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Photocatalytic oxidation of acetaldehyde with oxygen on TiO_2/ZSM-5 photocatalysts: Effect of hydrophobicity of zeolites

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Abstract

TiO_2 photocatalysts hybridized with ZSM-5 were prepared by the impregnation of $(NH_4)_2[TiO(C_2O_4)_2]$ aqueous solution. This is one of the most ideal green processes in establishing TiO_2 photocatalysts because of an organic solvent-free preparation method. The highly hydrophobic H-ZSM-5 with low Al_2O_3 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 TiO_2 prepared on zeolites compared with unloaded TiO_2 catalysts. However, acetaldehyde molecules were strongly trapped on the Na^+ sites of ZSM-5 and their efficient diffusion onto the TiO_2 sites was inhibited, resulting in low photocatalytic reactivity. The photocatalytic oxidation of acetaldehyde over TiO_2/ZSM-5 was improved in the coexistence of H_2O vapor. The role of the H_2O molecules was estimated to be the efficient formation of OH radicals and the prevention of strong adsorption of acetaldehyde on the TiO_2 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 TiO_2 photocatalysts have the potential to completely decompose various organic compounds into harmless CO_2 and H_2O 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 TiO_2 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 CO_2 and H_2O by photocatalytic oxidation. For this purpose, TiO_2 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 TiO_2 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 Al_2O_3 content are known to have highly hydrophobic surfaces [14]. H_2O 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 TiO_2 photocatalysts. In many cases, the improved photocatalytic reactivity from the addition of H_2O 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

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adsorbents and the photocatalytic reactivity of TiO_2 photocatalysts hybridized with zeolites can lead to the development of new photofunctional materials for environmental remediation.

In this work, the adsorption states of H_2O and acetaldehyde molecules on H^+ and Na^+ type ZSM-5 zeolites of different SiO_2/Al_2O_3 ratios were investigated by adsorption isotherm and temperature-programmed desorption (TPD) measurements. The TiO_2 photocatalysts hybridized with ZSM-5 zeolites were prepared by a simple impregnation method from an aqueous solution of titanium(IV) ammonium oxalate ($(NH_4)_2[TiO(C_2O_4)_2]$). The photocatalytic reactivity of the prepared TiO_2/ZSM-5 samples was evaluated by the complete oxidation of acetaldehyde with O_2, as was the effect of H_2O vapor addition on photocatalytic reactivity.

2. Experimental

Various ZSM-5 zeolite samples were supplied by Tosoh Co. Ltd. The ZSM-5 zeolite with a SiO_2/Al_2O_3 ratio of 1880 was supplied as the H^+-type zeolite and NH_4-ZSM-5 zeolites with SiO_2/Al_2O_3 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 NH_4NO_3 solution to obtain NH_4-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 NH_3 gas by TPD measurements.

TiO_2 photocatalysts hybridized with ZSM-5 zeolites were prepared by a simple impregnation method from a precursor solution of titanium(IV) ammonium oxalate $(NH_4)_2[TiO(C_2O_4)_2]$ (Kishida Chemicals Co.). After calcination at 723 K, the ZSM-5 zeolites were immersed in $(NH_4)_2[TiO(C_2O_4)_2]$ 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 TiO_2 content was adjusted to 10 wt%.

The adsorption isotherms of the H_2O and CH_3CHO molecules on various ZSM-5 zeolites were measured at room temperature. Before these measurements, the zeolite samples (30 mg) were placed in a Pyrex glass cell, degassed at 723 K for 2 h, treated in sufficient amounts of O_2 (ca. 6.7 kPa) at the same temperature for 2 h, and then degassed at 373 K for 2 h up to a 10^{-5} kPa range. To avoid temperature changes during adsorption isotherm measurements, the zeolite samples in the Pyrex glass cell were immersed in a water bath at ca. 300 K. Given amounts of H_2O or CH_3CHO vapor were admitted into the cell, step by step, and the pressure changes were then recorded once the adsorption equilibrium state was reached. The vapor pressures of H_2O and CH_3CHO at 300 K were 3.56 and 129.3 kPa, respectively.

For the TPD profiles of the H_2O and CH_3CHO molecules adsorbed on these ZSM-5 zeolites, the ion current for H_2O^+ (the ratio of molecular weight $[m]$ to charge careers $[z]$; $m/z = 18$) and CH_3CHO^+ ($m/z = 44$), which are ionized by high voltages of 1200 V, were monitored by a gas desorption analyzer (ANELVA, M-QA100TS) equipped with a quadrupole mass analyzer in a high-vacuum chamber of 10^{-9} kPa range. The zeolite samples (30 mg) in a quartz cell were pretreated in the same way as done for the adsorption isotherm measurements. Sufficient amounts of H_2O or CH_3CHO vapor were then adsorbed on these zeolite samples for 30 min. Before TPD measurements, the H_2O or CH_3CHO molecules in gas phase were degassed at room temperature for 1 h. TPD profiles were recorded by linear heating of the samples from 323 to 1023 K at a constant rate of 5 K/min.

The photocatalytic reactivities of the prepared TiO_2/ZSM-5 catalysts were evaluated by the decomposition of acetaldehyde in the presence of O_2 under UV light irradiation as a gas-phase reaction. TiO_2/ZSM-5 catalysts (50 mg) were placed onto a flat bottom quartz cell (volume, ca. 33 cm^3). The volume of the reaction area, including the cell volume, was ca. 100 cm^3. Pretreatment of the catalysts was carried out in the same way as done before the TPD and adsorption isotherm measurements. A gas mixture of CH_3CHO (0.27 kPa), O_2 (1.07 kPa), and H_2O (0–1.33 kPa) was then introduced into the reaction cell. The amount of acetaldehyde introduced into the reaction cell was calculated as ca. 7 µmol (ca. 1500 ppm). After an adsorption equilibrium was reached, UV light was irradiated at 275 K by a 100-W high-pressure Hg lamp (Toshiba, SHL-100UVQ-2) through a cutoff filter (Toshiba Glass, UV-27, $\lambda > 270$ nm). To avoid the heating effect from the Hg lamp, the photocatalysts in the quartz cell were cooled in ice water during the photoreaction. The amounts of CO_2 produced and acetaldehyde decomposed were analyzed by thermal conductivity and flame ionization detectors in a gas chromatograph (Shimadzu, GC-14A).

3. Results and discussion

The adsorption isotherms of the H_2O molecules on H and Na-ZSM-5 zeolites with SiO_2/Al_2O_3 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 Al_2O_3-containing zeolites. H-ZSM-5(1880), with a low Al_2O_3 content, exhibited the highest hydrophobicity among the ZSM-5 zeolites with different SiO_2/Al_2O_3 ratios. As the Al_2O_3 content increased to ca. 4 wt%, corresponding to a SiO_2/Al_2O_3 ratio of 23.8, the amount of H_2O adsorbed increased threefold more than the highly siliceous H-ZSM-5(1880). These results

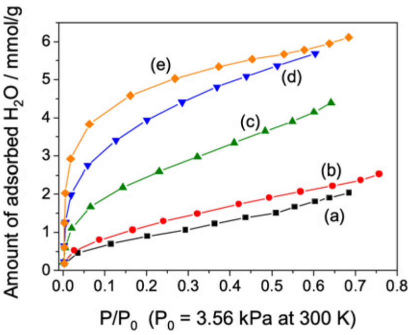


Fig. 1. Adsorption isotherms of H_2O molecules on (a–d) H-ZSM-5 and (e) Na-ZSM-5 zeolites. SiO_2/Al_2O_3 ratios: (a) 1880, (b) 220, (c) 68, (d) 23.8, and (e) 23.8. (Saturated vapor pressure of H_2O at 300 K: 3.56 kPa.)

clearly indicate that the Al^{3+} sites (i.e., Brönsted acid sites) play a major role as the adsorption sites of H_2O molecules. In fact, FTIR investigations have revealed that the H_2O molecules adsorb on the Brönsted acid sites of H-ZSM-5 or SAPO-34 to form oxonium ions (H_3O^+ or $H_2O_5^+$) [21–24] or H_2O molecules directly interacting with the H^+ moieties of the Brönsted acid sites by hydrogen bonding [25]. The strength of the interactions between the H_2O 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_2O 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_2O_3 within the zeolite frameworks gives rise to Brönsted acid sites, the surface of zeolites with high Al_2O_3 content have stronger adsorption sites for H_2O molecules compared with siliceous zeolites. This interpretation explains why the amount of H_2O molecules adsorbed strongly depends on the SiO_2/Al_2O_3 ratios of the zeolites. Investigations of Na-ZSM-5(23.8) and H-ZSM-5(23.8) showed that the adsorption of H_2O 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_2O 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_2O molecules.

TPD profiles of the H_2O molecules adsorbed on H and Na-ZSM-5 with different SiO_2/Al_2O_3 ratios are shown in Fig. 2. Desorption of the H_2O molecules can be seen at 373–573 K for H-ZSM-5 zeolites with low SiO_2/Al_2O_3 ratios of 23.8 and 68. However, very small amounts of H_2O desorbed from H-ZSM-5 with low Al_2O_3 content ($SiO_2/Al_2O_3 = 220$ and 1880). Moreover, as the SiO_2/Al_2O_3 ratio decreased, the desorption temperature shifted slightly toward higher-temperature regions. Generally, H_2O 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_2O molecules interacted with the surface silanol groups of siliceous H-ZSM-5 with low Al_2O_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_2O molecules adsorbed on the H^+ sites of the zeolite surfaces. The desorption of the H_2O molecules at around 823–973 K for H-ZSM-5 zeolites with low Al_2O_3 content could not be observed for the samples after outgassing at 873 K, suggesting that the desorption of H_2O 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_2O from Na-ZSM-5(23.8) broadened at higher temperatures compared with H-ZSM-5(23.8), suggesting the stronger interaction between the H_2O 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_2O molecules strongly interact with the cationic sites rather than with the hydroxyl groups on the oxide surfaces. Three kinds of adsorbed H_2O species are summarized in Table 1, according to the strength of the interactions between the H_2O molecules and surface sites: (A) the H_2O molecules interacting with the silanol groups are easily removed by evacuation at room temperature. On the other hand, two kinds of H_2O species are adsorbed on the H^+ sites neighboring the Al^{3+} of the zeolite surface, as proposed by FTIR investigations; (B-1) the H_2O molecules interact only by hydrogen bonding [25]; (B-2) the oxonium ions, as with H_3O^+ [21–24], desorb at 323–523 K from the H-ZSM-5 with high Al_2O_3 content; and (C) the H_2O 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.

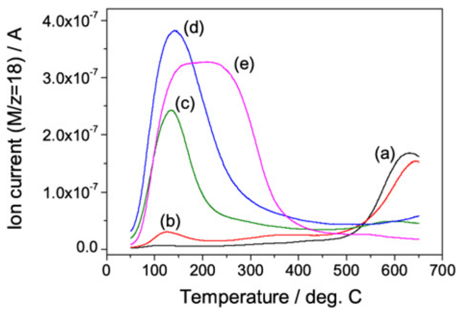


Fig. 2. TPD profiles of H_2O molecules adsorbed on (a–d) H-ZSM-5 and (e) Na-ZSM-5 zeolites. SiO_2/Al_2O_3 ratios: (a) 1880, (b) 220, (c) 68, (d, e) 23.8.

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_2O_3 ratios. These 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_2O_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-

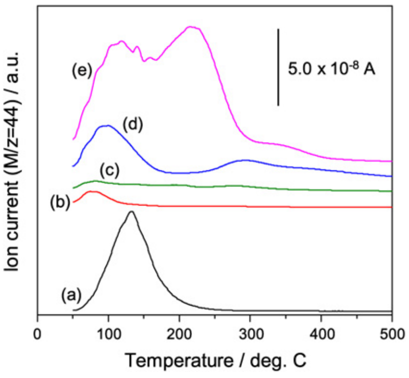
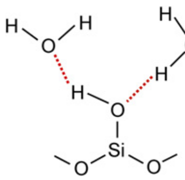
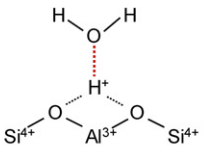
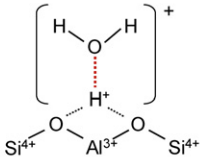
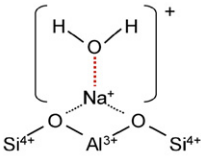


Fig. 3. TPD profiles of acetaldehyde molecules adsorbed on (a–d) H-ZSM-5 and (e) Na-ZSM-5 zeolites. SiO_2/Al_2O_3 ratios: (a) 1880, (b) 220, (c) 68, (d, e) 23.8.

Table 1
Interaction of H_2O molecules with various sites on the ZSM-5 zeolite surface

Species	(A)	(B)	(C)
		 **B-1**  **B-2**	
	H/ZSM-5 with low Al_2O_3 content	H/ZSM-5 with high Al_2O_3 content	Na/ZSM-5
Desorption temperature	Room temperature	323–523 K	523–673 K
Interaction	Hydrogen bonds Weak	B-l; Hydrogen bonds or B-2; Static electricity (oxonium ion) Medium	Static electricity Strong

ferences in their SiO_2/Al_2O_3 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 CH_3, CHO, and CH_3CO, respectively, as fragments of the CH_3CHO molecule. From these results, the desorbed species of $m/z = 44$ can be assigned to acetaldehyde and not to the CO_2 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 Al_2O_3, 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-ene 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 TiO_2 prepared on various ZSM-5 zeolites and of a commercial TiO_2 (Degussa, P-25) as reference are shown in Fig. 4. The absorption edges of the TiO_2/ZSM-5 samples were found to shift slightly toward shorter wavelength regions compared with P-25. The bandgap energies of the TiO_2 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 TiO_2/ZSM-5 catalysts (10 wt% as TiO_2) did not show any significant XRD peaks attributed to the TiO_2 particles; however, as the TiO_2 content increased up to 20 wt%, clear diffraction peaks attributed to the anatase structure of TiO_2 could be seen (data not shown). These results clearly suggest much smaller TiO_2 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, the major parts of the TiO_2 particles are considered to exist on the outer surfaces of the ZSM-5 zeolites. SEM images of the TiO_2/ZSM-5 samples in fact showed that the aggregated TiO_2 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 H_2O molecules adsorbed on the TiO_2/ZSM-5 zeolite samples are shown in Fig. 5. Compared with the TPD profiles of the ZSM-5 zeolites shown in Fig. 2,

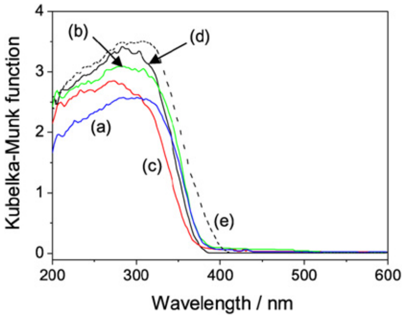


Fig. 4. Diffuse reflectance UV–vis absorption spectra of (a–d) TiO_2 prepared on H-ZSM-5 zeolites and (e) TiO_2 (Degussa, P-25) as reference. SiO_2/Al_2O_3 ratios: (a) 1880, (b) 220, (c) 68, (d) 23.8.

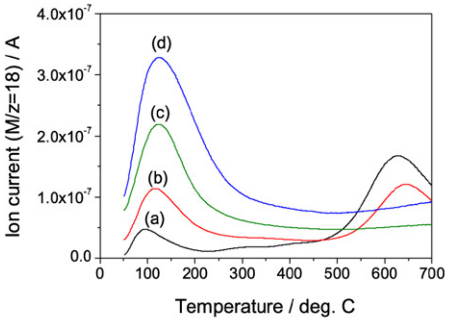


Fig. 5. TPD profiles of H_2O molecules adsorbed on TiO_2/H-ZSM-5 catalysts (10 wt% as TiO_2). SiO_2/Al_2O_3 ratios: (a) 1880, (b) 220, (c) 68, (d) 23.8.

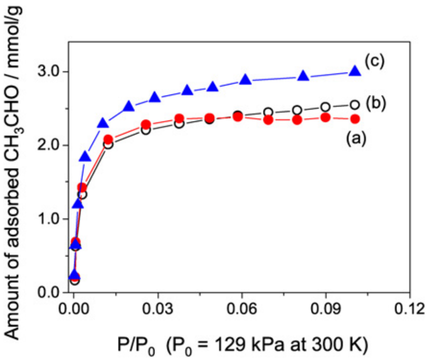


Fig. 6. Adsorption isotherms of CH_3CHO molecules on (a) dehydrated H-ZSM-5, (b) hydrated H-ZSM-5(1880), and (c) TiO_2/H-ZSM-5(1880). (Saturated vapor pressure of CH_3CHO at 300 K: 129.3 kPa.)

the desorption of H_2O can be seen at around 373–423 K, especially for the TiO_2 prepared on H-ZSM-5(1880 and 220) with low Al_2O_3 content. For the TiO_2 on H-ZSM-5(68, 23.8) with high Al_2O_3 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 TiO_2 particles. From these results, the order of interaction between the H_2O molecules and adsorption sites of the TiO_2/H-ZSM-5 zeolites can be estimated as follows: Brönsted acid sites neighboring Al^{3+} > TiO_2 photocatalytic sites > surface silanol groups of the zeolite framework.

The adsorption isotherms of the CH_3CHO molecules on the dehydrated, hydrated H-ZSM-5(1880), and TiO_2/H-ZSM-5(1880) zeolites are shown in Fig. 6. The hydrated surfaces were obtained through the preadsorption of H_2O vapor and then outgassing at room temperature. However, as shown in Fig. 2, because the major part of physisorbed H_2O molecules on the hydrophobic H-ZSM-5(1880) were degassed at room temperature, the amount of CH_3CHO adsorbed on the H-ZSM-5(1880) was hardly affected by the preadsorption of H_2O vapor. In contrast, the amount of CH_3CHO adsorbed on the hydrophilic H-ZSM-5(23.8) was decreased by the preadsorption of H_2O vapor (data not shown). Furthermore, the adsorption of CH_3CHO molecules on the TiO_2/H-ZSM-5(1880) increased by ca. 10–15% compared with the H-ZSM-5(1880). This result indicates that the CH_3CHO molecules easily interact with TiO_2 sites rather than siliceous H-ZSM-5 surfaces. It also suggests that once the CH_3CHO molecules adsorbed on TiO_2 photocatalytic sites are decomposed into CO_2 and H_2O by UV irradiation, the CH_3CHO molecules condensed in zeolite cavities are efficiently supplied onto the TiO_2 sites.

The photocatalytic reactivity of the TiO_2/ZSM-5 samples for the oxidation of acetaldehyde with O_2 in the absence of H_2O under UV light irradiation ($\lambda > 270$ nm) is shown in Fig. 7. The reactivity was found to depend on the SiO_2/Al_2O_3 ratio of the ZSM-5 zeolites. TiO_2 prepared on H-ZSM-5(1880) showed the highest photocatalytic reactivity among these hybrid photocatalysts. As the Al_2O_3 content increased, the reactivity decreased, whereas the TiO_2 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 TiO_2 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 TiO_2 photocatalytic sites, resulting in no photocatalytic reactivity. Although no experimental evidences for the formation of Na_2TiO_3 phases as a low photocatalytic active site could be obtained, the Na^+ sites migrated into the TiO_2 particles might work as a recombination center to suppress the photocatalytic reactivity.

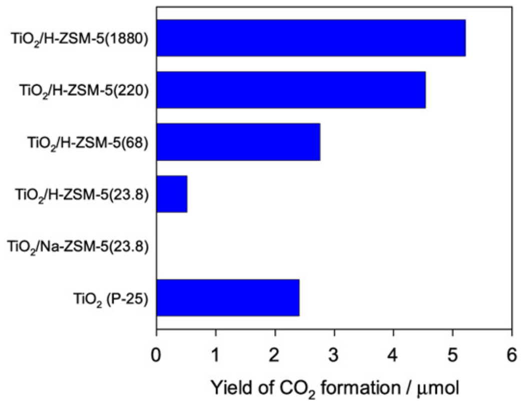


Fig. 7. Photocatalytic oxidation of acetaldehyde in the absence of H_2O vapor over the TiO_2 prepared on H- and Na-ZSM-5 zeolites under UV light irradiation.

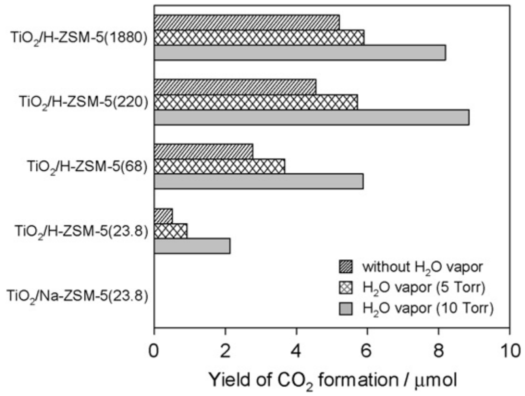


Fig. 8. Effect of the addition of H_2O vapor on the photocatalytic oxidation of acetaldehyde over TiO_2 prepared on H- and Na-ZSM-5 zeolites under UV light.

The effects of H_2O vapor on the photocatalytic oxidation reaction of acetaldehyde with O_2 on these TiO_2/ZSM-5 samples are shown Fig. 8. H_2O vapor effectively promoted the photocatalytic oxidation of acetaldehyde with O_2 on the TiO_2 photocatalysts prepared on H-ZSM-5. The role of H_2O 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 H_2O molecules strongly adsorb on the Ti^{4+} sites of TiO_2 surfaces, they may inhibit the strong adsorption of acetaldehyde as a reactant or acetic acid molecules as intermediate species on the TiO_2 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 H_2O vapor on the photocatalytic reaction mechanism will be undertaken.

4. Conclusion

TiO_2 photocatalysts were prepared on ZSM-5 zeolites by the impregnation of $(NH_4)_2[TiO(C_2O_4)_2]$ aqueous solution as a green process. TiO_2 prepared on siliceous H-ZSM-5 showed higher photocatalytic reactivity compared with the commercial TiO_2 photocatalyst, because the zeolite worked as an effective adsorbent to condense acetaldehyde molecules. The photocatalytic reactivity of TiO_2/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 TiO_2 sites, producing high photocatalytic reactivity. In contrast, the H-ZSM-5(220 and 68) with high Al_2O_3 content do not work as suitable adsorbents for acetaldehyde, resulting in decreased photocatalytic reactivity. Because the acetaldehyde molecules strongly trapped on the Na^+ sites of the zeolite could not hardly transfer onto the TiO_2 sites, TiO_2/Na-ZSM-5(23.8) showed no reactivity. Moreover, the oxidation of acetaldehyde over the TiO_2/ZSM-5 photocatalysts was effectively enhanced by the addition of H_2O vapor. The competitive adsorption of H_2O against acetaldehyde on the TiO_2 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 H_2O vapor.

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