STRUCTURAL CHARACTERIZATION OF A NEW MESOSTRUCTURED MANGANESE SILICATE MnKIL-1

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INTRODUCTION

The development of nanoporous inorganic materials is of great commercial and scientific interest. A large diversity in porous materials and their properties has been developed over the years, studied and evaluated by an interdisciplinary community ranging from chemist and physicists to pharmacists and mathematicians.

Manganese is an environmentally friendly active component for numerous catalyst systems [1]. To expand the available pore size range of highly ordered manganese containing porous silicates such as MnMCM-41 with pore widths of 4 nm[2] and MnSBA-15 with pore openings of 9 nm[3], manganese containing sponge-like MnTUD-1[1] with pore openings of 4 - 9 nm was recently prepared. TUD-1 and some other mesostructured silicates, including HMS, MSU and KIT-1 show disordered mesopores and amorphous pore walls.[4] 3D pores in disordered mesostructures are interpenetrating, uniform and adjustable. The characteristics of disordered mesostructures, such as uniform pores, high surface areas and easy modification offer good opportunities in catalysis, adsorption, separation and immobilization.

We present a structural characterization of new mesostructured manganese silicate MnKIL-1 (KIL denotes Kemijski Inštitut Ljubljana) with pore openings of 16 nm. The synthesis procedure of this material is cost-effective and environmental friendly, because it is surfactant-free. A non-surfactant synthesis of mesostructured materials still represents a great challenge because few molecules with size of several nanometers possess suitable spatial structure to direct the further construction.

EXPERIMENTAL

MnKIL-1 was prepared by a two-step method containing the gel preparation and solvothermal treatment of gel. [5] Template-free MnKIL-1 was prepared by calcination at 500 ºC for 10 h using a ramp rate of 1 ºC/min in the flow of air.

XRD patterns were obtained on a Siemens D5000 using CuKα radiation (λ = 1,5406 Å). The sample was scanned over a range of $0.5 - 10^{o}$ 2θ with a step of 0.04^{o} and in the range of 5 to 60° 2θ with the step of 0.02^{o} to detect the mesostructure and the presence of manganese oxides, respectively. The mesostructure was also investigated by TEM on a 200-kV field-emission gun (FEG) microscope JEOL JEM 2010F. SEM micrograph was obtained by scanning electron microscopy on Zeiss Supra^{TM} 3VP microscope. Elemental analysis was performed by EDX method with INCA Energy system attached to Zeiss Supra^{TM} 3VP microscope. Nitrogen physisorption measurement was preformed on a Micromeritics ASAP 2020 volumetric adsorption analyzer. The BET specific surface area[6], S_{BET}, was calculated using the adsorption branch in the relative pressure range between 0.05 and 0.25. The total pore volume was estimated from the amount adsorbed at a relative pressure of 0.98, converting it to the volume of liquid nitrogen at 77 K. The mesopore volume, V_{p}, the external surface area, S_{ex}, and the total surface area, S_{t}, were determined using the α_{s}-plot method[7]

from the adsorption data for mesostructured MnKIL-1. The pore size distribution (PSD) was calculated from nitrogen adsorption data using Barrett, Joyner, and Halenda (BJH) method[8]. The maximum on the PSD was considered as the primary mesopore diameter for given sample.

RESULTS AND DISCUSSION

The low-angle powder XRD pattern shown on Figure 1A exhibited a single broad diffraction peak in the range between 0.7 and 2° 2θ with a maximum at 0.97^{o} 2θ. This diffraction peak was not observed when the second step of the synthesis (solvothermal treatment) was not performed. Single broad diffraction peak indicated disordered mesoporous MnKIL-1 with wide pore size distribution. High-angle powder XRD was employed to detect the presence of manganese oxides in mesoporous MnKIL-1. High-angle powder XRD pattern (Fig. 1B) showed only two diffraction peaks at 38.29^{o} 2θ and 44.46^{o} 2θ corresponding to aluminum sample holder. XRD pattern did not show any diffraction peaks corresponding to manganese oxide phases as it was indicated from the results of N_2 sorption analysis, described below. This could be explained with the presence of highly dispersed manganese oxide clusters with nanosized dimensions that were not detectable by XRD technique and were located on the surface and within the mesopores.
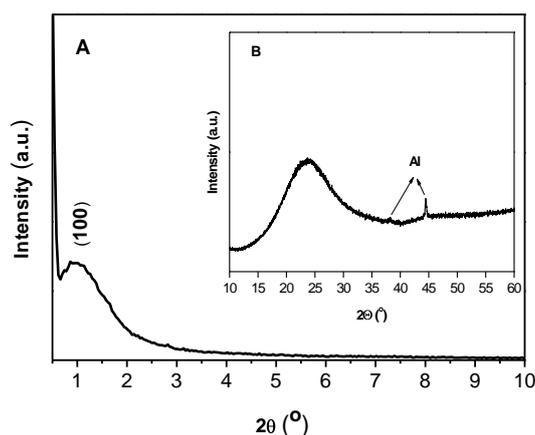

Figure 1: Low-angle XRD (A) and high-angle XRD (B Inset) patterns of new mesostructured MnKIL-1.

Mesostructure of MnKIL-1 was investigated by transmission electron microscopy (TEM) and nitrogen sorption. Figure 2A showed typical TEM image with disordered porous structure. TEM image revealed that this disordered mesostructured material possessed wormhole structure with pore openings in very broad range of dimensions (5 – 20 nm) which corresponded to low-angle XRD measurements. Mesostructured MnKIL-1 was shown by SEM micrograph (Figure 2B).
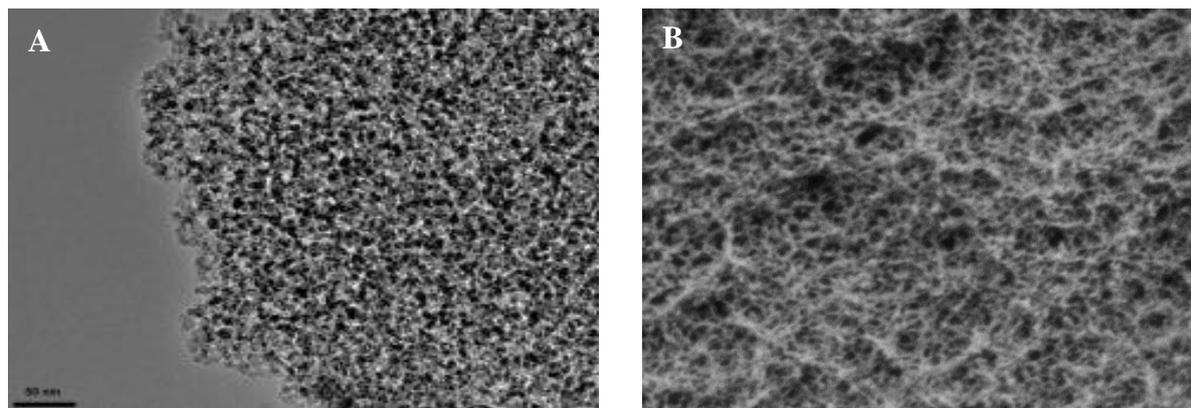
Figure 2: TEM image (A) and SEM micrograph (B) of new mesostructured MnKIL-1.

Nitrogen sorption isotherm for mesostructured MnKIL-1 was shown in Figure 3, whereas structural parameters determined on the basis of this isotherm were listed in Table 1. The nitrogen adsorption-desorption isotherm for the sample studied was typical type-IV isotherm[9,10] with a steep increase of adsorption branch at p/p_o 0.75 - 0.95 due to the capillary condensation of nitrogen in the mesopores. The BET surface area of the sample was 591 m^2g^{-1}. No micropores were present in MnKIL-1 according to α_s-plot method.
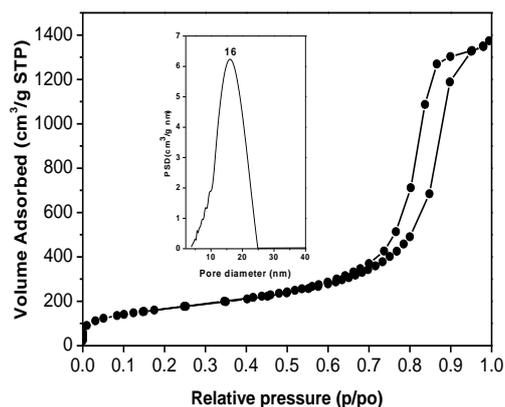

Figure 3: Nitrogen sorption isotherm with pore size distribution curve (Inset) of new mesostructured MnKIL-1.

The pore size distribution (PSD) obtained from the adsorption isotherm by BJH method was rather broad having a maximum at the pore width of 16 nm. The pore size distribution curve indicated smaller pore size uniformity as it was revealed from the results of low-angle XRD measurements and TEM micrograph, i.e. this disordered mesoporous material possessed pore widths from 5 to 25 nm.

Table 1: Textural properties of mesostructured MnKIL-1

Sample	Si/Mn	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{me} (cm^3/g)	S_{ex} (m^2/g)	S_t (m^2/g)	w_{BJH} (nm)
MnKIL-1	21.5	591	2.08	1.92	90	497	16.0

Abbreviations: S_{BET}, the BET surface area; V_t, total pore volume evaluated from adsorption isotherm at the relative pressure about 0.98; V_{me}, primary mesopore volume; S_{ex}, external surface area; S_t, total surface area; w_{BJH}, mesopore diameter.

CONCLUSION

In summary, new mesostructured manganese silicate named MnKIL-1 was synthesised using a cost-effective and environmental friendly two-step preparation method. Solvothermal treatment in ethanol in the second step of the synthesis gave rise of a wormhole silicate structure with the pore openings from 5 to 25 nm. The high surface area, large pore openings and manganese, placed in the framework with manganese oxides located in pores,[5] make this new material MnKIL-1 as an excellent candidate for catalysis and energy storage.

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