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ScienceDirect

Journal of Catalysis 244 (2006) 192–198

JOURNAL OF CATALYSIS

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Improvement in thermal stability and catalytic activity of titanium species in mesoporous titanosilicates by addition of ammonium salts

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Received 3 August 2006; revised 8 September 2006; accepted 8 September 2006

Abstract

Mesoporous titanosilicates (MTS-9A) with thermally stable titanium species were synthesized by adding ammonium salts in the preparation procedure. Characterization results show that hexagonal mesoporous titanosilicates (MTS-9A) contain primary and secondary structural building units of zeolite in the framework, in a similar manner to MTS-9. The promoted condensation of Ti-containing silica network in MTS-9A leads to higher thermal stability of four-coordinated titanium species compared with MTS-9, as evidenced by UV–vis and ^{29}Si NMR spectra. Catalytic tests indicate that MTS-9A samples show high activity in hydroxylation of both small (phenol) and bulky reactants (2,3,6-trimethylphenol) before and after calcination. Moreover, the recycled catalyst retains high conversion, confirming the high thermal stability of titanium species.

Keywords: Mesoporous titanosilicates; Four-coordinated titanium; Thermal stability; Hydrothermal stability; Ammonium salts

1. Introduction

Since the discovery of microporous crystal of TS-1 by Enichem Company [1], a series of microporous titanosilicates has been prepared in expectation of excellent catalytic activity in oxidation reactions for fine chemical production [2–8]. However, one disadvantage of these titanosilicate catalysts is that their pore sizes (generally <0.7 nm) are too small to allow access of bulky reactants to the active sites in the micropores, and such bulky reactants dominate most of the chemical transformations of importance in the fine chemical and pharmaceutical industries. Therefore, titanosilicates with relatively large pore size have always been sought. Mesoporous silica materials developed by Mobil scientists opened up a new route for preparing ordered mesoporous materials with large pore sizes of 2–20 nm [9–13].

Much attention has been paid to mesoporous titanosilicates in the last decade because of their potential use as catalysts for bulky substrates in the chemical industry. Some successful examples, including Ti-MCM-41 [14–16], Ti-HMS [17], Ti-MCM-48 [18], and Ti-SBA-15 [19,20], have shown remarkable catalytic activities in various reactions. However, for small substrates, the catalytic activities of these mesoporous titanosilicates are still low compared with those of microporous zeolite of TS-1 [1,16], which can be attributed to the amorphous nature of the mesoporous wall. Therefore, novel mesoporous titanosilicates with TS-1-like titanium species and high catalytic oxidation ability are still desirable.

Ordered mesoporous titanosilicate (MTS-9) prepared by the assembly of preformed titanosilicate precursors with triblock copolymers (P123) have been reported to show remarkable catalytic activity in a series of oxidations [21–23]. However, the thermal stability of titanium in MTS-9 is relatively low, and calcination results in the transformation of the coordination environment of titanium species, leading to decreased catalytic activity in oxidation [23]. The relatively low thermal stability of titanium has been attributed to the imperfectly condensed mesoporous walls formed at relatively low temperature (100 °C). Thus, Yang et al. prepared Ti-JLU-20 by assembling preformed titanosilicate precursors with a mixture of fluorinated surfactant (FC-4) and triblock copolymer (P123) at high temperature

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doi:10.1016/j.jcat.2006.09.007

(180 °C) [24]. Ti-JLU-20 has high thermal stability and active four-coordinated titanium species for oxidation, which is assigned to the well-condensed mesoporous walls; however, its surface area is small ($<400\ m^2/g$), much lower than that of most mesoporous materials. As a result, Ti-JLU-20 is catalytically less active than either TS-1 or as-synthesized MTS-9 samples. Consequently, mesoporous titanosilicates with relatively large surface area and high thermal stability are always sought.

Recently, the effect of ammonium salts on the synthesis and catalytic properties of TS-1 has been investigated in our laboratory [25]. Some ammonium salts can be used as crystallization-mediating agents to promote the condensation of framework as well as the catalytic activities of samples [25]. Here we show that thermal stability and catalytic activities of titanium species in MTS-9 are greatly improved by the addition of ammonium salts in the gel preparation procedure.

2. Experimental

2.1. Materials

The TCI products were titanium tetrabutoxide (TBOT), tetraethyl orthosilicate (TEOS), ethanol, acetonitrile, tetrapropylammonium hydroxide (TPAOH), hydrochloric acid, ammonium chloride, phenol, catechol, hydroquinone, benzoquinone, 2,3,6-trimethylphenol, trimethylhydroquinone, trimethylbenzoquinone, and H_2O_2 (30%). $EO_{20}PO_{70}EO_{20}$ (Pluronic P123) was purchased from Aldrich.

2.2. Synthesis

Mesoporous titanosilicates were synthesized from assembly of surfactant with preformed titanosilicate precursors [21–23] in strongly acidic media. As a typical example, MTS-9A was synthesized as follows:

1. The zeolite precursor solution with zeolite TS-1 primary structure units were prepared by mixing 6 mL of TPAOH aqueous solution (25%) with 12 mL of H_2O, followed by adding 0.3 mL of $Ti(OC_4H_9)_4$ and 5.6 mL of TEOS under stirring ($TiO_2/SiO_2/TPAOH/H_2O$ molar ratios of 1.0/30/8/1500). The mixture was then aged at 100 °C for 4 h. The final product was also a clear solution.
2. A 0.8-g sample of $EO_{20}PO_{70}EO_{20}$ was dissolved in 20 mL of H_2O containing the required amount of NH_4Cl mixed with 3 mL of HCl (10 M/L), followed by adding 9.0 mL of precursor solution (containing 8 mmol of SiO_2) obtained in step 1. The mixture was stirred at 40 °C for 20 h, then transferred into an autoclave for additional reaction at 100 °C for 24 h.
3. The products were collected by filtration, washed, and dried in air. Such products are defined as as-synthesized samples.
4. As-synthesized samples were treated in ethanol/HCl solution at 333 K overnight, to remove the templates.

By this procedure, the surfactant of P123 in the mesopores was removed completely, but a small amount of TPA^+ remained in the mesopores of extracted samples. The as-synthesized samples were calcined at 500 °C for 4 h to remove the residual TPA^+; the calcined samples had no organic templates. The products were designated as MTS-9A-x, where A represents ammonium chloride (NH_4Cl) and x is the amount of NH_4Cl added.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded by a MAC Science M3X 1030 X-ray diffractometer with Cu$K\alpha$ radiation (40 kV, 20 mA). The isotherms of nitrogen were measured at the temperature of liquid nitrogen using a Belsorp 28SA system. The samples were outgassed for 10 h at 250 °C before the measurements. The pore size distribution was calculated using the Barrett–Joyner–Halenda (BJH) model. The diffuse reflectance UV/vis spectra (DRS) were measured on a Jasco V-550 UV/vis spectrophotometer. Infrared (IR) spectra were acquired on a PE-1600 FTIR spectrometer. Scanning electron microscopy (SEM) experiments were performed on a Hitachi S-5200 electron microscope. ^{29}Si MAS NMR measurements were performed on a JEOL LA400WB 400-MHz nuclear magnetic resonance spectrometer at ambient temperature. The chemical shift was referenced to an external standard of polydimethylsilane. The spin rate of the rotor was 5.0 kHz. A pulse length of 7 ms was applied, and approximately 3000 scans were accumulated with a repetition time of 30 s. The spectra were deconvoluted with a Gaussian–Lorentzian mixed equation. The chemical composition of the samples was determined with an inductively coupled plasma–atomic emission spectrometer (Shimadzu ICPS-8000E).

2.4. Catalytic tests

Phenol hydroxylation experiments were run in a 50-mL glass reactor. In a standard run, 13.6 mmol of phenol, 50 mg of catalyst, and 10 mL of water were mixed, followed by addition of 4.53 mmol of H_2O_2 (30% aqueous). After reaction for 4 h at 353 K with magnetic stirring, the products were taken out from the system and analyzed by a Shimadazu GC-14B gas chromatograph, equipped with a 50-m OV-1 capillary column and a flame ionization detector. The amount of the unconverted H_2O_2 was determined by titrating with 0.1 m of $Ce(SO_4)_2$ aqueous solution.

The hydroxylation of 2,3,6-trimethylphenol was performed in a 50-mL glass reactor and stirred with a magnetic stirrer. In a standard run, 7.3 mmol of 2,3,6-trimethylphenol, 2.5 mL of acetonitrile as solvent, and 50 mg of catalyst were mixed in the reactor and heated to a given temperature. Then 2.78 mmol of H_2O_2 (30% aqueous) was added into the reactor. After the reaction for 2 h at 353 K with magnetic stirring, the products were removed from the system and analyzed as described above.

In catalyst recycling, the used catalysts were calcined at 550 °C for 6 h to remove the residual tar after being collected from the reaction solution before being reused in the next run.