Characterization of silicon-containing catalysts by ^{29}Si solid-state NMR

Spectroscopic background: ^{29}Si nuclei have a spin of I = 1/2 and no quadrupole moment. The ^{29}Si isotope has a natural abundance of 4.7 % and a sensitivity of 3.7 x 10^{-4} in comparison with ^{1}H nuclei (1.0). Therefore, it is at the limit for solid-state NMR studies being possible to investigate without isotopic enrichment. For basic principles of solid-state NMR, see lectures “Solid-State NMR Spectroscopy” for Bachelor students or PhD seminars, accessible via the link “Lectures for Students”.

The framework of crystalline aluminosilicates, such as zeolites, contains tetrahedrally coordinated silicon with Si-O-Si and Si-O-Al bridges. These local structures result in five different **Q^4** silicon environments, denoted as **Si(*n*Al) or Si((4-*n*)OSi,*n*OAl)) units**, with the number ***n* = 0, 1, 2, 3 or 4** of the aluminum atoms in the second coordination sphere. Each type of the various Si(*n*Al) units in **Fig. 1, top,** yields ^{29}Si MAS NMR signals in different ranges of chemical shifts between **δ_{29Si} = -70 and δ_{29Si} = -120 ppm** [1, 2].

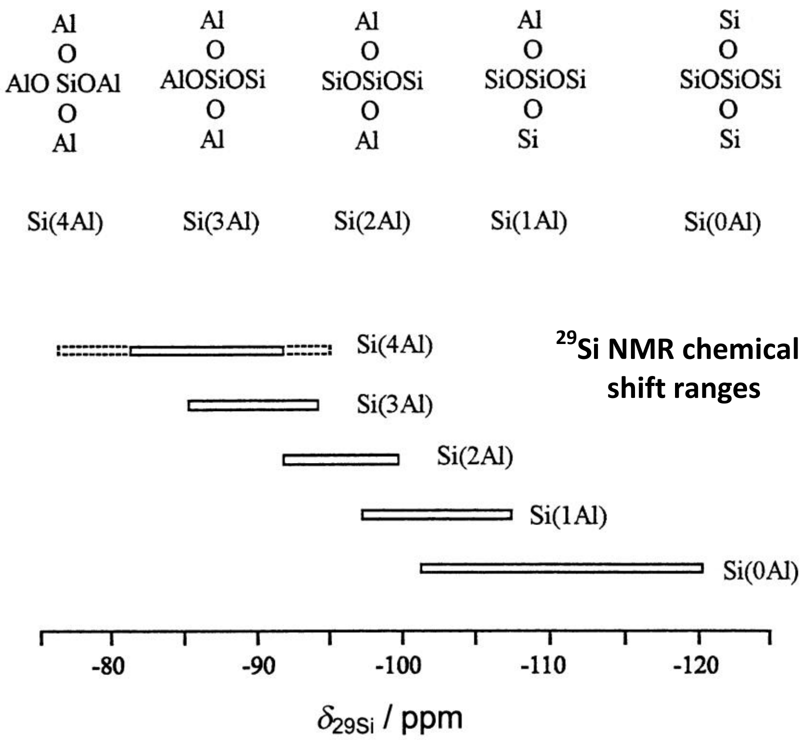

Fig. 1

For zeolite Y with a single crystallographic T-site, ^{29}Si MAS NMR spectra of aluminum-containing samples consist of Si(*n*Al) signals (**Fig. 2**, **top spectra**) with

^{29}Si MAS NMR

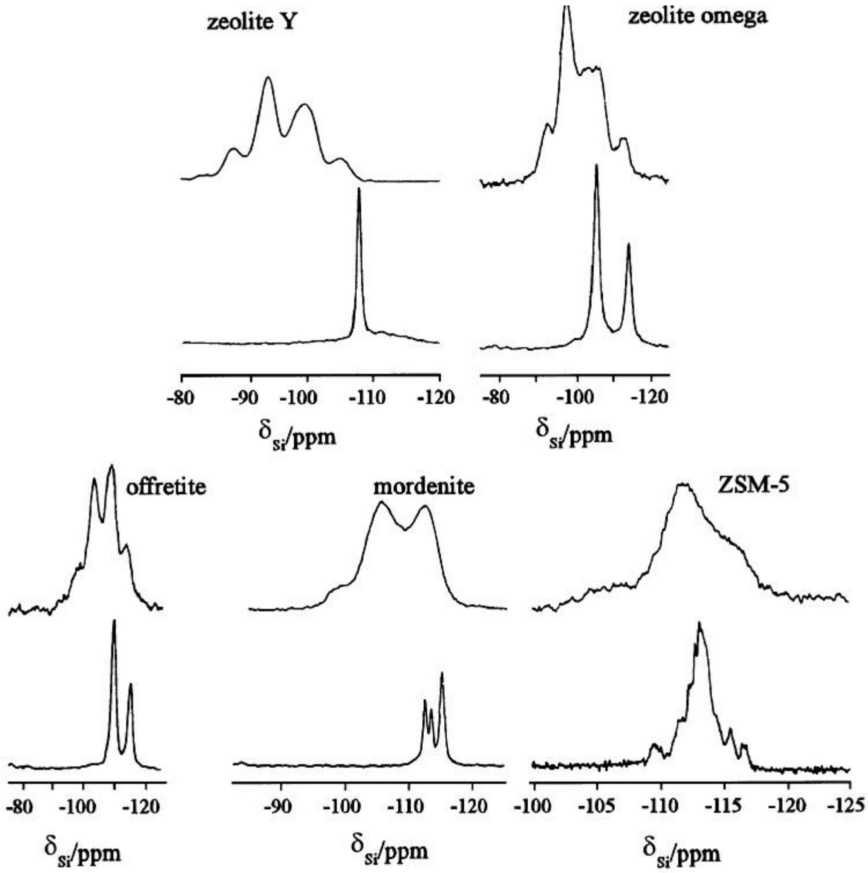

Fig. 2

intensities $I_{Si(nAl)}$, which are a function of the framework composition, i.e. of the aluminum content. Therefore, the framework n_{Si}/n_{Al} ratio of these materials can be calculated from the ^{29}Si MAS NMR intensities using the formula [1, 2]:

$$n_{Si} \,/\, n_{Al} = \sum_{n=0}^{4} I_{Si(nAl)} \,/\, \sum_{n=0}^{4} 0.25 \cdot n \cdot I_{Si(nAl)} \qquad (1)$$

By a comparison of the framework n_{Si}/n_{Al} ratio, calculated via **Equ. (1)**, with the bulk composition determined by chemical analysis, the amount of aluminum atoms at extra-framework positions can be obtained. However, in each zeolite, SiOH groups exist, bound to silicon atoms **(Q^3 units corresponding to Si(3OSi,1OH))** located at the outer surface of the zeolite particles or at framework defects. The chemical shifts of Si(3OSi,1OAl) units (δ_{29Si} = -95 to -105 ppm) are in the same range like those of Si(3OSi,1OH) units (**δ_{29Si} = -100 to -103 ppm**) [1, 2]. Therefore, the number of SiOH groups limits the range of n_{Si}/n_{Al} ratios, which can be derived by ^{29}Si MAS NMR spectroscopy, or their number must be previously determined by a complementary method, such as ^{1}H MAS NMR spectroscopy.

In the same manner, as above-mentioned for ^{29}Si MAS NMR spectroscopy on aluminosilicate-type zeolites, the chemical compositions of zincosilicates [3] and gallium-modified ZSM-5 (Ga-MFI) [4] can be determined. In the ^{29}Si MAS NMR spectra of the titanosilicate ETS-10 and the titanoaluminosilicate ETAS-10, signals of **Si(4OSi)** units at **δ_{29Si} = -103 ppm**, **Si(3OSi,1OTi)** units at **δ_{29Si} = -94 ppm to -97 ppm**, and **Si(2OSi,1OAl,1OTi)** units, ***ca.* 4 ppm down-field shifted from the signal of Si(3OSi,1OTi)** units occur [5]. Utilizing **Equ. (1)** with Si((4-*n*-*m*)OSi,*n*OGa,*m*OTi) instead of Si((4-*n*)OSi,*n*Al), and setting the corresponding factors *n* and *m* in the denominator, the framework n_{Si}/n_{Ga} and n_{Si}/n_{Ti} ratios, respectively, can be determined [3, 4].

Numerous zeolite frameworks are characterized by crystallographically non-equivalent T-sites, but chemically equivalent environments, being responsible for a chemical shift distribution and/or a split of the ^{29}Si MAS NMR signals of framework silicon atoms. Dealumination and ultrastabilization of zeolite frameworks, e.g. by steaming and calcination, result in an elimination of all Si(*n*Al) units and a strong decrease of the ^{29}Si MAS NMR signal widths (**Fig. 2**) [6, 7, 8]. The ^{29}Si MAS NMR spectra shown at the bottom of each spectra pair in **Fig. 2**, therefore, consists exclusively of narrow Si(4OSi) signals.

While the ^{29}Si MAS NMR spectrum of zeolite Y shows a single Si(4OSi) signal only, corresponding to one crystallographic T-site, most of the other zeolites cause ^{29}Si MAS NMR spectra with Si(4OSi) signals of at least two crystallographically non-equivalent T-sites. The intensity ratios of these lines, e.g. of 2 : 1 for zeolites omega and offretite, correspond to the population ratios of these different T-sites in the crystallographic structure. In **Table 1**, ^{29}Si chemical shift data of some selected zeolites are summarized (see also Ref. [9]).

As more sophisticated examples, the ^{29}Si MAS NMR spectra of a parent zeolite **MCM-22 (n_{Si}/n_{Al} = 11)** and its **dealuminated material (n_{Si}/n_{Al} = 20)** are shown in **Figs. 3a and 3b**, respectively [10]. Because of the low aluminum content of the dealuminated MCM-22, its ^{29}Si MAS NMR spectrum consists mainly of signals caused by Si(4OSi) units. Hence, the five ^{29}Si MAS NMR signals at δ_{29Si} =

Zeolites	n_{Si}/n_{Al}	Sites	Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	Si(0Al)
A	1.0	T	−89.6				
	∞	T					−112.9
Y	2.5	T	−83.8	−89.2	−94.5	−100.0	−105.5
	∞	T					−107.8
Omega	3.1	T1		−89.1	−93.7	−98.8	−103.4
		T2	−89.1	−93.7	−98.8	−107.0	−112.0
	∞	T1					−106.0
		T2					−114.4
Offretite	2.9	T1		−93.5	−97.5	−101.9	−106.9
		T2		−97.5	−101.9	−106.9	−112.5
	∞	T1					−109.7
		T2					−115.2
Mordenite	5.0	T1 to T4			−100.1	−105.7	−112.1
	∞	T1					−112.2
		T4					−113.1
		T2+T3					−115.0
ZSM-5	20	T1 to T12				−106.0	−112.0

Table 1

- 118.5 ppm, - 115.3 ppm, -112.3 ppm, -110.3 ppm, and -104.0 ppm in **Fig. 3b** are due to Si(4OSi) units at five crystallographically non-equivalent T-sites. For the zeolite with higher aluminum content (parent MCM-22, **Fig. 3a**), a corresponding set of Si(3OSi,1OAl) signals appears, which is shifted to higher δ_{29Si} values by about 5 to 6 ppm, like for the Si(*n*Al) signals of other zeolites in **Table 1**. Therefore, the ^{29}Si MAS NMR spectra in **Figs. 3a and 3b** were simulated using two sets of five signals: Five for Si(4OSi) and five for Si(3OSi,1OAl) units. Utilizing the relative intensities of the two sets of Si(3OSi,1OAl) and Si(4OSi) signals of 1:1.75 for the parent MCM-22 and 1:4 for the dealuminated MCM-22, the simulation of the ^{29}Si MAS NMR spectra in **Figs. 3a and 3b** yielded the resonance positions of the five Si(3OSi,1OAl) signals of δ_{29Si} = - 112.5 ppm, - 110.5 ppm, - 107.5 ppm, - 104.5 ppm, and -98.0 ppm. In addition, the simulation of the ^{29}Si MAS NMR spectrum of the parent MCM-22 (**Fig.3a**) required the assumption of a signal at δ_{29Si} = - 102 ppm due to surface SiOH groups (Q^3 corresponding to Si(3OSi,1OH)) with a relative intensity of *ca.* 5% [10].

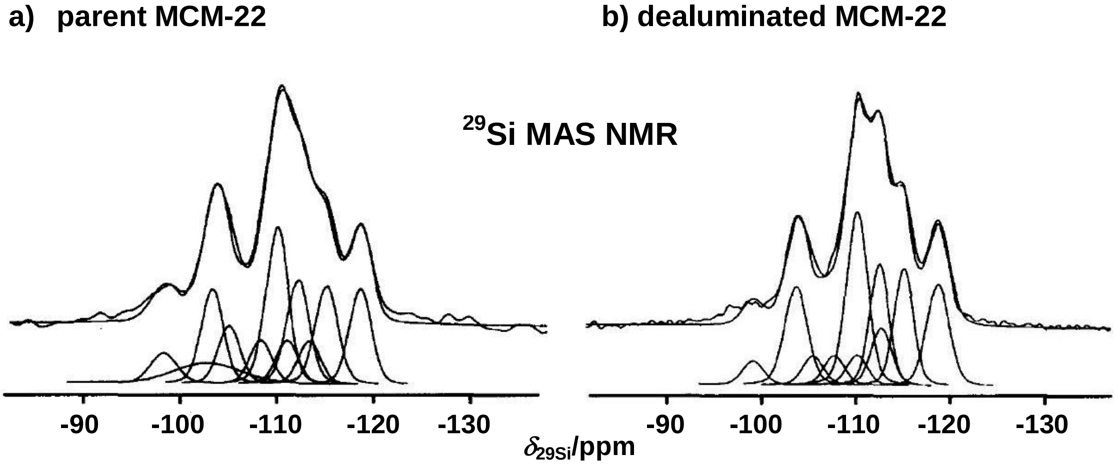

Fig. 3

Differences in the ^{29}Si MAS NMR shifts of framework silicon atoms located on crystallographically non-equivalent T-sites are mainly caused by different local geometries of the SiO_4 tetrahedra. Empirical correlations and theoretical considerations yielded that the ^{29}Si NMR shifts, δ_{Si}, of Si((4-*n*)OSi,*n*Al) units are linearly correlated to the mean value, $\overline{\alpha}$, of the four Si-O-T bond angles. With linear regression analysis, quantitative relationships between the values of δ_{Si} and $\overline{\alpha}$ have been derived. For Si(4OAl) units in sodalite, cancrinite, thomsonite, and zeolites A, X, Y, and ABW, the following correlation [11]:

$$\delta_{Si} / \text{ppm} = -5.230 - 0.570 \cdot \overline{\alpha} \quad (2)$$

was obtained. The correlation between δ_{Si} and $\overline{\cos\alpha / (\cos\alpha - 1)}$ was theoretically derived [12]:

$$\delta_{Si} / \text{ppm} = -223.9 \, \overline{\cos\alpha / (\cos\alpha - 1)} + 5n - 7.2 \quad (3)$$

where *n* corresponds to the number of aluminum atoms in the first coordination sphere of T-sites. Applying **Equs. (2) and (3)**, the ^{29}Si NMR shifts of silicon atoms at crystallographically non-equivalent T-sites of zeolite frameworks can be calculated from the Si-O-T bond angles, which are obtained by XRD. Therefore, is method allows the examination of structure models derived by XRD.

Three-dimensional connectivities between crystallographically non-equivalent T-sites in zeolites have been investigated applying COSY (Correlation Spectroscopy) and

INADEQUATE (Incredible Natural Abundance Double Quantum Transfer Experiment) pulse sequences [13]. The COSY experiment is based on the measurement of the J-coupling (direct bond coupling) within a molecular structure [13]. **Fig. 4a** shows the pulse sequence consisting of: (i) the preparation of the ^{29}Si spin system by magnetization transfer from the abundant *S*-spins (^{1}H nuclei) to the dilute *I*-spins (^{29}Si nuclei) by cross-polarization (CP), (ii) the evolution of the ^{29}Si spin system during the time period t_1, (iii) a fixed delay (FD) before and after a $\pi/2$ pulse, and (iv) the acquisition (AQ) of the free induction decay of the ^{29}Si magnetization during the time period t_2. The 2D ^{29}Si COSY MAS NMR spectrum of zeolite ZSM-39 in **Fig. 4c** was recorded with 128 increments in t_1 and 64 scans for each t_1. The contour plot in **Fig. 4d** shows diagonal peaks of silicon atoms at T1, T2 and T3 sites and off-diagonal peaks (cross-peaks) originating from silicon atoms at T1 and T2 (cross-peak T1T2) and at T2 and T3 (cross-peak T2T3) sites. Hence, the cross-peaks clearly indicate

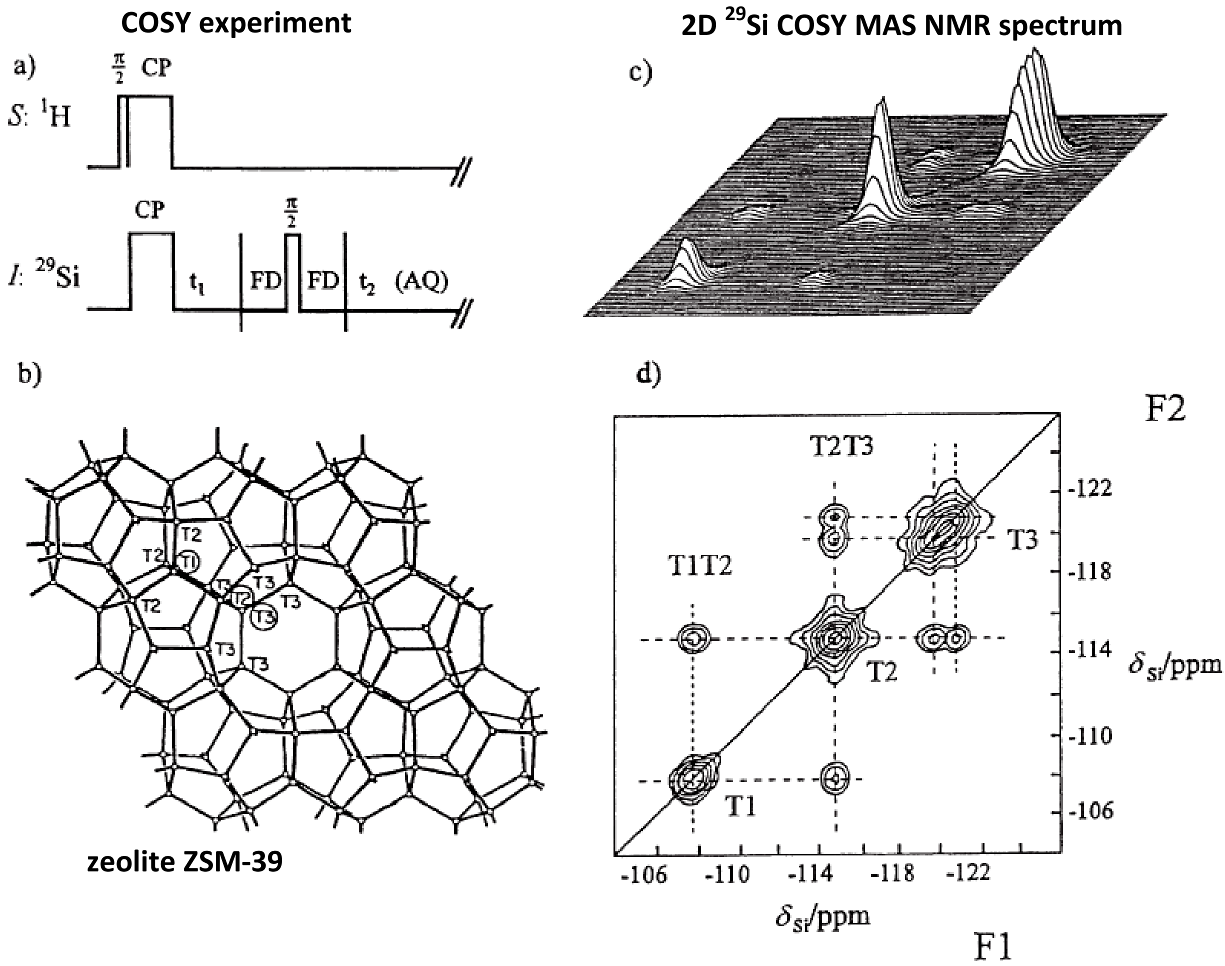

Fig. 4

connectivities between silicon atoms on T1 and T2 sites and between silicon atoms on T2 and T3 sites. These results agree with the structure model of zeolite ZSM-39 in **Fig. 4b**.

For reviews on ^{29}Si MAS NMR spectroscopy of silicon-containing solid catalysts, see Refs. [2], [6], and [9].

Catalyst preparation: Hydrated as well as dehydrated catalyst samples can be investigated by ^{29}Si MAS NMR. Adsorption of O_2 in the micropores of dehydrated samples can be helpful to decrease the T_1 time due to the paramagnetic properties of oxygen molecules.

^{29}Si MAS NMR studies: For decreasing the ^{29}Si MAS NMR line width, high-power ^{1}H decoupling should be applied for ^{29}Si MAS NMR studies. Typically, the nuclear spins of ^{29}Si nuclei in aluminosilicates have T_1 relaxation times allowing ^{29}Si MAS NMR measurements with a repetition time of 30 s. With decreasing aluminum content, however, the T_1 time can increase up to some minutes, which requires a correspondingly higher repetition time. In the case of exiting the ^{29}Si nuclei by cross-polarization (CP), the repetition time is limited by the T_1 time of the ^{1}H nuclei, which is typically significantly shorter than the T_1 time of ^{29}Si nuclei. In the case of ^{29}Si CP MAS NMR studies, however, the signal intensities do not correlate with the real spin numbers, which hinders the quantitative evaluation of obtained ^{29}Si CPMAS NMR spectra by Equ. (1). Chemical shifts are referenced to octakis(trimethylsiloxy)silsesquioxane powder (Q_8M_8, δ_{29Si} = 11.7 ppm) at spinning rates of ν_{rot} = 2 to 3 kHz. This reference is easier to handle in MAS NMR rotors in comparison with tetramethylsilane (TMS, δ_{29Si} = 0 ppm) with a boiling point of 299 to 301 K.

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