

Comparative Studies of Mesoporous Fe_2O_3/Al_2O_3 and Fe_2O_3/SiO_2 Fabricated by Temperature-Regulated Chemical Vapour Deposition as Catalysts for Acetaldehyde Oxidation

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Abstract Temperature-regulated chemical vapour desorption was used for deposition of Fe_2O_3 nanoparticles on the surface of mesoporous Al_2O_3 and SiO_2 . The entire internal structure of mesoporous substrates, with a mean particle diameter of several hundred micrometres, was coated by Fe_2O_3 nanoparticles < 2–3 nm in lateral size. Although Fe_2O_3/Al_2O_3 had a smaller mean Fe_2O_3 particle size with superior dispersion of Fe_2O_3 nanoparticles, Fe_2O_3/SiO_2 showed a higher CO_2 evolution rate than Fe_2O_3/Al_2O_3 . In combination with the results of acetaldehyde adsorption and desorption experiments, we suggest that acetaldehyde

interacts more strongly with Al_2O_3 than SiO_2 . This can reduce the collision frequency of acetaldehyde with catalytically active Fe_2O_3 nanoparticles deposited on Al_2O_3 , thereby reducing the total oxidation rate of acetaldehyde. We demonstrate that temperature regulated-chemical vapour deposition is a promising method for preparation of mesoporous substrate-based catalysts for efficient oxidation of volatile organic compounds with different mesoporous materials. Moreover, we show that interaction between supporting material surfaces and reactant molecules is a critical factor for determining activity in heterogeneous catalysis.



Graphical Abstract

Il Hee Kim and Chan Heum Park have contributed equally to this work.

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Interaction between SiO_2 and acetaldehyde is weaker than that of between Al_2O_3 and acetaldehyde.

A weaker interaction between substrate surface and reactant facilitates diffusion of reactant molecules to the catalytically active species, increasing total oxidation rate.

Keywords Temperature regulated-chemical vapour deposition (TR-CVD) · Heterogeneous catalysts · Acetaldehyde oxidation · Volatile organic compounds (VOCs)

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1 Introduction

The elimination of volatile organic compounds (VOCs) from outdoor and indoor environments has been receiving more attention recently because long-term inhalation of the vapours of these compounds can be detrimental [1–5]. As long as fossil fuels are used for energy, emission of these VOCs due to incomplete combustion is unavoidable [6–9]. In indoor environments, the use of organic solvents for interior construction can result in VOC emission, causing sick-building syndrome. Particular attention has been paid to acetaldehyde, which is regarded as the main cause of the aforementioned sick-building syndrome [10–13].

Several different strategies have been considered for removal of VOCs. The simplest and most efficient method for VOC removal is the use of high-surface-area adsorbent, such as activated carbon. Recently, other more efficient adsorbents such as metal–organic framework have been developed [14–17]. However, adsorbents are regularly regenerated, and VOCs can be re-emitted during this process, resulting in a secondary pollution problem. Alternatively, the use of catalysts for conversion of VOCs to CO_2 and H_2O can be considered. Photocatalysis and dark catalysis with thermal energy have been widely studied [18–20]. Although the use of solar light for photocatalytic decomposition of VOCs is an attractive strategy, its low efficiency limits practical applications [21, 22]. Conversely, dark catalysts are already widely used in a variety of applications [23–25].

Among various materials, Pt-group metal nanoparticles supported by high-surface area oxides are the most promising structures for catalytic conversion of VOCs in terms of catalytic activity and stability [26–28]. However, the low natural abundance and high price of Pt-group metals have triggered the development of non-Pt-group-based catalysts. Catalysts based on less expensive materials such as Au, Cu, Ni, and Fe as well as bimetallic structures have been tested for VOC oxidation [29-36]. Those non-Pt-group metal or metal-oxide nanoparticles are catalytically active, however, these nanoparticles generally show low stability, and therefore easily lose their catalytic activity due to the agglomeration of the particles upon catalytic operation at high temperatures for long time [37-40]. This is a hurdle of real application of these non-Pt-group catalysts, and a strategy for increasing stability of nanoparticles of non-Ptgroup metal and metal oxide, which are catalytically active, are needed.

One promising method for increasing catalytic activity and stability of transition metal nanoparticles is use of mesoporous materials as substrates. In this case, incorporation of catalytically active species into mesoporous structures is a challenging issue. The catalytically active species either can be incorporated into pre-formed mesoporous supporting materials [41–43], or can be introduced during the synthesis of mesoporous frameworks [32, 44-47]. The post-insertion of catalytically active nanoparticles into preformed mesoporous templates is advantageous, because commercially available and cost-effective mesoporous materials can be utilized. However, one can find several drawbacks here; diffusion of catalytically active nanoparticles is usually limited to less than several µm scale [39, 48], the nanoparticles often block the mesopores, lowering of the surface area of the substrate [49-52], and mass production of the catalysts in this way is challenging [53-55]. There are limited methods, such as atomic layer deposition (ALD), which allow insertion of catalytic nanoparticles into mesoporous frameworks without lowering the surface area of the substrate; however, ALD uses a high vacuum and complex control system, limiting its practical applications for the mass-production of catalysts.

In the previous studies [42, 43, 56], temperature-regulated chemical vapour deposition (TR-CVD), which is much simpler than ALD in terms of equipment structure and system control was introduced. With this method, we could insert catalytically active Ni-oxide and Fe-oxide nanoparticles into the core part of mesoporous Al_2O_3 substrate with size of ~1 mm, and the nanoparticles were evenly distributed. And, in the present work, we incorporated Fe-oxide nanoparticles into mesoporous Al₂O₃ and SiO₂, and examined further possibility of TR-CVD for applications in various substrates. Also, the resulting structures were used for acetaldehyde oxidation reaction. We demonstrate high efficiency of TR-CVD for evenly depositing catalytically active nanoparticles within the entire mesoporous network used as supporting media of nanoparticles. We compare the structure and catalytic activity of Fe₂O₃/Al₂O₃ and Fe₂O₃/SiO₂ and highlight that the use of different substrates can cause different activity not only due to various metal-support interactions, but also to dissimilar interactions between various substrate surfaces and reactant molecules.

2 Experimental

2.1 Sample Preparations

The Fe₂O₃/Al₂O₃ and Fe₂O₃/SiO₂ samples were prepared by the TR-CVD method [42, 43, 56]. Commercially available mesoporous Al₂O₃ (original bead size: 1 mm, mean pore size: 11.6 nm, Sasol) and SiO₂ [particle size: 250–500 μ m (35–60 mesh), mean pore size: 15 nm, Aldrich] were used as substrates. The Al₂O₃ bead was mechanically fractured and sieved so that fractured Al₂O₃ had similar lateral sizes to those of mesoporous SiO₂. Sieved mesoporous Al₂O₃ particles were used as supporting materials of Fe₂O₃ catalysts. SiO₂ was used as purchased without any additional mechanical treatment. Bis(cyclopentadienyl) iron [Fe(Cp)₂, Aldrich] was used as a metal precursor, and air or water vapour originally existing in the reactor chamber was used as an oxidizing agent. A total of 2.5 g of Fe(Cp)₂ in a quartz boat (internal size of $70 \times 20 \times 8 \text{ mm}^3$) was located at the bottom of the stainless-steel chamber, and mesoporous substrates (10 g of Al_2O_3 or 5.3 g of SiO_2) were also put inside the chamber. The amount of substrates was adjusted so that each substrate showed almost identical surface area. The chamber was closed with a lid and sealed with polyimide (PI) tape. In the first step, the temperature of the chamber increased to 60 °C, and this temperature was maintained for 2 h; this process is required for evaporation and diffusion of metal precursors into the mesoporous substrate. After maintaining the temperature for 2 h, the chamber temperature was further heated to 200 °C. This temperature was maintained for 12 h to oxidize the Fe species adsorbed on the internal surface of mesopores of Al₂O₃ or SiO₂.

2.2 Sample Characterization

After deposition of Fe₂O₃ on mesoporous substrate by TR-CVD, the elemental distribution of cross-sectional planes of Fe₂O₃/Al₂O₃ and Fe₂O₃/SiO₂ was analysed by scanning electron microscopy (SEM, JEOL, JSM-7100F) equipped with an energy dispersive spectrometer (EDS). To determine the Fe loadings in Fe_2O_3/Al_2O_3 and Fe_2O_3/SiO_2 , inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used. After Fe₂O₃/Al₂O₃ and Fe₂O₃/SiO₂ were annealed at 450 °C, the average pore diameter and surface area were determined by Barret-Joyner-Halenda (BJH) and Brunauer-Emmett-Teller (BET) methods based on N₂ isotherms (3Flex, Micromerities). The results were compared with those of bare Al₂O₃ and SiO₂ substrates. The X-ray diffraction (XRD) spectra of Fe_2O_3/SiO_2 and $Fe_2O_3/$ Al₂O₃ annealed at 450 °C were obtained, and compared with that of bare SiO_2 and Al_2O_3 [43]. Sample annealing at 450 °C was conducted under dry air flow of 30 sccm, and XRD spectra were obtained with an X-ray diffractometer (Rigaku, Ultima IV) using Cu Kα radiation (40 kV, 30 mA, $\lambda = 1.54$ Å) with a scanning rate of 4°/min. To obtain information about the structure of Fe₂O₃ nanoparticles deposited on the substrate, Fe₂O₃/Al₂O₃ and Fe₂O₃/SiO₂ annealed at 450 °C were ground and analysed by high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM, JEOL, JEM ARM 200F) or high-resolution transmission electron microscopy (HR-TEM, JEOL, JEM ARM 200F), respectively. The chemical states of the elements of Fe2O3/Al2O3 and Fe2O3/SiO2 were analysed by X-ray photoelectron spectroscopy (XPS). Fe₂O₃/Al₂O₃ and Fe₂O₃/SiO₂ were annealed at 450 °C under dry air flow of 30 sccm in a furnace located inside a glove box filled with Ar. The samples were then transferred to an ultra-high vacuum (UHV) system by high-vacuum sealing and portable magnetic transfer system without exposure to the atmosphere. This prevents possible contamination of the sample during transfer from the glove box to the UHV system. XPS analysis was carried out under a base pressure of 3×10^{-10} torr at UHV conditions [39, 41–43, 56]. The photon source for XPS was Mg K α X-ray line (1253.6 eV), and the XPS spectra were collected at a pass energy of 30 eV by a concentric hemisphere analyser (CHA, PHOIBOS-HAS 3500, SPECS). The binding energy of XPS spectra of each samples were calibrated with the respective C 1s peak centered at 284.5 eV [57]. The intensities of the Fe 2p core-level XPS peaks of Fe₂O₃/Al₂O₃ were normalized by the respective Al 2p peak area, and those of the Fe 2p core-level XPS peaks of Fe₂O₃/SiO₂ were normalized by the respective Si 2p peak area.

2.3 Catalytic Activity Test

The catalytic activity of Fe_2O_3/Al_2O_3 and Fe_2O_3/SiO_2 for acetaldehyde oxidation was evaluated in a gas flow type system comprised of a quartz tube (internal diameter of 21 mm, length of 300 mm) equipped with a temperature control system and mass flow controller. The concentration of acetaldehyde gas was controlled after addition of 200 mol ppm acetaldehyde gas diluted with N2 (AA/N2) and O2 gas; AA/ N₂ and O₂ were fed into the reactor at a flow rate of 16 and 4 ml/min, respectively. As a result, 160 mol ppm of acetaldehyde diluted with dry air was injected into the reactor at a flow rate of 20 ml/min. A total of 2.0 g of Fe₂O₃/Al₂O₃ or 1.2 g of Fe₂O₃/SiO₂ were used as catalysts; the amount of each catalyst was adjusted carefully based on the surface area and Fe loading of each sample, i.e., different weights of both samples were used in the reactivity experiments, resulting in similar surface areas and Fe loadings of both samples. The sample was placed in a quartz boat (internal size of $70 \times 20 \times 8 \text{ mm}^3$) located in the middle of the quartz reactor. Mixed gas that had passed through the reactor was analysed by on-line gas chromatography (GC, Hewlett Packard, HP 6890) using a capillary column (Agilent Technologies, HP-PLOT/Q, 30 m \times 0.53 μ m), methanizer, and flame ionization detector.

Before the acetaldehyde oxidation experiments, Fe_2O_3/Al_2O_3 and Fe_2O_3/SiO_2 were pre-annealed at 450 °C for 2 h under dry air flow of 30 ml/min. After the pre-annealing process, the catalytic activity of catalysts as a function of reaction temperature was evaluated. After annealing at 450 °C for 2 h, the reaction temperature was maintained at 450 °C, and 160 mol ppm gas was injected into the reactor. After acetaldehyde flow was stabilized, the reactor was cooled from 450 °C to 50 °C at a cooling rate of 1 °C/min. After evaluating the catalytic activity as a function of reaction temperature, the catalysts were again annealed at 450 °C for 2 h to regenerate catalytic activity. The catalytic activity ity of each catalyst was estimated at 250 °C for 24 h. The

24 h catalytic activity test of each catalyst was followed by purging of the remaining acetaldehyde in the reactor with 30 ml/min of N_2 flow for 1 h. Temperature programed oxidation (TPO) was then performed to determine the amount of carbon species remaining on catalysts during the catalytic activity test. For TPO, the reactor temperature was increased from 250 to 450 °C at a rate of 1 °C/min under dry air flow of 30 ml/min.

In addition, the catalytic activity of Fe_2O_3/SiO_2 and Fe_2O_3/Al_2O_3 for toluene oxidation as a function of reaction time was also evaluated. The catalyst amount and preannealing conditions were all identical to those of the aforementioned acetaldehyde oxidation experiments. After the pre-annealing step, reactor temperature was maintained at 450 °C, and 62 mol ppm toluene gas diluted with dry air was injected into the reactor at a flow rate of 30 ml/min. After the toluene flow was stabilized, the reactor temperature was cooled from 450 to 50 °C at a cooling rate of 1 °C/min.

2.4 Temperature Programed Desorption (TPD)

To elucidate the effects of the surface properties of mesoporous Al₂O₃ and SiO₂ on catalytic activity of acetaldehyde oxidation by Fe-loaded catalysts, temperature programed desorption (TPD) experiments of acetaldehyde from bare Al_2O_3 and SiO_2 were performed. To the reactor, 2.0 g of Al₂O₃ and 1.2 g of SiO₂ were added and annealed at 450 °C for 2 h under dry air flow of 30 ml/min in order to remove surface impurities. After this pre-annealing step, the reactor temperature was cooled to 30 °C, and 200 mol ppm of AA/N₂ gas with a flow rate of 10 ml/min for 60 h was applied to allow acetaldehyde adsorption on the surface. Subsequently, acetaldehyde in the reactor was purged by N_2 flow. Then, reactor temperature was increased from 30 to 450 °C under N₂ flow of 30 sccm at a heating rate of 1 °C/ min. The gas mixture that had passed through the reactor during TPD experiments was analysed by an identical GC system as was used for the aforementioned catalytic activity experiments.

3 Results and Discussion

3.1 Sample Characterizations

The elemental distribution inside Fe_2O_3/Al_2O_3 and Fe_2O_3/SiO_2 particles was analysed by measuring SEM-EDS images of the cut planes of mechanically fractured particles. The green trace in Fig. 1a represents Al species in the Fe_2O_3/Al_2O_3 sample, and the brown trace in Fig. 1c represents Si species in the Fe_2O_3/SiO_2 sample. These are elements of the mesoporous substrates that were found on the entire sample surface. Red traces in Fig. 1b, d correspond to Fe-species

in Fe₂O₃/Al₂O₃ and Fe₂O₃/SiO₂ samples, respectively, and Fe species were also distributed on the entire cutting plane of each sample. Fe was evenly deposited not only on the surface of the mesoporous substrate but also in the core part of substrates with a lateral dimension of 250–500 μ m. The diffusion of Fe precursor (ferrocene) in gas phase into the deeper part of SiO₂ or Al₂O₃ particles via the mesoporous network is facile, and Fe can be deposited evenly over the entire surface of mesoporous substrates.

To determine the structures of Fe species deposited on substrate, Fe_2O_3/Al_2O_3 was analysed by HAADF-STEM (Fig. 1e), and Fe_2O_3/SiO_2 was analysed by HR-TEM (Fig. 1f) after each sample was annealed at 450 °C under dry air flow for 2 h. Mean Fe-oxide particle size deposited on Al_2O_3 was 1 nm, whereas that deposited on SiO_2 was ~2 nm. Fe_2O_3 particles on SiO_2 were larger than those on Al_2O_3 , possibly due to a stronger metal-support interaction of Al_2O_3 as substrate than SiO_2 . Fe_2O_3 nanoparticles on Al_2O_3 were hardly identified by HR-TEM, most likely due to the overlap of Al_2O_3 and Fe_2O_3 lattices. Identification of Fe_2O_3 crystalline nanoparticles on amorphous SiO_2 substrate is easier.

 N_2 isotherms of bare SiO₂ and Fe₂O₃/SiO₂ annealed at 450 °C were obtained (Fig. S1), and those of bare Al₂O₃ and Fe₂O₃/Al₂O₃ annealed at 450 °C were studied as well [43]. Also, by using BET and BJH analyses of N₂ isotherms, the specific surface area and mean pore size of each sample were determined (Table 1). For Al₂O₃ substrate, surface area and pore diameter, and pore size distribution were barely changed after Fe deposition and subsequent annealing at 450 °C. However, the surface area of SiO₂, which is about double that of Al₂O₃, and the porosity of SiO₂ were slightly decreased upon Fe deposition and subsequent annealing, with a slight increase in the mean pore size. This result might be related to partial rupture of the porous structure of SiO_2 upon annealing; as the mesoporous SiO_2 network was exposed to high temperature as 450 °C, the structure started to partially collapse, resulting in decrease in the surface area, porosity, and increase in the mean pore size. The specific surface area of SiO_2 is much higher than that of Al_2O_3 due to the higher density of SiO_2 compared to Al_2O_3 [58, 59]. For a given apparent volume of SiO₂ and Al₂O₃ particles, internal pore-volumes are estimated to be almost identical. By ICP-OES, Fe loading on Fe₂O₃/SiO₂ (8.32 wt%) was more abundant than that of Fe_2O_3/Al_2O_3 (5.39 wt%). When considering the different surface areas of various substrates, Fe loading per unit area of Fe_2O_3/Al_2O_3 (0.35 mg/m²) and that of Fe_2O_3/SiO_2 (0.32 mg/m²) were almost identical.

XRD analysis of Fe_2O_3/SiO_2 sample was conducted, and the pattern was compared with that of bare SiO₂ (Fig. S2). Also, XRD pattern of Fe_2O_3/Al_2O_3 was compared with that of bare Al_2O_3 in the previous study [43]. No iron-oxide related peaks were found in both XRD spectra of $Fe_2O_3/$ SiO₂ and Fe_2O_3/Al_2O_3 . These results can be attributed to a Fig. 1 Cross-sectional EDS mapping images of **a** Al and **b** Fe species of mechanically cut Fe₂O₃/Al₂O₃ particles and those of **c** Si and **d** Fe species of Fe₂O₃/SiO₂. **e** HADDF-STEM image of Fe₂O₃/Al₂O₃ and **f** HR-TEM image of Fe₂O₃/SiO₂ annealed at 450 °C



Table 1 Surface area and average pore diameter of bare Al_2O_3 , Fe_2O_3/Al_2O_3 , bare SiO_2 , and Fe_2O_3/SiO_2

	Surface area (m ² /g)	Pore diameter (nm)
Bare Al_2O_3	158.0	12.1
450 °C-annealed Fe ₂ O ₃ /Al ₂ O ₃	151.8	11.6
Bare SiO ₂	302.60	13.06
450 °C-annealed Fe ₂ O ₃ /SiO ₂	259.02	14.51

low crystallinity of Fe_2O_3 nanoparticles, or the small size of Fe_2O_3 nanoparticles, which is in agreement with the TEM observation.

XPS analyses were carried out to identify the surface compositions and chemical states of elements in each catalyst. As shown in Fig. 2, each Fe 2p spectrum was de-convoluted using six different components of a Gaussian–Lorentzian function, and the normalized peak areas of each component were listed (Fig. 2). The Fe 2p core level spectrum of Fe(III) species shows complicated features due to multiplet splitting and other final state contributions [60, 61]. In addition, the lowest-binding energy peak corresponds to Fe ions with a lower oxidation state than the Fe(III) species. The highest-binding energy peak, centred at ~714 eV, is attributed to the surface Fe(III) species of bulk Fe₂O₃. The intensity of the highest-binding energy component of Fe₂O₃/ SiO₂ is higher than that of Fe₂O₃/Al₂O₃. This result is in line



Fig. 2 Fe $2p_{3/2}$ XPS spectra of Fe_2O_3/Al_2O_3 and Fe_2O_3/SiO_2 annealed at 450 °C. Fitting results are also displayed

with the aforementioned TEM results; for Fe_2O_3/Al_2O_3 , the smaller particle size of Fe_2O_3 and stronger metal-support interaction reduce the number of surface Fe species in bulk Fe_2O_3 , which originate from Fe_2O_3 surfaces with almost no electronic perturbation of Al_2O_3 to Fe_2O_3 . Larger particles of Fe_2O_3 on SiO₂ are electronically considered more bulk-like and therefore show a pronounced peak corresponding to the surface Fe species of bulk Fe_2O_3 .

3.2 Catalytic Activity Test for Acetaldehyde Oxidation

Catalytic oxidation of acetaldehyde using 2.0 g of Fe₂O₃/Al₂O₃ or 1.2 g of Fe₂O₃/SiO₂ annealed at 450 °C was studied with decreasing reaction temperature from 450 to 50 °C at a cooling rate of 1 °C/min. The amount of the catalysts was determined carefully, so that each catalyst has the same level of the surface area of the substrate, and the Fe loading (Table S1). The starting temperature was 450 °C in these light-off experiments because 100% conversion of acetal-dehyde to CO₂ was achieved at this temperature for both catalysts. As shown in Fig. 3a, the acetaldehyde consumption rates of both catalysts were similar. Almost all acetal-dehyde in the feed gas was removed over the entire reaction temperature range. On the other hand, the CO₂ evolution rate of both catalysts decreased with decreasing reaction



Fig. 3 a Acetaldehyde consumption rate and b CO_2 evolution rate of 450 °C-annealed Fe_2O_3/Al_2O_3 and Fe_2O_3/SiO_2 as a function of reaction temperature

temperature. In the entire temperature range of the catalyst, Fe_2O_3/SiO_2 generally showed a higher CO_2 evolution rate than Fe_2O_3/Al_2O_3 (Fig. 3b).

The results in Fig. 3 suggest that, at reaction temperatures above 300 °C, acetaldehyde is mostly removed by total oxidation into CO₂. Below 200 °C, partial oxidation of acetaldehyde followed by chemisorption of the partial oxidation products of acetaldehyde is responsible for acetaldehyde consumption. Total oxidation of acetaldehyde into CO₂ is more facile on Fe₂O₃/SiO₂ than Fe₂O₃/Al₂O₃. Because Fe₂O₃ nanoparticles are more highly dispersed on Al₂O₃ than SiO₂, Fe₂O₃/SiO₂ is not expected to show a higher activity for total oxidation of acetaldehyde to CO₂. This result is rationalized by assuming that diffusion of acetaldehyde molecules on the surface of SiO₂ is more facile than on Al₂O₃. Therefore, the collision frequency of acetaldehyde with catalytically active Fe₂O₃ is higher on SiO₂ than on Al₂O₃. Further studies using TPD also support this idea, which is explained more in detail in the forthcoming section. The results of light-off curves of Fe_2O_3/Al_2O_3 or Fe_2O_3/SiO_2 were compared with those from the previous studies in Table S2 [62–67]. Note that most of transition metal oxide catalysts showed ~90% of conversion to CO_2 at ~300 °C, which is comparable catalytic activity with those of Fe_2O_3/Al_2O_3 or Fe_2O_3/SiO_2 catalysts in the present work. It should be emphasized that our catalysts are comparable with other previously reported catalysts in terms of initial reactivity, yet long-term stability of the catalytic activity we tested in this work (which will be show next) has rarely been reported in the literature. Moreover, Fe is known to be one of the most cost-effective transition metals.

Catalytic oxidation of acetaldehyde at 250 °C using these two catalysts was studied for 24 h to test the long-term stability of the catalytic activity (Fig. 4). There was almost no difference between the two catalysts regarding acetaldehyde consumption rate, and both catalysts showed nearly 100% consumption of acetaldehyde for 24 h without a decrease in catalytic activity (Fig. 4a). There was almost no CO_2



Fig. 4 a Acetaldehyde consumption rate and b CO₂ evolution rate of Fe_2O_3/Al_2O_3 and Fe_2O_3/SiO_2 at 250 °C as a function of reaction time

evolution at the initial stage of both reactivity experiments, and CO₂ evolution rapidly increased with increasing reaction time (Fig. 4b). Analogous to the results of Fig. 3, the CO₂ evolution rate of Fe₂O₃/SiO₂ was generally higher than that of Fe_2O_3/Al_2O_3 . The amount of each sample was chosen to have the almost identical amount of Fe loading and surface area of both samples. According to TEM analysis, the lateral size of Fe_2O_3 nanoparticles on Fe_2O_3/SiO_2 is ~2 times larger than that on Fe₂O₃/Al₂O₃, therefore, the total number of Fe_2O_3 nanoparticles on Fe_2O_3/Al_2O_3 is ~8 times larger than that on Fe₂O₃/SiO₂ to have almost identical total volume of Fe₂O₃ nanoparticles, while surface area of an individual Fe₂O₃ nanoparticle on Fe₂O₃/SiO₂ is ~4 times larger than that on Fe_2O_3/Al_2O_3 . As a result, the total surface area of Fe₂O₃ nanoparticles on Fe₂O₃/SiO₂ samples should be ~2 times smaller than that on Fe₂O₃/Al₂O₃. Assuming that the CO₂ evolution rate is dependent on the number of active site of iron oxide, CO₂ evolution rate of Fe₂O₃/SiO₂ should be smaller than that of Fe₂O₃/Al₂O₃. However, CO₂ evolution rate of Fe₂O₃/SiO₂ was higher than that of Fe₂O₃/Al₂O₃, while acetaldehyde consumption rate was at the same level for 24 h. Therefore, it can be concluded that CO₂ evolution rate was mostly determined by the diffusion rate of acetaldehyde or its partial oxidation intermediates on substrate surface, not the number of catalytically active site, or the state of iron oxide particle. This point will be more clarified in the forthcoming discussion about TPD results. It is also worth mentioning that both substrates showed quite similar porosity, and therefore porosity does not seem to be a critical factor for determining the CO₂ evolution rate.

After each experiment shown in Fig. 4, a TPO experiment was subsequently carried out to determine the residual amount of carbon species remaining on the surfaces of both catalysts after catalytic reaction for 24 h (Fig. 5). It is notable



Fig. 5 CO $_2$ evolution rate during TPO of Fe $_2O_3/Al_2O_3$ and Fe $_2O_3/SiO_2$ after acetaldehyde oxidation for 24 h

that most of carbon species accumulated on the surface were removed during TPO. With increasing temperature, CO₂ desorption rate first increased and showed a maximum value at 330 °C. Above this temperature, the CO₂ desorption rate decreased, and no CO₂ desorption was detected at temperatures exceeding 450 °C (Fig. 5). The CO₂ evolution rate of Fe₂O₃/Al₂O₃ was generally higher than that of Fe_2O_3/SiO_2 , and the amount of carbon species remaining on Fe₂O₃/Al₂O₃ after the acetaldehyde oxidation experiment was much higher than that remaining on Fe₂O₃/SiO₂. During acetaldehyde oxidation, acetaldehyde adsorbed on the Fe_2O_3/SiO_2 surface was more easily removed into CO_2 , leaving only a small amount of carbon-containing species (reaction products of partial oxidation of acetaldehyde). Stabilization of the partial oxidation product of acetaldehyde is more pronounced on the Fe₂O₃/Al₂O₃ surface, resulting in a larger amount of residual carbon-containing species on the surface of catalysts during acetaldehyde reaction at 250 °C for 24 h.

3.3 Temperature Programed Desorption (TPD)

To investigate the interaction between acetaldehyde and mesoporous substrates (Al_2O_3 and SiO_2), TPD of acetaldehyde from bare SiO_2 and Al_2O_3 surfaces without Fe₂O₃ was performed. Before the TPD experiment, each sample was exposed to acetaldehyde flow (10 ml/min) with a concentration of 200 ppm (balanced N₂) for 60 h. During these experiments, the amount of acetaldehyde passed through the sample stage in the reactor was detected using GC (Fig. 6). Acetaldehyde contained in the flow gas can adsorb onto the surface of each sample. As the coverage of acetaldehyde on the surface increases, the amount of acetaldehyde passing



through samples and detected by GC increases [17, 68, 69]. When SiO_2 was used as adsorbent, the acetaldehyde evolution rate slowly increased with time. In contrast, almost no acetaldehyde was observed in the reactor outlet when Al_2O_3 was placed in the reactor. This indicates that all acetaldehyde molecules in the feed gas were adsorbed onto the surface of Al_2O_3 , and Al_2O_3 shows a much higher affinity towards acetaldehyde adsorption than SiO_2 (Fig. 6).

Subsequent to the breakthrough experiments shown in Fig. 6, TPD was performed as the reactor temperature increased from 30 to 450 °C. High purity N₂ gas passed through the substrate during TPD experiments. During TPD, desorption of various chemical species was identified, as shown in Fig. 7. From Al₂O₃, almost no acetaldehyde desorption was observed, whereas two acetaldehyde desorption states were identified from SiO₂ at ~ 120 and 350 °C, which are tentatively attributed to multilayer adsorption of acetaldehyde in SiO₂ pores (physisorption) and a monolayer of acetaldehyde (chemisorption),



Fig. 7 TPD results of 450 °C-annealed SiO_2 and 450 °C-annealed Al₂O₃. **a** Acetaldehyde evolution rate and **b** CO₂ evolution rate as a function of temperature for both adsorbents

respectively. Acetaldehyde adsorbed on the surface of SiO_2 was converted into CO_2 only when the temperature exceeded 350 °C, whereas acetaldehyde molecules adsorbed on Al₂O₃ were converted into CO₂ at 200 °C, much lower than the onset temperature of CO₂ evolution from SiO_2 (Fig. 7b). When the oxide surface is reducible, organic molecules can be oxidized by reaction between the molecules and the lattice oxygen of the oxide [70-72]. In case of SiO₂, the acetaldehyde can be oxidized by the lattice oxygen only when the reaction temperature was higher than 300 °C, and therefore the contribution of the substrate for CO_2 evolution can be neglected in the results of Fig. 4. In case of Al₂O₃, however, CO₂ is detected from 200 °C in the TPD, meaning that lattice oxygen of Al₂O₃ can totally oxidize acetaldehyde during the reactivity experiments in Fig. 4. However, the amount of CO_2 detected from 200 to 250 °C in the TPD is very is small compared to that above 250 °C and therefore, the contribution of the lattice oxygen of Al_2O_3 substrate in the acetaldehyde oxidation in Fig. 4 can be regarded to be a minor factor, even though this process cannot be fully excluded.

GC identified other species resulting from chemical reactions between acetaldehyde molecules on the surface and the substrate, and the formation of these chemical species was much more pronounced from Al_2O_3 than SiO_2 . This result indicates that acetaldehyde was adsorbed more strongly and more activated on the surface of Al_2O_3 than SiO_2 . The possible candidates for each species were speculated by its retention time of GC, and listed in Table S3 [73, 74]. According to the observation, polymerization of acetaldehyde was occurred, and C_3 , C_4 , and C_6 species were produced either on SiO_2 or Al_2O_3 . It is notable that the decomposition of acetaldehyde into CO and CH_4 was only occurred on Al_2O_3 .

Summarizing the results of Figs. 6 and 7, Al₂O₃ shows higher acetaldehyde uptake than SiO₂ at 30 °C. During TPD, acetaldehyde molecular desorption from SiO₂ prevailed, whereas conversion of acetaldehyde molecules into CO₂ and other chemical species was more dominant from Al_2O_3 . These results all imply that Al_2O_3 shows greater interaction with acetaldehyde than SiO₂. A higher Al₂O₃-acetaldehyde interaction hinders diffusion of acetaldehyde molecules on the surface. This reduces the collision frequency of Fe₂O₃ and adsorbed acetaldehyde species. Greater Al₂O₃-acetaldehyde interaction is suggested to be why partial oxidation of acetaldehyde is more dominant on the surface of Fe_2O_3/Al_2O_3 than total oxidation to CO_2 . Although SiO₂ shows a weaker metal-support interaction and lower dispersion of catalytically active Fe₂O₃ species, a weaker interaction between acetaldehyde and SiO₂ induces increased collision frequency between Fe₂O₃ and acetaldehyde adsorbed on the surface. This increases activity towards the total oxidation rate of acetaldehyde to CO₂.

3.4 Toluene Oxidation Using Fe₂O₃/Al₂O₃ or Fe₂O₃/ SiO₂

In order to test the potential of the Fe_2O_3/Al_2O_3 of Fe_2O_3/Al_2O_3 SiO₂ as the catalysts for oxidation of VOCs other than acetaldehyde, such as aromatic compounds represented by toluene, catalytic activity for toluene oxidation using those catalysts annealed at 450 °C was evaluated as a function of reaction temperature from 450 to 50 °C at a cooling rate of 1 °C/min (Fig. S3). Toluene gas (62 mol ppm) was injected into the reactor at a flow rate of 30 ml/min. A reaction temperature of 450 °C was chosen as the starting temperature for light-off experiments because 100% oxidation of toluene to CO₂ was achieved at this temperature for both catalysts. The CO₂ evolution rate of both catalysts decreased as reaction temperature decreased (Fig. S3b). Fe₂O₃/SiO₂ showed a higher CO₂ evolution rate than Fe₂O₃/Al₂O₃ within the entire temperature range, and these results are analogous to those of acetaldehyde. It can be said that the toluene-SiO₂ interaction is weaker than that of toluene-Al₂O₃, as acetaldehyde-SiO₂ interaction is weaker than that of acelaldehyde-Al₂O₃. Collision between adsorbed toluene and Fe₂O₃ nanoparticles is more facile on SiO₂ than on Al₂O₃, a reaction that is critical for total oxidation to CO2. Most toluene molecules were removed by total oxidation into CO₂ at 450 °C (Fig. S3a); however, with decreased reaction temperature to 250 °C, toluene removal rate remained at the maximum rate even though the CO₂ evolution rate drastically decreased. Toluene could not only be removed by total oxidation, but also by partial oxidation and chemisorption of the partial oxidation product on the surface of catalysts. As reactor temperature became lower than 200 °C, the toluene removal rate first decreased and then increased. The increase in toluene removal rate as reaction temperature decreased from 150 to 50 °C is attributed to molecular adsorption of toluene on the surface. Overall, Fe₂O₃/SiO₂ is more efficient for total oxidation of toluene, whereas Fe₂O₃/Al₂O₃ is superior to Fe₂O₃/ SiO₂ for molecular chemisorption and activation (or partial oxidation) of toluene, in line with the results of acetaldehyde oxidation.

4 Conclusion

Fe₂O₃ nanoparticles were deposited using the TR-CVD method and subsequent annealing. This allows deposition of catalytically active Fe₂O₃ nanoparticles both on the outermost surface layers and also the core part of mesoporous substrates. On Al₂O₃, the mean particle size of Fe₂O₃ was only ~1 nm, whereas that on SiO₂ was ~2 nm. Fe₂O₃ was more highly dispersed on the surface of Al₂O₃ due to the higher metal-support interaction of Al₂O₃ than SiO₂. Both Fe₂O₃/Al₂O₃ and Fe₂O₃/SiO₂ showed high catalytic activity

for acetaldehyde removal, with almost 100% acetaldehyde removal rate at 250 °C for 24 h. Regarding CO₂ evolution rate, however, Fe₂O₃/SiO₂ was superior to Fe₂O₃/Al₂O₃. Together with subsequent TPO results, this result implies that partial oxidation of acetaldehyde and adsorption of reaction intermediates for total oxidation significantly contribute to acetaldehyde removal by Fe₂O₃/Al₂O₃. Conversely, total oxidation of acetaldehyde to CO₂ is more dominant for Fe_2O_3/SiO_2 . In combination with acetaldehyde TPD results, we suggest that interaction of SiO₂ and acetaldehyde is weaker than interaction of Al_2O_3 and acetaldehyde. Weaker interaction between substrate surface and reactant facilitates diffusion of reactant molecules to the catalytically active species, increasing total oxidation rate. For toluene oxidation experiments using these two different catalysts, total oxidation of toluene into CO2 was more efficient when SiO₂ was used as a supporting material of Fe₂O₃ catalyst than when using Al₂O₃. This result is in line with that of acetaldehyde oxidation. Our results show that changes in substrate structure not only influence metal-support interaction, but also support-reactant interaction, a critical factor for determining catalytic activity and selectivity.

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