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Efficient adsorption and photocatalytic degradation of organic pollutants diluted in water using the fluoride-modified hydrophobic titanium oxide photocatalysts: Ti-containing Beta zeolite and TiO_2 loaded on HMS mesoporous silica

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Abstract

Using the F^- media, the hydrophobic zeolite and mesoporous silica can be synthesized. These hydrophobic porous materials exhibit the high ability for the adsorption of organic compounds diluted in water and become the useful supports of photocatalyst. The hydrophobic Ti-Beta(F) zeolite prepared in the F^- media exhibited high efficiency than the hydrophilic Ti-Beta(OH) zeolite prepared in OH^- media for the liquid-phase photocatalytic degradation of 2-propanol diluted in water to produce CO_2 and H_2O. The TiO_2 loaded on the hydrophobic mesoporous silica HMS(F) (TiO_2/HMS(F)), which was synthesized using tetraethyl orthosilicate, tetraethylammonium fluoride as the source of the fluoride and dodecylamine as templates, also exhibited the efficient photocatalytic performance for the degradation. The amount of adsorption of 2-propanol and the photocatalytic reactivity for the degradation increased with increasing the content of fluoride ions on these photocatalysts. The efficient photocatalytic degradation of 2-propanol diluted in water on Ti-Beta(F) zeolite and TiO_2/HMS(F) mesoporous silica can be attributed to the larger affinity for the adsorption of propanol molecules on the titanium oxide species depending on the hydrophobic surface properties of these photocatalysts.

Keywords: Photocatalysis; Titanium oxide; Zeolite; Mesoporous silica degradation; Hydrophobic property

1. Introduction

The design of highly efficient and selective photocatalytic systems is of vital interest. It has been found that the highly dispersed titanium oxide photocatalysts anchored on the porous silica-based materials exhibit high and characteristic photocatalytic reactivity compared to bulk TiO_2 powder. Especially the titanium oxide species prepared within the pores and frameworks of zeolite and mesoporous silica have been revealed to have unique local structures as well as high reactivities in the various photocatalytic reactions in the gas-phase [1].

Recently a large-pore Ti-containing zeolite, Ti-Beta, has been hydrothermally synthesized by various methods. Davis et al. have prepared aluminum-free Ti-Beta zeolite using N'-dibenzyl-4,4$'$-trimethylenebis(N-methylpiperidinium) dihydroxide as a structure-directing agent (SDA) in the absence of seeding [2] and found that the calcined sample exhibits the high H_2O affinity. On the other hand, Corma and co-workers have reported that aluminum-free Ti-Beta zeolite can be prepared in the F^- medium and performs as a hydrophobically selective oxidation catalyst [3]. The H_2O affinity of Ti-Beta zeolites changes significantly depending on the preparation methods and their hydrophobic–hydrophilic properties can modify not

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only the catalytic properties but also the photochemical process in the zeolite pores [4]. On the other hands, various types of mesoporous silica have been synthesized and been found to be useful as the supports of TiO_2 photocatalyst. Generally, these mesoporous silica has the hydrophilic surface property and this hydrophilic surface often affects to the photocatalytic reactions.

The photocatalytic degradation of organic toxic compounds dissolved in aqueous solutions at low concentrations using irradiated titanium oxide is one of the most promising applications of photocatalysts [5–10]. It is effective to use the hybrid materials, combined with adsorbents and photocatalysts for the purification of water. Zeolite and mesoporous silica, which have high surface area and porous structure, have been used as conventional adsorbents. The condensation properties of these adsorbents should depend on their surface hydrophilic–hydrophobic properties and the highly hydrophobic surface seems to be suitable for the adsorption of organic compounds diluted in water. The fine titanium oxide photocatalyst loaded on hydrophobic zeolite and mesoporous silica have opened new possibilities for photocatalytic degradation of various organic compounds diluted water.

In the present study, we have used the two types of Ti-Beta zeolites synthesized under different conditions as photocatalysts for the liquid-phase degradation of organic compounds (2-propanol) diluted in water to form CO_2 with H_2O and the effects of the hydrophobic–hydrophilic properties of zeolites on the photocatalytic reactivity have been investigated. Furthermore, the TiO_2 photocatalysts loaded on the fluoride-modified hydrophobic mesoporous silica were prepared. Using these hydrophobic supports and photocatalysts, the adsorption properties and photocatalytic reactivities for the degradation of 2-propanol diluted in water have been studied.

2. Experimental

2.1. Catalysts

Ti-Beta zeolites (Si/Ti = 60) were synthesized using two kinds of SDA: *N*′-dibenzyl-4,4′-trimethylenebis(*N*-methylpiperidinium) dihydroxide and tetraethylammonium fluoride (TEAF) [2,3]. The sources of the silica and titanium oxide were tetraethylorthosilicate and titaniumisopropoxide, respectively. The two types of Ti-Beta zeolites are denoted according to the kinds of SDA, i.e., Ti-Beta(OH) and Ti-Beta(F). The material mixture for Ti-Beta(OH) had the following composition: 1 SiO_2/0.02 TiO_2/0.2 *N*′-dibenzyl-4,4′-trimethylenebis(*N*-methylpiperidinium) dihydroxide/30 H_2O in molar ratio. The material mixture for Ti-Beta(F) had the following composition: 1 SiO_2/0.02 TiO_2/0.56 TEAF/7 H_2O. The gelation of the material mixtures were carried out at room temperature, and these gel mixtures were placed into Teflon-lined stainless autoclaves and heated at 413 K for 5 days while being rotated at 60 rpm. The product was collected by centrifugal filtration, washed with distilled water, and dried in air at 353 K. To remove the occluded organic molecules, the samples were heated under a flow of dry air at 823 K for 4 h. TS-1 (Si/Ti = 60, MFI) was prepared from a material mixture having the following composition: 1 SiO_2/0.02 TiO_2/0.4 tetrapropylammonium hydroxide (TPAOH)/30 H_2O. TiO_2 powdered catalysts (Degussa, P-25: anatase 92%, rutile 8%) were supplied as standard reference.

The synthesis of the hydrophobic mesoporous silica (denoted as HMS(F)) was performed using tetraethyl orthosilicate (TEOS), tetraethylammonium fluoride as the source of the fluoride and dodecylamine (DDA) [11]. TEOS dissolved in a mixture of 2-propanol and ethanol and DDA (0–7.75 g) dissolved in water with HCl (3 ml) are mixed, following to stirring at 295 K for 24 h. The precursor mixture was washed by distilled water, dried at 373 K for 24 h, and then calcined at 823 K for 7 h. The ratio of TEAF to DDA was 0 (HMS), 0.25 (HMS(F1)), 0.75 (HMS(F2)) and 1.25 (HMS(F3)). Furthermore, imp-TiO_2/HMS(F) (10 wt% as TiO_2) was prepared by impregnating HMS(F) with an aqueous titanium oxalate solution, then dried and calcined for 5 h at 773 K.

2.2. Photocatalytic reaction

2.2.1. Liquid-phase degradation

The photocatalytic reactions were carried out with the catalysts (50 mg) in the quartz tube with a 2-propanol aqueous solution (2.6×10^{-3} M, 25 ml). The sample was irradiated at 295 K using UV light ($\lambda > 280$ nm) from a 100 W high-pressure Hg lamp with stirring under O_2 atmosphere in the system [10]. The reaction products were analyzed by gas chromatography. The photocatalytic reactivity was estimated from the initial decrease in the concentration of 2-propanol after preadsorption of 2-propanol on the catalyst under dark condition for 60 min. The adsorption isotherms measurement was carried out stirring the catalysts (10 mg) dissolved in the solutions (5 ml) without the UV light irradiation at 295 K for 60 min.

2.2.2. Gas-phase reactions (reduction of CO_2 with H_2O, NO decomposition)

Prior to the photoreactions and spectroscopic measurements, the catalysts were degassed at 725 K for 2 h, heated in O_2 at the same temperature for 2 h and finally evacuated at 475 K to 10^{-6} Torr for 1 h. The photocatalytic reduction of CO_2 with H_2O was carried out with the catalysts (50 mg of the catalyst involving zeolite) in a quartz cell with a flat bottom (88 ml) connected to a conventional vacuum system (10^{-6} Torr range). UV-irradiation of the catalysts in the presence of CO_2 (36 μmol, 7.8 Torr) and gaseous H_2O (180 μmol, 39.0 Torr) was carried out using a 75-W high-pressure Hg lamp ($\lambda > 250$ nm) at 328 K. The photocatalytic reactions of NO molecules were carried out with the catalysts (150 mg) in a quartz cell with a flat bottom (60 ml) connected to a conventional vacuum system (10^{-6} Torr range). UV-irradiation of the catalysts in the presence of NO (7.8 μmol) was carried out using a 75 W high-pressure Hg lamp ($\lambda > 280$ nm) at 275 K. The reaction products collected in the gas-phase were analyzed by gas chromatography.

2.3. Characterization

The XAFS spectra (XANES and EXAFS) were measured at the BL-9A facility [12] of the Photon Factory at the National

Laboratory for High-Energy Physics, Tsukuba. A Si(1 1 1) double crystal was used to monochromatize the X-rays from the 2.5 GeV electron storage ring. The normalized spectra were obtained by a procedure described in previous literature [13] and Fourier transformation was performed on k^3-weighted EXAFS oscillations in the range of 3–10 Å^{-1}. The curve-fitting of the EXAFS data was carried out by employing the iterative nonlinear least-squares method and the empirical backscattering parameter sets extracted from the shell features of titanium compounds.

3. Results and discussion

3.1. Characterization of Ti-Beta zeolites

Fig. 1 shows the XANES spectra of the Ti-Beta zeolites. The XANES spectra of the Ti-containing compounds at the Ti K-edge show several well-defined preedge peaks that are related to the local structures surrounding the Ti atom. These relative intensities of the preedge peaks provide useful information on the coordination number surrounding the Ti atom [14]. As shown in Fig. 1, both Ti-Beta(OH) and Ti-Beta(F) zeolites exhibit an intense single preedge peak. Because a lack of an inversion center in the regular tetrahedron structure causes an intense single preedge peak [15], the observation of this intense single preedge peak indicates that the titanium oxide species in the Ti-Beta zeolites has a tetrahedral coordination. The Ti-Beta(OH) and Ti-Beta(F) zeolites exhibit the preedge peaks having the same intensities and positions indicating that both zeolites have the same titanium coordination.

Fig. 1 also shows the FT-EXAFS spectra of the zeolites and all data are given without corrections for phase shifts. Both Ti-Beta(OH) and Ti-Beta(F) zeolites exhibit only a strong peak at around 1.6 Å (uncorrected for the phase shift), which can be assigned to the neighboring oxygen atoms (a Ti–O bond), indicating the presence of the isolated titanium oxide species on these zeolites. From the results obtained by the curve-fitting analysis of the EXAFS spectra, it was found that the Ti-Beta zeolites consist of 4-coordinated titanium ions with an atomic distance of 1.84 Å for Ti-Beta(OH) and 1.83 Å for Ti-Beta(F).

The H_2O affinity of Ti-Beta zeolites can be evaluated by monitoring the H_2O adsorption isotherms. Fig. 2 shows the H_2O adsorption isotherms on the Ti-Beta zeolites. These results indicate that the Ti-Beta(OH) and Ti-Beta(F) zeolites synthesized using a typical OH^- ion and F^- ion as the anion of the SDA exhibit hydrophilic and hydrophobic properties, respectively. The large molecule of SDA, *N*′-dibenzyl-4,4′-trimethylenebis (*N*-methylpiperidinium) dihydroxide, for the

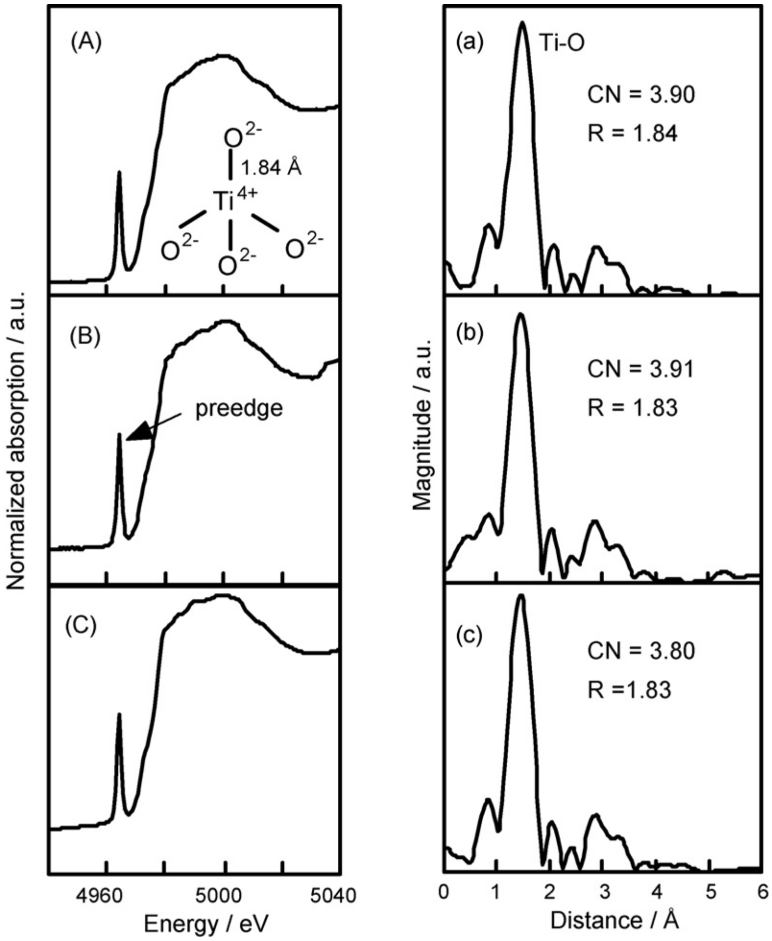


Fig. 1. The Ti K-edge XANES (left) and FT-EXAFS (right) spectra of Ti-Beta(OH) (A, a), Ti-Beta(F) (B, b) and TS-1 (C, c). CN: coordination number, R: Ti–O bond distance (Å).

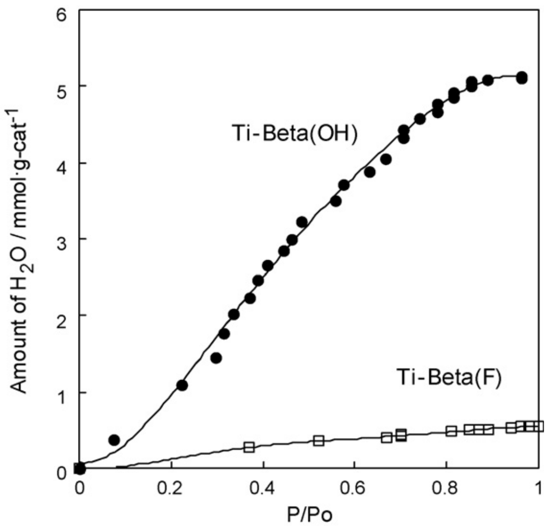


Fig. 2. Adsorption isotherms for H_2O molecules at 298 K on the Ti-Beta(OH) and Ti-Beta(F) zeolites.

synthesis of Ti-Beta(OH) can be removed only by calcination leaving many defect sites in the zeolite pore [2]. On the other hand, it has been reported that Ti-Beta free of detect sites can be prepared by using TEAF as SDA [3]. This difference in the numbers of defect sites between these Ti-Beta zeolites generates the unique hydrophilic and hydrophobic properties, respectively.

3.2. Adsorption properties and photocatalytic reactivities of Ti-Beta zeolites

The photocatalytic degradation of 2-propanol diluted in water was investigated using the Ti-Beta zeolite photocatalysts. Some amounts of 2-propanol were adsorbed on the photocatalyst without light irradiation, and then the photocatalytic reaction proceeds with the UV-irradiation. As shown in Fig. 3, the concentration of 2-propanol decreased and acetone increased as the intermediate, finally 2-propanol and acetone were degradated into CO_2 and H_2O. The other by-products were not observed.

Fig. 4 shows the adsorption properties and photocatalytic reactivities of Ti-Beta zeolites and TiO_2 powder (P-25) photocatalysts for the degradation of 2-propanol in water. Ti-Beta zeolites indicate the higher ability for 2-propanol adsorption and higher efficiency for the photocatalytic degradation than commercial TiO_2 powder (P-25) photocatalyst. Among the Ti-Beta zeolites, the amount of adsorbed 2-propanol on Ti-Beta(F) is higher than that of Ti-Beta(OH), indicating that efficient adsorption of organic compounds in the aqueous solutions can be realized by fluoride-modified hydrophobic zeolite. Because the Ti-Beta(F) exhibited the photocatalytic reactivity higher than Ti-Beta(OH), it can be also found that the more highly adsorption, the more efficiently photocatalytic reactivities were promoted.

UV-irradiation of powdered TiO_2 and Ti-Beta zeolite catalysts in the presence of a mixture of CO_2 and H_2O led to the evolution of CH_4 and CH_3OH in the gas-phase at 328 K. The yields of these photoformed products increased linearly against the UV-irradiation time, indicating the photocatalytic reduction of CO_2 with H_2O on the catalysts. The specific photocatalytic reactivity for the formation of CH_4 and CH_3OH

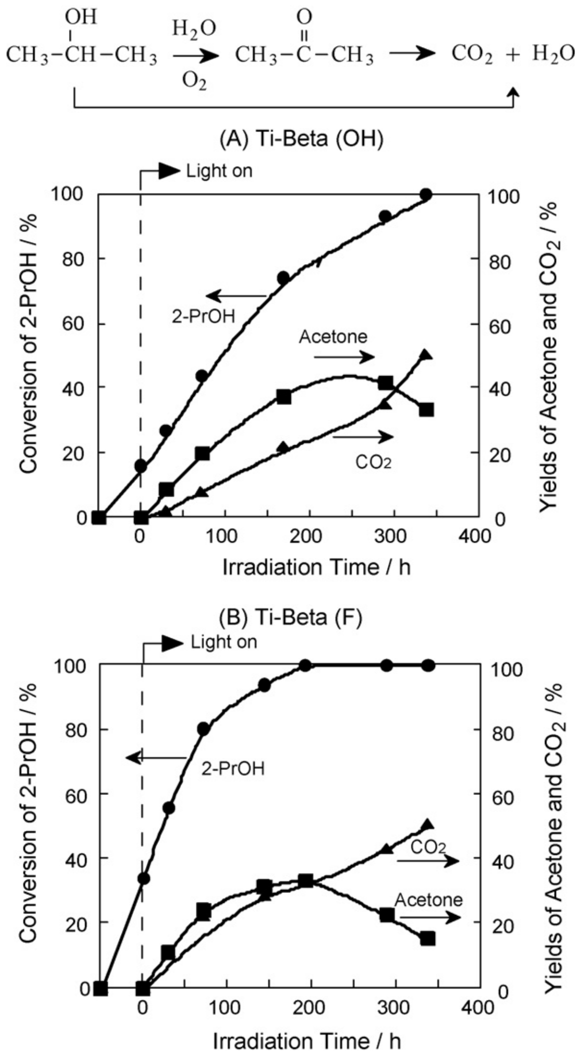


Fig. 3. Reaction time profiles of the photocatalytic oxidative degradation of 2-propanol diluted in water on (A) Ti-Beta(OH) and (B) Ti-Beta(F) zeolites.

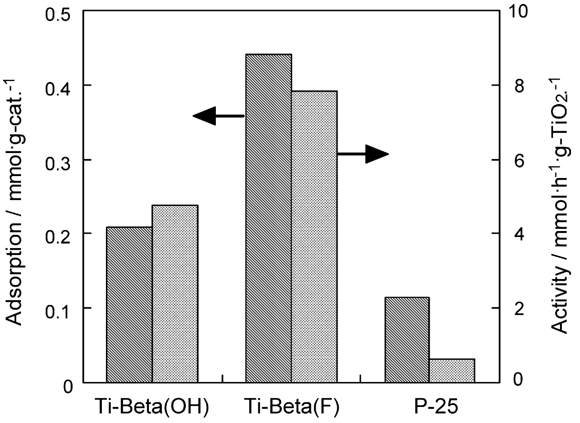


Fig. 4. The adsorption properties and photocatalytic reactivities of Ti-Beta zeolite and TiO_2 powder (P-25) photocatalysts for the degradation of 2-propanol in water.

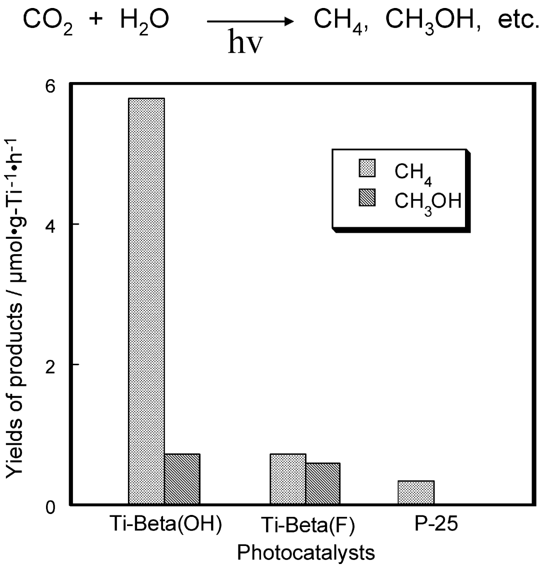


Fig. 5. The yields of CH_4 and CH_3OH in the photocatalytic reduction of CO_2 with H_2O at 323 K as the gas-phase reaction.

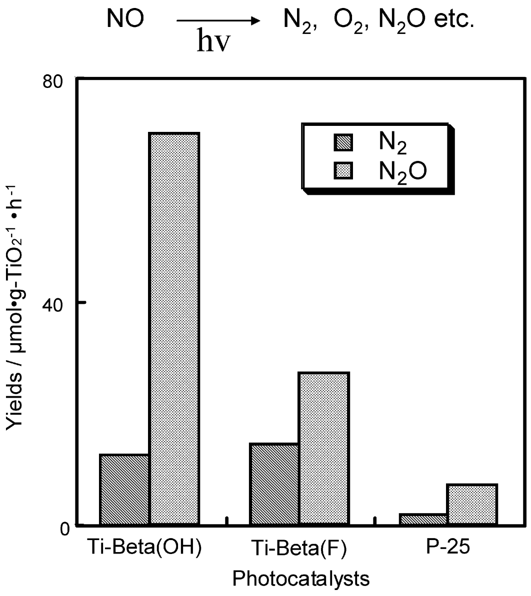


Fig. 6. The yields of N_2 and N_2O in the photocatalytic decomposition of NO at 273 K as the gas-phase reaction.

are shown in Fig. 5. The photocatalytic reduction of CO_2 with H_2O to produce CH_4 and CH_3OH was found to proceed in the gas-phase at 323 K with different reactivity and selectivity on hydrophilic Ti-Beta(OH) and hydrophobic Ti-Beta(F) zeolites. The higher reactivity for the formation of CH_4 observed with Ti-Beta(OH) and the higher selectivity for the formation of CH_3OH observed with the Ti-Beta(F) may be attributed to the different abilities of zeolite pores on the H_2O affinity. These results suggest that the hydrophilic–hydrophobic property of surface of zeolite cavities is one of important factors for the selectivity in the photocatalytic reduction of CO_2 and H_2O.

UV-irradiation of the powdered TiO_2 and the Ti-Beta zeolites in the presence of NO were found to lead to the evolution of N_2, O_2 and N_2O in the gas-phase at 275 K with different yields and different product selectivity. The efficiency and selectivity for the formation of N_2 strongly depend on the type of catalysts as shown in Fig. 6. The Ti-Beta zeolite exhibits a high reactivity and a high selectivity for the formation of N_2 while the formation of N_2O was found to be the major reaction on the powder TiO_2 catalyst.

As shown in Figs. 5 and 6, the Ti-Beta(OH) zeolite exhibits the higher photocatalytic reactivity than the Ti-Beta(F) for the gas-phase reactions; CO_2 reduction with H_2O and NO decomposition. On the other hand, Ti-Beta(F) exhibited the higher reactivity than Ti-Beta(OH) as shown in Figs. 3 and 4 for the liquid-phase reaction; degradation of 2-propanol diluted in water. These results suggest that the photocatalytic reactivity of active site of Ti-oxide moieties in zeolite is higher on the Ti-Beta(OH) than the Ti-Beta(F). However, in the liquid-phase reaction, the hydrophobic surface property of Ti-Beta(F) zeolite can realize the efficient adsorption of organic compounds and promote the photocatalytic degradation significantly. These results suggest that combination of photocatalyst and the hydrophobic porous supports is suitable for the liquid-phase photocatalytic reaction.

3.3. Characterization of imp-TiO_2/HMS(F)

The XRD patterns of the fluoride-modified hydrophobic mesoporous silica (HMS(F)) exhibited well-resolved peak typical of hexagonal structure of the HMS mesoporous molecular sieves having pores larger than 20 Å [11]. With increase the content of fluoride, the peak shifted to the lower angle with decrease in its intensity, suggesting the mesoporous hexagonal structure was distorted. The BET surface area of HMS(F) catalysts were measured by monitoring the physical adsorption of N_2 at 77 K: the values are 682 $m^2 g^{-1}$ (HMS), 581 (HMS(F1)), 487 (HMS(F2)) and 258 (HMS(F3)). The surface area decreased with increase the content of fluoride.

Fig. 7 shows the adsorption isotherm of H_2O molecules at 298 K obtained over various HMS(F) catalysts, indicating that the amount of adsorbed H_2O molecules decreases with increasing the content of fluoride in the HMS(F) mesoporous silica. The values of H_2O adsorption ability per unit surface area of catalysts at $P/P_0 = 1$ are 7.1 mmol/m^2-cat. (HMS), 2.6 (HMS(F1)), and 1.5 (HMS(F3)). This shows that fluoride-modified mesoporous silica can be hydrophobilized by the fluoride-modifications.

Fig. 8 shows the XAFS spectra of the imp-TiO_2/HMS catalysts. The XANES spectra of these catalysts at the Ti K-edge exhibit the preedge peak branched off into three distinct weak peaks. The FT-EXAFS spectra exhibit the existence of the peaks attributed to the neighboring O atoms (Ti–O) and the neighboring Ti atoms (Ti–O–Ti). These XAFS results indicate that the TiO_2 loaded on the mesoporous silica exists in the fine particles of anatase TiO_2 crystalline as main component [15].

3.4. Adsorption properties and photocatalytic reactivities of imp-TiO_2/HMS(F)

The photocatalytic degradation of alcohol diluted in water was investigated using the imp-TiO_2/HMS(F) photocatalysts.

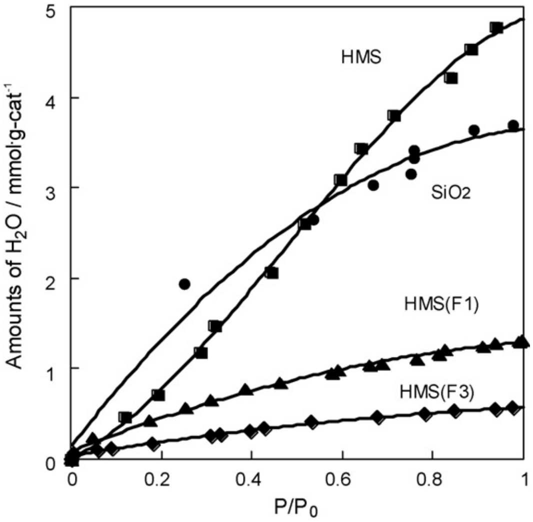


Fig. 7. Adsorption isotherms for H_2O molecules at 298 K on the HMS(F) mesoporous silica.

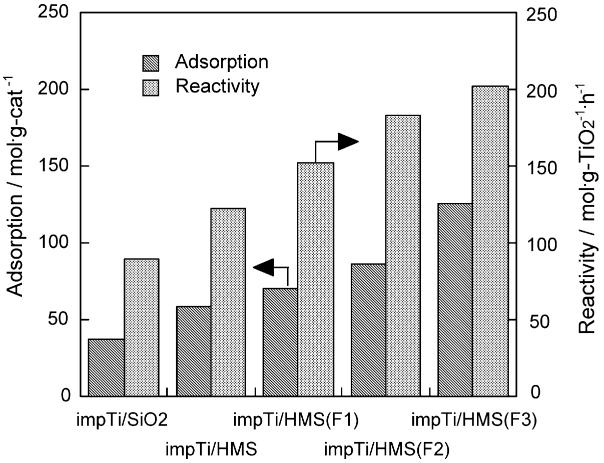


Fig. 9. The adsorption properties and photocatalytic reactivities of imp-TiO_2/HMS(F) photocatalysts for the degradation of 2-propanol in water.

Some amounts of 2-propanol were adsorbed on the photocatalyst without light irradiation, and then the photocatalytic reaction proceeded with the UV-irradiation. The concentration of 2-propanol decreased and acetone increased as the intermediate, finally 2-propanol and acetone were degradated into CO_2 and H_2O. Fig. 9 shows the adsorption properties and photocatalytic reactivities of imp-TiO_2/HMS(F) photocatalysts for the degradation of 2-propanol in water. The amount of adsorbed 2-propanol increased with increasing the amount of fluoride in HMS(F), indicating that efficient adsorption of organic compounds in their aqueous solutions can be realized by hydrophobilizing the support. Furthermore, it can be found that the more highly adsorption, the more efficiently photocatalytic reactivities were promoted on HMS(F).

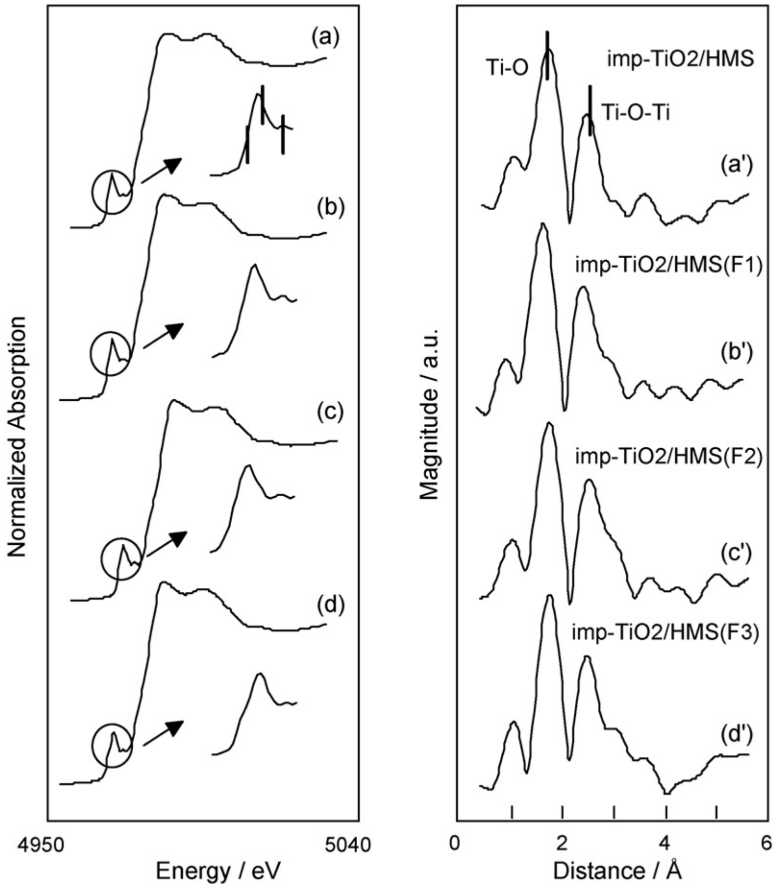
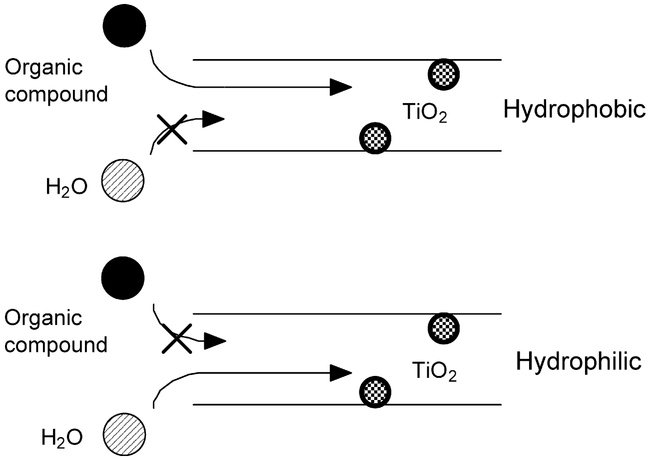


Fig. 8. XANES (a–d) and FT-EXAFS (a′–d′) spectra of the imp-TiO_2/HMS(F) photocatalysts.



Scheme 1. The difference of the adsorption of H_2O or organic compound on the system of TiO_2 photocatalyst and hydrophilic–hydrophobic adsorbents in the liquid-phase.

4. Conclusion

Ti-containing zeolites are good candidates as efficient photocatalysts. It has been revealed that the Ti-Beta zeolites synthesized in the media of OH^- ion and F^- ion exhibit hydrophilic and hydrophobic properties, respectively. The hydrophilic Ti-Beta(OH) and the hydrophobic Ti-Beta(F) exhibited the photocatalytic efficiency in the different manor for the gas-phase and liquid-phase reactions. Ti-Beta(F) exhibited a higher reactivity for the degradation of 2-propanol as compared to Ti-Beta(OH) due to the higher affinity of the 2-propanol molecules for adsorption in aqueous solutions, which was induced by the fluoride-modified hydrophobic surface. The TiO_2 photocatalysts loaded on the fluoride-modified hydrophobic mesoporous silica also exhibited the highly selective adsorption of organic compounds in the liquid-phase. The hydrophobic surface of HMS(F) supports was suitable for the adsorption of organic compounds and the larger amount of adsorbing organic compounds on the imp-TiO_2/HMS(F) led to the higher reactivity for photocatalytic degradation. The combination of the porous adsorbents with fluoride-modified hydrophobic surface and titanium oxide photocatalyst is a good candidate as the efficient system for the degradation of organic pollutants diluted in water as shown in Scheme 1.

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