



Al-rich beta zeolites. Distribution of Al atoms in the framework and related protonic and metal-ion species



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ABSTRACT

Al-rich BEA* zeolites with Si/Al 4.5 and 5.1, prepared by a template-free synthesis, were compared to a conventional (Si-rich) BEA* (Si/Al 11.3) regarding (i) the distribution of Al atoms in the framework, (ii) the behavior of the H-BEA* samples at high temperature, and (iii) the nature of charge balancing counter metal-ion species. ²⁷Al and ²⁹Si (CP) MAS NMR, and FTIR of adsorbed *d*₃-acetonitrile and UV–Vis spectroscopy of Co(II) ions as probes of close Al atoms were used and the study was further supported by DFT molecular dynamic calculations of Co(II) sites in the BEA* zeolites. In contrast to the Si-rich BEA*, the Al atoms in the Al-rich BEA* are mostly arranged in AlSiAl sequences with their Al atoms facing two different channels, which thus cannot bind bare divalent ions. Conversely, two Al atoms from two different AlSiAl sequences can face the same channel and they represent close unpaired Al atoms located in two different rings. They can be compensated by [Co(II)(H₂O)₆]²⁺, and in dehydrated zeolites by protons, monovalent metal-ions, and metal-oxo structures such as formally monovalent [Co(III)O]⁺. Only Al atoms in AlSiAl sequences in one ring and a minor fraction of AlSiAl sequences face the same channel and thus they can be balanced by bare divalent cations. Therefore, the Al-rich and conventional Si-rich BEA* differ substantially in the population of AlSiAl sequences, but not in the Si–Al arrangement in the inner surface of zeolite channels which is relevant for binding counter-ion species. The concentration of acid and redox sites in Al-rich BEA*, the potential catalytic active sites, is proportional to the increased Al content in the framework, but without marked change of their structure.

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1. Introduction

Beta zeolites (the BEA* topology, polymorphs A and B) of molar Si/Al > 11 composition belong to the most widely used aluminosilicates applied as catalysts in petrochemical technologies, syntheses of chemical commodities as well as fine specialties. The framework of the beta zeolite possesses three-dimensional intersecting channels of 6.6 × 6.7 Å size [1] providing advantageously easy diffusion even of voluminous organic molecules [2]. The recent discovery of the synthesis of new Al-rich beta zeolites with Si/Al molar ratios of 4–5 (i.e., a markedly increased concentration of framework Al atoms and thus the total negative charge of the framework) represents a substantial step ahead in future advanced applications of zeolites of the BEA* topology [3–9]. The high concentration of framework Al atoms enables the accommodation of a much higher

amount of protonic and/or metal-ion species compared to Si-rich BEA*. In addition, since Al-rich beta zeolites are prepared by employing a template-free hydrothermal synthesis route using seeding of BEA* crystals, their production in a large industrial scale could lead to great cost–benefits compared to conventional Si-rich beta zeolites synthesized exclusively in the presence of templates.

A high activity of Al-rich beta zeolites has been demonstrated for the first time for acid-catalyzed reactions, specifically of cumene [4] and n-decane cracking [10], and alkylation of benzene [6,7,10]. The benefit of a high concentration of Al in Al-rich BEA* and thus an increased concentration of various metal-ion and metal-oxo species has been manifested in the high activity of Al-rich Fe- and Cu-BEA* in selective reduction of nitrogen oxides and N₂O decomposition [10,11]. Since the structure and location of acidic or metal-ion sites, decisive for their catalytic function, are directly related to the location and distribution of Al atoms in the framework [12–18], we attempt to analyze the arrangements and properties of Al atoms in Al-rich BEA* and relate them to the structure of counter-ion species.

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AlSiAl sequences are absent in the framework of Si-rich pentasil-ring zeolites ($\text{Si}/\text{Al} > 8.5$) of the MFI, FER, MOR, and BEA* topology [13,15,16]. The framework Al atoms are predominantly organized as either isolated Al atoms located in different rings or Al atoms forming AlSiAl sequences located in 6MRs creating cationic sites for divalent cations [13,17,18]. On the contrary, ^{29}Si MAS NMR spectroscopy experiments on Al-rich BEA* [6,7,10] revealed a significant presence of Si(2Si,2Al) atoms, i.e. AlSiAl sequences in the framework. This finding shows significantly different Si–Al arrangements in the Al-rich and Si-rich beta zeolites. This study analyzes the Si–Al arrangements in the channel surface of the framework of Al-rich beta zeolites governing binding of counter metal-ion species, and compares them to those in Si-rich beta zeolites. It is based on the evaluation of (i) the coordination of Al atoms in the zeolite obtained from ^{27}Al MAS NMR spectroscopy and IR spectroscopy of OH groups and adsorbed d_3 -acetonitrile on acid sites, (ii) distribution of framework Al atoms as obtained from ^{29}Si (CP) MAS NMR, and (iii) related coordination of counter-ion Co(II) species in hydrated and dehydrated zeolites monitored by UV–Vis spectroscopy and IR spectra of adsorbed d_3 -acetonitrile, supported by molecular dynamic calculations.

2. Experimental

2.1. Preparation and characteristics of BEA* samples

Two Al-rich BEA* zeolites of Si/Al molar ratio of 4.5 and 5.1 (hereafter designated as BEA/4.5 and BEA/5.1) were synthesized hydrothermally from aluminosilicate mixtures of molar compositions of $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{NaOH}/\text{H}_2\text{O}$ of 1:26.2:17.2:911 and 1:40:26:1000, respectively, employing no organic template. Calcined crystals of the beta zeolite of Si/Al 11.5 (Lot. # TZB-212, Tricat) in amount of 0.052 g per 1 g SiO_2 or of Si/Al 12.0 (synthesized using TEOH) in amount of 0.100 g per 1 g SiO_2 were used for the seeding. Details are given in the [Supplementary Material](#), hereafter designated as SM, (SM1). The obtained BEA* products were four times ion-exchanged with 0.5 M NH_4NO_3 to yield NH_4 -BEA/4.5 and NH_4 -BEA/5.1 which were converted into H-BEA/4.5 and H-BEA/5.1 by deammonization at 500 °C.

The Si-rich beta zeolite (Si/Al 11.3, containing a template, hereafter designated as BEA/11) was kindly supplied by Zeolyst International (CP 814B-25, Lot. No. 814B-25-1597-77). The sample was heated in an ammonia stream at 420 °C for 3 h to remove the template by the procedure of Creighton et al. [19], which guarantees preserving Al atoms in the framework. NH_4 -BEA/11

was deammoniated in a stream of O_2 at 520 °C for 2 h to give H-BEA/11. Chemical composition of zeolites is given in [Table 1](#). A part of NH_4 -BEA* samples was ion-exchanged with Na^+ ions to obtain Na-BEA* (for NMR measurements), thereafter exchanged with Co (II) ions to yield Co-BEA* zeolites (see below).

XRD patterns (Bruker D8 Instrument, Bruker AXS, U.S.A.) and scanning electron microscopy images (Jeol JSM-03 Instrument) of the samples showed well-developed crystalline BEA* structure with crystal dimensions of ca 0.4 μm for BEA/4.5 and BEA/5.1, and 0.05 μm for BEA/11 (SM2A). The XRD patterns are typical for BEA* structure (SM2B). A higher intensity of XRD reflections for BEA/4.5 and BEA/5.1 compared to BEA/11 reflects their larger crystals of well-developed structure. The characteristic reflections were shifted by ca 0.3 2θ to lower values for BEA/4.5 and BEA/5.1 compared to BEA/11 due to the higher Al content and thus increased unit cell parameters. Also ^{27}Al and ^{29}Si MAS NMR spectroscopy of Na-BEA* indicated well-developed structures with Al atoms exclusively tetrahedrally coordinated and the $\text{Si}/\text{Al}_{\text{FR}}$ values close to those of chemical $\text{Si}/\text{Al}_{\text{bulk}}$ analysis. The XPS experiments showed that the distribution of Al along the crystals is homogeneous within the accuracy of the XPS Al 2p and Si 2p analysis, as the differences between $\text{Si}/\text{Al}_{\text{surf}}$ (XPS) and $\text{Si}/\text{Al}_{\text{bulk}}$ (chemical analysis) were below 10 rel.%.

For the purpose of analysis of the distribution of Al atoms in the framework of BEA* zeolites, the Co(II) ions were exchanged into Na-BEA* samples using 0.05 M $\text{Co}(\text{NO}_3)_2$ solution (strictly three-times at RT following by thorough washing) to guarantee the exclusive exchange of divalent $[\text{Co}(\text{II})(\text{H}_2\text{O})_6]^{2+}$ complexes (for details see Refs. [14,18,20]). The composition of Co-BEA* zeolites is given in [Table 2](#).

2.2. Structural analysis

The ^{29}Si and ^{27}Al MAS NMR spectra were measured employing a Bruker Avance 500 MHz (11.7 T) Wide Bore spectrometer using ZrO_2 rotors. For the ^{27}Al MAS NMR experiment, high-power decoupling pulse sequence with a $\pi/12$ (0.7 μs) excitation pulse, 1 s relaxation delay, and rotation speed of 12 kHz were applied to fully hydrated samples. The chemical shifts were referenced to the aqueous solution of $\text{Al}(\text{NO}_3)_3$. ^{29}Si MAS NMR single pulse and cross-polarization spectra were measured at a rotation speed of 7 kHz, with a $\pi/6$ (1.7 μs) excitation pulse and relaxation delay of 30 s for single pulse spectra. For the cross-polarization spectra, pulse sequences with 50% ramp CP pulse, 2000 μs contact time, high-power decoupling, and 5 s relaxation delays were employed. ^{29}Si high-power decoupling spectra were decomposed to the Gauss-Lorentzian bands using DMfit software [21]. The framework aluminum content ($\text{Si}/\text{Al}_{\text{FR}}$) was estimated using the standard approach from the single pulse spectrum according to the formula:

$$\text{Si}/\text{Al}_{\text{FR}} = I/(0.25I_1 + 0.5I_2) \quad (1)$$

where I_1 denotes the intensity of the NMR resonance of the Si (3Si,1Al) and I_2 corresponds to the Si(2Si,2Al) atoms, and I denotes the total ^{29}Si intensity; for details see Refs. [22,23].

The concentrations of Brønsted and Al-Lewis sites in H-BEA* zeolites, which depend on the temperature of their evacuation, were determined by adsorption of d_3 -acetonitrile (13 mbar CD_3CN at RT for 20 min) on the zeolite samples (prior evacuated at 450, 500, 550, and 600 °C) with a subsequent evacuation for 15 min at RT. The interactions of $\text{C}\equiv\text{N}$ groups with Brønsted and Lewis sites were manifested in their characteristic vibrations at 2292–2298 cm^{-1} and 2325 cm^{-1} , respectively. For quantitative analysis, the extinction coefficients of $\varepsilon_{\text{B}} = 2.05 \text{ cm} \mu\text{mol}^{-1}$ and $\varepsilon_{\text{L}} = 3.60 \text{ cm} \mu\text{mol}^{-1}$ obtained in Ref. [24] were used.

The concentration of bare Co(II) ions in cationic sites of Co-BEA* samples (dehydrated in vacuum at 500 °C) was obtained from the

Table 1
Composition and acid sites of H-BEA* zeolites.

| Sample | Si/Al | Acid sites | | |
|-----------|-------|------------------------|--|--|
| | | T^{a} (°C) | c_{B}^{b} (mmol g $^{-1}$) | c_{L}^{b} (mmol g $^{-1}$) |
| H-BEA/4.5 | 4.5 | 450 | 1.82 | 0.41 |
| | | 500 | 1.72 | 0.56 |
| | | 550 | 1.43 | 1.11 |
| | | 600 | 0.93 | 1.57 |
| H-BEA/5.1 | 5.1 | 450 | 1.61 | 0.60 |
| | | 500 | 1.24 | 0.82 |
| | | 550 | 1.23 | 0.86 |
| | | 600 | 1.21 | 0.99 |
| H-BEA/11 | 11.3 | 450 | 0.63 | 0.32 |
| | | 500 | 0.54 | 0.33 |
| | | 550 | 0.49 | 0.46 |
| | | 600 | 0.46 | 0.56 |

^a Temperature of evacuation for 3 h prior to the CD_3CN adsorption.

^b Concentration of Brønsted and Lewis sites, respectively, from FTIR spectra of adsorbed CD_3CN .

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