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Quantitative ⁶⁷Zn, ²⁷Al and ¹H MAS NMR spectroscopy for the characterization of Zn species in ZSM-5 catalysts†

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⁶⁷Zn MAS NMR spectroscopy was used to characterize the state of Zn in Zn-modified zeolites ZSM-5. Two ⁶⁷Zn enriched zeolite samples were prepared: by solid-state exchange with metal ⁶⁷Zn (Zn²⁺/ZSM-5 sample) and by ion exchange with zinc formate solution (ZnO/H-ZSM-5 sample), both containing ca. 3.8 wt% Zn. The elemental analysis, TEM, and quantitative BAS and aluminum analyses with 1 H and 27 Al MAS NMR have shown that Zn²⁺/ZSM-5 contains zinc in the form of Zn²⁺ cations, while both ZnO species and Zn²⁺ cations are present in ZnO/H-ZSM-5 besides BAS. ⁶⁷Zn MAS NMR has detected the signal of Zn in a tetrahedral environment from ZnO species for both the activated and hydrated ZnO/H-ZSM-5 zeolite. The signal of Zn in an octahedral environment was detected for the hydrated Zn²⁺/ZSM-5 and ZnO/H-ZSM-5 zeolites. This signal may belong to zinc cation [HOZn]⁺ or Zn(OH)₂ species surrounded by water molecules. Quantitative ⁶⁷Zn MAS NMR analysis has shown that only 27 and 38% of zinc loaded in the zeolite is visible for the activated and hydrated ZnO/H-ZSM-5 zeolite, and 24% of Zn is visible for the hydrated Zn²⁺/ZSM-5. Zinc in the form of ZnO species is entirely visible in both the activated and hydrated ZnO/H-ZSM-5 zeolite, while Zn²⁺ cations are not detected at all for the activated sample and only 29% of Zn²⁺ cations is visible for the hydrated zeolite. Detection of only a part of Zn²⁺ cations in the form of [HOZn]⁺ or Zn(OH)₂ species in octahedral environment presumes only partial hydrolysis of the bond of Zn²⁺ cation with framework oxygen and further solvation of the Zn species formed at hydrolysis by the adsorbed water.

Introduction

The conversion of light alkanes to highly valuable aromatic hydrocarbons can be effectively performed by Zn-modified zeolite catalysts. 1-4 Various approaches have been used 2,5 for zinc loading in the zeolite and, therefore, different types, dimensions, and localizations of zinc species, inside the zeolite pores and on the outer surface of the crystals, have been considered for the mechanism of catalysis. 6-8 In this regard, it is crucial to characterize properly the state of zinc species loaded into a zeolite. In our recent work, we have used the following experimental techniques to study Zn species in zeolites:8 extended X-ray absorption fine structure (EXAFS), X-ray photoelectron spectroscopy (XPS) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), the latter for

molecule complexes attached to the Zn species. An obvious idea is to use Zn NMR spectroscopy as well. However, there are certain difficulties regarding the application of the method. First, the only stable NMR-active isotope is ⁶⁷Zn, which has a natural abundance of 4.10%.9 Second, the low gyromagnetic ratio, γ , amounting to $\gamma/2\pi = 2.668532$ MHz T⁻¹, ¹⁰ downgrades the molar receptivity of ⁶⁷Zn nuclei with respect to ¹H nuclei by a factor of 2.87 \times 10⁻³. Third, the nuclear spin of ⁶⁷Zn is I = 5/2and the nuclear electric quadrupole moment of is 15.0 fm², ¹⁰ which limits the NMR observation of powders to the central transition (magnetic quantum numbers $-1/2 \leftrightarrow +1/2$) and causes a strong second-order quadrupole broadening of the NMR spectra. Fourth, the amount of Zn species usually loaded in a zeolite is relatively low, e.g., it is about 3.8 wt% our studies.8,11-13 A maximum value of 6 wt% can be found in the literature.14

The combination of the four factors lowers drastically the sensitivity of Zn NMR compared to the mostly used NMR isotopes. Only the first problem can be overcome by using ⁶⁷Zn enriched materials for Zn loading in zeolites. A corresponding study was performed by Qi et al.14 They used 89.6% ⁶⁷Zn enriched precursors for loading of 2 and 6 wt% of Zn in

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ZSM-5 zeolite and presented ⁶⁷Zn NMR spectra and ¹H spectra with dipolar ⁶⁷Zn recoupling by irradiation of the ⁶⁷Zn NMR frequency. The latter spectra were measured as a function of the irradiation time (up to 14.4 ms) and used for a quantitative determination of the synergic acid sites with the obtained amount being about 4 μ mol g⁻¹ for both, the 2 and 6 wt%, Zn-modified ZSM-5 samples.14 It turns out that the concentration of synergic acid sites, provided in the study of Qi et al., 14 is three orders of magnitude smaller than the concentration of Zn atoms.

NMR spectroscopy can be applied as a quantitative technique, if a one-pulse excitation (observation of the Bloch decay) and a reference sample with a known concentration of the nucleus under study are used. For echo measurements, the echo intensity loss by the transverse relaxation must be taken into account. The sensitivity-enhancement technique quadrupolar Carr-Purcell-Meiboom-Gill (QCPMG NMR)¹⁵ can be hardly used for concentration determinations because the obtained time-domain signal increases with the number of observed echoes. The present study applies 67Zn, 27Al, and 1H MAS NMR spectroscopy on zeolites ZSM-5 zeolites modified with ⁶⁷Zn enriched zinc, in order to find out which information for the characterization of Zn-containing catalysts can be obtained by quantitative NMR spectroscopy. ²⁷Al recoupled ¹H MAS NMR spectroscopy (TRAPDOR)^{16,17} was also applied to get additional information.

Methods

Synthesis of Zn²⁺/ZSM-5 zeolite and sample preparation

The parent zeolite is a template-free synthesized NH₄-ZSM-5 (Si/Al = 13) zeolite provided by the Tricat GmbH. The ammonium form was transformed into the hydrogen form by calcination at 500 $^{\circ}$ C for 5 h. The characteristics of this H-ZSM-5 zeolite were previously described.¹⁸ A solid-state exchange reaction between BAS of the acid H-ZSM-5 zeolite and zinc powder was used to prepare Zn2+ - exchanged zeolite. 19,20 The zeolite was activated under vacuum at 673 K for 20 h (residual pressure $< 10^{-3}$ Pa), and the reaction with zinc vapor was performed at 773 K for 7 h in a vacuumed glass ampule loaded with the activated zeolite and metallic zinc (Zn/Al = 5). We used a 90% ⁶⁷Zn enriched Zn metal of US Services Inc. (John Kilby), whereas a Zn metal with a 4.10% natural abundance of 67Zn was used for previous studies.19 It follows an evacuation at 773 K for 15 h. ¹H MAS NMR spectroscopy has shown¹⁹ that such a procedure leads to the removal of bridged SiOHAl groups. The concentration of Zn in the product in the resulting sample is 3.8 wt%, as determined by elemental analysis (ICP-OES). We denote this sample as activated Zn²⁺/ZSM-5. A portion of the Zn²⁺/ZSM-5 zeolite was exposed to atmospheric water for 24 h and then again activated at 673 K for 20 h under vacuum and further sealed in a 3-mm-glass ampoule for the NMR measurement. This sample is denoted as reactivated Zn²⁺/ZSM-5. Another sample, sealed in a glass tube, was opened and kept for 24 h under air before 67Zn NMR measurements meanwhile rehydration took place. We denote the sample as hydrated Zn²⁺/ZSM-5.

Synthesis of ZnO/H-ZSM-5 zeolite and sample preparation

Zn-modified ZSM-5 zeolite, containing both Zn²⁺ cations and highly dispersed ZnO species or small clusters of ZnO located in the channels of the zeolite, was synthesized by the ion exchange with zinc formate solution, ⁶⁷Zn(HCOO)₂. Details of the synthesis procedure is described further. The elemental analysis has shown that the content of Zn in the sample is 3.86 wt%.

ZnO/H-ZSM-5 zeolite was activated under vacuum (673 K for 20 h) and a portion of it was loaded with a small amount of adsorbed benzene and then sealed in a 3 mm-glass ampoule for the NMR measurement. We denote the sample as activated ZnO/H-ZSM-5. Another portion of the activated sample was kept in air for 24 h and further filled into the MAS rotor for the measurement. We denote the sample as hydrated ZnO/ H-ZSM-5.

Transmission electron microscopy

The Themis-Z 3.1 (TFS, USA) microscope, equipped with a field emission cathode with a monochromator and two aberration correctors, was used to study Zn-modified zeolite samples at an accelerating voltage of 200 kV. Energy dispersive X-ray spectroscopy (EDX) was performed with a four-segment Super-X detector (an energy resolution of 120 eV) in the scanning dark-field mode (HAADF-STEM) with elemental mapping along the characteristic lines of the spectrum from each point of the analyzing region. For the electron microscopy studies, Zn²⁺/ZSM-5 and ZnO/H-ZSM-5 zeolites were dispersed in ethanol using ultrasound and deposited on a perforated carbon-film-coated copper grid (3 mm diameter).

NMR methods

⁶⁷Zn and ²⁷Al MAS NMR experiments were performed at room temperature on a Bruker AVANCE 750 spectrometer at 17.6 T with high-power Bruker probes and a MAS frequency of 10 kHz. Larmor frequencies were about 195 and 47 MHz for ²⁷Al and ⁶⁷Zn, respectively. A narrow-bore X probe was used for ⁶⁷Zn MAS NMR spectroscopy. 67Zn MAS NMR measurements were done using a Hahn echo with a 16-phase cycle and a delay of one rotation period, 100 µs, between $\pi/2$ - and π -pulses. For each zeolite sample, the number of scans was 50 000 with a delay of 2 s between the scans, a dwell time of 20 μs, a size of 16 k, and a unique receiver gain. The estimated longitudinal 67Zn relaxation time for Zn-modified zeolite samples is smaller than 200 μs. We have $T_1 \approx 1$ s for ZnO powder and used a repetition delay of 5 s for the ZnO reference sample.

Additional 67Zn measurements with a Hahn-echo pulse delay of 200 µs did not show a significant signal decay compared to the 100 µs pulse distance for all samples. Therefore, transverse relaxation can be neglected for the 100 µs pulse distance. This is important for NMR concentration determinations by using the Hahn-echo intensity.

For ²⁷Al MAS NMR, the number of scans were 500 with a delay of 0.5 s between the scans, a dwell time of 20 µs, a size of 4 k and a unique receiver gain. A selective $\pi/4$ (non-selective $\pi/12$) **PCCP** Paper

pulse was used to get spectral intensities independent of different quadrupole coupling constants $C_{\rm O}$.

To determine the quantity of BAS in the zeolite samples with ¹H MAS NMR, the experiments were performed at 9.4 T on a Bruker Avance-400 spectrometer equipped with a broad-band double-resonance-MAS probe. Zirconia rotors (4 mm outer diameter) with the inserted sealed 3 mm glass tube were spun at 5-10 kHz by dried compressed air at room temperature (300 K). ¹H MAS NMR spectra were recorded by the Hahnecho pulse sequence $(\pi/2-\tau-\pi-\tau$ -acquisition), where τ equals one rotor period (100-200 µs). The excitation pulse length was 4.5 μ s (π /2), and typically 32 scans were accumulated with a 4-60 s delay. In double-resonance, ¹H{²⁷Al} TRAPDOR experiments^{16,17} Hahn-echo sequence was applied to the ¹H channel with irradiation of aluminum during both τ periods. The ²⁷Al nutation frequency of the irradiation field was about

All chemical shift references correspond to the IUPAC convention.21

Reference samples

NMR concentration determination requires a reference (internal or external) with a known concentration of the corresponding nucleus. For the determination of the concentration of zeolite OH groups (Brønsted acid sites, BAS) with ¹H MAS NMR, we have used a certain quantity of benzene adsorbed on activated (dehydrated) zeolite sample as an internal reference. 18,22

For determination of the quantity of Zn species by ⁶⁷Zn MAS NMR, ZnO powder with a molar mass of 81.41 g mol⁻¹ and a ⁶⁷Zn natural abundance of 4.10% was used as an external ⁶⁷Zn reference. We have 0.041 $N_A/81.41$ of 67 Zn nuclei per gram of ZnO (N_A is the Avogadro constant). Thus, the specific concentration (67 Zn number per 1g ZnO powder) is $c_{\rm s\,ZnO}$ = 5.036 \times $10^{-4} \times N_{\rm A} {\rm g}^{-1}$. 0.131 gram of ZnO powder was filled into the MAS rotor. It corresponds to $N_{\rm A} \times 6.6 \times 10^{-5}$ of ⁶⁷Zn nuclei in the rotor.

Aluminum concentration was determined by ²⁷Al MAS NMR measurements of the hydrated samples in comparison with the zeolite Na-ZSM-5 (Si/Al = 15) of the Tricat GmbH, which is the sodium form for the parent zeolite of the Zn-modified samples.

Results

Sample characterization by electron microscopy

Before studying by MAS NMR, ZnO/H-ZSM-5 and Zn²⁺/ZSM-5 zeolites were characterized by transmission electron microscopy. Fig. 1 shows the obtained TEM images. Both samples, originating from the same parent H-ZSM-5, display a crystal size of 0.5-5 µm and a rod-shaped morphology, which is typical of MFI-type zeolites.²³ The Zn²⁺/ZSM-5 sample represents the pure zeolite phase (Fig. 1a and b). For ZnO/H-ZSM-5, the particles notably different in size and mass density, compared to the zeolite crystals, can be seen (Fig. 1c and d). This evidences the presence of another phase deposited on the surface of the zeolite crystals.

For Zn²⁺/ZSM-5 (Fig. 1e and f), EDX elemental mapping shows Zn, Al, and Si are uniformly distributed in the zeolite crystals, with Al/Zn atomic ratio being around 2 (Table 1). This confirms the presence of only Zn2+ species in the sample and almost full substitution of BAS by zinc cations. For ZnO/H-ZSM-5 (Fig. 1g and h), there is a uniform distribution of Si and Al within the zeolite crystals, whereas the smaller particles, observed in HAADF-STEM images, are enriched with Zn. Therefore, it is reasonable to conclude that these particles are ZnO-like agglomerates on the external surface of ZSM-5 crystals. Elemental composition determined for different areas in Fig. 1h and presented in Table 1 demonstrates that the crystals of ZnO/H-ZSM-5

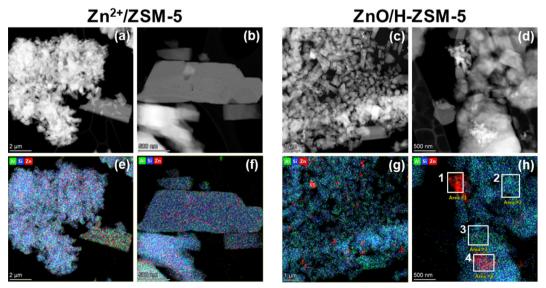


Fig. 1 HAADF-STEM images of ZnO/H-ZSM-5 (a) and (b) and Zn²⁺/ZSM-5 (c) and (d) zeolites. EDX elemental mapping images of Si (blue), Al (green), and Zn (red) in the crystals of ZnO/H-ZSM-5 (e) and (f) and Zn²⁺/ZSM-5 (g) and (h) zeolites. See also Table 1 for relative atomic content of the elements as obtained for whole studied area (e)-(h) or selected ones as depicted in (f).

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Table 1 Atomic content of Si, Al, and Zn for ZnO/H-ZSM-5 and Zn²⁺/ 7SM-5 zeolites

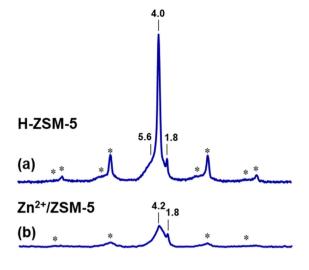
	Studied area	Atomic content/%			
Fig. 1 image		Al	Si	Zn	
e	Whole area	7.66	87.09	5.26	
f	Whole area	7.24	81.14	11.62	
	Area 1	0.73	8.39	90.88	
	Area 2	7.98	88.16	3.86	
	Area 3	9.62	83.32	7.06	
	Area 4	4.60	54.43	40.98	
g	Whole area	7.43	87.94	4.62	
h	Whole area	8.07	88.31	3.62	

zeolite also contain Zn, and its quantity is similar to that for the Zn²⁺/ZSM-5 sample. This may indicate the presence of Zn²⁺ cations and small ZnO-like clusters inside ZnO/H-ZSM-5 pores⁸ together with larger ZnO-agglomerates on the external surface.

Sample characterization by ¹H MAS NMR and evaluation of BAS quantity and zinc state

Zn²⁺/ZSM-5. Fig. 2 shows ¹H MAS NMR spectra of parent H-ZSM-5 and Zn²⁺/ZSM-5 zeolite samples. For the Zn²⁺/ZSM-5 sample, prepared by a solid-state exchange reaction between BAS of the zeolite and ⁶⁷Zn zinc powder, a minor signal at 1.8 ppm from SiOH groups does not change in intensity, compared to the same signal in parent H-ZSM-5, while the intensity of the signals at 4.0 and 5.6 ppm decreases dramatically. For H-ZSM-5, these two signals belong to isolated and hydrogen-bonded bridged SiOHAl groups, 22 respectively. TRAP-DOR experiments have shown that the intensity of the signals at 4.0 and 5.6 ppm decreases in the spectrum recorded with ²⁷Al irradiation for H-ZSM-5, whereas the intensity of the signal around 4.2 ppm is intact for Zn²⁺/ZSM-5 (Fig. 3). This implies that the signal at 4.2 ppm of Zn²⁺/ZSM-5 belongs presumably to hydrogen-bonded SiOH groups (silanol nests), rather than the residual, after solid-state exchange with metallic zinc, bridged SiOHAl groups (BAS). This means that about 100% exchange (full exchange) of acid OH groups of the zeolite for Zn²⁺ cations has occurred. The quantity of SiOHAl groups in parent H-ZSM-5 zeolite was determined by using adsorbed methane and benzene as the internal standards. 18,22 The quantity of 1290 µmol g⁻¹ [7.4 SiOHAl groups per zeolite unit cell (u.c.)] corresponds well with the quantity estimated from Si/Al ratio determined by ²⁹Si MAS NMR (Si/Al = 12).18 The concentration of BAS and Zn2+ species for Zn²⁺/ZSM-5 and H-ZSM-5 is presented in Table 2.

Reactivated Zn²⁺/ZSM-5. To inquire into the effect of water on the state of Zn in Zn2+/ZSM-5, the zeolite was exposed to atmospheric water at ambient temperature overnight. Further, the sample was again activated under vacuum at 673 K for 24 h, and then sealed in a 3 mm-glass ampoule for the NMR measurement. The spectrum of the reactivated Zn²⁺/ZSM-5 zeolite (Fig. 2c) shows the increase in the intensity of SiOHAl group signal at 4.0 ppm with respect to the signal in Zn²⁺/ZSM-5 sample (Fig. 2b) and the appearance of the new signals at 1.2 and 1.8 ppm. The TRAPDOR experiment 16 shows a decrease of the signal intensity at 4.0 ppm in the spectrum recorded with



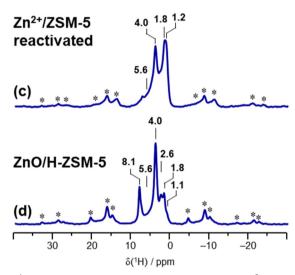


Fig. 2 ¹H MAS NMR spectra of parent H-ZSM-5 (a), Zn²⁺/ZSM-5 (b), reactivated Zn²⁺/ZSM-5 (c) and ZnO/H-ZSM-5 (d) zeolite samples. 23 µmol/g of benzene was adsorbed on sample (d), which is seen by the signal at 8.1 ppm.

²⁷Al irradiation, whereas the signals at 1.2 ppm and 1.8 ppm are not affected (Fig. 3). These signals are reasonably assigned to ZnOH groups¹⁴ formed at Zn²⁺-O⁻ bond hydrolysis by water, simultaneously SiOHAl groups are formed by Scheme 1. Note that the complete recovery of SiOHAl groups to their concentration in the parent H-ZSM-5 does not occur by the used procedure of zeolite treatment with water and its further activation.

ZnO/H-ZSM-5. Fig. 2d shows ¹H MAS NMR spectrum of activated ZnO/H-ZSM-5 zeolite sample with adsorbed benzene, which is used as an internal standard to determine the concentration of BAS. The signal at 8.1 ppm belongs to the adsorbed benzene. The signals at 4.0 ppm and ca. 5.6 ppm arise from the isolated and hydrogen-bonded SiOHAl groups. The minor signal at 1.8 ppm is due to isolated terminal SiOH groups, while the signal at 2.6 ppm is assigned to hydroxyl groups of extra framework or partially coordinated to zeolite framework

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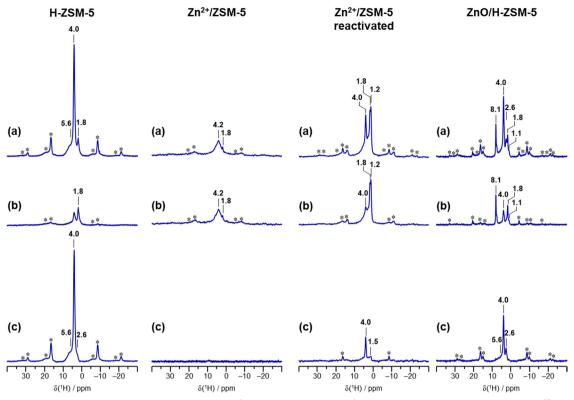


Fig. 3 ¹H MAS NMR Hahn-echo spectra of parent H-ZSM-5, Zn²⁺/ZSM-5, reactivated Zn²⁺/ZSM-5 and ZnO/H-ZSM-5: (a) without ²⁷Al irradiation and (b) with 27 Al irradiation (on-resonance). The difference spectrum of (a) and (b) is shown in (c). The spinning speed was set to 5 kHz, and τ was equal to one rotor period (200 µs)

Table 2 BAS concentration and zeolite unit cell composition for 7SM-5 zeolite samples

	OH concentration/μmol·g	-1			
Zeolite sample	Si-OH	Zn-OH	Al-OH	Si-OH-Al	Zeolite unit cell
H-ZSM-5 Zn ²⁺ /ZSM-5 (3.80 wt% ⁶⁷ Zn) ZnO/H-ZSM-5 (3.86 wt% ⁶⁷ Zn)	40 ± 8 (terminal) 400 ± 70 (silanol nests) 70 ± 50	17 ± 16	96 ± 5 140 ± 40	1290 ± 90 530 ± 170	$\begin{array}{c} \left Al_{0.47}^{\rm oct} H_{7.38} \right \left[Al_{}^{\rm tetr} I_{7.38}^{\rm si} Si_{88.62} O_{192} \right] \\ _{}^{67} Zn_{3}^{2+} J_{3.93} \right \left[Al_{}^{\rm tetr} I_{7.85}^{\rm si} Si_{88.15} O_{192} \right] \\ \left Al_{}^{\rm oct} I_{3.06}^{\rm $

AlOH species. 24 The signal at 1.1 ppm may be assigned to ZnOH groups. 14 Comparison of the BAS quantity, determined by the internal standard approach with that for parent H-ZSM-5 allowed us to calculate the composition of the zeolite unit cell and evaluate the state of Zn in the zeolite based on the known quantity of the loaded zinc (Table 2). This composition implies that zeolite contains both ZnO species and Zn²⁺ cations.

Concentrations of aluminum species determined by ²⁷Al MAS NMR spectroscopy

Fig. 4 presents the ²⁷Al MAS NMR spectra of the reference sample, a hydrated zeolite Na-ZSM-5 (A), and the samples under study, the hydrated Zn²⁺/ZSM-5 (B) and the hydrated ZnO/ H-ZSM-5 (C). The hydrated samples represent the activated samples that were opened and kept under air for 24 h. The weight analyses have shown that they contain 7 wt% water. Such value corresponds to the degree of hydration of about 25 water molecules per unit cell for Zn²⁺/ZSM-5 and ZnO/H-ZSM-5, respectively. Na-ZSM-5 reference sample contained 12 molecules of water per zeolite unit cell.

Spectra (A) and (B) show signals of tetrahedrally coordinated aluminum atoms AlO₄ at about 60 ppm. A spinning sideband is observed only in the spectrum (A). Spectrum (C) shows in addition a signal of octahedrally coordinated aluminum AlO₆ at about 3 ppm. No signal of five-fold coordinated aluminum AlO₅, which would be expected at about 35 ppm, is observed. For the determination of the aluminum concentration, we consider the integral intensities of the spectra, the weight of the samples and the different Si/Al ratios (those are 12 for the parent H-ZSM-5 and 15 for the reference Na-ZSM-5). The accuracy of this approach for concentration determinations by ²⁷Al MAS NMR is 15%. Within this limit, there is no significant deviation of the Si/Al ratio from the value 12 in the hydrated Zn²⁺/ZSM-5 and ZnO/H-ZSM-5 samples. Both samples

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Scheme 1 Hydrolysis of Zn²⁺-O⁻ bonds in Zn²⁺/ZSM-5 zeolite and further coordination of water molecules to the formed [HOZn]⁺ and Zn(OH)₂ species affording octahedrally coordinated Zn species.

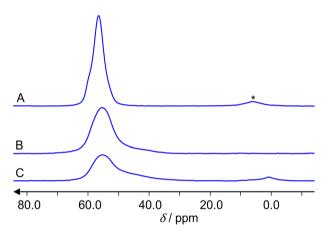


Fig. 4 ²⁷Al MAS NMR spectra of the hydrated zeolites: Na-ZSM-5 (A), Zn²⁺/ZSM-5 (B) and ZnO/H-/ZSM-5 (C). The asterisk (*) denotes a spinning sideband.

show mainly (100 and 94% integral intensity, respectively) AlO₄ coordination of framework aluminum atoms. Only the hydrated ZnO/H-ZSM-5 shows a weak (6% integral intensity) signal of extra-framework AlO₆ aluminum. Spectra (B) and (C) have a shoulder of the AlO₄ peak. Consequently, the spectra were deconvoluted by dmfit25 as presented for the ZnO/H-ZSM-5 sample in Fig. 5. The result is that the spectrum of ZnO/ H-ZSM-5 sample consists of three signals with the following values of the chemical shift δ , quadrupole coupling constant $C_{\rm O}$ and relative integral intensities I: δ = 60.5 ppm with $C_{\rm O}$ = 5.2 MHz and I = 59%, $\delta = 60.5$ ppm with $C_O = 8.2$ MHz and I = 35%, $\delta = 3.5$ ppm with $C_Q = 4.0$ MHz and I = 6%. The deconvolution of the spectrum of Zn²⁺/ZSM-5 gives two signals: δ = 60.5 ppm with $C_{\rm Q}$ = 5.2 MHz and I = 79%, δ = 60.5 ppm with $C_{\rm Q}$ = 8.2 MHz and I = 21%.

⁶⁷Zn MAS NMR spectra of the zeolite samples

Fig. 6 shows ⁶⁷Zn MAS NMR spectra of ZnO reference and the three samples under study. A fit of the spectrum in Fig. 6A by

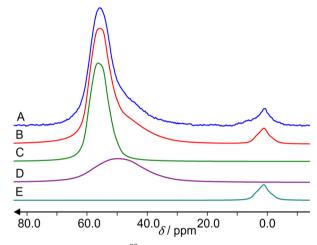


Fig. 5 Deconvolution of the ²⁷Al MAS NMR spectra of the hydrated ZnO/ H-ZSM-5 zeolite. (A) is the experimental spectrum, (B) the sum of the deconvoluted signals, (C) is the main AlO₄ signal with δ = 60.5 ppm, C_Q = 5.2 MHz, asymmetry parameter $\eta = 0.5$, (D) is a stronger guadrupolar broadened signal with the same chemical shift δ = 60.5 ppm, but C_{Ω} = 8.2 MHz, η = 0.5, (E) is the AlO₆ signal with δ = 4.0 ppm, $C_{\rm Q}$ = 4.0 MHz, η = 1. The deconvolution was performed by dmfit 25 using a broadening of Em = 600. The signals at 60.5 ppm with C_Q = 5.2 MHz, 60.5 ppm with C_Q = 8.2 MHz, and 3.5 ppm with C_Q = 4.0 MHz contain 59%, 35% and 6% of the total integral intensity, respectively.

the program dmfit²⁵ yields the following parameters for the ZnO signal: chemical shift δ = 240 ppm, quadrupole coupling constant $C_0 = 2.4$ MHz, asymmetry parameter $\eta = 0$. This is in accordance with the literature data.26 Spinning sidebands cannot be observed.

The hydrated Zn²⁺/ZSM-5 zeolite exhibits a signal in the region of 0 ppm (Fig. 6B), which belongs to octahedrally coordinated (ZnO₆) Zn.²⁷ A fit is less accurate due to the lower signal-to-noise ratio and a broadening of Em = 500 is used for the spectrum. It gives $\delta = 7$ ppm, $C_Q = 3$ MHz and $\eta = 0$.

The activated ZnO/H-ZSM-5 zeolite shows only the signal in the region of tetrahedrally coordinated (ZnO₄) Zn species (Fig. 6D). A fit gives $\delta = 240$ ppm, $C_{\rm O} = 2.5$ MHz and $\eta = 0$.

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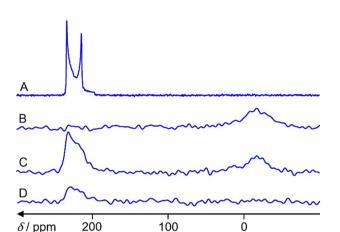


Fig. 6 67 Zn MAS NMR spectra of ZnO powder (A), the hydrated Zn $^{2+}$ /ZSM-5 (B), the hydrated ZnO/H-ZSM-5 (C), and the activated ZnO/H-ZSM-5 (D). The height of spectrum (A) is reduced by a factor of ten with respect to the other spectra.

The hydrated ZnO/H-ZSM-5 exhibits the signals of both tetrahedrally (ZnO₄) and octahedrally (ZnO₆) coordinated Zn species (Fig. 6C). A fit gives δ = 240 ppm, C_Q = 2.5 MHz and η = 0 with 2/3 integral intensity for the tetrahedrally coordinated Zn species and δ = 0 ppm, C_Q = 2.5 MHz and η = 0 with 1/3 integral intensity for the octahedrally coordinated Zn species. No ⁶⁷Zn MAS NMR signal is observed for the activated Zn²⁺/ZSM-5 zeolite.

Determination of Zn species concentration in zeolites by 67 Zn MAS NMR

For the determination of various Zn species concentration in the 90% 67 Zn enriched Zn²⁺/ZSM-5 and ZnO/H-ZSM-5 samples, we have assumed that both zeolite samples contain similar quantity of the loaded Zn (3.83 wt%). We neglect the weight of the adsorbed molecules in the fused samples. The atomic mass of 67 g mol⁻¹ for the 90% 67 Zn enriched zinc was used. In this case, the number of 67 Zn species per one gram of Zn-modified zeolite (specific concentration) is $c_{\rm s\, zeolite} = N_{\rm A} \times 0.9 \times 0.0383/67$. The comparison between $c_{\rm s}$ of the Zn-modified zeolites and ZnO powder (see section Reference Samples) gives $c_{\rm s\, Zn\, zeolite}/c_{\rm s\, ZnO} = 1.037$.

For the ZnO signal the Topspin integral intensity of the spectrum is 642571386. With a ZnO weight of 0.131 g in the rotor we obtain the specific intensity $I_{\rm s\,ZnO}$ = 96 627 per one scan and one gram sample.

The sample weight of the hydrated $\rm Zn^{2+}/ZSM-5$ is 0.053 g. The integral intensity of the spectrum (Fig. 4B) is 66975411. The specific intensity per one scan and one gram of sample is $I_{\rm s\,Zn2+/ZSM-5}=25274$. Presuming $c_{\rm s\,Zn2+/ZSM-5}/c_{\rm s\,ZnO}=I_{\rm s\,Zn2+/ZSM-5}/I_{\rm s\,ZnO}$ we have $c_{\rm s\,Zn2+/ZSM-5}/c_{\rm s\,ZnO}=0.2616$.

The sample weight (in the rotor) of the hydrated ZnO/H-ZSM-5 is 0.067 g. The integral intensity of the spectrum C in Fig. 6 is 128258318. $I_{\rm SZnO/H-ZSM-5} = 38$ 286. In this case $c_{\rm SZnO/H-ZSM-5}/c_{\rm SZnO} = 0.3962$.

The sample weight of the activated ZnO/H-ZSM-5 is 0.020 g in the fused glass ampoule. The integral intensity of the

spectrum (Fig. 4D) is 27196740. $I_{\rm s\,ZnO/H\text{-}ZSM\text{-}5}$ = 27197. We have $c_{\rm s\,ZnO/H\text{-}ZSM\text{-}5}/c_{\rm s\,ZnO}$ = 0.2815.

The accuracy of our approach to concentration determinations by 67 Zn MAS NMR is 20%. We would expect a ratio $c_{\rm s\,Znzeolite/cs\,ZnO}=1.037$ (see above), if the 67 Zn MAS NMR spectrum showed all 67 Zn nuclei in the sample according to 3.83 wt% Zn. The lower ratios, estimated above, demonstrate that we see only $38\pm8\%$ of the expected signal for the hydrated ZnO/H-ZSM-5, $24\pm5\%$ of the expected signal for the hydrated ZnO/H-ZSM-5, and less than 5% (detection limit) of the expected signal for the activated ZnO/H-ZSM-5, in a glass ampoule. For the hydrated ZnO/H-ZSM-5, the ratio 2:1 for ZnO₄ and ZnO₆ intensities implies that we detect 25% and 13% of Zn in tetrahedral and octahedral environments, correspondingly.

Discussion

Characterization of the zeolite samples with elemental analysis, TEM, ¹H and ²⁷Al MAS NMR allowed us to determine the state of Zn species in the zeolites and calculate the composition of the zeolite unit cell (Table 2). It follows that ZnO/H-ZSM-5 contains both ZnO and Zn²⁺ cation species. Only the signal of the tetrahedrally coordinated Zn species is detected for the activated ZnO/H-ZSM-5 by ⁶⁷Zn MAS NMR (Fig. 6D). This implies that highly dispersed ZnO species in the zeolite may represent the small ZnO-like clusters or ZnO-agglomerates in which Zn atoms are surrounded by tetrahedrally disposed oxygen atoms.

The zeolite exposed to water vapor from air atmosphere (hydrated ZnO/H-ZSM-5) displays the signal of octahedrally coordinated Zn species besides the signal of ZnO species (Fig. 6C). An appearance of this signal upon zeolite hydration implies hydrolysis of the bonds of Zn^{2+} cations with the oxygens of the zeolite framework and further hydration of the formed $[HOZn]^+$ cations or $Zn(OH)_2$ species with water molecules (Scheme 1). Presumably, $[HOZn(H_2O)_5]^+$ cations or $[(H_2O)_4Zn(OH)_2]$ species become detectable by ^{67}Zn MAS NMR.

The activated $\rm Zn^{2+}/ZSM$ -5 zeolite exhibits no $\rm ^{67}Zn$ MAS NMR signal. However, the hydration of the zeolite makes the signal visible (Fig. 6B), *e.g.*, in the form of $\rm [HOZn(H_2O)_5]^+$ cations, generated according to Scheme 1. Note that a notable part of loaded the Zn species (62–76%) remain invisible by $\rm ^{67}Zn$ MAS NMR even for the hydrated zeolites.

Why we cannot see the majority of zinc species in our 67 Zn MAS NMR spectra? 67 Zn has the nuclear spin I=5/2 and the second-order quadrupole broadening of the observed central transition is proportional to the square of the electric field gradient on the location of the nucleus. 28 $C_{\rm Q}$ is proportional to this gradient. In the reported spectra, the observed species have $C_{\rm Q}$ of 2.5 MHz and 3 MHz for tetrahedral or octahedral coordination, respectively. Quadrupole frequencies above 20 MHz for less symmetric coordination can be found in the literature. 27 If $C_{\rm Q}$ is larger, for example, by five times, this results in the line broadening by 25 times. This leads to a decrease in the amplitude

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of the signal by 25 times. Taking into account the signal-to-noise ratio for the spectra in Fig. 6, which is obtained with an acquisition time of one day, it is clear that the species with such a low symmetry of coordination cannot be observed. In this regard, the signal of Zn²⁺ cations without a hydration shell, which interacts directly with the oxygens of the zeolite framework is not detected.

Detection of 24% of the expected signal intensity for the hydrated Zn²⁺/ZSM-5 implies partial hydrolysis (with 25 adsorbed water molecules per u.c.) of the bonds of Zn²⁺ cations with oxygens of the zeolite framework. Most of the Zn²⁺ cations retain direct interaction with the oxygens of the zeolite framework and remain invisible in the ⁶⁷Zn MAS NMR spectrum.

It is interesting, the quantity of tetrahedrally coordinated Zn species visible in the hydrated and activated ZnO/H-ZSM-5 are similar, 25 and 27%, correspondingly. Presuming that Zn2+ is completely invisible for the activated ZnO/H-ZSM-5, it is reasonable to conclude that all Zn sites in the form of ZnO species are visible in both samples. Indeed, the composition of the zeolite unit cell of ZnO/H-ZSM-5 (Table 2) implies that 36% of Zn should be in the form of ZnO. This value is close to the experimentally observed quantity of ZnO species (25-27%), provided that the accuracy of Zn quantification by ⁶⁷Zn NMR is 20%.

Taking into account that the unit cell composition and the relative intensities of Zn signals in tetrahedral ZnO4 and octahedral ZnO₆ coordination is 2:1, one can infer that 71% of Zn in the form of Zn2+ cations remain invisible for the hydrated ZnO/H-ZSM-5.

Quantitative ²⁷Al MAS NMR spectroscopy of the hydrated samples can exclude that a significant dealumination takes place during the Zn modifications of the zeolite. The spectra of the Zn²⁺/ZSM-5 and ZnO/H-ZSM-5 samples show mainly (100 and 94% integral intensity, respectively) AlO₄ coordination of framework aluminum atoms as expected for a ZSM-5 zeolite. The loading of Zn does not destroy the zeolite structure, but provides some effect on the structure of AlO₄ tetrahedra. Each AlO₄ unit is negatively charged and requires a charge compensation by either BAS (H⁺) or zinc cation (Zn²⁺). The spectrum of the hydrated Zn²⁺/ZSM-5 sample does not show AlO₆ signal of extra-framework aluminum, whereas, in the hydrated sample ZnO/H-ZSM-5, 0.47 aluminum atoms per unit cell are in AlO₆ coordination. A deconvolution of the AlO₄ signal of both zeolites shows that it consists of two lines that have the same chemical shift of 60.5 ppm, but different quadrupole coupling constants of 5.2 and 8.2 MHz. The smaller $C_{\rm O}$ value corresponds to 59% and 79% and the larger one to 35% and 21% of the total intensity of ²⁷Al signal for the hydrated ZnO/H-ZSM-5 and Zn²⁺/ZSM-5 zeolites, respectively.

For the hydrated ZnO/H-ZSM-5, 29% of Zn²⁺ in the form, e.g., of [HOZn(H₂O)]⁺ species is visible. Visible cations correspond to 0.625 Zn²⁺ cations per u.c. Upon hydration of the zeolite, this quantity of the cations together with SiOHAl sites (3.06 H⁺ site per u.c.) can afford Al species in a tetrahedral oxygen environment (4.31 sites per u.c.) that are visible by ²⁷Al MAS NMR. This quantity of AlO₄ corresponds to 58% of the total quantity of AlO4 species in zeolite. This is in good

accordance with 59% of AlO₄ species measured by ²⁷Al MAS NMR with the signal with smaller $C_Q = 5.2$ MHz. This means that, for the hydrated ZnO/H-ZSM-5 zeolite, a narrower signal with smaller C_0 corresponds to AlO₄ tetrahedra in ²⁷Al MAS NMR spectrum, which have hydrated [HOZn]⁺ or/and Zn(OH)₂ and H⁺ cations in the neighborhood, while that with larger C_{Ω} belongs to the non-hydrated Zn2+ cations directly interacting with zeolite framework.

The situation seems to be completely different for the hydrated Zn²⁺/ZSM-5. If we accept that 76% of Zn in hydrated Zn²⁺/ZSM-5 remains invisible, while all Al in this sample is visible in ²⁷Al MAS NMR, then the larger signal with the relative intensity of 79% and smaller $C_{\rm O}$ should be assigned to Al in the AlO₄ tetrahedra, which have non-solvated Zn²⁺ cation in the neighborhood, that directly interact with the oxygen of zeolite framework. The broader Al signal with larger C_{O} should be assigned to Al of the AlO₄ tetrahedra with hydrated [HOZn]⁺ or H⁺ cations in the neighborhood.

Conclusions

The state of Zn species in Zn- modified ZSM-5 zeolite was characterized by a combination of 67Zn, 27Al, and 1H MAS NMR. Two 67Zn enriched zeolite samples were prepared, by solid-state exchange with metallic ⁶⁷Zn (Zn²⁺/ZSM-5 sample) and by ion exchange with a solution of zinc formate [⁶⁷Zn(HCOO)₂] (ZnO/H-ZSM-5 sample), both containing ca. 3.8 wt% Zn. The composition of the zeolite unit cell was established based on the elemental analysis and quantitative BAS and aluminum analyses with ¹H and ²⁷Al MAS NMR. It is inferred that Zn²⁺/ZSM-5 zeolite contains Zn in the form of Zn²⁺ cations, while BAS are absent in this sample. ZnO/H-ZSM-5 zeolite contains Zn in the form of Zn²⁺ cations and ZnO species and BAS are also present. 67Zn MAS NMR has detected the signal of Zn in a tetrahedral ZnO4 environment assigned to ZnO species for the activated (dehydrated) ZnO/H-ZSM-5 zeolite. For the hydrated ZnO/H-ZSM-5 zeolite, the signals of tetracoordinated, ZnO₄, and octacoordinated, ZnO₆, Zn are observed. The signal of Zn in an octahedral environment is assigned to zinc in the form of [HOZn]⁺ or Zn(OH)₂ species surrounded by water molecules. The activated (dehydrated) Zn²⁺/ZSM-5 zeolite with Zn²⁺ cations, directly interacting with the oxygens of the framework, exhibits no signal in 67 Zn MAS NMR spectrum. Hydration of the sample with 25 water molecules per u.c. makes the signal of Zn in an octahedral oxygen environment visible in the form of [HOZn]⁺ or Zn(OH)₂ species surrounded by water molecules. Quantitative analysis of Zn species detected by ⁶⁷Zn MAS NMR has shown that only 27 and 38% of zinc quantity loaded in zeolite is visible for the activated and hydrated ZnO/H-ZSM-5 zeolite, respectively. For the hydrated Zn²⁺/ZSM-5 zeolite, 24% of the loaded Zn is visible by ⁶⁷Zn MAS NMR, while zinc in the activated sample is not detected at all. Zinc in the form of ZnO species is entirely visible in both the activated and hydrated ZnO/H-ZSM-5 zeolite, while Zn in the form of Zn²⁺ is not detected at all for the activated sample and only 29% of Zn in

a form of Zn2+ cations is visible for the hydrated zeolite. Detection of only a part of Zn²⁺ cations in the form of [HOZn]⁺ or Zn(OH)₂ species in octahedral environment presumes partial hydrolysis of the bonds of Zn²⁺ cations with the framework oxygens and further coordination of the Zn sites by adsorbed water molecules. This affords octacoordinated Zn species

Author contributions

detectable by ⁶⁷Zn MAS NMR.

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M. A.: data curation, formal analysis, investigation; D. F.: methodology, data curation, investigation, writing (original draft); J. H.: funding acquisition; project administration; A. T.: data curation, investigation; S. S. A.: data curation, formal analysis, investigation; A. A. G.: data curation, investigation, visualization; A. G. S. conceptualization, writing (original draft), writing (review & editing), supervision.

Conflicts of interest

There are no conflicts to declare.

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