MnS-1 NANOCRYSTALS WITH MANGANESE LOCAL ENVIRONMENT ON DEMAND

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ABSTRACT

The diminution of the zeolite crystals from micro to nano scale is an important, but difficult step in the synthesis procedure. With the reduction of particle size the catalytic material gains larger surface area and consequently, higher surface activity. MnS-1 nanosized crystals with the size of 100 to 200 nm were synthesized under classical or microwave hydrothermal procedures. The local environment of manganese in MnS-1 nanocrystals was characterized by X-ray absorption spectroscopy (XANES and EXAFS techniques). The analysis of XANES and EXAFS spectra revealed different local environments of manganese: incorporated Mn^{3+} into the silicalite-1 framework as framework manganese or incorporated Mn^{3+} into the silicalite-1 framework as extra-framework manganese in MnO_x forms.

Keywords: MnS-1 Nanocrystals, Framework Manganese, Extra-Framework Manganese, Manganese Oxides , X-ray Absorption Spectroscopy

INTRODUCTION

Many structure types of zeolites are used as catalytic supports in chemical reactions [1]. Incorporation of transition metals into their framework generates different types of catalytically active sites. [2] Silicalite-1 is a microporous, silica-based molecular sieve with a MFI topology of the tetrahedral framework. The isomorphous substitution of Si^{4+} ions in silicalite-1 framework with tetra- and penta-valent ions such as Ti^{4+}, $V^{4+/5+}$ or Sn^{4+} has been reported to result in molecular sieves with selective oxidation properties. The isomorphous substitution of Si^{4+} ions in silicalite-1 with trivalent ions such as Al^{3+}, B^{3+}, Fe^{3+}, Ge^{3+} has been reported to result in high-quality inorganic membranes used for catalytic membrane reactors. The aluminum-containing silicalite-1 (ZSM-5) is a representative member of high-silica aluminosilicate molecular sieves (zeolites) exhibiting also considerable significance as catalytic materials. Manganese is one of the most intensively used elements for redox catalysis. This is, besides the non-toxic and cost-efficient nature, predominantly due to the multiple and wide range of stable oxidation states (2+, 3+, 4+, and 7+) of this element.

Incorporation of manganese into microsized crystals of zeolite with MFI topology generates catalitically active Lewis acid sites [3]. The diminution of the crystals from micrometer to nanometer scale means a larger specific surface area of the catalyst and thus, a higher activity. In addition, nanoparticles can be organised into a mesoporous catalyst or can be prepared in the form of thin films. In the frame of this work, the new synthesis routes for the preparation of nanocrystals of MnS-1 with sizes of 100 nm to 200 nm, are presented. Manganese local environment in these products were characterized by using X-ray absorption spectroscopic techniques.

EXPERIMENTAL

A conventional autoclave procedure (classical and microwave) was used with adequate source of silica, which plays the important role in the control of size of crystals obtained. Besides the silica source, important factors in controlling the size distribution are also the temperature and the time of crystallization. The MFI topology of the prepared product was identified by X-ray power diffraction (XRD). Scanning electron microscopy (SEM) revealed the information on the nanosized particles (Figure 1). Elemental analysis was performed using Energy dispersive spectroscopy (EDS). X-ray absorption spectroscopy (XANES and EXAFS techniques) provided direct information on valence state and local environment of Mn in the products.

RESULTS AND DISCUSSION

Products of one-step hydrothermal classical synthesis with TEOS as the silicon source and ageing of the reaction gel for 1 day are MnS-1 nanocrystals with MFI structure (Figure 1) and with the size of 150 nm (Figure 2).

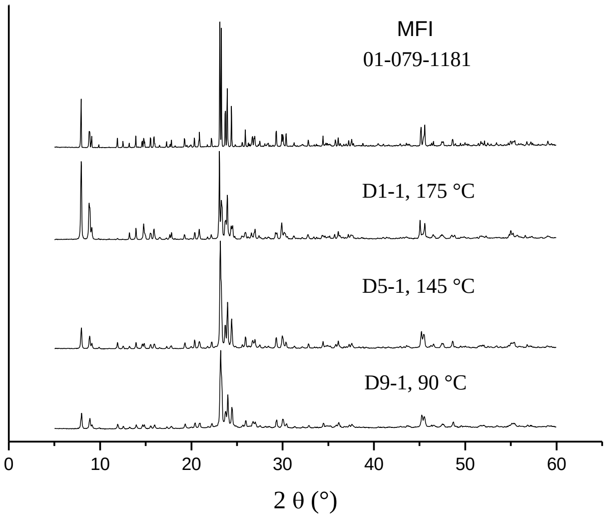

Figure 1: XRD patterns of the MnS-1 nanocrystals, synthesized by one-step classical hydrothermal procedure: D9-1 denotes crystals obtained at 90 ^{o}C, D5-1 denotes crystals obtained at 145 ^{o}C, D1-1 denotes crystals obtained at 175 ^{o}C and 01-079-1181 denotes reference patterns of MFI topology.

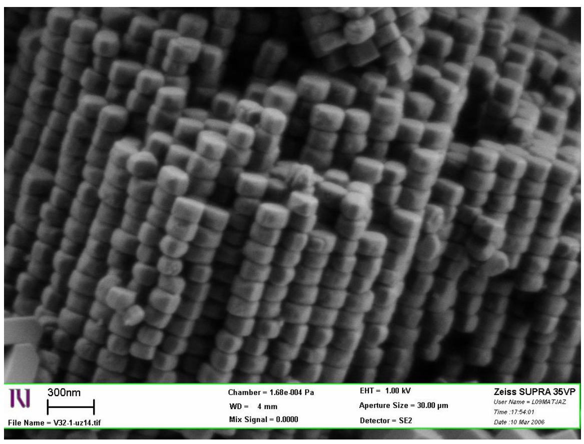

Figure 2: SEM image of the MnS-1 nanocrystals (synthesized by one-step classical hydrothermal procedure) having about 150 nm in size.

Products of two-step hydrothermal microwave synthesis with the TEOS as silicon source and ageing of the reaction gel for 1 day are MnS-1 nanocrystals with MFI structure (Figure 3) and with the size from 100 to 200 nm (Figure 4).

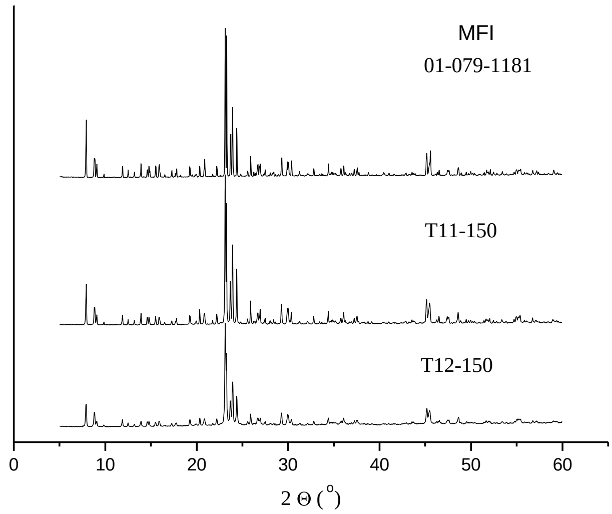

Figure 3: XRD patterns of the MnS-1 nanocrystals, synthesized by two-step microwave hydrothermal procedure: T12-150 denotes crystals obtained at 150 °C and higher amount of template in the synthesis gel, T11-150 denotes crystals obtained at 150 °C and lower amount of template in the synthesis gel, and 01-079-1181 denotes reference patterns of MFI topology.

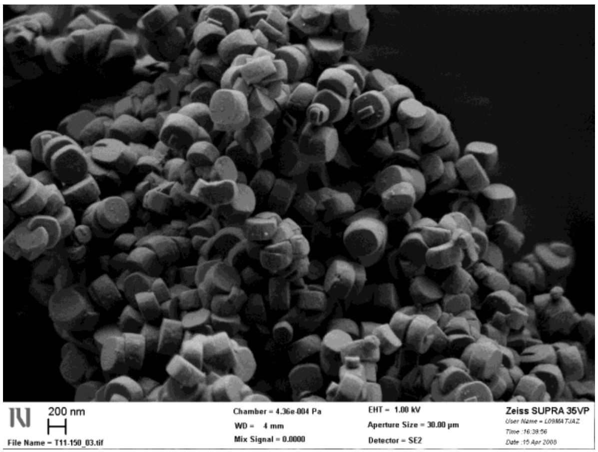

Figure 4: SEM image of the MnS-1 nanocrystals (synthesized by two-step microwave hydrothermal procedure) having about 200 nm in size.

The analysis of XANES (X-ray Absorption Near Edge Structure) spectra of MnS-1 show that the crystallization in the classic or microwave oven induces the incorporation of Mn^{3+} cations into the silicate framework of silicalite-1. The study of EXAFS (Extended X-ray Absorption Fine Structure) spectra show that the one-step hydrothermal procedure in the classical oven generate the isomorphous substitution of framework silicon in the silicalite-1 by manganese while the two-step procedure in the microwave oven bring about the incorporation of manganese into the silicate framework of silicalite-1 most probably in the form of manganese oxides.

CONCLUSION

MnS-1 nanosized crystals with the size of 100 to 200 nm were synthesized under classical or microwave hydrothermal procedures. The analysis of XANES and EXAFS spectra of the one-step-procedure-products via classical hydrothermal treatment show the incorporated Mn^{3+} into the silicalite-1 framework as framework manganese. The analysis of XANES and EXAFS spectra of the two-step-procedure-products via microwave hydrothermal treatment show the incorporated Mn^{3+} into the silicalite-1 framework most probably in the form of manganese oxides.

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