

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, therefore, no quadrupole moment. The ^{29}Si isotope has a natural abundance of 4.7 % only and, in this state, a sensitivity of 3.7×10^{-4} in comparison with ^1H 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 often performed 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 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 ^1H nuclei (spins I), which are dipolarly coupled with the spins S , is utilized for an enhancement of the low population difference ΔN_S of the spins S via a polarization transfer from spins I to spins S . An important prerequisite for this $I \Rightarrow S$ polarization transfer are equal energy level differences of the dipolarly coupled spins I and S in the magnetic field components $B_{1,I}$ and $B_{1,S}$ during long ($\tau = 1$ to 6 ms) radiofrequency pulses. These pulses are denoted contact pulses (**Fig. 1**). The initial $\pi/2$ pulse on

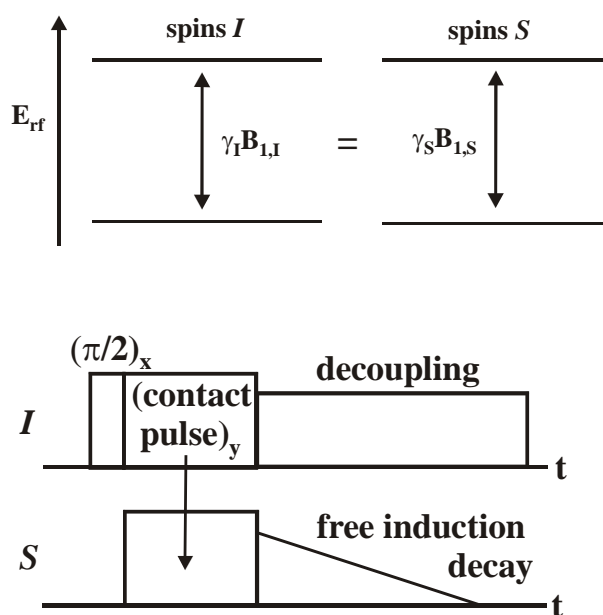


Fig. 1

the ^1H nuclei produces spin I polarization. The subsequent, simultaneous contact pulses allow the polarization transfer from spins I to dipolarly coupled spins S , if the following **Hartmann-Hahn condition** is valid [1]:

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

The parameters in **Eq. (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 pulses for the spins I and S , respectively. During the detection of the NMR signal (free induction decay) of the spins S , a weak and long decoupling pulse is irradiated on the spins I for removing dipolar I - S interactions, which may be responsible for a broadening of the spin S signals.

For the polarization transfer during the contact pulse, however, 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 $\text{Si}(n\text{Al})$ or $\text{Si}((4-n)\text{OSi}, n\text{Al})$ ($n = 0$ to 4), with typical ^{29}Si chemical shifts (see Section “method 11” and Refs. [2] and [3]). In addition, silicon atoms at the surface of pure or modified silicates 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 $\delta_{^{29}\text{Si}} = -103$ ppm and -113 ppm due to **SiOH groups of Q^3 ($\text{Si}(3\text{OSi}, 1\text{OH})$)** silicon species and due to tetrahedrally coordinated framework silicon atoms of **Q^4 ($\text{Si}(4\text{OSi})$)** silicon species, respectively. Upon saturation with H_2O , a weak decrease of these signals is observed (**Fig. 2a**), which is explained by a decreased $^1\text{H} \Rightarrow ^{29}\text{Si}$ polarization transfer upon water saturation. This is explained by an increase of the ^1H - ^{29}Si distance due to an increase of the O-H distance of the corresponding SiOH groups caused by hydrogen bonds 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 $\text{CD}_3\text{OH}/\text{SiOH}$ interactions compared with the $\text{H}_2\text{O}/\text{SiOH}$ interactions for Silicalite-1 [4].

The ^{29}Si CPMAS NMR spectrum of calcined ($T = 723 \text{ K}$) SBA-15 in **Fig. 2b** consists of **Q^3 ($\text{Si}(3\text{OSi},1\text{OH})$) and Q^2 ($\text{Si}(2\text{OSi},2\text{OH})$) signals** at $\delta_{^{29}\text{Si}} = -101 \text{ ppm}$ and **-92 ppm** , respectively, and a weak high-field shoulder at $\delta_{^{29}\text{Si}} = -110 \text{ ppm}$ 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 $^1\text{H} \Rightarrow ^{29}\text{Si}$ polarization transfer. In this case, the intensity decrease of the Q^2 signals of SiOH groups involved in hydrogen bonds to water molecules is overcompensated by the contribution of the additional ^1H spins of adsorbed water molecules to the $^1\text{H} \Rightarrow ^{29}\text{Si}$ 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 $\text{CD}_3\text{OH}/\text{SiOH}$ 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 hydrogen bonds to methanol molecules [4].

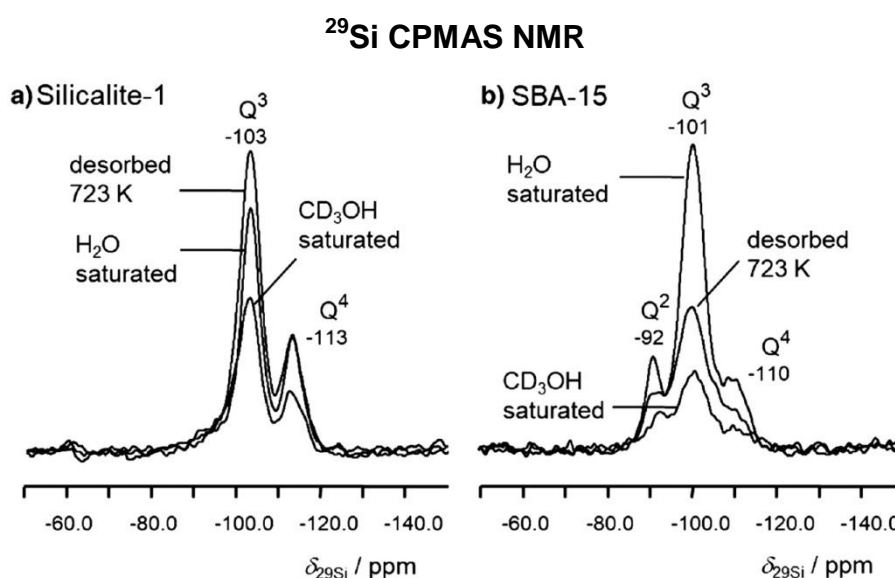

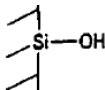

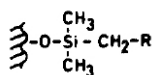
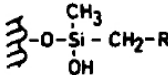
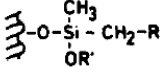
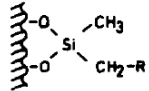
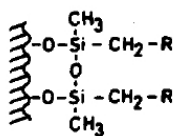


Fig. 2

Depending on the **technical application of siliceous materials** in adsorption or separation processes or for chromatography, **surface silicon atoms are bound via oxygen bridges to carbon or silicon atoms of surface-anchored complexes**. After reaction with octadecylmethyldichlorosilane with silica surfaces, ^{29}Si CP MAS NMR spectroscopy indicated the formation of D^1 ($\delta_{29\text{Si}} = -4$ ppm), D^2 ($\delta_{29\text{Si}} = -7$ ppm), D^3 ($\delta_{29\text{Si}} = -10$ ppm), and various $\text{D}^4 + \text{D}'^4$ species ($\delta_{29\text{Si}} = -14$ to -21 ppm) [5-8]. Reaction with octadecyltrichlorosilane cause additional signals of T^1 ($\delta_{29\text{Si}} = -46$ ppm), T'^1 ($\delta_{29\text{Si}} = -50$ ppm), T^2 ($\delta_{29\text{Si}} = -56$ ppm), $\text{T}^3 + \text{T}'^3$ ($\delta_{29\text{Si}} = -59$ ppm), and $\text{T}^4 + \text{T}'^4$ species ($\delta_{29\text{Si}} = -64$ to -70 ppm) [5-8]. See **Table 1** for an illustration of the above-mentioned surface complexes and a survey on their ^{29}Si chemical shift values.

| Surface complexes | Assignments | $\delta_{29\text{Si}}$ / ppm | Refs. |
|---|--------------|------------------------------|--------|
|  | Q^2 | -91 | [5, 6] |
|  | Q^3 | -101 | [5, 6] |
|  | Q^4 | -110 | [5, 6] |
|  | M | +13 to +15 | [8, 9] |
|  | D^1 | -4 | [5] |
|  | D^2 | -7.2 | [5] |
|  | D^3 | -10 | [5] |
|  | D^4 | -14 to -21 | [5] |

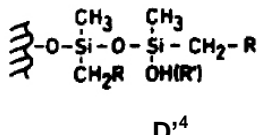
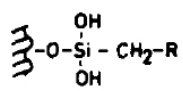
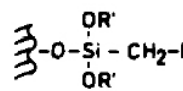
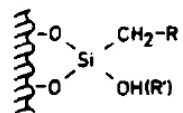
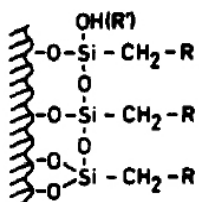
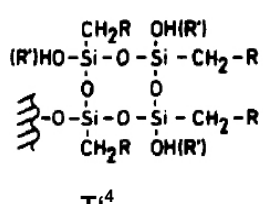
| | | | |
|--|--------------------------|--|----------------------|
|  <p style="text-align: center;">D'^4</p> | D'^4 | -14 to -21 | [5] |
|  | T^1 | -46 | [5] |
|  | T'^1 | -50 | [5] |
|  | T^2 | -55.5 to -58 $R \geq CH_3$ | [5, 8] |
|  | T^3 T^4 T'^4 | -59 $R \geq CH_3$ -64 to -70 -64 to -70 | [5, 8] [5] [5] |
|  <p style="text-align: center;">T'^4</p> | T'^3 T'^4 | -59 $R \geq CH_3$ -64 to -70 | [5] [5] |

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 (TF) octadecyl 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. 3a** and **3b** [9]. The ^{29}Si chemical shifts of the various species correspond to those in **Table 1**. The ^{29}Si CPMAS NMR signals at $\delta_{29\text{Si}} = -100$ 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

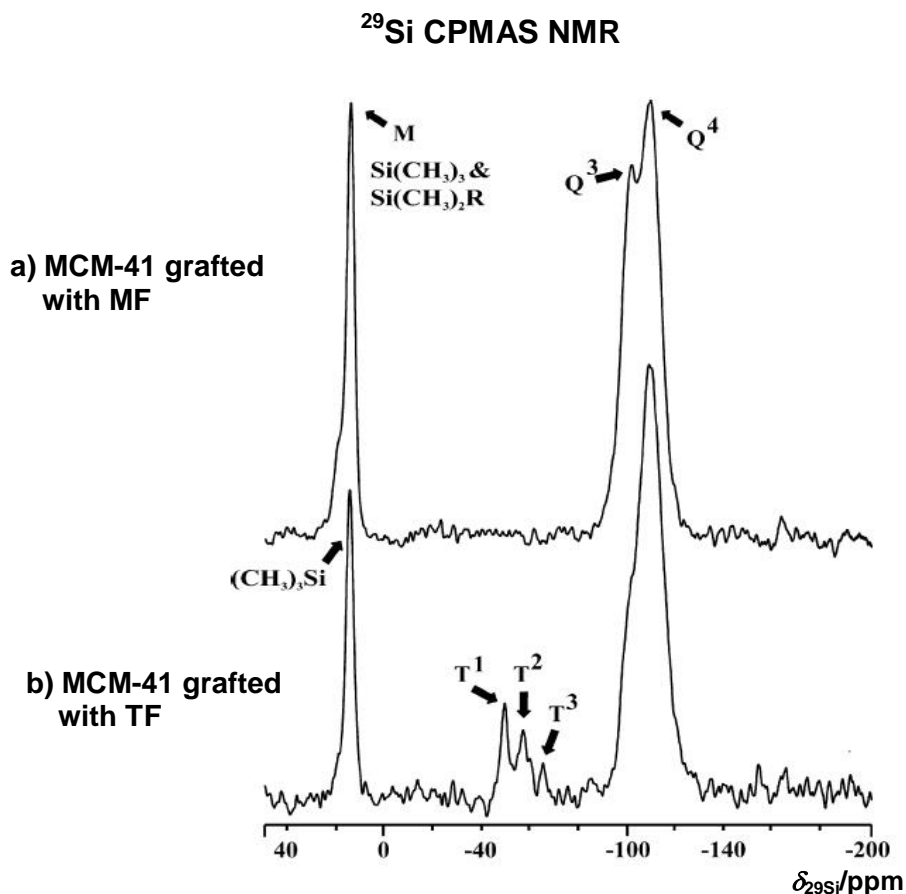


Fig. 3

of the calcined MCM-41 sample prior to the 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 ($\text{T}^n = \text{RSi}(\text{OSi})_n(\text{OH})_{3-n}$ with $n = 1, 2, 3$) between $\delta_{^{29}\text{Si}} = -45$ 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 $\delta_{^{29}\text{Si}} = 14.5$ ppm ($\text{R}_3\text{SiOSi} = \text{M}$ 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].

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 $\nu_{\text{rot}} = 3.5$ kHz. Too high ν_{rot} values may remove the dipolar I - S coupling and hinder the $I \Rightarrow S$ polarization transfer. The spectra were recorded at the resonance frequency of $\nu_0 = 79.5$ MHz, with a radiofrequency field of $\nu_{\text{rf}} = 41.67$ kHz, a ^1H - ^{29}Si contact pulse of $\tau = 3$ ms, and the repetition time of 4 s. For cross-polarization experiments, the repetition time is limited by the T_1 time of the ^1H nuclei, which is much shorter than for ^{29}Si nuclei. For decreasing the ^{29}Si MAS NMR line width, high-power ^1H decoupling was applied. In the case of ^{29}Si CPMAS NMR studies, the signal intensities do not correlate with the real spin numbers, which hinders the quantitative evaluation of obtained spectra (see text). Chemical shifts are referenced to octakis(trimethylsiloxy)silsesquioxane powder (Q_8M_8 , $\delta_{^{29}\text{Si}} = 11.7$ ppm) at spinning rates of $\nu_{\text{rot}} = 2$ to 3 kHz. This reference is easier to handle in MAS NMR rotors than liquid tetramethylsilane (TMS, $\delta_{^{29}\text{Si}} = 0$ ppm) with a boiling point of 299 to 301 K.

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