Transformation of the structural units of zeolites used in the synthesis of SSZ-13

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Abstract: Zeolite SSZ-13 was found as highly active and selective catalyst in NH_3-SCR, MTO reactions. SSZ-13 (CHA) is synthesized via various methods, including direct synthesis and conversion of zeolite Y. Using of zeolites of FAU topology (Y, USY) can suggest hexagonal prisms, common for both topologies as building blocks. Herein not only new synthesis procedure with the use of zeolites X (USY), A (LTA) and ZSM-5 (MFI) as Al source is presented in classic hydrothermal and mechanochemical approach. In this work also deeper insight into nature of building blocks used for the synthesis of SSZ-13 from other topologies is shown.

Keywords: SSZ-13 zeolite, Al distribution, synthesis of SSZ-13

1. Introduction

Zeolites are widely used catalysts in many fields of industry. Recently, SSZ-13, the zeolite of CHA topology, was intensively studied as a highly active and stabile catalyst in NH_3-SCR and MTO reactions as well as due to its interesting adsorption properties[1,2]. This zeolite can be obtained by direct synthesis from source of Si and $Al(OH)_3$ or by using zeolite with FAU topology (Y, USY) as Al source[3,4]. One can suggest that using zeolites with FAU topology as Al source allow transferring straight from parent to resulting zeolite hexagonal prisms as a common for FAU and CHA topology building blocks. Answer to this question lay not only in composition of synthesis gel but in components of the gel truly transfer into lattice of the product. This issue is nontrivial and here we are showing indirect way to follow relocation of AlSiAl sequences by the use of ^{29}Si MAS NMR combined with new synthesis approach, usage of zeolites X, A, ZSM-5 as a source of Al.

2. Experimental

Synthesis procedure was developed on the basis of recipe described by Fickel and Lobo[4]. Sodium silicate (26,5% SiO_2) was mixed with water and parent zeolite, that was used as a source of Al was added. Zeolites used for syntheses were Na-forms of commercial materials: Y (USY, Si/Al=3), X (USY, Si/Al=1.2), A (LTA, Si/Al=1), and synthesized ZSM-5 zeolite (MFI) with Si/Al=12.5. Then N,N,N-trimethyl-1-adamantanamine hydroxide (TMAdOH) was added to synthesis gels and placed in the Teflon lined steel autoclaves for 6 days at 140 °C under rotation. One sample was prepared with application of the mechanochemical treatment: source of Si (Tixosil 38A, Rhodia), source of Al ($Al(OH)_3$ Fluka), NaOH, TMAdOH (40% aq solution) were mixed and milled in a planetary mill. Obtained mixture underwent crystallization at standard static conditions for 4 days. The zeolite products were washed with distilled water, dried at 350 K and calcined in the air flow. Calcined samples were repeatedly exchanged with 1 M $NaNO_3$ at RT and obtained Na-forms were further exchanged to Co-forms by 0.05M solution of $Co(NO_3)_2$. All zeolites were characterized by X-ray diffraction, SEM and ^{27}Al and ^{29}Si MAS NMR.

3. Results and discussion

The synthesized SSZ-13 samples exhibited XRD reflections corresponding to SSZ-13 topology without showing any other crystalline phases. SEM micrographs show crystallites ranging in dimension from 0.5 to 5 μm. ^{27}Al MAS NMR spectra of all investigated samples exhibited only resonance with ^{27}Al observed chemical shift around 55 ppm, the resonance around 0 ppm was not observed. This evidences exclusive presence of framework Al atoms in investigated samples. The chemical composition of investigated samples together with the maximum $[Co(II)(H_2O)_6]^{2+}$ ion exchange capacity is concluded in the Table 1.

Table 1. Chemical composition of obtained SSZ-13 samples

Sample	Si/Al	Co/Al
SSZ-13-Y	7.6	0.35
SSZ-13-X	6.0	0.16
SSZ-13 (A)	5.6	0.15
SSZ-13 (ZSM-5)	13	0.06
SSZ-13 (machanochemical)	7.2	0.12

^{29}Si MAS NMR allows to analyze surrounding of Si atoms in the lattice and calculate percent of AlSiAl sequences transferred from parent zeolites into resulting SSZ-13 material. In X zeolite (LTA) (Si/Al 1), Si(4Al) atoms predominate in the framework followed by small fraction of Si(1Si, 3Al). In the hexagonal prism at least 3 Si atoms have 3 Al neighbors that will be reflected in SSZ-13 product as Si(1Si,3Al) or Si(4Al) atoms. The ^{29}Si MAS NMR spectrum of SSZ-13-X does not exhibit resonance attributable to Si(4Al) or Si(1Si, 3Al). This evidences that hexagonal prisms were not used in the building of SSZ-13 framework. X- and A-types zeolites contain 4-, 6- and 8-rings formed by only AlSiAl sequences that could be transfer to product. The AlSiAl sequences are well known to accommodate divalent cations. Thus, $[Co(II\ )(H_2O)_6]^{2+}$ ion exchange capacity supposed to be significantly higher than presented in Table 1. While synthesis of SSZ-13 from zeolite ZSM-5 of MFI topology with domination of 5-rings not present in CHA was successful, it can be assumed that disintegration of parent zeolite into noncyclic silicate and alumosilicate species is essential step in the synthesis. Low ion exchange capacity can be explained by formation of Al triads in 6-ring allowing accommodation of only one divalent cation.

4. Conclusions

The analysis of Si(1Si,3Al), Si(2Si,2Al), Si(3Si,1Al) and Si(4Si) atoms in SSZ-13 and parent zeolites X and A, together with comparison of CHA, FAU, LTA and MFI lattices allowed to suggest nature of building blocks used for the synthesis of SSZ-13 and coming from the disintegration of parent zeolites to linear alumosilicate (AlSiAlSiAl or SiAlSi) structures. AlSiAl sequences are transferred to SSZ-13 framework as chains with 3 Al atoms (at least 5 T atoms) – Al triads and form 6-ring Al. Triads in 6-MR are separated each from other and able to accommodate only one divalent cation (three Al to one M(II)) caused low ion exchange capacity for M(II) ions. Obtained results stress the crucial role of organic SDA in the building of the frameworks of Si-rich zeolites during synthesis without seeds. Parent zeolite serves thus rather as a source of oligomeric chains of tetrahedral Si and Al atoms which can be easy incorporated to the zeolite framework. A source of large building blocks of defined structure is not required. This opens the possibility to use zeolites without respect to similarity of structural units in the parent and targeted frameworks for the synthesis of zeolites with novel topologies.

References

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