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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 $[Co(II)(H_2O)_6]^{2+}$, and in dehydrated zeolites by protons, monovalent metal-ions, and metal-oxo structures such as formally monovalent [Co(III)O]⁺. Only Al atoms in AlSiSiAl 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

* Corresponding author. E-mail address: dedecek@jh-inst.cas.cz (J. Dedecek). 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 Alrich 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.







AlSiAl sequences are absent in the framework of Si-rich pentasil-ring zeolites (Si/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 AlSiSiAl sequences located in 6MRs creating cationic sites for divalent cations [13,17,18]. On the contrary, ²⁹Si 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 ²⁷Al 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 ²⁹Si (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 $Al_2O_3/SiO_2/NaOH/H_2O$ 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 SiO₂ or of Si/Al 12.0 (synthesized using TEAOH) in amount of 0.100 g per 1 g SiO₂ 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 NH₄NO₃ to yield NH₄-BEA/4.5 and NH₄-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 Creyghton et al. [19], which guarantees preserving Al atoms in the framework. NH₄-BEA/11

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Composition and acid sites of H-BEA [*] zeolite

Sample	Si/Al	Acid sites					
		<i>T</i> ^а (°C)	c _B ^b (mmol g ^{−1})	c_L^b (mmol g ⁻¹)			
H-BEA/4.5	4.5	450 500 550 600	1.82 1.72 1.43 0.93	0.41 0.56 1.11 1.57			
H-BEA/5.1	5.1	450 500 550 600	1.61 1.24 1.23 1.21	0.60 0.82 0.86 0.99			
H-BEA/11	11.3	450 500 550 600	0.63 0.54 0.49 0.46	0.32 0.33 0.46 0.56			

^a Temperature of evacuation for 3 h prior to the CD₃CN adsorption.

^b Concentration of Brønsted and Lewis sites, respectively, from FTIR spectra of adsorbed CD₃CN.

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 NH₄-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 ²⁷Al and ²⁹Si MAS NMR spectroscopy of Na-BEA* indicated well-developed structures with Al atoms exclusively tetrahedrally coordinated and the Si/Al_{FR} values close to those of chemical Si/Al_{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 Si/Al_{surf} (XPS) and Si/Al_{bulk} (chemical analvsis) 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 Co(NO₃)₂ solution (strictly three-times at RT following by thorough washing) to guarantee the exclusive exchange of divalent $[Co(II)(H_2O)_6]^{2+}$ complexes (for details see Refs. [14,18,20]). The composition of Co-BEA* zeolites is given in Table 2.

2.2. Structural analysis

The ²⁹Si and ²⁷Al MAS NMR spectra were measured employing a Bruker Avance 500 MHz (11.7 T) Wide Bore spectrometer using ZrO₂ rotors. For the ²⁷Al 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 Al(NO3)3. ²⁹Si 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. ²⁹Si high-power decoupling spectra were decomposed to the Gauss-Lorentzian bands using DMfit software [21]. The framework aluminum content (Si/Al_{FR}) was estimated using the standard approach from the single pulse spectrum according to the formula:

$$Si/Al_{FR} = I/(0.25I_1 + 0.5I_2)$$
 (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 ²⁹Si 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 CD₃CN 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 C=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 $\varepsilon_{\rm B} = 2.05$ cm µmol⁻¹ and $\varepsilon_{\rm L} = 3.60$ cm µmol⁻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 2

Sample	Co/Al ^a	<i>c</i> _{Comax} ^a	$c_{Co(II)-\beta}^{b}$	$c_{\mathrm{Co(II)}}{}^{c}$	$c_{\rm L}^{\rm d}$	Distribution of	Distribution of Al				
						Total Al ^a	Al _{pair} ^e		Al _{unpair} ^f		
		$(mmol g^{-1})$)			$(mmol g^{-1})$	$(\text{mmol } \text{g}^{-1})$	(%)	$(\text{mmol } \text{g}^{-1})$	(%)	
Co-BEA/4.5	0.48	1.34	0.38	0.47	0.05	2.79	0.94	34	1.85	66	
Co-BEA/5.1	0.48	1.21	0.48	0.66	0.03	2.53	1.32	52	1.21	48	
Co-BEA/11	0.50	0.65	0.18	0.20	0.03	1.30	0.41	32	0.89	68	

Analysis of the distribution of framework Al in BEA* using Co(II)-BEA*, FTIR of adsorbed d3-acetonitrile on Co(II), and Co(II) Vis spectra.

^a From chemical analysis of Co-BEA^{*} with the maximum degree of $[Co(II)(H_2O)_6]^{2+}$ exchange.

^b Concentration of bare Co(II)- β ions obtained from FTIR of adsorbed CD₃CN.

^c Total concentration of bare Co(II) ions estimated from the relative concentrations of Co(II)-α, Co(II)-β and Co(II)-γ ions from Vis spectra.

^d Concentration of Al-Lewis sites in dehydrated Co-BEA* from FTIR of adsorbed CD₃CN.

^e Concentration of Al atoms in AlSiSiAl (Al pairs) of 6MRs.

^f Concentration of Al atoms in unpaired Al balanced by [Co(II)(H₂O)₆]²⁺ in a hydrated Co-BEA*.

intensity of the characteristic C=N vibration at 3208 cm⁻¹ of adsorbed d_3 -acetonitrile (13 mbar at RT followed by evacuation at 200 °C for 30 min, suppressing adsorption of d_3 -acetonitrile on Brønsted sites). Details and the extinction coefficient of the C=N vibration associated with the bare Co(II) ions (2308 cm⁻¹), ε = 7.12 cm µmol⁻¹, were reported in Ref. [25]. The IR spectra were recorded at RT on a Nicolet 6700 FT spectrometer operating at a resolution of 1 cm⁻¹ by collecting 256 scans for a single spectrum.

The nature of Co species in the dehydrated Co-BEA* samples and siting as well as distribution of bare Co(II) ions in cationic sites were monitored by the UV–Vis–NIR spectroscopy. The UV–Vis–NIR reflectance spectra of Co-beta zeolites evacuated at 450 °C for 3 h up to $5 \cdot 10^{-2}$ Pa and sealed in a quartz cuvette were recorded on a Perkin–Elmer Lambda 950 UV–Vis–NIR spectrometer equipped with an integrating sphere for diffuse-reflectance measurements covered by Spectralon[®], which also served as a reference. The reflectance intensities were expressed using the Schuster–Kubelk a–Munk equation $F(R_{\infty}) = (1 - R_{\infty})^2/2R_{\infty}$, where R_{∞} is the diffuse reflectance from a semi-infinite layer and $F(R_{\infty})$ is proportional to the absorption coefficient. After the baseline abstraction, the spectra of Co-beta zeolites in the region of the Co(II) d–d transitions were simulated using Gaussian bands by the Fityk 0.9.8 software [26].

In contrast to AlSiAl sequences, the single Al atoms, Al pairs (AlSiSiAl in one ring) and unpaired Al atoms (close Al atoms balanced by a $[Co(II)(H_2O)_6]^{2+}$ complex, but unable to balance a bare divalent cation in dehydrated zeolites) (see Fig. 1) cannot be distinguished by ²⁹Si and ²⁷Al MAS NMR spectroscopy. But they can be analyzed by a combination of the Co(II) ion-exchange capacity of the hydrated Co-BEA* and the concentration of bare Co(II) ions coordinated with framework oxygen atoms of one ring in the dehydrated Co(II)-BEA* (for details see Refs. [13,18]). The methodology using bare Co(II) ions as probes of close Al atoms in various framework rings supplemented by ²⁷Al and ²⁹Si MAS NMR experiments was well-proven for pentasil-ring Si-rich zeolite structures [20,27–30] including BEA* topology [16,17], and it is reviewed in Ref. [13]. The analysis of the distribution of Al in the framework of Al-rich beta zeolites containing AlSiAl sequences requires modifications, as presented below.

 $[Co(II)(H_2O)_6]^{2+}$ complexes (under the strict absence of Co(II) hydroxo complexes) in a hydrated Co-BEA* sample are charge balanced by two close Al atoms located in a ring as well as in two different rings. The two Al atoms must be close enough to be able to charge balance the $[Co(II)(H_2O)_6]^{2+}$ complex. These $[Co(II)(H_2O)_6]^{2+}$ complexes are after a dehydration of Co-BEA* transformed into bare Co(II) ions coordinated exclusively with framework oxygen atoms in one ring containing two Al atoms. The rest of the $[Co(II)(H_2O)_6]^{2+}$ complexes, which is balanced by two close Al atoms in different rings, is rearranged into monovalent Co-oxo, $[Co(III)O]^+$ species each compensating only one AlO₄⁻. The concentration of

single Al atoms (unable to balance a divalent [Co(II)(H₂O)₆]²⁺ complex) in hydrated BEA* zeolites cannot be directly measured; for details see [18]. It is calculated as a difference of the concentration of Al in the framework and twice the ion-exchange capacity of [Co $(II)(H_2O)_6]^{2+}$ complexes. Single Al atoms represent AlO₄⁻ separated from the other Al atoms either by a long $(SiO)_{n>2}$ sequence or by a framework wall, and thus they are unable to charge balance a divalent counter-ion [13]. In dehydrated Co(II)-zeolites, bare Co(II) ions coordinated exclusively with framework oxygen atoms are in general charge balanced by two Al atoms in one ring [31]. It should be stressed that two Al atoms in one 6MR can be arranged only in AlSiSiAl sequences in Si-rich BEA* (Si/Al > 11) not possessing AlSiAl chains, while two Al atoms in Al-rich BEA* can also form AlSiAl sequences possibly located in 6MRs, 5MRs, and 4MRs. This is a matter of analysis in Results. Two Al atoms located in different rings, but close enough to be able to charge balance [Co(II) (H₂O)₆]²⁺ complexes in hydrated zeolites and forming Co-oxo species in dehydrated zeolites, are designated as close unpaired Al atoms. The concentrations of Al atoms in the individual Al arrangements are given by Eqs. (2)-(4) at the total balance of framework Al atoms (5):

$$Al_{1Al} = Al_{total} - 2Co_{max}$$
(2)

$$Al_{2A11R} = 2Co_{bare} \tag{3}$$

$$Al_{unpair} = 2(Co_{max} - Co_{bare})$$
(4)

$$Al_{total} = Al_{2A11R} + Al_{single} + Al_{unpair}$$
(5)

where the Co_{max} value corresponds to the $[Co(II)(H_2O)_6]^{2^+}$ ionexchange capacity, and Co_{bare} to the concentration of bare Co(II) ions in cationic sites, Al_{1AI} represents the concentration of single Al atoms (far distant or facing different channels unable to cooperate in binding $[Co(II)(H_2O)_6]^{2^+}$ complex in a hydrated zeolite), and Al_{2AI1R} means the concentration of Al atoms in AlSiSiAl or AlSiAl sequences located in one ring and with both Al atoms facing the same channel; in a specific case of AlSiSiAl sequence in 6MRs we designate it as Al pair (Al_{2AI}), and Al_{unpair} corresponds to the concentration of Al of two Al atoms in different rings unable to coordinate a bare divalent cation, but accommodating divalent $[Co(II)(H_2O)_6]^{2^+}$ complex or Co-oxo species in dehydrated zeolites.

2.3. Models and computational details

Periodic DFT calculations were employed to investigate siting of Co(II) ion probes in the dehydrated Co-BEA* zeolites. Two models possessing the P1 symmetry, designated as β_{TGTG} , β_{TAT4} , were employed to investigate two distinct possible arrangements of Co (II)- β cationic sites formed by the deformed 6MR, see Fig. 1 and SM3. They feature one unit cell of the beta zeolite with two



Fig. 1. Schematic representations of Al pairs, single Al atoms, unpaired Al atoms, and AlSiAl sequence in the zeolite framework, local structure of the α -, β -, and γ -sites and their positions in the BEA* framework.

differently oriented AlSiSiAl sequences in the 6MR accommodating one Co(II) ion. The starting orthorhombic structure was downloaded from the zeolite structural database [32]. In addition, four models featuring the Co(II) in α -type 6MRs of cationic sites of the FER, MFI, MOR, and BEA* zeolite topologies were used to compare the structures of the bare Co(II)- α ions in various pentasil-ring zeolites. The starting structures were obtained from the zeolite structural database [32]. Periodic DFT calculations were carried out employing the VASP code [33-36]. The high-spin electron configuration Co $d^5 \uparrow d^2 \downarrow$ was employed for the Co(II) ion accommodated in the zeolite [31]. The Kohn-Sham equations were solved variationally in a plane-wave basis set using the projectoraugmented wave (PAW) method of Blochl [37], as adapted by Kresse and Joubert [38]. The exchange–correlation energy was described by the PW91 generalized gradient approximation (GGA) functional [39,40]. Brillouin zone sampling was restricted to the Γ -point. The plane-wave cutoff of 400 eV was utilized for geometry optimizations while a smaller cutoff of 300 eV was used for the molecular dynamics simulations.

The atomic positions were optimized at constant volume employing a conjugate-gradient algorithm minimization of energies and forces while the lattice parameters were fixed at their experimental values. The molecular dynamics (MD) simulations used the exact Hellmann–Feynman forces acting on atoms and applied the statistics of the canonical ensemble to the motion of the atomic nuclei using the Verlet velocity algorithm to integrate Newton's equations of motion. The time step for the integration of the equations of motion was 1 fs. The simulations were run for 10 ps at 400 K. The structures of ten "snapshots" collected from the molecular dynamics simulations were optimized for each model.

3. Results

3.1. State of Al in H-BEA^{*}

²⁷Al MAS NMR spectra of fully hydrated Na-BEA/4.5, Na-BEA/5.1, and Na-BEA/11 (Fig. 2A) showed strong resonances centered around 57 ppm with the maxima at 58.0 and 55.0 ppm for BEA/4.5, at 57.8 and 54.0 ppm for BEA/5.1, and at 57.4 and 55.0 ppm for BEA/11. There is no intensity around 0 ppm of octahedrally coordinated Al atoms for all the three samples showing well-developed frameworks of zeolites with tetrahedrally coordinated Al atoms located exclusively in the framework with the absence of the extra-framework Al. This is supported by the values of Si/Al_{FR} of 4.8, 6.0, and 12.1 for BEA/4.5, BEA/5.1, and BEA/11, respectively, obtained from ²⁹Si MAS NMR (Fig. 2B), which are close to the corresponding values of Si/Al obtained from chemical analysis (Table 1). While the ²⁹Si MAS NMR spectra of all three Na-BEA/4.5, Na-BEA/5.1, and Na-BEA/11 exhibited resonances at ca -110 and -115 ppm reflecting Si(4Si,0Al) and at -105 ppm corresponding to Si(3Si,1Al) atoms, both the Al-rich BEA* samples showed another resonance at -98 ppm revealing the presence of Si(2Si,2Al) atoms [41,42].

Fig. 3 depicts the coordination of framework Al and Si in BEA/4.5 and BEA/11 depending on the cation-type presence. Regardless of the charge balance of framework AlO_4^- by either Na⁺ or NH⁺₄ ions (Fig. 3A) both the fully hydrated samples provided broad resonances with the maxima at around 58 and 54 ppm in their ²⁷Al MAS NMR spectra. For H-BEA* zeolites deammoniated at 500 °C followed by their full hydration at RT, the main resonance becomes broader with the maximum at around 56 ppm. Simultaneously, a new resonance at -1.5 ppm of octahedrally coordinated Al appeared in the spectra of both the H-BEA/4.5 and H-BEA/11 samples corresponding roughly to 25% and 20% of the total Al content, respectively. These results imply substantial, but reversible changes in the O_h/Td coordination of some framework Al atoms, which are able to increase their coordination up to the octahedral one. This behavior is further confirmed by ²⁹Si NMR yielding no significant differences in Si/Al_{FR} for Na-, NH₄-, H-, and Na (obtained from their H forms)-BEA* zeolites (Fig. 3B).

FTIR spectra of H-BEA/4.5, H-BEA/5.1, and H-BEA/11 in the region of the OH vibration mode showed characteristic bands for beta zeolites (Fig. 4A): terminal Si–OH groups at 3745 cm⁻¹ accompanied by a shoulder at around 3735 cm⁻¹ of internal Si–OH groups in the defective sites, and sharp absorptions at 3611 cm⁻¹ for H-BEA/11 and 3614 cm⁻¹ for H-BEA/4.5 and H-BEA/5.1 of non-interacting structural OH groups [43,44]. A broad absorption ranging from 3700 to 3200 cm⁻¹ observed in all the samples indicated mutually interacting SiOHAl groups. The H-BEA/5.1 sample possessed in addition a very low intensity band at 3783 cm⁻¹ and around 3650 cm⁻¹ reflecting trace amounts of Al–OH of perturbed framework Al atoms or extra-framework Al [44,45]. The intensities of absorptions of both the non-interacting and interacting SiOHAl groups (not shown in the figures) decreased roughly to the same degree when the temperature of zeolite evacuations increased from 450 to 600 °C.

FTIR spectroscopy of d_3 -acetonitrile adsorbed on H-BEA/4.5, H-BEA/-5.1, and H-BEA/11 evacuated at temperatures from 450 to 600 °C (see Fig. 4B and SM4) was employed to measure the concentrations of the Brønsted and Lewis sites. The quantitative analysis of the C=N mode vibrations on the Brønsted (3292–3298 cm⁻¹) and Lewis sites (3325 cm⁻¹) for H-BEA* (Table 1) yielded their respective concentrations. The relative decrease in the concentration of the Brønsted sites with the increasing temperature of the zeolite evacuation was roughly comparable for H-BEA/5.1 and H-BEA/11, but it was higher for BEA/4.5. This shows that Al-rich BEA* zeolites of 2.5 and 2.2 times higher concentrations of Al in the framework compared to H-BEA/-11 maintain a high fraction of Brønsted sites even at high temperatures of their evacuation (Table 1).



Fig. 2. MAS NMR spectra of hydrated Na-BEA* zeolites. (A) ²⁷Al MAS NMR spectra and (B) ²⁹Si MAS NMR spectra with relative areas of the individual resonances and their attribution to Si(xSi,yAl) atoms: (a) experimental data and (b) Gaussian bands of the individual resonances.

3.2. Computations on the structure and stability of the Co(II) ions in cationic sites

Our calculations of the two models of the β -type 6MRs with different location of AlSiSiAl sequences (β_{T6T6} and β_{T4T4}) yielded the structures of the exchanged Co(II) ions in β_{T6T6} and β_{T4T4} sites (Fig. 5A and B, respectively). The Co–O bond length ranged from 1.97 (Co-O_{Al}) to 2.00 (Co-O_{Al})Å and 1.96 (Co-O_{Al}) to 2.04 $(Co-O_{Si})$ Å for the β_{T6T6} and β_{T4T4} models of Co-BEA*, respectively. The bond lengths of the first Co-O shell determined by EXAFS in Co(II)-MFI and Co(II)-FER zeolites with prevailing population of the Co(II)- β type ions ranged from 1.99 to 2.00 Å with four or three oxygen ligand coordination [30]. This Co–O distance close to 2.00 Å satisfies requirements of Co(II) bonding to oxygen atoms in both zeolite structures. This is achieved by the deformation of the framework T-O bonds induced under the Co(II) ion coordination to framework rings, as previously observed by IR spectra of T-O framework vibrations [30,46]. The Co(II) ion accommodated in the β_{T6T6} site is ligated to four oxygen atoms of two AlO₄⁻ tetrahedra, while the Co(II) ion in β_{T4T4} coordinates with two O atoms of two AlO_4^- tetrahedra and two O atoms of two SiO_4 tetrahedra. This presumes that the ligand field of the Co(II) ions in β_{T6T6} and β_{T4T4} differs and thus, Co(II) ions in these sites should differ in their d-d spectra. Our prior computational studies of Fe(II)-FER, Co(II)-FER, and Cu (II)-FER showed significant rearrangements of the α and β rings of cationic sites upon binding the divalent cations [31,47]. The reason why the β_{T4T4} site accommodating Co(II) ion does not similarly rearrange to bind to four O atoms of two AlO₄⁻ tetrahedra, most likely is that the 6MR forming β site creates a rigid double 6MR (hexagonal prism) with another 6MR. The stabilization energy obtained from the preferential binding of Co(II) to four O atoms of two AlO₄⁻ tetrahedra is most probably smaller than the energy needed to deform the structure of the double 6MR to permit the preferential binding of Co(II). Similarities in the stability, coordination and Co-O bond distances of Co(II) ions in cationic sites were also indicated by MD simulations for the Co(II)- α ions bonding in BEA^{*} (Fig. 5C) and in MFI, FER, and MOR structures as shown in SM5.

The calculations of Co(II) ion coordination and Co–O bond length support structure stability of the bare Co(II) ions coordinated in the α - and β -type 6MRs of dehydrated BEA* and balancing the negative AlO₄⁻ charges of their AlSiSiAl sequences and the ability of the given rings to perturb their framework T—O—T angles (cf. Refs. [30,46]), which thus satisfies requirements of Co(II) ions to be bound to framework oxygen atoms. These results imply only small differences in the geometry of α - and β -type framework rings coordinated Co(II) ions of the respective pentasil-ring zeolites and thus in ligand field of Co(II) ions in the corresponding sites (cf. Table 3 below).

3.3. Distribution of Al atoms in the framework of BEA^{*}

²⁹Si MAS NMR experiments provide evidence that a considerable fraction of Al framework atoms form AlSiAl sequences in the framework of BEA/4.5 and BEA/5.1, as reflected in the resonance at 98.1 ppm corresponding to Si(2Si,2Al) atoms, while this resonance is missing in BEA/11 (see Fig. 2B, cf. Ref. [16]). Only the upper and lower limits of the concentration of the Al atoms in AlSiAl sequences can be estimated from the I_1 and I_2 intensities of the ²⁹Si MAS NMR resonances due to the fact that the exact arrangements of these sequences in the zeolite framework are unclear. In general, there are two limit situations of the arrangement of AlSiAl sequences in the framework:

(i) Infinite (AlSi)_n sequence or AlSiAl sequences forming rings in the framework. In this case, one Al atom of AlSiAl sequence corresponds to one Si(2Si,2Al) atom and two Si(3Si,1Al) atoms. The concentration of Al atoms in AlSiAl sequences is given by Eq. (6) and represents the lower bound of the concentration of Al in AlSiAl sequences:

$$Al_{AISIAI} = \frac{I_2}{I_2 + \frac{1}{4} * (I_1 - 2 * I_2)} * 100 \ [\%]$$
(6)

One isolated single Al atom (Al(Si)_{n>2}Al) or one Al atom of AlSi-SiAl sequence represents four Si(3Si,1Al) atoms. The concentrations of single Al atoms (Al_{1Al}) and of Al atoms in AlSiSiAl sequences (denoted here as Al pairs, Al_{2Al}) are given by Eq. (7):

$$Al_{1AI} + Al_{2AI} = \frac{\frac{1}{4} * (I_1 - 2 * I_2)}{I_2 + \frac{1}{4} * (I_1 - 2 * I_2)} * 100 \ [\%]$$
⁽⁷⁾





Fig. 3. Effect of the cationic forms on (A) ²⁷Al MAS NMR, and (B) ²⁹Si MAS NMR spectra of BEA/4.5 and BEA/11 zeolites. NH₄-BEA*, H-BEA*, and NaH-BEA* were obtained by an ion-exchange of the synthesized zeolites with a solution of NH₄NO₃, calcination of NH₄-BEA* in an O₂ stream at 475 °C for 1 h, and an ion-exchange of the H-BEA* with a solution of NAO₃, respectively.

(ii) Isolated AlSiAl sequences. In that case, two Al atoms of AlSiAl sequence correspond to one Si(2Si,2Al) atom and six Si (3Si,1Al) atoms. Concentration of Al atoms in these AlSiAl sequences is given by Eq. (8) and represents the upper bound of the concentration of Al in AlSiAl sequences:

$$Al_{AISIAI} = \frac{2 * I_2}{2 * I_2 + \frac{1}{4} * (I_1 - 6 * I_2)} * 100 \ [\%]$$
(8)

The sum of the concentrations of single Al atoms and Al atoms in AlSiSiAl sequences (Al pairs, Al_{2Al}) is then given by (9):

$$[AI_{1AI} + AI_{2AI}] = \frac{\frac{1}{4} * (I_1 - 6 * I_2)}{2 * I_2 + \frac{1}{4} * (I_1 - 6 * I_2)} * 100 \ [\%]$$
(9)

Thus the upper and lower bounds of the concentration of Al atoms in AlSiAl sequences estimated by using ²⁹Si MAS NMR spectroscopy (Eqs. (6)–(9)) are as follows: 82–100% of total Al atoms for BEA/4.5 with 17% of Si(2Si,2Al) and 49% of Si(3Si,1Al) atoms; and 42–100% of total Al atoms for BEA/5.1 with 7% of Si(2Si,2Al) and 52% of Si (3Si,1Al) atoms.



Fig. 4. FTIR spectra of H-BEA*. (A) OH vibrations after evacuation at 450 °C and (B) C=N vibrations after adsorption of d₃-acetonitrile (13 mbar) at RT and evacuation at RT.



Fig. 5. Optimized structures of the (A) β_{TGTG} , (B) β_{T4T4} , and (C) α sites after DFT molecular dynamics simulations. The distances are in Å. Silicon atoms are in gray, oxygen atoms in red, aluminum atoms in yellow, and cobalt atoms in blue.

The distribution of Al atoms between single Al atoms, unpaired two Al atoms (close but unable to accommodate a bare divalent cation) and two Al atoms in one ring facing the same channel cannot be distinguished by ²⁹Si and ²⁷Al MAS NMR spectra analysis. However, the Al distribution can be obtained from the combination

of the Co(II) ion-exchange capacity of the hydrated Co-BEA^{*} (Table 2) and the concentration of bare Co(II) ions coordinated with framework oxygen atoms of one ring in the dehydrated ion-exchanged Co-BEA^{*} (see Eqs. (2)–(5) and Ref. [13]).

The concentration of single Al atoms (Al_{1Al}) in both Al-rich and Si-rich Co-BEA* (see Table 2) is low as follows from Eq. (2) and the Co/Al ratio close to 0.5. The concentration of bare Co(II) ions (Eq. (3)) with an open coordination sphere coordinated with framework oxygen atoms of rings containing two Al atoms (AlSi-SiAl or AlSiAl sequences), facing one channel and accessible to d_3 -acetonitrile molecules, was derived from the intensity of the characteristic C N vibration (2308 cm⁻¹) of d_3 -acetonitrile adsorbed on dehydrated Co-BEA* (Fig. 6 and Table 2). It should be noted that the concentration of Al-Lewis sites was substantially lower compared to H-BEA*, indicating a stabilization of the T-O bonds due to the exchanged Co(II) ions. The MD simulations (see Fig. 5C) clearly showed that the Co(II)- α and Co(II)- γ sites in BEA* (not shown) are not accessible for d_3 -acetonitrile molecules. Thus, the quantity of adsorbed d₃-acetonitrile on Co-BEA* represents a measure of only the Co(II)- β sites in BEA^{*} (Table 2). The concentrations of Co(II)- α and Co(II)- γ ions were estimated by using their relative intensities of Vis d–d transitions to that of Co(II)- β ions (see below).

The UV-Vis spectra of dehydrated Co(II)-BEA* zeolites exhibited a broad complex absorption ranging from 13000 to 27000 cm⁻¹ ascribed to the d-d transitions of high-spin bare Co(II) ions coordinated exclusively with oxygen atoms of framework rings (Fig. 7). The simulation of the spectra supported by their 2nd derivative mode showed the presence of nine d-d bands for Sirich Co-BEA/11 as well as Al-rich Co-BEA/4.5 and Co-BEA/5.1 (Table 3). The analysis of the Vis spectra of Co-BEA/11 refers to Ref. [18], where the band positions of the predominant components in Si-rich Co-BEA* were determined by using Co-samples with the prevailing individual components. As the Co-BEA/11 zeolite did not possess Si(2Si,2Al) atoms and thus AlSiAl sequences in the framework (within the sensitivity of ²⁹Si MAS NMR spectroscopy, see Fig. 2B), the bare Co(II) ions should be exclusively balanced in that zeolite by AlO₄⁻ of AlSiSiAl sequences in 6MRs of the α , β , and γ cationic sites (Fig. 1). Table 3 lists the spectral

Table 3 Vis spectral components of Co(II) ions in the α , β , γ and ε cationic sites of dehydrated Co-BEA*.

Sample	Area (a.u.)				Wavenumber (cm ⁻¹)								
	α	β	γ	3	α	β	β	β	β	γ	γ	3	3
Co-BEA/4.5	390	4060	570	560	14850	15500	16300	17570	20100	19000	21700	25000	26600
Co-BEA/5.1	750	3910	710	380	14850	15500	16300	17570	20100	19000	21700	24500	26000
Co-BEA/11	900	3490	900	290	14600	15500	16300	17570	20100	18500	21700	24500	26000
Co-MFI ^a					15100	16000	17150	18600	21200	20100	22000		
Co-FER ^b					15000	16000	17100	18700	20600	20300	22000		
Co-MOR ^c					14800	15900	17 500	19200	21000	20150	22050		

^a Refs. [52].

^b Refs. [20].

^c Refs. [27].



Fig. 6. FTIR spectra of C \equiv N vibrations after adsorption of d_3 -acetonitrile (13 mbar) at RT and evacuation at 200 °C on Co-BEA^{*} prior evacuated at 450 °C for 3 h, and spectra simulations.

components of the individual types of Co(II) ions in Si-rich Co-BEA/11: a single band corresponds to the Co(II) ions in the α -site; the quartet of bands is attributed to the Co(II)- β ions, and the doublet is manifested by the Co(II)- γ ions.

The four Vis band positions observed for the Al-rich Co-BEA/4.5 and BEA/5.1 samples (Fig. 7) were clearly identical to those of the Co(II)- β ions of Co-BEA/11, and of Si-rich BEA* samples reported previously [16–18,25]. This indicates that the Co(II)- β ions are coordinated with either the β_{T6T6} or β_{T4T4} sites or their analogues (cf. Fig. 5 and Ref. [32]) within the sensitivity of frequency determination. Thus only one type of the local Al arrangement highly predominates with the β -type ring in both the Al-rich and Si-rich BEA*. The band positions of the Co(II)- α and Co(II)- γ type ions measured for Co-BEA/4.5 and BEA/5.1 were only slightly shifted to higher frequencies with respect to those of Co-BEA/11 (Table 3). The identical frequencies of the Co(II)- α and Co(II)- γ ions can hardly reflect a quite different Co(II) ion coordination which could be expected if Co(II) ions would be charge balanced by AlSiAl in 6MRs, 5MRs, and 4MRs. This assumption is supported by the close frequencies of the characteristic d-d transition of the Co(II) ions coordinated with the similar α -, β -, and γ -type framework rings of cationic sites reported for various pentasil-ring Si-rich zeolites given in Table 3. Also the results of MD calculations of the stability, coordination and Co–O bond length of Co(II) ions in the β - and α -type 6MRs (Fig. 5) imply that the small differences observed in Vis band positions of Co(II) ions coordinated in the α - and γ -type rings of the Al-rich and Si-rich BEA* structures can be accounted for small differences in the geometry of framework rings. They provide only slightly changed Co(II) ligand fields, and the ability of the given rings to perturb their framework T–O–T angles satisfies requirements of Co(II) ions to be bound to framework oxygen atoms. The calculations of Co(II) ion coordination and its stability thus support experimental results suggesting the bare Co(II) ions coordinated in one 6MR of dehydrated Al-rich BEA* balancing two AlO₄⁻ charges of AlSi-SiAl sequences.

The small differences in frequencies of the above mentioned d-d transitions can be accounted for small distortions of the rings containing AlSiSiAl sequences and coordinating the Co(II) ions owing to a higher total Al content in Al-rich Co-BEA^{*}. Therefore,



Fig. 7. Normalized UV–Vis–NIR spectra of Co-BEA* evacuated at 500 $^\circ C$ for 3 h and spectra simulations.

the identical or very similar band positions for the α -, β -, and γ -type Co(II) ions in Co-BEA/4.5, BEA/5.1, and BEA/11 indicate that the bare Co(II) ions are similarly coordinated with the α -, β -, and γ type 6MRs also in Al-rich Co-BEA*, despite containing high concentrations of AlSiAl sequences. These Co(II) ions charge-balance two AlO₄⁻ of AlSiSiAl in 6MRs and not two AlO₄⁻ of AlSiAl in the 6MRs, 5MRs, and 4MRs, which would lead to quite different Co(II) ion coordination and d-d transitions. Based on the intensities of the individual spectral α , β , and γ components and using the extinction coefficients for the Co(II)- α , Co(II)- β , and Co(II)- γ ions given in Ref. [18], it follows that both the Al-rich and Si-rich BEA* contain bare Co(II) ions predominantly coordinated with the β -type 6MRs of cationic sites. The Co(II)- β ions represent roughly 28% and 40% of all the Co(II) ions in Al-rich BEA/4.5 and BEA/5.1, respectively (Fig. 7). The concentration of the Co(II)- α and Co(II)- γ ions can be roughly estimated using the extinction coefficients for Si-rich BEA* zeolites. The total concentration of bare Co(II) ions ranges from ca 35% to 50% of the total Co species in Al-rich Co-BEA* (see Table 2). These values are similar to those for the Al-rich BEA* reported in Ref. [16] as well as for the Si-rich Co-BEA/11 sample. In addition to these characteristic intensive d-d absorptions, a low intensity doublet around 25000 cm⁻¹ appeared in Al-rich Co-BEA* zeolites reflecting the presence of some Co(II)- ε type ions (see Fig. 7 and Table 3). We have previously observed these Co(II) ions in trace concentrations in Si-rich Co-BEA* zeolites of Si/Al \sim 13 and at that time assumed that they correspond to Co(II) in some defective sites [18]. However, practically the measurement of the same frequencies of the doublet around 25000 cm^{-1} (Table 3) but with a substantially increased intensities (two and three times) for Co-BEA/5.1 and Co-BEA/4.5, respectively, encourages us to relate these ε -structures to the bare Co(II) ions charge balanced by two AlO₄⁻ of AlSiAl sequence located in one framework ring and facing the same channel. But their low relative intensity in the Vis spectra (ca 5% of total d-d intensity) indicates their low concentration. However, at the present time we cannot even estimate which of the rings (i.e., 6MRs, 5MRs, and 4MRs) these Co(II)- ε type ions are coordinated with. Nevertheless, considering the values of the extinction coefficients of Co(II) ions in the α . β , and γ cationic sites, these Co(II)- ε cations are of the low concentration, <10% of total Co(II) ions.

The bridged di-nuclear Co-oxo complexes, manifested by a broad band in the UV region around 30000 cm⁻¹ reflecting the oxygen ligand to metal transitions (LMCT) were not observed for any of the Co-BEA/4.5, Co-BEA/5.1, and Co-BEA/11 zeolites. However, we reported that not all Co-oxo species are reflected in the absorption around 30000 cm⁻¹ (for more information see Refs. [16,25]), but the LMCT transitions of specific Co-oxo species should extend beyond the monitored UV range above 50000 cm⁻¹ as indicated by quantum chemical calculations. The presence of such type of Co-oxo species is indicated by a substantial value of the difference of the $[Co(II)(H_2O)_6]^{2+}$ ion-exchange capacity (Co_{max}) and the sum of the concentrations of the bare Co(II) ions (Eq. (4), and Table 2). It implies a high relative concentration of close Al atoms in different rings able to charge balance $[Co(II)(H_2O)_6]^{2+}$ in a hydrated zeolite and transformed into some "monovalent" counter Co-oxo species in a dehydrated zeolite, but unable to accommodate bare divalent cations (Table 2). These "monovalent" Co-oxo species in Co-BEA^{*} zeolites, formed from $[Co(II)(H_2O)_6]^{2+}$ preferably at higher loadings, are reduced by hydrogen at much lower temperature (800 °C) compared to bare Co(II) ions (\geq 950 °C), but at a higher temperature compared to supported Co oxides (ca 450 °C, not present) as shown in the temperature-programmed reduction experiment by hydrogen over Co-BEA/11 of lower and higher Co loading (Fig. 8). The consumption of hydrogen related to the concentration of these Co-oxo species corresponds to a value 1, indicating presence of one O atom per Co. It is to be noted that the reduction of bare Co(II) ions occurs at very high temperature when they are released from the cationic sites. These findings imply that the Co-oxo species exhibiting LMCT above 50000 cm^{-1} , and thus non-visible by the standard UV–Vis spectrometer, correspond to counter-ion formally monovalent [Co(III) O]⁺ species balancing one AlO₄⁻ of the unpaired Al atoms, the second one being balanced by a proton (detailed study will be published elsewhere).

It can be summarized from Table 2 that the Al-rich BEA/4.5 and BEA/5.1 samples feature 34% and 52%, respectively, of AlO_4^- in Al pairs (Al_{2Al}, AlSiSiAl sequences) in 6MRs representing the sites for bare divalent cations, a very low concentration of single Al atoms (less than 3%), and a high content (66% and 48%, respectively) of close Al atoms located in different rings (Al_{unpair}) binding hexaaquo Co(II) complexes and the related formally monovalent Co-oxo [Co(III)O]⁺ species in a dehydrated beta zeolite, but not cooperating for binding bare divalent cations.

4. Discussion

4.1. Arrangement of Al atoms in the framework of Al-rich BEA^{*}

Both the hydrothermal syntheses of Al-rich BEA* samples yielded well-developed crystals and their BEA* structure as reported in Results. The main difference between the framework of Si-rich BEA* synthesized using TEAOH and that of the template-free Al-rich BEA* zeolites crystallized in the exclusive presence of Na⁺ ions lies in the organization of the framework Al atoms. While the arrangement of Al atoms in the channel surface (i.e., (i) Al pairs of AlSiSiAl sequences in 6MRs and (ii) close unpaired Al atoms located in different rings close enough to balance Co(II) hexaaquo complex, but unable to compensate bare Co (II) ions) is similar in the Al-rich and Si-rich BEA* zeolites, the incorporation of the closest possible Al atoms (i.e., AlSiAl sequences) occurs only in the framework of the Al-rich BEA* zeolites. The concentration of AlSiAl is estimated employing ²⁹Si NMR spectroscopy to be between 80% and 100% for BEA/4.5 and between 40% and 100% of the total Al content for BEA/5.1 (cf. Fig. 2B and Eqs. (6)-(9)). The exact values depend on the Al arrangement (see Eqs. (6)-(9)) and presumably might be affected by the gel composition and conditions of the hydrothermal synthesis.

The mutual detailed arrangements of Al atoms (see Fig. 1) in the framework relevant to the charge stabilization of bare divalent or monovalent cations or various metal-oxo species were analyzed using Co(II) ions as a probe in hydrated and dehydrated zeolites,



Fig. 8. H₂-TPR profiles of Co-BEA/11 (Co/Al 0.5, 0.44 mmol H₂ g⁻¹) and Co-BEA/11 (Co/Al 0.08, 0.04 mmol H₂ g⁻¹).

i.e., by the methodology developed and approved with Si-rich pentasil-ring zeolites of MFI, FER, MOR, and BEA* topologies [13].

Cooperation of two AlO_4^- charges in one ring (in principle as an AlSiSiAl or AlSiAl sequence) and facing the same channel (Eq. (2)) enables to bind a bare Co(II) ion coordinated exclusively with framework oxygen atoms. It should be noted that in the case of two Al atoms in different rings, the high reactivity of long-distance charge balanced Co(II) ion is supposed to lead to a formation of Co-oxo species adjacent to one AlO_4^- [48,49]. The concentrations of AlO₄ of AlSiSiAl and AlSiAl in one ring and facing the same channel, and thus enabling bind a bare divalent cation in Co-BEA^{*} (determined from d_3 -acetonitrile adsorbed exclusively on bare and accessible Co(II)- β ions, and for total Co(II) ions calculated from Vis spectra; see Figs. 6 and 7, and Table 2) differ for the individual BEA* samples, but are roughly about 35% and 50% of the total Al atoms for the Al-rich samples and of 30% for the Si-rich BEA* sample. The concentration of two Al atoms in one ring may depend on the conditions of hydrothermal synthesis, as it has been recently reported for ZSM-5 zeolites of various (commercial) provenience and laboratory synthesis protocols [14,50,51]. However, there are no data regarding the influence of hydrothermal synthesis conditions on the organization of Al atoms in the framework of Al-rich as well as Si-rich BEA* zeolites.

A majority of the Al atoms (80–100% in BEA/4.5 and 40–100% in BEA/5.1) form AlSiAl sequences while only ca 35% and 50%, respectively, of all the Al atoms can be charge balanced by bare Co(II) ions. Therefore, a vast amount of Al atoms in both the Al-rich samples should be located in AlSiAl sequences, where the two Al atoms face different channels (Fig. 1). This is an important finding with respect to the location of the negative AlO_4^- charges in individual channels and their ability to be balanced by variously positively charged counter-ion species. While AlSiSiAl sequences can occur only in 6MRs, two AlO_4^- of AlSiAl sequences in Al-rich BEA* can be located in 6MRs, 5MRs, and 4MRs.

In Si-rich zeolites, only AlSiSiAl sequences can be present in one 6MR where they form cationic sites for bare divalent cations. On the contrary, with Al rich BEA* zeolites both the AlSiSiAl and AlSiAl sequences can be located in one 6MR. To distinguish whether the two Al atoms located in one ring represent AlSiSiAl or AlSiAl sequences we applied our knowledge gained from previous studies on the distribution of Al atoms in the framework of Si-rich pentasil-ring zeolites of BEA*, MFI, FER and MOR topologies (not containing AlSiAl sequences) [13,18,20,27-30,50,52]. Quantitative analysis of Al atoms in AlSiSiAl sequences in 6MRs of cationic sites (Al pairs, Al_{2Al}) of Si-rich zeolites was obtained from the analysis of intensities of the characteristic Vis d-d transitions of the bare Co (II)- α , Co(II)- β and Co(II)- γ type ions (see Eq. (3)). The identical $(Co(II)-\beta)$ and very similar $(Co(II)-\alpha$ and $Co(II)-\gamma)$ frequencies of their characteristic spectral Vis d-d transition components for Sirich and Al-rich BEA* (Table 3 and Refs. [16,18,25]) indicate above given individual Co(II) ions coordinated with the same 6MRs containing AlSiSiAl sequences in Al-rich BEA*. This is further supported by the close d-d transitions and corresponding close coordinations of the Co(II)- α , Co(II)- β and Co(II)- γ type ions in MFI, FER and MOR structures (Table 3 and Refs. [27,29,30]). These similarities in the Co ion coordination are also confirmed by close Co-O bond lengths obtained here from DFT simulations of the Co(II) ions coordinated with the α -type rings of these zeolite structures (Fig. 5 and SM3B). The small differences in coordination (frequency) and Co-O bond lengths originate from differences in the geometry of the individual α -type rings as well as different perturbation of their T–O–T angles occurring for satisfying requirements of the Co(II) ions to be bound to oxygen atoms of the framework [30,46]. Also Co(II) ions coordinated in the β -type rings in BEA^{*} structure keep Co–O bond length around 2.00 Å as obtained from DFT simulations (Fig. 5). Most of the Al pairs of Al-rich BEA^{*} occurs in the β -type 6MRs, and the α - and γ -type rings are less populated. Nevertheless, in Si-rich BEA* the Al pairs (Table 2, Fig. 7 and Refs. [16,18,25]) are more significantly populated in the α -type rings compared to those in Al-rich BEA*.

If Al atoms of AlSiAl sequences (either presumably in 6MRs, 5MRs, and 4MRs) face the same channel, then they inevitably induce substantially different Co(II) coordination and d-d transitions compared to the above Co(II) ions charge balancing Al pairs (AlSiSiAl sequences) in 6MRs. The observed low intensity doublet (around 25000 cm⁻¹) of the Vis spectrum of Co(II)- ε ions is suggested to reflect Co(II) ions balancing AlO₄⁻ of AlSiAl sequences in one ring facing the same channel. This suggestion is supported by a similar Co(II) Vis spectrum observed with Co(II) ions in Atype zeolite [53]. The absence of any other distinct coordination of Co(II) ions beside the Co(II)- α , Co(II)- β , Co(II)- γ , and Co(II)- ε type ions in the Vis spectrum encourages us to suggest that most of AlSiAl present is unable to bind a bare divalent cation. AlSiAl in one ring with AlO_4^- facing one channel reflected by Co(II)- ε ions represent in maximum 4% of total Al atoms. Single far distant Al atoms, able to bind only monovalent species, also occur only in a very low concentration, less than 4% of total Al content as Co(II)/ Al equals to 0.48–0.50 for individual samples. Therefore, a predominant part of AlO₄ of AlSiAl sequences should participate with another AlO₄⁻ facing the same channel of another AlSiAl sequence located in a different ring, in formation of close unpaired Al atoms (for illustration see Figs. 1 and 9B in Section 4.2).

We summarize that the high concentration of Al atoms in Alrich BEA* zeolites (Si/Al 4.5 and 5.1) results in a quite different arrangement of framework Al atoms in Si(4-nSi,nAl) atoms, with predominant presence of AlSiAl sequences contrary to their absence in Si-rich BEA* and generally in Si-rich zeolites. However, the Al atoms of these AlSiAl sequences are arranged in the framework in a manner that they are manifested in the zeolite channels in similar Si–Al arrangements as Al atoms in Si-rich BEA*. The AlO₄ are organized in AlSiSiAl sequences in 6MRs of cationic sites (ca 35-50% of total Al) and as unpaired Al atoms originated from an AlSiAl sequence with Al atoms facing different channels and cooperating with an Al atom of the same channel from another AlSiAl sequence. Only a minority of Al atoms are presented as single Al atoms and in AlSiAl sequences with AlO_4^- facing the same channel. Such Al arrangement is possible at least for Al-rich BEA* with $Si/Al \ge 4.3$ (12 Al per U.C.) as it is demonstrated in Fig. 9. Nevertheless, the organization of framework Al atoms on the channel inner surface does not exhibit differences for Al-rich and Si-rich BEA* zeolites, and it differs only in their concentration.

4.2. Framework Al atoms and related acid sites and metal-ion species

High concentrations of Al atoms and AlSiAl sequences in the Al-rich BEA* zeolites do not result in a significant decrease in the strong acidity of protonic sites as reflected in very close frequency of O—H vibration of non-interacting SiOHAl groups at 3614 cm⁻¹ compared to 3611 cm⁻¹ for Si-rich BEA* of Si/Al 11.3 (Fig. 4). This is also manifested by a comparable activity per protonic site (sum of mutually interacting and non-interacting ones) of Al-rich and Si-rich BEA* in decane and cumene cracking [4,10] and ethylation of benzene [6,7,10] reported recently. The reason for a high acid strength may be the fact that protons related to the two Al atoms of AlSiAl sequences face different channels. That organization of Al atoms in the framework structure minimizes number of very close protons and provides strongly acidic protonic sites.

The higher concentration of framework Al atoms in Al-rich BEA* also does not induce a markedly increased tendency of Brønsted sites to dehydroxylation resulting in formation of Al-Lewis sites (Table 1 and SM4). The same susceptibility of both the Al-rich and Si-rich zeolites to yield Al-Lewis sites under



Fig. 9. Illustration of the prevailing structural arrangement of (A) Brønsted hydroxyl groups, and (B) $[Co(III)O]^*$ ions in Al-rich BEA*. The hydroxyls or $[Co(III)O]^*$ ions balancing the charge corresponding to a AlSiAl sequence are located in two different channels (oxygen atoms in red).

thermal treatment in the temperature range relevant to heterogeneous proton-catalyzed reactions is important for their selectivity in, e.g., hydrocarbon reactions, as it might be significantly affected by the presence of Al-Lewis sites [54]. Perturbed Al atoms with an open coordination sphere and electron-pair acceptor properties (see ²⁷Al and ²⁹Si MAS NMR spectra in Fig. 3 and IR spectra of adsorbed d_3 -acetonitrile in Fig. 4) are formed when NH₄-forms of BEA/4.6, BEA/5.1, and BEA/11 are deammonized employing a thermal treatment (above 450 °C). A high Al concentration in Al-rich H-BEA* cannot be accounted for a high relative concentration of Al-Lewis sites (cf. Fig. 4 and SM4) as also Si-rich H-BEA* zeolites exhibit relatively high tendency to dehydroxylation [44,55,56]. The significantly higher tendency of both Al-rich and Si-rich BEA* to form Al-Lewis sites compared, e.g., to H-MFI and H-FER zeolites, is thus induced by some structural or compositional parameters of the beta zeolites, and it is reported elsewhere [57].

Some of the perturbed Al atoms after a partial dehydroxylation of the beta zeolite can be proposed to accept three water molecules at RT, which together with three framework oxygen atoms yield an octahedral coordination (27 Al resonance at -1.5 ppm in Fig. 3A). But all Al atoms preserve their locations in the zeolite framework T sites since the samples are exchanged with Na⁺ ions, as exclusively Al atoms with tetrahedral coordination are observed. This indicates a high stability of Al atoms against releasing from the framework for the Si-rich as well as Al-rich H-BEA* zeolites despite a relative easy formation of Al-Lewis sites. On the other side, a purposed formation of high concentration of Al-Lewis sites in the framework of Al-rich BEA* has a high potential for their application as active sites in Al-Lewis catalyzed reactions, as, e.g., Meerwein– Ponndorf–Verley reduction of ketones to alcohols [58,59].

UV–Vis spectroscopy of Co(II) ions as probes of close Al atoms and ²⁹Si MAS NMR spectroscopy monitoring various AlSi_nAl sequences present a tool for analysis of the Al arrangements in the framework of Al-rich beta zeolites and also provide a more general view on the accommodation of various counter divalent metal-ion species. The increase in the maximum attainable concentration of bare divalent cations coordinated with 6MRs (Co(II) ions) in Al-rich BEA* is roughly proportional to the increased content of framework Al atoms, as shown for the Al-rich BEA* samples reported here. It is to be pointed out that on contrary to the other pentasil ring zeolites of MFI, FER, and MOR topologies, divalent cations in the α -sites are not accessible for guest molecules or reactants of relatively small kinetic diameter like acetonitrile molecule, as follows from MD simulation (not given). Thus, divalent cations only at the β -sites are accessible (note that access to cations in γ -sites is limited in all pentasil-ring zeolite structures).

The two Al atoms of AlSiAl of Al-rich BEA* face predominantly different channels (>90% of AlSiAl) and can participate with other Al atoms present in the same channels in a formation of close unpaired Al atoms located in different rings. These unpaired Al atoms have a potential to ion-exchange divalent hexaaquo complexes, $[Co(II)(H_2O)_6]^{2+}$, and if dehydrated to charge balance counter-ion Co-oxo ([Co(III)O]⁺) species similar to unpaired Al atoms of Si-rich BEA* zeolites which do not contain AlSiAl sequences in their frameworks. The described Al arrangements provide opportunities also for other metal ions (e.g., Cu, Fe, Ni) and their various counter-ion metal-oxo species to chargebalance the corresponding local negative charge of the framework. With this respect orientation of Al atoms to the same channel and their mutual arrangement in the channel with another Al atom is a necessary condition for binding bare divalent cations possessing open coordination sphere or formally monovalent [M(III)O]⁺ metal-oxo species.

The enhancement in activity compared to Si-rich zeolites has recently been manifested in kinetic studies of selective reduction of nitrogen oxides [11] and N₂O decomposition [10] for Al-rich Cu- and Fe-BEA*, respectively. With the synthesized Al-rich Co-BEA* we report in the following paper [60] the high unprecedented activity in propane-SCR-NO_x even in the presence of water vapour up to 10 %. The structure of highly active Co species surviving wet NO_x streams is deduced from the local distribution of Al atoms in the framework analyzed here, and their activity is attributed to the synergetic redox effect of high concentration of [Co(III)O]⁺ entities.

5. Conclusions

The arrangement of Si–Al atoms in the BEA* framework and that occurring in the inner surface of the channels was investigated for the synthesized template-free Al-rich beta zeolites and compared to that of Si-rich BEA*. While Si-rich BEA* (Si/Al > 12) do not exhibit AlSiAl sequences, in Al-rich BEA* (Si/Al ~ 4–5) the concentrations of Al atoms in AlSiAl range from 40% to 100% of the total Al depending on their actual arrangement (in rings or as infinite sequence) in the framework. The location of Al atoms of AlSiAl and AlSiSiAl sequences with respect to individual channels determines the ability of their AlO₄ to cooperate in binding bare divalent cations or formally "monovalent" metal-oxo species (e.g., $[Co(III)O]^+$). AlO₄ of Al pairs (AlSiSiAl in 6MRs) with a minor contribution of AlSiAl sequences in one ring (possibly in 6MRs, 5MRs, and 4MRs) facing the same channel are cationic sites for

bare divalent cations. Their concentration reaches 35-50% of the total Al depending on the zeolite synthesis in both the Al-rich and Si-rich BEA*. However, a predominant part of the Al atoms of AlSiAl sequences (>90%) faces different channels and thus cannot cooperate in binding bare divalent cation. The most populated (50–65% of total Al) are unpaired Al atoms located in different rings of the channel surface, but close enough to charge balance divalent metal aquo complexes. These unpaired Al atoms facing the same channel consist of two AlO₄ tetrahedra each from different AlSiAl sequences, where Al atoms face different channels. The AlO₄ unit of the unpaired Al atoms could be therefore in a dehydrated zeolite charge balanced by a "monovalent" counter metal-oxo species, while the second AlO₄ is balanced by a proton.

Although the AlSiAl sequences are present exclusively in the Alrich and not in Si-rich beta zeolites, the inner surface of their channels in both cases contains nearly exclusively Al pairs (AlSiSiAl sequences in 6MRs) able to charge balance bare divalent cations and unpaired Al atoms located in different rings balanced by "monovalent" metal-oxo species. There is only a minor concentration of AlO_4^- located in AlSiAl facing the same channel with possible charge balance of divalent cations. Thus the main difference between the Al-rich and Si-rich beta samples important with respect to counter-ion species is a great increase in the concentration of Al in the framework of Al-rich BEA* and thus the ionexchange capacity, without a dramatic change in the mutual Si—Al arrangement in the inner surface of the channels.

Similar mutual Si-Al arrangements in the framework rings regarding the surface of channels result in similar structures of the counter-ion species in Si-rich and Al-rich beta zeolites, represented by protons, bare divalent cations or metal-oxo species, the unique sites for acid-base and redox catalyzed reactions. A high total concentration of aluminum and the relative concentration of bare divalent cations and "monovalent" metal-oxo species in Al-rich BEA*, which dramatically differ in their redox properties, and thus in redox-catalyzed activity, come from the population of Al pairs and unpaired Al atoms. The protonic sites of a high concentration present in Al-rich BEA* exhibit a similar strong acid strength like those in Si-rich BEA*. Also their tendency to dehydroxylate and form Lewis sites is comparable for Si-rich and Al-rich beta zeolites, being for both higher compared to that for zeolites of the MFI and FER topologies. Nevertheless, a high concentration of protonic sites still remains in Al-rich BEA* even at temperatures typical for heterogeneously acid-base catalyzed reactions.

The high concentration and local distribution of framework Al atoms in Al-rich BEA* induces stabilization of a high concentration of both protonic sites of high acid strength and metal redox sites exhibiting synergetic effect.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2015.10.010.

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