Hydrophobic Modification of Ti-Containing Zeolite (TS-1) and Their Applications in Liquid-Phase Selective Catalytic Reactions

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Received October 6, 2009
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Hydrophobic modification of Ti-containing zeolite (TS-1) was performed by using triethoxyfluorosilane (TEFS). TS-1 after modification with TEFS ($w = 1\%$) showed higher catalytic activity for the ammoximation of cyclohexanone than those on unmodified and modified TS-1 with TEFS ($w = 5\%$) due to effective modification without covering the underlying catalytically active Ti-oxide species.

For many years, tetrahedrally coordinated transition-metal oxides (e.g., Ti-, Cr-, and Mo-oxide) containing porous materials such as zeolites and mesoporous silicas have attracted considerable attention because of their unique catalytic and photocatalytic activities.[1–19] Especially, tetrahedral Ti-oxide species exhibited excellent catalytic properties in selective oxidation processes, i.e., phenol to catechol and hydroquinone as well as olefins to epoxides, using alkyl hydroperoxide and hydrogen peroxide (H_2O_2).[3,4,10–19] Ammoximation also proceeded over tetrahedral Ti-oxide species with ammonia and H_2O_2. Cyclohexanone was efficiently transformed to cyclohexanone oxime as a precursor of ε-caprolactam, which was important for production of nylon-6.[18,19] These systems were also environmentally friendly and promising in reducing undesired by-products.

On the other hand, it is well known that both reaction rates and adsorption properties of reactants strongly depend on the surface hydrophilic–hydrophobic properties of catalysts and catalyst supports.[9,20] The large number of surface hydroxy groups showed affinity for water molecules, restricting the adsorption of reactants from air and aqueous solutions. Thus, in order to improve the adsorption properties of them, hydrophobically modified zeolites and mesoporous silicas were prepared in fluoride media using HF as well as fluorine containing structure-directing agent.[9,11] Surface hydrophobic modification has also been attempted using silylation reagent.[21–24] In our previous work, the enhancement of photocatalytic activities for decomposition of organic pollutants was successfully attained by simple modification using triethoxyfluorosilane (TEFS) as silylation reagent, which have a stable ≡Si–F bond and reduce the affinity of water molecules.[23,24]

In the present work, aiming at the development of more efficient catalytic reaction systems using Ti-containing porous materials, hydrophobically modified Ti-containing zeolite (TS-1) was prepared by using TEFS (Scheme 1). The effect of surface modification on their catalytic activities for the liquid-phase ammoximation of cyclohexanone was also investigated.

Results and Discussion

TS-1 showed typical X-ray diffraction peaks attributed to the MFI structure (Figure 1a).[25] The diffraction peaks assigned to the MFI structure were clearly observed and their intensities were scarcely changed even after surface modification by TEFS (Figures 1b and 1c).

The local structure of Ti-oxide species incorporated within the zeolite frameworks was also investigated by UV–vis and photoluminescence measurements. As shown in Figure 2A, the appearance of a distinct peak at around 220 nm can be assigned to the ligand to metal charge transfer (LMCT) transition of tetrahedrally coordinated Ti^{IV}-oxide.[26,27] Moreover, it was found that almost the same absorption spectra were observed before and after grafting of TEFS, suggesting that the local structure of Ti-oxide species were hardly affected by this surface modification treatment (data not shown).

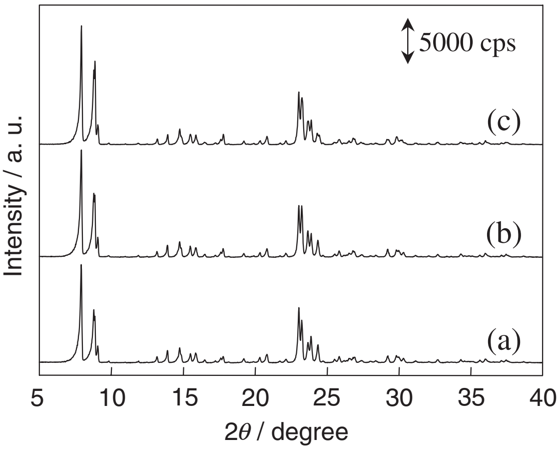
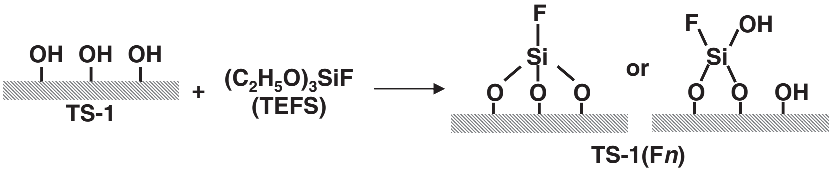


Figure 1. XRD patterns of (a) TS-1, (b) TS-1(F1), and (c) TS-1(F5).



Scheme 1. Reaction scheme for surface modification by TEFS.

Published on the web April 29, 2010; doi:10.1246/bcsj.20090265

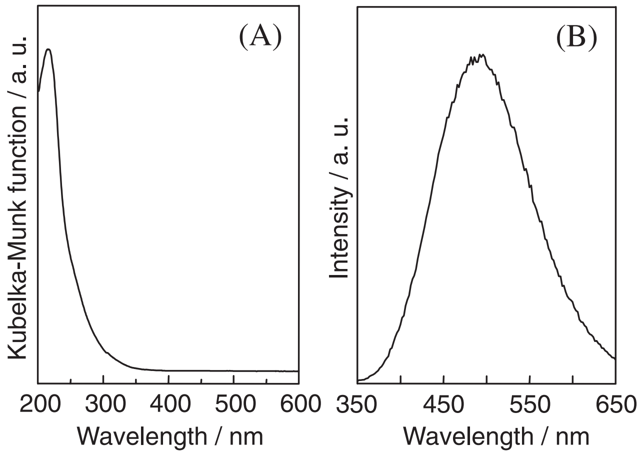


Figure 2. UV–vis (A) and photoluminescence spectrum (B) of TS-1(F1) measured at 298 K.

Table 1. Characteristics of TS-1 and Hydrophobically Modified TS-1

Sample	TEFS content$^{a)}$ /$w \times 10^2$	S_{BET} /m^2 g^{-1}	Relative percentage of $S_{\mathrm{BET}}$$^{b)}$/%	Water adsorption capacity$^{c)}$ /μmol m^{-2}
TS-1	0	434	100	3.65
TS-1(F1)	1.0	415	96	3.34
TS-1(F5)	5.0	362	83	1.00

a) TEFS content in 2-propanol. b) Relative percentages to BET surface area of unmodified TS-1. c) Calculated by division of water adsorption capacity at $P/P_0 = 0.5$ by the value of S_{BET}.

Figure 2B shows the photoluminescence spectrum of TS-1(F1), which was observed in the wavelength region from 400 to 600 nm upon excitation of its LMCT band at around 220 nm at 298 K. The peak position and intensity of photoluminescence was almost the same compared with original TS-1.

$$(\mathrm{Ti}^{4+}\text{–}\mathrm{O}^{2-}) \underset{h\nu'}{\overset{h\nu}{\rightleftarrows}} (\mathrm{Ti}^{3+}\text{–}\mathrm{O}^{-})^{*} \qquad (1)$$

This photoluminescence can be attributed to the radiative decay process from charge transfer excited triplet state of tetrahedrally coordinated Ti$^{\mathrm{IV}}$-oxide to its ground state (eq 1).[9,26,27]

These results clearly indicated the presence of tetrahedrally coordinated Ti$^{\mathrm{IV}}$-oxide as the dominant species within TS-1(F1).

The information about the nitrogen adsorption–desorption behavior on modified and unmodified TS-1 is summarized in Table 1. The typical type I isotherms were observed in each sample. The BET surface area (S_{BET}) of samples were slightly decreased with an increase in the grafted amount of TEFS, however TS-1(F1) and TS-1(F5) maintained large surface areas compared with original TS-1.

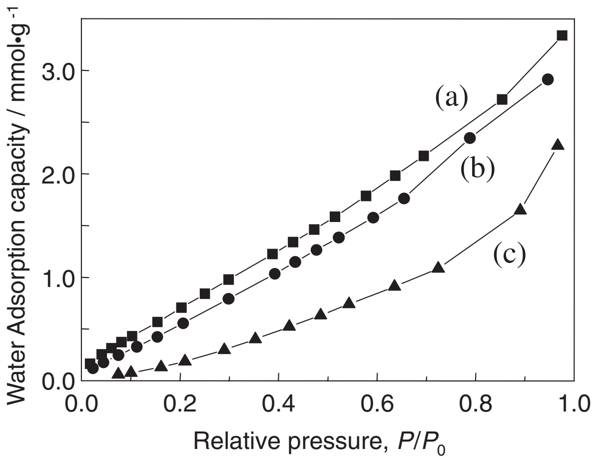


Figure 3. Water adsorption isotherms of (a) TS-1, (b) TS-1(F1), and (c) TS-1(F5) measured at 298 K.

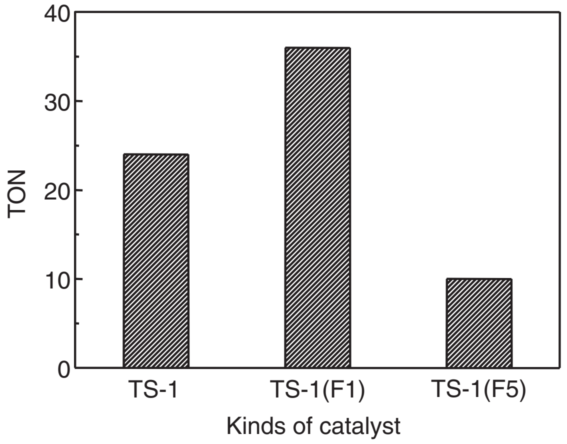


Figure 4. The turnover number (TON) for ammoximation of cyclohexanone to cyclohexanone oxime on each catalyst at 353 K. Reaction time: 1 h.

The effect of the grafting of TEFS on the surface hydrophilic–hydrophobic properties of TS-1 was investigated by water adsorption measurement. As shown in Figure 3 and Table 1, water adsorption capacity of TS-1 was gradually decreased with an increase in the grafted amount of TEFS. The differences in the amount of adsorbed water can be ascribable to the different concentrations of surface hydroxy groups in each sample. The presence of fluorine moieties on the surface of TS-1(F*n*) might also play significant roles for reducing the adsorbed amounts of water since the fluorine moieties tend to prevent the adsorption of water on the surface of TS-1.

XPS investigations also revealed the presence of fluorine moieties on the surface of TS-1(F*n*). F$_{1s}$ XPS peak was observed at around 689 eV, while no peak was detected in the case of original TS-1. This F$_{1s}$ XPS peak was assigned to the covalent F atoms,[28] which was different from the F^{-} ions on silica surface detected at around 685 eV,[28] suggesting the formation of fluorine moieties through the reaction as shown in Scheme 1.

It could be seen that the surface hydrophobic modification of TS-1 leading to the decrease in the adsorbed amount of water was successfully attained through the removal of surface hydroxy groups and anchoring of fluorine moieties by grafting of TEFS. The liquid-phase ammoximation of cyclohexanone was performed as the test reaction for investigating the effects of the surface hydrophobic modification of TS-1 on their catalytic activities. Figure 4 shows the turnover number (TON) defined as the ratio of produced cyclohexanone oxime to the amount of Ti-oxide species included in the catalyst. The selectivity of cyclohexanone oxime was as high as 99%. The enhancement of catalytic activity was observed for TS-1(F1), which showed less hydrophilicity compared to unmodified TS-1. Meanwhile, the catalytic activity of TS-1(F5) was lower than that on unmodified TS-1, although the hydrophobicity of TS-1(F5) was the highest among prepared catalysts. These results suggested that the catalytically active Ti-oxide species within the zeolite framework was gradually covered by fluorine moieties with increase in the amount of TEFS grafting, which play a crucial role for enhancement of surface hydrophobicity and may lead to inhibiting the adsorption of reactants on Ti-oxide species. Therefore, the surface modification with small amounts of TEFS was effective for enhancement of catalytic activities. Moreover, it was found that the recovered catalysts could be recycled without significant loss of their original catalytic activities.

In conclusions, hydrophobic Ti-containing zeolites (TS-1(F*n*)), which exhibited less water adsorption capacity, were successfully prepared by a simple surface modification of TS-1 by using TEFS. The MFI structures, large surface areas as well as the local structure of Ti-oxide species were scarcely changed after surface treatment. The grafting of a suitable amount of TEFS onto TS-1 effectively enhanced the liquid-phase ammoximation of cyclohexanone, showing the possibilities for application of this simple modification technique in other reaction systems.

Experimental

Preparation of TS-1. Ti-containing zeolite (TS-1, Si/Ti = 58) was synthesized by direct hydrothermal synthesis using tetraethyl orthosilicate, titanium isopropoxide, and Tetrapropylammonium hydroxide as template.[17] The mixture was transferred to a Teflon vessel autoclave and heated at 448 K for 24 h. After cooling to room temperature, the product was separated by centrifugation, washed several times with ion exchanged water, dried at 373 K for 12 h, and then calcined at 773 K for 5 h in air.

Hydrophobic Modification. The surface modification of TS-1 was performed by grafting TEFS onto TS-1 and is thought to proceed as shown in Scheme 1.[23,24] The mixture of TS-1 and 2-propanol solution of TEFS was stirred at 298 K for 5 h. Next, the sample was filtrated under vacuum, dried at 383 K for 12 h, and then calcined at 773 K for 5 h in air. TS-1 after grafting with TEFS were denoted as TS-1(F*n*), where *n* described the TEFS contents in 2-propanol ($w = 1, 5\%$).

Measurements. Prepared samples were characterized by XRD, UV–vis, and photoluminescence as well as nitrogen and water adsorption–desorption measurements. XRD measurements were performed using a Rigaku RINT 2500 diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). UV–vis and photoluminescence spectrum were measured at 298 K with a Shimadzu UV-2450A double-beam digital spectrophotometer and a Spex Fluorog-3 spectrophotometer, respectively. Prior to the spectroscopic measurements, the samples were calcined in O_2 (>2.66 kPa) at 723 K for 1 h and then degassed at 473 K for 1 h.

Catalytic Reaction. The ammoximation of cyclohexanone was used as the test reaction. Catalyst (50 mg), cyclohexanone (2 mmol), H_2O (5 mL), 30% H_2O_2 (0.5 mL), 25% aqueous solution of NH_3 (0.5 mL) and *tert*-butanol (5 mL) were charged into the reaction vessel and then heated at 353 K with stirring. The analysis of reaction product was performed on a gas chromatograph (Shimadzu GC-14B with FID detector) equipped with TC-1 capillary column.

The present work is supported by the Grant-in-Aid for Scientific Research (KAKENHI) from Ministry of Education, Culture, Sports, Science and Technology (No. 20360363 and No. 2156207).

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