DISTRIBUTION OF Al SITES IN SSZ-13 ZEOLITES

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ABSTRACT

CHA-type zeolites are commercially employed materials in the exhaust gas treatment for the selective catalytic reduction of nitrogen oxides and as the main catalyst in the methanol to olefin conversion technology. In line with general trends of modern society, there is a demand to develop more environment-friendly synthesis routes and improve their performance in the mentioned applications as well as in the other potential fields of usage. For this reason, numerous studies with the aim to meet these requirements are conducted. Acidic properties and particularly the distribution of Al species represent some of the crucial features that determine the efficiency of zeolite materials. Herein is investigated the correlation between the synthesis conditions of a series of SSZ-13 zeolite materials and their respective properties are evaluated by a range of characterization techniques.

Key words: CHA-type zeolites, SSZ-13 zeolite, Al distribution, acid sites, paired sites.

INTRODUCTION

The CHA zeolite framework is built of 4-, 6-, and 8-membered rings arranged to form a tridimensional system of channels perpendicular to each other. There are many CHA-type materials such as natural chabazite mineral, low-silica synthetic chabazite, high-silica (SSZ-13) and silicoaluminophosphate (SAPO-34) chabazites. They are applied in several commercial processes: SAPO-34 is an archetype catalyst in commercial Dalian methanol to olefins process (DMTO) [1]. Na,Ca-CHA is applied for drying of acidic gases in the industry [2] and Cu-CHA materials (Cu-SSZ-13 and Cu-SAPO-34) are highly effective in selective catalytic reduction of nitrogen oxides (NOx), so they are applied for the removal of NOx in transportation diesel-powered engines [3,4]. The synthesis of alumosilicate chabazite materials is usually performed by employing zeolite Y (FAU-type) as both Si and Al source and the most commonly used organic structure directing agent (OSDA) is N,N,N-trimethyl-1-adamantammonium hydroxide (TMADAOH) [5]. Still, there is a demand to develop more environment-friendly synthesis routes and improve their performance in the mentioned applications as well as in the other potential fields of usage. For this reason, numerous studies with the aim to meet these requirements are conducted.

The acidic properties of zeolites (quantity and strength of Brønsted and Lewis acid sites, Al location and distribution, presence of framework defect sites and extra-framework species) affect the overall performance of zeolites as catalysts, sorbents and ion-exchangers [6]. For instance, in methanol dehydration reaction, the samples with paired Al sites accelerate the turnover rates by order of magnitude compared to SSZ-13 material with isolated sites [7]. It seems that the paired acid sites stabilize the surface methoxy species involved in an alternate dehydration mechanism. Further, CHA-type zeolites prepared from systems with different proportions of Al-comprising chemicals ($Al(OH)_3$ and FAU-type zeolite) have similar amount of acid sites, yet differ in the distribution of Al atoms [8]. Herein, CHA-type zeolites will be prepared from reaction mixtures with varying amounts of the OSDA. The Si environment,

presence of various OH groups and diverse Al species will be identified in order to be able to prepare CHA-type zeolite materials of controllable acidic properties.

EXPERIMENTAL

A series of SSZ-13 zeolite materials was prepared using commercial FAU-type zeolite material CBV760 obtained from Zeolyst, KOH or NaOH, TMADAOH and doubly distilled water. The initial synthesis mixtures were obtained by admixing the appropriate amount of the chemicals and were subsequently heated at 150 °C. The respective molar oxide composition of the preparation systems as well as the corresponding heating period of time is listed in the Table 1. The obtained powders have been washed, dried, calcined at 600 °C and afterwards ion-exchanged with $[Co(H_2O)_6]^{2+}$ according to the procedure reported in [9]. The features of the prepared materials were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), dynamic light scattering (DLS), thermogravimetric analysis (TGA), UV–VIS spectroscopy, nitrogen adsorption/desorption, as well as nuclear magnetic resonance (NMR), atomic absorption (AAS) and infrared spectroscopy (IR).

RESULTS AND DISCUSSION

The XRD patterns of the studied materials demonstrates they all present chabazite structure (Figure 1). The samples present Si/Al ratios of rather similar values that lie in the range of 12 to 19 (Table 1). The nitrogen adsorption/desorption experiments show the initial CHA samples exhibit high specific surface areas and micropore volumes as well as maximums of pore width distribution curves at about 0.73 nm that corresponds to the dimensions of the *cha* cage-defining ring [10].

Table 1. Molar oxide compositions of the initial synthesis mixtures, the period of heating time at 150 °C and the Si/al ratio of the end product of each reaction.

system	molar ratio of chemicals used for SSZ-13 synthesis	t / d	Si/Al
A1	1 SiO_2 : 0.005 Al_2O_3 : 0.25 KOH : 0.25 TMADAOH : 15 H_2O	6	12
A2	1 SiO_2 : 0.005 Al_2O_3 : 0.25 KOH : 0.125 TMADAOH : 15 H_2O	6	18
A3	1 SiO_2 : 0.005 Al_2O_3 : 0.2 KOH : 0.125 TMADAOH : 15 H_2O	10	19
A4	1 SiO_2 : 0.005 Al_2O_3 : 0.3 KOH : 0.125 TMADAOH : 15 H_2O	5	14
B1	1 SiO_2 : 0.005 Al_2O_3 : 0.25 NaOH : 0.25 TMADAOH : 15 H_2O	6	14
B2	1 SiO_2 : 0.005 Al_2O_3 : 0.25 NaOH : 0.125 TMADAOH : 15 H_2O	6	17
B3	1 SiO_2 : 0.005 Al_2O_3 : 0.2 NaOH : 0.125 TMADAOH : 15 H_2O	10	18
B4	1 SiO_2 : 0.005 Al_2O_3 : 0.3 NaOH : 0.125 TMADAOH : 15 H_2O	5	14

According to the TG results displayed in the Figure 2, the average content of the OSDA in the as-prepared materials is about 22 wt%. Laser light scattering data indicate the majority of the crystals in all systems is smaller than 1 μm. Based on the SEM micrographs, the morphology of the harvested crystals in all systems is found to be cubic, with a few intergrown particles. The analysis of IR spectra of the samples in the silanols band region indicates that the studied samples present isolated silanol groups. In the samples A1, A2 and A4 is observed a band at 3669 cm^{-1}. It is attributed to Lewis acid sites that could be correlated with extra-framework aluminium connected to the zeolite structure. Besides, these samples exhibit band assigned to internal silanols and a very broad band arising due to the silanol nests. On the other hand, only in the spectrum of the sample A3 are found the bands associated with Brønsted acid sites. In ^{27}Al magic angle spinning (MAS) NMR spectra of the studied series of the samples are

observed both tetrahedral and octahedral Al species. Interestingly, there are two kinds of octahedral Al entities. A range of Si moieties (Q^4, Q^3, Q^2) was detected in the ^{29}Si MAS NMR spectra. Furthermore, the enhanced signals in ^{29}Si {^1H} CP MAS NMR spectra indicate the presence of the Q^3 Si(OH) groups as well as silanol nests defects.
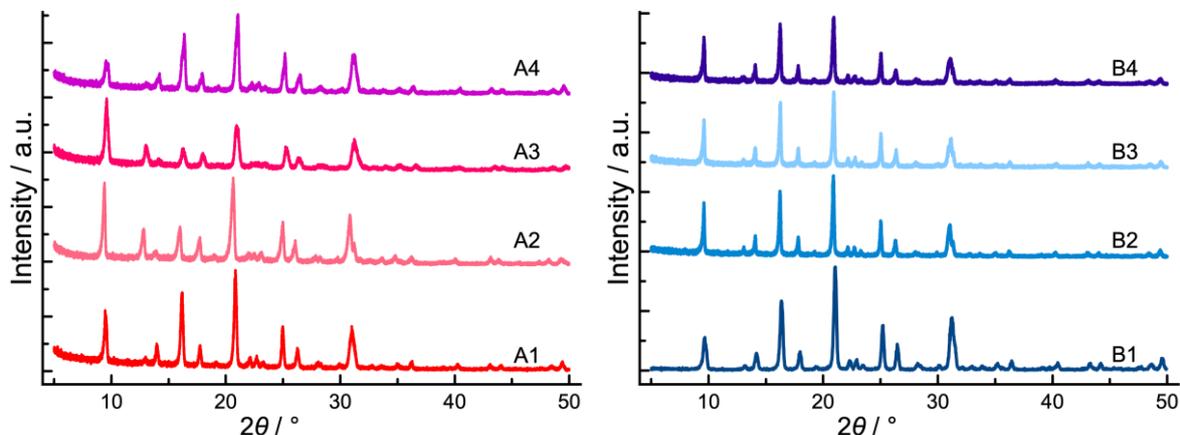

Figure 1. Powder X-ray diffraction patterns of the studied series of SSZ-13 materials.
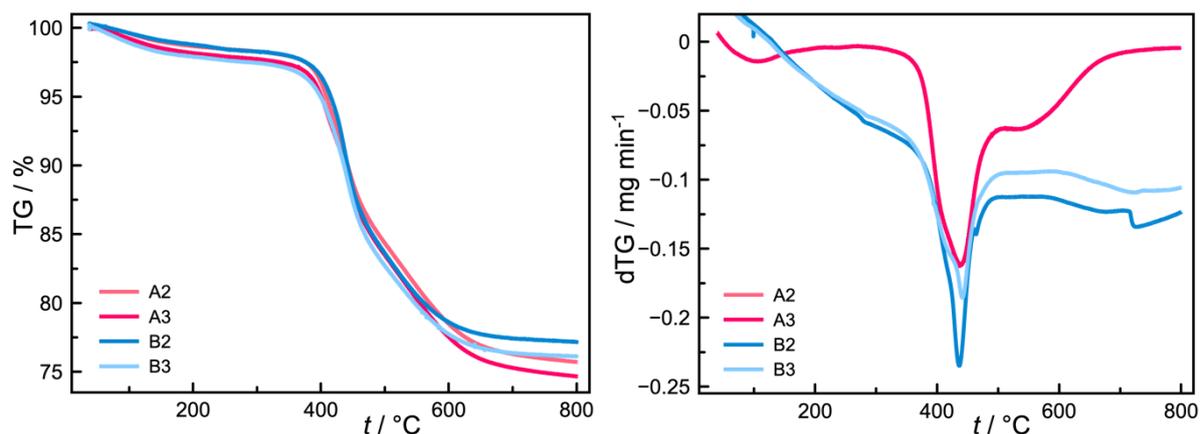

Figure 2. TGA and dTG curves of the selected studied SSZ-13 materials.

UV-VIS spectra confirm the presence of octahedrally coordinated Co entities in the samples. High weight fraction of Co in the exchanged samples suggests that there are paired Al sites (sequences Al−O(−Si−O)$_x$−Al, x = 1, 2, in the six-membered rings of the CHA framework) in the studied samples [11].

CONCLUSION

A series of nanosized high-silica SSZ-13 materials has been prepared employing TMADAOH as OSDA. Their properties have been modified via varying the alkali cation added to the initial synthesis mixture (K$^+$ or Na$^+$) as well as by changing the ratios K$^+$/TMADAOH and Na$^+$/TMADAOH. The impact of these parameters on the harvested CHA-type materials was investigated in terms of their phase, framework and chemical composition, morphological and textural features, acidic properties as well as structural defects. The results indicate that the present preparation method enables control of the Al distribution in the zeolite framework and consequently facilitated preparation of catalysts with predetermined performance.

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