Characterization of silicon species at catalyst surfaces by ^{29}Si CPMAS 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 % only and a sensitivity of 3.7 x 10^{-4} in comparison with ^{1}H nuclei (1.0). Therefore, this isotope is at the limit of those candidates for NMR studies of solids, which are possible to investigate without isotopic enrichment. Due to this low NMR sensitivity of ^{29}Si nuclei, the excitation of these nuclei for solid-state NMR studies is performed in some cases by the cross-polarization (CP) experiment (**Fig. 1** [1]). In this pulse experiment, a significant **enhancement of the signal intensities of spins S with low natural abundance and/or small gyromagnetic ratio (S: ^{13}C, ^{15}N, ^{29}Si etc.) is possible**.

In the CP experiment, the high population difference ΔN_{I} of the nuclear energy levels of the ^{1}H nuclei, which are dipolarly coupled with spins I, is utilized for an enhancement of the low population difference ΔN_{S} of the spins S via polarization transfer from spins I to spins S. An important prerequisite for this $I \Rightarrow S$ polarization transfer is an equalization of the energy levels of the dipolarly coupled spins I and S in the magnetic field components $B_{1,\mathrm{I}}$ and $B_{1,\mathrm{S}}$ of long (τ = 1 to 6 ms) radiofrequency pulses, also denoted contact pulses (**Fig. 1**, top). The $\pi/2$ pulse produces spins I

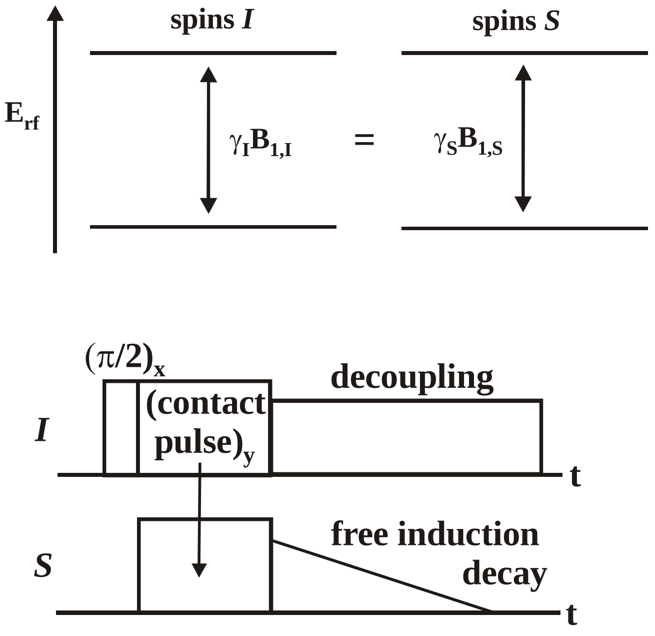


Fig. 1

polarization and the contact pulse allows the polarization transfer from spins I to dipolarly coupled spins S, if the following **Hartmann-Hahn condition** is valid [1]:

$$\gamma_I B_{1,I} = \gamma_S B_{1,S} \qquad (1)$$

The parameters in **Equ. (1)** are the gyromagnetic ratios γ_I and γ_S of the spins I and S and the magnetic field components $B_{1,I}$ and $B_{1,S}$ of the contact pulse for the spins I and S, respectively. During the detection of the NMR signal of the spins S, a weak and long decouple pulse is irradiated at the spins I for averaging dipolar I-S interactions being responsible for signal broadening. For the polarization transfer during the contact pulse, however, these dipolar I-S interactions are necessary. Therefore, the **mobility of the I-S coupled species under study must be low during the CP experiment**. Since the strength of the dipolar I-S interaction determined the effectivity of the $I \Rightarrow S$ polarization transfer, the **signal intensities in ^{29}Si CPMAS NMR spectra don't correlate with the number of ^{29}Si nuclei** in a direct manner.

Silicon atoms inside the framework of silicates and aluminosilicates are tetrahedrally oxygen coordinated (Q^4 or Q_4 species), resulting in different silicon environments, such as Si(*n*Al) or Si((4-*n*)OSi,*n*Al) (n = 0 to 4), with typical ^{29}Si chemical shifts (see "method 6" via link "NMR Methods for Heterogeneous Catalysis" and Refs. [2] and [3]). In addition, silicon atoms at the surface of pure or modified silicates and aluminosilicates are bound via oxygen bridges to hydroxyl protons, which can act as adsorptions sites. As an example, **Fig. 2** shows the ^{29}Si CPMAS NMR spectra of microporous Silicalite-1 (a) with MFI structure and of mesoporous SBA-15 (b) [4]. The spectrum of the calcined (T = 723 K) Silicalite-1 consists of signals at **δ_{29Si} = -103 ppm** and -113 ppm due to **SiOH groups of Q^3 (Si(3OSi,1OH))** silicon species and due to tetrahedrally coordinated framework silicon atoms of **Q^4 (Si(4OSi))** silicon species, respectively. Upon saturation with H_2O, a weak decrease of these signals is observed (**Fig. 2a**), which is explained by a decreased ^{1}H ⇒ ^{29}Si polarization transfer upon saturation. This is explained by an increase of the ^{1}H-^{29}Si distance due to an increase of the O-H distance of the corresponding SiOH groups caused by H-bondings to water molecules. Furthermore, a stronger decrease of the signal intensities occurred upon the saturation of Silicalite-1 with CD_3OH (CD_3OH

saturated). This finding hints at stronger CD_3OH/SiOH interactions compared with the H_2O/SiOH interactions for Silicalite-1 [4].

The ^{29}Si CPMAS NMR spectrum of calcined (T = 723 K) SBA-15 in **Fig. 2b** consists of **Q^3 (Si(3OSi,1OH)) and Q^2 (Si(2OSi,2OH)) signals** at **δ_{29Si} = -101 ppm and -92 ppm,** respectively, and a weak high-field shoulder at δ_{29Si} = -110 ppm due to Q^4 species [4]. In contrast to Silicalite-1, saturation of SBA-15 with water (H_2O saturated) led to a significant increase of the ^{29}Si CPMAS NMR signals. This effect may be due to an adsorption of water at the SiOH groups of well accessible Q^2 silicon species in such a manner that the H atoms of these water molecules are able to contribute to the $^1H \Rightarrow {}^{29}Si$ polarization transfer. In this case, the intensity decrease of the Q^2 signals of SiOH groups involved in H-bondings to water molecules is overcompensated by the contribution of the additional ^{1}H spins of adsorbed water molecules to the $^1H \Rightarrow {}^{29}Si$ polarization transfer. This effect cannot occur for Silicalite-1 since this material has no Q^2 silicon species. The ^{29}Si CPMAS NMR spectrum of SBA-15 saturated with CD_3OH (CD_3OH saturated), on the other hand, shows significantly lower signal intensities compared with the spectrum of calcined SBA-15, which is similar to the finding for methanol-loaded Silicalite-1. Also for SBA-15, therefore, strong CD_3OH/SiOH interactions can be assumed, leading to an increase of the ^1H-^{29}Si distance due to an increase of the O-H distance of the corresponding OH groups caused by H-bondings to methanol molecules [4].

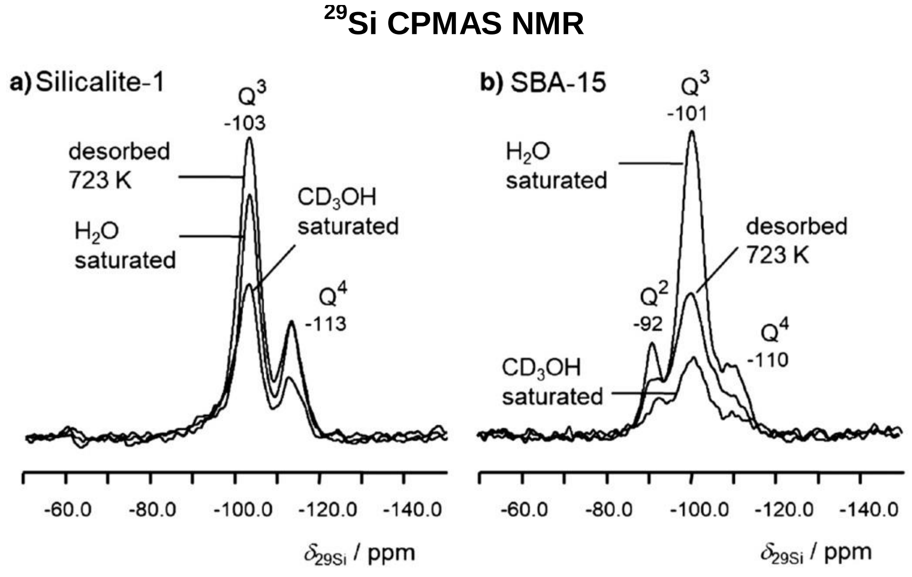


Fig. 2

Depending on the application of siliceous materials, silicon atoms at the surface are bound via oxygen bridges to carbon atoms or silicon atoms in surface-anchored complexes. After reaction with octadecylmethyldichlorosilane, signals of D_1 (δ_{29Si} = -4 ppm), D_2 (δ_{29Si} = -7 ppm), D_3 (δ_{29Si} = -10 ppm) and of various D_4 + D'_4 species (δ_{29Si} = -14 to -22 ppm) are obtained [5-8]. After reaction with octadecyltrichlorosilane, additional signals of T1 (δ_{29Si} = -46 ppm), T'_1 (δ_{29Si} = -50 ppm), T_2 (δ_{29Si} = -56 ppm), T_3 + T'_3 (δ_{29Si} = -59 ppm), and T_4 + T'_4 species (δ_{29Si} = -64 to -70 ppm) occur (see also **Fig. 3** and **Table 1**) [5-8].

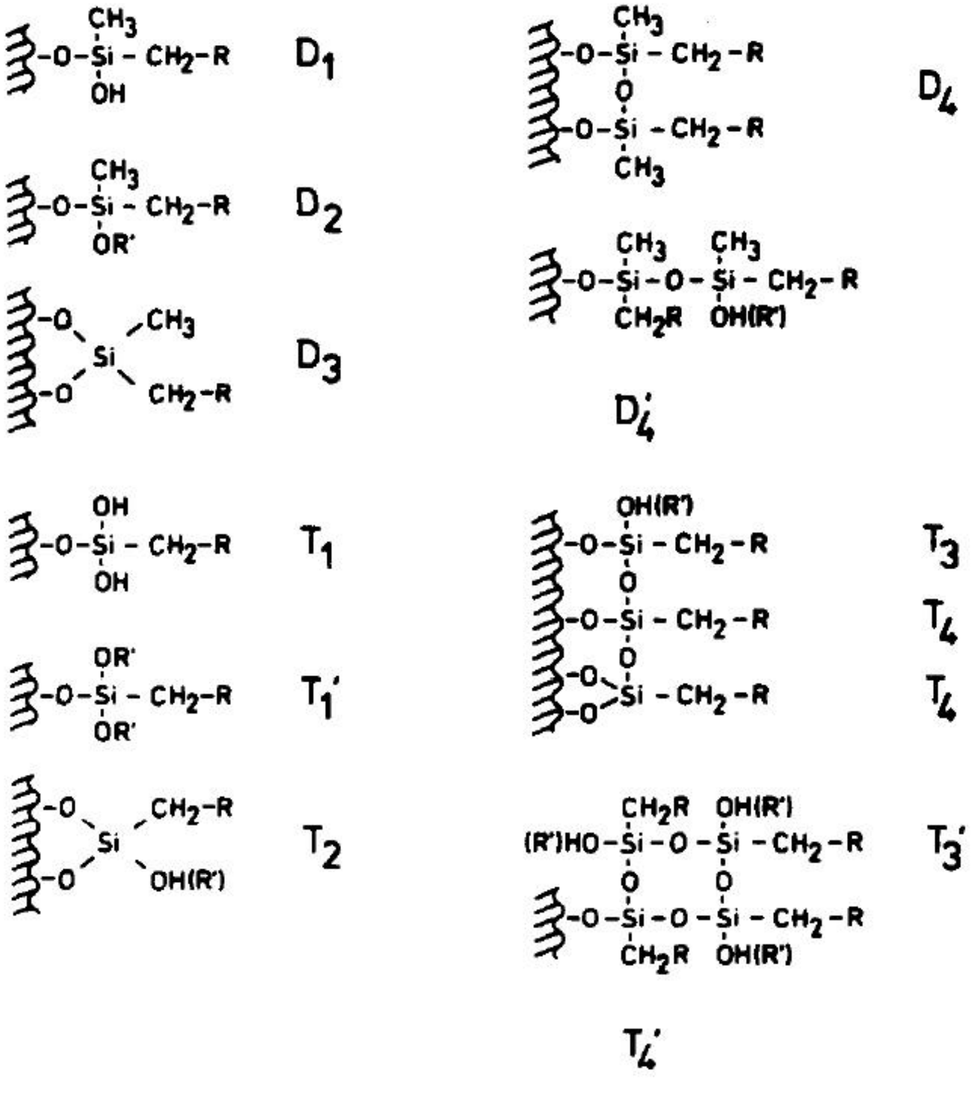
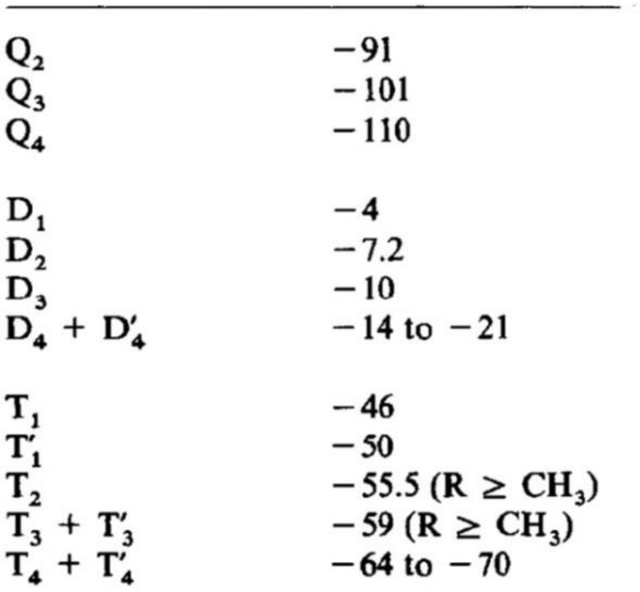


Fig. 3



Structural type	δ_{29Si}/ppm
Q_2	−91
Q_3	−101
Q_4	−110
D_1	−4
D_2	−7.2
D_3	−10
$D_4 + D'_4$	−14 to −21
T_1	−46
T'_1	−50
T_2	−55.5 ($R \geq CH_3$)
$T_3 + T'_3$	−59 ($R \geq CH_3$)
$T_4 + T'_4$	−64 to −70

Table 1

For applications as stationary phases in chromatography or as an easy-to-handle catalytic material, MCM-41 silica spheres were modified by grafting with mono- (MF) and trifunctional octadecyl (TF) alkyl chains and endcapping with hexamethyldisilazane [9]. ^{29}Si CPMAS NMR spectroscopy was utilized for determining the surface species, amount of alkyl chain grafting and degree of cross-linking of the attached alkylsilanes. The ^{29}Si CPMAS NMR spectra of the MCM-41 samples grafted with MF and TF are shown in **Figs. 4a** and **4b** [9]. The ^{29}Si chemical shifts of the various species correspond to those in **Table 1**. The ^{29}Si CPMAS NMR signals at δ_{29Si} = -100 ppm and -109 ppm originate from surface silanol groups (Q^3) and Q^4 species, respectively. The comparison with the ^{29}Si CPMAS NMR spectrum of the calcined MCM-41 sample prior to grafting (spectrum not shown), with a dominant Q^3 signal as well as Q^2 and Q^4 resonances, reveals a complete loss of the Q^2 signal and a noticeable reduction of the Q^3 signal after surface modification with the alkylsilanes and subsequent endcapping. The ^{29}Si CPMAS NMR spectrum of the MCM-41 sample grafted with TF contains signals of T^n groups ($T^n = RSi(OSi)_n(OH)_{3-n}$ with n = 1, 2, 3) between δ_{29Si} = −45 ppm and −70 ppm. These signals hint at the attachment and cross-linking of the C_{18} chains on the MCM-41 silica surface. Furthermore, intense ^{29}Si CPMAS NMR signals occur at about δ_{29Si} = 14.5 ppm (R_3SiOSi = M group), which are a superposition of the signals due to the attached monofunctional C_{18} chains and the trimethyl silyl groups from the endcapping reaction [9].

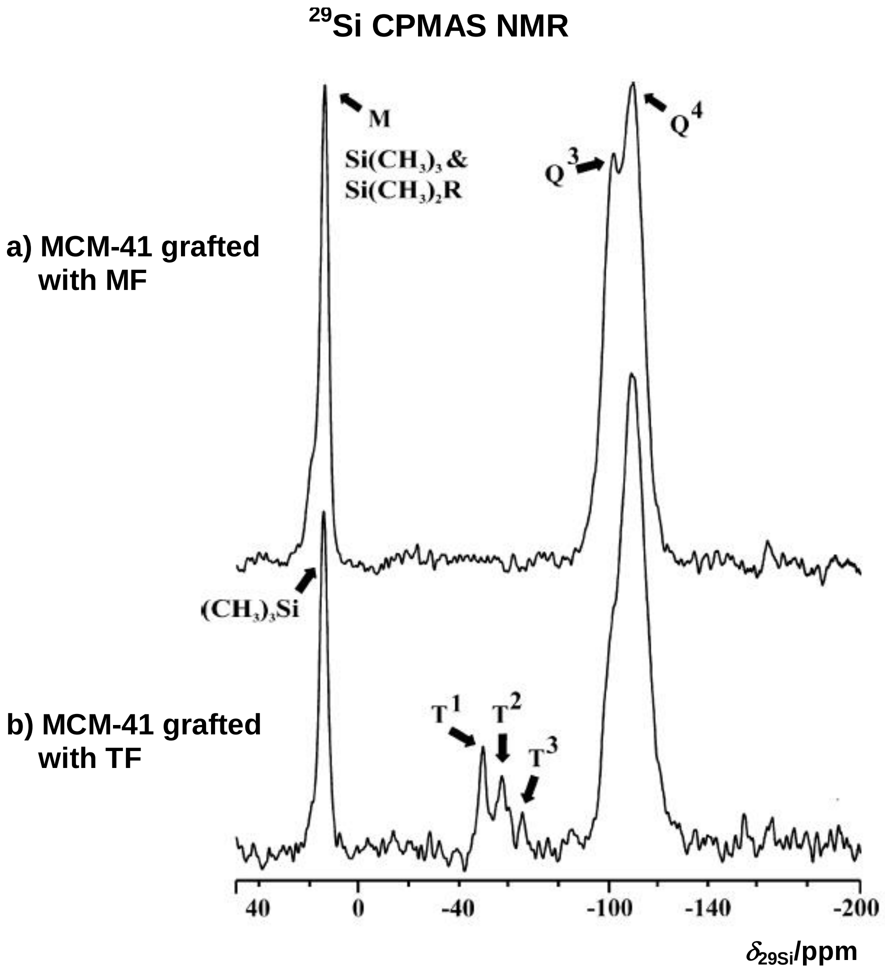


Fig. 4

Catalyst preparation: Most of the ^{29}Si CPMAS NMR studies of silicon atoms at the surface of pure or modified silicates and aluminosilicates are performed with sample materials in the hydrated state.

^{29}Si CPMAS NMR studies:. The ^{29}Si cross-polarization MAS NMR measurements (CPMAS NMR) in Fig. 2 were carried out using a 7.0 mm MAS NMR probe with a spinning rate of ν_{rot} = 3.5 kHz. These spectra were recorded at the resonance frequency of ν_0 = 79.5 MHz, with a radiofrequency field of ν_{rf} = 41.67 kHz, a ^{1}H–^{29}Si contact pulse of τ = 3 ms, and the repetition time of 4 s. For cross-polarization experiments, the repetition time is limited by the T_1 time of the ^{1}H nuclei, which is much shorter than for ^{29}Si nuclei. For decreasing the ^{29}Si MAS NMR line width, highpower ^{1}H decoupling was applied In the case of ^{29}Si CPMAS NMR studies, however, the signal intensities do not correlate with the real spin numbers, which hinders the quantitative evaluation of obtained spectra. Chemical shifts are referenced to octakis(trimethylsiloxy)silsesquioxane powder (Q_8M_8, $\delta_{29\mathrm{Si}}$ = 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, $\delta_{29\mathrm{Si}}$ = 0 ppm) with a boiling point of 299 to 301 K.

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