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Characterization of acidic property of sulfo-group functionalized microporous and mesoporous silica by adsorption microcalorimetry

Fei-Yee Yeoh [a], Akihiko Matsumoto [a,*], Yoshiyuki Iwase [b], Toshihide Baba [b]

[a] Department of Materials Science, Toyohashi University of Technology, 441-8122 Toyohashi, Japan
[b] Department of Environmental Chemistry and Engineering, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 226-8503 Yokohama, Japan

Abstract

Sulfo-group functionalized microporous and mesoporous silica based-on a MCM-41 framework which showed solid acid property were synthesized and characterized by adsorption microcalorimetry. Both the sulfo-functionalized microporous and mesoporous silica (Micro-SO_3H and Meso-SO_3H) were prepared by the oxidation of thiol group (–SH) included mesoporous silica which was obtained through the hydrolysis and co-condensation of tetramethoxysilane (TMOS) and mercaptopropyl trimethoxysilane (MPTMS). The samples have an ordered two-dimensional hexagonal pore array similar to that of MCM-41 as depicted from the XRD patterns. Nitrogen adsorption also shows that both microporous and mesoporous silica have pore characteristics similar to MCM-41, i.e. high surface area and high pore volume. However, pore regularity, surface area and pore volume decreased as the MPTMS loading increased. Solid-state ^{29}Si NMR indicated that the sulfo groups were successfully incorporated into both microporous and mesoporous silica frameworks. This sulfo-functionalized porous silica have high NH_3 uptakes and high differential heats of NH_3 adsorption, suggesting the presence of strong acidic sulfo groups on the silica surface. Acid catalyses of the samples were characterized by the isomerization reaction of but-1-ene to *cis*, *trans*-but-2-ene.

Keywords: Acid site; Adsorption microcalorimetry; Ammonia adsorption; Microporous silica; Mesoporous silica; Solid acids; Sulfo group

1. Introduction

Solid acids are important in many catalytic reactions [1–3]. Porous materials with high surface areas are good catalysts. However, many porous materials such as porous silica and porous carbon do not have strong acidic properties in nature. Thus, incorporation of acidic functional groups onto the surface of porous materials is a great challenge to obtain good solid acids [2,4–8]. MCM-41 is a well-known mesoporous silica with regular two-dimensional hexagonal structure [9–12]. The surface of MCM-41 has been chemically modified by various functional groups for different applications [13,14]. Research to incorporate metal and other functional groups to create Lewis and Brønsted acid sites in silica framework of MCM-41 have been reported [15–17]. Literature also show that the incorporation of strong acidic sulfo groups on ordered mesoporous silica such as MCM-41, SBA-15 and FSM-16 can efficiently catalyze various chemical reactions [18–29]. Pore size of a catalyst is one of the important features in selective adsorptions and reactions. Furthermore, in the case of adsorption in micropores, the adsorption is enhanced by overlapping interaction potential. In this study, synthesis and characterization of the sulfo-functionalized porous silica in both microporous and mesoporous ranges were attempted by the direct-hydrolysis and co-condensation of TMOS and MPTMS. The adsorption microcalorimetry of NH_3 and the catalytic activity of but-1-ene to *cis*, *trans*-but-2-ene of the samples were measured to elucidate the effect of pore size on the surface acidic property.

2. Experimental

2.1. Sample preparation

Sulfo-functionalized microporous and mesoporous silica were prepared in the same manner as reported [30,31]. The

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* Corresponding author. Tel.: +81 532 446811; fax: +81 532 485833.
E-mail address: aki@tutms.tut.ac.jp (A. Matsumoto).

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microporous silica included with sulfo groups were prepared as below. 3.08 g of decyltrimethylammonium bromide (C10TAB) was dissolved in 200 g mixed solution of water and methanol (300%, w/w). 4.32 ml of sodium hydroxide solution (NaOH aq., 1 M) was added to the surfactant solution as a basic catalyst. A mixture of 17.34 mmol tetramethoxysilane (TMOS) and mercaptopropyl trimethoxysilane (MPTMS) was then dropped into the basic surfactant solution to prepare a precursor gel of sulfo-functionalized microporous silica, namely Micro-SH-*n*%/C10TAB (where *n* is the molar percentage of MPTMS to total silica sources). The amount of thiol groups (–SH) was controlled by regulating the MPTMS amount. The mixture was then stirred at 298 K for 8 h. It was then filtered, washed and dried in an oven for 24 h. The as-synthesized sample was then refluxed in methanol for 24 h to extract the surfactant C10TAB. After surfactant removal, thiol-functionalized microporous silica was recovered and denoted as Micro-SH-*n*%. Finally, thiol groups on the surface of Micro-SH-*n*-% were oxidized into sulfo groups with a concentrated hydrogen peroxide solution (35% aq. H_2O_2) at room temperature to give sulfo-functionalized microporous silica, micro-SO_3H*n*%. As a control, microporous silica without any MPTMS loading (microporous MCM-41) was also synthesized and designated as micro-SH-0%.

The mesoporous silicas included with sulfo groups was prepared by a similar manner as micro-SO_3H-*n*%. 1.48 g of hexadecyltrymethylammonium bromide (C16TAB) was dissolved in 74 g of water–methanol mixed solution (methanol 30 mol%). A total of 1.3 mmol tetramethoxysilane (TMOS) and mercaptopropyl trimethoxysilane (MPTMS) mixture was then dripped in the surfactant solution. The amount of thiol groups was controlled from 0% to 30% by regulating the MPTMS amount. A precursor gel was formed when 8.2 g of tetramethylammonium hydroxide solution (TMAOH, 10%) was added into the mixture. The gel was stirred at room temperature and aged in a Teflon container at 368 K for 24 h. It was then filtered, washed and dried at 313 K for 15 h in an oven. The dried sample was designated as Meso-SH-*n*%/C16TAB (*n* = 10, 20 and 30 mol%). The template C16TAB was extracted in an ethanol and hydrochloric acid (9 mol%) mixed solution. After the surfactant removal, the thiol functionalized mesoporous silica was dried and designated as meso-SH-*n*%. Finally, meso-SH-*n*% was oxidized in a 35% hydrogen peroxide solution and denoted as meso-SO_3H-*n*%. Surfactant in meso-SH-0% (or mesoporous MCM-41) was removed by calcination at 823 K for 6 h as a control.

2.2. Characterizations

X-ray diffraction was measured by an automatic diffractometer (Rigaku RINT2000, Cu Kα). N_2 adsorption was measured volumetrically with an automatic adsorption apparatus (Quantachrome Autosorb I M) volumetrically at 77 K. A pretreatment was carried out at 383 K in 0.1 mPa for 11 h. Inclusion of sulfopropyl groups into silica framework was investigated with solid state ^{29}Si MAS-NMR with a 400 MHz spectrometer (Varian, VNMR400P).

2.3. NH_3 adsorption

Adsorption isotherm and differential heats of adsorption of NH_3 were measured simultaneously at 298 K by a volumetric adsorption apparatus attached with a twin-conduction type microcalorimeter (Tokyo Rico). Pretreatment was done at 383 K for 5 h in 0.1 mPa.

2.4. Catalytic activity

The catalyst (0.15 g) was packed in a continuous flow reactor (10 mm i.d. silica tubing) in a vertical furnace and heated under an N_2 stream at 0.15 K min^{-1} from room temperature to 423 K, and the sample was then heated at the same temperature for 1 h. After calcination of the catalyst, the reaction of but-1-ene was carried out using a continuous-flow reactor at atmospheric pressure. But-1-ene was fed with N_2 into the reactor via a mass flow meter. The partial pressure of but-1-ene and helium were 38 and 63 kPa, respectively. The contact time, *W*/*F* was 3.3 g h mol^{-1}, where *W* is the weight of the catalyst and *F* is a total feed rate (but-1-ene + He) (mol h^{-1}). Analyses for butenes, such as 2-methyl propene, and butanes were performed using Unicarbon A-400. The amounts of methane, ethane, propene and propane were determined using a Porapak Q column, and the amounts of hydrocarbons with more than three carbon atoms were determined using an OV-101 column.

3. Results and discussion

X-ray diffraction pattern of meso-SH-0% (Fig. 1) had a sharp peak at 2.4° and two smaller peaks at 4.1 and 4.8°, which were assigned to (1 0 0), (1 1 0) and (2 0 0) faces of *p*6*mm* structure of MCM-41 [10]. Meso-SH-*n*% showed a similar XRD pattern suggesting the retainment of regular pore structure. At a higher MPTMS loading, the intensity of the (1 0 0) peak was reduced and the high order peaks due to (1 1 0) and (2 0 0) faces were less obvious. XRD patterns of other micro-SH-*n*% showed similar patterns. The (1 0 0) peak was observed at 3.4° in the XRD pattern of Micro-SH-0%. Two

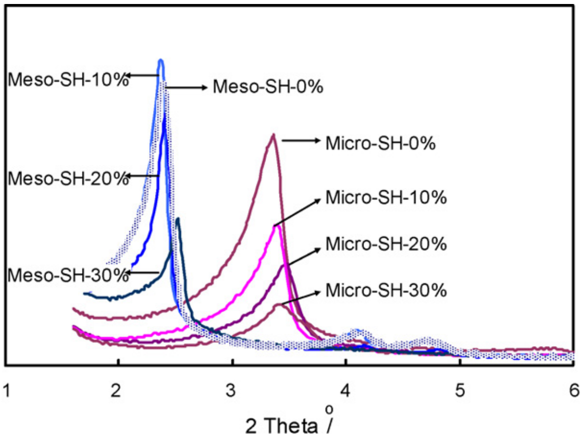

Fig. 1. XRD patterns of micro- and mesoporous silica with SH-0–30% after surfactant removal.