Photocatalytic oxidation of acetaldehyde with oxygen on TiO2/ZSM-5 photocatalysts: Effect of hydrophobicity of zeolites

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Abstract

TiO2 photocatalysts hybridized with ZSM-5 were prepared by the impregnation of (NH4)2[TiO(C2O4)2] aqueous solution. This is one of the most ideal green processes in establishing TiO2 photocatalysts because of an organic solvent-free preparation method. The highly hydrophobic H-ZSM-5 with low Al2O3 content was effective as an adsorbent for acetaldehyde molecules. These results suggest the close relationship between the hydrophobicity of the zeolite and the high photocatalytic reactivity of TiO2 prepared on zeolites compared with unloaded TiO2 catalysts. However, acetaldehyde molecules were strongly trapped on the Na+ sites of ZSM-5 and their efficient diffusion onto the TiO2 sites was inhibited, resulting in low photocatalytic reactivity. The photocatalytic oxidation of acetaldehyde over TiO2/ZSM-5 was improved in the coexistence of H2O vapor. The role of the H2O molecules was estimated to be the efficient formation of OH radicals and the prevention of strong adsorption of acetaldehyde on the TiO2 sites.

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1. Introduction

In recent years, volatile organic compounds (VOCs), including formaldehyde, acetaldehyde, toluene, and the like, emitted from building and interior materials in newly built houses have caused debilitating damage to our health in the so-called “sick house syndrome.” This has become one of the most serious environmental issues. Because TiO2 photocatalysts have the potential to completely decompose various organic compounds into harmless CO2 and H2O under UV light irradiation due to its high oxidative power, they have been widely studied for the purification of air, water, and soil polluted with organic compounds [1–3]. Removal systems incorporating TiO2 photocatalysts have been practically applied to purify water containing dilute amounts of harmful and toxic compounds [4–6], and because the diffusion of the reactants toward the surface is limited in aqueous solutions, adsorbents with large surface areas are not always needed to condense the reactants on the near surface. However, purifying polluted air requires hybrid photocatalysts that can efficiently adsorb organic compounds diffused in wide spaces and then decompose them into CO2 and H2O by photocatalytic oxidation. For this purpose, TiO2 fine particles with large surface areas prepared by a solvothermal method have been reported to show efficient photocatalytic reactivity for the oxidation of acetic acid [7,8]. The hybridization of adsorbents with large surface areas, such as zeolites [9–11] and active carbon [5,6,12,13], with TiO2 fine particles also has been reported to show efficient photocatalytic reactivity, especially for gas-phase reactions.

ZSM-5 zeolites, with highly ordered micropores, surface acidity, and ion-exchange capacities, are one of the most widely applied inorganic materials as catalyst supports, adsorbents, and molecular-sized spaces for various chemical or photochemical reactions. Highly siliceous ZSM-5 zeolites with low Al2O3 content are known to have highly hydrophobic surfaces [14]. H2O vapor has been reported to play an important role in the photocatalytic degradation of formic acid [15,16], toluene [17–19], and trichloroethylene (TCE) [20] over TiO2 photocatalysts. In many cases, the improved photocatalytic reactivity from the addition of H2O vapor could be explained by suppression of the strong adsorption of the reactants and/or intermediate species. From this standpoint, detailed investigations of the relationship between the adsorption properties of zeolites as...
adsorbents and the photocatalytic reactivity of TiO₂ photocatalysts hybridized with zeolites can lead to the development of new photofunctional materials for environmental remediation.

In this work, the adsorption states of H₂O and acetaldehyde molecules on H⁺ and Na⁺ type ZSM-5 zeolites of different SiO₂/Al₂O₃ ratios were investigated by adsorption isotherm and temperature-programmed desorption (TPD) measurements. The TiO₂ photocatalysts hybridized with ZSM-5 zeolites were prepared by a simple impregnation method from an aqueous solution of titanium(IV) ammonium oxalate ([(NH₄)₂[TiO(C₂O₄)₂]). The photocatalytic reactivity of the prepared TiO₂/ZSM-5 samples was evaluated by the complete oxidation of acetaldehyde with O₂, as was the effect of H₂O vapor addition on photocatalytic reactivity.

2. Experimental

Various ZSM-5 zeolite samples were supplied by Tosoh Co. Ltd. The ZSM-5 zeolite with a SiO₂/Al₂O₃ ratio of 1880 was supplied as the H⁺-type zeolite and NH₄-ZSM-5 zeolites with SiO₂/Al₂O₃ ratios of 220 and 68, respectively, were calcined in air at 723 K for 3 h to obtain H-ZSM-5(220) and H-ZSM-5(68), respectively. Na-ZSM-5(23.8) was ion-exchanged by a NH₄NO₃ solution to obtain NH₄-ZSM-5(23.8) and then calcined in air at 723 K for 3 h, resulting in the formation of H-ZSM-5(23.8). These latter three samples were confirmed to not desorb NH₃ gas by TPD measurements.

TiO₂ photocatalysts hybridized with ZSM-5 zeolites were prepared by a simple impregnation method from a precursor solution of titanium(IV) ammonium oxalate ([(NH₄)₂[TiO(C₂O₄)₂]) (Kishida Chemicals Co.). After calcination at 723 K, the ZSM-5 zeolites were immersed in (NH₄)₂[TiO(C₂O₄)₂] aqueous solution for 2 h, after which the water solvent was vaporized by a rotary evaporator. The white powder samples thus obtained were dried at 383 K for 12 h and then calcined at 773 K for 3 h. The TiO₂ content was adjusted to 10 wt%.

The adsorption isotherms of the H₂O molecules on H and Na-ZSM-5 zeolites with SiO₂/Al₂O₃ ratios of 1880, 220, 68, and 23.8 are shown in Fig. 1. It is well known that the surfaces of the siliceous zeolites (e.g., silicalite, dealuminated mordenite, USY-zeolites) show higher hydrophobic properties than Al₂O₃-containing zeolites. H-ZSM-5(1880), with a low Al₂O₃ content, exhibited the highest hydrophobicity among the ZSM-5 zeolites with different SiO₂/Al₂O₃ ratios. As the Al₂O₃ content increased to ca. 4 wt%, corresponding to a SiO₂/Al₂O₃ ratio of 23.8, the amount of H₂O adsorbed increased threefold more than the highly siliceous H-ZSM-5(1880). These results confirmed to not desorb NH₃ gas by TPD measurements.

3. Results and discussion

The adsorption isotherms of the H₂O molecules on H and Na-ZSM-5 zeolites with SiO₂/Al₂O₃ ratios of 1880, 220, 68, and 23.8 are shown in Fig. 1. It is well known that the surfaces of the siliceous zeolites (e.g., silicalite, dealuminated mordenite, USY-zeolites) show higher hydrophobic properties than Al₂O₃-containing zeolites. H-ZSM-5(1880), with a low Al₂O₃ content, exhibited the highest hydrophobicity among the ZSM-5 zeolites with different SiO₂/Al₂O₃ ratios. As the Al₂O₃ content increased to ca. 4 wt%, corresponding to a SiO₂/Al₂O₃ ratio of 23.8, the amount of H₂O adsorbed increased threefold more than the highly siliceous H-ZSM-5(1880). These results...
clearly indicate that the Al\(^{3+}\) sites (i.e., Brönsted acid sites) play a major role as the adsorption sites of H\(_2\)O molecules. In fact, FTIR investigations have revealed that the H\(_2\)O molecules adsorb on the Brönsted acid sites of H-ZSM-5 or SAPO-34 to form oxonium ions (H\(_3\)O\(^+\) or H\(_2\)O\(^+_2\)) \([21–24]\) or H\(_2\)O molecules directly interacting with the H\(^+\) moieties of the Brönsted acid sites by hydrogen bonding \([25]\). The strength of the interactions between the H\(_2\)O molecules and oxide surfaces can be described by the bonding characteristics of the oxide surfaces. The Si–O linkage is a covalent bond, whereas the Al–O linkage has a combination of 40\% covalent and 60\% ionic bond characters. Because H\(_2\)O molecules are strongly polarized due to the high electronegativity of the O atom, they strongly interact with the cationic surfaces rather than with neutral or anionic surfaces. Furthermore, because the addition of Al\(_2\)O\(_3\) within the zeolite frameworks gives rise to Brönsted acid sites, the surface of zeolites with high Al\(_2\)O\(_3\) content have stronger adsorption sites for H\(_2\)O molecules compared with siliceous zeolites. This interpretation explains why the amount of H\(_2\)O molecules adsorbed strongly depends on the SiO\(_2\)/Al\(_2\)O\(_3\) ratios of the zeolites. Investigations of Na-ZSM-5(23.8) and H-ZSM-5(23.8) showed that the adsorption of H\(_2\)O molecules on Na-ZSM-5(23.8) sharply increases even at low relative pressure compared with H-ZSM-5(23.8). However, the saturated amounts of H\(_2\)O adsorbed on these ZSM-5 zeolites were almost the same due to their similar surface areas. These results clearly suggest that the Na\(^+\) cation sites on zeolite surfaces work as strong adsorption sites for the H\(_2\)O molecules.

TPD profiles of the H\(_2\)O molecules adsorbed on H and Na-ZSM-5 with different SiO\(_2\)/Al\(_2\)O\(_3\) ratios are shown in Fig. 2. Desorption of the H\(_2\)O molecules can be seen at 373–573 K for H-ZSM-5 zeolites with low SiO\(_2\)/Al\(_2\)O\(_3\) ratios of 23.8 and 68. However, very small amounts of H\(_2\)O desorbed from H-ZSM-5 with low Al\(_2\)O\(_3\) content (SiO\(_2\)/Al\(_2\)O\(_3\) = 220 and 1880). Moreover, as the SiO\(_2\)/Al\(_2\)O\(_3\) ratio decreased, the desorption temperature shifted slightly toward higher-temperature regions. Generally, H\(_2\)O molecules weakly adsorb on surface hydroxyl groups by the hydrogen bonds and strongly adsorb on the cationic sites of oxide surfaces by electrostatic interactions. Here the H\(_2\)O molecules interacted with the surface silanol groups of siliceous H-ZSM-5 with low Al\(_2\)O\(_3\) content. In contrast, the desorption peak at around 373–573 K observed for the Al-containing H-ZSM-5 could be assigned to the H\(_2\)O molecules adsorbed on the H\(^+\) sites of the zeolite surfaces. The desorption of the H\(_2\)O molecules at around 823–973 K for H-ZSM-5 zeolites with low Al\(_2\)O\(_3\) content could not be observed for the samples after outgassing at 873 K, suggesting that the desorption of H\(_2\)O at higher than 823 K may be attributed to the condensation of the neighboring silanol groups on the zeolite surfaces. Furthermore, the desorption of H\(_2\)O from Na-ZSM-5(23.8) broadened at higher temperatures compared with H-ZSM-5(23.8), suggesting the stronger interaction between the H\(_2\)O molecules and Na-ZSM-5(23.8) compared with H-ZSM-5(23.8). These results clearly indicate that the desorption at 323–523 K and 523–673 K (as a shoulder) can be attributed to the H\(^+\) and Na\(^+\) zeolite sites, respectively. H\(_2\)O molecules strongly interact with the cationic sites rather than with the hydroxyl groups on the oxide surfaces. Three kinds of adsorbed H\(_2\)O species are summarized in Table 1, according to the strength of the interactions between the H\(_2\)O molecules and surface sites: (A) the H\(_2\)O molecules interacting with the silanol groups are easily removed by evacuation at room temperature. On the other hand, two kinds of H\(_2\)O species are adsorbed on the H\(^+\) sites neighboring the Al\(^{3+}\) of the zeolite surface, as proposed by FTIR investigations; (B-1) the H\(_2\)O molecules interact only by hydrogen bonding \([25]\); (B-2) the oxonium ions, as with H\(_3\)O\(^+\) \([21–24]\), desorb at 323–523 K from the H-ZSM-5 with high Al\(_2\)O\(_3\) content; and (C) the H\(_2\)O molecules interacting with the Na\(^+\) cation sites of Na-ZSM-5 by electrostatic interaction desorb at 523–673 K. The results of these adsorption and desorption measurements clearly indicate that the hydrophilic/hydrophobic properties of ZSM-5 zeolites can be explained by the cationic characteristics of the surface sites.

The adsorption properties of acetaldehyde molecules on ZSM-5 zeolites were also investigated by adsorption isotherm and TPD measurements. Adsorption isotherm analysis showed the saturated amount of acetaldehyde on the ZSM-5 zeolites to remain almost the same at ca. 2.0–2.5 mmol/g, despite their different SiO\(_2\)/Al\(_2\)O\(_3\) ratios. The results indicate that the amount of saturated adsorbed acetaldehyde depends on the surface areas of the ZSM-5 zeolites (ca. 300–350 m\(^2\)/g) but not on the surface chemical properties, which originate from changes in the SiO\(_2\)/Al\(_2\)O\(_3\) ratios. However, as shown in Fig. 3, the results of TPD measurements revealed that the interaction of acetaldehyde molecules with the ZSM-5 surface depends on the dif-

![Fig. 2. TPD profiles of H\(_2\)O molecules adsorbed on (a–d) H-ZSM-5 and (e) Na-ZSM-5 zeolites. SiO\(_2\)/Al\(_2\)O\(_3\) ratios: (a) 1880, (b) 220, (c) 68, (d, e) 23.8.](image)

![Fig. 3. TPD profiles of acetaldehyde molecules adsorbed on (a–d) H-ZSM-5 and (e) Na-ZSM-5 zeolites. SiO\(_2\)/Al\(_2\)O\(_3\) ratios: (a) 1880, (b) 220, (c) 68, (d, e) 23.8.](image)
Table 1
Interaction of H₂O molecules with various sites on the ZSM-5 zeolite surface

<table>
<thead>
<tr>
<th>Species</th>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desorption</td>
<td>H/ZSM-5 with low Al₂O₃ content</td>
<td>H/ZSM-5 with high Al₂O₃ content</td>
<td>Na/ZSM-5</td>
</tr>
<tr>
<td>temperature</td>
<td>Room temperature</td>
<td>323–523 K</td>
<td>523–673 K</td>
</tr>
<tr>
<td>Interaction</td>
<td>Hydrogen bonds</td>
<td>B-I; Hydrogen bonds or B-2;</td>
<td>Static electricity (oxonium ion)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Static electricity</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Weak</td>
<td>Strong</td>
</tr>
</tbody>
</table>

ferences in their SiO₂/Al₂O₃ ratios. The desorption spectrum of the molecule corresponding to the mass number (m/z = 44) showed the same tendency of the spectrum for the mass numbers of 15, 29, and 43 which are assigned to CH₃, CHO, and CH₃CO, respectively, as fragments of the CH₃CHO molecule. From these results, the desorbed species of m/z = 44 can be assigned to acetaldehyde and not to the CO₂ molecules. The desorption of acetaldehyde could be observed at 373–473 K for the siliceous H-ZSM-5(1880) zeolite, showing that the acetaldehyde molecules are well condensed on the surface hydroxyl groups in highly hydrophobic zeolite cavities. However, a significant desorption of acetaldehyde could not be observed for the H-ZSM-5 (220 and 68) containing Al₂O₃, suggesting that the Brönsted acid sites of the zeolite surfaces do not work as strong adsorption sites for acetaldehyde. Moreover, Na-ZSM-5(23.8) showed additional specific desorption profiles for acetaldehyde molecules at 473–523 K. Onaka et al. have reported that formaldehyde or acrolein molecules interacting with the Na⁺ sites in NaY or NaX zeolite cavities are stored in a stable form for long periods, and these formaldehyde or acrolein molecules highly stabilized on the Na⁺ sites catalyze the carbonyl-ylene reaction of olefins [26] and a Friedel-Crafts alkylation [27] with high selectivity, respectively. Acetaldehyde molecules desorbed at 473–523 K were also estimated to be highly stabilized on the Na⁺ sites of the Na-ZSM-5(23.8) zeolite. In our work, H-ZSM-5(23.8) showed desorption profiles not only at around 373 K, but also at ca. 573 K. H-ZSM-5(220 and 68) were supplied as H⁺-type zeolites; however, because H-ZSM-5(23.8) was prepared from H⁺ ion-exchange of Na-ZSM-5(23.8), some Na⁺ ions still remained within H-ZSM-5(23.8). These results suggest that the desorption peak at around 573 K may be attributed to the acetaldehyde molecules highly stabilized on the Na⁺ ion sites. The diffuse reflectance UV–vis absorption spectra of TiO₂ prepared on various ZSM-5 zeolites and of a commercial TiO₂ (Degussa, P-25) as reference are shown in Fig. 4. The absorption edges of the TiO₂/ZSM-5 samples were found to shift slightly toward shorter wavelength regions compared with P-25. The bandgap energies of the TiO₂ prepared on ZSM-5 zeolites were estimated to be 3.3–3.4 eV based on the absorption edges of ca. 365–375 nm. The TiO₂/ZSM-5 catalysts (10 wt% as TiO₂) did not show any significant XRD peaks attributed to the TiO₂ particles; however, as the TiO₂ content increased up to 20 wt%, clear diffraction peaks attributed to the anatase structure of TiO₂ could be seen (data not shown). These results clearly suggest much smaller TiO₂ primary crystalline particles of ca. 3–4 nm than the detection limit of XRD measurements. However, because the diameter of the ZSM-5 zeolite cavity is about 0.55 nm, most parts of the TiO₂ particles are considered to exist on the outer surfaces of the ZSM-5 zeolites. SEM images of the TiO₂/ZSM-5 samples in fact showed that the aggregated TiO₂ secondary particles of several 10 nm spread on the outer surfaces of the zeolite crystals of ca. 3–4 µm (data not shown).

The TPD profiles of the H₂O molecules adsorbed on TiO₂/H-ZSM-5 catalysts (10 wt% as TiO₂). SiO₂/Al₂O₃ ratios: (a) 1880, (b) 220, (c) 68, (d) 23.8.
the desorption of H2O can be seen at around 373–423 K, especially for the TiO2 prepared on H-ZSM-5(1880 and 220) with low Al2O3 content. For the TiO2 on H-ZSM-5(68, 23.8) with high Al2O3 content, the main desorption peaks can be seen at around 423 K, although the desorption profiles are broader than those of the original H-ZSM-5(68, 23.8) before impregnation with TiO2 particles. From these results, the order of interaction between the H2O molecules and adsorption sites of the TiO2/H-ZSM-5 zeolites can be estimated as follows: Brönsted acid sites \( \text{Al}^{3+} > \text{TiO2 photocatalytic sites} > \text{surface silanol groups of the zeolite framework.} \)

The adsorption isotherms of the CH3CHO molecules on the dehydrated, hydrated H-ZSM-5(1880), and TiO2/H-ZSM-5(1880) zeolites are shown in Fig. 6. The hydrated surfaces were obtained through the preadsorption of H2O vapor and then outgassing at room temperature. However, as shown in Fig. 2, because the major part of physisorbed H2O molecules on the hydrophobic H-ZSM-5(1880) were degassed at room temperature, the amount of CH3CHO adsorbed on the H-ZSM-5(1880) was hardly affected by the preadsorption of H2O vapor. In contrast, the amount of CH3CHO adsorbed on the hydrophilic H-ZSM-5(23.8) was decreased by the preadsorption of H2O vapor (data not shown). Furthermore, the adsorption of CH3CHO molecules on the TiO2/H-ZSM-5(1880) increased by ca. 10–15% compared with the H-ZSM-5(1880). This result indicates that the CH3CHO molecules easily interact with TiO2 sites rather than siliceous H-ZSM-5 surfaces. It also suggests that once the CH3CHO molecules adsorbed on TiO2 photocatalytic sites are decomposed into CO2 and H2O by UV irradiation, the CH3CHO molecules condensed in zeolite cavities are efficiently supplied onto the TiO2 sites.

The photocatalytic reactivity of the TiO2/ZSM-5 samples for the oxidation of acetaldehyde with O2 in the absence of H2O under UV light irradiation (\( \lambda > 270 \text{ nm} \)) is shown in Fig. 7. The reactivity was found to depend on the SiO2/Al2O3 ratio of the ZSM-5 zeolites. TiO2 prepared on H-ZSM-5(1880) showed the highest photocatalytic reactivity among these hybrid photocatalysts. As the Al2O3 content increased, the reactivity decreased, whereas the TiO2 prepared on Na-ZSM-5(23.8) showed no photocatalytic reactivity. Because the silanol groups in the H-ZSM-5(1880) zeolite cavities can condense acetaldehyde molecules and then efficiently provide them onto the TiO2 photocatalytic sites, high photocatalytic reactivity could be obtained. On the other hand, the H+ sites on H-ZSM-5(220 and 68) did not work as efficient adsorption sites for the acetaldehyde molecules, resulting in lower photocatalytic reactivity. Moreover, the acetaldehyde molecules highly stabilized on the Na+ sites of the Na-ZSM-5 zeolite could not efficiently spill over to the TiO2 photocatalytic sites, resulting in no photocatalytic activity. Although no experimental evidences for the formation of Na2TiO3 phases as a low photocatalytic active site could be obtained, the Na+ sites migrated into the TiO2 particles might work as a recombination center to suppress the photocatalytic reactivity.

The effects of H2O vapor on the photocatalytic oxidation reaction of acetaldehyde with O2 on these TiO2/ZSM-5 samples are shown Fig. 8. H2O vapor effectively promoted the photocatalytic oxidation of acetaldehyde with O2 on the TiO2 photocatalysts prepared on H-ZSM-5. The role of H2O molecules in the photocatalytic oxidation of acetaldehyde is considered to be the source supplying the OH⁻ species that are converted to active OH radicals by their reaction with the photoformed holes. Moreover, because H2O molecules strongly adsorb on the Ti4+ sites of TiO2 surfaces, they may inhibit the strong adsorption of acetaldehyde as a reactant or acetic acid molecules as intermediate species on the TiO2 photocatalytic sites, followed by
a decrease in photocatalytic reactivity. Further detailed spectroscopic investigations into the detection of the intermediate species to clarify the effect of the H₂O vapor on the photocatalytic reaction mechanism will be undertaken.

4. Conclusion

TiO₂ photocatalysts were prepared on ZSM-5 zeolites by the impregnation of (NH₄)₂[TiO(C₂O₄)₂] aqueous solution as a green process. TiO₂ prepared on siliceous H-ZSM-5 showed higher photocatalytic reactivity compared with the commercial TiO₂ photocatalyst, because the zeolite worked as an effective adsorbent to condense acetaldehyde molecules. The photocatalytic reactivity of TiO₂/ZSM-5 was largely dependent on the interaction of the reactants with the adsorption sites of the zeolite. The acetaldehyde molecules interacting with the silanol groups of the hydrophobic H-ZSM-5(1880) can efficiently spill over onto the TiO₂ sites, producing high photocatalytic reactivity. In contrast, the H-ZSM-5(220 and 68) with high Al₂O₃ content do not work as suitable adsorbents for acetaldehyde, resulting in decreased photocatalytic reactivity. The acetaldehyde molecules strongly trapped on the Na⁺ sites of the zeolite could not hardly transfer onto the TiO₂ sites, TiO₂/Na-ZSM-5(23.8) showed no reactivity. Moreover, the oxidation of acetaldehyde over the TiO₂/ZSM-5 photocatalysts was effectively enhanced by the addition of H₂O vapor. The competitive adsorption of H₂O against acetaldehyde on the TiO₂ photocatalytic sites may depress the highly stabilized acetaldehyde molecules as reactants and/or acetic acid as the intermediate species, resulting in enhanced photocatalytic reactivity from the addition of H₂O vapor.

References