Method for the determination of the density of Lewis acid sites by adsorption of trimethylphosphine oxide and ³¹P MAS NMR

Spectroscopic background: In contrast to the numerous applications of trimethylphosphine oxide (TMPO) as a probe molecule for the study of Broensted acid sites on solid catalysts, only few examples for solid-state NMR studies of Lewis acid sites on solid materials by adsorption of TMPO exist [1-8]. Furthermore, there are different assignments for ³¹P MAS NMR signals of TMPO interacting with Lewis acid sites on solids in literature [1-8]. For clarifying the interaction of TMPO with surface sites on typical Lewis acidic solids, ³¹P MAS NMR studies of TMPO interacting with γ -Al₂O₃, TiO₂/anatase, and partially lithium-exchanged zeolite Na-Y (52Li,48Na-Y) were performed [3]. The latter material is the mostly Lewis acidic zeolite Y. The ³¹P MAS NMR spectra of the above-mentioned materials, recorded after dehydration and TMPO loading, are shown in **Fig. 1** (Fig. 2 in Ref. [3]).

In Figs. 1b and 1c, the ³¹P MAS NMR spectra of 2.5 and 5 mg TMPO, respectively, loaded on ca. 50 mg dehydrated γ -Al₂O₃ are shown. These spectra consist of two signals at δ_{31P} = 48 and 65 ppm. Since the signal at δ_{31P} = 65 ppm is typical for TMPO interacting with Broensted acid sites (see Section "method 22"), the dominating signal at δ_{31P} = 48 ppm hints at an interaction of TMPO with Lewis acid sites. The weak shoulder at δ_{31P} = ca. 40 ppm in **Fig. 1c** is due to remaining bulk TMPO (compare with **Fig. 1a**). The ³¹P MAS NMR signal at δ_{31P} = 48 ppm for TMPO adsorbed on TiO₂ /anatase in Fig. 1d supports the above-mentioned assignment of TMPO interacting with Lewis acid sites. The weak low-field shoulder of this signal in Fig. 1d hints at a very small number of TMPO interacting with Broensted acid sites on TiO₂/anatase. The ³¹P MAS NMR spectrum of TMPO loaded on Lewis acidic **zeolite 52Li,48Na-Y** shows two strong signals at δ_{31P} = 49 and 51 ppm (Fig. 1e). The relative intensities of the two signals of roughly 1:1 indicates that these signals are due to TMPO adsorption at Li⁺ and Na⁺ cations. The signal at δ_{31P} = 42 ppm in Fig. 1e is caused by bulk TMPO, whereas the weak signal and shoulder at ca. 55 and 67 ppm are explained by TMPO adsorbed at few Broensted acidic OH groups in the supercages and sodalite cages, respectively, of the zeolite Y under study [10]. The above-mentioned solid-state NMR studies of three very different and well-



Fig. 1

For the quantitative evaluation of the ³¹P MAS NMR signal intensities of TMPO molecules adsorbed at Lewis acid sites, the procedure described by Eq. (3) of Section "method 1" is utilized. As an intensity standard, a well-known aluminosphosphate-type zeolite, such as VPI-5, is suitable.

Utilizing the assignment for TMPO interacting with Lewis acid sites on solid catalysts to ³¹P MAS NMR signals in the chemical shift range of $\delta_{31P} = 48$ to 51 ppm, the Lewis acidities of Sn-containing ZSM-5 zeolites [5], mesoporous Sn-MCM-41 materials [6], and yttrium-modified siliceous Beta zeolites [7] were investigated. Based on the results of the above-mentioned solid-state NMR spectroscopic studies, the conversion of dihydroxyacetone to methyl lactate [5], the conversion of 1,3-dihydroxyacetone to ethyl lactate [6], and the conversion of acetic acid to

isobutene [7] on these catalysts could be well explained by their Lewis acidic properties.

Alternative assignments of TMPO interacting with Lewis acid sites base on twodimensional solid-state NMR experiments with very complex samples, e.g. steamed H-ZSM-5 and H-[B]-ZSM-5, containing different types of Broensted acid sites, in addition to Lewis acid sites [2, 8]. These studies explain ³¹P MAS NMR signals in the chemical shift range of δ_{31P} = 55 to 88 ppm by TMPO interacting with Lewis acid sites [2, 8]. However, these resonance positions are identical with the chemical range of TMPO interacting with Broensted acid sites (see Section "method 22"). Furthermore, based on ³¹P MAS NMR studies of TMPO-loaded γ -Al₂O₃, Rakiewicz et al. assigned a signal occurring at δ_{31P} = 37 ppm in the ³¹P MAS NMR spectrum of TMPO-loaded dealuminated zeolite H-Y to TMPO interacting with Lewis acid sites [1]. On the other hand, Hayashi et al. observed a ³¹P MAS NMR signal at δ_{31P} = 37 ppm for physisorbed TMPO under steric restrictions in pores of silica surfaces [9]. For reviews on the above-mentioned topics, see Refs. [11], [12], and [13].

Catalyst preparation: Before the solid-state NMR studies, a standard dehydration of the solid catalyst inside a "sample tube system 1" at "vacuum line 1" (see Sections "sample tube system 1" and "vacuum line 1", accessible via link "*In Situ* Solid-State NMR Techniques") was performed. The dehydration starts with an evacuation at room temperature for ca. 10 minutes followed by a temperature ramp from room temperature to T = 393 K within 2 hours. At this temperature, the sample was dehydrated for 2 hours. Subsequently, the temperature was increased up to T = 723 K within 3 hours and the sample was evacuated at this temperature for 12 hours. After this treatment, the sample tube system was closed via the vacuum valve and disconnected from the vacuum line (after the line was ventilated with air).

For the studies demonstrated in Fig. 1, loading of dehydrated solid catalysts with TMPO of Alfa Aesar was performed by mixing of ca. 50 mg dehydrated solid catalyst with ca. 5 mg TMPO inside a rotor in a mini glove box (see Section "mini glove box", accessible via link "*In Situ* Solid-State NMR Techniques"), purged with dry nitrogen gas. Subsequently, the rotor was sealed with an O-ring-containing TORLON cap and heated at T = 433 K for 2 h for reaching a proper distribution of the TMPO on the catalyst surface. For alternative preparation routes of TMPO-loaded catalyst samples, see Ref. [14].

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³¹*P* MAS NMR studies: The ³¹P MAS NMR measurements were carried out at a Bruker Avance III 400WB spectrometer with a resonance frequency of $v_0 = 161.9$ MHz and using a 4 mm MAS NMR probe with a sample spinning rate of $v_{rot} = 10$ kHz. The spectra were recorded upon single pulse $\pi/2$ excitation, with a repetition time of 30 s, and high-power proton decoupling (HPDEC). Chemical shifts are referenced to 0.85 M H₃P0₄ ($\delta_{31P} = 0$ ppm).

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