Microporous and Mesoporous Materials 164 (2012) 44–48

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Direct synthesis of a titanosilicate molecular sieve containing large and medium pores in its structure

Manuel Moliner, Avelino Corma *

Instituto de Tecnología Química (UPV–CSIC), Universidad Politécnica de Valencia, Consejo Superior de Investigaciones Científicas, Valencia 46022, Spain

ARTICLE INFO

Article history:
Available online 1 July 2012

Dedicated to Professor Jens Weitkamp on his 70th birthday

Keywords:
Titanosilicate
ITQ-39 zeolite
Molecular sieve
Olefin epoxidation
Green chemistry

ABSTRACT

The direct synthesis of the titanosilicate form of ITQ-39 is reported. This is the first description of the direct preparation of a titanosilicate molecular sieve containing large and medium pores in the same structure. The characterization clearly indicates the presence of Ti atoms in tetrahedral coordination in the framework of ITQ-39 zeolite. This material is very active in the oxidation of lineal and cyclic olefins with H_2O_2, showing selectivities between TS-1 and Ti-Beta.

1. Introduction

The synthesis of molecular sieves containing interconnected different sized pores in the same structure can be very useful in catalysis since they would allow different diffusion rates of molecules along them, introducing remarkable changes in the product selectivities [1]. In this sense, diverse silicoaluminate molecular sieves with different sized pores have been successfully reported in the last years, showing unique catalytic behaviors [2]. Probably, the most outstanding materials are those containing large and medium pores in the same structure, due to the attractive industrial catalytic implications that those channel topologies introduce in several acid processes. Some interesting examples are CIT-1, which is an attractive additive catalyst in cracking reactions, since produces large ratios of i-C4/n-C4 and i-C5/n-C5 [3]; MCM-68, which shows higher propylene selectivity in comparison with other zeolites, allowing its application as FCC additive for highly selective propylene production [4]; and ITQ-39, which is a very active and stable catalyst for the conversion of naphta into diesel by alkylation [5].

Other transition elements, such as titanium, have been successfully introduced as isolated tetrahedral framework species in some zeolites, and those titanosilicate materials have been extensively applied as very selective catalysts for relevant oxidation reactions [6]. Several titanosilicates have been described in the literature (such as TS-1 [7], Ti-Beta [8], Ti-ZSM-12 [9], Ti-MOR [10], Ti-ITQ-7 [11], Ti-MWW [12], or Ti-BEC [13], among others), but only two examples of titanosilicates show large and medium pores in the same structure, Ti-SSZ-33 [14] and Ti-MCM-68 [15]. In those materials, Ti atoms can only be introduced by post-synthetic methodologies, due to both materials are prepared as borosilicate, SSZ-33, or aluminosilicate, MCM-68. Indeed, post-synthetic treatments are required for selectively removing B or Al framework atoms, followed by additional steps to introduce isolated Ti atoms in the framework. In the case of SSZ-33, Davis et al. described a procedure based on three steps: first, the calcined sample was treated with Ar at 300 °C; second, the Ar flow was bubbled through a vessel containing $TiCl_4$, and third, the argon stream was bubbled through methanol [14]. They claimed that the methanol allows the removal of boron atoms by producing volatile trimethyl borate, and then, titanium is inserted in the vacancy created. In the case of MCM-68, Tatsumi et al. [15] removed the framework Al atoms by acid treatments followed by gas-phase Ti insertion using $TiCl_4$.

Those post-synthetic methodologies on SSZ-33 and MCM-68 are effective for preparing the titanosilicate form of zeolites containing large and medium pores in the same structure, but the numerous steps required for their preparation result in an unproductive synthetic process. Moreover, the complete elimination of boron or aluminum from the framework or from the pores is not always possible and side reactions towards undesired by-products could also occur.

Recently, a new zeolite containing interconnected large and medium pores, ITQ-39, has been reported [5,16]. This novel material can be synthesized under broad synthesis conditions, even as

---

* Corresponding author. Address: Av. de los Naranjos s/n, Valencia 46022, Spain. Tel.: +34 96 3877800; fax: +34 96 3879444.

E-mail address: acorma@itq.upv.es (A. Corma).

1387-1811/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.micromeso.2012.06.035

pure silica polymorph, opening a very attractive route towards the direct preparation of a titanosilicate molecular sieve with interconnected large and medium pores.

Herein, we will show the direct synthesis of the titanosilicate form of ITQ-39 zeolite. This material will be properly characterized, showing the presence of isolated tetrahedral Ti species in the zeolite framework. Finally, its catalytic properties will be tested in the selective epoxidation reactions of two different sized olefins, revealing the presence of single active Ti species in both channel systems. This direct synthesis route towards the preparation of the titanosilicate ITQ-39 would open an attractive synthesis methodology for preparing other metallosilicate forms of this material, offering new promising active catalysts containing large and medium pores in the same structure that would introduce unique product selectivities in fine chemistry or biomass transformations [17].

2. Experimental

2.1. Organic structure directing agent (OSDA) synthesis

The OSDA cation required for the synthesis of the titanosilicate form of ITQ-39 was prepared as follows: 30 g of pyrrolidine (Sigma–Aldrich, 99%) was dissolved in 200 mL of methanol (Sigma–Aldrich, >99%). The solution was acidified with HCl (Fluka, 5 N in methanol) until pH = 7.5, cooling the mixture at 273 K. Next, 37 g of 1-propyl-4-piperidone (Sigma–Aldrich, 99%) was added, followed by 10.5 g of sodium cyanoborohydride ($NaBH_3CN$, Fluka, >95%). The resultant mixture was stirred during 72 h at room temperature.

After that, HCl was added slowly until reaching a pH close to 2, removing the HCN formed by flowing nitrogen. The solution was concentrated, and a 25 wt.% aqueous solution of KOH was added until pH > 12, achieving then a white precipitate. The mixture was saturated with NaCl, and the diamine 1-propyl-4-pyrrolidin-1-yl-piperidine was extracted with diethyl ether.

Twenty grams of the diamine 1-propyl-4-pyrrolidin-1-yl-piperidine was diluted in 70 ml of NaOH, and then 60 g of ethyl iodide was added dropwise. After 7 days under stirring at room temperature, a white precipitate was obtained, which was filtered and washed with methanol and diethyl ether. Finally, the solid was dried under high vacuum.

The iodide form of the organic salt was exchanged to the hydroxide form as follows: 44 mmol of cation in the iodide form was dissolved in water, and 89 g of Dower-SBR Anion Exchange resin in hydroxide form (total exchange capacity 1.4 eq/l) was added, maintaining under agitation overnight. The solution was filtered, and the dihydroxide cation was obtained.

2.2. Zeolite syntheses

Ti-ITQ-39 was synthesized as follows: 6.03 g of an aqueous solution of OSDA in hydroxide form (9.9 wt.%t) was mixed with 1.73 g of tetraethyl orthosilicate (TEOS, Sigma–Aldrich, 99 wt.%). After 30 min of stirring, 47 mg of titanium (IV) isopropoxide (TiISO, Sigma–Aldrich, 99 wt.%) was introduced. The mixture was maintained under stirring until complete hydrolysis of TEOS and TiISO. Then, 0.17 g of hydrofluoric acid (Sigma–Aldrich, 48 wt.%) was added to the gel, and the gel was stirred until evaporation of the excess of water. The final gel molar composition was fixed as: SiO_2:0.02 TiO_2:0.25 $OSDA(OH)_2$:0.50 HF:$3H_2O$. The gel was transferred to 10 ml Teflon lined autoclave and heated at 135 °C for 30 days. The resultant solids were filtered, washed, and dried at 100 °C.

Ti-Beta and TS-1 zeolites were synthesized following the procedures described in the literature [18].

The as-prepared samples were calcined in air at 580 °C for 6 h.

2.3. Characterization

Synthesized samples were characterized by powder X-ray diffraction (PXRD) using a multisample Philips X'Pert diffractometer equipped with a graphite monochromator, operating at 40 kV and 45 mA, and using Cu K_α radiation ($\lambda = 0.1542$ nm).

The chemical analysis was performed in a 715-ES ICP-Optical Emission spectrometer, after solid dissolution in HNO_3/HCl/HF aqueous solution. The organic content of the as-made materials was determined by elemental analysis performed on a SCHN FISONS elemental analyzer.

UV–vis spectra were obtained with a Perkin Elmer (Lambda 19) spectrometer equipped with an integrating sphere with $BaSO_4$ as reference.

2.4. Catalytic tests

Reactions were carried out in 2-mL glass flasks with magnetic stirring and heated by means of a temperature controlled aluminum rack. Catalytic tests by using H_2O_2 as oxidant were performed at 333 K, using 20 mg of catalyst and the following reaction mixture: 1.6 mmol of olefin (1-hexene or cyclohexene), 0.4 mmol of H_2O_2, 1.2 g of solvent (methanol or acetonitrile). All substances were available from Sigma–Aldrich Company (Acetonitrile, 99%; 1-hexene, 99%; cyclohexene, 99%; H_2O_2, 35 wt.% in water). Aliquots were analyzed online by gas chromatography using nonane as standard. H_2O_2 efficiency was calculated by iodemetric tritation.

3. Results

ITQ-39 zeolite is a very complex structure formed by the intergrowth of three different polymorphs, all of them containing large and medium pores in their structures [5]. This material can be synthesized under very broad synthesis conditions depending on the OSDA used in its preparation [16]. When the OSDA introduced in the synthesis media contains a combination of ethyl and propyl groups (see Fig. 1), the pure silica form of ITQ-39 can be achieved. Interestingly, this pure silica ITQ-39 can be obtained in the absence of alkali cations, such as potassium or sodium. This is an important point for attempting the isomorphic substitution of titanium atoms in the zeolite framework, since those cations preclude the insertion of isolated titanium in the framework due to the precipitation of alkali titanates during the synthesis process [19]. Then, we attempted the synthesis of the titanosilicate form of ITQ-39 under similar conditions to the pure silica ITQ-39, using the same OSDA

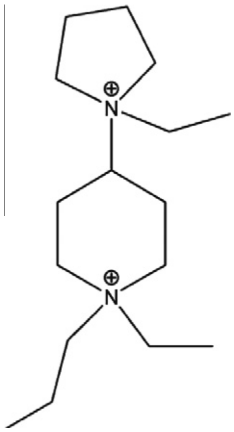

Fig. 1. OSDA used in the synthesis of the titanosilicate form of ITQ-39.