



Acid and redox activity of template-free Al-rich H-BEA⁺ and Fe-BEA⁺ zeolites



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ABSTRACT

Al-rich template-free BEA⁺ zeolite (Si/Al 4.6) was synthesized and its structure was analyzed in comparison with the conventional H-BEA⁺ zeolite of Si/Al 11.3 using XRD, N₂ sorption, SEM, FTIR, ²⁷Al 3Q and ²⁹Si MAS NMR spectroscopy, and DFT calculation of the deprotonation energies. The Al-rich H-BEA⁺ exhibited a high concentration of Brønsted and Lewis sites, both of high acid strength, although AlSiAl sequences were present in the framework. In Al-rich Fe-BEA⁺ the exchanged Fe ions, Fe-oxo species, and Fe-oxo oligomers were identified by UV-vis spectroscopy. Cracking of *n*-decane, alkylation of benzene with benzyl alcohol and hydroamination of styrene with aniline to (*anti*)Markovnikov phenyl-[2-phenylethyl]amine over H-BEA⁺, and decomposition of N₂O and NH₃-SCR-NO_x over Fe-BEA⁺ were investigated in relation to the concentration and nature of acid and Fe-redox sites. The high concentration of Al-related active sites and the highly regular structure of Al-rich beta zeolite are directly manifested in enhanced activity compared with conventional Si-rich beta zeolite.

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1. Introduction

High-silica zeolites possessing strongly acidic protons, such as dealuminated faujasites, mordenites, MFI, and beta (BEA⁺) zeolites, represent important zeolite structures employed as catalysts in fluid catalytic cracking and hydrocracking units converting oil fractions to valuable gasoline and diesel fuels, as well as in production of petrochemicals [1]. In addition, cationic species in zeolites with low Al concentrations with MFI, BEA⁺, or FER topologies exhibit extraordinary redox behavior employed in selective oxidation of hydrocarbons [2], selective conversion of N₂O/NO/NO₂ to molecular nitrogen by N₂O decomposition [3], and SCR of NO/NO₂ using NH₃ [4] or hydrocarbons [5], employed in the end-pipe gases of chemical plants, electric power stations, and exhaust gases of diesel engines.

Zeolite beta (BEA⁺, consisting of three A, B, and C polymorphs) [6] is assembled from 4-, 5-, and 6-membered rings forming an intersecting three-dimensional (3D) channel structure with 12-membered ring openings of 6.6 × 6.7 Å (Fig. 1). Its larger 3D 12-ring inner pores compared to 10-ring pores in MFI, only

monodimensional 12-ring pores of MOR, and absence of cavities existing in Y zeolites represent a great advantage for fast diffusion of bulkier molecules participating in oil processing, dewaxing and isomerization of paraffins, and benzene alkylation with low olefins, as well as organic specialty manufacturing. However, a substantial shortcoming for wider industrial application of the beta zeolite is the need to use expensive tetraethylammonium hydroxide (TEAOH) as a template for its hydrothermal synthesis, providing the beta framework for Si/Al > 11.

Since 2008, the successful synthesis of the template-free and Al-rich beta zeolite with Si/Al ~ 4.5 was reported by Xie et al. [7], Majano et al. [8], Kamimura et al. [9], and Kubota et al. [10] using calcined beta seeds added to the aluminosilicate gel. These procedures yielded a beta zeolite of high crystallinity and well-developed crystallites with dimensions about 0.3–0.5 μm. As could be expected, the increased concentration of Al in the beta zeolite with Si/Al ~ 4.5 obtained by the template-free route is accompanied by an increased ion-exchange capacity for protons, metal cations, and metal-oxo complexes.

Very recently, a collaborative effort among several laboratories [11,12] yielded a comparison of the structure, framework Al, and crystal size of the Al-rich beta zeolite (Si/Al 4.6) obtained by template-free synthesis with those of the standard BEA⁺ (Si/Al

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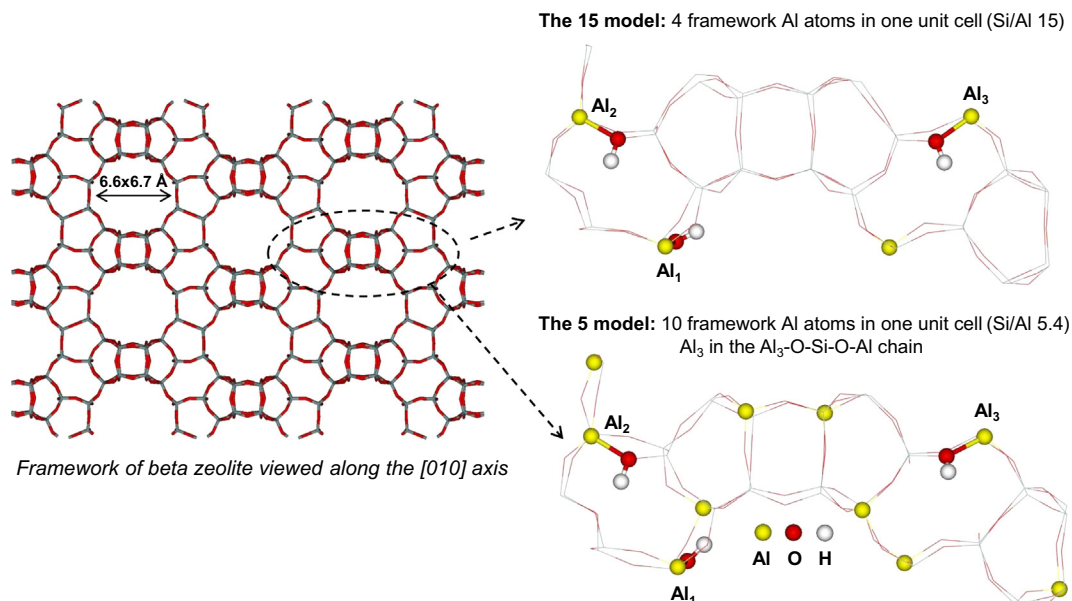


Fig. 1. Illustration of the structure of the beta zeolite and structural models of the zeolite with 4 and 10 Al atoms in one unit cell (molar Si/Al ratio of 15 and 5.4, respectively) used for the calculation of deprotonation energies of the corresponding Brønsted acid sites.

12) synthesized using TMAOH and of their activities in several acid-catalyzed reactions (hydrocarbon alkylation, hydroisomerization, and acylation). The authors showed that, in addition to the higher concentration of Al in the framework, the template-free beta zeolite exhibited more regular crystalline structure and slightly larger crystals (0.3–0.5 μm). While the larger crystals were connected with faster zeolite deactivation in benzene alkylation with ethylene, the higher concentration of strong acid sites greatly increased yields of cracked products in *n*-decane hydrocracking at low temperatures. Low activity in the acylation of anisole with acetic anhydride was observed over the Al-rich BEA⁺ and its dealumination to Si/Al 9 was necessary for a high 54% yield of *p*-methoxyacetophenone at 99% selectivity due to transport limitations [13]. Kubota et al. [10] showed that steaming of Al-rich BEA followed by partial dealumination using nitric acid provides a selective catalyst for high-temperature cracking of hexane to propene.

The results obtained to date on the activity of template-free BEA⁺ in acid-catalyzed reactions raised new questions on (i) the strength of bridging OH groups in Al-rich BEA⁺, (ii) the structure and concentration of the metal counter-ions and metal-oxo species, and (iii) the related activity of H- and metal-Al-rich BEA⁺ zeolite in acid- and redox-catalyzed reactions.

In the present study, we compare the synthesized template-free BEA⁺ (Si/Al 4.6) and commercial beta zeolite (Si/Al 11.3, synthesized using TMAOH) with respect to (i) the concentration and strength of the protonic Brønsted sites and the occurrence of Lewis sites, (ii) the ion-exchange capacity for Fe ions and Fe-oxo complexes, and (iii) the crystal size and texture. These parameters are related to the activity and selectivity of BEA⁺ zeolites with quite different Al content in their H-form for acid-catalyzed and Fe-BEA⁺ in redox-catalyzed reactions. In this respect, it is demonstrated that enhancement is attained in cracking of *n*-decane to olefins and paraffins as well as transformation of bulkier molecules, the precursors for synthesis of natural products, pharmaceuticals, cosmetics, etc. In the alkylation of benzene by benzyl alcohol to diphenylmethane and hydroamination of styrene with aniline, the shape-selective effects, crystal size, and diffusion constraints are considered in addition to the increased concentrations of active acid sites. For redox-catalyzed reactions, we demonstrate a marked increase in the concentration of Fe ions and Fe-oxo species and an

enhancement of the activity of Al-rich Fe-BEA⁺ compared to conventional Si-rich Fe-BEA⁺ in N₂O decomposition and NH₃-SCR-NO_x to molecular nitrogen.

2. Experimental

2.1. Preparation of H-BEA⁺ and FeH-BEA⁺

Al-rich beta zeolite was hydrothermally synthesized by a procedure based on the reports in Refs. [7–9,14] using seeding of calcined beta crystals of Si/Al 11.5 (TZB-212, Tricat) in an amount of 0.052 g per 1 g SiO₂. A starting aluminosilicate mixture with a molar ratio of Al₂O₃/SiO₂/NaOH/H₂O 1:26.2:17.2:911 was prepared from NaAlO₂ and fumed silica (Cabosil). An amount of 10 g NaAlO₂ was dissolved in 1000 ml deionized water followed by addition of 42 g NaOH, stirring for 40 min, addition of 96 g silica, stirring for 10 min, and addition of 5 g of beta zeolite seeds, after which mixture homogenization took place for 5 min at room temperature. The mixture was treated hydrothermally at 120 °C for 125 h in a 2500-ml autoclave with very slow stirring under autogenic pressure. The obtained solid product was separated by filtration, washed with deionized water, and dried at 80 °C for 6 h. The zeolite product has a molar Si/Al ratio of 4.6 and was denoted as BEA-5. The BEA-5 sample was ion-exchanged three times with 1.0 M NH₄NO₃, yielding NH₄-BEA-5 and, after deammonization at 500 °C, obtaining H-BEA-5. The beta zeolite (containing template) with Si/Al 11.3 was kindly supplied by Zeolyst International (CP 814B -25, Lot. No. 814B-25-1597-77). This type of beta sample is widely used for preparation of zeolite catalysts and as a standard for comparing the activities of various zeolites. The sample denoted as BEA-11 was prepared from this zeolite by calcination in an ammonia stream at 420 °C for 8 h to remove the template, according to the procedure first described by Creighton et al. [15]. This procedure yields a charge balance of the framework AlO₄⁻ by NH₄⁺ ions and thus preserves Al in the framework sites [16]. The NH₄-BEA-11 was deammoniated by calcination in a stream of O₂ at 520 °C for 2 h to H-BEA-11. The chemical compositions of both H-BEA⁺ samples are given in Table 1. Na-forms of beta zeolites for NMR measurements were obtained by Na⁺ ion exchange with NaNO₃ of part of the NH₄-BEA-5 and H-BEA-11.

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