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

Spectroscopic background: Numerous studies demonstrated that trimethylphosphine oxide (TMPO) is a useful molecular probe for characterizing the strength and location of Broensted acid sites on solid catalysts (Cat) [1-10]. Bulk TPMO causes a narrow ^{31}P MAS NMR signal at δ_{31P} = 41 ppm [9, 11], while 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 [12].

DFT calculations have shown that the ^{31}P 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 (Equ. (8) in [13]):

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

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

$$\text{Cat(OH)}_{ac} + \text{P(CH}_3)_3\text{O} \rightarrow \text{Cat(OH)}_{ac}\cdots\text{OP(CH}_3)_3 \qquad (2)$$
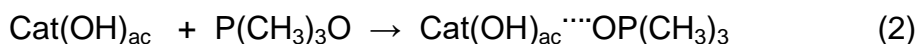
is δ_{31P} **= 60 to 70 ppm**. For adsorption of TMPO at Broensted acidic OH groups in small pores or cages, such as in the small sodalite cages of zeolite Y, a high-field shift by approximately δ_{31P} = 10 to ca. 55 ppm occurs [7]. This sterically induced high-field shift of the ^{31}P MAS NMR signals 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 molecule:

$$\text{Cat(OH)}_{ac} + \text{P(CH}_3)_3\text{O} \rightarrow \text{Cat(O)}^- + \text{P(CH}_3)_3\text{OH}^+ \qquad (3)$$

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

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For the quantitative evaluation of the ^{31}P MAS NMR signal intensities of TMPO molecules adsorbed at Broensted acid sites, the procedure described by Equ. (3) of the Section "method 12" 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)Al) in noble metal-loaded zeolites Y was investigated by ^{31}P MAS NMR spectroscopy (**Fig. 1** shown below and Fig. 5 in Ref. [7]). Si(OH)Al 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)Al groups in these cages of zeolites Y, a homologous series of H,Na-Y zeolites, prepared by ammonium exchange and deammoniation (exchange degrees of 10, 20, 30 and 80%), was loaded with TMPO and investigated by ^{31}P 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
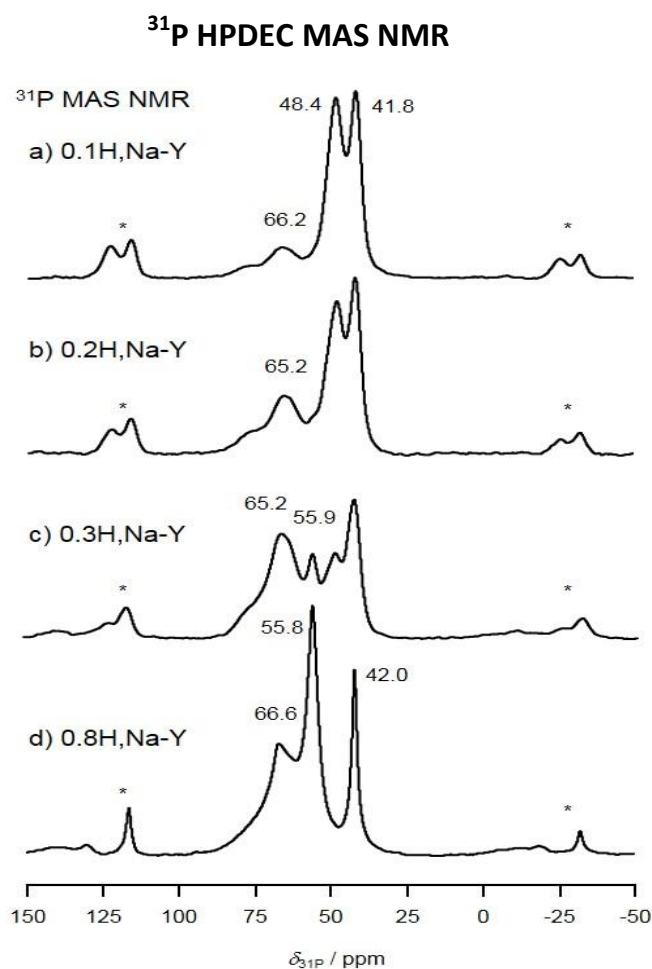
^{31}P HPDEC MAS NMR

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 ^{31}P MAS NMR spectrum of the TMPO-loaded zeolite 0.1H,Na-Y in Figure 1a consists of a strong signal of bulk TMPO at δ_{31P} = 42 ppm and TMPO physisorbed at Na$^+$ cations at δ_{31P} = 48 ppm. The weak signal at δ_{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 ^{31}P MAS NMR signals at δ_{31P} = 66 ppm in **Figs. 1b to 1d** increase and additional signals occur at δ_{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: At first, a standard activation of the solid catalyst inside a „sample tube system 1" at „vacuum line 1" is performed (see link "*In Situ* Solid-State NMR Techniques"). 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 Figure 1, loading of dehydrated solid catalysts with TMPO of Alfa Aesar is performed by mixing of ca. 50 mg dehydrated solid catalyst with ca. 10 mg TMPO inside a rotor using, e.g., a mini glove box purged with dry nitrogen (see Section "mini glove box" accessible 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. [13].

^{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 ν_0 = 161.9 MHz,

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using a 4 mm MAS NMR probe, and with a sample spinning rate of ν_{rot} = 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_3PO_4 (δ_{31P} = 0 ppm).

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