

A TWO-STEP MICROWAVE SYNTHESIS OF NANOCRYSTALLINE IRON SILICALITE PARTICLES

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ABSTRACT

The influence of microwave synthesis conditions (time, temperature) and aging of clear solutions on the size, morphology, iron content, and aggregation of nanocrystalline particles were studied for iron silicalite-1 (FeS-1). The smallest round FeS-1 intergrown crystals with a mean diameter of 300 nm composed of 40-nm particles were obtained by the two-step microwave-assisted hydrothermal syntheses. TEM investigation reveals the presence of an amorphous shell around the intergrown crystals. The study of iron local structure in FeS-1 by using UV-Vis spectroscopy evidences framework and extra-framework iron species.

Keywords: microwave synthesis, iron silicalite, nanocrystalline, TEM, UV-VIS.

INTRODUCTION

Application of a microwave technique in hydrothermal synthesis is of great importance, especially in the synthesis of nanoporous materials. Microwave heating is regarded as a synthesis tool with several benefits, such as homogeneous nucleation, promotion of faster crystallization, rapid synthesis, small crystallites, the avoidance of undesirable phases by shortening the synthesis time and so on. Recently, it was found that microwave synthesis provides an effective way to control the particle size distribution, crystal morphology, orientation, and even the type of crystalline phase [1]. A two-step synthesis procedure consisting of a treatment at lower temperature followed by a rapid change in temperature during the course of the crystallization have already been used for the preparation of colloidal silicalite-1 by microwave and conventional hydrothermal heating [2].

The method of iron silicates preparation strongly influences the nature and distribution of the resulting iron species, which basically determines the catalyst performance. Iron can be incorporated by isomorphous substitution, ion exchange, and chemical vapor deposition [3]. The introduction of iron into the silicate matrix is typically followed by a high-temperature calcination or steam treatment [4]. These treatments are crucial to yield active sites in isomorphously substituted silicates by the extraction of framework iron to extra-framework positions [5].

We present here the new preparation using microwave heating and characterization of isomorphously substituted FeS-1 nanocrystalline particles. The influence of the microwave synthesis conditions on the characteristics, such as size, shape, and aggregation of FeS-1 nanocrystalline particles as well as iron content have been studied in detail. The nature of iron species in FeS-1 has also been examined.

EXPERIMENTAL

The clear solutions were prepared by mixing deionized water, FeCl₃·6H₂O (purum, Merck), tetraethyl ortho- silicate (TEOS, 98%, Acros) and tetraethylammonium hydroxide (TPAOH, 40%, Alfa Aesar) at room temperature, respectively. The clear solution molar compositions was 10 TEOS : 0.2 FeCl₃ : 3 TPAOH : 245 H₂O. The clear solutions were aged under stirring for 1 hour at room temperature. After aging, 20 ml of each clear solution was transferred into one Teflon autoclave and put in the microwave oven ETHOS 1600 (Milestone). This oven is a computer controlled and can operate with 10 Teflon autoclaves with temperature sensor in one of them. The two-step microwave heating was

performed by the following regime: the first step from at temperatures from 100 - 130 °C for 180 min and the second step at 140 and 150 °C for 50 to 270 minutes. After the syntheses, the autoclaves were cooled down and the suspensions were removed from the autoclaves. The solid products were separated by centrifugation at 9500 rpm (Hettich) and washed with distilled water until the pH of filtrate was neutral. The recovered products were dried at 60 °C for several hours and calcined at 500 °C for 5 hours in oxygen flow.

All as-synthesized samples were characterized with different techniques including X-ray powder diffraction (XRD), scanning and transmission electron microscopies (SEM, TEM), energy dispersive X-ray spectroscopy (EDXS) and dynamic light scattering (DLS). The X-ray powder diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO high-resolution diffractometer with Alpha1 configuration using CuK α 1 radiation (1.5406 Å) in the 2 θ range from 5 to 35 °2 θ using step 0.034 o and collection time of 100 s per step at fully opened X'Celerator detector. SEM micrographs were obtained by scanning electron microscopy on Zeiss SupraTM 3VP microscope. Elemental analysis was performed by EDX method with INCA Energy system attached to Zeiss SupraTM 3VP microscope. The microstructure was investigated by high resolution transmission electron microscopy (HRTEM) on a 200-kV field-emission gun (FEG) microscope JEOL JEM 2100. The particle size analysis of FeS-1 nanocrystalline particles in the ethanol was performed with a Microtrac 3500S particle size analyzer. Diffuse reflectance UV-Vis spectra of the selected as-synthesized and calcined sample as well as of reference material were recorded at room temperature using a Perkin-Elmer Lambda 40P UV-Vis spectrophotometer equipped with the RSA-PE-19M Praying Mantis accessory. The Spectralon® white reflectance standard was used to perform the instrument background correction in the range of 200-800 nm.

RESULTS AND DISCUSSION

A great care was needed for microwave synthesis of pure iron silicalite-1 (FeS-1) nanocrystalline particles. FeS-1 was prepared by hydrothermal microwave syntheses from clear solutions with molar composition 10 TEOS : 0.2 FeCl₃ : 3 TPAOH : 245 H₂O [6]. The pure products crystallized from the gels with the initial pH of 12. Lower amounts of the TEOS and the template (lower initial gel pH) were favorable for the formation of amorphous phase as a major phase. The primary step of heating was performed at 100, 110, 120 and 130 °C for the equal duration of heating 180 minutes, while the secondary step of heating was carried out at 140 or 150 °C for different duration of heating from 50 to 270 minutes. Powder products did not crystallize from clear solutions when the primary step of heating was lower than 100 °C. Most of the powder products were obtained after the crystallization time of the secondary step of 180 minutes. The exceptions were two products, which were prepared after 50 and 60 minutes at the second step at 140 °C, while the first step of crystallization temperature was carried out at 110 °C.

The following characterization work and discussion in this paper is focused on the phase-pure product of FeS-1 (denoted FS-17) prepared after 50 min in the second step with the smallest intergrown crystals.

Powder XRD patterns (not shown) of the selected as-synthesized and calcined sample contains only diffraction peaks corresponding to silicalite-1.

Scanning electron microscopy reveals that iron silicalite-1 powders contain nanocrystalline particles with different shapes, which built round and/or angular intergrown crystals, depending on the crystallization time, and the temperature. Most of the products prepared by the two-step heating procedure possess round intergrown crystals composed of small 40-nm particles [6]. The selected FeS-1 product has 300 nm spherical intergrown crystals composed of 40-nm particles (Figure 1A).

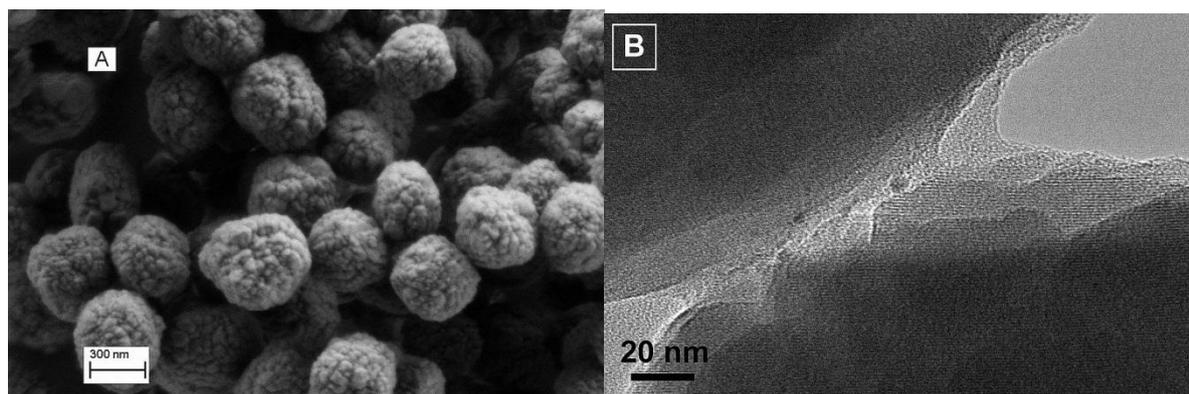


Figure 1. SEM micrograph of the selected FeS-1 prepared at 110°C for 180 min and 140°C for 50 min (A) and TEM image of the close view of the amorphous shell material between two FeS-1 nanocrystalline particles (B).

All FeS-1 samples were studied by dynamic light scattering (DLS) in order to evaluate the particle size distribution. According to this investigation, suspensions with a relatively broad (200 nm - 10 μ m) particle size distributions are obtained in general. The particle size distribution by number for the sample FS-17 shows a peak centered at about 377 nm.

The selected sample was further studied by HRTEM to understand the reason for the difference in the crystal size measured by DLS and SEM techniques. According to the TEM study (Figure 1B), the product containing mostly intergrown crystals are built of individual crystals. The careful inspection of these intergrown crystals reveals that all crystals are covered with a shell of material with amorphous appearance, because of the absence of lattice fringes and a substantial difference in the contrast between this material and underlying zeolite. The same observation was found by Valtchev et al. in his study of nanosized zeolite A prepared at room temperature [7]. Having in mind that both zeolite and amorphous material were obtained from the same clear solution, the contrast difference was attributed to the formation of a shell of highly hydrated amorphous material. This material covers the individual crystals and the intergrown crystals with a 5-10 nm shell. XRD analysis indicates that the amount of the amorphous material is low. Valtchev explains that residual amount of amorphous precursor serves as contact cement binding the well-shaped individual crystals into random aggregates [7]. The TEM investigation reveals the presence of an amorphous shell around the intergrown crystals.

Diffuse reflectance UV-Vis spectroscopy was used to investigate the nature of the Fe(III) species (i.e. ferric iron) in the selected iron silicalites-1. As shown previously, UV-Vis spectra of Fe-containing zeolites are characterized by intense $\text{Fe}^{3+} \rightarrow \text{O}$ charge-transfer (CT) bands, the position of which provided information on the coordination and degree of agglomeration [8]. Thus, isolated Fe^{3+} ions gave rise to bands below 300 nm while signals of small oligonuclear Fe_xO_y clusters within the pores appeared between 300 and 400 nm and Fe_2O_3 nanoparticles at the external surface of the crystal above 400 nm [5]. Two CT transitions are observed for more or less distorted isolated Fe^{3+} sites. For tetrahedral Fe^{3+} in framework positions of iron silicalite they are observed at 215 and 241 nm [5]. CT bands of isolated Fe^{3+} in octahedral symmetry appear below 300 nm; they are found at 285 [5] and at 291 nm [9] in iron silicates. The analysis of UV-Vis spectroscopy reveals that the selected as-synthesized FeS-1 sample shows two bands at 216 and 243 nm. According to the above considerations, they can be attributed to isomorphously

substituted Fe³⁺ sites in tetrahedral positions of the corresponding silicalite-1 lattice. In addition, UV-Vis spectrum of the calcined sample shows three sub-bands below 300 nm, which can be assigned to isolated Fe³⁺ species in framework (215 and 240 nm) and extra-framework positions (280 nm). This result clearly indicates that removal of the template by calcination of the as-synthesized selected FeS-1 induces a substantial dislodgment of framework Fe³⁺ ions.

CONCLUSION

The two-step microwave-assisted hydrothermal synthesis was used to prepare nanocrystalline FeS-1 particles. The synthesis could be accomplished within 4 hours at relatively low crystallization temperatures. All FeS-1 powders crystallized from clear solutions as intergrown crystals. Lower crystallization temperatures resulted in the formation of smaller round intergrown crystals composed of 40-nm particles. The results of UV-Vis spectroscopic characterization proved the presence of extra-framework iron species in the selected FeS-1.

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REFERENCES

- [1] G. A. Tompsett, W. C. Conner and K. S. Yngvesson, *Chem.Phys. Chem.*, 2006, **7**, 296-319.
- [2] J. Motuzas, A. Julbe, R. D. Noble, C. Guizard, Z. J. Bersnevičius and D. Cot, *Micropor. Mesopor. Mater.*, 2005, **80**, 73-83.
- [3] J. Pérez-Ramírez, J. C. Groen, A. Brückner, M. S. Kumar, S. Bentrup, M. N. Debbagh and L.A. Villaescusa, *J. Catal.*, 2005, **232**, 318-334.
- [4] J. Pérez-Ramírez, F. Kapteijn, J. C. Groen, A. Doménech, G. Mul and J. A. Moulijn, *J. Catal.*, 2003, **214**, 33-45.
- [5] S. Bordiga, R. Buzzoni, F. Geobaldo, C. Lamberti, E. Giamello, A. Zecchina, G. Leofanti, G. Petrini, G. Tozzola and G. Vlaic, *J. Catal.*, 1996, **158**, 486-501.
- [6] A. Ristić, K. Lázár, H. Solt and V. Kaučič, *Cryst. Eng. Comm.*, 2011, **13**, 1946-1952.
- [7] V. P. Valtchev, L. Tosheva and K. N. Bozhilov, *Langmuir*, 2005, **21**, 10724-10729.
- [8] J. Pérez-Ramírez, M. S. Kumar and A. Brückner, *J. Catal.*, 2004, **223**, 13-27.
- [9] M. S. Kumar, J. Pérez-Ramírez, M. N. Debbagh, B. Smarsly, U. Bentrup and A. Brückner, *Appl. Catal. B: Environ.*, 2006, **62**, 244-254.