Adsorption and Oxidative Desorption of Acetaldehyde over Mesoporous FeₓOᵧHₓ/Al₂O₃

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Supporting Information

ABSTRACT: FeₓOᵧHₓ nanostructures were incorporated into commercially available and highly porous alumina using the temperature-regulated chemical vapor deposition method with ferrocene as an Fe precursor and subsequent annealing. All processes were conducted under ambient pressure conditions without using any high-vacuum equipment. The entire internal micro- and mesopores of the Al₂O₃ substrate with a bead diameter of ~2 mm were evenly decorated with FeₓOᵧHₓ nanoparticles. The FeₓOᵧHₓ/Al₂O₃ structures showed substantially high activity for acetaldehyde oxidation. Most importantly, FeₓOᵧHₓ/Al₂O₃ with a high surface area (~200 m²/g) and abundant mesopores was found to uptake a large amount of acetaldehyde at room temperature, and subsequent thermal regeneration of FeₓOᵧHₓ/Al₂O₃ in air resulted in the emission of CO₂ with only a negligibly small amount of acetaldehyde because FeₓOᵧHₓ nanoparticles can catalyze total oxidation of adsorbed acetaldehyde during the thermal treatment. Increase in the humidity of the atmosphere decreased the amount of acetaldehyde adsorbed on the surface due to the competitive adsorption of acetaldehyde and water molecules, although the adsorptive removal of acetaldehyde and total oxidative regeneration were verified under a broad range of humidity conditions (0~70%). Combinatory use of room-temperature adsorption and catalytic oxidation of adsorbed volatile organic compounds using FeₓOᵧHₓ/Al₂O₃ can be of potential application in indoor and outdoor pollution treatments.

1. INTRODUCTION

Volatile organic compounds exist in indoor and outdoor environments. Indoor atmospheres contain materials used for interior construction such as paints and adhesives that consist of organic solvents, which are volatile and known to cause “sick-building syndrome.” In the outdoor atmosphere, volatile organic compounds are emitted from vehicles, power plants, and anything using fossil fuels. In these cases, incomplete combustion of fuel and subsequent emission of volatile organic compounds are unavoidable. Volatile organic compounds in outdoor environments are recently of more concern because these molecules act as seeds for secondary organic aerosols under atmospheric conditions by interacting with light and nitrogen-containing compounds. Toxicity of the volatile organic compounds themselves and that of the secondary organic aerosols induced by volatile organic compounds have been widely reported in the literature. Therefore, removal of volatile organic compounds has become more and more important in environmental science and engineering.

Adsorbents with very high surface area materials are one of the most widely used methods for removing volatile organic compounds. Activated carbon is the most widely used adsorbent for pollutants in air, and more recently, novel materials with high surface areas and porosities such as metal–organic frameworks have shown potential for applications as adsorbents. Adsorbents are one of the most efficient ways for removing volatile organic compounds, and they also have the advantage that the energy consumption for operation of an adsorbent-based filtering system seems to be quite low. However, once all the surface adsorption sites are occupied by molecules, the adsorbent should be replaced by a new one, and the used adsorbents should be regenerated (e.g., by thermal treatment). During the thermal regeneration process, adsorbed species can be re-emitted into the air, causing a secondary pollution problem. An alternative way of removing volatile organic compounds is heterogeneous catalysis. Here, volatile organic compounds consisting of C, H, and O and oxygen gas (or water vapor) can adsorb on the surface of catalysts and react to form CO₂ and H₂O. Ideally, heterogeneous catalysts can be permanently used because the reaction products (CO₂ and H₂O) desorb from the surface of the catalyst, thus always providing free adsorption sites to the next volatile organic compound. Generally, nanoparticles of Pt-group metals supported by mesoporous alumina or silica are widely used for the catalytic oxidation of volatile organic compounds. Catalytic converters are widely used for exhaust gas treatments in vehicles. In this case, emitted gas is at a relatively high temperature (<150 °C) at which Pt-group catalysts can work.

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properly. However, the use of such catalysts for indoor pollution treatment is limited due to the energy cost needed for heating the catalysts to their operating temperatures. Another hurdle for the use of Pt-group catalysts is the high prices of these materials and their low natural abundance.

Alternative materials to Pt-group metals such as Ni, Co, Cu, and Au have been widely considered as candidates of the key components of catalytic converters for polluted atmospheres. Some of these cost-effective materials (in the form of nanoparticles smaller than ~5 nm in diameter) can be as efficient as Pt group-based catalysts for the total oxidation of volatile organic compounds. However, these catalytically active nanoparticles exhibit lower thermal stability and therefore easily agglomerate into larger particles, losing the effective surface area and catalytic activity within a short time.

One of the promising methods for increasing the thermal stability and catalytic activity of nanoparticles is incorporating them into mesoporous media. There have been many works devoted to fabricating mesoporous substrates in which catalyst nanoparticles are highly dispersed. Many works related to this issue are based on the synthesis of mesoporous materials and incorporation of catalytically active species during the synthesis process of the mesoporous structures. Alternatively, one can consider the use of already commercially available and cost-effective mesoporous alumina or silica as substrates and post-incorporation of catalytically active nanoparticles into the mesoporous templates. However, wet-chemical processes based on the capillary force of the solvent often hinder diffusion of metal salt ions or metal nanoparticles into the deeper part of mesoporous templates. Vapor deposition methods such as atomic layer deposition (ALD) can effectively incorporate catalytically active nanoparticles into mesoporous media. We have recently reported that temperature-regulated chemical vapor deposition (TR-CVD), which does not require complex equipment like ALD, can efficiently incorporate NiO and FeOxH2 nanoparticles at the internal structure of bead-type substrate of mesoporous alumina and silica substrates.

In this work, FeOxHx was incorporated into a very cost-effective commercially available alumina bead with not only mesopores but also micropores using TR-CVD. The resulting structures were used as catalysts for acetaldehyde oxidation. Our results suggest the possibility of fabricating more cost-effective FeOxHx/Al2O3 catalysts, which are efficient for total oxidation of volatile organic compounds. It is worth mentioning that the Al2O3 sample we used is currently as cost-effective as activated carbon, which is a widely used adsorbent for air purification. The most crucial result of this work is that our FeOxHx/Al2O3 can operate as an effective adsorbent of volatile organic compounds at room temperature, and thermal regeneration of the used adsorbent results in dominant emission of CO2 with only negligibly small amounts of volatile organic compounds due to the total catalytic oxidation of adsorbed volatile organic compounds molecules into CO2 by FeOxHx nanoparticles evenly dispersed within the mesoporous Al2O3 beads. The cycle of adsorption of volatile organic compounds on FeOxHx/Al2O3 and its regeneration without pollutant emission can work under a broad range of humidity and be repeated many times.

2. RESULTS AND DISCUSSION

2.1. Characterization of Bulk and FeOxHx-Decorated Al2O3 Beads. Table 1 summarizes the specific surface areas and mean pore sizes of alumina substrates before and after FeOxHx deposition and subsequent postannealing. Before FeOxHx deposition, Al2O3 shows a relatively high surface area (305.1 m²/g) and a small mean pore size (5.5 nm). For all characterizations of FeOxHx-deposited Al2O3, the sample with Fe loading of 10 wt % was used. After FeOxHx deposition using TR-CVD and subsequent postannealing at 450 °C under ambient conditions, the surface area of the sample significantly decreased (from 305.1 to 204.3 m²/g), and the mean pore size slightly increased (from 5.5 to 5.8 nm). This result can be interpreted in two ways: the pores smaller than ~3–4 nm existing in Al2O3 ruptured during the TR-CVD and postannealing process, or those pores were blocked by FeOxHx nanoparticles. In fact, the pore size distribution of these samples displayed in Figure 1 clearly shows that the number of pores smaller than ~3–4 nm existing in fresh Al2O3 disappeared upon FeOxHx deposition and postannealing. For further shedding light on the structure of FeOxHx overlayer deposited in Al2O3, TEM was used. Even though the use of high-resolution TEM and high-angle annular dark-field (HAADF) imaging was not successful in obtaining information about the structure of FeOxHx, Fe elemental mapping image clearly showed that nanoparticles smaller than ~3–4 nm in lateral size of the Fe-containing structure were finely distributed on the surface of Al2O3 (Figure 2). One can

| compound | surface area (m²/g) | average pore diameter (nm) |
|----------|---------------------|----------------------------|
| Al2O3    | 305.1               | 5.5                        |
| FeOxHx/Al2O3 | 204.3               | 5.8                        |

Figure 1. BJH pore volume distributions of bulk Al2O3 and FeOxHx/Al2O3 (10 wt % Fe) based on N2 adsorption isotherm.

Figure 2. EDS mapping image of Fe element of FeOxHx/Al2O3 (10 wt % Fe) sample prepared by TR-CVD and a subsequent heat treatment.
Therefore suggest that FeO$_x$H$_y$ nanoparticles with a mean size of $\sim$3–4 nm could fill the pores of Al$_2$O$_3$, reducing the specific surface area and increasing the mean pore size of the substrate. However, the possibility that the pores ruptured during TR-CVD and postannealing cannot be ruled out.

To shed light on the distribution of FeO$_x$H$_y$ within the porous Al$_2$O$_3$ bead after deposition of Fe using TR-CVD, cross sections of FeO$_x$H$_y$/Al$_2$O$_3$ were monitored using EDS elemental mapping of the sides of the mechanically fractured samples (Figure 3). As shown in Figure 3a,b, both Al and Fe were evenly distributed over the entire plane of the side of the mechanically fractured FeO$_x$H$_y$/Al$_2$O$_3$, indicating that FeO$_x$H$_y$ was deposited on the surface of the alumina bead and evenly distributed in the entire internal structure of the alumina bead. We have previously shown that such even decoration of the internal structure of $\gamma$-Al$_2$O$_3$ with larger pores with Fe could be realized using the TR-CVD method. Note that the Al$_2$O$_3$ substrate used in the present work consists of a higher portion of micropores, and therefore, diffusion of the Fe precursor into deeper layers of the Al$_2$O$_3$ bead during the TR-CVD process could be much more kinetically hindered. As shown in Figure 3a,b, however, an even distribution of Al and Fe was observed in the entire internal structure of FeO$_x$H$_y$/Al$_2$O$_3$ in the present work. Thus, our TR-CVD technique allows efficient incorporation of FeO$_x$H$_y$ nanoparticles in the core part of the alumina beads, consisting of both meso- and micropores in size.

Figure 4 shows XRD patterns of bulk and FeO$_x$H$_y$-deposited Al$_2$O$_3$. For the bulk Al$_2$O$_3$, the appearance of a pronounced peak at 67° was accompanied by multiple broad peaks in the 2θ range from 20° to 50°. This pattern can be attributed to the $\gamma$-phase of Al$_2$O$_3$, even though we cannot exclude the existence of other phases of Al$_2$O$_3$ such as $\gamma$-Al$_2$O$_3$. After deposition of Fe$_x$O$_y$H$_z$, no additional feature could be clearly seen, most likely due to the small particle size of FeO$_x$H$_y$ and its poor crystallinity.

Figure 5 shows XPS Fe 2p$_{3/2}$ spectra of FeO$_x$H$_y$-deposited Al$_2$O$_3$. Fe 2p$_{3/2}$ spectra of FeO$_x$ show multiple features, which can be attributed to surface and bulk components of FeO$_x$ and many other states related to final state relaxation effects. In the literature, different phases of Fe oxide such as $\alpha$-FeO$_x$, $\gamma$-FeO$_x$, and FeO$_x$ exhibited different shapes of Fe 2p spectra. The Fe 2p$_{3/2}$ spectrum in Figure 5 was deconvoluted into five different components based on the information from the literature; however, considering the ratio between areas of five different components used for fitting the Fe 2p$_{3/2}$ spectrum in Figure 5, one cannot attribute our Fe 2p$_{3/2}$ spectra to a specific phase of Fe oxide, even though the binding energy of the peaks can be mostly attributed to Fe(III) ($\sim$709–712 eV) with some minor contribution of Fe(II) ($\sim$706–709 eV). UV–Vis diffuse reflectance spectroscopy also does not provide a clear clue to the crystalline structure of the FeO$_x$H$_y$ (Figure S1).

XRD, XPS, and UV–Vis diffuse reflectance spectroscopy failed to provide a deep insight into the structure of FeO$_x$H$_y$. To shed light on the detailed structure of FeO$_x$H$_y$ nanoparticles on Al$_2$O$_3$, we employed Mössbauer spectroscopy. The spectrum obtained at $-268.95$ °C together with the results of fitting of the spectrum is shown in Figure 6. It is notable that there is a strong doublet structure centered at $\sim$0 mm/s of the velocity, and this feature can be attributed to the ferrihydrite structure (FeO$_x$(OH)4H$_2$O). The ferrihydrite structure is known to be very defective and exists only in the form of nanostructures. For completely fitting the experimentally obtained Mössbauer spectra, A and B sites of FeO$_x$ as well as $\alpha$-FeO$_x$ should be included, each of which can be represented by a sextet feature with different shifts and splittings (Figure S2). It is worth noting that FeO$_x$ consists of a mixture of Fe(II) and Fe(III), and therefore, two different sites for FeO$_x$ should be included in the fitting process. As summarized in Figure 6, our FeO$_x$H$_y$ structure can be attributed to a complex mixture of ferrihydrite, Fe$_3$O$_4$, and $\alpha$-FeO$_x$.

2.2. Catalytic Oxidation of Acetaldehyde. Figure 7 shows the results of the light-off experiments using FeO$_x$H$_y$/Al$_2$O$_3$ samples with three different Fe loadings (3, 6, and 10 wt %). Starting from 450 °C, the reactor temperature was decreased with a constant cooling rate under a constant feed of acetaldehyde vapor with dry air, and at the same time, the gases in the outlet of the reactor were analyzed using GC. For the sample with 10 wt % Fe, the CO$_2$ evolution rate is close to the corresponding value of the total oxidation of the acetaldehyde fed into the reactor at above 300 °C (Figure 6). When the reactor temperature became lower than 300 °C, the CO$_2$ evolution rate drastically decreased with decreasing temperature; however, the acetaldehyde consumption rate shown in Figure 7b remained nearly constant within the temperature range of 50–450 °C, and most of the acetaldehyde molecules introduced into the reactor were consumed inside the reactor. Acetaldehyde is removed mostly by total oxidation to CO$_2$ and H$_2$O above 300 °C. Below this temperature, partial oxidation of acetaldehyde and adsorption of the partially oxidized species take place on the surface of FeO$_x$H$_y$/Al$_2$O$_3$. Molecular chemisorption of acetaldehyde is most likely the removal path of acetaldehyde in the lower temperature range, where the acetaldehyde consumption rate is close to 100%, yet almost no CO$_2$ was observed. With decreasing Fe loading from 10 wt % to 6 and 3 wt %, the CO$_2$ evolution rate slightly decreased; decrease in the CO$_2$
The evolution rate with decreasing Fe loading was pronounced in the temperature range above 300 °C. On the other hand, the sample with 6 wt % Fe loading showed nearly complete consumption of acetaldehyde from 450 to 500 °C, whereas 3 and 10 wt % samples showed very slight decrease in the acetaldehyde consumption below 300 °C. The total oxidation rate of acetaldehyde correlates with the amount of Fe, implying that Fe₃O₄H₂ should be an active species for acetaldehyde total oxidation. Regarding acetaldehyde adsorption and partial oxidation activity, which do not correlate with the amount of Fe, not only Fe₃O₄H₂ but also Fe₅O₇H/Al₂O₃ interface sites and Al₂O₃ can come into play.

To shed light on the stability of the catalytic activity of Fe₅O₇H/Al₂O₃ with 10 wt % Fe loading, acetaldehyde was fed into the reactor with the catalyst at a temperature of 250 °C, and the reaction products were measured using a GC connected to the outlet of the reactor. As shown in Figure 7c, a nearly constant acetaldehyde consumption rate was shown for 1440 min, indicating high stability of the catalyst structures. The CO₂ evolution was not observed at the initial stage of each experiment (Figure 7d) because acetaldehyde is most likely consumed by partial oxidation and molecular chemisorption on the Al₂O₃ surface. This chemisorption was a different case from the physisorption mentioned in Figure 9c. As the Al₂O₃ surface is saturated by acetaldehyde and its partial oxidation products, further incoming acetaldehyde can diffuse more efficiently to Fe₅O₇H/Al₂O₃ catalysts in the form of an extrinsic precursor, and CO₂ evolution was then observed. After the catalytic activity experiment, a temperature programmed desorption (TPD) experiment was subsequently performed, and the only desorption species detected by GC was CO₂ (Figure 7e). Residual carbon from chemisorbed acetaldehyde or partially oxidized species of acetaldehyde, which was not totally oxidized at the initial stage of the long-term catalytic activity experiment, remained on the catalyst surface, resulting in a large amount of CO₂ desorption in the subsequently performed TPD experiment. Most of CO₂ in the TPD experiment was desorbed below 400 °C.

The greatest advantage of using Fe₅O₇H/Al₂O₃ could be addressed via TPD experiments, which shows how the
adsorbed acetaldehyde molecules are desorbed from the surface (Figure 8). The TPD experiment was subsequently performed after the adsorption of acetaldehyde for 60 h, and the results are shown in Figure 8. It is worth noting that the TPD experiments can imitate the oxygen-limited situations when instant and intensive heat is treated as in the practical regeneration process of catalysts. One can see that a much larger amount of CO\textsubscript{2} was generated when Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z} was deposited on the Al\textsubscript{2}O\textsubscript{3} structure, which implies higher incomplete oxidation of acetaldehyde in the case of bulk Al\textsubscript{2}O\textsubscript{3}. Moreover, in the chromatogram of the gases passed through the reactor at 350 °C (Figure S3), various toxic organic molecules (e.g., CO, CH\textsubscript{4}, C\textsubscript{n}) were additionally produced in the case of bulk Al\textsubscript{2}O\textsubscript{3}, while only CO\textsubscript{2} was generated in Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3}. Unlike bulk Al\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3} did not emit any secondary pollutants during the regeneration process.

Figure 7. (a) CO\textsubscript{2} evolution rates and (b) acetaldehyde consumption rates of Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3} with three different Fe contents (3, 6, and 10 wt %) as a function of temperature. (c) Acetaldehyde consumption rate and (d) CO\textsubscript{2} evolution rate of the Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3} (10 wt % Fe) as a function of reaction time at the fixed temperature of 250 °C. (e) TPD results after the acetaldehyde oxidation for 24 h at 250 °C using Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3} (10 wt % Fe).

Figure 8. TPD results of bulk Al\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3} (10 wt % Fe). Prior to TPD, acetaldehyde adsorption was carried out for 60 h under dry condition.
2.3. Adsorption of Acetaldehyde on Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3} at Room-Temperature and Thermal Oxidative Regeneration of Adsorbents. The porous Al\textsubscript{2}O\textsubscript{3} substrate used in the present work is well known for its cost effectiveness, and the TR-CVD process for Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z} deposition based on thermal evaporation with ferrocene as an Fe precursor under ambient conditions also shows the potential for cost-effective fabrication of catalysts in a larger scale. Our Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3} samples should be potential candidates of adsorbents of various volatile organic compounds. Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z} nanoparticles incorporated within porous alumina substrate can also efficiently catalyze total oxidation of volatile organic compounds, yielding CO\textsubscript{2} and H\textsubscript{2}O. Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3} can capture volatile organic compounds at lower temperatures, and along with thermal regeneration of the saturated adsorbents, Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z} can catalyze the conversion of volatile organic compounds to CO\textsubscript{2}. Assuming that this scenario can be realized, it can overcome problems of conventional adsorbents and catalysts. For example, widely used adsorbents such as activated carbon emit volatile organic compounds upon thermal regeneration of the saturated adsorbents. In addition, thermal catalysts require high temperature, and therefore, energy cost for constantly operating thermal catalysts is of concern.

Our attempt reveals that Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3} shows the high adsorption capacity of acetaldehyde near room temperature. On the other hand, most of the adsorbed acetaldehyde is converted into CO\textsubscript{2} upon thermal regeneration of the adsorbents under atmospheric conditions. As shown in Figure 9a, the acetaldehyde molecules fed into the reactor (concentration of acetaldehyde at the inlet of the reactor was 160 mol ppm) with 1 g of Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3} were almost completely removed by Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3} under dry air conditions for 12 h. When Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3} exposed to acetaldehyde-containing dry air for 12 h was subsequently heated with a constant heating rate under dry air flow, a large amount of CO\textsubscript{2} was desorbed from Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3} in the reactor temperature range of 100–450 °C with a pronounced desorption peak at 270 °C (Figure 9b). The amount of acetaldehyde desorbed during this thermal treatment of Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3} exposed to acetaldehyde-containing dry air is negligibly small with respect to the CO\textsubscript{2} desorption (Figure 9c). This acetaldehyde adsorption/oxidative regeneration of Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3} can be repeated many times (Figure S4).

We also studied the influence of the humidity of the atmosphere to the adsorption capacity of Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3} toward acetaldehyde as well as thermal oxidative regeneration of acetaldehyde-saturated surfaces. With increasing humidity of the air with acetaldehyde, acetaldehyde adsorption capacity of the surface decreased; for dry conditions, no acetaldehyde could be seen in the outlet of the reactor during 12 h by complete adsorption of all incoming acetaldehyde molecules into the reactor at Fe\textsubscript{x}O\textsubscript{y}H\textsubscript{z}/Al\textsubscript{2}O\textsubscript{3}; however, with increasing humidity of the atmosphere from 0 to 30%, increase in the acetaldehyde concentration at the outlet of the reactor could be found. With further increase in the humidity level, increase
in the acetaldehyde concentration at the outlet of the reactor with time became more pronounced, indicating that humidity decreases the adsorption capacity of acetaldehyde due to the competitive adsorption. This result can suggest that the surface of our Fe\textsubscript{2}O\textsubscript{3} catalyst is quite hydrophilic, probably due to the existence of hydroxyl groups from the ferrhydrite phase on the surface of Fe\textsubscript{2}O\textsubscript{3} particles. As an attempt to increase resistance against humidity, one can possibly consider coating a hydrophobic silicon-based polymer layer on the surface of porous materials. However, this hydrophobic silicon layer lacks thermal stability; this hydrophobic layer starts to decompose at 250 °C.\textsuperscript{30} Formation of thermally stable and humidity-resistant surface warrants further studies, yet the highlight of the present work is the complete oxidation of acetaldehyde of Fe\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}.

In the subsequently performed thermal regeneration experiment using air flow with the humidity used for the respective adsorption experiments near the room temperature, CO\textsubscript{2} desorption could be found at 300–450 °C with the maximum desorption rate at ∼400 °C, which is much higher that the CO\textsubscript{2} maximum desorption temperature of dry condition experiments. Water vapor shows a blocking effect not only for the adsorption of acetaldehyde near the room temperature but also for total oxidation of acetaldehyde to CO\textsubscript{2} at ∼300 °C.

We have calculated the amount of acetaldehyde taken from the Fe\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} surface under conditions of various humidity levels and how much adsorbed acetaldehyde was either desorbed as an acetaldehyde molecule or converted into CO\textsubscript{2} in each experiment (Figure 9d), and the details of the calculations are given in Figure S5. Even though increase in the humidity in this experiment decreased acetaldehyde uptake, nearly all adsorbed acetaldehyde near room temperature was converted into CO\textsubscript{2} in the subsequently performed TPO experiments. Therefore, we can conclude that our Fe\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} can be used as adsorbents of acetaldehyde, which can be regularly thermally regenerated, thereby emitting almost no acetaldehyde but only CO\textsubscript{2} under a wide range of humidity levels of atmosphere.

3. CONCLUSIONS

Fe\textsubscript{2}O\textsubscript{3} nanoparticles smaller than ∼3–4 nm were incorpo- rated into commercially available and highly porous alumina using TR-CVD and subsequent annealing. We showed that Fe\textsubscript{2}O\textsubscript{3} nanoparticles were evenly spread throughout the substrates, even for Al\textsubscript{2}O\textsubscript{3} beads with a diameter exceeding 1–2 mm consisting of micro- and mesopores. This indicates that the whole structure of mesoporous bead-type substrates can serve as supports for Fe\textsubscript{2}O\textsubscript{3} catalysts. Fe\textsubscript{2}O\textsubscript{3}-decorated Al\textsubscript{2}O\textsubscript{3} shows high catalytic activity for acetaldehyde total oxidation at ∼250 °C or above. It is worth noting that the porous alumina used in the present work is nearly as economical as activated carbon, which is a widely used adsorbent in commercial air-purifying systems. Most importantly, we found that Fe\textsubscript{2}O\textsubscript{3}-decorated Al\textsubscript{2}O\textsubscript{3} can adsorb a large amount of acetaldehyde at room temperature, and subsequent thermal regeneration of the Fe\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} adsorbent resulted in emission of CO\textsubscript{2} with only a negligible amount of acetaldehyde because Fe\textsubscript{2}O\textsubscript{3} nanoparticles can catalyze the total oxidation of acetaldehyde adsorbed on the surface during the thermal treatment of Fe\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}. The adsorption of acetaldehyde and oxidative regeneration of the Fe\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} adsorbents can be repeated several times. The room-temperature adsorption of acetaldehyde and subsequent thermal oxidative regeneration for Fe\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} were verified under a wide range of humidity levels of the atmosphere. Conventional adsorbents such as activated carbon generally emit volatile organic compounds adsorbed on the surface into the air during regeneration, causing a secondary pollution problem. On the other hand, current thermal catalysts for oxidation of volatile organic compounds should constantly operate at high temperature, requiring high energy cost for operation. Room-temperature adsorption and catalytic oxidation of adsorbed volatile organic compounds with the Fe\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} can be used in indoor and outdoor pollution treatments in the future due to the fact that secondary pollutant emission during regeneration can be avoided, and thermal energy need not be constantly supplied (but only be provided at regular intervals) using Fe\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}. This saves energy costs as compared to the thermal catalysts.

4. EXPERIMENTAL SECTION

4.1. Materials. The highly porous spherical Al\textsubscript{2}O\textsubscript{3} substrate (particle size: 2.0 mm (7 × 14 Tyler mesh), total pore volume: 0.5 mL/g) was purchased from BASF (Germany). Bis-(cyclopentadienyl)iron (Fe(Cp)\textsubscript{2}) was purchased from Sigma Aldrich (USA). Acetaldehyde (200 ppm) diluted with N\textsubscript{2} was purchased from JC Gas (Korea).

4.2. Preparation of Fe\textsubscript{2}O\textsubscript{3}-Incorporated Mesoporous Al\textsubscript{2}O\textsubscript{3}. The Fe\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} catalysts were prepared by the TR-CVD method.\textsuperscript{21,33} Bis(cyclopentadienyl)iron (Fe(Cp)\textsubscript{2}) was used as a metal precursor, and water vapor or oxygen gas in the reaction chamber was used as the oxidizing agent. Fe(Cp)\textsubscript{2} (10, 21, or 67.5 g) in a foil container was located at the bottom of the box-type stainless-steel chamber (size: 56 × 37 × 9 cm\textsuperscript{3}), and 100 g of Al\textsubscript{2}O\textsubscript{3} loaded in a mesh container was placed in the middle of the chamber. Different amounts of Fe(Cp)\textsubscript{2} resulted in various Fe loadings on Al\textsubscript{2}O\textsubscript{3}. The chamber was equipped with a heating band, k-type thermocouple, temperature controller, and power supply. For the TR-CVD process, the chamber was closed with a lid and space between the chamber body, and the lid was sealed with a polyimide (PI) tape. First, the chamber was heated to 60 °C for evaporation of the iron precursor (Fe(Cp)\textsubscript{2}), and this temperature was maintained for 2 h. After 2 h, the temperature of the chamber was further raised to 200 °C, and this temperature was then maintained for 12 h to deposit Fe\textsubscript{2}O\textsubscript{3} nanoparticles on the internal surface of porous Al\textsubscript{2}O\textsubscript{3} substrates. After the TR-CVD process, the Fe\textsubscript{2}O\textsubscript{3}-deposited Al\textsubscript{2}O\textsubscript{3} sample was preannealed at 450 °C for 8 h under a dry air flow of 30 mL/min to remove carbon impurities on the surface of the sample. The preannealing time for the sample was adjusted on the basis of the level of carbon impurities on the surface of the sample; that is, annealing was carried out at this temperature and under dry air until no CO\textsubscript{2} desorption could be identified.

4.3. Characterization of Materials. The surface area and average pore diameter of the samples were analyzed by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods based on N\textsubscript{2} isotherms (3Flex, Micromeritics). The Fe\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} sample was analyzed by scanning transmission electron microscopy (STEM, JEOL, JEM-ARM200F) equipped with energy dispersive spectroscopy (EDS) to confirm the dispersion of Fe\textsubscript{2}O\textsubscript{3} nanoparticles on the Al\textsubscript{2}O\textsubscript{3} substrate. XRD spectra were obtained using an X-ray diffractometer (Rigaku, Ultima IV) using Cu Kα radiation (40 kV, 30 mA, λ = 1.54 Å) with a scanning rate of 4°/min.\textsuperscript{21}
Scanning electron microscopy (SEM, JEOL, JSM-7100F) equipped with energy dispersive spectroscopy (EDS) was used to analyze the elemental distribution of cross-sectional planes of Fe$_2$O$_3$/Al$_2$O$_3$. Fe loading was analyzed by using inductively coupled plasma optical emission spectrometry (ICP-OES, Varian). Also, the chemical states of elements of the Fe$_2$O$_3$/Al$_2$O$_3$ were analyzed by X-ray photoelectron spectroscopy (XPS). For the XPS analysis, the Fe$_2$O$_3$/Al$_2$O$_3$ sample prior to preannealing was located in a furnace inside a glove box filled with Ar, and it was annealed at 450 °C under a dry air flow of 30 mL/min for 8 h. After the annealing process, the sample was transferred from the glove box to an ultrahigh vacuum (UHV) system using a magnetic transfer system without exposing the sample to the air. XPS analysis proceeded under UHV conditions with a base pressure of $3 \times 10^{-10}$ Torr. The Mg Kα X-ray (1253.6 eV) was used as the photon source for XPS. XPS spectra were collected at a pass energy of 30 eV by a concentric hemisphere analyzer (CHA, PHOIBOS-HAS 3500, SPECS).

The hyperfine interaction and site occupancy of magnetic ions of the Fe$_2$O$_3$/Al$_2$O$_3$ sample were investigated by $^{57}$Fe Mössbauer spectroscopy at $-268.95$ °C and room temperature. Mössbauer spectra were recorded by using a conventional spectrometer of the electromechanical type with a single $^{57}$Co γ-ray source in an Rh matrix, which was calibrated by using an α-Fe foil. The source was accelerated through a range of velocities from −12 to 12 mm/s using a driving unit to produce a Doppler effect and scanned the γ-ray energy. Mössbauer spectra were analyzed by a least-squares fitting procedure, and we obtained the relative area ratio of various Fe sites, magnetic hyperfine field ($H_{hf}$), isomer shift ($\delta$), and electric quadrupole splitting (EQ).

4.4. Catalytic Activity Test. The catalytic activity of Fe$_2$O$_3$/Al$_2$O$_3$ for acetaldehyde oxidation was tested with a flowing system consisting of a quartz tube (internal diameter of 21 mm, length of 300 mm) reactor, temperature controller, mass flow controller (MFC), and gas chromatograph (GC, Hewlett Packard, HP 6890) equipped with a capillary column (Agilent Technologies, HP-5/60, 0.3 mm × 50 mm), methanizer, and flame ionization detector. Here, 1.0 g of Fe$_2$O$_3$/Al$_2$O$_3$-deposited Al$_2$O$_3$ was used as catalysts for the acetaldehyde oxidation experiment. The catalyst was in a quartz boat (internal size: $70 \times 20 \times 8$ mm$^3$) placed in the center of the quartz tube.

Before the acetaldehyde oxidation experiments, each Fe$_2$O$_3$/Al$_2$O$_3$-deposited Al$_2$O$_3$ sample was preannealed at 450 °C for 8 h under a dry air flow condition of 30 mL/min until the removal of all carbon impurities on the surface of the catalyst was achieved. After the preannealing step, the catalytic activities of the samples as a function of reaction temperature were analyzed.

The temperature of the reactor was maintained at 450 °C, and then the reagent gas, that is, 160 ppm acetaldehyde gas diluted by dry air with a total flow rate of 20 mL/min (200 ppm acetaldehyde gas diluted with N$_2$ with 16 mL/min + O$_2$ gas of 4 mL/min; flow rate of each gas was regulated by MFC), was fed into the reactor. After the acetaldehyde flow was stabilized, the reactor temperature decreased from 450 to 50 °C at a rate of 1 °C/min. The concentrations of acetaldehyde and CO$_2$ in the outlet of the reactor with catalysts were analyzed using online GC. For these experiments, samples with Fe loadings of 3, 6, and 10 wt % were used.

The catalytic activity of the sample with Fe loading of 10 wt % was also measured at a constant reaction temperature of 250 °C as a function of time for 24 h. After the preannealing process, the temperature of the reactor was maintained at 250 °C, and the reagent gas was fed into the reactor with the previously mentioned flow rate. After the experiment, 30 mL/min N$_2$ gas was used for purging the reactor for 1 h at 250 °C, and temperature-programmed oxidation (TPO) experiments over used catalysts were subsequently conducted to determine the amount of remaining carbon species on the surface of catalysts. For TPO, the temperature of the reactor was raised from 250 to 450 °C at a ramping rate of 1 °C/min under a dry air flow of 30 mL/min.

4.5. Temperature Programmed Desorption. To elucidate the effects of Fe$_2$O$_3$/H$_2$ on the catalytic activity of acetaldehyde oxidation, temperature programmed desorption (TPD) experiments of acetaldehyde from bulk Al$_2$O$_3$ and Fe$_2$O$_3$/H$_2$/Al$_2$O$_3$ were performed. To the reactor, 1.0 g of Al$_2$O$_3$, and 1.0 g of Fe$_2$O$_3$/H$_2$/Al$_2$O$_3$ were added and annealed at 450 °C for 2 h under a dry air flow of 30 mL/min to remove surface impurities. After this preannealing step, the reactor temperature was cooled to 30 °C, and 200 mol ppm acetaldehyde diluted with balanced N$_2$ gas with a flow rate 10 mL/min for 60 h was applied to allow acetaldehyde adsorption on the surface. Subsequently, acetaldehyde in the reactor was purged by a N$_2$ flow of 30 mL/min. Then, the reactor temperature was increased from 30 to 450 °C at a heating rate of 1 °C/min under N$_2$ flow. The gas mixture that had passed through the reactor during TPD experiments was analyzed by an identical GC system as was used for the aforementioned catalytic activity experiments.

4.6. Adsorption of Acetaldehyde at Room-Temperature and Thermal Oxidative Regeneration. The potential use of Fe$_2$O$_3$/H$_2$/Al$_2$O$_3$ as a recyclable absorbent for acetaldehyde was tested using experiments consisting of near-room-temperature adsorption of acetaldehyde on Fe$_2$O$_3$/H$_2$/Al$_2$O$_3$ and its thermal oxidative regeneration at various humidity conditions. The experiments were tested with a stainless-steel reactor (inner diameter of $1/2$ in, length of 5 cm). The gas preparation stage comprised three mass flow controllers (MFCs) and a bottle filled with distilled water (Figure S6). Humidity of the reagent gas was controlled by the temperature of the distilled water bottle sealed with heating band (24 °C (30% RH), 58.5 °C (50% RH), and 69.5 °C (70% RH)). Before the acetaldehyde oxidation experiments, 1.0 g of Fe$_2$O$_3$/H$_2$/Al$_2$O$_3$-deposited Al$_2$O$_3$, which has 10 wt % Fe loading, was preannealed at 450 °C for 8 h under a dry air flow condition of 30 mL/min. After the preannealing process, the temperature of the reactor containing the sample was cooled down to 30 °C, and this temperature was maintained. Then, the reagent gas, that is, 107 ppm acetaldehyde gas diluted by either dry air or air with various humidity levels with a total flow rate of 30 mL/min (200 ppm acetaldehyde gas diluted with N$_2$ with 16 mL/min + O$_2$ gas of 4 mL/min + air with humidity of 10 mol ppm; flow rate of each gas was regulated by MFC), was fed into the reactor for 12 h at 30 °C. Subsequently, purging gas (N$_2$, 30 mL/min) was fed into the reactor for 1 h to remove any weakly bound acetaldehyde from the surface of the sample. After the purging process, TPO over the Fe$_2$O$_3$/H$_2$/Al$_2$O$_3$ was performed. The reactor temperature was increased from 30 to 450 °C at a rate of 1 °C/min under air, with the humidity used for the respective adsorption experiment with a total flow of 30 mL/min (N$_2$ gas of 16 mL/
Experiment setup for acetaldehyde adsorption and oxidative desorption at humid condition, UV–Vis DRS spectra and Mössbauer spectrum of FeO/H2O/Al2O3. GC chromatogram of bulk Al2O3 and FeO/H2O/Al2O3 at 350 °C during TPD, acetaldehyde flow rate at the outlet of the reactor with FeO/H2O/Al2O3 during acetaldehyde adsorption experiment as a function of time, CO2 evolution rate and acetaldehyde desorption rate during TPO of FeO/H2O/Al2O3 after acetaldehyde adsorption for 1150 min, percentages of the amount of weakly bound acetaldehyde desorbed at 30 °C during purging, molecularly desorbed acetaldehyde and emitted CO2 during TPO from FeO/H2O/Al2O3 after acetaldehyde adsorption for 1150 min (these experiments were all conducted under dry conditions, and the samples were put in a quartz boat, which was located in the middle of a quartz reactor), and detailed description about the calculations of the desorption rate and percentage of acetaldehyde and CO2 (PDF).

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