Fabrication of hydrophobic zeolites using triethoxyfluorosilane and their application as supports for TiO_2 photocatalysts†

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Hydrophobically modified Y-zeolites were prepared by simple modification with triethoxyfluorosilane (TEFS). These zeolites, used as supports, enhanced the efficiency of deposited TiO_2 for the photocatalytic degradation of organics diluted in water.

Hybrid materials combined with dispersed transition metal oxides and mesoporous materials with large surface areas and ordered porous structures have been attractive because of their efficient adsorption of guest molecules and unique catalytic reactions.[1–3] As a representative catalyst, TiO_2 has been frequently utilized as a photocatalyst due to its practicability and strong oxidation potential under UV-light irradiation.[4,5] The majority of these hybrid materials are based on zeolites and mesoporous silicas such as HMS and MCM-41, primarily because silica substrates offer large surface areas due to their excellent chemical and thermal stability.[6–8] In our previous studies concerning TiO_2 and mesoporous silica photocatalytic hybrid systems, it was demonstrated that the smooth transfer of guest molecules into the pores and the photocatalytic properties for degradation of organic compounds much depend on the hydrophilic–hydrophobic properties of the silica surface, which arises from the SiO_2/Al_2O_3 ratio. Moreover, the number of surface hydroxyl groups induces an interaction with water molecules and inhibits the adsorption of organics. Hence the zeolite with a higher SiO_2/Al_2O_3 ratio and mesoporous silica with fluorine embedded in its framework can be used as useful supports for high adsorption of organics.[9,10] Silylation of the silica surface using conventional silica coupling agents has also been attempted in order to remove the hydroxyl groups on the surface. Modification of mesoporous silicas by silylation is very useful for designing multifunctionalized spaces and for a variety of reactions on them.[11–14] Although this method can substitute surface hydroxyl groups with organosilicon or silicon alkoxide groups through condensation polymerization, few methods are available for their usage under high temperature because the terminal hydrocarbon groups of reagents are easily oxidized above 700 K, and additional hydroxyl groups are formed.[15]

In the present study, therefore, the surface-modified hydrophobic zeolites were prepared using triethoxyfluorosilane (TEFS) as a fluorine-containing silylation reagent. TEFS was employed because it was expected to substitute surface hydroxyl groups with a robust O–Si–F bond and not to obstruct zeolite pores by unnecessary long carbon chains. Although it is well known that fluorinated materials exhibit chemical stability, it has been also reported that silica surfaces with fewer hydroxyl groups can lead to high crystallization of TiO_2 species due to the decrease in interaction with titanium ions introduced into zeolite pores.[10] Hence, this modification process would be a dual-purpose means of achieving both chemical stability and high crystal growth of TiO_2 particles (as well as hydrophobicity) into the porous silica structure. The adsorption properties and surface state of the prepared hydrophobic zeolites were investigated in detail. Moreover, these modified zeolites were applied as the supports of TiO_2 photocatalysts, and the practical photocatalytic degradation of organics under UV-light irradiation was performed to assess the advantages of modification.

The surface modification was performed by impregnating proton type Y-zeolite into triethoxyfluorosilane (TEFS) solution diluted in 2-propanol, followed by calcination at 773 K for 5 h. The prepared samples were denoted as FS*m*-Y(*n*), where *m* and *n* describe the ratio of TEFS reagent (10, 20 and 40 mol%) and SiO_2/Al_2O_3 ratio (5, 40 and 200), respectively. The incorporation of 10 wt% of TiO_2 particles into zeolite pores was carried out by an impregnation method. The modified Y-zeolite was stirred in ammonium titanyl oxalate ($(NH_4)_2[TiO(C_2O_4)_2]\cdot nH_2O$) solution at room temperature for 6 h, followed by drying *in vacuo* and calcination at 823 K for 5 h in air.

From the XRD patterns, although the intensities of low-angle XRD peaks slightly decreased after modification, the diffraction peaks assigned to the ordered zeolite structure were clearly observed, confirming that the ordered zeolite microstructures were still maintained even after the surface modification, and that they were thermally stable even at 773 K. N_2 adsorption–desorption analysis showed the typical type I isotherm, also indicating that the uniform zeolite micropores were unchanged. With an increase in the amount of TEFS reagent, a slight change from type I behavior of the unmodified zeolite into type II behavior with gradual inflection was observed in the relative pressure range from 0.5 to 1.0. The pore structural parameters derived from the N_2 adsorption–desorption isotherms are summarized in Table 1. It was confirmed that the large surface areas were almost maintained, although S_{BET} and pore volume slightly decreased due to the introduction of TEFS reagent on the zeolite surfaces. Considering the

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Table 1 Textual properties of surface modified zeolite materials

Sample	TEFS grafted (mol%)	SiO_2/Al_2O_3	$S_{BET}/m^2\ g^{-1}$	Relative percentage of $S_{BET}{}^a$ (%)	Pore volume^b/cm^3 g^{-1}	Water adsorption^c/μmol m^{-2}
HY(5)	0	5	606	100	0.25	13.8
FS1-Y(5)	10	5	563	93	0.21	13.7
FS4-Y(5)	40	5	482	80	0.17	12.1
HY(40)	0	40	672	100	0.24	9.1
FS1-Y(40)	10	40	584	87	0.17	5.5
FS4-Y(40)	40	40	472	70	0.14	5.2
HY(200)	0	200	727	100	0.28	6.6
FS1-Y(200)	10	200	696	96	0.25	3.3
FS4-Y(200)	40	200	551	76	0.17	2.8

[a] Relative percentage to BET surface area of unmodified Y-zeolites. [b] Determined from BJH adsorption. [c] Calculated by division of water adsorption capacity at $P/P_0 = 0.75$ by the value of S_{BET}.

behaviour of N_2 adsorption, it was estimated that new silicate layer was partially formed in zeolite micropores by the addition of excess TEFS reagent.[16] The decrease in S_{BET} and pore volume was proportional to the grafted amount.

Fig. S1† shows the F_{1s} XPS spectra of HY(200) and FS-Y(200). The distinguishing peak derived from F species was detected at around 689 eV in modified samples but not in the unmodified sample. Generally, the F_{1s} binding energy at around 685 eV corresponds to the adsorbed F^- ions on silica surface, while that at 689 eV is ascribed to the covalent F atoms.[17] From the FT-IR analysis, an overlap of two kinds of peaks centered at around 950 and 970 cm^{-1}, attributable to Si–F and Si–OH stretching vibrations, respectively,[18] were observed. A definite shift of this overlap peak toward the lower wavenumber was seen with increasing TEFS content, confirming that fluorine atoms are present as a Si–F covalent bond in all of the modified samples. These results prove that the TEFS reagent is grafted on the zeolite surface.

Fig. 1 shows the adsorption isotherms of H_2O molecules at room temperature. After the surface modification, the water adsorption capacity and that per unit surface area (shown in Table 1) dramatically decreased compared to the values of the original Y-zeolite, suggesting that the surface hydrophobization was successfully achieved. Additionally, the effects of modification were different depending on the SiO_2/Al_2O_3 ratio. In the case of FS-Y(5), the water adsorption capacity decreased proportionately to the amount of added TEFS reagent. In the case of Y-zeolites with higher SiO_2/Al_2O_3 ratio, the water adsorption capacity also decreased with the addition of TEFS, but at an insignificant rate. This tendency indicates that the amount of TEFS reagent is suitable and corresponds to the number of surface hydroxyl groups, and that excessive addition of TEFS over fully grafted silica surface is scarcely effective for hydrophobization.

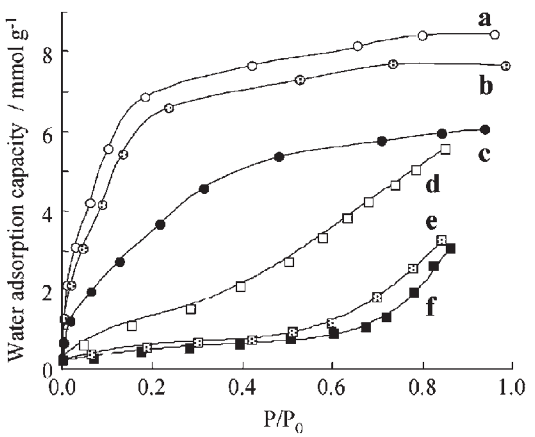

Fig. 1 The adsorption isotherms of H_2O at room temperature on (a) HY(5), (b) FS1-Y(5), (c) FS4-(5), (d) HY(200), (e) FS1-Y(200) and (f) FS4-Y(200).

Water contact angle measurements were conducted on these surface-modified zeolites, to evaluate their actual surface hydrophobicity. The contact angles were measured by dropping 3 μl water droplets on pellet-type modified zeolites which were compressed to the same thickness. As seen in Fig. 2, the contact angle became larger with highly modified zeolite samples, revealing that the prepared samples were more hydrophobic. In particular, FS4-Y(200), which showed extremely high contact angle of 132°, is thought to be fully silylated, with the new hydrophobic silica layer being formed by the TEFS reagent.

Fig. 3 shows the results of Ti K-edge XAFS analyses of tetraisopropyl orthotitanate (TPOT: $Ti(OC_3H_7)_4$) and anatase TiO_2 as reference samples, and TiO_2 loaded on FS-Y(5) samples. A sharp pre-edge peak at around 4970 eV observed in the XANES spectra is due to the presence of isolated titanium atoms surrounded by four tetrahedral oxygen atoms. The peak at around 2.5 Å in the FT-EXAFS spectra is due to neighboring titanium atoms, indicating the formation of nano-size titanium oxide.[10] A medium intensity pre-edge peak was observed with TiO_2/Y(5), suggesting that the restricted porous structure of Y-zeolite might inhibit formation of large crystals of titanium oxide, nano-size TiO_2 particles being formed instead. In contrast, TiO_2/FS4-Y(5) showed XANES and EXAFS spectra more similar to those for anatase-type TiO_2,

Fig. 2 Images of water droplets on pellet-type (a) HY(200), (b) FS1-Y(200) and (c) FS4-Y(200).

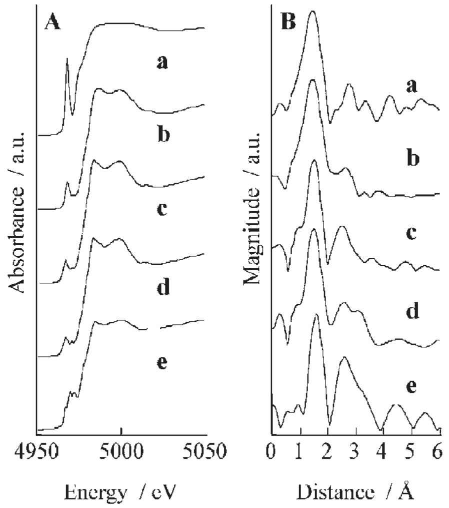

Fig. 3 (A) Ti K-edge XANES spectra and (B) FT-EXAFS spectra of (a) Ti(O*i*Pr)$_4$, (b) TiO_2/Y(5), (c) TiO_2/FS1-Y(5), (d) TiO_2/FS4-Y(5) and (e) TiO_2 (anatase).

suggesting that well-crystallized TiO_2 particles were obtained in hydrophobic pores. The TiO_2 particles in the TiO_2/Y systems are confirmed to be an anatase phase from the XRD patterns; however, the intensities of the diffraction peaks were low due to the smaller size of the particles. This can be attributed to the smaller interaction between the modified surface and the titanium species because of decrease in number of surface hydroxyl groups. Consequently, it is thought that the titanium species were aggregated, and that crystallization of TiO_2 was promoted in the modified zeolite pores.

The influence of the above modifications on the photocatalytic activity of the photocatalyst was evaluated by the degradation of aqueous 2-propanol (2.6×10^{-3} mol L^{-1}) under UV-light at room temperature. The photocatalyst and the aqueous 2-propanol were first stirred in a flow of O_2 for 1 h in the dark. When irradiated with UV-light, the TiO_2 photocatalyst eventually decomposed 2-propanol completely into CO_2 and H_2O, *via* acetone as an intermediate. Fig. 4 shows the comparison of photocatalytic activities for the degradation of 2-propanol diluted in water per unit quantity of TiO_2 photocatalyst. TiO_2 photocatalysts loaded on zeolites with a higher SiO_2/Al_2O_3 ratio exhibited higher photocatalytic activity. The TiO_2 loaded on the modified zeolites exhibited much higher photocatalytic activity than those on the unmodified zeolites. These results indicate that the modified zeolites are more appropriate supports for the TiO_2 photocatalyst, and can enhance the photocatalytic degradation of organics diluted in water due to their ability to selectively adsorb organic molecules onto the zeolite surface in aqueous solution. Additionally, TiO_2 photocatalysts loaded on FS-Y(200) were photocatalytically more effective than pure TiO_2 powder (P-25).

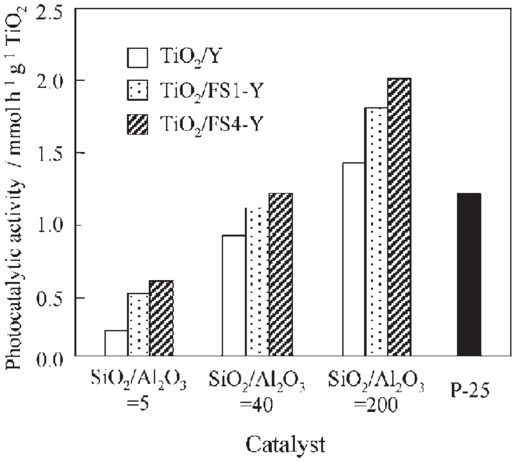

Fig. 4 Photocatalytic activity for degradation of 2-propanol diluted in water on 10 wt% TiO_2 photocatalyst loaded on the original Y-zeolites, surface modified Y-zeolites and TiO_2 powder (P-25).

In summary, the hydrophobic surface modification of zeolite was successfully achieved by modification with TEFS, while retaining the thermal stability of the microporous structure and the large surface area. The advantages of this modification technique are the simplicity of the modification process and its applicability to any materials whose surface consists of a silica base. This modification technique should prove to be a promising approach to improve the surface hydrophobic properties of porous silica materials, and should assist not only photocatalytic reactions but also other catalytic reactions.

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Notes and references

1 H. Yamashita and K. Mori, *Chem. Lett.*, 2007, **36**, 348.
2 H. Yamashita and M. Anpo, *Curr. Opin. Solid State Mater. Sci.*, 2003, **7**, 471.
3 H. Yamashita, K. Yoshizawa, M. Ariyuki, S. Higashimoto, M. Che and M. Anpo, *Chem. Commun.*, 2001, 435.
4 G. Palmisano, V. Augugliaro, M. Pagliaro and L. Palmisano, *Chem. Commun.*, 2007, 3425.
5 S. Horikoshi, N. Watanabe, M. Mukae, H. Hidaka and N. Serpone, *New J. Chem.*, 2001, **25**, 999.
6 N. Takeda, M. Ohtani, T. Torimoto, S. Kuwabata and H. Yoneyama, *J. Phys. Chem. B*, 1997, **101**, 2644.
7 X. Liu, K. K. Iu and J. K. Thomas, *Chem. Phys. Lett.*, 1992, **195**, 2.
8 H. Chen, A. Matsumoto, N. Nishimiya and K. Tsutsumi, *Colloids Surf., A*, 1999, **157**, 296.
9 K. Ikeue, H. Yamashita and M. Anpo, *J. Phys. Chem. B*, 2001, **105**, 8350.
10 H. Yamashita, K. Maekawa, H. Nakao and M. Anpo, *Appl. Surf. Sci.*, 2004, **237**, 393.
11 P. K. Jal, S. Patel and B. K. Mishra, *Talanta*, 2004, **62**, 1005.
12 K. Lin, L. Wang, F. Meng, Z. Sun, Q. Yang, Y. Cui, D. Jiang and F. S. Xiao, *J. Catal.*, 2005, **235**, 423.
13 H. Zhang, Y. Kim and P. K. Dutta, *Microporous Mesoporous Mater.*, 2006, **88**, 312.
14 T. Kasahara, K. Inumaru and S. Yamanaka, *Microporous Mesoporous Mater.*, 2004, **76**, 123.
15 M. V. Cagnoli, S. G. Casuscelli, A. M. Alvarez, J. F. Bengoa, N. G. Gallegos, M. E. Crivello, E. R. Herrero and S. G. Marchetti, *Catal. Today*, 2005, **107**, 402.
16 T. Kimura, M. Suzuki, M. Maeda and S. Tomura, *Microporous Mesoporous Mater.*, 2006, **95**, 213.
17 Y. Q. Wang and P. M. A. Sherwood, *Chem. Mater.*, 2004, **16**, 5427.
18 R. A. Orozco-Teran, B. P. Gorman, D. W. Mueller, M. R. Baklanov and R. F. Reidy, *Thin Solid Films*, 2005, **471**, 145.