Available online at www.sciencedirect.com

ScienceDirect

Microporous and Mesoporous Materials 104 (2007) 269–280

MICROPOROUS AND MESOPOROUS MATERIALS

www.elsevier.com/locate/micromeso

Catalytical studies on trimethylsilylated Ti-MCM-41 and Ti-MCM-48 materials

Naoko Igarashi [a], Kazuhito Hashimoto [a], Takashi Tatsumi [b,*]

[a] *Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan*
[b] *Division of Catalytic Chemistry, Chemical Resources Laboratory, Tokyo Institute of Technology, 4259-R1-9 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

Received 5 November 2006; received in revised form 19 February 2007; accepted 19 February 2007

Abstract

Titanium-incorporated MCM-41 and MCM-48 materials (Ti-MCM-41 and Ti-MCM-48, respectively) have been trimethylsilylated by employing various silylating agents (i.e., hexamethyldisilazane (HMDZ) and trimethylchlorosilane (TMCS) in toluene, and a mixture of TMCS and hexametyldisiloxane (HMDS)). Their catalytic activities in various oxidation reactions as well as their physical properties are compared. The highly reactive HMDZ has achieved the maximum degree of silylation to introduce 2.35 and 2.06 trimethylsilyl groups per 1 nm^2 on the surface of Ti-MCM-41 and -48, respectively. IR spectra have confirmed that HMDZ can react with hydrogen-bonded silanol groups as well as isolated silanol groups, generating a new band at 3700 cm^{-1}, while TMCS does not. These silylated materials show remarkably high catalytic activity in the oxidation of substrates with various molecular sizes (from C_6 to C_{12}) with H_2O_2 and *tert*-butyl hydroperoxide (TBHP) compared to non-silylated samples. Introducing a small amount of H_2O so as to double the H_2O content in a reaction system for the oxidation of cyclododecene using TBHP has approximately doubled the catalytic activity. Such unexpected results were only observed with highly hydrophobic samples, Furthermore, by conducting the reaction at 343 K for 6 h over highly silylated Ti-MCM-48, high conversion of 98% has been attained.

Keywords: Ti-MCM-41; Ti-MCM-48; Hydrophobicity; Trimethylsilylation; Epoxidation catalyst

1. Introduction

The discovery of titanium-incorporated molecular sieves has greatly extended the field of catalytic science and technology [1]. In particular, microporous titanosilicates such as TS-1, Ti-beta and Ti-MWW with the MFI, BEA and MWW structures, respectively, have shown high catalytic activity in the selective oxidation of various organic substrates with H_2O_2 [2–6]. However, their applications are rather limited to the reactants with the molecular sizes smaller than 7 Å due to their small micropore openings. On the other hand, the emergence of the M41S family [7,8] and a wide variety of mesoporous materials synthesized by the surfactant-templating method, having mesopores with uniform sizes ranging from 15 to 100 Å, has mitigated the size limitation of microporous materials. Titanium-substituted mesoporous molecular sieves have actually demonstrated the ability to catalyze the oxidation of bulky reactant molecules which cannot enter into the micropores of titanium-incorporated zeolites [9–11]. However, they show much lower catalytic activity than TS-1 or Ti-beta in the oxidation of small reactant molecules with H_2O_2.

In the preliminary communication we have reported that the activity of titanium-containing mesoporous molecular sieves in the oxidation of alkenes with H_2O_2 is remarkably enhanced by trimethylsilylation of silanol groups [12]. We assumed that the low activity of titanium-containing

---

[*] Corresponding author. Tel.: +81 45 339 3943; fax: +81 45 339 3941.
E-mail address: ttatsumi@cat.res.titech.ac.jp (T. Tatsumi).

doi:10.1016/j.micromeso.2007.02.041

mesoporous molecular sieves is caused by the poisoning of catalytically active Ti sites by H_2O molecules adsorbed on the surface with relatively high hydrophilicity derived from a large number of silanol groups [10]. This hypothesis has been verified by the remarkable enhancement of the activity in the liquid phase oxidation regardless of the method for introducing organic groups into the titanium-incorporated mesoporous catalysts; we have also reported that the oxidation activity has been successfully improved by direct one-step synthesis of organically modified mesoporous titanium-substituted MCM-41 [13–15].

Catalytic activities can be improved by taking a different approach to the control of the surface hydrophobicity. It has been recently reported that the titanium-impregnated NaY having an amphiphilic external surface obtained by partly loading alkylsilane is an active phase-boundary heterogeneous epoxidation catalyst [16,17]. In this case, the surface hydrophobicity benefits the catalytic activity in a macroscopic point of view by allowing the catalyst particles to lay at the liquid–liquid phase boundary where catalyst is accessible to both upper organic and lower aqueous phases.

For the trimethylsilylation of silanol groups, various reagents have been used such as hexamethyldisilazane (HMDZ), trimethylchlorosilane (TMCS), *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA), trimethylsilylimidazole, and hexamethyldisiloxane (HMDS) with/without a solvent [8,18–34], and it has been claimed that the degree of trimethylsilylation is affected by various factors such as the dose and reactivity of silylating agent and reaction temperature. Hertl and Hair estimated the activation energies in the silylation with TMCS and HMDZ at 22.0 and 18.5 kcal/mol, respectively [19,20], showing the higher reactivity of HMDZ. Actually, TMCS generally requires higher temperature in silylation than HMDZ. It is also reported that the conditions for the pre-treatment of silica surface are important, where the dehydration occurs to change the environment of silanol groups to be modified by silylating reagents [23]. A number of researchers suggested that TMCS and HMDS can react with hydrogen-bonded vicinal silanol groups [18,24,25], and that geminal silanol groups (${=}Si(OH)_2$) are more reactive with silylating agents than single ones ($\equiv Si(OH)$) [22,30,31].

Thus, a lot of researches have been pursued into the trimethylsilylation of silica materials. However, as far as we know, systematic studies on the trimethylsilylation of titanium-containing mesoporous molecular sieves and its effect on their catalytic performance have not yet been reported.

In this study, Ti-MCM-41 and Ti-MCM-48 samples are silylated under various silylating conditions, and the effective trimethylsilylating method for obtaining a highly active catalyst is investigated. Thus silylated materials are employed as catalysts in the oxidation of cyclic alkenes and unsaturated alcohols, whose molecular sizes are larger than micropore sizes of titanium-incorporated zeolites, using an aqueous solution of H_2O_2 or TBHP as an oxidant.

2. Experimental

2.1. Materials

Ti-MCM-41 was synthesized as follows. An aqueous solution of NaOH and hexadecyltrimethylammonium bromide (C_{16}TMABr) was added to TEOS under vigorous stirring, and immediately tetrabutyl orthotitanate (TBOT) was added dropwise. The resulting mixture was stirred for 1 day at room temperature, followed by the hydrothermal treatment at 373 K for 6 days. The molar composition was TEOS:0.12C_{16}TMABr:0.3NaOH:100H_2O:0.02TBOT. Tetramethylammonium hydroxide (TMAOH) was used instead of NaOH as a base in the synthesis of Ti-MCM-41(TMA) for control. Ti-MCM-48 was synthesized in a similar manner from the mother gel with the molar composition of TEOS:0.67C_{16}TMABr:0.64NaOH:103H_2O:0.02TBOT.

The organic templates were removed by the acid treatment using 1 M HCl solution in ethanol at 353 K for 16 h, followed by the calcination at 813 K for 5 h at a heating rate of 1 K/min. In this treatment, Na cations were completely removed by ion-exchange, as verified by inductively coupled plasma (ICP) analyses.

2.1.1. Post-synthesis trimethylsilylation

In the post-synthesis trimethylsilylation, TMCS, HMDZ, or HMDS were used as silylating agents. A typical surface modification was conducted as follows. 1.0 g of template-free Ti-MCM-41 was evacuated at 473 K for a given time and then subsequently dispersed in the mixture of TMCS and HMDS (total silylating reagent/Ti-MCM-41 = 0.55 mol/g) at refluxing under N_2 atmosphere for 16 h. After filtration of the reaction mixture, the dry powder obtained was thoroughly washed with dry acetone, and dried at 393 K.

2.1.2. Analytical procedure

Powder X-ray diffraction (XRD) patterns were collected on a Mac Science M3X HF-22E instrument equipped with a CuK_α X-ray source. ICP analyses were performed on a Shimadzu ICPS-8000E spectrometer. The nitrogen and water adsorption/desorption isotherm measurements were carried out using Belsorp 28SA and 18 apparatus, respectively. Solid-state ^{29}Si MAS NMR spectra were recorded on a JEOL JNM-ECA400 spectrometer at a frequency of 79.27 MHz for ^{29}Si. Chemical shifts were referenced to external tetramethylsilane. A sample spinning rate of 5 kHz, recycle delay time of 15 s, pulse width of 7.0 μs, and 5000–10,000 scans were taken. Ultraviolet–visible (UV–VIS) spectroscopy was performed on a Hitachi 340 spectrometer with a diffuse reflectance mode. The *in situ* silylated and non-silylated Ti-MCM-41 samples were prepared as self-supporting pellets and placed inside a cell which allows IR spectrum to be measured after outgassed at various temperatures. The spectra were recorded on a Perkin–Elmer 1600 spectrometer.