Method for the determining of the spatial distribution of noble metals on porous solids by complex formation with triphenylphosphine and ^{31}P MAS NMR

Spectroscopic background: Due to the high reactivity of triphenylphosphine (PPh_3) in the complex formation with noble metals (NM: Pt, Rh, Pd, Ru) and the molecular diameter of 0.72 nm, this molecule is suitable for determining the spatial distribution of noble metals on microporous zeolites, such as zeolite Y characterized by a faujasite structure (FAU) with 12-ring pores (diameter 0.74 nm), supercages (inner diameter 1.14 nm), and small sodalite cages accessible by 6-ring windows (diameter 0.265 nm). On amorphous silica (A200 or A300) and mesoporous SBA-15, on the other hand, all well-dispersed noble metal atoms are available for complex formation with PPh_3 due to the open surfaces and large pores of these materials (see **Fig. 1**) [1, 2].

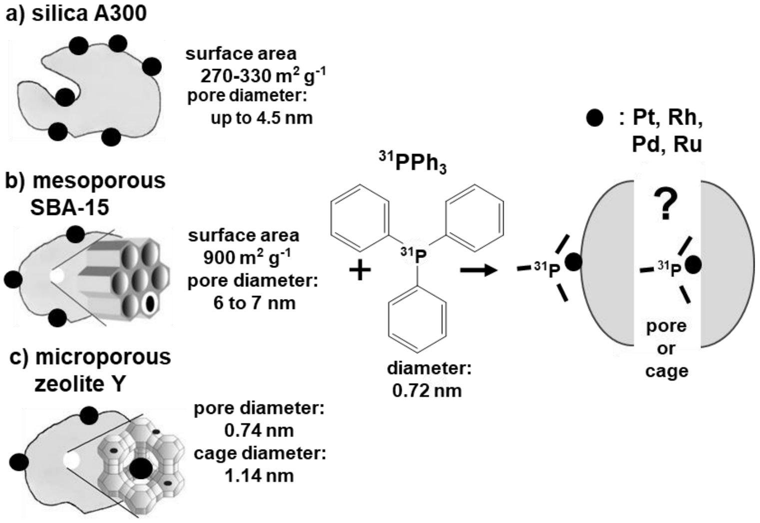

Fig. 1

Because of the natural abundance of 100% and a nuclear spin of I = ½ of the ^{31}P isotope, quantitative ^{31}P MAS NMR spectroscopy is a suitable tool for the investigation of PPh_3 complexes formed at noble metals on porous supports with high sensitivity. While bulk PPh_3 causes a narrow ^{31}P MAS NMR signal at δ_{31P} = -9 ppm (**Fig. 2a** shown below and Fig. 2a in Ref. [1]), physisorption of this molecule on open silica surfaces and in mesopores leads to a low-field resonance shift to δ_{31P} = -6 ppm (**Fig. 2b** show below and Figs. 1a and 1b in Ref. [1]). In empty micropores and supercages of dealuminated zeolite Y (DeA-Y), the ^{31}P MAS NMR signal of PPh_3 is further shifted to δ_{31P} = -3 ppm, while interactions with sodium cations and Broensted acidic bridging OH groups in the supercages of zeolites Na-Y and H-Y lead to signals at δ_{31P} ca. -1 ppm and 8 ppm, respectively (**Figs. 2c to 2e** shown below and Figs. 1c to 1e in Ref. [1]).

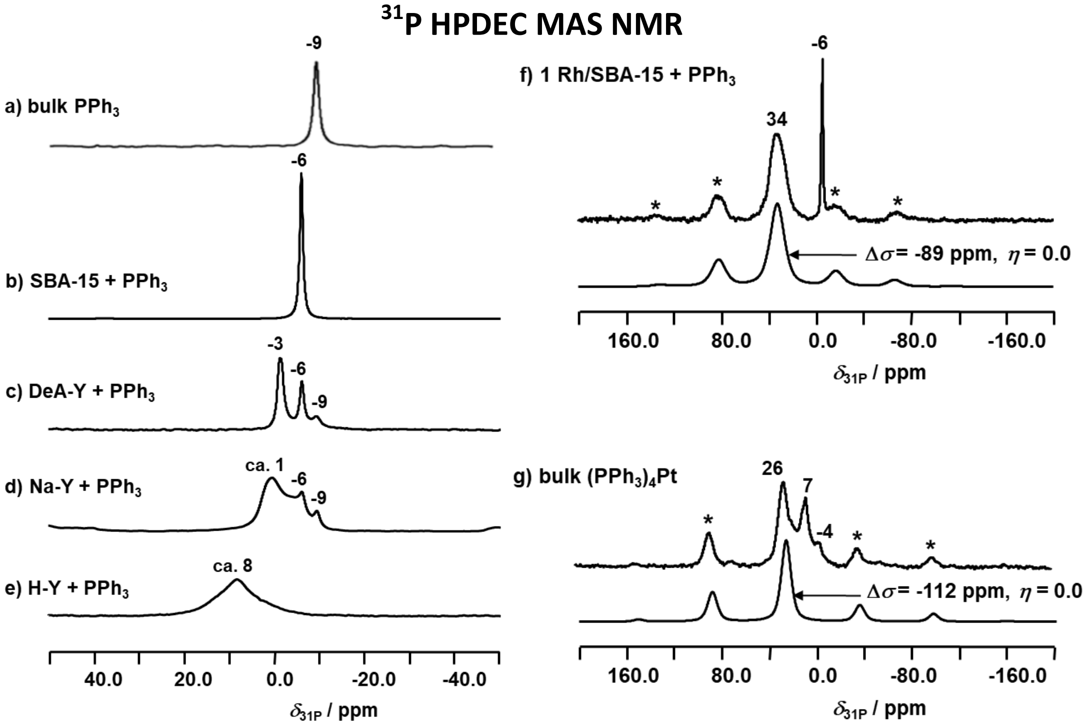

Fig. 2

For studying the complex formation of PPh_3 with noble metals, H_2-reduced Pt-, Rh-, Pd-, and Ru-loaded meso- and microporous support materials were prepared as described in Refs. [1-5]. In their H_2-reduced state, these catalysts demonstrated a high activity in the hydrogenation of propene and the dehydrogenation of propane [4, 5]. The complex formation of PPh_3 with noble metals, such as rhodium, on a well accessible surface is indicated by broad ^{31}P MAS NMR signals in the shift range of δ_{31P} ca. 33 to 35 ppm, additionally characterized by a high shielding anisotropy (**Fig. 2f shown** above and Fig. 5b in Ref. [1]). These signals are comparable with that of noble metal tetrakis(triphenylphosphine) complexes at δ_{31P} = 26 ppm in **Fig. 2g** (Fig. 2c in Ref. [1]) having regard to the additional low-field shift in the case of a physisorption on silica surfaces. Due to the steric restrictions for complexes formed by PPh_3 with noble metals in the supercages of zeolite Y, a similar low-field shift of the above-mentioned complex signals at δ_{31P} = 33 to 35 ppm to a resonance position

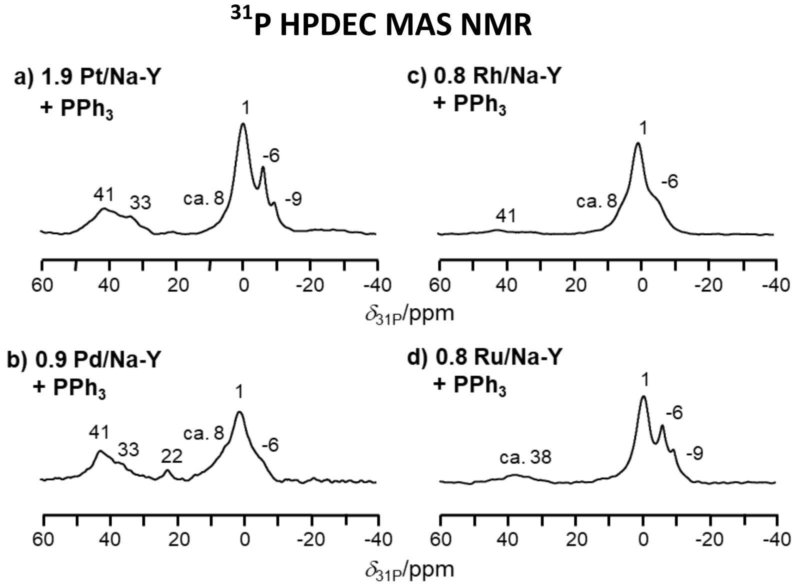

Fig. 3

of δ_{31P} = 41 ppm is observed (**Fig. 3** shown above and Fig. 3 in Ref. [2]). A summary of the above- mentioned ^{31}P chemical shift values of bulk and physisorbed PPh_3 as well as of complexes of PPh_3 with noble metals is given in Table 1. Considering these values, the **location of noble metals on the outer surface or inside the supercages of zeolites Y can be distinguished by** formation of complexes with PPh_3 (**signals at δ_{31P} = 33 ppm and ca. 41 ppm, respectively**). Furthermore, the presence of sodium cations and Broensted acid sites can be detected (signals at δ_{31P} = 1 ppm and 8 ppm, respectively). No ^{31}P MAS NMR signals were observed for complex formation inside the sodalite cages. Contact of H_2-reduced noble metal-containing catalysts under study with oxygen (e.g. air) must be strictly avoided.

δ_{31P} / ppm	Assignments of PPh_3 species
-9	bulk PPh_3
-6	physisorbed PPh_3 on open surfaces and in mesopores
-3	physisorbed PPh_3 in supercages of zeolite Y
ca. 1	PPh_3 coordinated at Na^+ cations in supercages of zeolite Y
8	protonated PPh_3 (PPh_3H^+) in supercages of zeolite Y
ca. 22	decomposed oxidation products of PPh_3
ca. 33	$(PPh_3)_nNM$ complexes on open surfaces and in mesopores
ca. 41	$(PPh_3)_nNM$ complexes in supercages of zeolite Y

Table 1

Otherwise, oxidation of PPh_3 can occur, leading to ^{31}P MAS NMR signals with chemical shifts near the range of signals due to complex formation with noble metals (line 7 of **Table 1**).

For the quantitative evaluation of the ^{31}P MAS NMR signal intensities of noble metal complexes with phosphines, 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. In this case, the repetition times t_{rep} of the ^{31}P MAS NMR measurements can be optimized by solely evaluating the ^{31}P MAS NMR signals of phosphines complexed with noble metals, recorded with t_{rep} = 20 s, while the VPI-5 standard is recorded with t_{rep} = 240 s. Phosphines physisorbed at the support surfaces without noble metals in their vicinity have much higher T_1 relaxation times compared with phosphines involved in complex formation with noble metals.

If PPh_3 is applied together with $P(PhOMe)_3$ (see Section "method 22") as a molecular probe for the study of the spatial distribution of noble metals on zeolite Y, the noble metal locations summarized in **Table 2** (Table 4 in Ref. [2]) and visualized in **Fig. 4** can be distinguished by their complex formation with phosphines. Ref. [6] gives a survey on the above-mentioned topics.

Positions in Fig. 4	Noble metal location	Complexation with phosphines	^{31}P MAS NMR signal (ppm)
1	on outer particle surface of DeA-Y and Na-Y	PPh_3 and $P(PhOMe)_3$	ca. 33 and 35
2	in secondary mesopores of DeA-Y	PPh_3	ca. 33
3	in supercages (SII position) of Na-Y	PPh_3	41
4	in sodalite cages (SII' position)	no	no
5	in hexagonal prisms (SI position)	no	no

Table 2

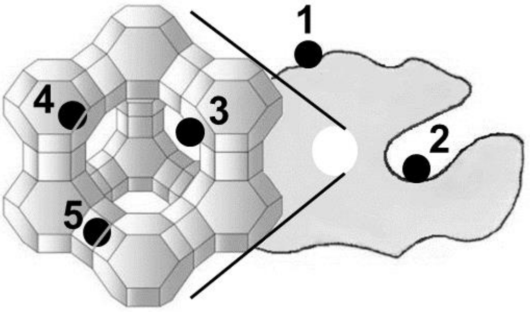

Fig. 4

Catalyst preparation: The noble metal-containing catalysts, prepared as described in Refs. [1-5], were calcined in synthetic air (970 mL/min) by heating with a rate of 2 K/min up to 573 K and further calcined at this temperature for 3 h, excluding the Ru-containing support materials. The materials were reduced in flowing hydrogen (100 mL/min) at 623 K (Pt-, Rh-, Pd-containing samples) or at 673 K (Ru-containing samples) for 2 h, transferred into glass tubes inside a glove box under nitrogen atmosphere, evacuated ($p < 10^{-2}$ Pa) at a vacuum line (see Section „vacuum line 1" via link "*In Situ* Solid-State NMR Techniques") at 298 K for 12 h, and sealed in glass tubes until their use.

For studies as those demonstrated in Figs. 2 and 3, loading of H_2-reduced catalysts with triphenylphosphine (PPh_3) of Sigma-Aldrich is performed by mixing of 40 to 50 mg catalyst with ca. 10 mg PPh_3 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 363 K for 20 h for reaching a proper distribution of the PPh_3 on the catalyst.

^{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 of the PPh_3-loaded noble metal containing catalysts are recorded upon single pulse $\pi/2$ excitation with the repetition time of 20 s and high-power proton decoupling (HPDEC). The intensity standard VPI-5 is measured with a repetition time of 240 s. Chemical shifts are referenced to 0.85 M H_3P0_4 (δ_{31P} = 0 ppm).

References:

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