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Unprecedented propane–SCR-NO$_x$ activity over template-free synthesized Al-rich Co-BEA* zeolite

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ABSTRACT

An Al-rich Co-BEA* zeolite (Si/Al 4.2, Co/Al 0.5) was prepared by organotemplate-free hydrothermal synthesis and $[Co(II)(H_2O)_6]^{2+}$ ion exchange. The structure of the Co species and their activity in C_3H_8–SCR-NO$_x$ were compared to that of Si-rich Co-BEA* (Si/Al 11.3). The high population of AlSiAl sequences in Al-rich BEA* with AlO_4^- facing different channels, contrary to their absence in Si-rich BEA*, results in dehydrated Co-BEA* in easily reducible counter-ion $[Co(III)O]^+$ species attached to one AlO_4^-. The high concentration and density of these Co-oxo species in Al-rich Co-BEA* facilitates extraordinarily high SCR-NO$_x$ rate even under water vapor up to 10 vol.%, twelve-times outperforming Si-rich Co-BEA*. The five-to-six times increased TOF and easier reducibility suggest a synergetic redox effect of water-resistant Co-oxo species. The Al-rich Co-BEA* provides the highest reaction rate at conditions of wet NO$_x$ streams, exceeding that previously reported for metal ion/oxo zeolite catalysts, with a high selectivity to molecular nitrogen and efficient utilization of propane.

1. Introduction

Development of a functional catalyst for selective catalytic reduction of nitrogen oxides by hydrocarbons, particularly propane, methane or long-chain paraffins (SCR-NO$_x$) under real NO$_x$ streams containing low concentrations of NO/NO$_2$ (~1000 ppm) in the presence of high concentration of water vapor (1–10%) remains a great challenge for heterogeneous catalysis [1–5]. Cobalt counter-ion species in conventional (Si-rich, Si/Al > 12) zeolites of BEA* and MFI topology have so far exhibited the highest SCR-NO$_x$ activity and selectivity in reduction of NO$_x$ to nitrogen by propane in a broad temperature range among all the types of investigated catalysts [2,6–8]. Besides stabilization of various types of counter-ion Co species, the advantage of these crystalline matrices lies in their three-dimensional channel structures with 10-member ring (10MR) openings for MFI and particularly with 12MR openings for BEA* topology offering fast intra-crystalline diffusion of reactants and products through zeolite pores [7].

The concentration, structure and location of incorporated Co species represent key parameters governing the SCR activity and selectivity for nitrogen [9–18], which are inevitably controlled by the overall and local negative charge of the zeolite framework [19,20]. For the Si-rich Co-beta and Co-ZSM-5 zeolites, it has been shown that the single exchanged Co(II) ions coordinated exclusively with the oxygen atoms of the framework rings containing Al pairs (AlSiSiAl sequences) and forming cationic sites are active in propane–SCR-NO$_x$ [21,22] only in the absence of water vapor or at temperatures when water adsorption does not take place on these electron-acceptor Co sites. Much higher activity, which is moreover preserved in wet gas streams, was found for counter-ion Co-oxo species adjacent to isolated framework Al atoms and populated predominantly at higher Co loadings in ZSM-5 and beta zeolites [21,22].

To reach high concentration of incorporated counter-ion Co species, moreover, of appropriate structure and redox properties relevant for the SCR-NO$_x$ reaction, a high concentration of Al atoms in the framework and their optimal mutual arrangement are necessary [22]. The concentration of the active Co-oxo species could be increased at the expense of less active bare Co(II) species by

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optimizing the distribution of Al atoms in the framework of the parent zeolites [21].

The recently discovered new procedure for the hydrothermal synthesis of the Al-rich beta zeolite with a high concentration of Al in the framework has opened the way for preparation of Co zeolite-based catalysts with a high concentration of Co species. Borade and Clearfield [23,24] developed a new synthesis route for high substitution of Al in the tetrahedrally coordinated SiO_4 framework of the beta zeolite (Si/Al 4.5) from a dense system containing a minimum of template. Later studies [25–37] led to the synthesis of Al-rich beta zeolites of Si/Al $\geqslant$ 4 employing seeding of Si-rich BEA* crystals and in the complete absence of an organic structure-directing agent like tetraethyl ammonium hydroxide (TEAOH). The first results showing the prospect for Al-rich beta zeolites as a base for redox catalysts have been reported for Fe [37,38], Cu [39], and Pt [40] catalysts. Al-rich Fe-BEA* reached the highest activity among Fe-zeolite catalysts in NH_3–SCR-NO_x, and substantially enhanced the reaction rate in N_2O decomposition [37] and capture of NO at low concentrations [41].

In this study we show the superior activity of the Al-rich Co-beta zeolite in propane–SCR-NO_x, even in the presence of water vapor, remarkably outperforming that of the so-far most active Si-rich Co-BEA* and Co-MFI catalysts. Detail analysis of the arrangement of Al atoms in the framework of Al-rich beta zeolites described in an preceded paper [42] enabled investigation of the structure, location and activity of Co species in propane–SCR-NO_x with regard to the arrangement of framework Al atoms and to compare it to those of Si-rich Co-BEA*.

2. Experimental

2.1. Preparation of Co-zeolites

Al-rich BEA* was hydrothermally synthesized using a template-free procedure with seeding of calcined beta crystals (TBZ 212, Tricat) and an aluminosilicate mixture with a molar ratio of Al_2O_3/SiO_2/NaOH/H_2O 1.00:31.7:20.7:1110.5 originating from $NaAlO_2$ (Sigma Aldrich, 13404, Lot # SZBA2440), fumed silica (Aerosil) and NaOH. The synthesis gel was prepared by mixing 8.0 g of fumed silica, 3.475 g of NaOH, 0.775 g of $NaAlO_2$, 82.00 g H_2O and 0.400 g of zeolite seeds. Hydrothermal synthesis was performed in 200 ml autoclaves without agitation at a temperature of 120 °C under autogeneous pressure for 120 h. The obtained zeolite with a molar Si/Al ratio 4.2 was denoted as BEA/4.2. The beta zeolite with Si/Al 11.3 (CP814B-25, Lot. No. 814B-25-1597-77, denoted as BEA/11), was kindly supplied by Zeolyst International as a material widely used for preparation of zeolite catalysts. The template was removed by careful zeolite heating in an ammonia stream followed by calcination up to 550 °C according to the procedure described in Ref. [37]. ZSM-5 with Si/Al (15.3) provided by the Research Institute of Petroleum and Hydrocarbon Gases (Slovnaft, Slovakia) was denoted as ZSM-5/15 (see the Supplementary Materials). The composition of BEA* zeolites is given in Table 1. Detailed structural analysis of the BEA/11 and ZSM-5/15 parent zeolites has been reported elsewhere [37,43].

All the zeolites were ion-exchanged three times with 0.5 M NH_4NO_3 to obtain the NH_4^+-form. Co-BEA/4.2, Co-BEA/11 and Co-ZSM-5/15 were prepared by threefold ion-exchange at RT (24 h) of the respective zeolites in their NH_4^+ forms with 0.05 M aqueous $Co(NO_3)_2$ solution (100 ml g^{-1}) followed by washing with demineralized water and drying in the open air. The chemical composition of Co-BEA* zeolites is given in Table 2.

2.2. Structural analysis

X-ray diffractograms were recorded using a Bruker D8 instrument (Bruker AXS), the N_2 sorption at 77 K and scanning electron micrographs were obtained by an ASAP2020 Micromeritics apparatus and Jeol JSM-03 microscope, respectively. A Bruker Avance 500 MHz (11.7 T) Wide Bore spectrometer was used to measure the ^{27}Al and ^{29}Si MAS NMR spectra of the fully hydrated parent zeolites. ZrO_2 rotors with a rotation speed of 12 kHz and high-power decoupling pulse sequences with a $\pi/12\pi$ (0.7 μs) excitation pulse and 1 s relaxation delay were used. Chemical shifts were referenced to an aqueous solution of $Al(NO_3)_3$. ^{29}Si MAS NMR single pulse spectra were measured at a rotation speed of 5 kHz with a $\pi/6$ (1.7 μs) excitation pulse and relaxation delay of 30 s. The framework Si/Al_{FR} ratio was estimated according to the equation

$$Si/Al_{FR} = I/(0.25I_1 + 0.5I_2) \qquad (1)$$

where I_1 denotes the intensity of the NMR lines corresponding to the Si(3Si,1Al) atoms, I_2 to Si(2Si,2Al) atoms and I denotes the total ^{29}Si intensity; for details see Ref. [44].

The FTIR spectra of H- and Co-BEA* zeolites were measured, after evacuation at 450 °C for 3 h, in the region of the OH mode and after adsorption of d_3-acetonitrile (13 mbar) at RT followed by evacuation at RT for 20 min (for H-BEA*) and after evacuation at 200 °C for 30 min (for Co-BEA*). The latter procedure suppressed adsorption of CD_3CN on Brønsted sites (2293 cm^{-1}) and enabled quantitative analysis of the intensity of the C≡N vibrations connected with bare Co(II) ions (2308 cm^{-1}) by using extinction coefficient ε = 7.12 cm μmol^{-1} [22]. A Nicolet 6700 FTIR spectrometer operating at a resolution of 1 cm^{-1} and collecting 256 scans for a single spectrum was employed. Temperature-programmed reduction of Co-zeolites by hydrogen (H_2-TPR) was monitored by an Altamira AMI-200 instrument on samples pre-treated in a stream of air at 450 °C for 1 h and then cooled to 35 °C. Reduction of samples by hydrogen was carried out at a heating rate of 10 °C min^{-1} from 35 to 1000 °C using an H_2/Ar stream (9.44 vol.% H_2) with a flow rate of 30 ml min^{-1}. The UV–Vis–NIR reflectance spectra of Co-zeolites evacuated at 500 °C were recorded on a Perkin-Elmer Lambda 950 UV–Vis–NIR spectrometer equipped with an integrating sphere covered by Spectralon®, which also served as a reference. The reflectance was calculated using the Schuster–Kubelka–Munk function $F(R_\infty) = (1 - R_\infty)^2/2R_\infty$, where R_∞ is the diffuse reflectance from a semi-infinite layer. $F(R_\infty)$ is proportional to the absorption coefficient for $F(R_\infty) < 0.5$.

The concentration of bare Co(II) ions in dehydrated Co-BEA* was estimated from the intensity of the characteristic IR band at 2308 cm^{-1} of adsorbed d_3-acetonitrile on Co(II)-β ions (the only one of Co(II) ions accessible to CD_3CN molecules in both the

Table 1
Characteristics of parent zeolites.

Sample	Si/Al[a]	Si/Al_{FR}[b]	c_{Al}[a] (mol g^{-1})	c_B[c] (mol g^{-1})	c_L[c] (mol g^{-1})	Crystal size (μm)	S (m^2 g^{-1})
BEA/4.2	4.2	4.7	3.0	1.80	0.22	~0.4	510
BEA/11	11.3	11.5	1.4	0.63	0.32	~0.05	617

[a] From chemical analysis of Na-BEA*.
[b] From ^{29}Si MAS NMR spectra of Na-BEA*.
[c] Concentration of Brønsted and Al-Lewis sites from FTIR spectra of adsorbed d_3-acetonitrile.