

Introduction of Mesoporosity in Zeolites Using Nanoparticles as Hard Templates

A.I. Carrillo, N. Linares, J. García Martínez *

Department of Inorganic Chemistry. University of Alicante, Carretera San Vicente s/n,
E-03690, Alicante, Spain.
e-mail: j.garcia@ua.es URL: www.ua.es/grupo/nanolab

ABSTRACT

Silicalite-1 zeolite with intracrystalline mesoporosity has been synthesized by using nanosized MgO as a hard template. The inorganic nanoparticles have been embedded inside the silicalite-1 crystals during the crystallization step and then easily removed by simple acid wash. All the mesoporous materials have been obtained by hydrothermal treatment using tetrapropylammonium as a structure directing agent. All samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and N₂ physisorption at 77K. The results suggest that MgO nanoparticles are suitable hard templates for the synthesis of hierarchical porous materials.

Keywords: Silicalite-1; Mesoporous; Hard template, Nanoparticles.

1 INTRODUCTION

The development of ordered, thermal and hydrothermal stable mesoporous materials with zeolite-like crystalline frameworks is highly desirable to reduce the diffusion limitations of these microporous materials.[1] Zeolites are widely used in catalysis, purification, adsorption, separation and other industrial applications because their stability, high internal surface, and controllable chemistry.[2] However, their small channels and cavities (typically below 1 nm) significantly reduce some of their applications. Different strategies have been tried to overcome this limitation. Among them, the direct incorporation of mesoporosity (intracrystalline mesoporosity) is especially desirable. Mesopores have been introduced into zeolites mostly by dealumination,[3] recrystallitation,[4] or by using various templates such as surfactants,[5] cationic polymers,[6] carbon black,[7] and nanoparticles.[8]

The use of templates is especially convenient because it allows for an easy pore size control. The templates used so far include tree types, namely soft, hard, and hierarchical templates. The soft templates, which can be subsequently removed by heat treatment, are usually organic-based molecules, such as polymers and surfactant micelles. The hard templates, which can be leached away by using alkali or acid washes or calcination, actually refer to nanosized solids, for example carbon black, or polymer microspheres.

In some cases, nanocasting was used to produce inverse replicas of a porous structure. The pores are filled with a secondary material, followed by a post-treatment, and the removal of the template. The hard template method has been recently used to fabricate various novel porous structures, which are difficult to synthesize using the soft template method. For example, zeolites, ordered mesoporous silicas (*e.g.*, MCM-48, SBA-15, and SBA-16), and inverse opals have been used to fabricate microporous, mesoporous and macroporous carbons, respectively. Finally, hierarchical templates, which combines different templates with controlled structures at different length scales, have been used to prepare bi-modal and tri-modal porous structures with the primary objective of minimizing diffusion resistance.[9]

A wide variety of nanoparticles have been used as hard templates to produce mesoporous zeolites. H. Kato et al. describe the synthesis of mesoporous zeolites by using platinum nanoparticles as mesopore-forming templates.[8] A.H. Janssen et al. present an exploratory study on the generation of mesopores by templating with carbon during zeolite synthesis.[7] H. Zhu et al. have recently reported the preparation of silicalite-1 single crystal with intracrystal pores in the range of 50-100 nm by using the nanosized CaCO₃ as a hard template. In this case, the CaCO₃ nanoparticles embedded in the silicalite-1 crystals are removed by acid wash, which give rise to intracrystal mesopores within the zeolite crystal.[2]

Herein, we describe the use of MgO nanoparticles as hard templates to obtain mesoporous zeolites [2,8]. These nanoparticles can be conveniently removed by chemical treatment (usually acid wash) without damaging the zeolite. The final mesoporous materials prepared using this strategy shows a bimodal pore size distribution, *i.e.* the pores due to their crystalline framework (micropores) and the mesopores resulting from the removal of the nanoparticles

2 EXPERIMENTAL SECTION

2.1 Materials.

MgO nanoparticles used as a hard template were obtained from Sigma-Aldrich. According to the vendor, the particle size distribution of MgO is in the range of 25-50 nm.

3-mercaptopropyltriethoxysilane (MPTES, 80%, Fluka), NaOH (99%), tetrapropylammonium bromide (98%, Aldrich, denoted as TPABr), tetraethoxysilane (98%, Aldrich, denoted as TEOS) were commercial available and used in the synthesis without further purification.

Finally, sulfuric acid (96%) from Panreac was used to remove the MgO nanoparticles after convenient dilution.

2.2 Synthesis of Silicalite-1 with Intracrystal Mesopores.

In a typical synthesis of mesoporous silicalite-1, 0.10 g of MgO nanoparticles was added to a clear solution of tetrapropylammonium bromide, water, NaOH, TEOS as silica precursor and MPTES to functionalize MgO nanoparticles. The resulting solution underwent ultrasonic agitation for 15 min in order to produce a homogeneous dispersion of MgO nanoparticles in the silica gel. The final mixture has a molar composition of about 0.05TPABr:0.15NaOH:1TEOS:43.2H₂O, the ratio molar of MPTES:MgO nanoparticles is 1:1. The resulting gel was transferred into a Teflon-lined stainless steel autoclave, where it was heated under autogeneous pressure for 72 h in an oven at 150 °C. After cooling to room temperature, the products were recovered by filtration, washed with water and dried at room temperature for 24 h. The organic structure-directing agent trapped in the pores was thoroughly removed by calcination at 550 °C for 8 h. Finally, the inorganic MgO nanoparticles were removed by chemical treatment with sulfuric acid using a 0.01 M H₂SO₄ solution during 10 min or citric acid to pH =3 during 30 min. The resulting zeolite was water washed, filtered out, and dried at room temperature for 24 h.

For comparison purposes, silicalite-1 without MgO nanoparticles was synthesized using the same experimental conditions and procedure.

2.3 Characterization Methods.

X-ray powder diffraction patterns (XRD) were obtained with a Bruker D8-Advance diffractometer using CuK α radiation; the scanning velocity was 0.1%/min over the range of 1.7-50° (2 θ). Scanning electron microscopy (SEM) features of all the samples were observed by SEM (JEOL JSM-840). Transmission electron microscopy (TEM) experiments were performed on a JEM-2010 electron microscope (JEOL, Japan) having 0.14 nm instrumental resolution equipment operated at 200 kV. Samples for TEM studies were prepared by dipping a carbon-coated copper grid into a suspension of samples in ethanol that was presonicated. N₂ adsorption/desorption isotherms were measured at 77 K on a Quantacrome Autosorb-6 volumetric adsorption analyzer. Before the adsorption measurements, all samples were outgassed at 523 K for 4 h. The pore size distribution was calculated from adsorption branches of isotherms using the BJH method, with the software attached to the equipment.

3 RESULTS AND DISCUSSION

3.1 X-ray diffraction (XRD).

Figure 1 shows the XRD patterns of a) silicalite, b) silicalite with 10 % of MgO nanoparticles functionalized with MPTES, c) silicalite with 25 % of hard template and functionalize with MPTES, and d) silicalite with 50 % of MgO nanoparticles and functionalize with MPTES. Sample b show high crystallinity and all the peaks are located at the same angles, which correspond to the pure silica MFI structure. No peaks due to the MgO nanoparticles were observed, as expected because their small size. Therefore, the incorporation of MgO nanoparticles does not hinder the crystallization of silicalite.

Figures 1c and 1d show than silicalites with high quantity of hard template lose the structure crystalline of zeolite. TEM image of silicalite-1b, with 25 % of MgO nanoparticles, show an opening structure of the crystal that corresponds with the adsorption branch in nitrogen physisorption when we can see that these samples have more mesoporosity than silicalite-1a.

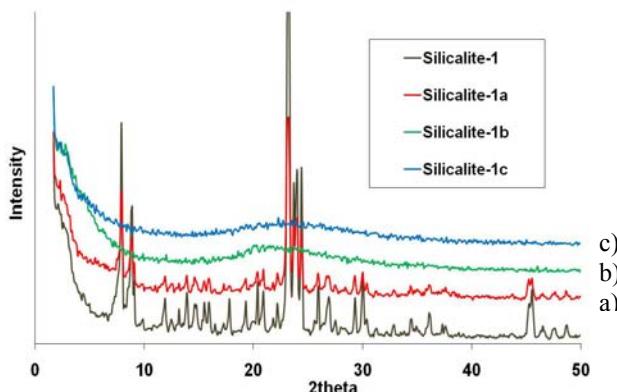


Figure 1: XRD patterns of silicalites with a different quantity of the hard template MgO: a) silicalite without MgO b) silicalite with 10 % of nanoparticles, c) silicalite with 50 % of hard template and d) silicalite with 50 % of MgO nanoparticles.

3.2 Transmission electron microscopy (TEM)

The transmission electron microscopy is a powerful technique for direct observation of secondary pores in zeolites.[6]

Figure 2 shows a TEM image of mesoporous silicalite-1b. The zeolite has lost the crystallinity and we can see an opening structure.

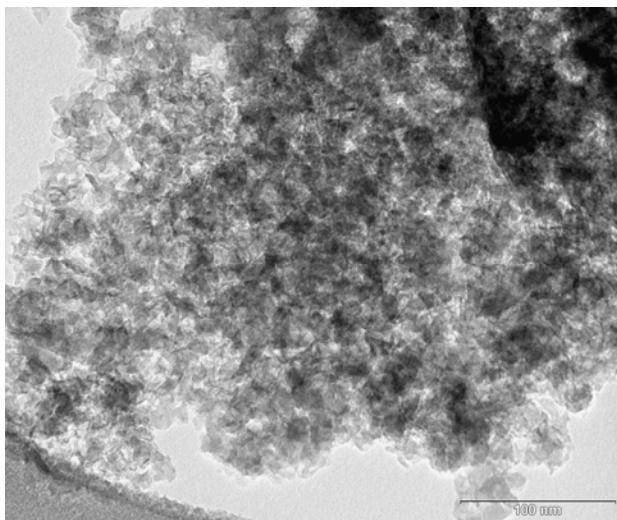


Figure 2: TEM image of silicalite-1b after it has been washed by sulfuric acid.

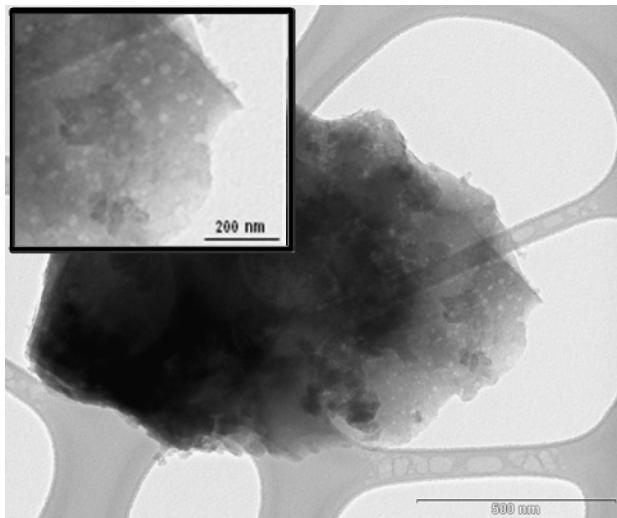


Figure 3: Low magnification TEM micrograph of mesoporous silicalite-1a. In this case we can see the crystallinity of silicalite-1.

The crystals are not well faceted, as some irregularly shaped intracrystalline mesoporosity is observed throughout the sample. The TEM micrographs show that the intracrystalline pores are not ordered as the regular mesopores observed in the more conventional amorphous mesoporous materials, like MCM-41 silica.

3.3 Scanning electron microscopy (SEM)

The SEM images in Figures 4-5 give details on silicalite-1 morphology. The low magnification image shows that particles are uniform.

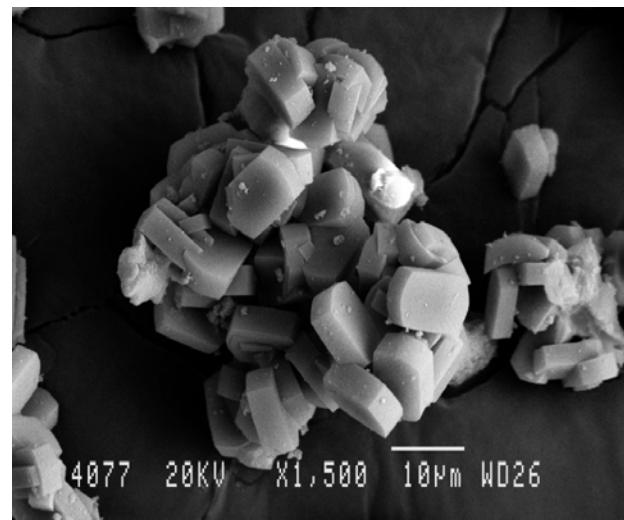


Figure 4: SEM image of the silicalite-1a, with 10 % of MgO nanoparticles.

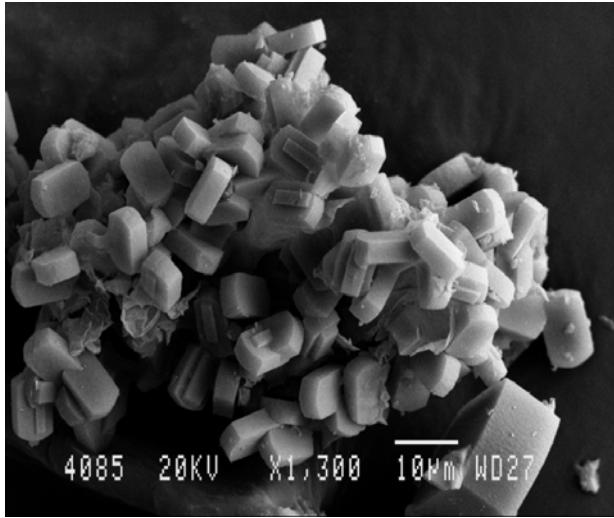


Figure 5: SEM image of mesoporous silicalite-1a.

The results of scanning electron microscopy for the hard-templated-directed silicalite-1 show that samples are highly crystalline. Estimated from the SEM overview, the average crystal size of silicalite-1a/MgO composite and the mesoporous silicalite-1 are in the range of 10 microns. So the morphology and size of crystals has been maintained after MgO removal.

3.4 Nitrogen physisorption

Figure 6 shows the isotherms of silicalite with 10 wt% of MgO washed with citric acid during 30 min (circles and dotted line), silicalite with 10 wt% MgO washed with sulfuric acid 2 M during 10 min (crosses and solid line), silicalite with 25 wt% MgO washed with sulfuric acid 2 M for 10 min (squares), and silicalite with 50 wt% MgO

washed with sulfuric acid 2 M for 10 min (triangles). The materials with higher amount of mesoporosity are silicalite 1b and 1c, i.e. those that were prepared using 25 wt% and 50% wt MgO. These materials, however do not show any crystallinity, (see Figure 1), which suggest that there is a limit in the amount of template that can be used.

Figure 7 shows the pore size distribution of mesoporous silicalite-1a-1 washed with citric acid 30 min and silicalite-1a-2 washed with sulfuric acid 10 min. In both cases, there is a peak around of 20 nm that it corresponds with the size of nanoparticles. This is an evidence of the template effect of the MgO.

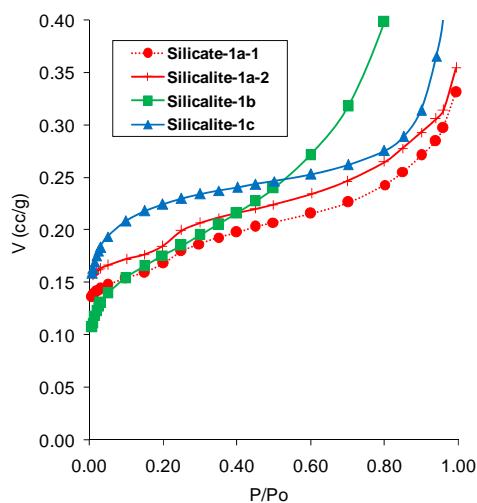


Figure 6: N_2 adsorption isotherm of mesoporous silicalite obtained by using different concentrations of hard template. Curve of silicalite-1a-1 is shifted +0.02 cc/g for clarity.

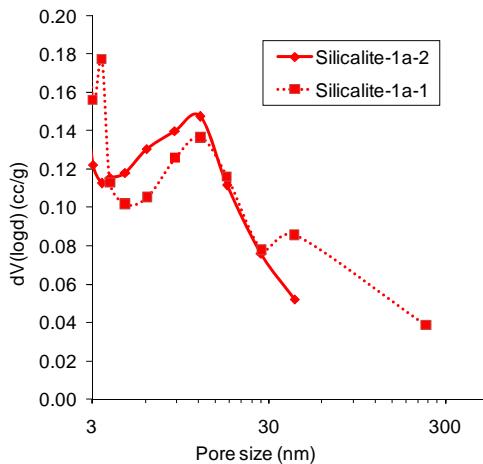


Figure 7: Mesopore size distributions of silicalite-1a-1, dot line, and silicalite-1a-2, solid line, calculated from the adsorption branch by the BJH method.

4 CONCLUSIONS

Silicalite-1 with intracrystalline mesopores (average pore size approx. 20 nm) was prepared using different concentrations of MgO nanoparticles as hard template. The MgO nanoparticles were embedded in the silicalite-1 crystal during the crystallization process. Afterwards, they were removed by controlled acid wash without damaging the silicalite crystals besides producing intracrystalline mesoporosity. We have used MPTES to functionalize the MgO nanoparticles. The pore size distribution obtained by using BJH method exhibits a pore size distribution centered at 20 nm that it corresponds with size of MgO nanoparticles. The combined use of X-ray diffraction, TEM and SEM images analysis show that the crystallinity is preserved even after the acid wash step when the concentration in MgO nanoparticles is small.

Mesoporous zeolites with both microporosity and intracrystalline mesoporosity, like the ones herein described, are desirable because their enhanced diffusion properties and therefore potential application in catalysis, separation, and adsorption of bulky molecules.[10,11]

ACKNOWLEDGEMENT

This research has been funded by the Ministerio de Educacin y Ciencia (CTQ2005 - 09385 - C03 - 02). J.G.M. is grateful for financial support under the Ramn y Cajal program and N.L. for a FPI fellowship.

REFERENCES

- [1] H. Li et al., Micropor. Mater., 106, 174-179, 2007.
- [2] H. Zhu et al., Chem. Mater., 20, 1134-1139, 2008.
- [3] A.H. Janssen, A.J. Koster, K.P. de Jong, Angew. Chem. Int. Ed., 40, 1102, 2001.
- [4] I. Ivanova et al., Stud. Srf. Sci. Catal., 158, 121, 2005.
- [5] F.-S. Xiao, L. Wang, C. Yin, Y. Di, J. Li, R. Xu, D. Su, R. Schlogl, T. Yokoi, T. Tatsumi, Angew. Chem., Int. Ed. 45, 3090, 2006.
- [6] M. Choi, H.S. Cho, R. Srivastava, C. Venkatesan, D.-H. Choi, R. Ryoo, Nature Mater., 5, 718, 2006.
- [7] A.H. Janssen, I. Schmidt, C.J.H. Jacobsen, A.J. Koster, K.P. de Jong, Micropor. Mesopor. Mater., 65, 59-75, 2003.
- [8] H. Kato, T. Minami, T. Kanazawa, Y. Sasaki, Angew. Chem., Int. Ed. 43, 1271-1274, 2004.
- [9] X.S. Zhao, J. Mater. Chem., 16, 623-625, 2006.
- [10] C. H. Christensen, I. Schmidt, A. Carlsson, K. Johannsen, K. Herbst, J. Am. Chem., 127, 8098, 2005.
- [11] I. Schmidt, A. Krogh, K. Wienberg, A. Carlsson, M. Brorson, C. J. H. Jacobsen, Chem. Commun., 2157, 2157.