Method for the determination of the strength, density, and location of Broensted acid sites by adsorption of trimethylphosphine oxide and ³¹P MAS NMR

Spectroscopic background: Trimethylphosphine oxide (TMPO) is a useful molecular probe for characterizing the strength and location of Broensted acid sites on solid catalysts [1-10]. Bulk TPMO causes a narrow ³¹P MAS NMR signal at δ_{31P} = 41 ppm [9, 11], while a resonance shift of the ³¹P MAS NMR signal to δ_{31P} = 37 ppm was observed for physisorbed TMPO under steric restrictions on silica surfaces [12]. DFT calculations have shown that the ³¹P chemical shift of TMPO (δ_{31P} (TMPO)) adsorbed at well-accessible Broensted acidic hydroxyl groups on solid catalysts (Cat(OH)_{ac}) correlates with the proton affinity (PA in kcal/mol) of these surface sites (Eq. (8) in Ref. [13]):

$$\delta_{31P}(\text{TMPO}) / \text{ppm} = 182.87 - 0.390 \text{ x PA}$$
 (1)

Typically, the experimentally observed ³¹P MAS NMR shift range of TMPO adsorbed via hydrogen bonds at well accessible **Broensted acid sites**:

$$Cat(OH)_{ac} + P(CH_3)_3 O \rightarrow Cat(OH)_{ac} \cdots OP(CH_3)_3$$
 (2)

is $\delta_{31P} = 60$ to 70 ppm. For adsorption of TMPO at Broensted acidic OH groups in small pores or cages, such as in the small sodalite cages of zeolite Y, a high-field shift by approximately $\delta_{31P} = 10$ to ca. 55 ppm occurs [7]. This sterically induced highfield shift of the ³¹P MAS NMR signals of physisorbed TMPO is the reason for the potential of this method for studying the spatial distribution of hydroxyl groups in microporous catalysts.

In the presence of **superacidic Broensted sites**, able to protonate TMPO molecules:

$$Cat(OH)_{ac} + P(CH_3)_3O \rightarrow Cat(O)^- + P(CH_3)_3OH^+$$
(3)

³¹P MAS NMR signals occur at δ_{31P} = 87.7 to 92.1 ppm, such as observed for TMPO-loaded heteropoly acids [14].

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

Utilizing TMPO, the spatial distribution of bridging OH groups (Si(OH)AI) in noble metal-loaded zeolites Y was investigated by ³¹P MAS NMR spectroscopy (**Fig. 1** and Fig. 5 in Ref. [7]). Si(OH)AI groups in zeolites Y can be located in small sodalite cages with 6-ring windows with a diameter of 0.22 nm or in large supercages with an inner diameter of 1.2 nm and 12-ring windows with a diameter of 0.74 nm. For the assignment of TMPO interacting with Si(OH)AI groups in these cages of zeolites Y, a homologous series of H,Na-Y zeolites, prepared by ammonium exchange (exchange degrees of 10, 20, 30 and 80%) and deammoniation, was loaded with TMPO and investigated by ³¹P MAS NMR spectroscopy (**Fig. 1**). It is well-accepted that ammonium exchange of zeolite Na-Y with a low exchange degree (< 50%) leads to a



Fig. 1

preferential formation of Si(OH)Al groups in the large supercages, before formation of these hydroxyl groups occurs in the small sodalite cages at higher exchange degrees (see Figs. 4 and 5 in Ref. [15]). The ³¹P MAS NMR spectrum of the TMPO-loaded zeolite 0.1H,Na-Y in **Fig. 1a** consists of a strong signal of bulk TMPO at $\delta_{31P} = 42$ ppm and TMPO physisorbed at Na⁺ cations at $\delta_{31P} = 48$ ppm. The weak signal at $\delta_{31P} = 66$ ppm is due to a small amount of TMPO interacting with Si(OH)Al groups located in the large supercages of zeolite 0.1H,Na-Y. With increasing ammonium exchange degree of up to 80%, the ³¹P MAS NMR signals at $\delta_{31P} = 66$ ppm in **Figs. 1b to 1d** increase and additional signals occur at $\delta_{31P} = 56$ ppm, which are assigned to Si(OH)Al groups in the small sodalite cages. The latter signals are high-field shifted due to the steric restrictions for the interaction of TMPO with Si(OH)Al groups in the small cages.

For reviews on the above-mentioned topics, see Refs. [16], [17], and [18].

Catalyst preparation: Before the ³¹P MAS 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 this line was ventilated with air).

For studies as those 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. 10 mg TMPO inside an MAS NMR 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. [13].

³¹*P* MAS NMR studies: The above-mentioned 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 $v_{\text{rot}} = 10$ 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 were referenced to 0.85 M H₃P0₄ ($\delta_{31P} = 0$ ppm).

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