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

Spectroscopic background: In contrast to the numerous applications of trimethylphosphine oxide (TMPO) as a probe molecule for 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, very different assignments for ^{31}P MAS NMR signals of TMPO interacting with Lewis acid sites on solids exist in literature [1-8]. Some of these assignments base on two-dimensional solid-state NMR experiments with complex samples (e.g. steamed H-ZSM-5, H-[B]-ZSM-5) containing different types of Broensted acid sites in addition to Lewis acid sites. These studies explain ^{31}P MAS NMR signals in the chemical shift range of $\boldsymbol{\delta_{31P} = 55}$ **to 88 ppm** by **TMPO interacting with Lewis acid sites** [2, 8], which is identical with the chemical range of TMPO interacting with Broensted acid sites (see Section “method 17”). Additionally, based on ^{31}P MAS NMR studies of TMPO-loaded γ-Al_2O_3, Rakiewicz et al. assigned a signal occurring at δ_{31P} = 37 ppm in the ^{31}P MAS NMR spectrum of TMPO-loaded dealuminated zeolite H-Y to TMPO interacting with Lewis acid sites [1]. While bulk TPMO causes a narrow ^{31}P MAS NMR signal at δ_{31P} = 41 ppm (see **Fig. 1a**) [3, 5], for physisorbed TMPO under steric restrictions in pores of silica surfaces, a high-field shift of the ^{31}P MAS NMR signal to δ_{31P} = 37 ppm was observed [9]. Obviously, there is a significant discrepancy in the assignment of ^{31}P MAS NMR signals for TMPO interacting with Lewis acid sites on solid materials.

In another experimental approach, therefore, the interaction of TMPO with surface sites on typical Lewis acidic solids was investigated by one-dimensional ^{31}P MAS NMR spectroscopy [3]. These Lewis acidic solids are γ-Al_2O_3, TiO_2/anatase, and partially lithium-exchanged zeolite Na-Y (52Li,48Na-Y). The latter material is the mostly Lewis acidic, alkali-exchanged zeolite Y. The ^{31}P MAS NMR spectra of these materials, recorded after dehydration and TMPO loading as described below, are shown in **Fig. 1** (Fig. 2 in Ref. [3]).

In **Figs. 1b and 1c**, the ^{31}P MAS NMR spectra of 2.5 and 5 mg TMPO, respectively, loaded on ca. 50 mg dehydrated γ-Al_2O_3 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 17”), 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 earlier assignment of a ^{31}P MAS NMR signal at δ_{31P} = 37 ppm to TMPO interacting with Lewis acid sites on γ-Al_2O_3 may be caused by physisorbed TMPO in small pores at the surface [9] and the very high TMPO loading of this material [1]. The ^{31}P MAS NMR signal at δ_{31P} = 48 ppm for TMPO adsorbed on TiO_2 /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 TiO_2/anatase. The ^{31}P 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 (compare Fig. 1a in Section “method 17”). 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 can be explained by TMPO adsorbed at few Broensted acidic OH groups

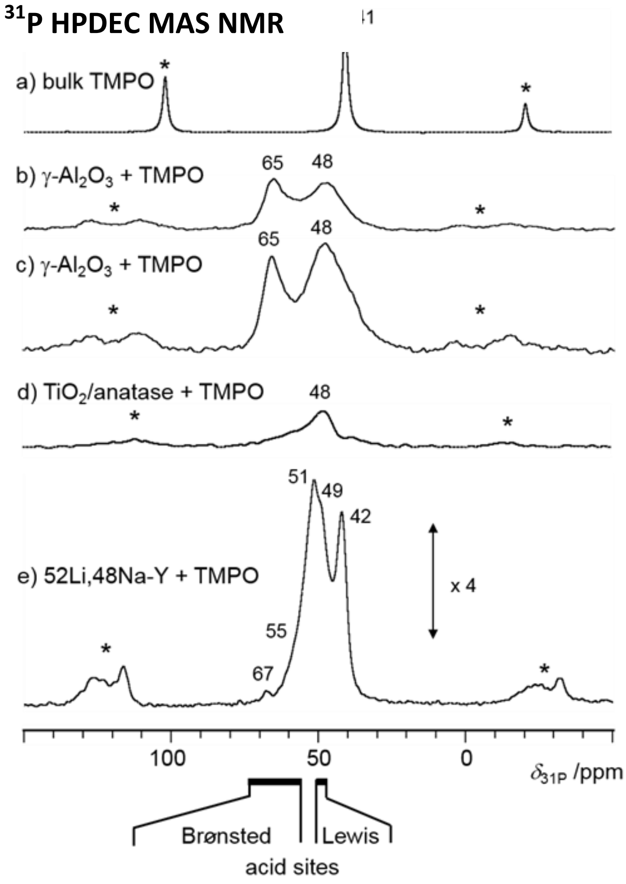

Fig. 1

in the supercages and sodalite cages, respectively, of the zeolite Y under study [10]. The above described solid-state NMR studies of three very different and well-accepted Lewis acidic solids support an assignment of **^{31}P MAS NMR signals at δ_{31P} = 48 to 51 ppm to TMPO at Lewis acid sites** on solid catalysts (see **Fig. 1, bottom**) [3].

For the quantitative evaluation of the ^{31}P MAS NMR signal intensities of TMPO molecules adsorbed at Lewis acid sites, the procedure described by Equ. (3) of Section “method 12” 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 ^{31}P MAS NMR signals in the chemical shift range of δ_{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 these 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 the above-mentioned catalysts could be well explained by the Lewis acidic properties of these materials. For reviews on the above-mentioned topics, see Refs. [11], [12], and [13].

Catalyst preparation: At first, a standard activation of the solid catalyst inside a „sample tube system 1“ is performed on „vacuum line 1“. The activation starts with an evacuation at room temperature for ca. 10 minutes followed by a temperature ramp from room temperature to 393 K within 2 hours. At this temperature, the sample is dehydrated for 2 hours. Subsequently, the temperature is increased up to 723 K within 3 hours and the sample is evacuated at this temperature for 12 hours. After this treatment, the sample tube system is closed via the vacuum valve and disconnected from „vacuum line 1“ after this line was ventilated with air.

For studies as those demonstrated in Fig. 1, loading of dehydrated solid catalysts with TMPO of Alfa Aesar is performed by mixing of ca. 50 mg dehydrated solid catalyst with ca. 5 mg TMPO inside a rotor using e.g. a mini glove box purged with dry nitrogen gas (see Section “mini glove box” via link “In Situ Solid-State NMR Techniques”). Subsequently, the rotor is sealed with an O-ring-containing TORLON cap and heated at 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].

^{31}P MAS NMR studies: ^{31}P MAS NMR measurements were carried out using a Bruker Avance III 400WB spectrometer at a resonance frequency of 161.9 MHz using a 4 mm MAS NMR probe with a sample spinning rate of 10 kHz. The spectra are recorded upon single pulse $\pi/2$ excitation with the repetition time of 30 s and high-power proton decoupling (HPDEC). Chemical shifts are referenced to 0.85 M H_3P0_4 (δ_{31P} = 0 ppm).

References:

[1] E. F. Rakiewicz, A. P. Peters, R. F. Wormsbecher, K. J. Sutovich, K. T. Mueller, *Characterization of acid sites in zeolitic and other inorganic systems using solid-state ^{31}P NMR of the probe molecule trimethylphosphine oxide*, J. Phys. Chem. B 102 (1998) 2890-2896, DOI: 10.1021/jp980808u.

[2] P.V. Wiper, J. Amelse, L. Mafra, *Multinuclear solid-state NMR characterization of the Bronsted/Lewis acid properties in the BP HAMS-1B (H-[B]-ZSM-5) borosilicate molecular sieve using adsorbed TMPO and TBPO probe molecules*, J. Catal. 316 (2014) 240-250, DOI: 10.1016/j.jcat.2014.05.017.

[3] S. Lang, M. Benz, U. Obenaus, R. Himmelmann, M. Hunger, *Novel approach for the characterization of Lewis acidic solid catalysts by solid-state NMR spectroscopy*, ChemCatChem 8 (2016) 2031-2036, DOI: 10.1002/cctc.201600372.

[4] R. Zhao, Z. Zhao, S. Li, W. Zhang, *Insights into the correlation of aluminum distribution and Bronsted acidity in H-Beta zeolites from solid-state NMR spectroscopy and DFT calculations*, J. Phys. Chem. Lett. 8 (2017) 2323-2327, DOI: 10.1021/acs.jpclett.7b00711.

[5] E. Yuan, W. Dai, G. Wu, N. Guan, M. Hunger, L. Li, *Facile synthesis of Sn-containing MFI zeolites as versatile solid acid catalysts,* Microporous Mesoporous Mater. 270 (2018) 265-273, DOI: 10.1016/j.micromeso.2018.05.032.

[6] K.D. Kim, Z. Wang, M. Hunger, J. Huang, *The cooperative effect of Lewis acid and Broensted acid on Sn-MCM-41 catalysts for the conversion of 1,3-dihydroxyacetone to ethyl lactate,* Green Chemistry 21 (2019) 3383-3393, DOI: 10.1039/C9GC00820a.

[7] T. Yan, L. Yang, W. Dai, G. Wu, N. Guan, M. Hunger, L. Li, *Cascade conversion of acetic acid to isobutene over yttrium-modified siliceous Beta zeolites,* ACS Catal. 9 (2019) 9726-9738, DOI: 10.1021/acscatal.9b02850.

[8] C. Bornes, M. Sardo, Z. Lin, J. Amelse, A. Fernandes, M.F. Ribeiro, C. Geraldes, J. Rocha, L. Mafra, *^{1}H-^{31}P HETCOR NMR elucidates the nature of acid sites in zeolite HZSM-5 probed with trimethylphosphine oxide*, Chem. Commun. 55 (2019) 12635-12638, DOI: 10.1039/c9cc06763a.

[9] S. Hayashi, K. Jimura, N. Kojima, *Adsorption of trimethylphosphine oxide on silicalite studied by solid-state NMR*, Bull. Chem. Soc. Jpn. 87 (2014) 69-75, DOI: 10.1246/bcsj.20130192.

[10] U. Obenaus, M. Dyballa, S. Lang, M. Scheibe, M. Hunger, *Generation and properties of Broensted acid sites in bifunctional Rh-, Ir-, Pd-, and Pt-containing zeolites Y investigated by solid-state NMR spectroscopy,* J. Phys. Chem. C 119 (2015) 15254-15262, DOI: 10.1021/acs.jpcc.5b03149.

[11] Y. Jiang, J. Huang, W. Dai, M. Hunger, *Solid-state nuclear magnetic resonance investigations of the nature, property, and activity of acid sites on solid catalysts*, Solid State Nucl. Magn. Reson. 39 (2011) 116-141, DOI: 10.1016/j.ssnmr.2011.03.007.

[12] W. Yang, Z. Wang, J. Huang, Y. Jiang, *Qualitative and Quantitative Analysis of Acid Properties for Solid Acids by Solid-State Nuclear Magnetic Resonance Spectroscopy*, J. Phys. Chem. C 125(19) (2021) 10179-10197, DOI: 10.1021/acs.jpcc.1c01887.

[13] M. Dyballa, *Solid-State NMR Probe Molecules for Catalysts and Adsorbents: Concepts, Quantification, Accessibility, and Spatial Distribution*, Energy & Fuels 37(23) (2023) 18517-18559, DOI: 10.1021/acs.energyfuels.3c03815.

[14] A. Zheng, S.-B. Liu, F. Deng, *^{31}P NMR chemical shifts of phosphorus probes as reliable and practical acidity scales for solid and liquid catalysts*, Chem. Rev. 117 (2017) 12475-12531, DOI: 10.1021/acs.chemrev.7b00289.