PCCP

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Phys. Chem. Chem. Phys.*, 2023, **25**, 28043

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

Marija Avramovska,[a] Dieter Freude,*[a] Jürgen Haase,[a] Alexander V. Toktarev,[b] Sergei S. Arzumanov,[b] Anton A. Gabrienko[b] and Alexander G. Stepanov *[b]

^{67}Zn MAS NMR spectroscopy was used to characterize the state of Zn in Zn-modified zeolites ZSM-5. Two ^{67}Zn enriched zeolite samples were prepared: by solid-state exchange with metal ^{67}Zn (Zn^{2+}/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 Zn^{2+}/ZSM-5 contains zinc in the form of Zn^{2+} cations, while both ZnO species and Zn^{2+} cations are present in ZnO/H-ZSM-5 besides BAS. ^{67}Zn 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 Zn^{2+}/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 ^{67}Zn 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 Zn^{2+}/ZSM-5. Zinc in the form of ZnO species is entirely visible in both the activated and hydrated ZnO/H-ZSM-5 zeolite, while Zn^{2+} cations are not detected at all for the activated sample and only 29% of Zn^{2+} cations is visible for the hydrated zeolite. Detection of only a part of Zn^{2+} cations in the form of $[HOZn]^{+}$ or $Zn(OH)_2$ species in octahedral environment presumes only partial hydrolysis of the bond of Zn^{2+} cation with framework oxygen and further solvation of the Zn species formed at hydrolysis by the adsorbed water.

Received 4th July 2023,
Accepted 10th October 2023

DOI: 10.1039/d3cp03136e

rsc.li/pccp

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 ^{67}Zn, 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 ^{67}Zn nuclei with respect to ^{1}H nuclei by a factor of 2.87×10^{-3}. Third, the nuclear spin of ^{67}Zn is $I = 5/2$ and the nuclear electric quadrupole moment of is 15.0 fm^{2},[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 ^{67}Zn enriched materials for Zn loading in zeolites. A corresponding study was performed by Qi *et al.*[14] They used 89.6% ^{67}Zn enriched precursors for loading of 2 and 6 wt% of Zn in

---

[a] *Faculty of Physics and Earth Sciences, Leipzig University, Linnéstraße 5, 04103 Leipzig, Germany. E-mail: freude@uni-leipzig.de*

[b] *Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Prospekt Akademika Lavrentieva 5, Novosibirsk 630090, Russia. E-mail: stepanov@catalysis.ru*

† Electronic supplementary information (ESI) available. See DOI: **https://doi.org/10.1039/d3cp03136e**

ZSM-5 zeolite and presented ^{67}Zn NMR spectra and ^{1}H spectra with dipolar ^{67}Zn recoupling by irradiation of the ^{67}Zn 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 μmol 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 ^{67}Zn, ^{27}Al, and ^{1}H MAS NMR spectroscopy on zeolites ZSM-5 zeolites modified with ^{67}Zn enriched zinc, in order to find out which information for the characterization of Zn-containing catalysts can be obtained by quantitative NMR spectroscopy. ^{27}Al recoupled ^{1}H MAS NMR spectroscopy (TRAPDOR)[16,17] was also applied to get additional information.

Methods

Synthesis of Zn^{2+}/ZSM-5 zeolite and sample preparation

The parent zeolite is a template-free synthesized NH$_4$-ZSM-5 (Si/Al = 13) zeolite provided by the Tricat GmbH. The ammonium form was transformed into the hydrogen form by calcination at 500 °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 Zn^{2+} – 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% ^{67}Zn enriched Zn metal of US Services Inc. (John Kilby), whereas a Zn metal with a 4.10% natural abundance of ^{67}Zn was used for previous studies.[19] It follows an evacuation at 773 K for 15 h. ^{1}H MAS NMR spectroscopy has shown[19] 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 Zn^{2+}/ZSM-5. A portion of the Zn^{2+}/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* Zn^{2+}/ZSM-5. Another sample, sealed in a glass tube, was opened and kept for 24 h under air before ^{67}Zn NMR measurements meanwhile rehydration took place. We denote the sample as hydrated Zn^{2+}/ZSM-5.

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

Zn-modified ZSM-5 zeolite, containing both Zn^{2+} 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, ^{67}Zn(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, Zn^{2+}/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

^{67}Zn and ^{27}Al 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 ^{27}Al and ^{67}Zn, respectively. A narrow-bore X probe was used for ^{67}Zn MAS NMR spectroscopy. ^{67}Zn MAS NMR measurements were done using a Hahn echo with a 16-phase cycle and a delay of one rotation period, 100 μs, between π/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 ^{67}Zn 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 ^{67}Zn 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 ^{27}Al 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 π/4 (non-selective π/12) pulse was used to get spectral intensities independent of different quadrupole coupling constants C_Q.

To determine the quantity of BAS in the zeolite samples with ^{1}H 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). ^{1}H MAS NMR spectra were recorded by the Hahn-echo pulse sequence ($\pi/2$–τ–π–τ-acquisition), where τ equals one rotor period (100–200 μs). The excitation pulse length was 4.5 μs ($\pi/2$), and typically 32 scans were accumulated with a 4–60 s delay. In double-resonance, ^{1}H{^{27}Al} TRAPDOR experiments[16,17] Hahn-echo sequence was applied to the ^{1}H channel with irradiation of aluminum during both τ periods. The ^{27}Al nutation frequency of the irradiation field was about 100 kHz.

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 ^{1}H 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 ^{67}Zn MAS NMR, ZnO powder with a molar mass of 81.41 g mol^{-1} and a ^{67}Zn natural abundance of 4.10% was used as an external ^{67}Zn 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 $\boldsymbol{c}_{\mathrm{s\,ZnO}} = 5.036 \times 10^{-4} \times N_A$ g^{-1}. 0.131 gram of ZnO powder was filled into the MAS rotor. It corresponds to $N_A \times 6.6 \times 10^{-5}$ of ^{67}Zn nuclei in the rotor.

Aluminum concentration was determined by ^{27}Al 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 Zn^{2+}/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 Zn^{2+}/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 Zn^{2+}/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 Zn^{2+} 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

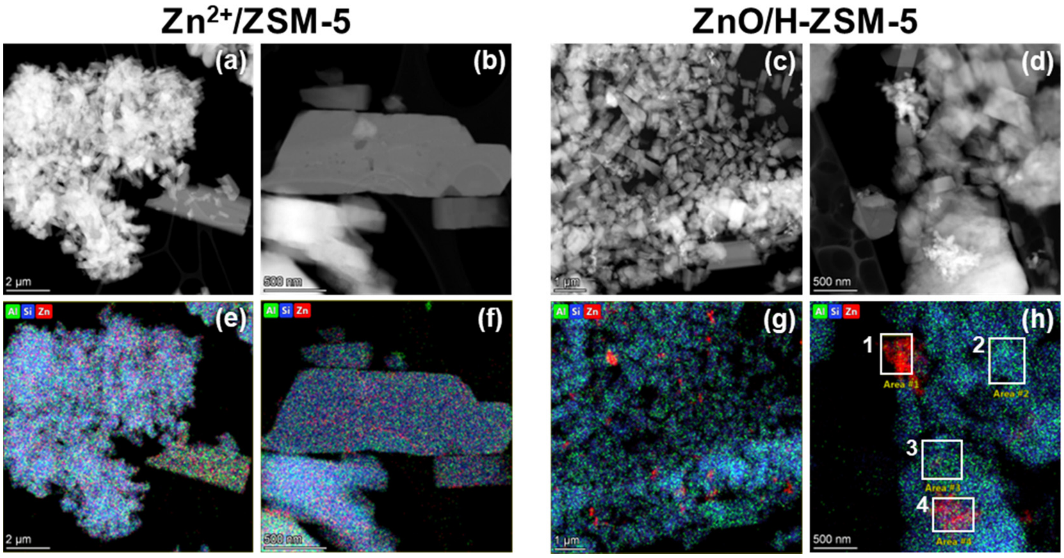


Fig. 1 HAADF-STEM images of ZnO/H-ZSM-5 (a) and (b) and Zn^{2+}/ZSM-5 (c) and (d) zeolites. EDX elemental mapping images of Si (blue), Al (green), and Zn (red) in the crystals of ZnO/H-ZSM-5 (e) and (f) and Zn^{2+}/ZSM-5 (g) and (h) zeolites. See also Table 1 for relative atomic content of the elements as obtained for whole studied area (e)–(h) or selected ones as depicted in (f).

Table 1 Atomic content of Si, Al, and Zn for ZnO/H-ZSM-5 and Zn^{2+}/ZSM-5 zeolites

		Atomic content/%		
Fig. 1 image	Studied area	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 Zn^{2+}/ZSM-5 sample. This may indicate the presence of Zn^{2+} cations and small ZnO-like clusters inside ZnO/H-ZSM-5 pores[8] together with larger ZnO-agglomerates on the external surface.

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

Zn^{2+}/ZSM-5. Fig. 2 shows ^{1}H MAS NMR spectra of parent H-ZSM-5 and Zn^{2+}/ZSM-5 zeolite samples. For the Zn^{2+}/ZSM-5 sample, prepared by a solid-state exchange reaction between BAS of the zeolite and ^{67}Zn 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. TRAPDOR experiments have shown that the intensity of the signals at 4.0 and 5.6 ppm decreases in the spectrum recorded with ^{27}Al irradiation for H-ZSM-5, whereas the intensity of the signal around 4.2 ppm is intact for Zn^{2+}/ZSM-5 (Fig. 3). This implies that the signal at 4.2 ppm of Zn^{2+}/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 Zn^{2+} 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 ^{29}Si MAS NMR (Si/Al = 12).[18] The concentration of BAS and Zn^{2+} species for Zn^{2+}/ZSM-5 and H-ZSM-5 is presented in Table 2.

Reactivated Zn^{2+}/ZSM-5. To inquire into the effect of water on the state of Zn in Zn^{2+}/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 Zn^{2+}/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 Zn^{2+}/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 ^{27}Al irradiation, whereas the signals at 1.2 ppm and 1.8 ppm are not affected (Fig. 3). These signals are reasonably assigned to ZnOH groups[14] formed at $Zn^{2+}–O^{-}$ 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.

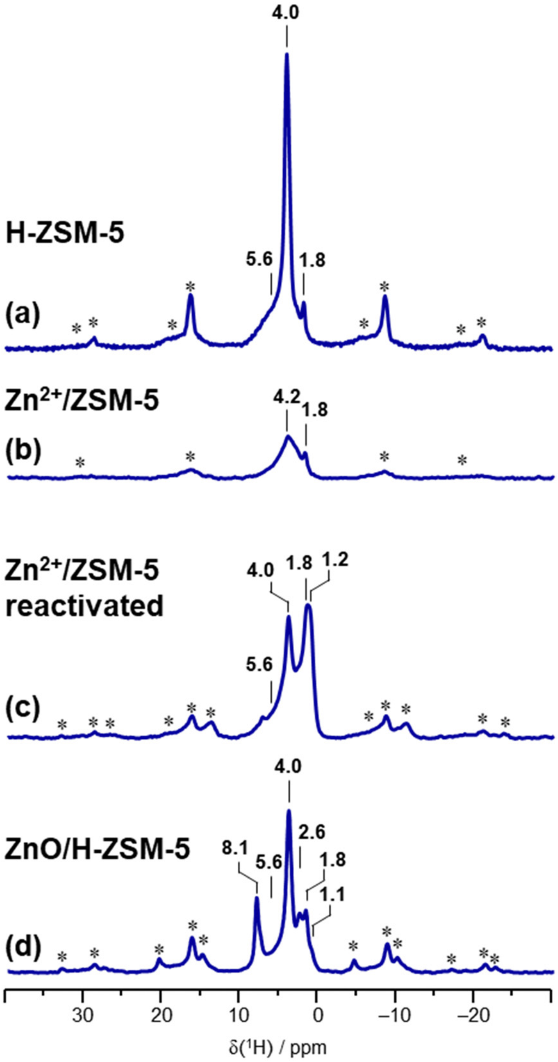


Fig. 2 ^{1}H MAS NMR spectra of parent H-ZSM-5 (a), Zn^{2+}/ZSM-5 (b), reactivated Zn^{2+}/ZSM-5 (c) and ZnO/H-ZSM-5 (d) zeolite samples. 23 μmol/g of benzene was adsorbed on sample (d), which is seen by the signal at 8.1 ppm.

ZnO/H-ZSM-5. Fig. 2d shows ^{1}H 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

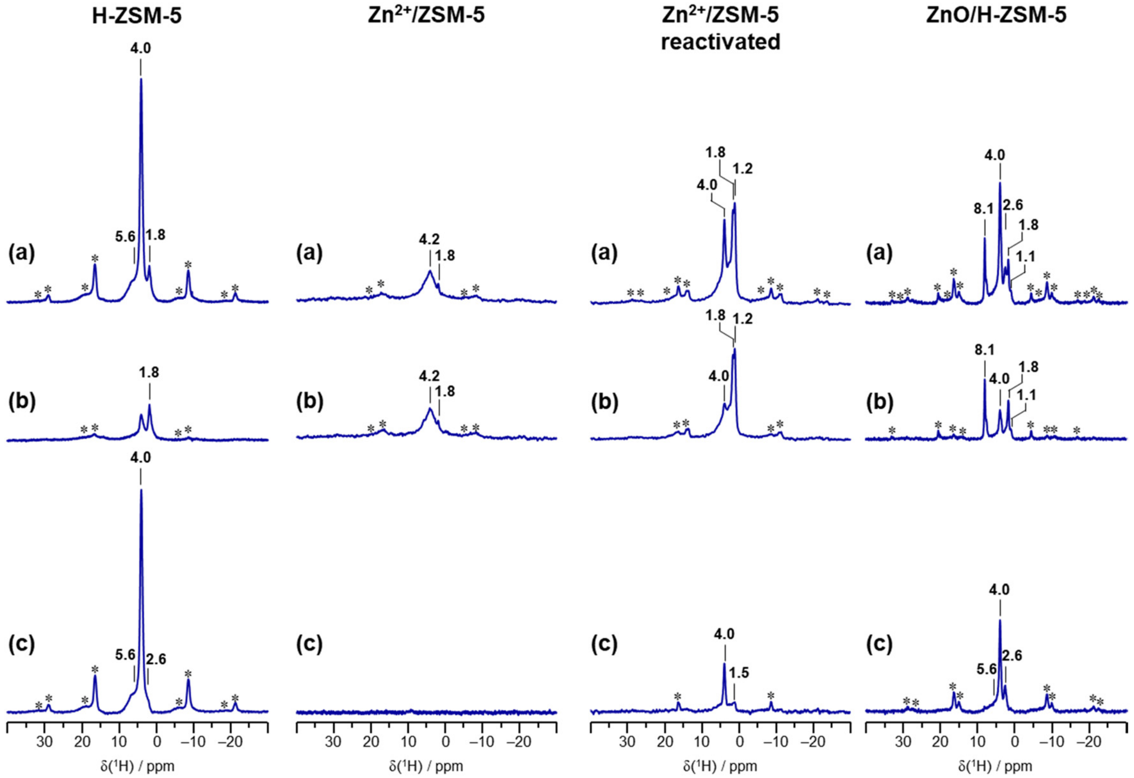


Fig. 3 ^{1}H MAS NMR Hahn-echo spectra of parent H-ZSM-5, Zn^{2+}/ZSM-5, reactivated Zn^{2+}/ZSM-5 and ZnO/H-ZSM-5: (a) without ^{27}Al irradiation and (b) with ^{27}Al irradiation (on-resonance). The difference spectrum of (a) and (b) is shown in (c). The spinning speed was set to 5 kHz, and τ was equal to one rotor period (200 μs).

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

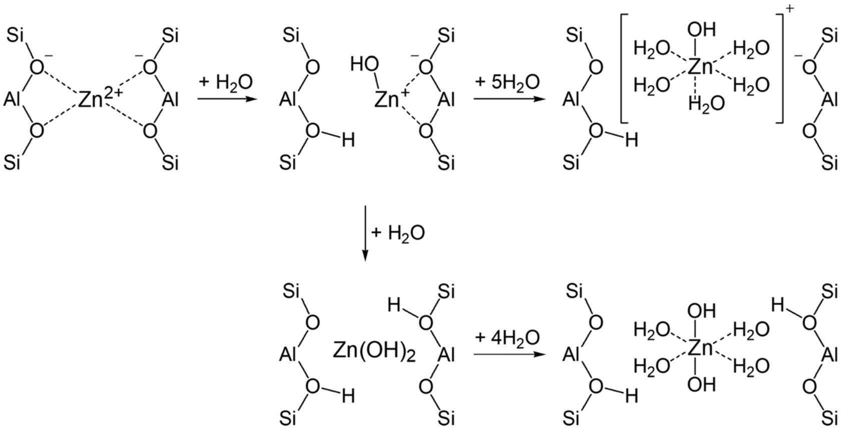
	OH concentration/$\mu mol \cdot g^{-1}$				
Zeolite sample	Si–OH	Zn–OH	Al–OH	Si–OH–Al	Zeolite unit cell
H-ZSM-5	40 ± 8 (terminal)		96 ± 5	1290 ± 90	$\lvert Al^{oct}_{0.47}\ H_{7.38}\rvert\ [Al^{tetr}_{7.38}\ Si_{88.62}\ O_{192}]$
Zn^{2+}/ZSM-5 (3.80 wt% ^{67}Zn)	400 ± 70 (silanol nests)				$\lvert {}^{67}Zn^{2+}_{3.93}\rvert\ [Al^{tetr}_{7.85}\ Si_{88.15}\ O_{192}]$
ZnO/H-ZSM-5 (3.86 wt% ^{67}Zn)	70 ± 50	17 ± 16	140 ± 40	530 ± 170	$\lvert Al^{oct}_{0.47}\ ({}^{67}ZnO)_{1.25}\ ({}^{67}Zn^{2+})_{2.16}\ H_{3.06}\rvert\ [Al^{tetr}_{7.38}\ Si_{88.62}\ O_{192}]$

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 Zn^{2+} cations.

Concentrations of aluminum species determined by ^{27}Al MAS NMR spectroscopy

Fig. 4 presents the ^{27}Al MAS NMR spectra of the reference sample, a hydrated zeolite Na-ZSM-5 (A), and the samples under study, the hydrated Zn^{2+}/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 Zn^{2+}/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 AlO_4 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 AlO_6 at about 3 ppm. No signal of five-fold coordinated aluminum AlO_5, 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 ^{27}Al MAS NMR is 15%. Within this limit, there is no significant deviation of the Si/Al ratio from the value 12 in the hydrated Zn^{2+}/ZSM-5 and ZnO/H-ZSM-5 samples. Both samples



Scheme 1 Hydrolysis of Zn^{2+}–O^- bonds in Zn^{2+}/ZSM-5 zeolite and further coordination of water molecules to the formed $[HOZn]^+$ and $Zn(OH)_2$ species affording octahedrally coordinated Zn species.

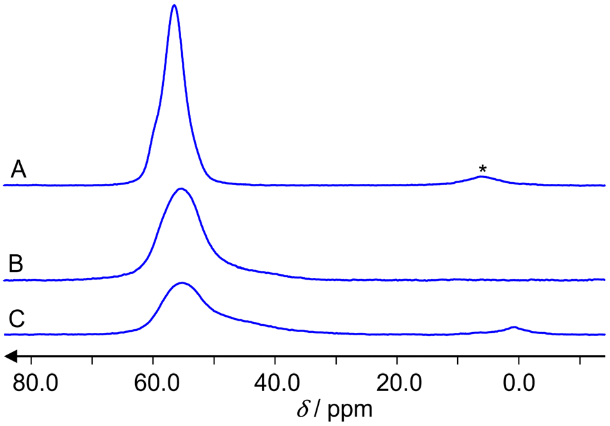


Fig. 4 ^{27}Al MAS NMR spectra of the hydrated zeolites: Na-ZSM-5 (A), Zn^{2+}/ZSM-5 (B) and ZnO/H-/ZSM-5 (C). The asterisk (*) denotes a spinning sideband.

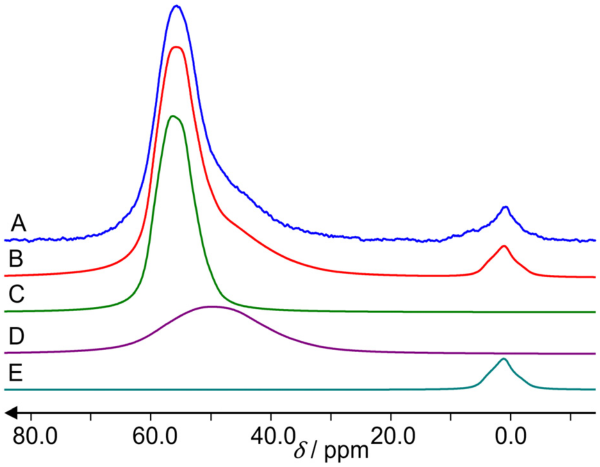


Fig. 5 Deconvolution of the ^{27}Al MAS NMR spectra of the hydrated ZnO/H-ZSM-5 zeolite. (A) is the experimental spectrum, (B) the sum of the deconvoluted signals, (C) is the main AlO_4 signal with δ = 60.5 ppm, C_Q = 5.2 MHz, asymmetry parameter η = 0.5, (D) is a stronger quadrupolar broadened signal with the same chemical shift δ = 60.5 ppm, but C_Q = 8.2 MHz, η = 0.5, (E) is the AlO_6 signal with δ = 4.0 ppm, C_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.

show mainly (100 and 94% integral intensity, respectively) AlO_4 coordination of framework aluminum atoms. Only the hydrated ZnO/H-ZSM-5 shows a weak (6% integral intensity) signal of extra-framework AlO_6 aluminum. Spectra (B) and (C) have a shoulder of the AlO_4 peak. Consequently, the spectra were deconvoluted by dmfit[25] 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_Q and relative integral intensities I: δ = 60.5 ppm with C_Q = 5.2 MHz and I = 59%, δ = 60.5 ppm with C_Q = 8.2 MHz and I = 35%, δ = 3.5 ppm with C_Q = 4.0 MHz and I = 6%. The deconvolution of the spectrum of Zn^{2+}/ZSM-5 gives two signals: δ = 60.5 ppm with C_Q = 5.2 MHz and I = 79%, δ = 60.5 ppm with C_Q = 8.2 MHz and I = 21%.

^{67}Zn MAS NMR spectra of the zeolite samples

Fig. 6 shows ^{67}Zn MAS NMR spectra of ZnO reference and the three samples under study. A fit of the spectrum in Fig. 6A by the program dmfit[25] yields the following parameters for the ZnO signal: chemical shift δ = 240 ppm, quadrupole coupling constant C_Q = 2.4 MHz, asymmetry parameter η = 0. This is in accordance with the literature data.[26] Spinning sidebands cannot be observed.

The hydrated Zn^{2+}/ZSM-5 zeolite exhibits a signal in the region of 0 ppm (Fig. 6B), which belongs to octahedrally coordinated (ZnO_6) 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 δ = 7 ppm, C_Q = 3 MHz and η = 0.

The activated ZnO/H-ZSM-5 zeolite shows only the signal in the region of tetrahedrally coordinated (ZnO_4) Zn species (Fig. 6D).[27] A fit gives δ = 240 ppm, C_Q = 2.5 MHz and η = 0.

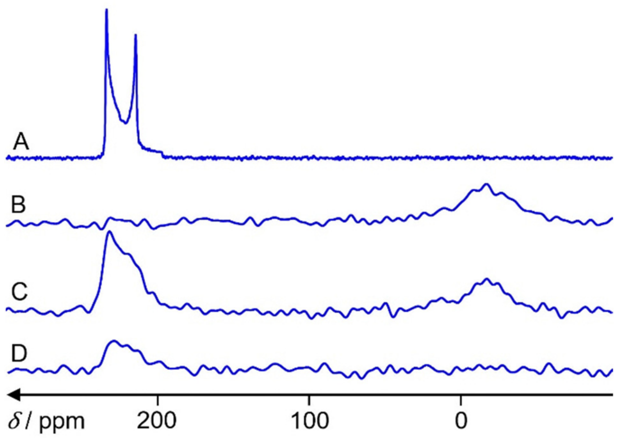


Fig. 6 ^{67}Zn MAS NMR spectra of ZnO powder (A), the hydrated Zn^{2+}/ZSM-5 (B), the hydrated ZnO/H-ZSM-5 (C), and the activated ZnO/H-ZSM-5 (D). The height of spectrum (A) is reduced by a factor of ten with respect to the other spectra.

The hydrated ZnO/H-ZSM-5 exhibits the signals of both tetrahedrally (ZnO_4) and octahedrally (ZnO_6) coordinated Zn species (Fig. 6C). A fit gives $\delta = 240$ ppm, $C_Q = 2.5$ MHz and $\eta = 0$ with 2/3 integral intensity for the tetrahedrally coordinated Zn species and $\delta = 0$ ppm, $C_Q = 2.5$ MHz and $\eta = 0$ with 1/3 integral intensity for the octahedrally coordinated Zn species. No ^{67}Zn MAS NMR signal is observed for the activated Zn^{2+}/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 Zn^{2+}/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 $c_{\mathrm{s\,zeolite}} = N_A \times 0.9 \times 0.0383/67$. The comparison between c_s of the Zn-modified zeolites and ZnO powder (see section Reference Samples) gives $c_{\mathrm{s\,Zn\,zeolite}}/c_{\mathrm{s\,ZnO}} = 1.037$.

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 $I_{\mathrm{s\,ZnO}} = 96\,627$ per one scan and one gram sample.

The sample weight of the hydrated 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 $I_{\mathrm{s\,Zn2+/ZSM\text{-}5}} = 25274$. Presuming $c_{\mathrm{s\,Zn2+/ZSM\text{-}5}}/c_{\mathrm{s\,ZnO}} = I_{\mathrm{s\,Zn2+/ZSM\text{-}5}}/I_{\mathrm{s\,ZnO}}$ we have $c_{\mathrm{s\,Zn2+/ZSM\text{-}5}}/c_{\mathrm{s\,ZnO}} = 0.2616$.

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. $I_{\mathrm{s\,ZnO/H\text{-}ZSM\text{-}5}} = 38\,286$. In this case $c_{\mathrm{s\,ZnO/H\text{-}ZSM\text{-}5}}/c_{\mathrm{s\,ZnO}} = 0.3962$.

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. $I_{\mathrm{s\,ZnO/H\text{-}ZSM\text{-}5}} = 27197$. We have $c_{\mathrm{s\,ZnO/H\text{-}ZSM\text{-}5}}/c_{\mathrm{s\,ZnO}} = 0.2815$.

The accuracy of our approach to concentration determinations by ^{67}Zn MAS NMR is 20%. We would expect a ratio $c_{\mathrm{s\,Znzeolite}/\mathrm{cs\,ZnO}} = 1.037$ (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 ± 8% of the expected signal for the hydrated ZnO/H-ZSM-5, 24 ± 5% of the expected signal for the hydrated Zn^{2+}/ZSM-5, 27 ± 5% of the expected signal for the activated ZnO/H-ZSM-5, and less than 5% (detection limit) of the expected signal for the activated Zn^{2+}/ZSM-5 in a glass ampoule. For the hydrated ZnO/H-ZSM-5, the ratio 2 : 1 for ZnO_4 and ZnO_6 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, ^{1}H and ^{27}Al 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 Zn^{2+} cation species. Only the signal of the tetrahedrally coordinated Zn species is detected for the activated ZnO/H-ZSM-5 by ^{67}Zn 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 Zn^{2+}/ZSM-5 zeolite exhibits no ^{67}Zn MAS NMR signal. However, the hydration of the zeolite makes the signal visible (Fig. 6B), *e.g.*, in the form of $[HOZn(H_2O)_5]^+$ cations, generated according to Scheme 1. Note that a notable part of loaded the Zn species (62–76%) remain invisible by ^{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_Q is proportional to this gradient. In the reported spectra, the observed species have C_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_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 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 Zn^{2+} 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 Zn^{2+}/ZSM-5 implies partial hydrolysis (with 25 adsorbed water molecules per u.c.) of the bonds of Zn^{2+} cations with oxygens of the zeolite framework. Most of the Zn^{2+} cations retain direct interaction with the oxygens of the zeolite framework and remain invisible in the ^{67}Zn 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 Zn^{2+} 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 ^{67}Zn NMR is 20%.

Taking into account that the unit cell composition and the relative intensities of Zn signals in tetrahedral ZnO_4 and octahedral ZnO_6 coordination is 2 : 1, one can infer that 71% of Zn in the form of Zn^{2+} cations remain invisible for the hydrated ZnO/H-ZSM-5.

Quantitative ^{27}Al 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 Zn^{2+}/ZSM-5 and ZnO/H-ZSM-5 samples show mainly (100 and 94% integral intensity, respectively) AlO_4 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 AlO_4 tetrahedra. Each AlO_4 unit is negatively charged and requires a charge compensation by either BAS (H^+) or zinc cation (Zn^{2+}). The spectrum of the hydrated Zn^{2+}/ZSM-5 sample does not show AlO_6 signal of extra-framework aluminum, whereas, in the hydrated sample ZnO/H-ZSM-5, 0.47 aluminum atoms per unit cell are in AlO_6 coordination. A deconvolution of the AlO_4 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_Q value corresponds to 59% and 79% and the larger one to 35% and 21% of the total intensity of ^{27}Al signal for the hydrated ZnO/H-ZSM-5 and Zn^{2+}/ZSM-5 zeolites, respectively.

For the hydrated ZnO/H-ZSM-5, 29% of Zn^{2+} in the form, *e.g.*, of $[HOZn(H_2O)]^+$ species is visible. Visible cations correspond to 0.625 Zn^{2+} 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 ^{27}Al MAS NMR. This quantity of AlO_4 corresponds to 58% of the total quantity of AlO_4 species in zeolite. This is in good accordance with 59% of AlO_4 species measured by ^{27}Al 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_Q corresponds to AlO_4 tetrahedra in ^{27}Al MAS NMR spectrum, which have hydrated $[HOZn]^+$ or/and $Zn(OH)_2$ and H^+ cations in the neighborhood, while that with larger C_Q belongs to the non-hydrated Zn^{2+} cations directly interacting with zeolite framework.

The situation seems to be completely different for the hydrated Zn^{2+}/ZSM-5. If we accept that 76% of Zn in hydrated Zn^{2+}/ZSM-5 remains invisible, while all Al in this sample is visible in ^{27}Al MAS NMR, then the larger signal with the relative intensity of 79% and smaller C_Q should be assigned to Al in the AlO_4 tetrahedra, which have non-solvated Zn^{2+} cation in the neighborhood, that directly interact with the oxygen of zeolite framework. The broader Al signal with larger C_Q should be assigned to Al of the AlO_4 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 ^{67}Zn, ^{27}Al, and ^{1}H MAS NMR. Two ^{67}Zn enriched zeolite samples were prepared, by solid-state exchange with metallic ^{67}Zn (Zn^{2+}/ZSM-5 sample) and by ion exchange with a solution of zinc formate $[^{67}Zn(HCOO)_2]$ (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 ^{1}H and ^{27}Al MAS NMR. It is inferred that Zn^{2+}/ZSM-5 zeolite contains Zn in the form of Zn^{2+} cations, while BAS are absent in this sample. ZnO/H-ZSM-5 zeolite contains Zn in the form of Zn^{2+} cations and ZnO species and BAS are also present. ^{67}Zn MAS NMR has detected the signal of Zn in a tetrahedral ZnO_4 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, ZnO_4, and octacoordinated, ZnO_6, 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) Zn^{2+}/ZSM-5 zeolite with Zn^{2+} 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 ^{67}Zn 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 Zn^{2+}/ZSM-5 zeolite, 24% of the loaded Zn is visible by ^{67}Zn 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 Zn^{2+} is not detected at all for the activated sample and only 29% of Zn in a form of Zn^{2+} cations is visible for the hydrated zeolite. Detection of only a part of Zn^{2+} cations in the form of $[HOZn]^+$ or $Zn(OH)_2$ species in octahedral environment presumes partial hydrolysis of the bonds of Zn^{2+} cations with the framework oxygens and further coordination of the Zn sites by adsorbed water molecules. This affords octacoordinated Zn species detectable by ^{67}Zn MAS NMR.

Author contributions

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.

Acknowledgements

A. G., S. A. and A. S. acknowledge the financial support from Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project AAAA-A21-121011390053-4). M. A., D. F., and J. J. acknowledge the support by the Deutsche Forschungsgemeinschaft (grant no. HA 1893/22-1).

References

1 Y. Ono, *Catal. Rev.: Sci. Eng.*, 1992, **34**, 179–226.
2 H. Berndt, G. Lietz, B. Lücke and J. Völter, *Appl. Catal., A*, 1996, **146**, 351–363.
3 J. A. Biscardi and E. Iglesia, *Catal. Today*, 1996, **31**, 207–231.
4 A. Hagen and F. Roessner, *Catal. Rev.: Sci. Eng.*, 2000, **42**, 403–437.
5 J. Heemsoth, E. Tegeler, F. Roessner and A. Hagen, *Microporous Mesoporous Mater.*, 2001, **46**, 185–190.
6 Y. G. Kolyagin, V. V. Ordomsky, Y. Z. Khimyak, A. I. Rebrov, F. Fajula and I. I. Ivanova, *J. Catal.*, 2006, **238**, 122–133.
7 S. M. T. Almutairi, B. Mezari, P. C. M. M. Magusin, E. A. Pidko and E. J. M. Hensen, *ACS Catal.*, 2012, **2**, 71–83.
8 A. A. Gabrienko, S. S. Arzumanov, A. V. Toktarev, I. G. Danilova, I. P. Prosvirin, V. V. Kriventsov, V. I. Zaikovskii, D. Freude and A. G. Stepanov, *ACS Catal.*, 2017, **7**, 1818–1830.
9 K. J. R. Rosman and P. D. P. Taylor, *Pure Appl. Chem.*, 1998, **70**, 217–235.
10 R. K. Harris, E. D. Becker, S. M. C. De Menezes, R. Goodfellow and P. Granger, *Pure Appl. Chem.*, 2001, **73**, 1795–1818.
11 A. A. Gabrienko, I. G. Danilova, S. S. Arzumanov, D. Freude and A. G. Stepanov, *ChemCatChem*, 2020, **12**, 478–487.
12 A. A. Gabrienko, S. S. Arzumanov, Z. N. Lashchinskaya, A. V. Toktarev, D. Freude, J. Haase and A. G. Stepanov, *J. Catal.*, 2020, **391**, 69–79.
13 S. S. Arzumanov, A. A. Gabrienko, A. V. Toktarev, D. Freude, J. Haase and A. G. Stepanov, *J. Phys. Chem. C*, 2020, **124**, 20270–20279.
14 G. D. Qi, Q. Wang, J. Xu, J. Trebosc, O. Lafon, C. Wang, J. P. Amoureux and F. Deng, *Angew. Chem., Int. Ed.*, 2016, **55**, 15826–15830.
15 F. H. Larsen, A. S. Lipton, H. J. Jakobsen, N. C. Nielsen and P. D. Ellis, *J. Am. Chem. Soc.*, 1999, **121**, 3783–3784.
16 C. P. Grey and A. J. Vega, *J. Am. Chem. Soc.*, 1995, **117**, 8232–8242.
17 E. R. H. van Eck, R. Janssen, W. E. J. R. Maas and W. S. Veeman, *Chem. Phys. Lett.*, 1990, **174**, 428–432.
18 A. A. Gabrienko, I. G. Danilova, S. S. Arzumanov, L. V. Pirutko, D. Freude and A. G. Stepanov, *J. Phys. Chem. C*, 2018, **122**, 25386–25395.
19 A. A. Gabrienko, S. S. Arzumanov, M. V. Luzgin, A. G. Stepanov and V. N. Parmon, *J. Phys. Chem. C*, 2015, **119**, 24910–24918.
20 A. A. Gabrienko, S. S. Arzumanov, A. V. Toktarev, D. Freude, J. Haase and A. G. Stepanov, *J. Phys. Chem. C*, 2019, **123**, 27573–27583.
21 R. K. Harris, E. D. Becker, S. M. C. De Menezes, R. Goodfellow and P. Granger, *Solid State Nucl. Magn. Reson.*, 2002, **22**, 458–483.
22 A. G. Stepanov, in *Zeolites and Zeolite-like Materials*, ed. B. F. Sels and L. M. Kustov, Elsevier Inc., 2016, pp. 137–188, DOI: 10.1016/b978-0-444-63506-8.00004-5.
23 A. Petushkov, S. Yoon and S. C. Larsen, *Microporous Mesoporous Mater.*, 2011, **137**, 92–100.
24 M. Hunger, *Catal. Rev.: Sci. Eng.*, 1997, **39**, 345–393.
25 D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan and G. Hoatson, *Magn. Reson. Chem.*, 2002, **40**, 70–76.
26 G. Wu, *Chem. Phys. Lett.*, 1998, **298**, 375–380.
27 Y. Huang and A. Sutrisno, *Annu. Rep. NMR Spectrosc.*, 2014, **81**, 1–46.
28 D. Freude and J. Haase, https:/www.quad-nmr.de (accessed 13.09.2022).