Photocatalyst and mesoporous transition metal oxides for air purification under ambient conditions

Kenichiro Suzuki

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| 著者（英） | Kenichiro Suzuki |
| 学位名 | 博士 工学士 |
| 学位授与番号 | 33333号 |
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(常温下での空気浄化のための
光触媒ならびに遷移金属酸化物メソ多孔体)

2013

Kenichirou Suzuki
(鈴木賢一郎)
Abstract

The increasing concern of reducing air pollution in view of its adverse effects on the human health and the climate urges me to research and develop novel materials for rapid elimination of volatile organic compounds (VOCs) and ground level ozone (O₃) under ambient conditions. Strongly motivated by this interest, I am focusing on developing novel heterogeneous catalysts that can be used to remove and decompose air pollutants such as VOCs, O₃, and so forth. In this thesis, synthesis, characterization and evaluation of various transition metal oxides and analysis of the reaction kinetic were conducted for the catalytic elimination of VOCs and O₃.

Initially, the photocatalytic decomposition of VOCs over TiO₂ was investigated. Nowadays, photocatalysis is a common word and well known as an effective oxidation method for organic compounds in air and applied for photocatalytic functions to control environmental pollution. When I started my study, it was not proved whether this effect would be applicable for purifying a low level of noxious contaminants existing in air. My developing effort was focused on the fixation of the ultrafine titania semiconductor catalyst and then the effectiveness was examined. The photocatalytic oxidation of acetaldehyde, which proceeded stoichiometrically, was demonstrated as a representative VOCs de-pollution. TiO₂, oxygen, and UV-light were essential for the decomposition reactions. The feasibility test on a new vehicle and many vehicles in actual use by TiO₂ photocatalyst were widely conducted. Noticeable purification ability of the air purifier was clearly confirmed through both chemical analysis and human sensitivity test. Using photocatalyst TiO₂ by supporting over a monolith-like
carrier, it has demonstrated that air purification of the car cabin could be performed in air at room temperature. This research became a forerunner of subsequent photocatalytic air purification research.

Next, I focused on mesoporous based material for air purification application. I demonstrated for the first time that three-dimensional (3D) mesoporous oxides of Cu, Co, Ni, Mn, Fe, Cr and Ce, which were prepared by neutral templating route, showed exceptionally high VOCs (toluene, acetaldehyde, n-hexane) removal/oxidation ability. Characterization and evaluation made it clear that these materials had 3D mesoporosity, high surface area, and high oxidizing activity along with probable ready evolution of active lattice oxygen. Furthermore, I developed mesoporous ceria-titania mixed oxides with uniform pore size which were prepared by a neutral templating route preparation, and proposed their potential application as VOCs removal material at room temperature. High-surface-area mesoporous metal oxide materials were proved to be capable of eliminating VOCs at ambient temperature. Regarding these promising results, I investigated a range of metal oxides and noble metal catalysts. The catalyst of gold nanoparticles/γ-MnO₂ (Au/MnO₂) with high surface area could efficiently eliminate a wide range of VOCs under ambient conditions.

The abatement of air contaminants by mesoporous metal oxides, such as Cr₂O₃ and Au/MnO₂, has been proved to be a versatile approach and the performance is superior to activated carbon and mesoporous silica. However, these oxides had the non-environmentally friendly nature and/or were used expensive metal. This result promoted me to focus on environmentally compatible and highly available iron-based oxides. I found the high efficiency of mesoporous two-line ferrihydrite (Fh) for VOCs and O₃ removal for the first time. This study demonstrated the promise of highly
favorable electronic and textural structures of mesoporous Fh or Fh-based iron oxides in environmental catalysis.

The present results of mesoporous-based mesostructured material and their performances in air contaminants removal demonstrate the high efficacy of such a dual functional material which can act as an adsorbent as well as a catalyst that is decomposition of them. Furthermore, another important aspect of the present work is that a detailed structure-activity study is essential from the perspective of VOCs and O3 removal since these systems are newly introduced for air purification application. Therefore, such systems have been studied in detail from structure-activity point of view for air purification application for the first time.

While proposing novel transition metal oxide materials for air purification through this research, it also succeeded in developing the practical use level which contributes to realize safe and secure indoor environment with these materials.

The work concludes that these transition metal oxides are very promising for application in indoor air purification as well as outdoor emission control.
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Chapter 1

Introduction

Abstract
This chapter presents the rationale which motivates the present study of transition metal oxides for air purification material under ambient conditions. Section 1 presents a general overview of the issues associated with volatile organic compounds (VOCs) and ozone (O₃) and of the major sources of these contaminants in air. Additionally, the trends of VOCs and O₃ regulations for indoor as well as outdoor clean air are presented in this section. In Section 2, a brief review of the past research trend on the preparation method of the transition metal oxides catalysts and adsorbents are discussed. Finally, the scope and objectives of this thesis is presented in Section 3.
1.1. Overview

1.1.1. Volatile Organic Compounds (VOCs) and related issues

Today, people face a number of environmental problems including indoor air contamination and global warming. Especially, indoor air quality has become an important environmental issue [1]. Since many people spend most of their time indoor, such as in houses, office buildings, vehicles etc., exposing themselves to various artificial indoor environments. Most of the recently constructed buildings are designed to be insulated from the open air and to regulate their indoor environment artificially, and it is customary for vehicles also. As a result, the level of contaminants in such environments has growingly become several times higher than that in the open air. For this reason, a potential effect of deteriorating indoor air quality and the associated health risks is becoming a serious problem [1]. In particular, there is growing consensus regarding the possible effect of these contaminants on infants, the sick and the aged who are susceptible to them. Poor indoor air quality is considered to be linked to a number of symptoms, which are defined as sick building syndrome (SBS) or sick house syndrome (SHS) by the World Health Organization (WHO) [2, 3]. These symptoms include headaches, irritation of the eyes, drowsiness and general malaise.

Volatile organic compounds (VOCs) are some of the major indoor air pollutants. Particularly, toluene is considered as one of the causes of SBS/SHS because it is a major VOCs component that could be found in indoor atmosphere such as in house or in vehicles.

However, in contrast to the occupational environments, finding a certain kind of contaminant at high concentration level in general indoor environment is quite unlikely to occur. Instead, in such cases, a variety of contaminants with relatively low
concentrations are most common. For example, the cumulative contamination due to various human activities include smoking, pet odor, heating and cooking, which causes serious detrimental problems such as asthma and allergies. Among those contaminants are smelly volatile compounds such as toluene and acetaldehyde, nitrogen compounds such as trimethylamine, ammonia which is known or its high threshold value and odorless but hazardous carbon monoxide.

Besides the above mentioned indoor air pollution issues, the atmospheric pollutants like VOCs and NO\textsubscript{x} are the major reasons for photochemical smog and ground-level ozone [4]. VOCs and NO\textsubscript{x} emitted from industrial, automobile and biogenic process undergo photochemical reaction in the presence of sunlight to form ozone. The photochemical oxidant is a causative agent of the photochemical smog. 90\% of photochemical oxidant is ground-level ozone. The concentration of ozone is high in a summer. Ozone is also detected in the room. It is considered that ozone generated in the outside environment is introduced in indoors through infiltration [5]. Gaseous ozone in the troposphere is considered to be one of the most harmful air pollutants in view of its high reactivity and immediate action to the surroundings, which causes both short- and long-term adverse health effect and disrupts plant growth [6-8]. The rapid and irreversible chemical changes that may be caused by the ground-level ozone [4a] as well as the severe ecological impacts and the adverse health conditions that resulted by a wide range of VOCs and the aftereffect smog components in the atmosphere [9] have made it imperative to develop highly efficient functional materials for limiting organic pollutants from several industrial sectors [10].
1.1.2. VOCs and O₃ regulations

The USA was the first country to install legislation, known as the Clean Air Act (CAA) established by the Environmental Protection Agency (EPA) to complement the enforcement of the point source regulations [11]. The CAA establishes a pair of programs, known as New Source Review (NSR), which regulate the construction and modification of large stationary sources of air pollution. Recent studies of ambient air quality have highlighted the issues with VOCs in the atmosphere contributing to the indoor concentrations of various hydrocarbons. Regulation of VOCs emissions has further expanded to the state level in the United States. The California Air Resource Board (CARB) and several northeastern states that are members of the Ozone Transport Commission (OTC) are now regulating the VOCs levels of many consumer products with the goal of improving air quality [12, 13a]. The ozone is lumped together as a photochemical oxidant in Japan. On the other hand, in the United States the environmental standard value of ozone alone is determined by the environmental protection agency (EPA). The value is under 0.075ppm for 8-hour average. There is also a regulation level about the indoor ozone density standard in the United States. The maximum permissible concentration of ozone in indoor environment is set with 0.05ppm for 24-hour average by the American food and drug administration (FDA). According to ACGIH (American conference of industrial hygienists), the permissible concentration of ozone (TWA; time weighted average) during the hard labor work is about 0.05 ppm, whereas for normal labor it is 0.08ppm [14].

For ozone, entirely new approaches are required to achieve the substantial improvement that will be needed to meet the health standard in several areas such as Southern California, New York, etc. in the United States. The CARB has adopted
direct ozone reduction (DOR) technologies as an emission control alternative [15]. An automaker can get non-methane organic gas (NMOG) emission credits, which may be applied to offset vehicles tailpipe emissions or evaporative emissions from fuel tanks by applying to DOR technologies on vehicles [13b].

In Japan, by regulating the bad smell which occurs in connection with the active conduct of business in a factory or offices, bad smell preventive measures were promoted and odor control law was enforced on July 1, 1971 for the purpose of contributing a living environment to preservation and protection of national health. There are two kinds of regulations, one is Offensive Odor Substances and another is Odor Index. In Offensive Odor Substances, the 22 substances specified in the list include ammonia [NH₃], methyl mercaptan [CH₃SH], hydrogen sulfide [H₂S], methyl sulfide [(CH₃)₂S], methyl disulfide [CH₃SSCH₃], trimethylamine [(CH₃)₃N], acetaldehyde [CH₃CHO], propionaldehyde [CH₃CH₂CHO], n-butyl aldehyde [CH₃(CH₂)₂CHO], isobutyl aldehyde [(CH₃)₂CHCH₂CHO], isovaleraldehyde [(CH₃)₂CHCH₂CHO], isobutyl alcohol [(CH₃)₂CHCH₂OH], ethyl acetate [CH₃COOC₂H₅], methyl isobutyl ketone [CH₃COCH₂CH(CH₃)₂], toluene [C₆H₅CH₃], styrene [C₆H₅CHCH₂], xylene [C₆H₅(CH₃)₂], propionic acid [CH₃CH₂COOH], butyric acid [CH₃CH₂CH₂C₂OOH], valeric acid [CH₃(CH₂)₃COOH], isovaleric acid [(CH₃)₂CHCH₂COOH].

In order to prevent sick house syndrome from the Ministry of Health and Welfare in 1997, the guideline place of the formaldehyde concentration of indoor environment was released. Henceforth, 13 substances and the guideline value of Total Volatile Organic Compounds (TVOC) are released [16].
1.1.3. VOCs and O₃ removal technologies

Several technologies have been demonstrated in the literature to reduce the VOCs emissions to a desired level. Adsorption, incineration, and condensation were all considered. Adsorption of VOCs on a solid adsorbent has been used successfully and especially useful for relatively low concentration gas in indoor environment at ambient temperature. Activated carbon can adsorb more or less every organic vapor at ambient temperature except methane. The draw back of a solid adsorbent is to release the adsorbed compounds by temperature stress. In a manufacturing plant, the regeneration and eventual organic recovery or disposal of carbon that carried out saturated adsorption is the primary operating cost factors for this technology [17]. Steam desorption followed by condensation and recovery is the most common on-side regeneration method. Incineration (both direct fired and catalytic) is the most common technologies for removing the VOCs emissions especially at a plant. The fuel that obtains a temperature of about 650 to 1000 °C is the main factor affecting operating costs. Although the catalytic incinerate system is also operated in a similar way, catalyst is used at lower temperature of about 350 to 550 °C in this case. The higher initial cost of a catalytic device is offset by the lower fuel cost. In order to reduce fuel requirements, heat recovery is almost always used to pre-heat the incoming gas stream by heat exchange [17]. Incineration is not easily applicable to the use in a house. For condensation, it is not suitable for practical use because the applications were outside the practical limits of the technology.

The amelioration methods such as using activated carbon, conventional oxides and O₃ are utilized for air purifying system. And air purifier equipped these methods
are available on the market but they often have shortcomings such as their performance drop in a relatively short period of time or their safety is doubtful.

Materials explored for eliminating O$_3$ in several applications include activated carbon or carbon-promoted oxide materials, noble-metal-supported catalysts, and various transition-metal oxides [8, 18-20]. These materials have diverse drawbacks: They must often be deposited on high-surface-area metal oxides or mixed with organic additives to enhance their performance, they use expensive metal components, they are not very environmentally friendly, and they are not flexible enough to use as a common choice in a wide range of sectors.

1.2. Background

The trapping and decomposition of air contaminants are highly demanding in view of reducing pollution that directly or indirectly causes health problem and greenhouse effect. Here I will review the background of technology regarding with the contents of this thesis, i.e. photocatalyst and mesoporous materials. Also, the standpoint of this work is described.

1.2.1. Photocatalyst

Photocatalyst is a type of catalyst which can repeat the cycle of driving the redox as a result of the photoexitation. The photocatalysis is a redox reaction with those active species of holes and electrons generated from semiconductor catalyst when it is excited by light. This sensitization reaction principal is based on the Honda-Fujishima effect [21]. The principle of the Honda-Fujishima effect briefly explained as follows [22]: when a semiconductor electrode adsorbs photons with energy
greater than its band gap, electrons can be excited to the conduction band, thus creating electron-hole pairs [23]. In the case of an n-type semiconductor, the electric field drives photogenerated holes toward the interfacial region and electrons toward the interior of the electrode. Such photogenerated holes can oxidize various chemical species. The oxidizing ability in a semiconductor depends mainly on the energy level of the valence band. The valence band edge of n-type titanium oxide (TiO$_2$) is reported to be 2.6V (vs. SCE) at pH7 [24], thus acts as a strong oxidizer and causes various photochemical reactions. By using a system in which the TiO$_2$ electrode was connected to a platinum black electrode, the possibility of solar photoelectrolysis of water was demonstrated by Honda and Fujishima for the first time [21]. This photo-assisted electrolysis of water was defined as Honda-Fujishima effect. Since that time, photoelectrochemistry of semiconductors has been studied extensively, and much of this work has been associated with solar energy applications and photochemical energy conversion devices [25-28]. In experiments investigating the conversion of solar energy to chemical energy, systems of TiO$_2$ particles have also been used, because each TiO$_2$ particle can be considered as a microphotocell [22].

Nowadays, photocatalysis is a common word and well known as an effective oxidation method for organic compounds in air and applied for photocatalytic functions to control environmental pollution. But when I started my study around 1985, almost all studies on photocatalysis had been done regarding aqueous solution suspended with different kinds of semiconductor catalyst. A few gas phase studies have been reported. Ingenious application of sensitization in water hydrolysis with titania semiconductor electrode for gas phase was the key point for forming this practical air purification. Also in the past, much effort has been made for suppressing the photocatalysis that was
noticeable as the chalking phenomenon on paint film. However, there was no way of thinking to utilize this photocatalytic reaction as we did, rather than preventing it. Therefore, it was not proved whether this effect would be applicable for purifying a low level of noxious contaminants existing in gas phase when I began the study.

1.2.2. Mesoporous materials: Fundamental aspects

The introduction of supramolecular templating of silicate frameworks by Mobil and Japanese scientists in the early 1990s marked the beginning of ordered mesostructured materials [29-31]. Since then, silica has been the most widely studied mesostructured material because, compared to that of the majority of inorganics, the sol–gel chemistry silica species is simple to control. The basic concept of synthesizing mesoporous materials starts with aluminosilicates (often called by the general term zeolite) [32]. In contrast to isolated molecules employed for zeolite synthesis, supramolecular assemblies of amphiphilic organic molecules could act as templates for large-pore inorganic frameworks [29-31]. These micelle-forming organic molecules, termed structure-directing agents (SDAs), come in a variety of forms such as ionic surfactants, 1-3 block-copolymers [33], and even biomolecules like phospholipids [34] have been shown to template mesostructured oxides. The essential feature of SDAs is the presence of chemically bonded hydrophobic and hydrophilic components that phase segregate on the nanoscale. The hydrophobic component can solubilize organic species, while the hydrophilic component interacts with charged inorganic precursors to direct the formation of the inorganic framework. When the structure of the inorganic framework, defined by the geometry of the SDA, exhibits mesoscale (2–50 nm) periodicity, these materials are termed ordered mesostructured materials.
Silica-based mesostructured powders are generally synthesized from tetraethylorthosilicate (TEOS) and SDAs in either basic or acidic [33, 35, 36]. water/ethanol mixtures. The pH of this solution is critical for organic–inorganic co-assembly; reaction of the inorganic precursor with water to liberate alcohol (hydrolysis) and yield hydrophilic hydroxysilicate monomers should be fast, but the linkage of two monomers via an oxide bridge (condensation) must be slow enough for co-assembly with the SDA rather than precipitation of bulk silica or disordered composites [37]. Consequently, the highest quality ordered mesoporous silicas are synthesized in either basic media (pH ~13) or acidic media (pH <2) where molecular silica species are stable and negatively or positively charged, respectively. Charged inorganic species strongly interact with charged surfactant head groups or block-copolymer hydrophilic components, either directly or through counterion and hydrogen bond mediated pathways. These important interactions have been integrated into a generalized cooperative assembly mechanism: soluble inorganic species and surfactant molecules combine to form hybrid intermediates that are the building blocks of the final mesostructured hybrid. The critical aspects of sol-gel chemistry and mesostructure assembly are depicted in Figure 1 (Source: Ref. 38).

Synthesized in basic medium, the M41S family is made up of three welldefined mesostructures; MCM-41, MCM-48, and MCM-50. MCM-41 has a hexagonally packed array of non-interconnecting cylindrical pores. The structure of MCM-48 belongs to the cubic space group $Ia3d$. The structure can be thought of as two intertwined networks of spherical cages separated by a continuous silicate framework. MCM-50 contains a lamellar structure in the uncalcined form; a mesoporous pillared layered material results when the surfactant is removed after post-treatment with TEOS.
The dependence of surfactant/silica molar ratio in a ternary synthesis system containing tetraethylorthosilicate (TEOS, silica source), water and cetyltrimethylammonium (C16-TMA, surfactant) at 100°C on appearance of different phases of M41S family is summarized in Table 1.

<table>
<thead>
<tr>
<th>Surfactant/Silica ratio</th>
<th>Different Phases of M41S type materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1.0</td>
<td>Hexagonal (p6mm, MCM-41)</td>
</tr>
<tr>
<td>1.0-1.5</td>
<td>Cubic (Ia3d, MCM-48)</td>
</tr>
<tr>
<td>1.2-2.0</td>
<td>Lamellar (p2, MCM-50)</td>
</tr>
<tr>
<td>2.0</td>
<td>Cubic octamer [(C_{16}TMA)SiO_{2.5}]^8</td>
</tr>
</tbody>
</table>

The most outstanding feature of M41S material synthesis, in contrast to the traditional single organic molecule or metal ion templating preparation, is that the templates used are surfactants, having an alky chain length greater than ten carbon atoms. The surfactants has a hydrophilic head group and a long chain hydrophobic tail group, within the same molecule, and in solution they will aggregate and self-organize in such a way so as to minimize the contact between the incompatible ends. Therefore, the mechanism responsible for the formation of M41S materials from its precursors had attracted much scientific attention. Moreover, an improved understanding about the self-organization of surfactant-silicate assembly can provide significant impact in the development of new application-oriented materials.

Hence, a number of models have been proposed to rationalize the mechanism of formation of mesoporous materials by various synthesis routes. All these models are based on the role of surfactants in solution to direct the formation of silicate
mesostructure. However, these models quite often use for explaining the mesostructure ordering in non-siliceous mesostructured systems.

Figure 1.  The critical aspects of sol-gel chemistry and mesostructure assembly [Source: Ref. 38].
With the preparation of mesoporous silica in 1991, a new area of chemistry was opened up [29]. Non-siliceous mesostructured systems, such as transition metal oxides (TMOs), are often of greater interest than silicate mesostructures [39, 40], which is expected to play a pivotal role in advancing disciplines such as catalysis, energy conversion, sensing, optics, and biotechnology. The metal oxides, preferably transition metal oxides, either as a single component or as a multicomponent, with mesoporous structure and redox properties are considered to be the preferable candidate to solve the above issue. However, there are two additional challenges for non-siliceous oxide synthesis. First, metal oxide precursors (generally chlorides or alkoxides) are much more reactive than silica-based analogues; uncontrolled condensation yields macroscopic phase segregation. Second, redox reactions, phase transformations, and crystallization can collapse the framework at elevated temperatures. Various strategies for controlling the hydrolysis–condensation rates of metal oxide precursors that include utilizing specific pH ranges, stabilizing ligands, nonaqueous media, preformed nanoclusters, controlled hydrolysis, or some combination thereof have been extensively tried out. Block-copolymer SDAs that yield thicker inorganic walls and careful heat treatment are often preferred for synthesizing mesoporous metal oxides. In the following, the various strategies adopted for the mesoporous metal oxides are briefly discussed.

1.2.3. Methods of preparation of non-silicate mesoporous metal oxides

(a) Evaporation-induced self-assembly (EISA)

Evaporation-induced self-assembly (EISA) described by Brinker and colleagues for mesostructured silicates has proven to be an extremely useful process for
both controlling macroscopic form (thin films, membranes, and monoliths) and enabling the synthesis of mesostructured TMOs [41, 42]. Here, the evaporation of a volatile solvent (usually ethanol) following deposition concentrates the surfactant molecules and inorganic precursors, driving their co-assembly to form ordered mesophases. Subsequent aging, heat, or chemical treatments induce inorganic precursor condensation and lock in the mesostructure. The power of this process is twofold. First, the macroscopic morphology of the product can be tailored into application-specific geometries. Second, the co-assembly of the surfactant and inorganic precursors can be decoupled from the condensation reactions of the inorganic precursors, which is particularly useful for mesostructured TMO synthesis.

(b) Liquid crystal templating approach

The first foray into mesostructured materials of non-silicate compositions started with the generalized LCT mechanism of Huo and co-workers [35, 36]. Mesostructured oxides of metals such as Sb, Fe, Zn, Pb, W, and Mo were possible to obtain [35, 43]. However, most mesophases were layered and did not yield porous materials when the surfactants were removed. The few hexagonal phases derived underwent mesostructure collapse upon surfactant removal (either by solvent extraction or by calcination), probably due to the lack of complete condensation of the inorganic framework.

(c) Nanocasting by exo templatic method

Nanocasting is a process in which a mold with relevant structures on the length scale of nanometers is filled with another material, and the initial mold is removed
afterwards. Generally, two kinds of templates, defined as hard and soft templates, have been described as molds for nanocasting processes. Nanocasting from soft templates was developed and organic precursor species, often polymers, which allow the formation of liquid crystals, can be used as soft templates. However, this is often not considered as a real nanocasting process, because the soft templates do not really provide a rigid framework, but rather are nanoreactors. In contrast, in cases where a hard template is used, the synthesis indeed corresponds to a direct casting mechanism, where a relatively precise negative replica of the template is created. Schüth has suggested the term “endotemplating” for soft template method and “exotemplating” for hard template approach. An important advantage of using a hard template is the fact that the syntheses are relatively easy to control, since the template structures are fixed. Contrarily, soft template structures are often much more flexible, and can be dependent on temperature, solvent, ionic strength, and other parameters, which makes the prediction of the resulting negative replica more difficult. The first report by Ryoo’s group on this pathway described the synthesis of mesoporous carbon with an ordered structure, where the replication of the MCM-48 structure led to the formation of a new type of mesoporous carbon material (CMK-1) [44].

The general principle of structure replication by exotemplate (hard template) method is very straightforward. A porous solid material is used as a rigid matrix (template); that is, its pores are filled with one or more precursor species which react in situ to form the desired material. The matrix is finally removed to yield the product as its negative replica.

For the creation of periodically ordered porous materials by structure replication, two distinct types of structure matrices (exotemplates) are commonly used:
(i) On the one hand, porous silica or aluminosilicate materials (e.g., mesoporous SiO$_2$ such as MCM-48, SBA-15, or KIT-6, as well as microporous zeolites) frequently serve as structure matrices; they are synthesized by “soft” templating procedures (endotemplating). (ii) On the other hand, mesoporous carbon materials (e.g., CMK-3) are increasingly being utilized as structure matrices; their synthesis already involves the utilization of a “hard” structure matrix (exotemplate), usually silica. In both cases, the entire process can be envisaged as a repeated templating mechanism, namely, “soft/hard” templating in the former case and “soft/hard/hard” templating in the latter case. The exo templating approach has afforded a large variety of new, periodically ordered materials, such as carbon, noble metals, metal oxides, metal chalcogenides, or silicon carbide.

(d) Ligand-assisted templating

In this approach the surfactants usually pretreated with the metal alkoxides in the absence of water to form metal-ligated surfactants. The highest quality materials came from the use of amine surfactants, due to the strong affinity for nitrogen-metal bond formation between the surfactant head group and the metal precursors (for example, niobium or tantalum alkoxide precursor). Upon water addition to the alkoxide-surfactant mixture, mesoporous structured material is obtained. Here water actd as both a solvent and a reactant, to initiate surfactant self-assembly and alkoxide hydrolysis/condensation, respectively. In this ligandassisted templating (LAT) approach, control of mesostructure phases was found possible by adjustment of the metal / surfactant ratio, and led to a family of mesoporous transition metal oxides analogous to the M41S family of aluminosilicates.
1.3. Scope and Purpose of the thesis

As stated in Section 1, air pollution especially indoors by VOCs and O₃ have been a matter of growing concern over past decade which has resulted in strict legislation for concerning nearly any kind of chemical emission into the atmosphere. Regarding the health problems and the severe ecological impacts caused by contaminants in the atmosphere, the development of efficient functional materials for the removal of VOCs and O₃ in air at ambient conditions is of great importance. One favorable approach for dealing with VOCs and O₃ are catalytic combustion, yielding CO₂, H₂O and O₂ as final reaction products.

The main objective of the present thesis work is to develop a gas phase catalysis process that could be used to remove and destroy VOCs and also O₃ in air under ambient conditions. These efforts are also intended to the realization of new generation vehicles, where vehicle itself acts as an air-purifying device. The vehicle equipped with the presently developed dual functional catalysts on the surface of its component disclosed at a site where air stream is formed when the vehicle is moving. The vehicle removes the air contaminants and cleans the air when it runs.

By considering the present situations, I focused on transition metal oxides for removing contaminants. Transition metal oxides possess a multitude of different coordination numbers and oxidation states and are more susceptible to redox reactions or phase transitions [45]. Especially, oxides of transition metals such as Mn, Cr, Cu and Co are the typical cost-effective catalysis for complete oxidation of VOCs [46-49]. Also, crystalline chromium oxide that favors the formation of CO₂ could be the most promising candidate for the total oxidation of organics [50]. However, the conventionally prepared transitions metal oxides show very poor catalytic reactions
Chapter 1

under ambient temperature. Usually, conventional transition metal oxides require relatively high temperature (more than 100°C) for initiating the activity and keep oxidizing VOCs.

Initially, the photocatalytic decomposition of VOCs over TiO₂ was investigated. As stated in Section 2, it was not proved whether photocatalytic reaction could be applicable for purifying a low level of noxious contaminants existing in gas phase when I began the study. I found that the photocatalytic reaction was quite promising for the removal of various contaminants that existed at extremely low concentrations. Also, noticeable purification ability of the air purifier by using TiO₂ photocatalyst was confirmed for various contaminants. This air purifier, which was deduced from the experimental results, is promising technology for a range of applications. For these reactions to proceed, TiO₂, oxygen and UV-light are essential and it is demonstrated. However, since UV-light source has to be equipped for undergoing the photocatalytic reaction, it is not economical for practical use.

The disadvantage of photocatalytic system has led me to focus on developing novel and highly efficient mesoporous transition material oxides for contaminant removal applications. This is because mesostructured materials have some of the unique properties such as high surface area and large pore volume, large uniform pore size, high adsorption capacity and presence of mobile lattice oxygen with potentially high oxygen storage capacity [40]. Especially, mesoporous three-dimensional (3D) structure of these oxides are more suitable for application as catalyst or adsorbent due to easier diffusion of reactants by overcoming mass-transfer limitations [51]. After that I found mesoporous transition metal oxides such as Cr₂O₃, Au/γ-MnO₂ has been shown to be the most active catalysts for the elimination of organic contaminants in air at room
temperature [52b, 52e]. However, the non-environmentally friendly nature of these metal oxides is a primary impediment to consider them in several sectors, especially for indoor applications. This prompted me to look for highly active and environmentally compatible candidates, preferably from the category of the most abundant transition metal of iron-based materials.

In Chapter 2, TiO$_2$ photocatalyst is systematically examined for its activity at room temperature in terms of purifying the gaseous contaminants present in air at extremely low concentration. An on-board type air purifier by using TiO$_2$ photocatalyst was practically evaluated. These results suggest that the photocatalytic reaction is promising for purifying various contaminants which present at extremely low concentrations in air.

In Chapter 3, the preparation of three-dimensional mesoporous metal oxides of Cu, Co, Ni, Mn, Fe, Cr and Ce using an interaction between various nonionic polyethylene oxide based surfactants as template and neutral inorganic metal nitrate precursors in non-aqueous solution is reported for the first time. Such mesoporous oxides are expected to have unique catalytic activity. Such novel metal oxides with 3-dimensional mesoporosity were examined for their toluene removal ability at ambient temperature.

In Chapter 4, in order to identify the mechanism of VOCs removal over these materials, a detailed characterization of the nature of chromium site in three-dimensional mesoporous chromium oxides samples and also a more detailed evaluation of the VOCs removal ability are reported.
In Chapter 5, the synthesis of mesoporous ceria using the same method as in Chapter 3 is reported. The unique structure of this material was characterized and its VOCs removal activity was evaluated.

In Chapter 6, mesoporous ceria-titania mixed oxides with uniform pore size and enhanced thermal stability is reported. A neutral templating method is employed to produce such novel mesoporous mixed oxides. Further, a detailed characterization of these materials and their potential application as novel indoor VOCs removal material at room temperature is presented in this chapter.

In Chapter 7, the detailed results on a simple route for the bulk synthesis of mesoporous manganese oxides (γ-MnO₂) are presented. Structurally these mesoporous manganese oxides γ-MnO₂ are composed of nanofiborous aggregates with intraparticle mesoporosity. Application of these materials to low-temperature VOCs elimination before and after modification with gold nanoparticles is also discussed. Detailed characterization studies have been done to understand the reasons for high activities of these materials.

In Chapter 8, the environmentally compatible and highly available iron-based oxides is prepared and investigated. A template assisted synthesis route to produce stable mesoporous 2-line ferrihydrite (M2LFh) was reported. A detailed characterization of M2LFh and the evaluation of the acetaldehyde and O₃ removal ability were performed. Furthermore, the fundamental aspect of structure-property relationship for these materials was achieved and the adsorption behavior of O₃ on ferrihydrite was performed. A unique biocompatible and cost effective catalyst system active at room temperature for the above two processes is reported for the first time.
Finally, in Chapter 9, all the results of this thesis are summarized, and the main conclusions of this thesis and outlook are presented.

1.4. References


Introduction


Photocatalytic air purification on TiO$_2$

Abstract

Photocatalytic deodorization on TiO$_2$ coated honeycomb supports were systematically examined in extremely low concentrations at room temperature. The decomposition of acetaldehyde, isobutylic acid, toluene, hydrogen sulphide, methyl mercaptan and trimethyl amine were investigated. In case of acetaldehyde, the photocatalytic oxidation proceeds stoichiometrically as at the given initial concentration of acetaldehyde the molar ratio of CO$_2$ produced to CH$_3$CHO decomposed is always two was demonstrated. I also demonstrated that oxygen, TiO$_2$ and UV-light was essential for these reactions to proceeds. The results encouraged me to evaluate an on-board air purifier by using TiO$_2$ photocatalyst. The feasibility test on a new vehicle and many vehicles in actual use were widely conducted. As a result, noticeable purification ability of the air purifier was clearly confirmed through both chemical analysis and human sensitivity test.
2.1. Introduction

The photocatalytic reactions of ethylselosolve [1], ammonia [2], hydrocarbons [3], carboxylic acid [4], fluoroalkens [5], chlorinated organics [6-7], formic acid [8], nitrogen oxides [9], etc. in gaseous state have been already reported. However, the results and/or mechanisms obtained from these reports are far from the standpoints of practical application to an air purifier because of high concentration of the reactants or low concentration of oxygen. After that, the photocatalysis of various oxygenates and aromatic in air was reported on a trace level by Ollis, et al. [10]. Therefore, it was not proved whether this photocatalytic reaction could be applicable for purifying a low level of noxious contaminants existing in gas phase when I began research.

Thus, the fundamental evaluations of photocatalyst were systematically conducted using a recycling reactor on various odor contaminants, and the excellent results of the experiments have encouraged me to develop a new, compact air purifier based on the photocatalysis principle mentioned above [11, 12].

The air purifier was evaluated using a stirred large box. Furthermore, feasibility tests on a new vehicle and a number of vehicles in actual use were widely conducted. As a result, noticeable purification ability of the air purifier was confirmed for various contaminants [13].

This air purifier deduced from the above experimental results can promise a wider application to vehicles as well as to domestic rooms. To attain these purposes, the specifications of the air purifier must be further optimized for the proper uses.
2.2. Experimental

Prior to the experimental evaluations of photocatalysts in terms of the purification ability, the preparation methods of photocatalyst were systematically examined in order to draw the best catalytic activity from the various parameters such as the material of support, the structure of support, the source of TiO₂ powder as a catalyst ingredient.

2.2.1. Preparation photocatalyst

First of all, my effort was focused on the fixation of ultrafine titania semiconductor catalyst and the effectiveness was examined. It is well known in the field of catalyst engineering that a honeycomb catalyst gives a low pressure drop, a wide reaction zone and uniform flow distribution within a channel matrix [14]. Therefore, the honeycomb supports made of cordierite (NGK; HONEYCERAM) and active carbon (KOBELCO; ACH-3) were selected. The density of both the cells was 300 cells/in². Among the preparation parameters, the loading technique of TiO₂ powder on the surface of the supports is the most important. In this experiment, a conventional, "washcoat" method, used worldwide for preparing automotive honeycomb catalysts, was successfully transferred to prepare the present photocatalyst.

On the other hand, the selection of TiO₂ powder as a catalyst ingredient is also very important. For this reason, thirteen kinds of TiO₂ powders obtained from different manufacturers were examined, and the TiO₂ powder Degussa P-25 was found to be excellent. The total loading amount of TiO₂ power on the supports was 84 g/L-catalyst. The surface of the photocatalyst was examined by a scanning electron microscope (SEM) and an electron probe microanalyzer (EPMA).
2.2.2. Analytical method

In the laboratory evaluations of the photocatalyst, acetaldehyde (Merck), toluene (Wako Pure Chemical), isobutyric acid (Wako Pure Chemical), isoprene (Wako Pure Chemical), ammonia (Nacalai Tesque), methyl mercaptan and hydrogen sulfide, were used as the contaminants. These contaminants were used without further purifications. Methyl mercaptan and hydrogen sulfide were obtained from a gas cylinder (Nippon Sanso). On the other hand, toluene, xylene, hydrogen sulfide, carbon disulfide, and nitrogen-containing organic substances existing in a new vehicle were examined in the feasibility test of the air purifier with the photocatalyst. In the laboratory examinations, the concentrations of these contaminants except hydrogen sulfide, methyl mercaptan and ammonia, were determined using the gas chromatograph (GC) with a flame ionization detector (Shimadzu; HCM-1B) and/or the gas chromatograph-mass spectroscopy (GC-MS; Hewlett Packard; HP5890-5971A) during the reaction time. The concentrations of hydrogen sulfide and methyl mercaptan were determined using the GC with a flame photometric detector (FPD; Shimadzu; GC-9A), and the concentration of ammonia was determined by gas detector tubes (Gastec; No. 3L). In the feasibility test, the concentrations of the contaminants in a new vehicle were determined as follows [15]: Gas samples were collected with adsorption tubes containing TENAX-GC for hydrocarbons and nitrogen-containing organics, Chromosorb 101 for sulfur compounds. Following thermal desorption, the contaminants were quantitated by a gas chromatograph with FID (Hewlett-Packard; HP5890) for hydrocarbons, a flame thermoionic detector (FTD; Shimadzu; GC-14A) for nitrogen-containing organics, and a GC with FPD for sulfur compounds. These data were used for calculating percentage conversion and rate constant. The reaction
products which may be generated, except CO₂, were traced over the entire reaction process by means of GC-MS. CO₂ concentration was determined by back titration of Ba(OH)₂ with 0.1N HCl [16]. On the other hand, in the feasibility test using the vehicles in actual use, the evaluation of the air purifier was conducted with a human sensitivity test.

2.2.3. Evaluation apparatus-recycling and stirred box reactor

First, the fundamental evaluation of photocatalyst was carried out using a recycling reactor system shown in Figure 1. This system consists of a photocatalyst, TiO₂ powder coated on cordierite type honeycomb structured support, a 500 watt high pressure Hg lamp (USHIO; UI-501C), a 20 L gas container (GL Sciences; tedler-c-c-k-20) made of polyvinyl fluoride, and a pump.

![Figure 1. Recycling reactor system for evaluation of photocatalyst.](image)

Figure 2 shows the entire photocatalyst. The photocatalyst, 30 mm in diameter and 50 mm in length, was inserted into a quartz tube, and was irradiated with the Hg lamp from one side. The output wavelength spectrum of this lamp ranged from 200 to 500 nm, with a maximum intensity near 365 nm. The contaminants were diluted with air to a given concentration and held in the gas container. The diluted
contaminants were recycled with the pump in a flow rate of 5L/min. In the reaction involving water, water vapor was added into the reactor before reaction. The vapor pressure of the water was estimated to be about 24 torr, assuming that the saturation was kept in the bubbler. All the reactions occurred at room temperature. The concentration of the contaminant was determined at the given reaction times.

Second, the stirred large box experiment was conducted. Figure 3 shows this system. A reactor that consists of two pieces of photocatalyst and a small 5 watt UV lamp (OSRAM; HNS GIE 5W ofr), and a fan were placed on the bottom of the box. Figure 4 shows the reactor. The photocatalysts were placed on both sides of the lamp. Figure 5 shows an outside view of the photocatalyst. The support is made of active carbon, and its dimension is about 80 mm × 60 mm × 20 mm. The output wavelength of this light ranged from 200 to 500 nm, with a maximum intensity of 254 nm.
The purification ability of this reactor was examined in a 1 m$^3$ stirred box made of acrylic sheet. The experimental procedure was as follows: First, the reaction gas was stirred with the fan by a flow rate of 0.5 m$^3$/min.
Next, the contaminant was added into the stirred box through an inlet, with its concentration adjusted to become about 20ppm. Then, the UV lamp and the fan were operated for 30 min., and the concentration of the contaminant was determined every 10 min. This 30 min. experimental run is defined as “one cycle” and the cycle was repeated many times. Prior to each cycle, the contaminant was added into the box so that its concentration could reach the initial value of about 20ppm. The purification ability was examined for three contaminants, hydrogen sulfide, isopurene and ammonia, which are known as the noxious substances in cigarette smoke.

2.2.4. Feasibility test

The feasibility tests of a new, compact air purifier designed on the bases of the above experiments were conducted using a new vehicle as well as a number of vehicles in use. Figure 6 shows an outside view of air purifier with the photocatalyst.
For the case of new vehicle, the purification was evaluated by the determination of various contaminants before and after a two-hour operation of the air purifier. For the vehicles in use, on the other hand, twenty-five air purifiers were prepared and their purification abilities were evaluated. In this evaluation, the results were discriminated by twenty-five user’s human sensitivity.

2.3. Results and discussions

2.3.1. Physical state of TiO\textsubscript{2} coated photocatalyst

Figure 7 shows the physical state of the photocatalyst coated on cordierite type honeycomb structured support observed by SEM with a magnification of 200,000. The size of the TiO\textsubscript{2} particle (Degussa; P-25) was several ten nanometers.

Figure 8 shows across section of the photocatalyst observed by an EPMA. In this figure, the black- and gray- colored areas correspond to elemental TiO\textsubscript{2} and cordierite substrate, respectively. It is clear that the TiO\textsubscript{2} particles do not enter into a cordierite phase. It is apparent from this figure that the distribution of TiO\textsubscript{2} is accumulated around a concave corner of the honeycomb support. The thickness of the TiO\textsubscript{2} layer ranged from 0.01 to 0.08 mm.

This photocatalyst was used only for the following fundamental experiments using a 500 watt UV lamp, which are discussed from Section 2.3.2. to 2.3.4.
2.3.2. Fundamental evaluation of photocatalyst

In the first place, the effects of various reaction parameters on the decrease rate of acetaldehyde were systematically examined, and the typical results were briefly described. Acetaldehyde was adopted as the representative contaminant. Its smells fishy even in an extremely low concentration, with an offensive threshold value of 0.014ppm.
Figure 9 shows the decrease profiles in the acetaldehyde concentration as a function of the reaction time with and without photocatalyst. It is clear from this figure that the desired reaction is accelerated with the photocatalyst.

![Figure 9. Photocatalytic reaction of acetaldehyde in air at room temperature.](image)

Next, the influence of water vapor on the decrease rate of acetaldehyde was examined as shown in Figure 10. In this experiment, water vapor was introduced by the flowing air through a bubbler held at room temperature. The vapor pressure of the water in the reaction gas was estimated to be about 24 torr, assuming that the saturation was kept throughout the bubbling process. As seen from this figure, the acetaldehyde concentration decrease but is only slightly suppressed by the presence of water vapor with and without UV irradiation.
Figure 10. Influence of water vapor on photocatalytic reaction.

Figure 11 shows the effect of support materials, active carbon and cordierite, on percentage conversion of acetaldehyde through the photocatalytic reaction. The conversion on the active carbon support is larger than that on the cordierite support. This fact results from the difference in adsorption capacity of the supports rather than the difference in the reactivity of TiO$_2$ on the supports.

Figure 11. Effect of support material: active carbon and cordierite.
Finally, three kinds of blank tests were conducted. Among the three reaction conditions, photocatalyst, oxygen, and UV irradiation, each of the reactive each of the reaction systems lacking any one of the conditions was compared with the normal photocatalytic condition. In Table 1, the first row is the normal condition, the second row is without the photocatalyst, the third row is without oxygen, and fourth row is without UV irradiation, respectively.

Table 1. Results of the normal condition and three kinds of blank tests.

<table>
<thead>
<tr>
<th>CH₃CHO (ppm)</th>
<th>Photocatalyst</th>
<th>Atmosphere</th>
<th>Irradiation</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.2</td>
<td>yes</td>
<td>Air</td>
<td>yes (60 min)</td>
<td>99.5</td>
</tr>
<tr>
<td>19.0</td>
<td>no</td>
<td>Air</td>
<td>yes (60 min)</td>
<td>6.3</td>
</tr>
<tr>
<td>22.5</td>
<td>yes</td>
<td>Ar-N₂</td>
<td>yes (60 min)</td>
<td>10.6</td>
</tr>
<tr>
<td>21.0</td>
<td>yes</td>
<td>Air</td>
<td>no</td>
<td>13.7</td>
</tr>
</tbody>
</table>

The percentage conversions described in the right column of Table 1 were obtained after a reaction time of 60 min. In this table, the value of the conversion under the normal condition is clearly larger than those of the others. Therefore, it is concluded that the photocatalysis for oxidizing acetaldehyde requires coexistence of photocatalyst and oxygen under UV irradiation.

2.3.3. Reaction mechanism

In the above section, how the gas phase photocatalysis of acetaldehyde depends on the various parameters has been roughly outlined. In this stage, the most important point is what kinds of products will be formed through the photocatalytic reaction. To clarify this point, the reaction products that may be generated through the photocatalytic
process were traced by mean of GC-MS. As a result, no product other than CO$_2$ was detected. In this experiment, the amounts of the acetaldehyde decomposed and the CO$_2$ produced in the reaction gas were determined by varying the initial concentration of acetaldehyde. The result is shown in Figure 12. As shown in this figure, the molar ratio of CO$_2$ produced to the acetaldehyde decomposed through the photocatalytic process always becomes "2".

![Figure 12. Relation between CO$_2$ produced and CH$_3$CHO decomposed after 60 min. irradiation.](image)

In the following experiment, both the amounts of the CO$_2$ produced and the acetaldehyde decomposed were determined as a function of UV irradiation time under the initial concentration of acetaldehyde kept at 340ppm. As seen from Figure 13, the molar ratios of the CO$_2$ produced to the acetaldehyde decomposed also becomes "2", which is consistent with the finding by Ollis, et al., on the photocatalytic oxidation of formaldehyde [10].

The figures "2" obtained from the two cases of the above experiments clearly indicate that the photocatalytic reaction of acetaldehyde proceeds stoichiometrically. In other words, the reaction is just characterized by complete oxidation. This fact is very favorable for the use of the photocatalyst for purifying the contaminants in the
aspect of human safety. For example, in the case of an air purifier using \( O_3 \), the partially oxidized substances are produced due to insufficient supply of \( O_3 \) and remain as the noxious contaminants. On the contrary, excess supply of \( O_3 \) causes some damage due to the toxicity of \( O_3 \).

![Graph](image_url)

Figure 13. Amount of \( CO_2 \) produced and \( CH_3CHO \) decomposed as a function of irradiation time at initial \( CH_3CHO \) concentration of 340 ppm.

2.3.4. Kinetic evaluation

The decrease profiles of other contaminants, toluene, isobutyric acid, methyl mercaptan and hydrogen sulfide, are shown in Figure 14. In each figure, the abscissa is the UV irradiation time and the ordinate is the logarithmic concentration. For these contaminants, it is clear that the desired reaction is accelerated under UV irradiation, and that the reaction proceeds according to the pseudo first order.
Figure 14. Reactions of contaminants in air at room temperature in the presence of TiO$_2$ photocatalyst: (a) toluene, (b) isobutyric acid, (c) methyl mercaptan, and (d) hydrogen sulfide.
Table 2 shows the rate constant for each contaminant. These results suggest that the photocatalytic reaction is promising for purifying the various contaminants which exist in extremely low concentrations.

<table>
<thead>
<tr>
<th>Odor</th>
<th>Rate constant (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CHO</td>
<td>0.11</td>
</tr>
<tr>
<td>CH₃C₆H₅</td>
<td>0.059</td>
</tr>
<tr>
<td>(CH₃)₂COOH</td>
<td>0.0078</td>
</tr>
<tr>
<td>CH₃SH</td>
<td>0.13</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.13</td>
</tr>
</tbody>
</table>

2.3.5. Stirred box experiment

In the laboratory experiment mentioned above, a powerful lamp of 500 watt was used. However, since this lamp is not suitable for installation into a small air purifier, a small UV lamp of 5 watt was substituted hereafter.

Figure 15 (a) shows the results of the cyclic tests for hydrogen sulfide. The abscissa is the number of cycles and the ordinate is the concentration of hydrogen sulfide. The upper figure shows the result for the support without TiO₂, and the lower for the support with TiO₂. Both the supports with and without TiO₂ shows sufficient purification ability with in 20 cycles.

Figure 15 (b) shows the results for isoprene. In spite of the use of a small lamp, the desired reaction is fully achieved at each cycle and the repeatability of every
cycle is excellent. However, in the case for the support without TiO₂, the purification ability gradually decreased.

Figure 15. Profiles of cyclic tests of contaminants in stirred box: (a) hydrogen sulfide, (b) isoprene, and (c) ammonia
Figure 15 (c) shows the results for ammonia. The reaction behavior is somewhat different from the cases of hydrogen sulfide and isoprene. Although the deviation at each cycle largely depends on poor precision of the analytical method due to the use of a detection tube, it is apparent that purification ability of the photocatalyst is gradually weakened beyond 11 cycles.

Fortunately, the deteriorated photocatalysts could be easily regenerated by exposing it to clean air in the box under the irradiation with a 5 watt UV lamp. After the regeneration, the photocatalyst behaves like the initial one as shown in the right side of this figure.

Figure 15 also shows the behavior of the support without TiO$_2$. Its purification ability rapidly decreased compared with that of the support with photocatalyst especially the result for ammonia. This fact verifies that the function of TiO$_2$ coated photocatalyst does not largely depend on the adsorption capacity of the active carbon support.

Through the stirred box experiment mentioned above, it is confirmed that the sufficient purification ability is demonstrated by the reactor with the small UV lamp of 5 watt.

2.3.6. Feasibility tests using the air purifier for vehicle

Referring to the above experiments, a new, compact air purifier was prepared (Figure 6), and its feasibility tests were conducted within a new vehicle and vehicles in use. This air purifier can be operated by a DC12 volt battery, and its electric power
consumed is to be as small as 10 watt in total. These specifications are adequate for an on-board air purifier.

First, the feasibility test of the prototype air purifier was conducted using a new vehicle. Table 3 shows the percentage conversions of toluene, xylene, hydrogen sulfide, carbon disulfide, and nitrogen-containing organic substances coexisting in the new vehicle after a 2-hour operation of the air purifier. In this table, percentage conversion of nitrogen-containing organic substances, which are mainly amines such as trimethylamine, propylamine, is a gross figure because each component is too low for the quantitative analysis.

Table 3. Apparent purification ability of air purifier in new vehicle through 2-hour operation.

<table>
<thead>
<tr>
<th></th>
<th>Concentration (ppb)</th>
<th>Purification rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>Toluene</td>
<td>51</td>
<td>17</td>
</tr>
<tr>
<td>Xylene</td>
<td>267</td>
<td>118</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>5.7</td>
<td>4.3</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>3.2</td>
<td>1.6</td>
</tr>
<tr>
<td>Organic nitrogen compound</td>
<td>3.4*</td>
<td>ND</td>
</tr>
</tbody>
</table>

* : ng/l

It is noticeable from the results of this feasibility test that the above contaminants in the new vehicle are continuously supplied from the various interior materials and adhesives. Considering this fact, the “net” purification ability of the photocatalyst is superior to the values of percentage conversion. The evaluation test
using the simple chemical and coexisted contaminants, conventionally called “new car odors”, has been proved that the prototype air purifier is excellent.

Second, twenty-five prototypes of this air purifier were prepared to examine the purification ability within twenty-five users' vehicles at the same time for three months. In this case, there are different and complex odor sources, such as cigarette smoke, body odors, and unpleasant odors from pets of air conditioner.

![Figure 16. Results of 3-month human sensitivity test.](image)

The prototype of the air purifier was programmed to work only when the vehicle was driving. Figure 16 shows the results of the human sensitivity test. More than “70%” of the testers recognized certain effectiveness of the prototype air purifier. In these human sensitivity tests, the figure “70%” obtained from the twenty-five cases is very significant.
2.3.7. Application examples

The photocatalyst type air purifier other than a vehicle in a house under actual working conditions was tested and was accepted with the excellent performance. The preparation work for practical applications was advancing in the following areas; (1) Air purifier for living environment was effective for the removal of cigarette smoke, cooking smells and unpleasant odors from bedridden people and pet. This type air purifier for office was practically marketed from Matsushita Seiko Co., Ltd. based on these our knowledge and technology. (2) Air purifier for use in toilet was effective for removal of toilet odors. Both built-in and incorporated types were developed. We knew further efforts were required for optimization of the purifier's specifications in this development.

2.4. Summary

The TiO₂ coated photocatalysts were evaluated using a recycling reactor and a stirred large box, and the purification ability was confirmed to be excellent for various contaminants. On the bases of these results, the prototype air purifiers with the photocatalyst were prepared for the purpose of on-board use. The favorable effectiveness of these air purifiers was demonstrated in a new vehicle as well as vehicles in use. In addition, these air purifiers were easily applicable to the use in various domestic rooms contaminated by cooking, pets, or toilet smells. In fact, a part of these applications were evaluated in the respective fields. An air purifier for living environment has been practically marketed based on these knowledge and technology.
2.5. References


Abstract

Novel mesoporous oxides of Cu, Co, Ni, Mn, Fe, Cr and Ce were successfully prepared by neutral templating route in a mixed organic medium using triblock copolymer and metal nitrate or acetate as the template and inorganic source, respectively. These materials had three-dimensional (3D) cubic arrangement of mesopores with semi-crystalline walls. The materials showed the volatile organic compounds (VOCs) removal ability. Under ambient conditions the materials act as selective sorbents and oxidation catalysts for VOCs. Results suggest that these mesoporous oxides are promising for air-purification applications.
3.1. Introduction

In this chapter, I focused on the mesoporous transition metal oxides and lanthanide oxides, because these structured materials have some of the unique properties such as high surface area and large pore volume, large uniform pore size, high adsorption capacity and presence of mobile lattice oxygen with potentially high oxygen storage capacity [1]. With the preparation in 1991 of mesoporous silica a new area of chemistry was opened up [2]. Ordered structures formed by the assembly of transition metal oxides are of great interest in the area of material science [3]. Oxides of Mn, Cr, Cu, Co are the typical cost-effective catalysts for the decomposition VOCs [4-8]. Preparation of stable mesoporous oxide of transition metals and lanthanides has been most difficult though it has been possible to prepare unstable mesostructures and lamellar phases of these materials. Preparation of well-ordered mesoporous oxide of Mn has been successfully reported [9]. Recently hexagonally ordered mesoporous Ni oxide [10] and wormhole-like mesoporous Fe oxide [11] have been reported. But, mesoporous three-dimensional (3D) structure of these oxides is more suitable for application as catalyst or adsorbent due to easier diffusion of reactants by overcoming mass-transfer limitations [12]. Transition metal oxides possess a multitude of different coordination numbers and oxidation states and are more susceptible to redox reactions or phase transitions, making it rather difficult to prepare their mesoporous structure unlike silica and alminosilicates which can easily form stable mesoporous structure [13]. The neutral templating route has been successfully used for the synthesis of metal oxides [3, 14] that have been less readily accessible by electrostatic templating pathways [7, 15]. Here, I describe my work on the preparation of three-dimensionally ordered mesoporous metal oxides [16] of Cu, Co, Cr [17], Ni, Mn, Fe and Ce using
nitrate salt or acetate salt precursor in a mixed non-aqueous ethylene glycol-propanol medium and using poly (alkylene oxide) block copolymers as template by evaporation–induced self-assembly (EISA). These materials show exceptionally high VOCs removal ability. Results suggest that these mesoporous oxides are promising for air-purification applications.

3.2. Experimental

3.2.1. Preparation of mesoporous metal oxides

Mesoporous metal oxides were prepared by neutral templating route in a mixed organic medium of propanol and ethylene glycol (EG). Non-ionic amphiphilic triblock copolymer F-127 \([\text{HO(CH}_2\text{CH}_2\text{O})_{106}\text{CH}_2\text{CH}({\text{CH}}_3)\text{O})_{70}\text{CH}_2\text{CH}_2\text{O})_{106}\text{H}]\) and metal nitrate or acetate were used as the template and inorganic source, respectively. The method uses an interaction between various nonionic polyethylene oxide based surfactants and neutral inorganic metal nitrate precursors in a non-aqueous solution. Typical molar gel composition was 65-170 M: 115 propanol: 1080 EG: 1 F-127 (M= Cu, Co, Cr, Ni, Mn, Fe and Ce). In a typical synthesis 1 g of F-127 block copolymer (Sigma-Aldrich) was dissolved in 5 g of propanol (Wako Pure Chemical) and 5 g of ethylene glycol (Wako Pure Chemical) mixture. To this solution required amount of metal nitrate (or acetate) salt (Wako Pure Chemical) was added with vigorous stirring for 30-40min. The resulting sol solution was then aged at 40-50 °C for 3-7 days and then heated gradually (1 °C/min) to 100-200 °C and finally the organic template molecules were removed by extracting with ethanol. As-made samples were transparent which changed to fluffy foam-like material after heating in air to 200 °C.
3.2.2. Characterization

The powder X-ray diffraction (XRD) patterns were obtained on Rigaku Rint 2400 instrument equipped with a rotating anode and using Cu Kα radiation (wavelength = 0.1542 nm). Nitrogen adsorption/desorption isotherms were obtained at -196°C on an Autosorb-1 apparatus. Prior to measurement, samples were heated at 200°C for 2 h and finally outgassed to 10⁻³ torr. BET and BJH analysis were used to determine the total specific surface area, pore volume and pore size distribution of the samples. Scanning electron microscopy (SEM) observations were made using a Hitachi S-3600N instrument. Transmission electron microscopy (TEM) observations were made using a JEOL JEM200CX instrument. The XPS measurements were performed on a PHI-5500MC spectrometer by using Mg Ka(1253.6 eV) radiation as the excitation source and with an analysis area of about 800 μm². Charging of the catalyst samples was corrected by setting the binding energy of the adventitious carbon (C 1s) to 284.6 eV [18-19]. The XPS analysis was done at ambient temperature and pressures typically on the order of 10⁻⁷ Pa. Prior to analysis, the samples were outgassed in a vacuum oven overnight. The EPR spectrums were obtained on Bruker Electron Spin Resonance ESP 300 spectrometer. All the samples were evacuated at 400°C to 10⁻⁴ torr (4h), then cooled down to R.T. and exposed to O₂ (100 torr).

3.2.3. Toluene removal ability analysis method

All the mesoporous metal oxides were tested and compared for their toluene removal performance. As an evaluation gas, a gas mixture was used which contained, toluene: 80ppm, oxygen: 20% and the balance of nitrogen. 1.0 g each of the aforementioned catalyst samples and the evaluation gas were put in a 5-liter gas
In the case of a detailed evaluation of chromium oxide, the concentration of toluene was 103.3ppm and the amount of sample was 0.4 g. The gas was analyzed after different time intervals by Gas Chromatograph (Shimazu; GC-14B) and CO₂ analyzer (LI-COR; LI6262). The toluene conversion was determined from the following equation.

\[
\text{Toluene Removal (\%)} = \frac{\text{(Toluene Concentration on gas container without catalyst) - (Toluene Concentration in gas container with catalyst)}}{\text{Toluene Concentration in gas container without catalyst}} \times 100
\]

### 3.3. Results and Discussions

Table 1 shows the preparation conditions and starting materials used for the various 3D mesoporous metal oxides.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Composition</th>
<th>Aging</th>
<th>Heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Cu(NO₃)₂3H₂O 3.624g</td>
<td>F-127:1g</td>
<td>Propanol:5g Ethylene glycol:5g</td>
</tr>
<tr>
<td>Co</td>
<td>Co(NO₃)₂6H₂O 2.3793g</td>
<td>F-127:1g</td>
<td>Propanol:7g Ethylene glycol:3g</td>
</tr>
<tr>
<td>Cr</td>
<td>Cr(NO₃)₂9H₂O 4.0015g</td>
<td>F-127:1g</td>
<td>Propanol:7g Ethylene glycol:3g</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni(NO₃)₂6H₂O 2.9079g</td>
<td>F-127:1g</td>
<td>Propanol:7g Ethylene glycol:3g</td>
</tr>
<tr>
<td>Mn</td>
<td>Mn(NO₃)₂6H₂O 2.8704g</td>
<td>F-127:1g</td>
<td>Propanol:7g Ethylene glycol:3g</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron Acetate 2.0g</td>
<td>F-127:1g</td>
<td>Propanol:10g</td>
</tr>
<tr>
<td>Ce</td>
<td>Ce(NO₃)₂6H₂O 4.3422g</td>
<td>F-127:1g</td>
<td>Propanol:10g</td>
</tr>
</tbody>
</table>
Figure 1 shows typical XRD patterns for mesostructured metal oxides before and after organic template removal.

![XRD Patterns](image)

Figure 1. XRD pattern of mesoporous: (1) copper oxide, (a) as-made (b) after template removal, (2) cobalt oxide, and (3) cerium oxide.
The as-made copper inorganic/polymer mesostructure shows diffraction peaks with lattice spacings $d = 173, 122, 100$ Å. The $d$-value ratios for these peaks are $\sqrt{2} : \sqrt{4} : \sqrt{6}$ which are indexable as (110), (200), (211) reflection respectively, in the cubic $Im\bar{3}m$ space group. After removal of the organic block copolymer template, five XRD peaks are observed with $d$ spacings of 150, 106, 87, 67, 61 with ratios $\sqrt{2} : \sqrt{4} : \sqrt{6} : \sqrt{10} : \sqrt{12}$ which are similarly indexable as (110), (200), (211), (310) and (222) reflections of the cubic $Im\bar{3}m$ space group. Upon removal of the template by thermal treatment (to promote metal oxide cross-linking) followed by extraction with ethanol, the basal spacing is observed to decrease by 23 Å. Wide-angle X-ray diffraction studies of calcined samples also clearly show broad peaks that can be indexed according to crystalline metal oxide phases that indicate that the mesopore walls are crystalline in nature.

Figure 2 shows the results of thermogravimetric analysis of as-made 3D mesoporous metal oxide.

![Figure 2: Thermogravimetric weight loss and DTA curves for as-synthesized mesoporous copper oxide.](image)

Figure 2. Thermogravimetric weight loss and DTA curves for as-synthesized mesoporous copper oxide.
Thermogravimetric experiment results indicate that the block copolymers are completely removed upon calcinations in air at 400 °C.

The XRD peak assignment was further confirmed by TEM. TEM image for the mesopore arrangement is shown in Figure 3.

![Figure 3. TEM image of mesoporous: (a) copper oxide and (b) cerium oxide.](image)

A regular arrangement of bright spots and well-ordered large channels reveals that the mesoporous material is of the three-dimensional-cage type. A square lattice of pores can be clearly seen in the inset conforming a cubic arrangement of 3D mesopores.

Figure 4 shows the SEM image of mesoporous copper oxide and cerium oxide.
SEM analysis showed that the copper oxide and cerium oxide materials consisted of particles with tens of micrometer size and these particles clearly showed the presence of the macropores with size ranging from about 100 nm to 700 nm.

The N$_2$ adsorption-desorption isotherm and BJH pore size distribution for mesoporous copper oxide are presented in Figure 5.

Figure 5. N$_2$ sorption and pore size analysis (inset) of mesoporous CuO.
The sample exhibits isotherm of type IV, typical of mesoporous materials with a well-defined step in the adsorption curve between partial pressures $P/P_0$ of 0.4 to 0.8 and a large hysteresis loop, due to capillary condensation in the mesoporous channels and/or cages. Barret-Joyner-Halenda (BJH) analysis shows that the calcined mesoporous copper oxide exhibited mean pore size of 79 Å. All the mesoporous metal oxides exhibited similar pore size. Absence of textural mesoporosity is indicated by a plateau at the relative pressure of about 0.8 to 1.0.

Table 2 lists the pore size and surface areas of various mesoporous metal oxides

<table>
<thead>
<tr>
<th>Element</th>
<th>Pore size (nm)</th>
<th>Area ($m^2g^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>8.2</td>
<td>133.6</td>
</tr>
<tr>
<td>Co</td>
<td>7.9</td>
<td>113.9</td>
</tr>
<tr>
<td>Cr</td>
<td>7.6</td>
<td>96.2</td>
</tr>
<tr>
<td>Ni</td>
<td>6.7</td>
<td>89.5</td>
</tr>
<tr>
<td>Mn</td>
<td>8.1</td>
<td>79.9</td>
</tr>
<tr>
<td>Fe</td>
<td>7.8</td>
<td>105.1</td>
</tr>
<tr>
<td>Ce</td>
<td>8.5</td>
<td>256.2</td>
</tr>
</tbody>
</table>

A variety of pathways have been used for the synthesis of silicious mesoporous materials such as liquid templating, cooperative templating, neutral templating and ligand assisted templating that have been extended to form mesoporous metal oxides. The majority of these routes entail the use of organic precursor species such as molecular surfactants or block copolymers which allow the formation of liquid crystals.
The neutral templating route using amphiphilic poly (alkylene oxide) block copolymers as structure-directing agents and inorganic salt precursors in non-aqueous solution provides for the synthesis of metal oxide mesostructured that may be less readily accessible by electrostatic templating pathways. For oxides, the rates of hydrolysis and condensation of the inorganic species relative to the rate of assembly of the mesostructure is crucial. Deterrence of crystallization is an import prerequisite for enhanced framework cross-linking. For example, by using inorganic salt precursors in a predominantly nonaqueous media, the rates of precursor hydrolysis, condensation of metal species and precipitation of mesostructured oxides can be performed in a controlled manner and I have been able to obtain very stable mesostructures of Cu, Co, Cr, Ni, Mn, Fe, Ce.

Figure 6 shows the toluene concentration decrease profile as a function of the reaction time using the developed mesoporous oxides. Figure 7 shows the toluene removal performance after 25 hours.

![Figure 6. Decrease in toluene concentration with time for different mesoporous metal oxides.](image-url)
It can be observed from Figures 6, 7 that chromium oxide (Cr_2O_3) shows the best toluene removal performance with about 93.2% removal rate after 25 h. Cerium oxide shows about 15% removal toluene removal activity after 25 h. All the mesoporous metal oxides of Cu, Co, Fe, Mn, and Ni show <10% of toluene conversion after 25 h of reaction.

Presence of high density of mobile lattice oxygen due to large structural strain in the mesoporous chromium oxide framework could be responsible for the very strong chemical interaction of toluene with these lattice oxygen resulting in high toluene removal capacity for mesoporous chromium oxide. Such strong interactions between lattice oxygen and adsorbed toluene species are probably not present in other mesoporous metal oxides. In addition, partial oxidation and/or decomposition of
toluene can not be ruled out due to very powerful oxidizing property of Cr$_2$O$_3$. In fact, formation of some CO$_2$ could be observed after 25 h of reaction. Further characterization of these highly active mesoporous chromium oxides by methods like EXAFS, XPS, and so forth is necessary in order to determine the exact nature of Cr species in the mesoporous structure.

3.4. Summary

I have successfully prepared novel mesoporous oxide of Cu, Co, Ni, Mn, Fe, Cr and Ce for the first time by neutral templating route in a mixed organic medium using triblock copolymer as the template and metal nitrate as the inorganic source. These materials have three-dimensional (3D) cubic arrangement of mesopores with semi-crystalline walls as confirmed by XRD and TEM analysis. All the mesoporous metal oxides exhibited similar pore sizes. Among different metal oxides, mesoporous chromium oxide showed best toluene elimination activity with >93% toluene removal after 25 h under ambient temperature. All other mesoporous metal oxides of Cu, Co, Ni, Mn, Fe, and Ce, showed <15% of toluene conversion under ambient temperature. Results suggest that these mesoporous oxides are promising good candidate for VOCs removal.
3.5. References


Chapter 4

3D mesoporous chromium oxide as efficient material for VOCs elimination

Abstract

A 3D mesoporous chromium oxide prepared by a neutral templating route showed exceptionally high capacity for the elimination of volatile organic compounds (VOCs). The toluene removal was both by sorption as well as catalytic as indicated by CO₂ evolution. The material contains chromium species with mixed oxidation states mainly between +2 and +5 was observed XPS analysis. 3D mesoporosity, high surface areas, high oxidizing power along with probable ready evolution of active lattice oxygen, are responsible for efficient removal of VOCs at low temperatures. Although the 3D mesoporous chromium oxide had ~0.1 times the surface area than that of mesoporous silica, the chromium oxide showed much better toluene removal ability. At ambient conditions, the material acts as a selective sorbent for VOCs, while at higher reaction temperature it can be an effective and selective deep oxidation catalyst for VOCs.
4.1. Introduction

Crystalline chromium oxide, which favors the formation of CO₂, could be the most promising candidate for the total oxidation of organics [1]. Ordered mesostructures of transition metal oxide [2, 3] are of immense interest in the areas such as catalysis, sorption, chemical and biological separation, photonic and electronic devices, and drug delivery [4]. Preparations of well-ordered mesoporous oxides of Mn [5], Ti [6, 7], V [8], Zr [9], W [6], Nb [6, 8], Ta [6, 9] have been successfully reported. But the preparation of three-dimensionally (3D) ordered mesoporous oxides of Cu, Co, Cr, Ni, Fe have been most difficult though it has been possible to prepare unstable lamellar phases of these materials. Recently hexagonally ordered mesoporous nickel oxide [10] and wormhole-like mesoporous iron oxide [11] have been reported. But, a nanoporous 3D structure of oxides is more suitable for application as catalyst or adsorbent due to an easier diffusion of reactants by overcoming mass-transfer limitations [12]. Transitional metal oxides are more susceptible to hydrolysis, redox reactions or phase transitions and possess a number of different coordination numbers and oxidation states [13], making it rather difficult to prepare their mesoporous structure unlike silica and aluminosilicates which can easily form stable mesoporous structure. The neutral templating route has been successfully used for the synthesis of metal oxide mesostructures [2, 6] that have been less readily accessible by electrostatic templating pathways [3, 7]. In chapter 3, I demonstrated for the first time that a 3D mesoporous transition metal oxide material could be prepared by a neutral templating route [14]. I observed that mesoporous chromium oxide showed exceptionally high toluene removal/oxidation ability. My intention was to exploit such material with 3D mesoporosity, high surface area and high oxidizing power along with probable ready
evolution of active lattice oxygen, to prepare a commercially viable, cost-effective catalyst/sorbent system for efficient removal of VOCs at low temperatures.

Herein, I present a detailed characterization of the nature of chromium site in the mesoporous chromium oxide samples and also more detailed evaluation of the VOCs removal ability, in order to identify the mechanism of VOC removal over these materials.

4.2. Experimental

4.2.1. Synthesis 3D mesoporous chromium oxide

Triblock copolymer and chromium nitrate were used as the template and inorganic source, respectively. Typical molar gel composition was 134 Cr : 1115 propanol : 1080 EG : 1 F-127 (or P-123; Sigma-Aldrich). The samples were calcined by heating gradually (1 °C /min.) to 300-500 °C. As-made mesoporous chromium oxide samples were transparent which changed to fluffy foam-like material after heating in air to 150°C. Thermogravimetric experiments indicated that the template molecules are completely removed by calcinations of as-made sample at 400°C.

4.2.2. VOC removal analysis

As an evaluation gas, a gas mixture was used which contained, toluene: 103.3 ppm, oxygen: 20% and the balance of nitrogen. 0.4 g each of the aforementioned catalyst samples and the evaluation gas were put in a 5-liter gas container. The gas was analyzed after different time intervals by GC (Shimadzu; GC-14B) and CO₂
analyzer (LI-COR; LI-6242). The toluene conversion was determined from the equation:

\[
\text{Toluene removal (\%) = \left\{ \frac{(\text{Toluene Concentration in gas container without catalyst}) - (\text{Toluene concentration in gas container with catalyst})}{\text{Toluene Concentration in gas container without catalyst}} \right\} \times 100.}
\]

A packed-bed reactor was used to evaluate catalysts activity in the complete oxidation of toluene as a function of temperature (space velocity 30000 h\(^{-1}\), catalysts \(\sim 2.0\text{g}\), particle size 20-40 mesh, toluene: 100ppm, oxygen: 18% and the balance of nitrogen). At the onset of reaction, the catalyst was pretreated with reactant mixture at 180\(^{\circ}\)C for 1.5 h to prevent over-estimation of toluene conversion caused by adsorption of toluene in the initial stages of test. The temperature was lowered to 60\(^{\circ}\)C and then at each temperature analysis of reaction products were taken for a time-on-stream of 30 min. The reaction temperature was increased by 5-25\(^{\circ}\)C for each measurement. For toluene removal capacity analysis different desired volumes of liquid toluene were injected using a microsyringe into a stream of flowing air and evaporated via a preheater (kept at 80\(^{\circ}\)C) and filled into a gas container taking 5 L of flowing air (containing the toluene vapor) to obtain different initial toluene concentrations, varying from 5 to 105ppm. The initial and final toluene concentrations were confirmed by GC analysis.

4.3. Results and discussion

4.3.1. Characterization

Typical X-ray diffraction (XRD) patterns for mesostructured chromium oxide before and after organic template removal are shown in Figure 1. The as-made
chromium inorganic/polymer mesostructure shows diffraction peaks with lattice spacings, \(d\) of 173, 122, and 100 Å. The \(d\)-value ratios for these peaks are \(\sqrt{2}:\sqrt{4}:\sqrt{6}:\), and they are indexable as (110), (200), (211) reflections respectively, in the cubic \(Im3m\) space group. Five major XRD peaks, with \(d\) spacings of 150, 106, 87, 67, 61 Å and \(d\)-value ratios \(\sqrt{2}:\sqrt{4}:\sqrt{6}:\sqrt{10}:\sqrt{12}\), are observed after removal of the organic block copolymer template. They are similarly indexable as the (110), (200), (211), (310) and (222) reflections of the cubic \(Im3m\) space group. The basal spacing is observed to decrease by 23 Å upon removal of the template due to lattice contraction.

![Figure 1. XRD pattern of mesoporous chromium oxide: 1) as-made and 2) template-free (150°C treated and ethanol extracted).](image)

The wide-angle X-ray diffraction pattern of the template-free calcined sample (Figure 1, inset) clearly shows peaks that can be indexed according to the rhombohedral phase of crystalline Cr\(_2\)O\(_3\), thus indicating the presence of trivalent Cr in the sample. However,
the presence of other mixed-valent Cr species cannot be ruled out because XPS analysis revealed the presence of Cr species with different oxidation states.

The XRD peak assignment was further confirmed by transmission electron microscopy (TEM). The TEM image for the mesopore arrangement is shown in Figure 2, where a regular arrangement of bright spots and ordered channels is observed that is attributed to the three-dimensional cubic ordered arrangement of mesopores.

![Figure 2. TEM of mesoporous chromium oxide sample.]

Barret-Joyner-Halenda (BJH) analysis of the nitrogen adsorption data, assuming cylindrical pores, shows that the calcined mesoporous chromium oxide exhibit mean pore size of 7.9 nm and wall thickness of 13.3 nm, estimated using XRD unit cell parameter ($a_o$) value of 21.2 nm. The template-free sample (after ethanol extraction) had 212 m$^2$/g surface area, which decreased to 96 m$^2$/g after calcinations at 400 °C and further decreased to 78 m$^2$/g after calcinations at 500 °C.
In order to assign the oxidation state of chromium species the sample was analyzed by EPR spectroscopy. Figure 3 shows the ESR spectrum of calcined mesoporous chromium oxide. The ESR spectrum shows a broad isotropic signal at \( g = 1.98 \) with a peak-to-peak line width of 500 G which is the so-called \( \beta \)-signal ascribed to \( \text{Cr}_2\text{O}_3 \)-like clusters [15]. This signal is therefore assigned to \( \text{Cr}^{3+} \) clusters of \( \alpha \)-\( \text{Cr}_2\text{O}_3 \) phase. No signal due to higher valent Cr species could be observed even though XPS analysis indicates the presence of different oxidation states. It is probably due to masking of the narrower signal due to higher oxidation states (so-called \( \gamma \)-signal [15]) by the very broad and intense \( \beta \)-signal ascribed to \( \text{Cr}_2\text{O}_3 \)-like clusters.

![Figure 3. EPR spectra of mesoporous and commercial chromium oxide samples.](image)

Figure 4a shows the Cr 2p XPS spectra of mesoporous chromium oxide and commercial \( \text{Cr}_2\text{O}_3 \) samples. The commercial \( \text{Cr}_2\text{O}_3 \) material’s spectrum shows a
symmetrical band with a peak position at 576.5 eV for Cr 2p\textsubscript{3/2} corresponding to trivalent Cr\textsuperscript{3+} species. However, mesoporous chromium oxide samples show a broad and complicated band indicating presence of Cr in multiple oxidation states from +2 to +6. From the literature, it can been noted that Cr\textsuperscript{2+}, Cr\textsuperscript{3+}, Cr\textsuperscript{5+}, Cr\textsuperscript{6+} species appear at the binding energies of 576, 577, 579, 580 eV respectively [16]. Deconvolution of the Cr 2p\textsubscript{3/2} XPS spectra of the mesoporous chromium oxide samples shown in Figure 4b clearly indicates the presence of multiple oxidation states of chromium. The mesoporous chromium oxide has about 94.3% of Cr present in +2 to +5 oxidation state while the sample.

![Figure 4 (a). Cr 2p XPS spectra of mesoporous chromium oxide (Meso-CrOx) and commercial Cr\textsubscript{2}O\textsubscript{3} samples.](image-url)
4.3.2. Activity

A sample (0.4 g) of the 3D mesoporous chromium oxide calcined at 500 °C showed the highest toluene removal ability among all these materials, with 52% toluene removal and 11 ppm CO₂ formation (2% conversion) after 25 h at room temperature (sample 3 in Figure 5). The toluene-removal performance increased to 65%, with 66 ppm CO₂ formation (12% conversion), when the temperature was increased to 85 °C (sample 4). An increase in toluene-removal ability with increasing temperature is an indication of catalytic oxidation of toluene at low temperatures. This is the first report of partial catalytic decomposition of VOCs by mesoporous transition-metal oxides at low temperature. In comparison, mesoporous silica with a surface area of 1120 m²/g showed 42% toluene removal at room temperature (sample 5), which decreased to 26%
when the reaction temperature was increased to 85 °C (sample 6). Even though the 3D mesoporous chromium oxide has a surface area about 10 times lower surface area than that of mesoporous silica, it still shows a much higher toluene removal ability.

Figure 5. Toluene removal (x) over various chromium oxide samples: (1) commercial Cr₂O₃, (2) commercial CrO₃, (3) mesoporous CrOₓ (at room temperature), (4) mesoporous CrOₓ (at 85 °C), (5) mesoporous SiO₂ (room temperature), and (6) mesoporous SiO₂ (at 85 °C). Inset shows the toluene removal rate per unit area of the samples (x/a).

The toluene-removal ability per unit area is about 18 times higher at room temperature, and about 35 times higher at 85 °C, for mesoporous chromium oxide than for mesoporous silica (Figure 5, inset). It was possible to achieve 94% toluene removal ability using 1.0 g of 3D mesoporous chromium oxide. Commercial hexavalent and trivalent chromium oxide (Wako Pure Chemical) samples (sample 1 and 2) gave less than 1% toluene removal. A high-surface-area amorphous chromia aerogel (278 m²/g)
[17], which contains mostly trivalent chromium species (from XPS analysis), showed a low toluene-removal performance (<10%).

When the toluene combustion reaction was evaluated in a continuous-flow reactor, the toluene decomposition started well below 100 °C and it was possible to reach 100% toluene combustion at temperature of 280-300 °C (Figure 6).

The same 3D mesoporous chromium oxide catalyst (0.4 g) also showed 94% acetaldehyde removal performance after 25 h of reaction, at room temperature (from a 27 ppm acetaldehyde feed in air) (Figure. 7). It was also observed that commercial Cr$_2$O$_3$ and CrO$_3$ samples show very low acetaldehyde removal performance.
The above results imply that the 3D mesoporous chromium oxide with mixed oxidation state are the most active material for toluene removal. Strong $\pi$-$d$ interaction resulting from the overlapping between the $d$ orbitals of metal cation in mesoporous Cr$_2$O$_3$ structure and $\pi$ orbitals of toluene molecules resulting in the formation of so-called $\pi$-complex [12, 13] is probably responsible for the high toluene removal performance (Figure 8). In addition the possibility of the interaction of C-H bonds with metal cations via hydrogen bondings [14] and to cause C-H bond breaking by oxidative addition [17] is well known. These interactions are thought to primarily involve overlapping of $d$ orbitals of the metal with $\sigma$ and $\sigma^*$ orbitals of the C-H bond. These overlappings can cause the breaking of the C-H bond and the formation of C-Cr and Cr-H new bonds (oxidative addition) leading to further oxidation via C-O bond formation [18] which is probably favored by active lattice oxygen species in mesoporous chromium oxide. That is to say, the mixed oxidation state of the 3D mesoporous chromium oxide sample, as well as its high surface area and 3D
mesoporosity, is probably responsible for the exceptionally high toluene-removal ability. Strong π-d [18] and d-σ interactions [19], the possibility of ready evolution of active lattice oxygen species, as well as the high oxidizing power of higher valent Cr species favored by lattice strain, is probably responsible for the excellent toluene-removal ability of this mesoporous chromium oxide.

These 3D mesoporous oxides can be excellent materials for sorption of VOCs at room temperature from indoor, which can be directly decomposed over the same catalyst at higher temperatures, thereby eliminating the need of recovery of VOCs from the sorbent as is done in case of conventionally used VOCs removal materials such as activated carbon or porous silica. We were able to completely decompose the toluene adsorbed on the surface of the catalyst by thermal treatment at around 350°C, and the regenerated catalyst could be reused without any loss in activity. XPS analysis did not show any change in the oxidation state of Cr after regenerating the 3D mesoporous oxide. There was little change in the surface area of the regenerated catalysts.

![Figure 8. Probable reaction mechanism for toluene adsorption and decomposition over 3D mesoporous chromium oxide.](image-url)
4.4. Summary

I report on a novel promising mesoporous chromium oxide sorbent/catalyst with high VOCs elimination ability. The material is prepared by a neutral templating route using a block co-polymer template in a non-aqueous medium. XRD and ESR analysis showed the presence of Cr$^{3+}$ species in a $\alpha$-Cr$_2$O$_3$ phase. XPS analysis showed that the material contains chromium species with mixed oxidation states between +2 and +5. The 3D mesoporous chromium oxide had ~0.1 times the specific surface area of that of mesoporous silica, but it showed much better toluene removal ability. I expect to develop a novel dual-function sorbent/catalyst medium under ambient conditions, the material acts as a selective sorbent for the VOCs. When the solid is heated to higher reaction temperature, it can be an effective and selective deep oxidation catalyst for the VOCs so that the recovery and/or incineration step required in the case of current commercial VOCs adsorbents can be eliminated. These mesoporous oxides can also have potential applications as catalysts for various selective organic transformations, as supports, adsorbents, separation materials and in sensors, porous electrodes or electrolytes, electromagnetic and electronic devices.

4.5. References


Monodisperse, bimodal mesoporous ceria catalysts and adsorbents for VOCs elimination

Abstract

I report for the first time a novel bimodal mesoporous crystalline ceria with nanometer-sized, pseudo-spherical, monodisperse particles. This mesoporous ceria was prepared using block-copolymer templates and non-aqueous solvent. The surface areas, mesopore structure and thermal stabilities of the final product is found to depend on the gel composition. The material shows very high sorption and catalytic property for the elimination of acetaldehyde compared to semicrystalline mesoporous ceria and non-porous crystalline ceria materials. The material also showed nearly 2-times or higher acetaldehyde elimination ability than conventional materials.
5.1. Introduction

CeO$_2$-based mixed oxides and supported CeO$_2$ are effective catalysts for the oxidation of different hydrocarbons, for the production and purification of H$_2$ and for the removal of organics from polluted water [1, 2]. Such catalytic prowess of ceria comes from its ability to shift between two oxidation states, Ce(III) and Ce(IV), and the high mobility of bulk oxygen species—properties that allow ceria to behave as an oxygen buffer [3]. Moreover, Namai et al. reported defect mobility even at room temperature due to hopping of lattice oxygen [4] which would be important for making ceria a very promising ambient temperature catalyst. Ceria and ceria-based compounds obtained in nanostructured forms are expected to be promising as materials that show interesting properties through shape-specific and/or quantum size effect [5]. In addition, a bimodal mesoporous structure with monodisperse spherical particles would result in very high surface area, thermally stable material that are more amenable to practical applications in areas such as catalysis. Accordingly, several studies report the fabrication of mesoporous crystalline ceria [6-10]. However, the ceria mesostructure often undergoes a severe breakdown during the final crystallization step, which leads to rather ill-defined porosity without controlled nanocrystallinity in the pore walls, in terms of the spatial distribution and the size of the oxide nanocrystals. Lyons et al. [6] reported a hexagonal structure for CeO$_2$ with well crystallized walls after calcination at 600 °C. Similar results were previously reported by Terribile et al. [7]. Recently preparation of well ordered, thermally stable mesoporous ceria has been reported, but these methods have limitations in terms of the cumbersome procedures involved—such as using preformed nanoparticle colloids [8-10], functionalization of these nanoparticles [8] and self-assembly using specially prepared block-polymers [9, 10] and ionic-liquids
Monodisperse, bimodal ceria catalysts and adsorbents for VOCs elimination

[10]. In Chapter 4, I reported mesoporous chromia material that showed very promising results for the elimination of volatile organic compounds [11]. Herein, I report a simple method to prepare mesoporous ceria with different porosities depending on the gel composition using a modified sol-gel technique and evaporation induced self-assembly (EISA) in a non-aqueous medium using a nitrate salt precursor and a commercially available block-polymer template.

5.2. Experimental

5.2.1. Synthesis

Triblock copolymer and cerium nitrate were used as the template and inorganic source, respectively for preparing the material. The cerium precursor concentration was varied for the preparations, and samples prepared at two different concentrations are reported here. In a typical synthesis, 1 g of Pluronic F-127 block copolymer (Sigma-Aldrich) was dissolved in 10 g of propanol. To this solution 0.01 mol of Ce(NO₃)₂₃H₂O (Wako Pure Chemical) was added with vigorous stirring for 30 min. The typical molar gel composition was 70-134 Ce : 2230 propanol : 1 F-127 (sample ‘A’ gel composition 134 Ce : 2230 propanol : 1 F-127; sample ‘B’ gel composition 70 Ce : 2230 propanol : 1 F-127). The resulting sol solution was then aged at 40-50 °C for 2-7 days and then heated gradually (heating rate, 1 °C/min.) to 120-200 °C and finally the organic template molecules were removed by extracting with ethanol. In a specific synthesis, the sol was aged at 45 °C for 7 days followed by heating at 120 °C for 6 h. The resulting product was extracted overnight with ethanol and then calcined at 400 °C (heating rate, 1 °C/min.) for 6 h. To find the optimum synthesis conditions,
samples with higher (>140) and lower (<60) Ce/template ratios were also prepared. For comparison, a commercial crystalline ceria (sample ‘C’) (Wako Pure Chemical) was used.

5.2.2. Characterization

The powder X-ray diffraction (XRD) patterns were obtained on a Rigaku Rint-2400 instrument equipped with a rotating anode and using Cu Kα radiation (wavelength = 0.1542 nm) in the range 1–10° 2θ and 10–75° 2θ. An accelerating voltage of 40 kV and current of 30 mA were used. Nitrogen adsorption-desorption isotherms were obtained at −196 °C on a Micromeritics ASAP 2010 apparatus. Prior to measurement, the samples were heated at 200 °C for 2 h and finally outgassed to 10⁻³ Torr. BET and BJH analysis were used to determine the total specific surface areas ($S_{BET}$), pore volumes and pore size distribution of the samples. Transmission electron microscopy (TEM) observations were made using a JEOL JEM200CX instrument at an accelerating voltage of 200 kV. For TEM, samples were dispersed in absolute ethanol ultrasonically, then the suspension was dropped onto copper grids coated with amorphous carbon film, and the solvents determine the macropore volume and allowed to evaporate. Scanning electron microscopy (SEM) observations were made using a JEOL JSM890 instrument. A Quantachrome Autoscan 60 Mercury Porosimeter was used to determine the volume and size.
5.2.3. Stability test

The material was heat treated in air to 700°C (heating rate, 1°C/min.) to check the thermal stability. The material was heat treated under reducing condition, in 5% hydrogen in nitrogen to 300°C (1°C/min.).

5.2.4. Feasibility test

As an evaluation gas, a gas mixture was used which contained, 80 ppm acetaldehyde, 20% oxygen and the balance of nitrogen. Acetaldehyde is a major indoor air pollutant responsible for sick-building syndrome so it was selected as a model volatile organic compound (VOC) [11, 12]. 100 mg each of the catalyst/adsorbent samples and the evaluation gas mixture were put in a 5-liter gas container. The gas was analyzed after different time intervals by GC (Shimadzu; GC14B) and CO₂ analyzer (LI-COR; LI6262). The acetaldehyde conversion was determined from the equation: acetaldehyde removal (%) = [{(acetaldehyde concentration in gas container without catalyst) – (acetaldehyde concentration in gas container with catalyst)}/acetaldehyde concentration in gas container without catalyst] × 100.

For comparison conventional VOCs removal materials, activated carbon (BFG from CATALAR Corporation with 1060 m²/g surface area), titania photocatalyst (UV-100 from Sachtleben Chemie GmbH, under UV irradiation using 500 watt high-pressure mercury arc lamp), mesoporous silica (996 m²/g surface area) and microporous zeolite beta (Süd-Chemie) were used.
5.3. Results and discussions

5.3.1. Physical and morphological properties

Samples prepared from gel composition 134 Ce : 2230 propanol : 1 F-127 (Sample ‘A’), and calcined at 400 °C showed formation of pseudo-spherical, 240 ± 40 nm size monodisperse particles, as observed from FE-SEM analysis (Figure 1a). TEM observation showed the presence of particles of smaller sizes, and further revealed that the pseudo-spherical, monodisperse particles (Figure 1b) are made of tight aggregation of ceria nanoparticles, resulting in disordered wormhole-like mesopores (~5 nm in size) (Figure 1c). High resolution TEM analysis shows the presence of (<2 nm size) secondary, intracrystalline mesoporosity inside the ceria nanoparticles (Figure 1d). Figure1d clearly shows that the pore walls exhibit well-defined (111) surface planes. Also, the selected area electron diffraction (SAED) pattern (Figure 1e) confirms the formation of the (111) surface plane. Ceria crystallizes in a cubic fluorite structure and exposes the thermodynamically most stable (111) surface [4]. This surface is the oxygen termination of stoichiometric O-Ce-O trilayers stacked along the (111) direction and also represents the major fraction of the catalytic surface in the ceria nanocrystallites [13].
Monodisperse, bimodal ceria catalysts and adsorbents for VOCs elimination

Figure 1. (a) FE-SEM, (b) TEM, (c) high-magnification TEM showing wormhole-like primary mesopores (~5nm), and (d) high-resolution TEM showing intra-particle secondary mesopores (<2nm), for monodisperse, psuedo-spherical CeO$_2$ nanostructure with bimodal mesoporosity. (e) Selected area electron diffraction pattern.
XRD analysis showed a very broad peak in the low-angle region due to disordered mesoporosity (Figure 2a). Wide angle XRD analysis clearly shows peaks corresponding to the crystalline cubic fluorite ceria phase (PDF-ICDD34-0394) (Figure 2b). This material was thermally stable up to 700 °C without any considerable change in structure and porosity. The sample after reduction in H₂ (300 °C) did not show any change in structure and porosity.

Figure 2a. Low-angle XRD pattern of mesoporous crystalline ceria.

Figure 2b. Wide-angle XRD pattern of mesoporous crystalline ceria.
The sample exhibits N\textsubscript{2} adsorption-desorption isotherm with steps between partial pressures $P/P_0$ of 0.3 to 0.8, and hysteresis loop, due to capillary condensation in the mesoporous channels and/or cages (Figure 3). The sharp increase in adsorption at higher $P/P_0 (>0.9)$ could be due to the presence of macropores at the contact sites between the spherical particles, but from mercury porosimetry analysis no pores with $>10$ nm size could be measured (Figure 4). It is interesting to note that the sample prior to calcination at 400 °C (i.e. the sample heated to 120 °C and extracted with ethanol) showed only one type of mesopores with mean pore size 5.0 nm (Figure 5) and 266 m\textsuperscript{2}/g surface areas. However, BJH analysis of the adsorption isotherm for the calcined mesoporous cerium oxide shows two peaks corresponding to mean pore sizes of 1.9 nm and 5.0 nm indicating a bimodal pore size distribution (Figure 3, inset). The sample had 193 m\textsuperscript{2}/g BET surface areas. This implies that secondary pores (about 1.9 nm in size) are created during the heat treatment process due to the sintering and crystallization of ceria nanoparticles. t-plot analysis of the adsorption isotherm did not show the presence of any micropores.

![Figure 3. Nitrogen sorption isotherm of crystalline, monodisperse, psuedo-spherical, mesoporous ceria (sample A). Inset shows the bimodal pore size distribution.](image-url)
Figure 4. Pore size distribution analysis using mercury porosimetry for crystalline, monodisperse, pseudo-spherical, mesoporous ceria.

Figure 5. Nitrogen sorption isotherm of monodisperse, pseudo-spherical mesoporous ceria sample before calcination (sample A, extracted). Inset shows the pore size distribution.

The mesoporous ceria samples prepared at lower Ce/template ratios, (gel with composition 70 Ce : 2230 propanol : 1 F-127), had a very low surface area of 12 m$^2$/g after calcination at 400°C. But the surface area before calcination (and after template removal by extraction) was 112 m$^2$/g and the material was semicrystalline as observed
from wide-angle XRD analysis. This semicrystalline sample showed a type IV $N_2$ sorption isotherm with mean pore diameter (BJH) of 4.0 nm (Figure 6). The extracted sample showed disordered aggregation of ceria particles at lower magnification with 100 nm range macropores (Figure 7) while a higher magnification image shows the presence of intracrystalline mesoporosity in the material (Figure 8). During calcination as the material crystallizes there is rapid sintering and agglomeration of ceria nanoparticles resulting in mesopore collapse as observed also from TEM analysis (Figure 9).

Samples prepared with higher Ce/template ratio (>140) were completely amorphous without any mesoporosity. While, samples prepared with Ce/template ratios <60 were completely amorphous without any mesoporosity. These results indicate that the Ce/template ratio is very crucial, and there is an optimum ratio (~ 140) to obtain the desired thermally stable material with high surface area. The samples prepared at higher ratios are not mesoporous while those prepared at lower ratios (~ 70) are mesoporous but have poor thermal stability and low surface area.

Figure 6. Nitrogen sorption isotherm of mesoporous ceria (sample B, extracted) prepared from gel composition 70 Ce : 2230 propanol : 1 F-127. Inset shows the pore size distribution.
Figure 7. TEM image of mesoporous semicrystalline ceria samples (sample B, extracted) prepared from gel composition 70 Ce : 2230 propanol : 1 F-127.

Figure 8. High-resolution TEM image of mesoporous ceria samples (sample B, extracted) prepared from gel composition 70 Ce : 2230 propanol : 1 F-127.
5.3.2. Acetaldehyde removal ability

Acetaldehyde is a major component of indoor air pollutants. I evaluated my materials for the elimination of acetaldehyde and compared them with other available VOCs adsorbents/catalysts. Figure 10 shows the acetaldehyde removal ability of mesoporous ceria sample ‘A’ (prepared from gel with composition 134 Ce : 2230 propanol : 1 F-127), sample ‘B’ (prepared from gel with composition 70 Ce : 2230 propanol : 1 F-127) and non-porous commercial ceria (sample ‘C’) at 25 °C and 80 °C.
Figure 10. Acetaldehyde removal ability of ceria samples at 25°C and 80°C (24h): sample “A” is crystalline monodisperse, psuedo-spherical, bimodal mesoporous ceria (193 m²/g), “B” is semicrystalline mesoporous ceria (112 m²/g), “C” is non-porous crystalline ceria (11 m²/g).

Crystalline monodisperse, bimodal mesoporous ceria (sample ‘A’) showed high acetaldehyde removal ability at ambient temperature (25°C), with about 92% acetaldehyde removal (after 24 h) and about 33% conversion (in terms of CO₂ formation from acetaldehyde decomposition reaction, CH₃CHO + 5/2O₂ → 2CO₂ + 2H₂O wherein 1 mole of decomposed CH₃CHO is converted to 2 moles of CO₂). Interestingly, by increasing the reaction temperature to 80°C, 100% acetaldehyde removal could be obtained. This acetaldehyde removal performance is nearly twice as high as that for the conventional VOCs removal materials such as activated carbon or mesoporous silica with much higher surface areas (Table 1). In contrast uncalcined semicrystalline mesoporous ceria (sample ‘B’ prepared from gel composition 70 Ce : 2230 propanol : 1 F-127, heated at 120 °C and extracted) showed only 65% acetaldehyde removal (with about 4% CO₂ formation), and when the reaction
temperature was raised to 80 °C most of the acetaldehyde was desorbed and the acetaldehyde removal ability dropped to only 9%. This implies that a completely crystalline ceria structure rather than a semicrystalline structure is necessary to obtain high VOCs elimination ability. Commercial non-porous crystalline ceria with about 11 m²/g surface area showed only about 8-11% acetaldehyde removal at temperatures ranging from 25 to 80 °C. This low removal ability is attributable to the very low surface area of this commercial ceria. The mesoporous ceria (sample ‘A’) reduced in H₂ showed similar removal performance as the calcined sample (see Table 1) but lower conversion (about 18%). The possibility of reoxidation of reduced ceria surface during evaluation can not be ruled out.
Table 1. Acetaldehyde removal ability of crystalline mesoporous ceria, and conventional materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface area m²/g</th>
<th>Pore volume cm³/g</th>
<th>Pore size nm</th>
<th>Morphology</th>
<th>Acetaldehyde removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25 °C (1h) 80 °C (24h)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>1060</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>35 31</td>
</tr>
<tr>
<td>Mesoporous silica</td>
<td>996</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>45 36</td>
</tr>
<tr>
<td>Commercial ceria (C)</td>
<td>11</td>
<td>-</td>
<td>-</td>
<td>Irregular</td>
<td>8 11</td>
</tr>
<tr>
<td>Semi-crystalline mesoporous ceria (B)</td>
<td>112</td>
<td>0.24</td>
<td>4.0</td>
<td>Irregular</td>
<td>65 9</td>
</tr>
<tr>
<td>Crystalline mesoporous ceria (A) (400 °C)</td>
<td>193</td>
<td>0.46</td>
<td>1.9, 5.0</td>
<td>Pseudo-spherical</td>
<td>81 100</td>
</tr>
<tr>
<td>Crystalline mesoporous ceria (A) (reduced)</td>
<td>139</td>
<td>0.28</td>
<td>1.9, 5.0</td>
<td>Pseudo-spherical</td>
<td>78 100</td>
</tr>
<tr>
<td>Crystalline mesoporous ceria (A) (700 °C)</td>
<td>156</td>
<td>0.35</td>
<td>1.9, 5.0</td>
<td>Pseudo-spherical</td>
<td>- -</td>
</tr>
</tbody>
</table>
5.4. Summary

Thus, I report for the first time that it is possible to prepare bimodal mesoporous, monodisperse ceria nanostructures with high surface area and high thermal stability, by a very straightforward modified sol-gel technique using a commercially available block-polymer template. The formation of these materials was highly dependent on the gel composition as well as the pretreatment method. The material shows very high acetaldehyde removal ability at ambient conditions, which could find application in air-purification materials. Besides, this simple sol-gel technique to prepare monodisperse, spherical, bimodal mesoporous ceria is highly amenable to the preparation of homogeneous coatings for several other catalytic applications.

5.5. References


Chapter 6

Preparation and characterization of mesoporous ceria-titania

Abstract

A mesoporous ceria-titania using a neutral templating route is reported. The as-made inorganic-template hybrid mesostructured matrix showed a broad low-angle XRD peak characteristic of mesoporous materials. Careful thermal treatment of the matrix allowed the subsequent densification of the inorganic component and removal of the organic component so that a high quality mesoporous ceria-titania was formed as observed. The calcined material showed the formation of fluorite type structure of CeO$_2$ but no crystalline titania phase was observed. The mesoporous structure remained even after high temperature treatment. The material had high surface area after calcination up to the temperatures of 700°C, with well-dispersed ceria and titania components and negligible bulk oxide formation. These novel mesoporous ceria-titania materials showed high performance for the removal of toluene.
Chapter 6

6.1. Introduction

Ceria-based materials have received enormous attention due to their applications in various fields such as high temperature ceramics, catalysis and solid oxide fuel cells [1]. CeO$_2$ is a well-known additive in the so-called three-way catalysts for automobile exhaust [2]. In particular, supported CeO$_2$ and CeO$_2$-based mixed oxides are the effective catalysts for the oxidation of different hydrocarbons and for the removal of organics from polluted water from different sources [3-6]. The incorporation of CeO$_2$ to the formulation of oxidation catalysts promotes various catalytic reactions such as CO$_2$ activation [7], CO oxidation [3], CO/NO removal [8], and combustion of hydrocarbons [9]. In all of these applications, two features are mainly responsible for making CeO$_2$ a promising material for use either as a support or as an active catalyst: (i) the redox couple Ce$^{3+}$/Ce$^{4+}$, with the ability of ceria to shift between CeO$_2$ and Ce$_2$O$_3$ under oxidizing and reducing conditions, respectively, and (ii) the ease of formation of labile oxygen vacancies and the relatively high mobility of bulk oxygen species [10]. However, pure ceria is known to be poorly thermostable and undergoes rapid sintering under high temperature conditions, thereby losing oxygen buffer capacity [11, 12]. Therefore, there have been several attempts to overcome this problem. One approach is the substitution of another metal or metal oxide into the ceria lattice, thereby facilitating the formation of mixed oxides [13-18]. Replacing cerium ions by cations of different size and/or charge modifies ion mobility inside the modified lattice, resulting in the formation of a defective fluorite-structured solid solution. Such modifications in the defect structure of ceria confer new properties to the catalyst such as better resistance to sintering at high temperatures and high catalytic activity for various reactions [19]. The mixing of two different oxides could result in
the formation of new stable compounds that may lead to totally different physicochemical properties and catalytic behavior [18]. Ceria can be photoactivated by near-UV-Vis range irradiation [20] while titania is most active photocatalyst. These characteristics suggest that ceria modified titania could be potentially used as a photocatalyst as well as can find application in electrochromic devices [21]. These mixed oxide materials could find application in removal of pollutants like volatile organic compounds (VOCs). Plastics, paints, varnishes, disinfectants, cosmetics, tobacco smoke, and fuels are some of the household sources of VOCs.

High surface area non-porous ceria and ceria-zirconia [22] as well as their mesoporous structures [23] have been prepared by different methods, namely, template-assisted method or homogeneous precipitation and microemulsion methods [22]. Such materials by virtue of their large surface area exhibit greater catalytic activity. With the preparation in 1991 of mesoporous silica a new area of chemistry, allowing the exploitation of high surface area materials, was opened up [24]. The use of surfactants as liquid crystal templating agents so as to create a regular three-dimensional micellar array about which an inorganic precursor could form a framework gives a reliable method to produce ordered mesoporous solids. The subsequent removal of surfactant in a controlled manner yields a material with an open framework with uniform pore dimensions in the range 2-10 nm. This silica-based synthesis has been extended to a number of transition metal and main group oxides using various surfactants and inorganic precursors under different reaction conditions [25, 26]. Herein is reported a neutral templating method employed to form a true mesoporous ceria-titania of uniform pore size with enhanced thermal stability after surfactant removal. Also reported is the detailed characterization of these materials.
and their potential application as novel indoor VOCs removal material at room temperature.

6.2. Experimental

6.2.1. Synthesis mesoporous ceria-titania

Mesoporous ceria-titania with different Ce/Ti ratios (0.5/1, 1/1, 1/1.5) were prepared by a neutral templating route using hexadecylamine as structure directing reagent and triethanolamine as an additive in mixed propanol-water medium. Role of triethanolamine additive is to act as a complexing agent for the inorganic precursor ions resulting in gradual and homogeneous crystallization of the mixed inorganic oxide phase. In a specific synthesis hexadecylamine (2.0 g, Wako Pure Chemical) was dissolved in propanol (6 g) at 35°C followed by the addition of cerium (III) acetate monohydrate (0.69 g, 99%, Wako Pure Chemical) and titanium isopropoxide (0.59 g, 95%, Wako Pure Chemical) (for Ce/Ti = 1/1) and the mixture stirred for 1 h. Then triethanolamine (0.31 g, 98%, Wako Pure Chemical) and water (6.0 g) were added to the gel followed by stirring for 6 h. The final gel was treated at 60°C in a closed vessel for 6 h followed by washing the solid product with ethanol and calcining at 450°C for 6 h. Reference mesoporous ceria, mesoporous titania materials were also prepared by a similar reported procedures using hexadecylamine template. Non-porous ceria-titania was also prepared according to reported procedure [29]. The samples were impregnated with 1 wt% of Pt by incipient-wetness method using aqueous solution of Pt(NO$_3$)$_2$(NH$_3$)$_2$ complex (Tanaka Kikinzoku Kogyo) and reduction in H$_2$ atmosphere at 500°C.
6.2.2. Characterization

The powder X-ray diffraction (XRD) patterns were obtained on a Rigaku Rint-2400 instrument equipped with a rotating anode and using Cu Kα radiation (wavelength = 0.1542 nm). UV-vis diffuse reflectance spectra were measured at room temperature on a Photal Otsuka Electronics, MC-2530 instrument. Nitrogen adsorption/desorption isotherms were obtained at –196 °C on an Autosorb-1 apparatus. Prior to measurement, the samples were heated at 200 °C for 2 h and finally outgassed to 10⁻³ Torr. BET and BJH analysis were used to determine the total specific surface area (S_BET), pore volume and pore size distribution of the samples.

The XPS measurements were performed on a PHI-5500MC spectrometer by using Mg Kα (1253.6 eV) radiation as the excitation source and with an analysis area of about 800 μm². Charging of the catalyst samples was corrected by setting the binding energy of the adventitious carbon (C 1s) to 284.6 eV [29, 30]. The XPS analysis was done at ambient temperature and pressures typically on the order of 10⁻⁷ Pa. Prior to analysis, the samples were outgassed in a vacuum oven overnight. The O1s, Ce3d and Ti2p core-level spectra were recorded. Transmission electron microscopy (TEM) observations were made using a JEM200CX instrument. Scanning electron microscopy (SEM) observations were made using a JSM890 instrument. Ti and Ce contents in the catalysts were determined by inductively coupled plasma (ICP) technique.

6.2.3. Toluene removal analysis

Mesoporous oxides and Pt (1 wt%) impregnated materials were tested for their toluene removal ability at room temperature. As an evaluation gas, a gas mixture was
used which contained, toluene: 103ppm, oxygen: 20% and the balance of nitrogen. 0.5 g each of the oxide samples and the evaluation gas (5 L) were put in a 5-liter gas container. The gas was analyzed after different time intervals by gas chromatography (Shimadzu GC-12A) equipped with FID and a CO$_2$ analyzer (LI-6262, LI-COR, Inc.). The toluene removal was determined from the following equation:

$$\text{toluene Removal (\%)} = \left[ \frac{\text{toluene concentration in gas container without catalyst} - \text{toluene concentration in gas container with catalyst}}{\text{toluene concentration in gas container without catalyst}} \right] \times 100$$

The toluene conversion to CO$_2$ was determined from the following equation:

$$\text{toluene Conversion (\%)} = \left[ \frac{\text{CO}_2 \text{ concentration in gas container with catalyst} - \text{CO}_2 \text{ concentration in gas container without catalyst}}{\text{theoretical } \text{CO}_2 \text{ concentration in gas container assuming complete toluene decomposition}} \right] \times 100$$

A packed-bed reactor was used to evaluate catalyst activity in the complete oxidation of toluene (space velocity, 30,000 h$^{-1}$; toluene, 100ppm; oxygen, 18%; and the balance of nitrogen). At the onset of reaction, the catalyst was pretreated with reactant mixture at 180°C for 1.5 h to prevent over-estimation of toluene conversion caused by adsorption of toluene in the initial stages of test.

### 6.3. Results and Discussions

Thermogravimetric analysis (TGA) of the as-made ceria-titania mesoporous material showed that organic template molecules could be completely removed by calcining the powders up to 400°C and the weight loss between 400°C and 800°C was extremely small. From ICP analysis it was found that the Ce:Ti atomic ratios in the
final calcined product was almost the same as the input Ce:Ti ratio during synthesis (Table 1).

Table 1. Surface properties of mesoporous Ceria-Titania calcined at different temperatures and those of reference materials.

<table>
<thead>
<tr>
<th>Oxide samples, temp.</th>
<th>Area (m²/g)</th>
<th>Pore Size (nm)</th>
<th>Pore Volume (cm³/g)</th>
<th>Ce : Ti (mol ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial gel</td>
<td>final calcined</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce-Ti (Meso), 400°C</td>
<td>357</td>
<td>3.6</td>
<td>0.63</td>
<td>1 : 1</td>
</tr>
<tr>
<td>Ce-Ti (Meso), 500°C</td>
<td>349</td>
<td>3.6</td>
<td>0.61</td>
<td>1 : 1</td>
</tr>
<tr>
<td>Ce-Ti (Meso), 600°C</td>
<td>336</td>
<td>3.4</td>
<td>0.58</td>
<td>1 : 1</td>
</tr>
<tr>
<td>Ce-Ti (Meso), 800°C</td>
<td>286</td>
<td>3.2</td>
<td>0.41</td>
<td>1 : 1</td>
</tr>
<tr>
<td>Ce-Ti (Meso), 500°C</td>
<td>366</td>
<td>3.8</td>
<td>0.59</td>
<td>0.5 : 1</td>
</tr>
<tr>
<td>Ce-Ti (Meso), 500°C</td>
<td>351</td>
<td>3.4</td>
<td>0.55</td>
<td>1.5 : 1</td>
</tr>
<tr>
<td>Ce (Meso), 500°C</td>
<td>263</td>
<td>2.9</td>
<td>0.46</td>
<td>-</td>
</tr>
<tr>
<td>Ti (Meso), 500°C</td>
<td>389</td>
<td>3.9</td>
<td>0.66</td>
<td>-</td>
</tr>
<tr>
<td>Ce-Ti, 500°C</td>
<td>68</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pt/Ce-Ti (Meso)</td>
<td>332</td>
<td>3.4</td>
<td>0.55</td>
<td>-</td>
</tr>
</tbody>
</table>

When the Ce/Ti ratio in the initial synthesis mixture was 1/1 (confirmed by ICP analysis) the ratio in the final calcined product was 0.8/1. Similarly, when the Ce/Ti ratio in the initial synthesis mixture were 0.5/1 and 1.5/1, the actual ratio in the final calcined product were 0.45/1 and 1.4/1, respectively. This indicates that there is only a
slight difference in the Ce/Ti ratio before and after hydrothermal crystallization. A slight decrease in Ce concentration in the calcined product is due to washing out of some ceria component as observed by ICP analysis of the filtrate. The surface Ce/Ti ratio measured by XPS analysis was also the same as the bulk ratio.

Figure 1 shows typical X-ray diffraction (XRD) patterns for mesostructured ceria-titania (Ce/Ti = 1/1). A very broad XRD peak is observed at $2\theta = 1-3^\circ$ typical for mesostructured materials (Figure 1(i)). All the other samples with different Ce/Ti ratios (0.5/1, 1/1.5) also showed similar XRD patterns. It is observed that the broad peak in the $2\theta$ range 1-3$^\circ$ in the as-made template containing ceria-titania sample becomes narrower and sharper after calcinations of the material up to 500$^\circ$C. When the sample is further heated to 600 and 700$^\circ$C, the low angle XRD peaks shift slightly toward higher $2\theta$ value and there is a decrease in the peak intensities. This could be due to wall structuring during the template removal and higher temperature thermal treatment which is also accompanied by pore shrinkage. On further calcining the sample to 800$^\circ$C, the characteristic low-angle XRD peak due to framework-confined mesoporosity vanishes because of breakdown in the mesoporous structure.
Figure 1. XRD pattern of mesoporous ceria-titania: (i) low angle pattern; (ii) high angle pattern.

Figure 1(ii) shows the wide angle X-ray diffraction patterns of the CeO$_2$-TiO$_2$ sample calcined at different temperatures. All the diffraction peaks can be assigned to cubic, fluorite CeO$_2$ (PDF-ICDD 34-0394) and no peaks because the TiO$_2$ phase could be observed indicating the absence of bulk titania phase (with crystallite size >3 nm) in these mesoporous materials. Preuss and Gruehn have reported various Ce-Ti-O oxides, namely, Ce$_2$TiO$_5$, Ce$_2$Ti$_2$O$_7$, and Ce$_4$Ti$_6$O$_{24}$, by heating appropriate mixture of solids containing Ce and Ti at 1250°C [31]. However, no such crystalline phases could be observed in the present study. The absence of crystalline Ce-Ti-O phases may be due to the differences in the preparation methods and lower calcinations temperatures employed in the present investigation. With increasing calcinations temperature, a little peak narrowing and an increase in the intensity of the lines because of cubic CeO$_2$
can be observed. This implies that there is little sintering and agglomeration of ceria crystallites with increasing temperature, which is probably due to the effect of dispersed titania phase which inhibits the agglomeration of ceria phase. Also, there was no observable change in the ceria particle size in the mesoporous mixed oxides with different Ce/Ti compositions. In CeO$_2$-TiO$_2$ mixed oxides prepared by coprecipitation method, the presence of anatase titania phase along with cubic ceria phase has been invariably observed [29] by XRD, but in the present mesoporous CeO$_2$-TiO$_2$ materials, I do not observe any bulk titania phase; this could be due to very fine dispersion of titania nanocrystallites resulting from Ce-O-Ti type bonds. Such a fine dispersion of Ti in ceria matrix prevents the aggregation of titania even after heating the sample up to 800 $^\circ$C. The $\alpha$ cell-parameter values for the CeO$_2$ (111) base peak [27] were calculated using the cubic indexing method. The $\alpha$ cell-parameter value for the calcined sample was 0.536 nm which was smaller than the 0.540-nm value for the pure CeO$_2$ phase which indicates that Ti$^{4+}$ cation could enter the ceria lattice, resulting in the formation of solid solutions because the Ti$^{4+}$ ionic radius (0.064 nm) is smaller than that of Ce$^{4+}$ (0.097 nm).

The XRD results were verified by transmission electron microscopy, Figure 2. The micrograph displays a TEM of the calcined material. The presence of a disordered mesostructure is apparent. The observed disorder is consistent with the XRD of the mixed metal oxide, which shows the absence of additional indexable peaks in the pattern besides the broad d$_{100}$ peak. The TEM of the sample heated to 700 $^\circ$C shows the presence of dense wormholelike mesopores resulting from the densification of the mesopore walls at higher temperatures and consequent pore shrinkage (as observed from pore size analysis). In the samples heated to 800 $^\circ$C, the TEM does not
show clearly the presence of disordered mesopores but a rather foamlike structure resulting from closely aggregated metal oxide nanoparticles is observed (Figure 3). The aggregation resembles aerogel materials such as titania-silica prepared by sol-gel method [33].

Figure 2. TEM image of mesoporous oxides (i) ceria-titania (500 °C), (ii) Ceria-titania (700 °C).

Figure 3. TEM image of mesoporous oxides ceria-titania (800 °C).
The porous properties of calcined mesoporous ceria-titania and other reference materials are shown in Table 1. The N$_2$ adsorption-desorption isotherm for mesoporous ceria-titania is presented in Figure 4. The sample exhibits isotherm of type IV, typical of mesoporous materials with a well-defined step in the adsorption curve between partial pressures $P/P_0$ of 0.4-0.8, and a large hysteresis loop due to capillary condensation in the mesoporous channels or cages. Barret-Joyner-Halenda (BJH) analysis of adsorption isotherm shows that the mesoporous ceria-titania mixed oxide (Ce/Ti = 1/1) calcined at 500 °C exhibits a broad pore-size distribution with a mean pore size of 3.6 nm. The sample calcined at 800 °C shows smaller average pore size of 3.2 nm but the pore size distribution is broad even though the XRD analysis of the sample did not show any observable peaks in low 2θ range which indicates that the sample still retains the mesoporous structure but the local organization of pores is lost at 800 °C.

Figure 4. N$_2$ sorption analysis of mesoporous ceria-titania (500 °C) [inset pore size distribution (a) 500 °C (b) 800 °C].
UV-vis diffuse reflectance spectra (DRS) of the mesoporous samples are plotted in Figure 5. Although the mesoporous CeO$_2$ sample presents its absorption edge at ca. 370 nm, the spectrum of mesoporous ceria-titania (Ce/Ti = 1/1) shows that ceria incorporation to TiO$_2$ induces a small red-shift of the electronic absorption with respect to the pure titania and significant blue-shift with respect to pure ceria. Previous studies on supported ceria samples have shown an increasing blue shift of the absorption edge of this material with decreasing the ceria loading and, consequently, the ceria average particle size [34-36]. This fact has been proposed to arise as a consequence of either the quantum size effect originated by the diminution of ceria particle size or the existence of larger contribution of Ce$^{4+}$-O$^{2-}$ charge-transfer transitions, which yields a relatively broad band with a maximum at ca. 280 nm [34]. Accordingly, small ceria particles, or highly dispersed cerium entities (either isolated or forming two-dimensional ceria patches on the support surface), display a larger intensity of the charge-transfer transition than the corresponding bulk oxide [34, 36]. On this basis, the modification of the spectrum of mesoporous ceria-titania with respect to ceria is consistent with the presence of a dispersed ceria component.
The nature of interactions in the samples of \( \text{CeO}_2\)-\( \text{TiO}_2 \) calcined at different temperatures has been investigated by XPS technique. The electron-binding energies (eV) of the photoelectron peaks pertaining to O 1s, Ti 2p, and Ce 3d are shown in Table 2 and agree well with the values reported in the literature [29, 30, 36].

Table 2. XPS core-level binding energies (eV) of \( \text{CeO}_2\)-\( \text{TiO}_2 \) sample calcined at different temperatures.

<table>
<thead>
<tr>
<th>Material</th>
<th>O(1s), eV</th>
<th>Ti(2p_{3/2}), eV</th>
<th>Ce (3d_{5/2}), eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CeO}_2)-( \text{TiO}_2 ) (600 °C)</td>
<td>529.1</td>
<td>531.7</td>
<td>458.0</td>
</tr>
<tr>
<td>( \text{CeO}_2)-( \text{TiO}_2 ) (800 °C)</td>
<td>529.2</td>
<td>531.7</td>
<td>458.2</td>
</tr>
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</table>
The representative photoelectron peaks of O 1s, Ti 2p, and Ce 3d pertaining to the mesoporous CeO$_2$-TiO$_2$ samples are depicted in Figures 6, 7 and 8, respectively. Figure 6 displays the O 1s XPS spectra of CeO$_2$-TiO$_2$ samples calcined at different temperatures. As shown in Figure 6, the O 1s peak is, in general, broad and complicated because of the nonequivalence of surface oxygen ions. The peak shape suggests that it is composed of more than one peak arising from the overlapping contribution of oxygen from ceria, titania, and Ce-Ti-O compounds. The binding energy of the most intense O 1s peak slightly increased for the 800°C calcined sample. The Ti 2p photoemission spectra of the sample exhibited typical XPS peaks around 458 eV for Ti 2p$_{3/2}$ and at around 464 eV for Ti 2p$_{1/2}$ (Figure 7). The peak separation between Ti(2p$_{1/2}$) and Ti(2p$_{3/2}$) signals is 5.8 eV, which is in agreement with the reported literature value [37]. The intensity of the Ti 2p core-level spectra increased with increasing calcination temperature probably because of better crystallization of TiO$_2$ because of elimination of residual carbon during calcination of samples in air at higher temperatures.
Figure 6. O 1s XPS spectra of mesoporous ceria-titania calcined at different temperatures.

Figure 7. Ti 2p XPS spectra of mesoporous ceria-titania calcined at different temperatures.
The Ce 3d XPS spectra of mesoporous CeO$_2$-TiO$_2$ samples calcined at different temperatures are shown in Figure 8. The XPS core-level spectra of Ce 3d are generally characterized by complex but distinct features that are related to the final-state occupation of the Ce 4f level [38]. On the basis of the works of Burroughs et al. [39], Pfau and Schierbaum [36], and Creaser et al. [40], the Ce 3d spectrum can be assigned as follows: The peaks labeled u are due to 3d$_{3/2}$ spin-orbit states, and those labeled v are the corresponding 3d$_{5/2}$ states. The u'''/v''' doublet is due to the primary photoemission from Ce(IV)O$_2$. The u/v and u''/v'' doublets are shakedown features resulting from the transfer of one or two electrons from a filled O 2p orbital to an empty Ce 4f orbital. The u'/v' doublet is due to photoemission from Ce (III) cations. The Ce 3d spectrum of the CeO$_2$-TiO$_2$ sample basically denotes a mixture of Ce$^{3+}$/Ce$^{4+}$ oxidation states giving rise to a myriad of peaks indicating that the surface of the sample is not fully oxidized. With increasing calcination temperature, the intensity of the u'/v'
doublet due to primary photoemission from Ce$^{3+}$ relative to the intensities of the peaks due to photoemission from Ce$^{4+}$ (u''/v'') did not show any clear change. The presence of u'/v' doublet peaks in the spectrum indicates that the CeO$_2$-TiO$_2$ sample contains some oxygen vacancies and is in a partially reduced state. Partial photoreduction of CeO$_2$ during XPS measurements is a well-known fact in the literature [41-43]. The reduction is mainly due to the progressive elimination of surface hydroxyls and oxygen ions from the CeO$_2$ surface upon vacuum treatment.

Figure 9 shows the results for the removal of toluene as representative volatile organic compound (VOC) after 24 h over the ceria-titania materials (with Ce/Ti = 1/1) calcined at 500 °C which showed best performance among ceria-titania materials with different Ce/Ti ratios. The material showed considerable toluene removal ability at room temperature (about 30%) along with 19 ppm CO$_2$ formation indicating 3.4% partial oxidation/degradation of the toluene. When the same reaction was carried under daylight, there was no change in overall toluene removal but the CO$_2$ formation nearly doubled indicating photocatalytic decomposition of adsorbed toluene with 7.1% conversion.
Figure 9. Toluene removal ability of mesoporous ceria-titania (Ce-Ti(Meso)), mesoporous ceria (Ce(Meso)), mesoporous titania (Ti(meso)), non-porous ceria-titania (Ce-Ti), and Pt impregnated mesoporous ceria-titania (Pt/Ce-Ti(Meso)) samples.

The toluene removal ability increased with temperature and reached about 40% along with 35ppm CO₂ formation at 85 °C (Figure 10) indicating 6.3% partial oxidation/degradation of the toluene. The result indicates that these materials are
promising for developing indoor air-purification materials. This could be attributed to the presence of labile oxygen vacancies and mobile bulk oxygen species, as also indicated by Ce 3d XPS analysis (*vide supra*).

In comparison, under similar conditions non-porous ceria-titania prepared by co-precipitation method [27] showed very low toluene removal ability (< 5%) (Figure 9). The toluene removal performance per unit area was about 1.2 times higher at room temperature, and about 1.3 times higher at 85°C for mesoporous ceria-titania compared to non-porous ceria-titania. Mesoporous ceria and mesoporous titania samples also showed lower intrinsic toluene removal ability (per square meter surface area) than mixed mesoporous ceria-titania and only about 3-5 ppm of CO₂ was observed (<1% toluene conversion), implying that there was little toluene decomposition over these materials at room temperature (Figure 9). Also, the mesoporous ceria and mesoporous titania samples showed decreasing toluene removal ability with increasing temperature (up to 85°C) implying weak adsorption of toluene over these materials (Figure 10).

The toluene removal ability further improved after Pt impregnation (about 58%) (Figure 9) and reached about 67% at 85°C (Figure 10). Noble metals such as Pt are efficient total oxidation catalysts for which reaction may start at temperature as low as room temperature [44]. So in Pt deposited mesoporous ceria-titania, there is a synergetic effect; the noble metal site is a highly efficient oxidation site for toluene while the metal oxide site acts not only as an oxidation site but also provides active oxygen species for reaction. Hence, the toluene removal ability almost doubled after Pt impregnation.
6.4. Summary

Thermally stable mesoporous ceria-titania mixed oxide has been successfully prepared. The material had high surface areas with a narrow pore size distribution in the mesoporous range after calcination up to 700 °C. UV-vis and XPS analysis indicated the presence of well-dispersed ceria and titania components with negligible bulk oxide formation. The material showed high VOC (toluene) removal ability at room temperature compared to non-porous ceria-titania, mesoporous ceria, and mesoporous titania. The toluene removal ability almost doubled after Pt impregnation on mesoporous ceria-titania, most likely because of the synergetic effect between the Pt sites and the metal oxide sites. These results suggest that mesoporous ceria-titania mixed oxides are very promising for air-purification applications. So these materials will be further evaluated for their performance as photocatalysts and as total oxidation catalysts for VOCs wherein more interesting and useful results can be anticipated.

6.5. References


Chapter 7

Mesostructured manganese oxide/gold nanoparticles for extensive air purification

Abstract

A novel mesoporous manganese oxide-nanogold catalyst for efficient elimination of VOCs is reported. Mesoporous $\gamma$-MnO$_2$ was obtained through a surfactant-assisted wet-chemistry route. It had very high surface area (>300 m$^2$/g) due to mesoporous, nanofibrous particles hierarchically aggregated into spherical microparticles. Au nanoparticles were homogeneously deposited on the mesoporous oxide by a high energy vacuum ultraviolet radiation assisted laser ablation (VALA) method to induce lattice-defects and strong metal-support interactions. The material showed exceptionally high VOCs removal ability at ambient temperature and the ability increased with increasing temperature. I observed the formation of radical species on the catalyst surface in the presence of oxygen and the material could easily undergo oxidation-reduction cycle even at low temperature, which explains the high activity of these materials.
7.1. Introduction

Manganese oxide structures can form mixed-valent octahedral molecular sieves (OMS). These OMS materials have extensive applications in energy storage applications, as acid catalysts, and in ion-exchange processes [1, 2]. Various types of manganese oxides with fibrous and flaky morphologies have been synthesized [3]. An electrochemically active form of manganese oxides is $\gamma$-MnO$_2$; this form of Mn oxide has been commercially used as cathodic materials in alkaline batteries. $\gamma$-MnO$_2$ is a ramsdellite matrix with randomly distributed intergrowth microdomains of pyrolusite, which are constructed of MnO$_6$ octahedral units with edge or corner sharing [4]. Conventionally, $\gamma$-MnO$_2$ was prepared by electrolysis (EMD), redox reactions, or disproportionation. However, to the best of our knowledge, the $\gamma$-MnO$_2$ synthesized using the above methods has irregular morphologies and surface areas no higher than 80 m$^2$/g [5]. MnO$_2$'s electrochemical performance is greatly affected by morphology, surface area, and the pore size distribution [6]. Here I report on a simple route to the bulk synthesis of manganese oxide microspheres, which are composed of mesoporous $\gamma$-MnO$_2$ hexagonal nanofibrous aggregates [7]. Au nanoparticles supported on metal oxides have been well reported as efficient oxidation catalysts [8]. I also report a catalyst composed of Au nanoparticles supported on the novel high surface area mesoporous $\gamma$-MnO$_2$ by V-UV-Laser Ablation (VALA) method [9]. This shows high efficiency for total VOCs removal and can have potential application as novel indoor VOCs removal material at room temperature. Here I present a detailed characterization of these catalysts to identify the local structure of the catalyst and to understand the mechanism of VOCs removal using XPS, EXAFS-XANES and in-situ ESR techniques.
7.2. Experimental

7.2.1. Synthesis mesoporous manganese oxide

In a specific synthesis 16.7 g of Mn(NO$_3$)$_2$6H$_2$O (Wako Pure Chemical) was dissolved in 150 ml of H$_2$O followed by addition of 4.8 g NaOH dissolved in 50 ml water. The resulting precipitate was mixed drop wise with an aqueous solution of 67 g of cetyltrimethylammonium bromide (CTAB, Kishida Chemical) in 150 ml water and stirred at 75°C for 1 h, and then heated for 12 h at 75°C. The supernatant was then decanted, and the solid residue was washed copiously with water, dried in air at room temperature followed by calcinations at 550°C for 6 h. The calcined sample (6.0 g) was treated with 120 ml 10M H$_2$SO$_4$ solution in a beaker for 1 h, filtered, washed copiously with water and dried at 105°C.

7.2.2. Deposition of gold nanoparticles.

The second harmonic of a Nd: YAG pulsed laser (4.8 GW/cm$^2$) [9] with pulse width 7 nanosec., energy of 1 J/pulse and V-UV wavelength of 60-80 nm is used to vaporize the Au metal from the Au disk which creates a plasma. Cluster nucleation and growth occur when a continuous flux of inert gas (He) is introduced into the vacuum chamber. (The deposition rates were monitored using a quartz microbalance.) To deposit the clusters on the metal oxide supports, the supports prepared as thin self supported wafers (200 µm thick) were placed in front of the cluster beam. Each side of the wafer was exposed to cluster beam for same time interval: 15 min (high Au loading) and 7.5 min (low Au loading). After deposition, the samples are air transferred, characterized, and/or used in catalytic reactions. For these experiments, a
gold disk of 99.99% purity from Tanaka Kikinzoku Co., Japan was used. The metal content of each catalyst were measured by chemical analysis (ICP or ICP-MS).

7.2.3. Characterization.

Analysis of the product was performed by X-ray diffraction (XRD) on a Rigaku Rint-2400 instrument equipped with a rotating anode and using Cu Kα radiation (wavelength = 0.1542 nm) operating at 45 kV and 40 mA, scanning electron microscopy (SEM), transmission electron microscopy (TEM) using a JEM200CX instrument. A Bruker Electron Spin Resonance ESP 300 spectrometer was used to obtain EPR spectra. Nitrogen adsorption/desorption isotherms were obtained at -196°C on a Micromeritics ASAP 2010 apparatus. Prior to measurement, the samples were heated at 200°C for 2 h and finally outgassed to 10⁻³ torr. BET and BJH (Barrett-Joyner-Halenda) analysis were used to determine the total specific surface area (S_BET), pore volume and pore size distribution of the samples. Au and Mn contents in the catalysts were determined by inductively coupled plasma (ICP) technique.

The XPS measurements were performed on a PHI-5500MC spectrometer by using Mg Kα (1253.6 eV) radiation as the excitation source and with an analysis area of about 800 µm². Charging of the catalyst samples was corrected by setting the binding energy of the adventitious carbon (C 1s) to 284.6 eV. The XPS analysis was done at ambient temperature and pressures typically on the order of 10⁻⁷ Pa. Prior to analysis, the samples were outgassed in a vacuum oven overnight. The O1s, Mn2p and Au4f core-level spectra were recorded.
Mn K-edge EXAFS measurements were performed using beamline BL16B2 at SPring-8 (Hyogo, Japan). Incident X-rays were monochromatized using a Si(111) double-crystal monochromator, and the harmonic content of the beam was minimized using a Rh-coated Si mirror inclined at 5 mrad. X-ray intensities were monitored using ionization chambers filled with nitrogen gas for the incident beam and a mixture of argon (25%) and nitrogen (75%) for the transmitted beam. The data were recorded in transmission mode at PF, with BL-7C beam line using Si(111) sagittal focusing double crystal monochromators and a focusing double mirror for harmonic rejection. The absolute energy scales were calibrated by using value of Mn metal. Fourier transformations were performed over the k range 3–12 Å using k3 weighting. The structural parameters were determined by curve-fitting procedures using Rigaku REX2000 data analysis software. Theoretical parameters of backscattering factors and phase shifts used in the curve-fitting analysis were calculated by XAS code FEFF8.

A Bruker Electron Spin Resonance ESP 300 spectrometer was used to obtain EPR spectra. All the samples were evacuated at 400 °C to 10^-4 torr (4 h), then cooled down to R.T. and exposed to O2 (100 torr).

7.2.4. VOCs removal analysis.

Mesoporous oxides were tested for their ability to remove total volatile organic compounds (TVOCs) as well as individual VOC at room temperature. As an evaluation gas, a gas mixture was used which contained, VOC (toluene: 101ppm or acetaldehyde: 61ppm), oxygen: 20% and the balance of nitrogen. 0.3 g each of the oxide samples and the evaluation gas (5 L) were put in a 5-liter gas container. As an evaluation gas, a gas mixture was used which contained, toluene: 103.3ppm (or
acetaldehyde: 200ppm or a mixture of toluene: 19.5ppm + acetaldehyde: 27ppm +
\(n\)-hexane: 50ppm), oxygen: 20% and the balance of nitrogen. 0.4 g each of the
aforementioned catalyst samples and the evaluation gas were put in a 5-liter gas
container. The gas was analyzed after different time intervals by gas chromatography
(Shimadzu; GC-12A, FID detector, column SP-1000) and a CO\(_2\) analyzer (LI-COR,
Inc.; LI-6262,). The VOC removal was determined from the following equation:
VOC removal (%) = \[\frac{\{\text{VOC concentration in gas container without catalyst} - \text{VOC}
\text{concentration in gas container with catalyst}\}}{\text{VOC concentration in gas container}
\text{without catalyst}}\] \times 100.
The toluene/acetaldehyde conversion to CO\(_2\) was determined from the following
equation:
Toluene/acetaldehyde conversion (%) = \[\frac{\{\text{CO}_2 \text{ concentration in gas container with}
\text{catalyst} \} - \text{(CO}_2 \text{ concentration in gas container without catalyst)\}}{\text{theoretical CO}_2
\text{ concentration in gas container assuming complete toluene/acetaldehyde decomposition}}\]
\times 100

7.3. Results and Discussions

7.3.1. Characterization of mesoporous manganese mixed nanostructure.

It was observed that all the samples showed a single peak at small angle which
is generally ascribed to mesostructured materials (Figure 1). The wide angle XRD
analysis for the as-made material (brownish colored) showed weak diffraction peaks
which could be ascribed to a mixed microcrystalline phase, Mn\(_2\)O\(_3\) (gamma phase) and
Mn\(_3\)O\(_4\) (Hausmannite) (Figure 2a). After calcination the sample turns brownish-black
and the XRD peaks due to Mn\(_3\)O\(_4\) (Hausmannite) phase are only observed (Figure 2b).
After treatment with H$_2$SO$_4$, the peaks due to crystalline hausmannite phase completely disappeared and new peaks which correlate to pure hexagonal $\gamma$-MnO$_2$ phase are observed (Figure 2c). In short, the sample undergoes the following phase transformations on calcinations followed by H$_2$SO$_4$ treatment: Mn$_2$O$_3$ ($\gamma$ phase) + Mn$_3$O$_4$ (Hausmanite) [as-made] $\rightarrow$ Mn$_3$O$_4$ (Hausmanite) [calcined] $\rightarrow$ $\gamma$-MnO$_2$ [H$_2$SO$_4$ treated].

Figure 1. Small angle XRD patterns of mesoporous manganese oxides: (a) as-made, (b) calcined, and (c) H$_2$SO$_4$ treated.

Figure 2. Wide angle XRD patterns of mesoporous manganese oxides: (a) as-made, (b) calcined, and (c) H$_2$SO$_4$ treated.
The pore size distribution of the nanoparticles was calculated from nitrogen desorption isotherm using the BJH model. The results show a narrow distribution centered at 3.6 nm (Figure 3) for the H$_2$SO$_4$ treated calcined mesoporous manganese oxide material. The pore size distribution was broader in the case of the calcined samples prior to H$_2$SO$_4$ treatment.

![Figure 3. Nitrogen sorption isotherm of calcined H$_2$SO$_4$ treated mesoporous manganese oxide sample (inset shows the pore size distributions of (a) calcined, (b) H$_2$SO$_4$ treated samples).](image)

The nature of adsorption-desorption isotherm and the shape of the hysteresis loop is indicative of the pores that are poorly defined and due to the presence of thick and dense wall structure. From the inter-lattice d spacing of the (100) reflection (9.1 nm, Figure 1) and the pore diameter (3.7 nm) the wall thickness of the mesopores was deduced to be about 5.4 nm. Thus these mesoporous oxides have a relatively very thick wall which is responsible for their high stability. The BET surface area of calcined mesoporous manganese oxide was 72.6 m$^2$/g (density-normalized surface area, 380
The same mesoporous material after H$_2$SO$_4$ treatment showed more than four-times higher surface area of 315.8 m$^2$/g (density-normalized surface area, 1600 m$^2$/cm$^3$). This is the highest surface area observed for mesoporous manganese oxide material, nearly 2.4 times more than the highest reported [10].

SEM images of the samples revealed that the calcined manganese oxide samples consist of particles with irregular shape and size (Figure 4a), but the same sample after H$_2$SO$_4$ treatment shows aggregate of almost spherical microcrystallites less than 1 μm in size (Figure 4b, inset) which are assembled together into millimeter length films of several micrometer size thickness. These thin films show presence of micrometer size holes (Figure 4c).

TEM analysis showed that the calcined samples consist of nearly sphere-like nanoparticles <100 nm in size (Figure 5a-1) and high-resolution TEM confirmed the presence of mesoporous channels of ≈3 nm width within these particles (Figure 5a-2). But when these calcined manganese oxide samples were treated with 10M H$_2$SO$_4$, interwoven nanofibrous aggregates were formed (Figure 5b-1) and high-resolution TEM analysis revealed that these fibrous nanoparticles had intraparticle disordered, wormhole-like mesoporosity (Figure 5b-2). These micrograms clearly show that calcined manganese oxide nanoparticles with well-defined mesoporosity, under controlled acid-treatment conditions in solution, transform into nanofibrous entities yielding an open-wave structure with disordered (wormhole-like) mesoporosity.

Thus, it can be expected that such a nanostructured material would have structural distortions, a larger number of defect-sites/active-sites, readily available lattice oxygen for oxidation, high porosity, and large surface area. These can be
expected to translate into such high sorption capacities and high activity as observed by me.

Figure 4. SEM images of mesoporous manganese oxides: (a) calcined and (b), (c) H$_2$SO$_4$ treated.
The mechanism involved in the formation of the fibrous nanoparticles from spherical nanoparticles is not very clear. Most probable possibility is that the strong acidic condition breaks down the spherical nanoparticles into fibrous aggregates while maintaining the intraparticle mesoporosity, though the mesopores become disordered.
This breakdown of the larger spherical particles into smaller fibrous aggregates is responsible for the large increase in the surface area. The breakdown in the structure is reflected in the wide-angle XRD analysis of the samples after $\text{H}_2\text{SO}_4$ treatment wherein more crystalline peaks for $\text{Mn}_2\text{O}_3$ change to weaker and broader peaks corresponding to the $\gamma$-$\text{MnO}_2$ phase resulting from complete phase transformation of Hausmannite-type $\text{Mn}_3\text{O}_4$, which undergoes oxidation. Such transformations of the $\text{Mn}_3\text{O}_4$ phase to $\text{MnO}_2$ by acid treatment are also reported in the literature [11]. The dissolving of the $\text{Mn}_3\text{O}_4$ phase during acid treatment can be ruled out as the weight loss during acid treatment is not significant. The formation of high surface area fibrous mesoporous manganese oxide was found to be dependent on the nature and concentration of the acid used [11], $10\text{ M }\text{H}_2\text{SO}_4$ being the best.

EPR spectra of the acid treated sample show a hyperfine splitting of six lines centered at $3300\text{ G}$ that are separated by $92.8\text{ G}$, indicative of octahedral symmetry (Figure. 6).

![Figure 6. EPR spectra of mesoporous $\gamma$-$\text{MnO}_2$.](image)
7.3.2. Characterization of Au supported mesoporous manganese oxide nanostructure.

Manganese oxide/gold catalysts prepared by a co-precipitation method have been reported to be active catalysts for low-temperature CO oxidation reactions [12]. In the present study, deposition of gold nanoparticles on mesoporous $\gamma$-MnO$_2$ by the classical deposition-precipitation method [13] resulted in a catalyst with poor activity (XRD showed formation of a mixed manganese oxide phase after Au deposition, while TEM showed Au agglomerates of over 25 nm in size). Attempts to use the low-energy (200 MW/cm$^2$) laser-ablation process to deposit metal nanoparticles resulted in very little improvement in the performance of the catalyst in the removal of VOCs. However, surprisingly, a dramatic enhancement in the ability of the substrate to remove VOCs was observed after the deposition of Au by VALA method. The VALA method [9] produces laser plasma containing highly energetic ablated Au nanoparticles that deposit on the mesoporous substrate. VUV photons produced during this process (in the wavelength region 60-80 nm) can induce both thermal activation and lattice defects [14, 15]. $\gamma$-MnO$_2$ shows a strong absorption at $\lambda \approx$60 nm in the VUV region (Figure. 7) which can be expected to result in rapid activation of this material during Au deposition by the VALA method.
Au nanoparticles 3-6 nm in size were well dispersed (Figure 8a) and clearly seen to be embedded in the support lattice (Figure 8b), which is due to the high-energy Au deposition method, as well as the easily penetrable mesoporous support structure. Some Au nanoparticles were observed inside mesoporous channels (Figure 8a, inset). These observations indicate very strong metal-support interactions [4] after Au deposition, which creates a unique interface that results in enhanced activity. High-resolution (HR)-TEM revealed that the Au nanoparticles were well faceted (Figure 8c).
Mesostructured manganese oxide/gold nanoparticles for extensive air purification

Figure 8. a: TEM images of 3-10 nm Au nanoparticles on the mesoporous $\gamma$-MnO$_2$ surface (inset showing Au nanoparticles in mesopore). b: High-magnification transmission electron micrograph shows Au nanoparticles embedded in the $\gamma$-MnO$_2$ lattice to create a unique interface. c: HRTEM image shows the formation of well-faceted Au nanoparticles.

Au L₃-edge XANES analysis (Figure 9) confirmed that Au nanoparticles are completely metallic. However, XPS analysis revealed Au$^0$ binding energies at 84.6 and 88.2 eV, which are 0.6 eV higher than those for bulk metallic Au (84.0, 87.6 eV) (Figure 10). This small shift in binding energy indicates a partial positive charge (δ+) on Au sites resulting from strong electronic interaction between the metal and the support.
Figure 9. Au L3 edge XANES spectra of Au deposited mesoporous $\gamma$-MnO$_2$: fresh sample (red) was reduced by toluene at 85 $^\circ$C (yellow) and at 200 $^\circ$C (cyan). Spectrum of Au foil (blue) is also shown for comparison.

Figure 10. Au 4F(a) and 4d5(b) X-ray photoelectron spectra of Au deposited mesoporous $\gamma$-MnO$_2$ samples with 1.6 wt% (low Au) and 2.8wt% (high Au) gold loadings.
The Mn 2p spectra consisted of a spin-orbit doublet with an Mn 2p\(_{1/2}\) binding energy of 653.7 eV and an Mn 2p\(_{3/2}\) binding energy of 642.5 eV. The binding energy for Mn 2p\(_{3/2}\) species are the same for Au loaded and free samples (642.5 eV) which correspond to Mn in the +4 oxidation state (642.8 eV) (Figure 11a). The results confirm that Mn is present as MnO\(_2\) species. Mn 3p spectra are also shown in Figure 11b. The selection of Mn 3p to establish the chemical shifts of Mn in order to distinguish its different oxidation states has been considered. The single main peak at 50.1 eV is due to Mn\(^{4+}\) ions, which is reported to have a binding energy of 50.4 eV [16]. This seems to be a strong evidence for the presence of Mn\(^{4+}\) ions in that sample.

![Figure 11. Mn2p(a) and Mn3p(b) X-ray photoelectron spectra of γ-MnO\(_2\)(Meso-MnO\(_2\)), Au loaded mesoporous γ-MnO\(_2\) samples with 1.6 wt% (low Au) and 2.8wt% (high Au) gold loadings.](image-url)
XPS analysis did not reveal any change in the oxidation states (binding energies) of Au and Mn following their reaction to remove VOCs. However, Mn K-edge XANES spectra of a sample of Au deposited mesoporous $\gamma$-MnO$_2$ after exposure to toluene (100 ppm in air, 24 h) revealed that the oxidation state of Mn decreases slightly (reduction, $\approx$1.1 eV edge shift, Figure 12) and that this decrease in oxidation state is greater at higher temperature ($\approx$2.6 eV edge shift, Figure 12). Interestingly, the material easily readopted its original oxidation state after heating the reduced sample in air at 100$^\circ$C (Figure 12).

![Figure 12. Mn K-edge XANES spectra of Au deposited mesoporous $\gamma$-MnO$_2$: fresh sample (blue) was reduced by toluene at 85$^\circ$C (black) and at 200$^\circ$C (green) and then reoxidized in air at 100$^\circ$C (red).](image)

These observations clearly show that the MnO$_2$ lattice oxygen atoms are readily available for oxidation and are involved in the oxidation of the VOCs, in accordance with the Mars-van Krevelen mechanism [17]. A two-step Mars–van Krevelen model involving an exchange between the gas phase and lattice oxygen has
also been proposed for the oxidation of benzyl alcohol by molecular O₂ in the liquid phase using an octahedral molecular sieve (OMS) catalyst [2, 18]. Analysis of local structure parameters around Mn shows that the coordination number of Mn (Table 1) is lowered after Au deposition, possibly as a result of strong metal-support interactions. The coordination numbers (N) also decreased after exposure of the sample to toluene, and this decrease is greater at higher temperatures, thus indicating a strong interaction between the adsorbed toluene and the oxide lattice. It is to be noted that the coordination number around first coordination shell (Mn-O) is less than 4, whereas it should be 6 for a perfectly octahedral coordination. Such low values obtained in these calculations could be due to large structural distortions, lattice vacancies, and defects as well as partly due to inherent limitation of such analysis.

Table 1. Local structure parameters around Mn estimated by Mn K-edge EXAFS analysis, Using a nonlinear least-squares fitting method.

<table>
<thead>
<tr>
<th></th>
<th>Mn-O</th>
<th>Mn-Mn (edge sharing)</th>
<th>Mn-Mn (corner sharing)</th>
<th>R factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>r (Å)</td>
<td>D.W. (Å²)</td>
<td>N</td>
</tr>
<tr>
<td>(1) Mesoporous γ-MnO₂</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>3.598</td>
<td>1.909</td>
<td>0.051</td>
<td>2.585</td>
</tr>
<tr>
<td>(2) Au deposited on (1)</td>
<td>3.304</td>
<td>1.908</td>
<td>0.042</td>
<td>2.308</td>
</tr>
<tr>
<td>(3) sample (2) reduced in toluene at 85°C</td>
<td>2.92</td>
<td>1.913</td>
<td>0.05</td>
<td>2.107</td>
</tr>
<tr>
<td>(4) sample (2) reduced in toluene at 200°C</td>
<td>2.145</td>
<td>1.923</td>
<td>0.048</td>
<td>0.806</td>
</tr>
<tr>
<td>(5) sample (3) re-oxidized in air at 100°C</td>
<td>3.651</td>
<td>1.908</td>
<td>0.055</td>
<td>1.973</td>
</tr>
</tbody>
</table>

The discrepancy (R) factor is defined as \( \Sigma (k^3 \chi_{\text{obs}} - k^3 \chi_{\text{calc}})^2 / \Sigma (k^3 \chi_{\text{obs}})^2 \) where k, \( \chi_{\text{obs}} \) and \( \chi_{\text{calc}} \) are the wavenumber of a photoelectron excited from the X-ray absorbing atom, experimental and theoretical EXAFS functions, respectively. The interatomic distance (r) and thermal parameter (Debye-waller factor, D.W.) show very little variation for all the samples.
It is also likely that oxygen can dissociate on the Au surface and spillover from Au to the oxygen vacancies in the oxide, which synergetically promotes the adsorption/dissociation of VOCs. In situ ESR analysis of Au/MnO₂ samples after evacuation and exposure to oxygen showed a weak anisotropic signal which can be attributed to the formation of radical species on the surface of this catalyst (Figure. 13). The ability to form such radical species in the presence of oxygen [19] is probably the reason for the enhanced performance of the Au-deposited material in removing VOCs.

![Figure 13](image13.png)

Figure 13. In-situ ESR spectra of: (a) Mesoporous γ-MnO₂ evacuated to 10⁻⁴ torr at 400°C (4 h), then cooled down to R.T. and exposed to O₂ (100 torr) did not show any ESR signal, (b) Au loaded mesoporous γ-MnO₂ evacuated to 10⁻⁴ torr at 400°C (4 h), then cooled down to R.T. did not show any ESR signal, and (c) Au loaded mesoporous γ-MnO₂ evacuated to 10⁻⁴ torr at 400°C (4 h), then cooled down to R.T. and exposed to O₂ (100 torr) showed a weak anisotropic signal.

7.3.3. VOCs removal ability

The acid treated mesoporous manganese oxide sample (0.3 g) showed the highest VOCs removal ability among all the samples, with 73% toluene removal and 5% CO₂ formation, after 25 h at room temperature (sample γ-MnO₂ 25°C in Figure 14).
The toluene removal performance increased to 95% with 55% CO₂ formation, when the temperature was increased to 85 °C (sample γ-MnO₂ 85 °C in Figure 14). Large increase in toluene removal performance with increasing temperature indicates catalytic oxidation of toluene at low temperatures (up to 85 °C). This is the first report of enhanced catalytic decomposition of VOCs by mesoporous manganese oxides at low temperature. In our earlier work, we had reported that mesoporous chromium oxide as an efficient toluene removal material [7]. But the present mesoporous manganese oxide shows 2.5-times higher CO₂ conversion at room temperature and about 4.6-times more CO₂ conversion at 85 °C. In comparison mesoporous Mn₂O₃ (before acid treatment) with surface area of 76 m²/g and non-porous commercial MnO₂ (99.9%, Aldrich) showed less than 10% toluene removal performance at room temperature (sample c-MnO₂ and Mn₂O₃ 25 °C in Figure 14) and no CO₂ formation was observed.

![Figure 14. Toluene removal and CO₂ formation (after 24 h) over commercial MnO₂ (c-MnO₂), mesoporous Mn₂O₃, and mesoporous γ-MnO₂.](image-url)
Au deposited mesoporous \( \gamma\)-MnO\(_2\) showed much enhanced activity for a mixture of toluene, acetaldehyde and \( n \)-hexane. The material showed 95\% toluene removal and 30\% \( n \)-hexane removal (sample 3 in Figure 15). The removal ability was further enhanced by increasing the reaction temperature to 85 °C, with 99\% toluene removal and 77\% \( n \)-hexane removal (sample 4).

![Figure 15. TVOC removal performance (after 24 h) of various manganese oxide samples: (1) mesoporous \( \gamma\)-MnO\(_2\) (room temp.), (2) mesoporous \( \gamma\)-MnO\(_2\) (at 85 °C), (3) Au deposited mesoporous \( \gamma\)-MnO\(_2\) (room temp.), and (4) Au deposited mesoporous \( \gamma\)-MnO\(_2\) (at 85 °C).](image-url)
It can be seen from Figure 16 that sample with higher Au loading (double ablation time) shows much higher \(n\)-hexane removal ability.

![Figure 16. TVOC removal ability at different temperatures for \(\gamma\)-MnO\(_2\) samples with different Au loading: \(\text{Au/MnO (15m \times 2)}\) was VALA treated twice for 15 min each; \(\text{Au/MnO (15m)}\) was VALA treated for 15 min once; \(\text{MnO}\) is Au free sample.](image)

I also prepared Au nanoparticles supported on mesoporous silica, silica-titania and ceria materials by chemical, DP method as well as by physical, VALA method but none of these catalysts showed any activity enhancement compared to unsupported catalyst. So, the activity enhancement after Au deposition appears to be unique for mesoporous \(\gamma\)-MnO\(_2\). Commercial non-porous \(\gamma\)-MnO\(_2\) also did not show any activity enhancement after Au deposition (maximum toluene removal was 49\%, hexane removal was 2\%).

Thus, mesoporous \(\gamma\)-MnO\(_2\) can be excellent materials for sorption of VOCs at room temperature from indoors, which can be directly decomposed over the same
catalyst at higher temperatures. Strong π-d interactions [20] and d-σ interactions [21], the possibility of ready evolution of active lattice oxygen species, as well as high oxidizing power of higher valent Mn species favored by the lattice strain are probably responsible for the high VOCs removal performance of the mesoporous manganese oxide.

7.4. Summary

High surface area mesoporous manganese oxide materials γ-MnO₂, with novel fibrous structures and uniform particle size were synthesized in bulk by a facile two step process: template-assisted assembly followed by treatment in a strong acidic medium.

The presence of wormhole-like mesoporosity was confirmed by TEM and FE-SEM analysis. A narrow pore size distribution was observed from BJH analysis of the adsorption isotherm. XPS analysis confirmed the presence of manganese on the +4 oxidation state while Au deposited as metallic gold with partial positive charge (δ+).

These findings clearly showed the efficacy of high surface-area mesoporous γ-MnO₂ materials in the removal of VOC (toluene).

Moreover, the materials after deposition of gold nanoparticles on the substrate by a vacuum-assisted laser ablation (VALA) method showed exceptionally high VOCs (toluene, acetaldehyde, n-hexane) removal ability at low temperature and the ability increases with increasing temperature.

Detailed characterization results clearly established the role of lattice defects/vacancies and strong metal–support interactions in the elimination of VOCs.
Mn K-edge XANES-EXAFS analysis indicated strong adsorbate-adsorbent interaction due to readily available lattice oxygen for oxidation.

These results indicate that these materials are very promising for application in emission control in indoor air purification applications as sorbent and catalyst.

7.5. References


Chapter 8

Mesosporous ferrihydrite-based iron oxide nanoparticles for removal VOCs and O₃ in air

Abstract

This chapter deals with a solution phase assembly process for producing 2-line ferrihydrite as a partially dehydroxylated material with accessible mesopores and its exceptionally high performance in eliminating VOCs (acetaldehyde removal in the present study) and ozone (O₃) in air at room temperature. My objective was to identify a highly active iron-based biocompatible material for decomposition/removal of these gases with high conversion level at room temperature. Although ferrihydrite has been recognized as an industrially as well as naturally important material, the bulk ferrihydrite in the literature is extensively hydrated, non mesoporous and moreover
highly vulnerable to phase transition. This hampers its use for advanced applications including air purification, catalysis etc. The current template assisted solution phase process allowed me to prepare it in a partially dehydroxylated and stable form with accessible mesopores while keeping the desirable ferrihydrite phase properties intact. I also show here for the first time the presence of Fh nanoparticles in disordered mesostructured iron oxide has significant effect to the bulk and surface structure of the material and to the activity. The fundamental aspect of structure-property relation of these materials was achieved by performing various X-ray absorption spectroscopic characterizations and the adsorption behavior of O₃ on ferrihydrite was performed by density functional theory (DFT) calculation. My study demonstrate the promise of the highly favorable electronic and textural structures of mesoporous Fh or Fh-based iron oxides in environmental catalysis, especially for treating some of the most dangerous gases in the atmosphere at moderate reaction conditions.
8.1. Introduction

The abatement of air contaminants using mesoporous transition metal oxides such as Cr$_2$O$_3$ and Au/MnO$_2$ has been proved to be a versatile approach and their performance was superior to materials including activated carbon, zeolites and mesoporous silica [1]. However, the non-environmentally friendly nature of these oxides and/or use of expensive metal components prompted us to focus on the environmentally compatible and largely available iron-based oxides. Iron oxyhydroxides and oxides are of technological importance as catalytic materials, sorbents, pigments, flocculants, coatings, gas sensors and ion exchangers [2-9]. Several iron-based materials have been used in various catalytic applications. For example, it has been used in the production of clean transportation fuels and high molecular weight hydrocarbons from synthesis gas (H$_2$/CO mixture) by Fischer-Tropsch synthesis [10]. An amorphous $\alpha$-Fe$_2$O$_3$ thin film deposited on a fused quartz substrate has shown photocatalytic degradation of an oxygenated aqueous solution of phenol upon visible light illumination [11]. Iron oxide-based materials have been found to be good candidates as cheap, efficient and non-hazardous catalysts, especially in environmental catalysis. As for example, iron oxide based catalysts are attractive candidates amongst the readily available carbon monoxide oxidation catalysts especially in the removal of carbon monoxide in a burning cigarette, where the potential toxicity of other catalysts would be undesirable. Various organic contaminants (for example, toxic 2-chlorophenol) in water or soil could be oxidized by hydrogen peroxide in the presence of iron oxides [3]. Several studies have shown that iron oxides and composites containing iron oxides have a significant potential to adsorb and catalytically decompose volatile organic compounds [12, 13] including chlorinated...
hydrocarbons [14-20]. To date, the most widely studied chemical method to prepare iron oxides has been the precipitation of iron ions from aqueous solutions of their nitrate, chloride, perchlorate, or sulfate salts. This method has been reviewed and is well established in the literature [21-23]. Goethite (α-FeOOH), ferrihydrite (Fe₅HO₈₄H₂O) or akagenite (β-FeOOH) are usually the initial precipitates, which are converted to crystalline low surface area α-Fe₂O₃ upon moderate heat treatment [2, 24]. Because of low surface area and no ordered pores, these preparation methods are useful only for very limited applications. In view of the versatility of iron oxide materials for its diverse applications, the development of iron oxide-based materials with meso structure and high surface area is of great interest. There is intense interest in mesoporous transition metal oxides because confining ‘d’ electrons to the thin walls between pores can endow such materials with unusual magnetic, electrical, and optical properties, whereas the high internal pore surface area can lead to new and unique catalytic properties [25-30]. The high internal pore surface area is very important when it is meant to use as a catalyst material for adsorption and subsequent transformation process. Several authors have extensively reviewed the application of the mesoporous materials in catalysis [31, 32]. Similar to magnetic properties, catalytic properties have also been studied after filling the catalysts inside the pores of the mesoporous framework. Previous such studies have shown considerably high conversion of cyclohexane to cyclohexanol and cyclohexanone [33]. The preparation of mesoporous phase-pure iron oxides has been a real challenge due to the difficulties that usually accompany this process [34-36]. This is, in part, due to the different iron oxidation states, which can lead to various oxides, FeO, Fe₂O₃, and Fe₃O₄. Moreover, Fe₂O₃ exhibits different phases (for example, α- Fe₂O₃ and γ- Fe₂O₃), among which is hematite, α- Fe₂O₃, the
most thermodynamically stable form. The preparation of mesoporous iron oxide is
effected either by using a soft template (e.g., alkyl amine, block co polymers, CTAB,
dodecyl sulfate, etc.) around which the mesoporous solid is assembled or a hard
template (e.g., mesoporous silica, mesoporous C) within the pores of which the
mesoporous transition metal oxide is formed, followed by template dissolution. In
both case, a solution step is required, which can limit the synthesis of mesoporous
transition metal oxides to those containing transition metals in oxidation states that are
stable in solution [37]. Also, if the temperature range within which the target phase
forms does not coincide with the stability range of the template, the desired phase may
not be obtained.

Among all iron oxides and oxyhydroxides studied so far, ferrihydrite (Fh) is
known for its harmonious role in the nature, numerous industrial applications, and
excellent adsorption capacity towards a number of inorganic species [38-43]. The
poorly crystalline 2-line ferrihydrite (2LFh) and the relatively more ordered 6-line
ferrihydrite are the most common in this category. However, the surface-structured
hydration layer in the Fh nanoparticles slows down the diffusion of organic gas
molecules to the active iron sites and thereby adsorption and reaction processes [44].
Other drawbacks that limit the use of Fhs in removal of organic contaminants are lack
of mesoporosity, low pore volume and/or high vulnerability to phase transformation [41,
45]. The synthesis of mesoporous 2LFh under calcined condition has recently been
reported by using mesoporous silica as a hard template [46]. Si is an essential
component to maintain the Fh phase and modify the surface property of Fh in this case
[41, 45a]. If we consider the previous evidences on the complexities involved in the
micellar assembly of iron species and their poor thermal stability [47], the synthesis of
iron oxide in a partially dehydroxylated form with accessible mesopores and maintained the Fh-phase properties is a major challenge.

I have explored several strategies to obtain mesoporous iron oxides with high surface area and different pore sizes by varying synthesis parameters as well as process methodology. However, all my strategy that based on Evaporation Induced Self Assembly (EISA) process resulted \( \gamma \)-Fe\(_2\)O\(_3\) irrespective of the template and the additives. Herein I have adopted a precipitation induced self assembly using polyoxyethylene (20) cetyl ether as template in an aim to obtain mesoporous iron oxide with other kinds of phases such as \( \alpha \)-Fe\(_2\)O\(_3\) and Fh. According to this synthesis strategy, since the precipitated iron oxyhydroxide are assembled to the template through a relatively weak H bonding interaction rather than the strong covalent linkage between Fe\(^{3+}\) ion and template (the latter usually happens with EISA process), it is quite easy to remove most of the template by simple water washing and thereby phase transformation to \( \gamma \)-Fe\(_2\)O\(_3\) can be suppressed to a great extend.

In this Chapter, I report a template-assisted solution-phase synthesis to obtain 2LFh as a partially dehydroxylated material with accessible mesopores and the efficacy of the 2LFh towards VOCs and ozone (O\(_3\)) decomposition.

8.2. Experimental

8.2.1. Preparation of mesoporous two-line ferrihydrite

For producing mesoporous two-line ferrihydrite (M2LFh), I performed the precipitation reaction between iron nitrate and NH\(_3\) in a clear solution of 1-propanol-polyoxyethylene (20) cetyl ether surfactant mixture. The precipitation in
1-propanol produces Fh nanoparticles as predominant iron precipitate [48], while the surfactant plays a major role in stabilizing them through H bonding interaction. These organic matters in the coordination sphere of the Fh nanoparticles also impede the nucleation of the primary particles and the solution phase crystal growth through steric effect [49]. Thus, the combined use of 1-propanol and the surfactant bring a cooperative effect and efficiently organize the Fh nanoparticles into an assembly. The interparticle mesopore network established through this assembly process offers extra stability to the 2LFh lattice. This limits particle growth and maintains the Fh phase characteristics during the elimination of structured water and partial dehydroxylation by heat treatment at 300°C. A schematic illustration of the preparation method is shown in Figure 1.

![Figure 1. A schematic illustration of the synthesis of Fh.](image)

In a specific synthesis, reagents used are Fe(NO₃)₃·9H₂O (Wako Pure Chemical), 28 wt % NH₃ (Wako Pure Chemical) and Polyoxyethylene (20) Cetyl Ether
Mesoporous iron oxide was prepared by the precipitation of Fe(NO$_3$)$_3$9H$_2$O in Brij 58 containing 1-propanol using 28% NH$_3$ solution. In a typical procedure, 17.02 g Brij 58 (0.015 mole of Brij 58) dissolved in 100 ml 1-propanol (17.54 wt % Brij 58 in 1-propanol) by gently heating at ~ 35°C and cooled to room temperature (RT). About 12.12 g solid Fe(NO$_3$)$_3$9H$_2$O (0.03 mole) was then added to the above solution at room temperature (RT) and stirred for 2 h. Precipitation was carried out by adding 8 g 28% NH$_3$ solution to the iron containing template solution followed by vigorous stirring for 3 h. The pH of the resulting solution was ~ 8.0-8.5. The resultant iron precipitate containing mixture is kept for ageing at 50°C in an oven for 3 days followed by filtration, washed with ~ 500-750 ml water while gently stirring the precipitate during the washing procedure. The precipitate was dried at 50°C and grinded well to a fine powder. About 3 g of the fine powder was then mixed with 100 ml ethanol and stir at room temperature for 24 h to remove the template. The iron powder containing ethanol mixture was finally filtered, washed with water, followed by drying at 50°C. The dried powder is calcined at 300°C by heating from room temperature to 300°C in 5 h and finally maintained at that temperature for 3 h.

As for comparison purpose, 2-line ferrihydrite (2LFh) was prepared according to a literature procedure [39]. Briefly, about 1 M solution of NaOH was added slowly (approximately at a rate of 2 mL/minute) to a 0.2 M solution of Fe(NO$_3$)$_3$9H$_2$O (300 ml solution) at room temperature with constant stirring till the pH becomes 7.5. The resulting precipitate was filtered, washed with water to remove the Na and nitrate species, and finally dried at room temperature.
Additionally, a mesostructured semicrystalline iron oxide in which the amorphous Fh nanoparticles co-exist with γ-Fe₂O₃ phase (MSIO), and a crystalline iron oxide with no well-defined mesopores (CIO) were prepared for comparison purpose towards gaseous ozone (O₃) decomposition. MSIO was prepared through a sol-gel process in which iron nitrate, oleic acid, a triblock polymer template F-127 (Sigma-Aldrich) and 1-propanol were mixed, followed by ageing and calcination. CIO was prepared by an assembly process of iron oxyhydroxide in water-ethylene glycol mixture in the presence of cetyltrimethylammonium bromide (CTAB, Kishida Chemical). In a typical procedure, MSIO was 134 Fe: 2230 1-propanol: 67 oleic acid: 1 F-127 [(HO(CH₂CH₂O)₁₀₆(CH₂CH(CH₃)O)₇₀(CH₂CH₂O)₁₀₆H). Briefly, 10 g F-127 was dissolved in a mixture of 100 g 1-propanol and 14.12 g oleic acid. Fe(NO₃)₃·9H₂O (40.4 g) was then added followed by vigorous stirring for 2 h. The resulting solution was then aged at 50 °C on a hot plate for 3 days and then gradually heated to 75-80 °C and maintain at this temperature for another 3 days. The dried pasty mass was then heated at 120 °C for 2 h followed by template removal by ethanol extraction. The ethanol treated sample was first dried at 120 °C (2 h) and finally heating gradually (1 °C/min) to 300 °C and kept at 300 °C for 3 h.

For CIO synthesis, the iron hydroxide formed by the precipitation reaction between an aqueous solution of Fe(NO₃)₃·9H₂O (24.2 g in 25 mL water) and NaOH (8 g in 25 mL water) was added to an aqueous solution of CTAB (60 g in 250 mL water) and ethylene glycol (1.84 g) solution mixture at 75 °C with continuous stirring. The resulting gel (maintained at pH around 10.5) after stirring for 2 h at 75 °C was further heated for 40 h at 75 °C in an oven (closed condition). The solid mass was centrifuged, washed several times with water, dried and finally calcined at 500 °C for 4 h.
8.2.2. Characterization

XRD patterns were obtained on a Rigaku Rint-2400 instrument using Cu Ka radiation operating at 40 kV and 30 mA. TEM observations were made with a JEM200CX instrument (Hitachi) at an accelerating voltage of 200 kV. N₂ adsorption analysis was carried out on a BELSORP 18 apparatus (BEL Japan, INC). ⁵⁷Fe Mössbauer spectra were measured on a constant acceleration spectrometer with ⁵⁷Co in an Rh matrix source at ambient temperature and calibrated the velocity scale using the standard magnetic sextuplet spectrum of a high-purity iron foil absorber. All the spectra were deconvoluted with calculated Mössbauer spectra consisting of Lorentzian-shaped lines. The Fe K-edge EXAFS and XANES measurements were carried out at BL33XU of SPring-8 (Hyogo, Japan). The O K-edge NEXAFS measurement was carried out at BL12 of SAGA-LS, Japan (1.4GeV light source). The NEXAFS spectral measurements were obtained by total-electron-yield (TEY) method. The XPS measurements were carried out on a Quantera SXM (Ulvac-PHI) spectrometer. The temperature programmed reduction by hydrogen (H₂-TPR) analysis was performed on a TP5000 apparatus (Ohkura, Riken). All surface structures calculation of Fh was carried out using density functional theory (DFT) with PWscf code [50]. Exchange correlation was treated in the generalized gradient approximation (GGA) with Perdew Burk, and Ernzerhof (PBE) [51]. The pseudo potentials were 3d⁷4s¹ for Fe, 2s²2p⁴ for O, and 1s¹ for H. We also utilized GGA+U method in order to modify GGA energies with an explicit correction for the Coulomb interaction of the 3d electrons of Fe [52]. The Hubbard U parameter was set to 4eV (Ueff = 3eV). The U value was utilized by Pinney et al. and Rollman et al. [53, 54]. The geometry optimization of bulk structure was performed with a 4 × 4 × 3 Monkhorst-Pack k-point grid and a plane wave kinetic
cutoff energy of 30Ry. The (110) surface structural optimization was performed with a $2 \times 2 \times 1$ Monkhorst-Pack k-point grid and a planewave kinetic cutoff energy of 30Ry. For surface structure calculation, the most exposed (110) surface cluster was generated from the DFT optimized bulk structure of ferrihydrite (Fh). Subsequently, geometry optimization of (110) surface was performed for each case by keeping the bottom layer of the (110) cluster atoms to a fixed position. The optimized surface structural model of Fh was further used for O$_3$ adsorption calculation.

8.2.3. CH$_3$CHO and O$_3$ removal Analysis

For CH$_3$CHO removal test (static condition), a gas mixture comprised of CH$_3$CHO (31.7ppm), O$_2$ (20%), and the balance of N$_2$, and sample (1g) were introduced in a 5 L container. The gas was analyzed by a GC and the percentage removal of CH$_3$CHO was calculated according to the equation: $% \text{CH}_3\text{CHO removal} = [1 - \frac{\text{concentration of CH}_3\text{CHO with catalyst}}{\text{concentration of CH}_3\text{CHO without catalyst}}] \times 100$. To check the CO$_2$ formation, M2LFh (≈0.1 g) and CH$_3$CHO (1000ppm) containing an air mixture were used (0.5L bottle). Several blank tests were also performed and the analysis was conducted in a separate GC equipped with a methanizer.

The O$_3$ removal measurement was carried out on a fixed bed down flow reactor using 0.2 g catalyst material of pellet size 0.5 mm. O$_3$ was generated by the electric discharge of O$_2$ under a suitable voltage. The resulting (O$_2$ + O$_3$) gas mixture at a flow rate of 0.5 L/min was then mixed with N$_2$ gas of flow rate 4.5 L/min, making a total gas flow rate of 5 L/min (initial concentration of O$_3$ was 600ppm). The O$_3$ concentration was measured by a chemiluminescence method by reacting the residual O$_3$ with
1000ppm NO, and the O$_3$ removal was calculated with respect to the initial concentration.

8.3. Results and Discussions

8.3.1. Characterization of two-line ferrifydrite

The low angle XRD pattern (Figure 2a) of M2LFh shows a broad peak at $2\theta = 0.5-2^\circ$, which is typical of disordered mesostructured materials. The wide-angle XRD pattern in Figure 2b displays characteristic broad reflections of 2LFh phase at $d$-values 0.26 nm (110) and 0.15 nm (300) [41, 46]. The Mössbauer analysis at room temperature resulted a doublet with an isomer shift and quadruple splitting values of 0.34 mm/s and 0.72 mm/s, respectively (Figure 3). These values are typical of 2LFh [41, 55].

The aggregation of Fh nanoparticles into a disordered mesoporous structure was evidenced from the TEM analysis of M2LFh (Figure 4). Within the aggregate, the lighter regions in the THM contrast can be recognized as mesoporous due to interparticle distance as previously described for self-assembled nanoparticles of metals and metal oxides [56]. The TEM analysis over a large domains confirmed the particle size was less than 10 nm. The majority was in the size range of 5-8 nm. The selected area electron diffraction (SAED) pattern showed two broad rings at 0.26 nm and 0.15 nm (inset of Figure 4), which is in agreement with the wide angle XRD ‘$d$’ spacings. The high-resolution TEM image and the corresponding fast Fourier transform diffraction pattern illustrate the nanocrystalline nature of the material as reported for the case of 2LFh [39, 40] (Figure 5). The characteristic type IV isotherm and the
Barrett-Joyner-Halenda (BJH) pore size distribution resulted by N\textsubscript{2} adsorption analysis also confirmed the material has well defined mesopores with a pore size distribution centered at 5.6 nm (Figure 6). The BET surface area and the pore volume were 180 m\textsuperscript{2}/g and 0.36 cm\textsuperscript{3}/g, respectively.

Figure 2. Low-angle (a) and wide-angle (b) XRD patterns of M2LFh

Figure 3. Mössbauer spectrum of M2LFh obtained at room temperature.
Figure 4. TEM image and SAED pattern (inset) of M2LFh.

Figure 5. HRTEM image and the corresponding fast Fourier transform diffraction pattern (in the inset) of M2LFh.
Figure 6. Nitrogen adsorption-desorption isotherms of M2LFh. The Barrett-Joyner-Halenda (BJH) analysis of pore size distribution is given in the inset.

A comparison of the Fe K-edge EXAFS spectra of M2LFh and various bulk iron oxides (Figure 7a) as well as the curve-fitting analysis of M2LFh (Figure 8 & Table 1) confirmed that the local structure of M2LFh is essentially the same as that reported for 2LFh [17]. The second peak corresponding to Fe-Fe distances in the Fourier transformed (FT) spectrum of M2LFh is low in intensity with respect to crystalline iron oxides, but it is similar to 2LFh (Figure 7b), suggesting that a long-range structural order was lacking in M2LFh as is the case for 2LFh.
Figure 7. Fe-K edge EXAFS spectra (a) and the corresponding FT spectra (b) of M2LFh (black), 2LFh (red), $\alpha$-Fe$_2$O$_3$ (blue), and $\gamma$-Fe$_2$O$_3$ (green). $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ are commercial supplied by High Purity Chemicals. The purity is 99.99% and 99% respectively.

Figure 8. Multi-shell fit to Fe EXAFS data for M2LFh.
Table 1. Multi-shell fit parameters obtained by curve-fitting analysis for NAMF.

<table>
<thead>
<tr>
<th>Atom Pair</th>
<th>CN</th>
<th>R(Å)</th>
<th>σ²(Å²)</th>
<th>ΔE₀</th>
<th>MF</th>
<th>R-range</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-O1</td>
<td>2.7</td>
<td>1.91</td>
<td>0.005</td>
<td>-2.97</td>
<td>3.96</td>
<td>1.3-4.7</td>
<td>0.011</td>
</tr>
<tr>
<td>Fe-O2</td>
<td>2.7</td>
<td>2.03</td>
<td>0.007</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-Fe1</td>
<td>3.7</td>
<td>3.01</td>
<td>0.010</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-Fe3</td>
<td>1.4</td>
<td>3.45</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CN is the coordination number, R is the interatomic distance, σ² is the mean-square displacement of bond length, and ΔE₀ is the threshold energy, MF is mean free path. The crystal structure of goethite (Gualtieri and Venturelli, 1999) was used.

The characteristic pre-edge peak in the Fe K-edge XANES spectrum shows M2LFh has several non-centrosymmetric iron sites (Figure 9). In terms of relative peak intensity, the number of these sites in M2LFh may be close to 2LFh rather than to crystalline iron oxides. If we consider the previous XANES studies on Fh [10a] and iron oxide nanoparticles [18], the main contribution of the pre-edge peak area for M2LFh must be from unsaturated Fe coordination sites on the particle surface.

Figure 9. The pre-edge peak from Fe-K edge XANES spectra for each sample: M2LFh (black), 2LFh (red), α-Fe₂O₃ (blue), and γ-Fe₂O₃ (green).
A corroboration to this XANES-based interpretation was obtained from density functional theory (DFT) calculation of the Fh(110) surface. I used the recently reported Michel’s model of Fh structure (Fe$_3$O$_8$H) [39] for DFT study and the surface-structure calculation show the Fh surface is enriched with two different kinds of unsaturated iron sites, that is, tetracoordinated and tricoordinated iron (Figure 10).

Figure 10. The geometry-optimized (110) surface of Fh by DFT calculation shows tetra- and tricoordinated iron sites on the Fh surface.
As a consequence of this structural disorder and unsaturated iron coordination sites on the particle surface, Fh samples have several electrophilic O species. This was evidenced from the broadening of O 1s main peak component to a higher binding energy (BE) of 531 eV in the O 1s XPS spectra of the Fh samples (Figure 11). The spectral feature at around 531-533.5 eV for the Fh sample is mainly characteristic of O species from iron hydroxyl group [19]. This shows that the structurally intact OH in Fh is only partially consumed during the calcination. Nonetheless, by a deconvolution analysis (Figure 12), I found that the relative amount of O species at 531-533.5 eV in M2LFh (28.6%) was less than in 2LFh (34.5%). Thus, by partial dehydroxylation, the proportion of lattice and electrophilic O in M2LFh on relative basis has certainly increased at the expense of hydroxyl oxygen.

Figure 11. O1s XPS spectra of M2LFh (black), 2LFh (red), and α-Fe₂O₃ (blue).
Figure 12. The deconvoluted O1 XPS spectra of (1) M2LFh and (2) 2-line ferrihydrite (2LFh).

The H$_2$-TPR analysis also confirmed M2LFh was easily reducible, suggesting that these electrophilic oxygen species are highly reactive (Figure 13). This aspect of M2LFh is highly beneficial in adsorption and catalysis that involve a redox reaction.

Figure 13. The temperature programmed reduction (H$_2$-TPR) profiles of (1) M2LFh, (2) 2-line ferrihydrite (2LFh), (3) $\alpha$-Fe$_2$O$_3$, and (4) $\gamma$-Fe$_2$O$_3$. Note that the small intensity dip at around 145$^\circ$C observed for 2LFh was due to variation in the TCD signal by water evolution from this hydrated material.
8.3.2. CH$_3$CHO removal ability

Among the various iron-based materials I tested, M2LFh was found to be the most efficient candidate for the rapid removal of CH$_3$CHO at room temperature (RT). As evidenced in Figure 14a, within 1 h, about 84% CH$_3$CHO was removed over M2LFh (0.1 g at 31.7ppm CH$_3$CHO). The non-mesoporous 2LFh showed only 19% CH$_3$CHO removal under similar experimental conditions. The CH$_3$CHO removal efficiency of M2LFh was also remarkably better than $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$. The surface-area-normalized CH$_3$CHO removal by M2LFh was about 5.8 times higher than by 2LFh in the first hour, whereas 3.9 times enhancement was shown with respect to crystalline iron oxides. The time-dependent organic-contaminant removal test at RT confirmed that CH$_3$CHO can be more rapidly and completely removed over M2LFh. For example, by M2LFh 100% CH$_3$CHO removal was achieved in 3 h (Figure 14b). Further, the performance of M2LFh was not affected by about 40% relative-humidity conditions (100% removal at RT, 3 h). No other catalysts showed 100% CH$_3$CHO removal even after 24 h in our study at RT.

Recycled M2LFh (i.e., M2LFh obtained after heating at 105 $^\circ$C in an oven) also showed 100% CH$_3$CHO removal within 3 h at RT (Figure 15), suggesting that M2LFh can be efficiently reused. Further, I could not find any change in the XRD pattern of the used and/or regenerated catalyst under mild reaction condition. Under similar experimental conditions (1 h, RT), I also verified M2LFh (84%) can remove CH$_3$CHO faster than mesoporous silica (43%) or zeolite $\beta$ (48%). With respect to the previously reported ordered mesoporous Cr$_2$O$_3$ (94% removal in 24 h at RT using 0.4 g catalyst and 27ppm CH$_3$CHO) [1a], the CH$_3$CHO removal ability of M2LFh is gauged to be higher. However, mesoporous $\gamma$-MnO$_2$ and Au/$\gamma$-MnO$_2$ are considered to be the
highest-performing material for CH$_3$CHO elimination (100% removal, 1 h, RT)\[1b\]. Although, in a recent study, metal-organic-framework compound (MOF-5) was reported for adsorption/separation of HCHO, to my knowledge, the scope of such a material for destructing VOC’s even at elevated temperature is doubtful [57].

Figure 14. a) Comparison of the first hour CH$_3$CHO removal efficiency of (1) M2LFh, (2) 2LFh, (3) α-Fe$_2$O$_3$, and (4) γ-Fe$_2$O$_3$. b) The time-dependent CH$_3$CHO removal efficiency of the corresponding materials.

Figure 15. The CH$_3$CHO removal performance of recycled M2LFh (spent M2LFh after heating in an oven at 105°C) and one-year-old M2LFh. In both cases, activity was performed at room temperature using 0.1 g catalyst and 31.7ppm CH$_3$CHO as initial concentration.
At 1000 ppm CH$_3$CHO and 0.1 g catalyst, I also experimented to know whether M2LFh is efficient in oxidizing at ambient temperature. Under these conditions, CO$_2$ was not detected at room temperature. However, when the temperature was increased to 80 $^\circ$C, about 246 ppm CO$_2$ was detected after 20 h, corresponding to 12.3% CO$_2$ formation. This shows that M2LFh can act as a sorbent as well as an oxidation catalyst even at low temperatures. I also verified that the CH$_3$CHO removal ability of one-year-old M2LFh (i.e., M2LFh kept idle in the lab for one year) is close to the activity of freshly prepared M2LFh (Figure 15). If I consider the storage and the practical difficulty of handling the extensively hydrated 2LFh, the latter aspect of M2LFh is also advantageous for practical use and making the process commercially viable. The catalytic performances of M2LFh under various reaction conditions and gas compositions as well as the long-term stability are major concerns of my future research. Thus, from the above structure-activity results, it is obvious that the mesoporous structure and the physico-chemical properties of the Fh phase, which is devoid of a surface-structured hydration layer, are essential to achieve high CH$_3$CHO removal. As evidenced from TEM and N$_2$ adsorption results, the interparticle mesopore network in such a partially dehydroxylated 2LFh is favorable for creating a diffusion-free pathway for CH$_3$CHO molecules to access several reactive surface sites with great ease. EXAFS, XANES, and XPS analyses as well as DFT calculations convincingly proved that the disordered structure of M2LFh introduce numerous tetra- and tricoordinated Fe sites and electrophilic oxygen species on the particle surface, allowing M2LFh to be a highly valuable candidate for organic adsorption. Thus, M2LFh can accommodate an increased amount of CH$_3$CHO molecules at a greater rate than any other iron-oxide material in the present study. The DFT calculation of
CH$_3$CHO adsorption on a few small cluster models of FeO$_x$ (where $x = 0$, 1 and 2) suggests that the tetra- and tricoordinated iron sites in Fh nanoparticles must be better adsorption sites for CH$_3$CHO than a metallic centers in iron nanoparticles (Table 3 & Supporting Information).

### Table 3. The adsorption energy of CH$_3$CHO on iron cluster models, such as Fe, FeO and FeO$_2$.

<table>
<thead>
<tr>
<th>Cluster Type</th>
<th>Adsorption Energy, eV</th>
<th>Spin Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe…CH$_3$CHO</td>
<td>0.82</td>
<td>5</td>
</tr>
<tr>
<td>FeO…CH$_3$CHO</td>
<td>2.74</td>
<td>5</td>
</tr>
<tr>
<td>FeO$_2$…CH$_3$CHO</td>
<td>5.04</td>
<td>3</td>
</tr>
</tbody>
</table>

The DFT calculations of cluster models of iron (FeO$_x$ where $x = 0$, 1 and 2) have been performed with Gaussian 03 program package (see below for complete citation). Here Fe is equivalent to a simple surface atomic model in metallic iron and the latter two a similar situation corresponding to dicoordinated and tetracoordinated iron, respectively, in iron oxides/xydroxides. Adsorption energies and optimized structures of CH$_3$CHO onto FeO$_x$ were obtained by hybrid density functional B3PW91, and by LANL2DZ (for Fe) and 6-31+G(d) (for H, C, O) basis set. Adsorption energy ($E_{ad}$) is defined as $E_{ad} = E_{FeOx} + E_{CH3CHO} - E_{CH3CHO/FeOx}$.

### 8.3.3. O$_3$ removal analysis

I have also evaluated M2LFh towards gaseous ozone (O$_3$) decomposition. Because O$_3$ in the troposphere is considered to be one of the most harmful air pollutions in view of its high reactivity and immediate action to the surroundings, which causes both short- and long-term adverse health effect and also disrupts plant growth [58]. In this evaluation, MSIO and CIO were used as a comparative iron oxide material. Although the amorphous Fh-phase reflections in the XRD pattern of MSIO (Figure 16a, B) were disguised to a great extent by the crystalline peaks of $\gamma$-Fe$_2$O$_3$, the analysis of the Mössbauer spectrum indicated that MISO was composed of about 47% Fh and 53% $\gamma$-Fe$_2$O$_3$ (Table 4). In the case of CIO, all the diffraction peaks (Figure 16a, C) are in
good agreement with the standard XRD pattern of the hexagonal phase of \( \alpha{-}\text{Fe}_2\text{O}_3 \) (JCPDS No. 80-2377) and the Mössbauer result gives a further confirmation of this characteristic phase (Table 4).

A broad, low-angle XRD peak at \( 2\theta = 0.5\text{-}3.0^\circ \) (Figure 17) and a characteristic type IV isotherm with a homogeneous pore size distribution in the range 4-6 nm by N\(_2\) adsorption analyses (Figure 18) are critical pieces of evidence that both M2LFh and MSIO are mesoporous. The low-angle XRD reflections observed for M2LFh and MSIO were supported by TEM images. The TEM images illustrate the presence of a disordered mesoporous structure in both cases (Figure 16b, c). In M2LFh, primary nanoparticles smaller than 10 nm aggregated to form a disordered mesoporous structure. In the case of MSIO, a mixture of spherical and fibrous particles was apparent. Although the above mesoporous characteristics are missing for CIO, the TEM image of CIO illustrates that it is crystallized largely as tubular particles with irregular intraparticle pores (Figure 16d). The Scherrer analysis revealed that the wall structures of MSIO and CIO were made up of particles with an average crystallite size about 8 and 18 nm, respectively. The BET surface area of M2LFh, MSIO, and CIO were 180, 140, and 82 m\(^2\)/g, respectively.
Figure 16. a) Wide-angle XRD patterns of (A) M2LFh, (B) MSIO, and (C) CIO. TEM images of b) M2LFh, c) MSIO, and d) CIO.

Figure 17. The low-angle XRD pattern of M2LFh, MSIO, and CIO.
Table 4. $^{57}$Fe Mössbauer hyperfine parameters and relative integrated intensities of M2LFh, MSIO and CIO. The Mössbauer analysis was carried out at ambient temperature and various components were identified by curve-fitting analysis.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Identification</th>
<th>Isomer Shift (mm/s)</th>
<th>Quadrupole Splitting (mm/s)</th>
<th>Hyperfine Field (kOe)</th>
<th>Relative Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M2LFh</td>
<td>Doublet</td>
<td>+0.34</td>
<td>+0.72</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>MSIO</td>
<td>Sextet (I)</td>
<td>+0.34</td>
<td>0.00</td>
<td>485</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Sextet (II)</td>
<td>+0.34</td>
<td>0.06</td>
<td>422</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Doublet</td>
<td>+0.33</td>
<td>0.74</td>
<td>0</td>
<td>47</td>
</tr>
<tr>
<td>CIO</td>
<td>Sextet (I)</td>
<td>+0.38</td>
<td>-0.21</td>
<td>505</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>Sextet (II)</td>
<td>+0.38</td>
<td>-0.22</td>
<td>480</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Doublet</td>
<td>+0.36</td>
<td>+0.67</td>
<td>0</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure 18. The N$_2$ adsorption-desorption isotherms and the Barrett-Joyner-Halenda (BJH) analysis of pore size distribution for (a) M2LFh, (b) MSIO, and (c) CIO.
Among a wide range of materials tested at room temperature (RT), I found M2LFh to be the most efficient candidate for O\textsubscript{3} removal; it showed about 95 % O\textsubscript{3} removal with high reproducibility (sample A, Figure 19). MSIO (sample B) effected an O\textsubscript{3} removal of 87%, whereas CIO (sample C) showed 71% removal. The O\textsubscript{3} elimination efficiencies of these materials were remarkably better than those of $\gamma$-Fe\textsubscript{2}O\textsubscript{3} (sample D; 17.5 m\textsuperscript{2}/g) and the microporous Fe-incorporated 5 wt\% Fe/ZSM-5 (sample E; 258 m\textsuperscript{2}/g); both of these materials showed less than 5% O\textsubscript{3} removal at RT. Manganese oxide has been reported to be the most active oxide material for O\textsubscript{3} removal and is the commercial catalyst in applications such as electrostatic copying machines [59]. In my study, a commercially availed manganese oxide based O\textsubscript{3} removal catalyst (sample F; 200 m\textsuperscript{2}/g, CMD 200, Chuo Denki Kagaku Kogyo) exhibited only about 71% removal at RT. The O\textsubscript{3} removal activity of other materials, such as microporous Fe-Si composites, noble-metal-supported catalysts, mesoporous and non-mesoporous oxides, and so forth, are provided in Table 5. All these materials showed less than 75% O\textsubscript{3} removal at RT.

![Graph](image.png)

Figure 19. Comparison of the O\textsubscript{3} removal performances of various samples at RT: (A) M2LFh, (B) MSIO, (C) CIO, (D) $\gamma$-Fe\textsubscript{2}O\textsubscript{3}, (E) 5 wt\% Fe/ZSM-5, and (F) commercial MnO\textsubscript{2}.
Table 5. The $O_3$ decomposition activity of various samples at room temperature.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Physico-chemical Characteristics</th>
<th>Surface Area (m²/g)</th>
<th>$O_3$ conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5 wt% Pd/Al₂O₃</td>
<td>Non-mesoporous</td>
<td>200</td>
<td>62</td>
</tr>
<tr>
<td>Fe-Si composites</td>
<td>Microporous Fe/Si = 4</td>
<td>200</td>
<td>41</td>
</tr>
<tr>
<td>Fe-Si composites</td>
<td>Microporous Fe/Si = 2</td>
<td>401</td>
<td>38</td>
</tr>
<tr>
<td>Iron oxyhydroxide</td>
<td>Non-mesoporous</td>
<td>241</td>
<td>74</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>Non-mesoporous</td>
<td>47</td>
<td>48</td>
</tr>
<tr>
<td>Mesoporous Silica (SBA-15)</td>
<td>Mesoporous</td>
<td>-</td>
<td>15</td>
</tr>
</tbody>
</table>

I verified that the non-mesoporous 2LFh (223 m²/g) prepared by a conventional route [39] was less effective for $O_3$ removal than M2LFh; it showed only 71% $O_3$ removal at RT. This finding demonstrates that the mesoporous structure in M2LFh was advantageous in that it offered an increased number of exposed surface sites for $O_3$ adsorption and thereby enhanced performance in $O_3$ removal. The importance of mesoporous structure and the key role played by Fh nanoparticles in $O_3$ removal is also evidenced if the activity of the non-porous $\gamma$-Fe₂O₃ (sample D) and MSIO are compared. The latter is mesoporous and contains about 47% Fh, although it looks like $\gamma$-Fe₂O₃ by XRD. MSIO showed about 43.5 times higher $O_3$ removal rate than $\gamma$-Fe₂O₃ at RT. I believe that the mesoporous structure and the characteristics of the Fh phase are useful when other gases or reactants may be included in the air stream, such as when the reaction is carried out in the presence of water vapor or if the air stream contains other contaminants as ‘spectator’ species. For example, among all iron-based materials, M2LFh showed distinctly high activity when $O_3$ removal was performed at 75 °C with water vapor (Figure 20).
I have studied the X-ray absorption characteristics of M2LFh, MSIO, and CIO to have knowledge of the relative changes in the surface and bulk structural features of these materials and accordingly of their O$_3$ removal performance. The Fe K-edge extended X-ray absorption fine structure (EXAFS) analysis showed softened EXAFS oscillations (Figure 21a, left) and a much lower peak intensity in the corresponding Fourier transformed (FT) spectra at 2-4 Å (Figure 21a, right) for both M2LFh (black) and MISO (red) in comparison with CIO (blue), thus suggesting that a long-range structural order was lacking in mesoporous Fh-based materials [60].

A characteristic pre-edge peak in the Fe K-edge X-ray absorption near edge structure (XANES) spectra of M2LFh, MISO, and CIO illustrates the presence of non-centrosymmetric Fe sites [61] in all of them (Figure 21b). Of the three materials in this study, CIO with α-Fe$_2$O$_3$ phase showed the lowest pre-edge peak intensity, because the oxygen atoms in α-Fe$_2$O$_3$ are almost packed with same density around Fe$^{3+}$.
and thereby offer only a slight distortion in the octahedral ($Oh$) environment of Fe$^{3+}$ [62]. Nonetheless, although M2LFh and MSIO have high surface areas and smaller particles with lot of probable surface imperfection, I found that the pre-edge peak intensities of these materials are lower than that of pure $\gamma$-Fe$_2$O$_3$, which contains about 33% tetrahedral ($Td$) iron sites. I believe that the abundant unsaturated Fe sites on the Fh particle surface have different symmetry and coordination number and thereby affect the pre-edge peak feature and its intensity differently. Unlike the case with pure $\gamma$-Fe$_2$O$_3$, where the non-centrosymmetric iron sites are more like those in the bulk, the surface-enriched Fe sites in mesostructured Fh-based materials are readily available for adsorption and reaction. Thus, M2LFh showed the highest O$_3$ removal activity.

Further fruitful information on the electronic states of these materials was obtained by O K-edge near edge X-ray absorption fine structure (NEXAFS) spectroscopy, which is more surface-sensitive than both EXAFS and XANES (Figure 21c). The NEXAFS spectrum of CIO showed a well-resolved splitting of Fe 3d states into $t_{2g}$ and $e_g$ symmetry bands in the region A (corresponding to Fe 3d + O 2p bands) with a relatively high peak intensity in the region B (corresponding to Fe 4sp + O 2p bands) [62]. This result is a clear indication of the high packing density of oxygen atoms around iron atoms in CIO. In contrast, the splitting of the 3d state is not well-resolved for M2LFh and MSIO, and a broad peak is detected with decreased intensity of the A’ peak feature. This finding is ascribed to the inherent convoluted splitting of iron in different coordination environments with less closely packed oxygen atoms and the presence of more isolated FeO$_x$ groups [62] in M2LFh and MSIO.

Thus, the high O$_3$ removal activity of mesostructured Fh-based material is due to the abundantly available surface unsaturated iron sites with less oxygen packing
around them and the presence of isolated FeO₅ species. Probably the mesoporosity and the presence of these isolated FeO₅ units in M2LFh and MSIO make them more easily reducible than CIO and other crystalline iron oxides (evidenced from temperature-programmed reduction analysis by H₂ [63]), and accordingly, they showed the highest activity. This finding is in accordance with the literature, which suggests that an easily reducible metal oxide is more active for O₃ removal and decomposition [64]. Furthermore, with respect to CIO, the relatively low peak intensity of the Fe 4sp + O 2p states in Fh-based materials (region B, Figure 21c) and the less dense packing of oxygen around iron sites indicate that the metal electrons in the latter materials are more localized around iron-atom sites. Thus, the Fe 3d + O 2p states with electrons more localized around their iron-atom sites can readily interact with electron-deficient O₃ molecules through both π and σ bonds. Contrarily, with respect to M2LFh and MSIO, the relatively high peak intensity of Fe 4sp + O 2p states of CIO suggests that there is more electron density spread to the weekly structured Fe 4sp states in the latter case. As the electron cloud in Fe 4sp + O 2p states is less localized around iron-atom sites, O₃ interaction with CIO leads to an overall smaller charge transfer from its oxide surface to the O₃ molecule. Thus, a plot of the peak maxima of the Fe 4sp + O 2p states of these iron oxides expressed in electron yield versus O₃ removal activity showed a clear trend that CIO, with the greatest contribution of Fe 4sp states, showed the lowest activity, and vice versa (Figure 21d).
Figure 21. a) The Fe K-edge EXAFS spectra (left) and the corresponding FT spectra (right) of M2LFh (black), MSIO (red), and CIO (blue). b) The pre-edge peak from Fe K-edge XANES spectra. c) The O K-edge NEXAFS spectra. d) A plot of electron yield obtained from the O K-edge NEXAFS peak maximum in the region B (corresponding to Fe 4sp+O 2p states) versus O₃ removal activity for each sample at RT (indicated by the respective color). The activity decreases with relative increase of Fe 4sp contribution in the bonding.
8.3.4. The interaction between O₃ and Fh surface by DFT calculation

On the basis of the previously proposed calculation model of Fh (Figure 10), I have examined the interaction between O₃ and Fh (110) surface by density functional calculations (DFT) to gain a fundamental understanding of the adsorption behavior of O₃ on Fh nanoparticles. The moieties of the most stable structure that resulted after O₃ adsorption on tri- and tetracoordinated Fe sites on the Fh (110) surface are shown in Figure 22 a, b. The integrated change density difference (Δρ(r)) for each atom of the O₃-adsorbed Fh system was calculated. A qualitative picture of the amount of electron transfer during O₃ adsorption on tri- and tetracoordinated iron sites is depicted in Figure 22c, d (the charge flows from blue to orange regions). The extent of charge (electron) transfer from O₃ to Fh (O₃→Fh) and vice versa (Fh→O₃) in those adsorbed complexes were examined with Löwdin charge population (LCP) analysis, as reported in the literature [65]. This method shows that the charge population of O(I) 2p of O₃ has been increased from 4.26 to 4.59 on O₃ adsorption at tricoordinated iron sites (Table 6). In contrast, and with respect to gas-phase O₃, the charge densities of both the terminal oxygen atoms of O₃ at O(I) (O(III)) on tetracoordinated Fe sites has been increased to 4.56 (4.50). I observed that the magnitude of charge transfer from O₃ to Fh was smaller than that of back-donation during the adsorption process in both sites. A comparison of the bond length between the gas-phase O₃ (1.28 Å) and the adsorbed O₃ revealed that the O(I)-O(II) bond length (1.52 Å) of O₃ on tricoordinated sites has been elongated and that the O(II)-O(III) bond length (1.27 Å) had double-bond character, which is more or less similar to the gas-phase O₃. This result suggests that O₃ has a strong tendency to dissociate over tricoordinated iron sites, thus producing a reactive atomic ‘O’ and an O₂ molecule (see Figure 23 for a comparison of density of states of
O$_3$ before and after adsorption. Although the deformation of O$_3$ on tetracoordinated Fe sites was less pronounced than in the case of O$_3$ on tricoordinated iron sites, the former case of O$_3$ also resulted in elongation of O-O bonds (1.33–1.37 Å) with respect to gas phase O$_3$.

Figure 22. a) The partial structure derived from the optimized structure of O$_3$ adsorbed on Fh (110) tricoordinated Fe site. b) The partial structure derived from the optimized structure of O$_3$ adsorbed on Fh (110) tetracoordinated iron site. c, d) Charge density difference $\Delta \rho(r) = \rho_{O_3/Fh}(r) - \rho_{O_3}(r) - \rho_{Fh}(r)$ for O$_3$ adsorbed on Fh (110), where $\rho$ is the charge and $r$ donates the position vector. The charge flows from blue regions to orange regions. c) O$_3$ adsorbed on Fh (110) tricoordinated iron site, and d) O$_3$ adsorbed on Fh (110) tetracoordinated iron site.
Table 6. The Löwdin Charge Population (LCP) results for ozone before and after adsorption on the tri- and tetracoordinated iron sites of Fh(110) surface.

<table>
<thead>
<tr>
<th></th>
<th>Before adsorption</th>
<th>Total</th>
<th>After adsorption1)</th>
<th>Total</th>
<th>After adsorption2)</th>
<th>Total</th>
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<tr>
<td></td>
<td>s orbital</td>
<td>p orbitals</td>
<td>s orbital</td>
<td>p orbitals</td>
<td>s orbital</td>
<td>p orbitals</td>
</tr>
<tr>
<td>O(I)</td>
<td>1.86</td>
<td>4.26</td>
<td>6.12</td>
<td>1.88</td>
<td>4.59</td>
<td>6.47</td>
</tr>
<tr>
<td>O(II)</td>
<td>1.68</td>
<td>3.91</td>
<td>5.60</td>
<td>1.76</td>
<td>4.05</td>
<td>5.81</td>
</tr>
<tr>
<td>O(III)</td>
<td>1.85</td>
<td>4.26</td>
<td>6.12</td>
<td>1.86</td>
<td>4.26</td>
<td>6.13</td>
</tr>
</tbody>
</table>

1) For O₃ adsorbed on tricoordinated sites of Fh (110) surface.  2) For O₃ adsorbed on tetracoordinated sites of Fh (110) surface.

Figure 23. a) The density of states (DOS) of O₃ after adsorption on the tricoordinated iron sites of Fh (110) surface.  b) The DOS of O₃ after adsorption on the tetracoordinated iron sites of Fh (110) surface.  c) The DOS of free ozone molecule.  A comparison of the density of states of (DOS) free O₃ and O₃ after adsorbed on the iron sites of Fh (110) revealed that both σ and π bonds of O₃ are essentially involved in the interaction process.  A vanishing σ-bond of O₃ was apparent when O₃ adsorbed on tricoordinated iron sites of Fh (110) surface, suggesting that a dissociative adsorption of O₃ on such sites.
Thus, as previously proposed [66], the O$_3$ decomposition on Fh surface may proceed by an Eley-Riedel type mechanism in which the dissociatively adsorbed atomic ‘O’ that was produced on tricoordinated iron sites or the more highly charged O$_3$ on tetracoordinated iron sites undergo reaction with another O$_3$ molecule from the gaseous phase, resulting in gaseous O$_2$ and reactive peroxide species.

**8.4. Summary**

I have reported a solution-phase assembly process to obtain mesoporous 2-line ferrihydrite as a partially dehydroxylated material and demonstrated that it can be used as a new attractive and environmentally friendly material for the removal of not only organic contaminants but also O$_3$ in the air under ambient condition. My investigation on the CH$_3$CHO and O$_3$ removal performance of various iron oxides and the structure-activity study proved that both mesoporous structure and the physico-chemical characteristics of the Fh phase devoid of surface-structured water were indispensable for high activity at room temperature. These studies also demonstrate the promise of the highly favorable electronic and textural structures of mesoporous Fh or Fh-based iron oxides in environmental catalysis, especially for treating some of the most noxious gases in the atmosphere at moderate reaction conditions. I expect that the present finding will provide a new insight to design highly active and less expensive Fh-based composite materials for the rapid removal and decomposition of different kinds of noxious gases present in the atmosphere under ambient conditions.
8.5. References


Mesoporous ferrihydrite-based iron oxide nanoparticles for removal VOCs and O3 in air


Mesoporous ferrihydrite-based iron oxide nanoparticles for removal VOCs and O$_3$ in air


Chapter 9

Conclusions
9.1. Summary

The present thesis deals with the study of efficient functional materials for the removal of VOCs and O₃ in air at ambient conditions. Towards this purpose, focus was given on transition metal oxide-based catalyst materials. Various transition metal oxide materials have been prepared and examined their performance in terms of purifying the gaseous contaminants in low concentration at room temperature. Additionally, by several characterization techniques and density functional theory calculation, a detailed structure-activity study was performed to understand the VOCs and O₃ removal mechanism and the nature of active sites in the catalyst. The thesis achieved two aims of work; a) identification of active TiO₂ photocatalyst and mesoporous transition oxides and development of high active, durable, eco-friendly mesoporous transition oxides catalysts (Chapter 2-8), and b) a detailed structure-activity study and elucidation of catalyst activity to find the nature of active sites and catalytic states involved in the reaction (Chapter 4, 7, 8).

In Chapter 2, TiO₂ photocatalyst was systematically examined to evaluate their performance in purifying the gaseous contaminants in extremely low concentration at room temperature. It is found that the photocatalytic oxidation of acetaldehyde over TiO₂ photocatalyst proceeds stoichiometrically as at a given initial concentration of acetaldehyde the molar ratio of CO₂ produced to CH₃CHO decomposed was always two. I also demonstrated that oxygen, TiO₂ and light were essential for these reactions to proceed. An on-board type air purifier by using TiO₂ photocatalyst was practically evaluated. Using photocatalyst TiO₂ by supporting over a monolith-like carrier, it has been demonstrated that air purification of the vehicle interior could be performed in air
Conclusions

at room temperature. This research became a forerunner of subsequent photocatalytic air purification research.

In Chapter 3, the preparation of three-dimensional mesoporous metal oxides of Cu, Co, Ni, Mn, Fe, Cr and Ce was reported for the first time by using an interaction between various nonionic polyethylene oxide-based surfactants as template and neutral inorganic metal nitrate precursors in non-aqueous solution. Such mesoporous oxides are expected to have unique catalytic activity. These materials have 3D cubic arrangement of mesopores with semi-crystalline walls. These materials are dual functional in the sense that they are capable of capturing VOCs and catalyze their oxidation to CO₂ at the same time.

In Chapter 4, a detailed characterization of the nature of chromium site in three-dimensional mesoporous chromium oxides samples and also more detailed evaluation of the VOCs removal ability were presented. A three-dimensional cubic network of chromium oxide in which chromium was in the oxidation states ranging from +2 to +6 was observed. The average pore size was 7.9 nm, and the wall thickness was 13.3 nm. Mesoporous chromium oxide was the first reported material that not only showed high VOCs adsorption (VOCs removal) at room temperature, but also catalyzed their decomposition under these mild conditions. Toluene was thus reduced by 52% within 25 hours at room temperature, while acetaldehyde could be eliminated by up to 94%.

In Chapter 5, a mesoporous ceria using the same method as in Chapter 3 was reported. This method resulted in a unique hierarchically structured mesoporous crystalline ceria with nanometer-sized monodisperse particles with exposed most-active (111) ceria planes. The material showed very high sorption and catalytic property for
the elimination of acetaldehyde, compared to semicrystalline mesoporous ceria and non-porous crystalline ceria materials.

In Chapter 6, mesoporous ceria-titania mixed oxides with uniform pore size and enhanced thermal stability was reported. A neutral templating method was employed to produce such novel mesoporous mixed oxides. The material after calcination had high surface area with a narrow pore size distribution in the mesoporous range. The presence of well-dispersed ceria and titania components with negligible bulk oxide formation was confirmed by spectroscopic analysis. The material showed high removal ability for toluene at room temperature compared to non-porous ceria-titania, mesoporous ceria, and mesoporous titania materials, along with some CO₂ formation indicating partial oxidation/degradation of toluene.

In Chapter 7, a novel mesoporous manganese oxide–nanogold catalyst for air purification application has been reported for the first time, which can store a wide range of organic pollutants from air, as well as their decomposition. These “Memory Catalysts” have been realized only by the state-of-art combination of mesoporous γ-MnO₂ and gold nanoparticles by a VUV radiation assisted laser ablation method resulting in very strong metal-support interactions. The mesoporous γ-MnO₂ could itself efficiently eliminate acetaldehyde and toluene and this efficiency was dramatically enhanced in the presence of gold. For example, there was about 15-fold enhancement in n-hexane removal ability after Au deposition. This material also showed up to 50-times higher acetaldehyde removal ability than conventional activated carbon sorbent. Such surprisingly high performance was not possible using conventional Au-deposition techniques. Spectroscopic evidences clearly indicated the role of lattice oxygen and radical species in enhanced performance.
In Chapter 8, the environmentally compatible and highly available iron-based oxides were prepared and investigated their performance in air purification application. A template assisted synthesis route to produce stable mesoporous 2-line ferrihydrite (M2LFh) was reported for the first time. A detailed characterization of M2LFh and the evaluation of the acetaldehyde and O₃ removal ability were performed. The presence of Fh nanoparticles in disordered mesostructured iron oxide had significant effect on the bulk and surface structure of the material and the activity.

Through Chapter 2-8, highly active, durable and environmentally friendly transition metal oxides catalysts were found. In Chapter 3-8, the main intention was to exploit such a material with mesoporosity, large surface area, high oxidizing power, and probable ready evolution of active lattice oxygen, to prepare a commercially viable, cost-effective catalyst/sorbent system for efficient removal of VOCs and O₃ at low temperature. Additionally the major factors affecting VOCs and O₃ removal ability were elucidated in Chapter 4, 7, 8. The present results of mesoporous-based material and their performances in air contaminants removal demonstrate the high efficacy of such a dual functional material employing in air purification system. The advantage of such a dual functional transition metal oxide-based mesostructured material over the conventionally practiced high surface area materials and/or other material systems is that the former can act as an adsorbent as well as a catalyst (that is decomposition of them), which is not possible with the latter systems. This would be able to remove the air pollutants at a faster rate and on-board they can destruct them in a continuous process. On the other hand, the conventional catalyst (non mesoporous) cannot act as an efficient adsorbent. Therefore, the fast removal of pollutants is not possible with the conventional catalysts. Moreover, such system needs much higher temperature for
decomposing the pollutants, which is energy consuming. Furthermore, another important aspect of the present work is that a detailed structure-activity study is essential from the perspective of VOCs and O\textsubscript{3} removal since these systems are newly introduced for air purification application. Therefore, such systems have been studied in detail from structure-activity point of view for air purification application for the first time.

My study demonstrate the promise of the highly favorable electronic and textural structures of mesoporous transition metal oxides in environmental catalysis, especially for treating some of the most dangerous gases in the atmosphere at moderate reaction conditions. Thus, this investigation provided very important information and techniques required for further improvement of VOCs and O\textsubscript{3} removal catalysts. I expect my findings can contribute toward designing highly active and less expensive transition metal oxides materials for rapid removal and their decomposition of different kinds of noxious gases in the atmosphere under ambient conditions.

In conclusion, I believe that this work could trigger further work into new applications of transition metal oxides catalysts or new clean air treatment systems under ambient conditions, as well as other interdisciplinary research areas such as material science and environmental chemistry. Further, it is expected that this thesis will inspire other scientists and engineers to continuous development of environmental catalysis technology.

\subsection{9.2. Outlook}

I have found that the mesoporous transition metal oxides have great utility as catalysts and separation media for industrial applications. The openness of the
Conclusions

Microstructure allows molecular access to the internal surface of the materials that enhance their catalytic and sorption activity. Furthermore, a multitude of different coordination numbers and oxidation states of transition metal oxides can be utilized in partial oxidation, complete combustion of organic compounds and solid acid catalysis. Further work on characterization of mesoporous metal oxides is underway to establish the nature of metal at different temperatures, modification in synthesis procedure to enhance the long range order and to enhance the thermal stability of the material. The materials are also being evaluated for their performance in low temperature catalytic combustion of adsorbed contaminants in air such as VOCs, O3 where in more enhanced performance can be anticipated due to very high VOCs, O3 adsorption capacity of these materials. It is expected to develop a dual function sorbent/catalyst medium, at ambient conditions, the medium acts as a selective adsorbent for the contaminants, then, when the medium is raised to higher reaction temperature, it is an effective and selective deep oxidation catalyst for the contaminants so that the recovery and/or incineration step in case of the current commercial VOCs, O3 adsorbents can be eliminated. So these mesoporous transition metal oxides are of immense commercial importance. The present study is also intended to contribute to the realization a vehicle acts as an air-purifying device. The vehicle equipped with this newly developed catalysts on the surface of its component disclosed at a site where air stream is formed when the vehicle is moving. The vehicle cleans air as it runs.

Besides, these mesoporous transition metal oxides offer many new opportunities to study fundamental surface processes in a controlled manner and this in turn leads to fabrication of new devices. Mesoporous structure unavoidably amplify the surface character of electrically conductive transition metal oxides, which can
translated into new properties for cation-insertion battery materials based on these materials and an improved understanding of mixed-valent, mixed electron-proton conducting oxides of interest in ultracapacitors and fuel cells. Mesoporous materials whose low density and high surface area result from synthesis methods enable the solvent/template in the pore to be removed without collapsing the solid network phase. The interconnected porosity provides both molecular accessibility and rapid mass transport via diffusion, and for these reasons mesoporous transition metal oxides are interesting as intercalation electrode materials for lithium-ion batteries. Furthermore, the application of these mesostructured materials can be extended to photochromic and electrochromic displays, optical switches, chemical sensors, heat-reflecting and UV-adsorbing layers, coating to improve chemical and mechanical stability of glass, dyesensitized heterojunctions, where photo-induced charge separation occurs at the interface between the mesoporous oxide and the hole conductor or the electrolyte. To obtain the final goal, further efforts are required for optimization of the target's specifications.
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“Photocatalytic deodorization on TiO₂ coated honeycomb ceramics”

Kenichirou Suzuki


“Photocatalytic air purification on TiO₂ coated honeycomb support”

Chapter 3

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“Novel promising 3-D mesoporous metal oxides sorbent/catalyst with volatile organic compounds elimination ability”

Chapter 4

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“Novel promising 3-D mesoporous metal oxides sorbent/catalyst with volatile organic compounds elimination ability”
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**Chapter 6**  
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Patent

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