

MICRO/MESOPOROUS ALUMINOSILICATE MATERIALS VIA DUAL TEMPLATING, PART 1: SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

In a quest for optimal synthesis procedure of hierarchically porous zeolite by dual template method, a series of materials was prepared starting from zeolite yielding precursor with an addition of surfactant as a mesopore. Characterization of the obtained materials showed that all samples possess micro and mesoporous structures, which ratio depends on the amount of surfactant present in the reaction mixture. However, in the most of the samples separation of phases occurred, and crystalline zeolite phase along amorphous MCM-41 like phase were detected, except for the sample obtained from the modified precursor, where only crystalline zeolite phase was obtained, with a specific and unusual morphology. Adsorption isotherm of that sample resembles the isotherms obtained for post synthesis modified samples.

Keywords: micro/mesoporous aluminosilicate, dual template method.

INTRODUCTION

Owing to specific microporous structure, uniform sizes of channels, cages and pore openings, as well as to the presence of aluminum in the framework, zeolites are very important materials intensively applied as, for example, ion exchangers, molecular sieves, adsorbents or catalysts. However, in some cases this exceptional microporous structure presents an obstacle, for example in petrochemical or biomass catalytic reactions, when large or bulk molecules are involved [1]. Mesoporous materials, like MCM-41, that have much larger pores could satisfy these pore size demands, but they suffer, as amorphous materials, from low thermal and/or hydrothermal stability, which are usual working demands for catalytic reactions. To overcome these problems a new type of zeolite materials, hierarchical or mesoporous zeolites, has started to attract a scientific interest. Compared to microporous ones, hierarchical zeolites enclose an additional level of porosity, and thus combine and preserve important zeolite properties like hydrothermal resistance, acidity and shape selectivity, with large pores or voids for improved accessibility of active sites and increased diffusion rates of molecules [2].

Many different approaches have been introduced for preparation of hierarchical zeolites. Generally, an additional porosity could be obtained by zeolite synthesis in the presence of different mesopore or macropore forming templates or by post synthesis removal of framework atoms [3]. One of the synthetic approaches is a dual template method where, besides the usually applied micropore forming for zeolite synthesis, a surfactant as a mesopore forming has been included. However, many of dual template synthesis attempts resulted in separated micro- and mesoporous phases. It seemed that instead of working in cooperation, micro and mesopore forming acted in competition and separated phases of zeolite crystals and mesoporous materials have been obtained [4]. Better results have been reached if zeolite nanoclusters have been formed before addition of surfactant or by application of poly quaternary surfactant where the same surfactant molecule acted as micro and mesopore forming [5].

In here presented work we have applied a dual template method in attempt to avoid pitfalls of up-to-date studies and to prepare single phase, crystalline hierarchical zeolite. The main gears were modification of zeolite ZSM-5 yielding precursor and variation of surfactant hexadecyltrimethylammonium bromide (CTAB) concentrations.

EXPERIMENTAL

Chemicals used were: sodium aluminate (NaAlO_2 , Riedel de Haen, 54 % Al_2O_3 , 41 % Na_2O), sodium hydroxide (NaOH , 98 %, Kemika), Tetrapropylammonium bromide (TPABr, Sigma), hexadecyltrimethylammonium bromide (CTAB, 98 %, Alfa Aesar), Ludox30, demineralised water. The zeolite ZSM-5 precursor with the oxide formula $12.5 \text{ Na}_2\text{O}:60 \text{ SiO}_2:1 \text{ Al}_2\text{O}_3:8\text{TPABr}:4000 \text{ H}_2\text{O}$ was prepared by dissolving sodium aluminate in proper amount of NaOH solution. After obtaining a clear solution a proper amount of TPABr was added. When clear, Ludox was added; obtained gel was homogenized at room temperature for 1 hour. Afterwards a proper amount of CTAB solution was added and additionally homogenized for half an hour; CTAB/ SiO_2 ratio was varied, values 0.2, 0.1 and 0.04 were applied (samples S1, S2 and S3 respectively). For CTAB/ $\text{SiO}_2 = 0.1$, CTAB was added immediately (sample S2), or after aging at 80 °C during 3 h (S4) or 6 h (S5). Thus obtained reaction mixtures were then aged at 60 °C for 24 hours in static conditions and afterwards synthesized at 150 °C for 48 hours. After synthesis, the obtained materials were filtered, washed with copious amount of distilled water and dried overnight at 80 °C. Dry samples were calcined at 550 °C for 4 hours and subsequently converted to their hydrogen forms. The samples were characterized by XRD (RigakuUltima IV), FE SEM (ULTRA plus, Carl Zeiss) and N_2 adsorption (Micromeritics).

RESULTS AND DISCUSSION

Figure 1 shows well resolved XRD patterns characteristic for MFI type of zeolite for samples S2-S5, while S1 is evidently amorphous.

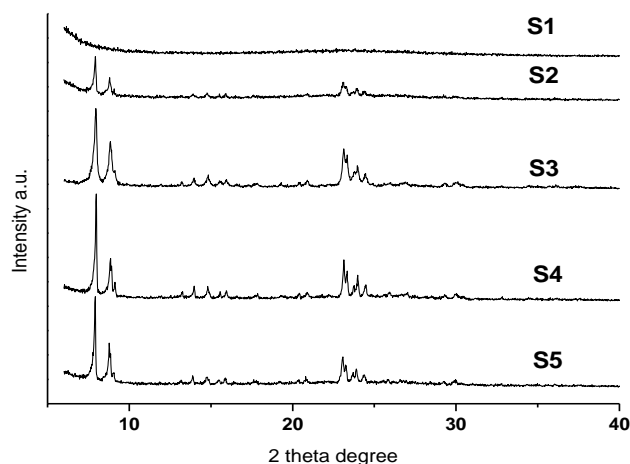


Figure 1. XRD patterns of samples S1-S5.

The morphology of prepared samples is shown in following FE SEM micrographs. Decreasing the amount of surfactant present in the reacting mixture resulted in final materials with rather pronounced morphology inconsistencies, showing irregular bulk material, some large spherical particles inside bulk matrix, and higher amount of smaller spherical particles in samples S1, S2 and S3, respectively (Figure 2).

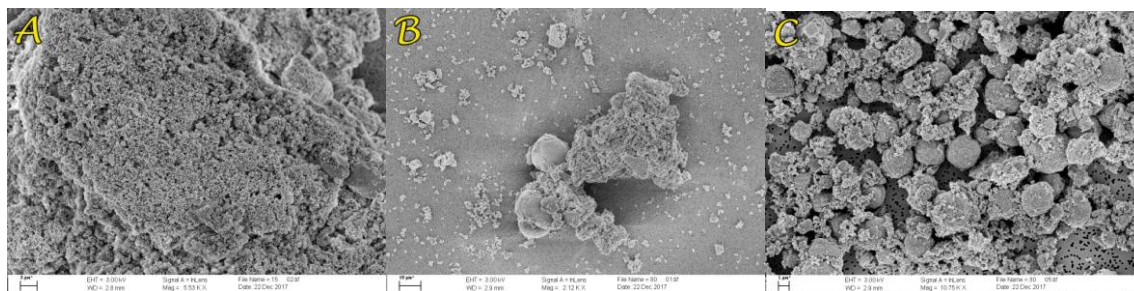


Figure 2. SEM images of sample S1(a), sample S2(b) and sample S3 (c).

Furthermore, the nitrogen adsorption measurements showed that decrease of CTAB amount in the reaction mixture resulted in reduced specific surface, decreased mesoporous and increased microporous volume of the obtained materials. Thus, mesoporous volume obtained for sample S1 (the highest amount of CTAB) was $0.87 \text{ cm}^3/\text{g}$, while for sample S3 (the lowest amount of CTAB) mesoporous volume was $0.24 \text{ m}^3/\text{g}$. At the same time microporous volume of the samples increased, and whereas in the sample S2 it had value of $0.027 \text{ cm}^3/\text{g}$, microporous volume of the sample S3 was $0.09 \text{ cm}^3/\text{g}$.

A specific morphology of the bulk in all samples resembles specific worm-like morphology. The worm like morphology of the particles was also found in investigation of the ZSM-5 zeolite crystallization, in the solid phase of the reaction mixture from the same precursor as used in this work [6]. As it was established in that investigation, ZSM-5 crystallization process goes in the sequence: gel \rightarrow worm-like particles \rightarrow condensed aggregates \rightarrow product. The worm-like particles are formed after heating of the precursor from silicate and aluminate reactive species present in the reaction mixture. They eventually aggregate into so-called condensed aggregates, which in time transform into polycrystalline spheres. The morphology of the sample S1 (Figure 2a) could be explained by high amount of CTAB in the reaction mixture that hinders aggregation of worm like particles and formation of spherical aggregates. On the other side in the samples S2 and S3 where concentration of CTAB is lower, spherical aggregates form. However, it can be seen from Fig 2b and 2c that in samples S2 and S3, respectively, a separation of phases occurred. By detailed inspection of the higher magnification of the Figure 2b, it was noticed that in sample S2, beside condensed wormlike particles and large spheres, a specific morphological features were present. These particles have laminar, leaf like morphology, which was not found in other samples. However, in spite of such morphological diversity, as the nitrogen adsorption results show, all samples include both microporous and mesoporous structure.

Figure 3 shows FESEM micrographs of the samples obtained in further experiments where zeolite precursor was aged prior the addition of the surfactant in concentration of 0.1 M. It is worth noticing that in aged samples lamellar spheroid features, sparsely found in sample S2, are present in higher amount. Large spheroid aggregates formed in sample S4 (Figure 3a) are rather rare, but are formed from elongated particles with sharp edges. In sample S5 (Figure 3b) only lamellar particles were found.

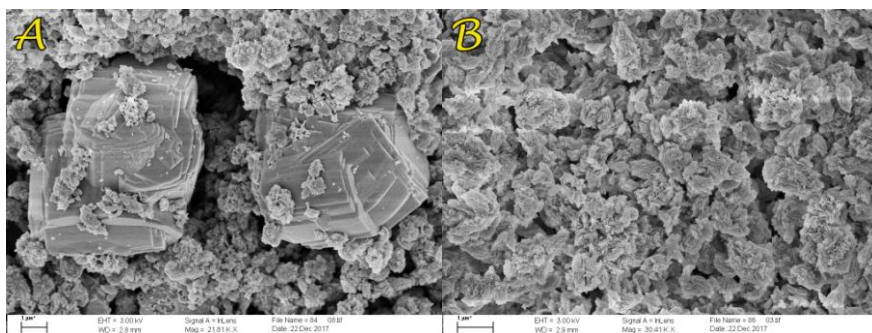


Figure 3. SEM images of sample S4 (a) and sample S5 (b).

XRD diffractogram of this sample (Figure 1) shows a well resolved pattern characteristic for zeolite of MFI structural type. Specific surface area of this lamellar ZSM-5 determined by nitrogen adsorption is 649 m²/g, and total volume $V_{\text{mic+meso}}$ is approximately 0.44 cm³/g. While the surface area of here obtained lamellar ZSM-5 is slightly higher, total volume is in agreement with the values obtained for MFI nanosheet assemblies synthesized in the presence of polyquaternary ammonium surfactant as a the only template [5] or co-template [7].

CONCLUSION

In attempt to prepare hierarchical zeolite ZSM-5 by dual template method, syntheses were performed in which a surfactant, CTAB, as a mesoporegen was added to the zeolite ZSM-5 yielding precursor. In most cases obtained materials showed separation of microporous and mesoporous phases. In syntheses where the zeolite yielding precursor was aged prior to addition of surfactant, a crystalline zeolite ZSM-5 with specific laminar morphology was obtained.

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