

the ^{31}P MAS NMR signal of PPh_3 is further shifted to $\delta_{31\text{P}} = -3$ ppm, while interactions with sodium cations and Brønsted acidic bridging OH groups in the supercages of zeolites Na-Y and H-Y lead to signals at $\delta_{31\text{P}}$ ca. -1 ppm and 8 ppm, respectively (**Figs. 2c to 2e** and Figs. 1c to 1e in Ref. [1]).

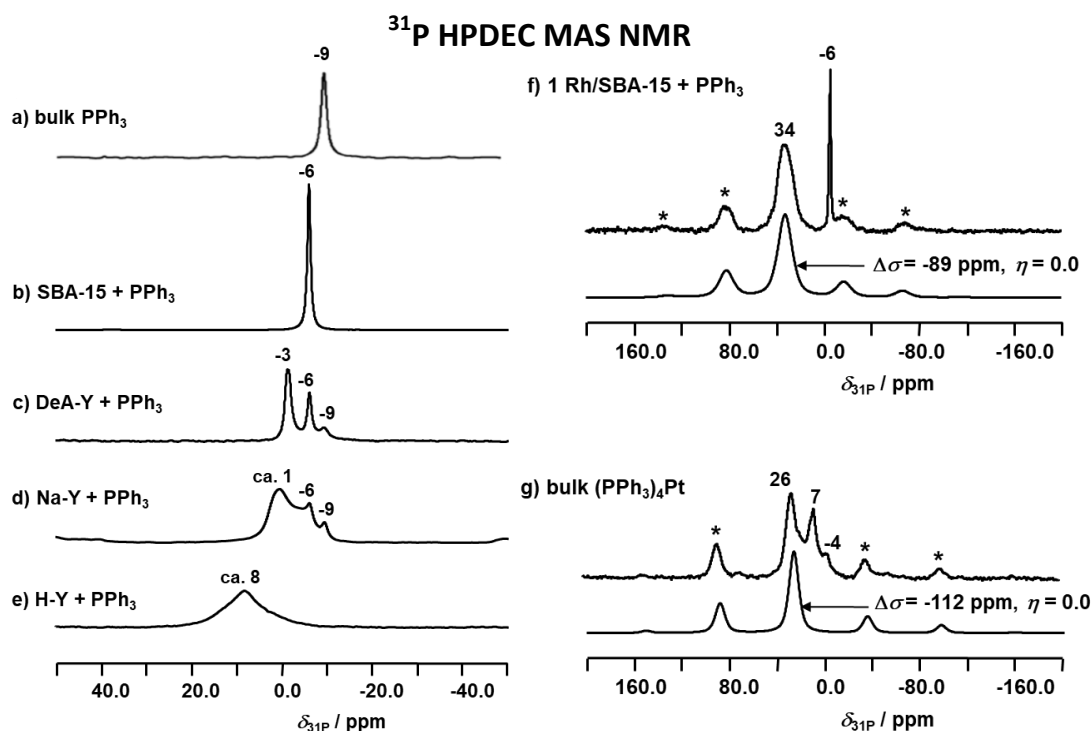
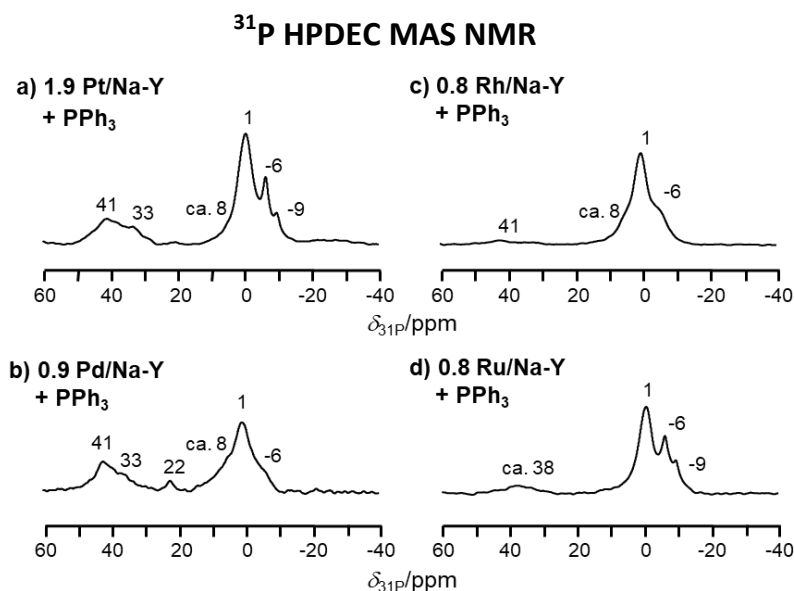


Fig. 2

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 $\delta_{31\text{P}}$ 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 $\delta_{31\text{P}} = 26$ ppm in **Fig. 2g** (Fig. 2c in Ref. [1]), responsible for the additional low-field shift in the case of a physisorption on silica surfaces. Due to steric restrictions for complexes formed by PPh_3 with noble metals in the supercages of zeolite Y, a similar low-field resonance shift of the signals of the above-mentioned complex from $\delta_{31\text{P}} = 33$ to 35 ppm to a

**Fig. 3**

resonance position of $\delta_{31\text{P}} = 41$ ppm is observed (**Fig. 3** and Fig. 3 in Ref. [2]). **Table 1** is a summary of the above-mentioned ^{31}P chemical shift values of bulk and physisorbed PPh₃ as well as of complexes of PPh₃ with noble metals. Considering these values, the **location of noble metals on the outer surface and inside the supercages of zeolites Y** can be distinguished by formation of complexes with PPh₃ (signals at $\delta_{31\text{P}} = 33$ ppm and **ca. 41 ppm**, respectively). Furthermore, the presence of sodium cations and Brønsted acid sites can be detected (signals at $\delta_{31\text{P}} = 1$ ppm and 8 ppm, respectively). No ^{31}P MAS NMR signals were observed for complex formation inside the sodalite cages.

$\delta_{31\text{P}} / \text{ppm}$	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 ₃ H ⁺) in supercages of zeolite Y
ca. 22	decomposed oxidation products of PPh ₃
ca. 33	(PPh ₃) _n NM complexes on open surfaces and in mesopores
ca. 41	(PPh ₃) _n NM complexes in supercages of zeolite Y

Table 1

Contact of H₂-reduced noble metal-containing catalysts under study with oxygen (e.g. air) must be strictly avoided. Otherwise, oxidation of PPh₃ may occur, leading to ³¹P 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 ³¹P MAS NMR signal intensities of noble metal complexes with phosphines, the procedure described by Eq. (3) of the Section “method 1” 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 ³¹P MAS NMR measurements can be optimized by solely evaluating the ³¹P MAS NMR signals of phosphines complexed with noble metals, recorded with $t_{\text{rep}} = 20$ s, while the VPI-5 standard must be recorded with $t_{\text{rep}} = 240$ s. Phosphines physisorbed at the support surfaces without noble metals in their vicinity have much higher T₁ relaxation times compared with phosphines involved in complex formation with noble metals.

If PPh₃ is applied together with P(PhOMe)₃ (see Section “method 28”) 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

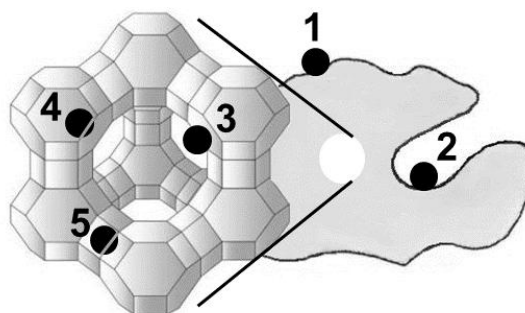


Fig. 4

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 $T = 573$ 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 $T = 623$ K (Pt-, Rh-, Pd-containing samples) or at $T = 673$ K (Ru-containing samples) for 2 h and, subsequently, transferred into without air contact inside a glove box (purged with dry nitrogen gas) into a “sample tube system 1” (see Section “sample tube system 1”, accessible via link “*In Situ* Solid-State NMR Techniques”). Then, the materials were evacuated ($p < 10^{-2}$ Pa) at “vacuum line 1” (see Section “vacuum line 1”, accessible via link “*In Situ* Solid-State NMR Techniques”) at $T = 298$ K for 12 h. Finally, the materials were sealed in the glass tubes of the “sample tube system 1” until their further use.

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

^{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 $\nu_0 = 161.9$ MHz using a 4 mm MAS NMR probe with a sample spinning rate of $\nu_{rot} = 10$ kHz. The spectra of the PPh_3 -loaded noble metal containing catalysts were 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 was measured with a repetition time of 240 s. Chemical shifts were referenced to 0.85 M H_3PO_4 ($\delta_{31\text{P}} = 0$ ppm).

References:

- [1] M. Dyballa, C. Rieg, D. Dittmann, Z. Li, M. Buchmeiser, B. Plietker, M. Hunger, *Potential of triphenylphosphine as solid-state NMR probe for studying the noble metal distribution on porous supports*, Microporous & Mesoporous Mater. 293 (2020) 109778, DOI: 10.1016/j.micromeso.2019.109778.
- [2] C. Rieg, D. Dittmann, Z. Li, D. Estes, M. Buchmeiser, M. Dyballa, M. Hunger, *Noble metal distribution on porous supports determined by reaction with phosphines*, Microporous & Mesoporous Mater. 310 (2021) 110594, DOI: 10.1016/j.micromeso.2020.110594.
- [3] U. Obenaus, M. Dyballa, S. Lang, M. Scheibe, M. Hunger, *Generation and properties of Brønsted 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.
- [4] U. Obenaus, F. Neher, M. Scheibe, M. Dyballa, S. Lang, M. Hunger, *Relationships between the hydrogenation and dehydrogenation properties of Rh-, Ir-, Pd-, and Pt-containing zeolites Y studied by in situ MAS NMR spectroscopy and conventional heterogeneous catalysis*, J. Phys. Chem. C 120 (2016) 2284-2291, DOI: 10.1021/acs.jpcc.5b11367.
- [5] U. Obenaus, S. Lang, R. Himmelmann, M. Hunger, *In situ MAS NMR investigation of parahydrogen induced hyperpolarization inside meso- and micropores of Ir-, Pt-, Rh-, and Pd-containing solid catalysts*, J. Phys. Chem. C 121 (2017) 9953-9962, DOI: 10.1021/acs.jpcc.7b01899.
- [6] 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.