Zeolites

Location of Framework Al Atoms in the Channels of ZSM-5: Effect of the (Hydrothermal) Synthesis

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Abstract: ²⁷AI 3Q MAS NMR and UV/Vis spectroscopy with bare Co^{II} ions as probes of AI pairs in the zeolite framework were employed to analyze the location of framework Al atoms in the channel system of zeolite ZSM-5. Furthermore, the effect of Na⁺ ions together with tetrapropylammonium cation (TPA⁺) in the ZSM-5 synthesis gel on the location of Al in the channel system was investigated. Zeolites prepared using exclusively TPA⁺ as a structure-directing agent (i.e., in the absence of Na⁺ ions) led to 55-90% of AI atoms located at the channel intersection, regardless the presence or absence of Al pairs [Al-O-(Si-O)₂-Al sequences in one ring] in the zeolite framework. The presence of Na⁺ ions in the synthesis gel did not modify the Al location at the channel intersection (55-95% of Al atoms) and led only to changes in i) the distribution of framework AI atoms between AI pairs (decrease) and single isolated Al atoms (increase), and ii) the siting of Al in distinguishable framework tetrahedral sites.

Zeolites are crystalline microporous aluminosilicates built from corner-sharing $SiO_{4/2}$ and $[AIO_{4/2}]^-$ tetrahedra. They represent the most important group of heterogeneous catalysts widely applied in oil and petrochemical processing, syntheses of bulk and fine chemicals, and deNO, processes. Isomorphous Al/Si framework substitutions introduce a negative charge of [AlO₄]⁻ tetrahedra into the framework, which is balanced by protons and extra-framework metal cations and metal-oxo species, which represent active sites for acid-, base-, and redox-catalyzed reactions. These active sites are located in the microporous channel system and exhibit significant variability in size, organization, and channel dimensionality for zeolites with different topologies. The confinement of transition states and reaction intermediates in the pore-void volume of the zeolite channels plays a crucial role in the shape selectivity of zeolite catalysts.^[1] Si-rich (Si/Al > 12) pentasil-ring ZSM-5 zeolites with MFI topology have found particular attention and represent the most widely applied Si-rich zeolite catalysts. The 3D channel system of the MFI structure is formed by intersecting tenmember ring straight and sinusoidal channels of similar sizes (Figure 1). A decreased confinement in the less confining void



Figure 1. Schematic depiction of the ZSM-5 channel system^[3] (left) and the location of T2 (\bigcirc), T6 (\bigcirc), T11 (\bigcirc), T21(\bigcirc), and T23 (\bigcirc) atoms at the channel intersection [views along the main (middle) and sinusoidal (right) channels].

volume of channel intersections (the maximum diameter of sphere that can be included is 6.36 Å) compared to the two channels (the maximum diameters of spheres that can be included are 4.70 and 4.46 Å) has been suggested as a key parameter to explain the selectivity in, for example, alkane cracking and dehydrogenation.^[2] Thus the location of the active sites, which can be in either the channels or at the channel intersections, is of great importance. However, there is no straightforward knowledge regarding the location of Al in ZSM-5 zeolites.

Since cationic species bind to [AlO₄]⁻ tetrahedra, the positions of AI in zeolite frameworks govern the locations of the active sites. The Al siting in the zeolite frameworks [i.e., the crystallographically distinguishable tetrahedral (T) sites that are occupied by Al] was clearly shown to be neither random nor controlled by simple rules, but to depend on the conditions of their hydrothermal synthesis.^[4] This means that Al atoms can be located in zeolites of the same topology and Al concentration at various crystallographically distinguishable T sites.^[4b,e,g,h] Therefore, obtaining insights into the Al locations in the channel system of ZSM-5 is of crucial importance for development of highly selective catalysts. Diffraction techniques cannot distinguish between AI and Si atoms and thus do not allow direct identification of the Al location, whereas application of probe molecules is restricted to materials with different channel sizes.^[5]

It was shown that the addition of Na⁺ ions to the structuredirecting agent (SDA) tetrapropylammonium cation (TPA⁺) in the synthesis mixture can markedly affect the incorporation of single isolated Al atoms (hereafter single Al atoms) and Al–O– (Si–O)₂–Al sequences in one ring (hereafter Al pairs) into the zeolite framework.^[6] Moreover, our ²⁷Al triple quantum magic angle spinning (3Q MAS) NMR spectroscopic measurements revealed that the addition of Na⁺ also alters the Al siting in the

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framework T sites.^[6] These findings suggest that the presence of Na⁺ ions during the synthesis can possibly affect the Al location in the ZSM-5 channel system. Since no syntheses of ZSM-5 zeolites have been reported with Si/Al $\leq 22^{[6]}$ and with Na⁺ absent from the synthesis gel, all such ZSM-5 zeolites, which are highly relevant for catalysis, exhibit an organization of framework Al atoms that is affected by the presence of Na⁺ in the synthesis gel. Thus, knowledge of the effect of Na⁺ ions on the location of Al atoms in the zeolite channel system is of crucial importance. Recently Tatsumi and co-workers reported a comparison regarding the constraint indices for cracking of n-hexane and 3-methyl pentane over ZSM-5 zeolites synthesized either by employing exclusively TPA⁺ or TPA⁺ and Na⁺ as SDAs.^[7] They suggested that the application of only TPA⁺ led to Al atoms located at channel intersections. Conversely, based on their constraint index results, they suggested that Al atoms are located in the channels (straight and sinusoidal) when Na⁺ ions are present in the synthesis gel. Despite its historical contribution to zeolite science, the applicability of the constraint index on a detailed study of zeolites is significantly limited.^[8] Moreover, the observed differences in constraint indices for their ZSM-5 samples cannot be readily attributed to the location of Al atoms in the channels and intersections but could rather be associated with a substantial effect of Na⁺ ions in the synthesis gel on the incorporation of Al atoms as Al pairs rather than single AI atoms.^[6] The high importance of the concentrations of Al pairs and single Al atoms, which are the most important arrangements of Al atoms in the framework of ZSM-5 zeolites,^[9] has already been manifested in butene cracking and its aromatization^[10] and in the ratio of butane cracking and dehydrogenation.^[2d]

Herein, we analyze the locations of framework AI atoms in the channel system by employing ²⁷AI multiple quantum (MQ) MAS NMR spectroscopy and applying bare Co^{II} ions as probes of AI pairs. The Co^{II} ions in dehydrated zeolites are monitored by UV/Vis spectroscopy. In other words, we study whether the framework AI atoms are present in the channels and/or at the channel intersections. The ZSM-5 samples used were synthesized by using TPA⁺ as SDA. In addition, we investigate the effect of the employment of Na⁺ ions together with TPA⁺ in ZSM-5 synthesis on the Al location in the channel system. Al atoms in different framework T sites can be distinguished by ²⁷Al 3Q MAS NMR experiments^[4b,e] only in the absence of Al pairs, since they can change the isotropic chemical shifts of framework Al atoms up to 4 ppm.^[4g,9,11] Therefore, ²⁷Al 3Q MAS NMR spectroscopy was used only for samples in which single Al atoms are prevalent, whereas UV/Vis spectroscopy of bare Co^{II} ions in dehydrated zeolites was employed to study ZSM-5 samples containing Al pairs.^[4g,9,11]

High-resolution ²⁷Al MAS NMR experiments, that is, high-field (500 MHz) 3Q MAS NMR and ultrahigh-field (900 MHz) single-pulse MAS NMR measurements, have recently been shown be able to distinguish Al atoms in different T sites of zeolites with a high number of framework T sites, such as ferrierite, β -zeolite, and ZSM-5.^[4b,e-h] ²⁷Al (3Q) MAS NMR spectra of the hydrated Na-ZSM-5 zeolite samples A–C (Figures 2 and 3), in which single Al atoms are prevalent (according to the Co²⁺ ion exchange capacity; see Table 1), prepared using TPA⁺ ions (TPAOH or TPABr; see Table 1^[12]) in the absence of Na⁺ in the synthesis mixture exhibit a dominant ²⁷Al NMR resonance (>55% of Al) with an isotropic chemical shift of δ =56.4 ppm (Figure 4).

Simulations of the ²⁷Al single-pulse MAS NMR spectra were employed to quantitatively analyze the Al siting.^[4b,e] X-ray crystallography studies showed that the TPA⁺ ion was located at the intersection of the two channels.^[13] Since the TPA⁺ ions represent the only species capable of compensating [AlO₄]⁻ tetrahedra, the Al atoms corresponding to the ²⁷Al NMR resonance at 56.4 ppm are likely located at the channel intersection. Based on our prior studies,^[4b,e] the calculated ²⁷Al isotropic chemical shifts of δ_{iso} =56.7, 57.0, 57.1, 57.1, and 57.2 ppm are assigned to Al substitution into the T11, T21, T2, T16, and T23 sites of monoclinic ZSM-5^[4b,e] (see the Supporting Information, Table S2). All T sites with the exception of the T16 site, which are assignable to the ²⁷Al NMR resonance at 56.4 ppm, are located at the channel intersection (Figure 1).

This result supports our assumption, based on previous reports,^[13] that the Al atoms related to the ²⁷Al NMR resonance



Figure 2. ²⁷AI MAS NMR spectra of samples A, D, J, and K, and 2D plot of ²⁷AI 3Q MAS NMR spectrum of sample D, with the F1 and F2 projections and slices and their simulations for the individual resonances.

Chem. Eur. J. 2016, 22, 3937 - 3941

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Figure 3. ²⁷AI MAS NMR spectra of samples B, C, E, F, G, H and I, and 2D plot of ²⁷AI 3Q MAS NMR spectrum of sample B with the F1 and F2 projections and slices and their simulations for the individual resonances.

Table 1. Descriptions of ZSM-5 samples and their syntheses.									
Sample	Si/Al ^[a]	Co/Al	Na source	Al source					
A ^[b]	25.0	0.03	-	AICI					
В	24.5	0.03	-	AI(NO ₃) ₃					
С	34.0	0.06	-	[c]					
D ^[d]	18.0	0.04	[e]	[e]					
E	30.0	0.07	Na ₂ CO ₃	AICI ₃					
F	12.8	0.11	NaNO ₃	AI(NO ₃) ₃					
G	15.0	0.12	NaOH	AICI ₃					
Н	26.5	0.15	NaOH	AICI ₃					
I ^[f]	15.1	0.02	[g]	AICI ₃					
J ^[f]	20.5	0.05	[g]	AI(NO ₃) ₃					
К	22.5	0.08	NaCl	AI(NO ₃) ₃					
L ^[d]	14.1	0.42	[e]	[e]					
M ^[h]	25.0	0.34	-	AICI ₃					

[a] Determined by EDS; [b] TPABr used instead of TPAOH as SDA; [c] Al isopropoxide; [d] Na aluminosilicate precursor used instead of TEOS as Si source; [e] Na aluminosilicate; [f] Na silicate used instead of TEOS as Si source; [g] Na silicate; [h] Si source added to the mixture of Al source and TPAOH.



Figure 4. Effect of synthesis conditions on the Al concentration in T11, T21, T2, T16, and T23 (all of these T sites: black) and T6 (crosshatched) sites in ZSM-5 samples A–K.

at 56.4 ppm are most likely present at the channel intersection. The ZSM-5 samples A and B further exhibit ²⁷Al NMR resonances at 54.6 and 56.0 ppm, respectively. That at 54.6 ppm represents Al located in the T6 site at the channel intersection and the ²⁷Al NMR resonance at 56.0 ppm can be attributed to one of the same T sites as the dominant resonance at 56.4 ppm (see the Supporting Information, Table S2). Thus, the Al atoms in ZSM-5 samples A–C, prepared exclusively with the TPA⁺ ion, are predominantly located at the channel intersection (> 55% of Al) and the ²⁷Al NMR resonances at 54.6, 56.0, and 56.4 ppm characterize such Al atoms (Figure 4).

²⁷AI (3Q) MAS NMR spectra of the ZSM-5 samples D–H, with prevalent single AI atoms (Table 1), synthesized with TPA⁺ and Na⁺ ions (Figures 2 and 3) are similar to those of samples A–C and do not exhibit a decrease in the intensity of the resonance at 56.4 ppm. Therefore, the AI sittings in ZSM-5 samples D–H are not significantly changed and the AI atoms are located mainly at the channel intersections (Figure 4).

A significant decrease in the intensity (to ca 40% Al) of the ²⁷Al NMR resonance at 56.4 ppm was observed for the ZSM-5 samples I–K, with prevalent single Al atoms (Table 1), that were also synthesized with TPA⁺ and Na⁺ ions (NaOH, Na silicate, and NaCl; Figures 2 and 3). Nevertheless, this decrease is compensated for by a significant increase in the intensity of the resonance at 54.6 ppm of Al atoms located at the T6 site at the channel intersection. Thus, the location of Al atoms at the channel intersections is also predominant for ZSM-5 samples I–K (Figure 4).

There is no way to analyze the effect of Na⁺ ions on the Al siting for the ZSM-5 samples D, F, G, and I, with Si/Al < 18 and prepared using TPA⁺, since the presence of Na⁺ is required to obtain crystalline products of the MFI topology. Nevertheless, the location of Al atoms in samples with mainly single Al atoms is similar to that of their analogues with a significantly higher Si/Al ratio (i.e., samples G and H, synthesized from NaOH, and samples I and J, prepared from Na silicate).

Besides isolated single Al atoms, Al pairs of Al–O– $(Si–O)_2$ –Al sequences in one ring represent a typical Al arrangement in the framework of Si-rich zeolites, as follows from ion-exchange

Chem	Fur I	2016	22	3937 - 3941	
Chem.	Lui. J.	2010,	ZZ ,	2221 - 2241	

www.chemeurj.org



capacity of Si-rich zeolites for divalent cations.^{[9] 27}AI MQ MAS NMR spectroscopy fails to determine the Al location in the channel system of ZSM-5 zeolites in which Al pairs are prevalent since ²⁷AI NMR resonances are significantly affected by next-next-nearest neighbor AI atoms in the AI-O-(Si-O)2-AI sequences.^[11a] Therefore, a different experimental method has to be employed to estimate the locations of Al pairs in Si-rich zeolites. UV/Vis spectroscopy of bare Co²⁺ ions was developed for this purpose.^[9,14] Bare Co²⁺ ions in dehydrated zeolites monitored by UV/Vis spectroscopy serve as probes for the presence of two Al atoms located in one ring. Quantitative analysis of the spectra then reveals the concentration of Al pairs in individual rings with two Al atoms. Three rings containing Al pairs and accommodating Co²⁺ ions (α , β , and γ cationic sites) were reported for ZSM-5.^[9,15] The Al atoms of the α and β sites are located at the channel intersection. The exact location of the Al atoms forming the γ sites is not known. However, the concentration of the γ sites in ZSM-5 samples is very $\mathsf{low}^{\scriptscriptstyle[6,\,15]}$ and therefore we do not consider this site in this study. The concentrations of Al atoms in the α and β sites of the samples in this study with prevalent Al pairs have been previously reported.^[6, 15] The ZSM-5 samples L^[15] and M,^[6] with Si/Al ratios of 14.1 and 25.0, respectively, contain 84 and 68% of framework aluminum atoms in AI pairs, respectively (Co_{MAX}/ Al=0.42 and 0.34, respectively). ZSM-5 sample L was synthesized with Na⁺, whereas ZSM-5 sample M was prepared without Na⁺. Therefore, at least 84% of Al atoms are located at the channel intersection for the sample with Na⁺ in the synthesis mixture, compared to at least 68% for that prepared without Na⁺. We can conclude that the addition of Na⁺ ions to TPA⁺, which is essential for the synthesis of ZSM-5 zeolites with Si/Al ratios of 12-18, does not result in a significant decrease in the proportion of Al atoms located at channel intersections.

Generally, ZSM-5 samples with the presence, as well as the absence, of AI pairs, prepared using TPA⁺ as SDA, contain AI atoms predominantly at the channel intersections. Adding Na⁺ ions to the synthesis mixture can only serve to i) increase the content of framework Al (i.e., ZSM-5 with Si/Al < 22) and ii) tune the distribution of AI between AI pairs and single AI atoms, without changing the locations of Al atoms in the channel system. The function of Na⁺ ions in the synthesis gel is to balance additional Al atoms of aluminosilicate fragments (i.e., building blocks) from which the zeolite is synthesized and thus Na⁺ ions influence the Al siting and also the distribution of AI between AI pairs and single AI atoms. Thus the differences in the performance of ZSM-5 catalysts with similar Si/Al ratios prepared by using either TPA⁺ or TPA⁺ and Na⁺ as SDAs can be attributed to variations in the distribution between AI pairs and single AI atoms, as well as to different AI siting at the channel intersections (i.e., different T sites),^[6,16] rather than to differences in the Al location within the channel system.

We conclude that the framework Al atoms in ZSM-5 highly prefer locations at the channel intersections (at least 55% of framework Al atoms) regardless of the synthesis conditions when TPA⁺ serve as SDA. The source of the Na⁺ ions in the synthesis mixture of ZSM-5 samples without Al pairs affects

only the occupation of various distinguishable framework T sites by Al atoms (i.e., Al siting). Our results reveal that Na⁺ ions can be employed to tune the Al distribution between Al pairs and single Al atoms in ZSM-5 without a change in the location of Al atoms at the intersection of the channels. In addition, it should be stressed that Na⁺ ions do not change the predominant location of Al atoms at the intersection of the channels when Na⁺ ions are added to attain Si/Al < 22. We believe that the identification of Al framework sites in ZSM-5 regarding their locations in either the channels or at their intersections and their distribution between Al pairs and single Al atoms is of high importance for understanding the individual reaction steps in the pore-void volume of the zeolite channels and channel intersections and the related shape selectivities of zeolites in acid-catalyzed reactions of hydrocarbons.

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Chom	Fur I	2016	22	3037 - 3041	
Chem.	Lui. J.	2010,	22,	3937 - 3941	



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