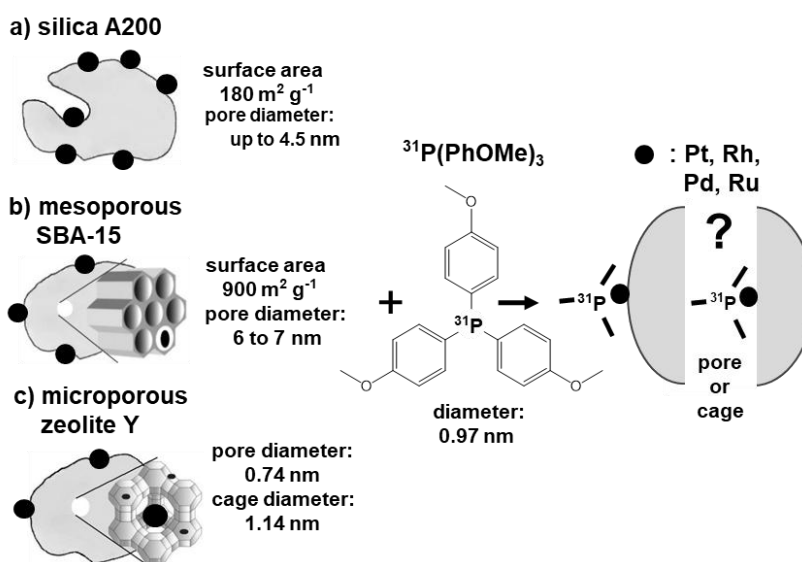


## Method for the determining of the spatial distribution of noble metals on porous solids by complex formation with tris(methoxyphenyl)phosphine and $^{31}\text{P}$ MAS NMR

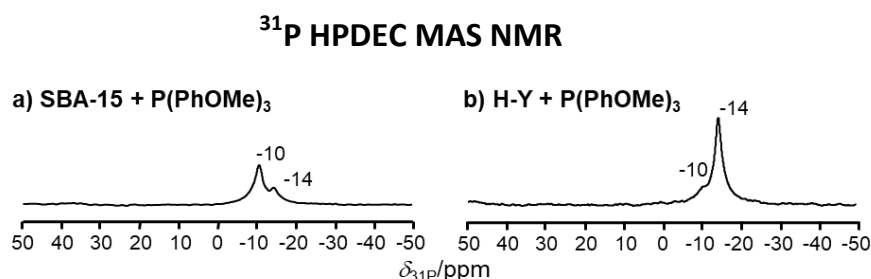
**Spectroscopic background:** Due to the high reactivity of tris(methoxyphenyl)phosphine ( $\text{P}(\text{PhOMe})_3$ ) in the complex formation with noble metals (NM: Pt, Rh, Pd, Ru) and the molecular diameter of 0.97 nm, this molecule is suitable for determining the presence of noble metals at the outer particle surface of microporous zeolites, such as zeolite Y (structure type FAU), since the micropores and cages, such as the 12-ring pores of this zeolite with a diameter of 0.74 nm, are not accessible for this molecule. 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  $\text{P}(\text{PhOMe})_3$  due to the open surfaces and large pores of these materials (see **Fig. 1**) [1].



**Fig. 1**

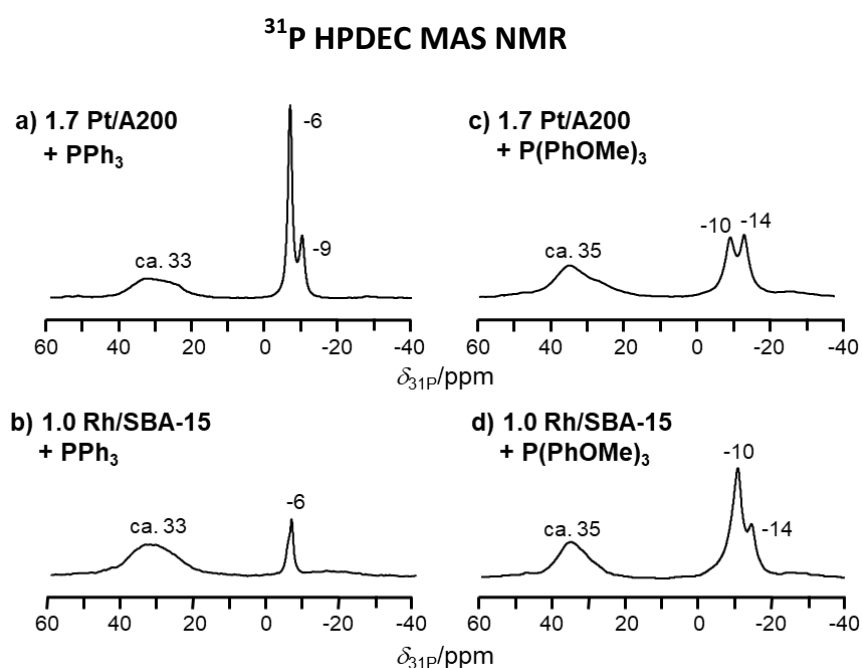
Because of the natural abundance of 100% and a nuclear spin of  $I = \frac{1}{2}$  of the  $^{31}\text{P}$  isotope,  $^{31}\text{P}$  MAS NMR spectroscopy is a suitable tool for the investigation of  $\text{P}(\text{PhOMe})_3$  complexes, formed at noble metals on porous supports with high sensitivity and in a quantitative manner. While **bulk  $\text{P}(\text{PhOMe})_3$**  causes a narrow  $^{31}\text{P}$  MAS NMR signal at  $\delta_{^{31}\text{P}} = -14 \text{ ppm}$  (Table 1 in [1]), **physisorption** of this molecule on open silica surfaces and in mesopores leads to a low-field resonance shift to  $\delta_{^{31}\text{P}} = -10 \text{ ppm}$  (**Fig. 2a** and Fig. 1 in Ref. [1]). Same types of  $^{31}\text{P}$  MAS NMR signals are observed for adsorption of  $\text{P}(\text{PhOMe})_3$  on zeolite H-Y (**Fig. 2b** and Fig. 1 in Ref. [1]).

The latter finding indicates that  $\text{P(PhOMe)}_3$ , in contrast to  $\text{PPh}_3$  (see Fig. 2e in Section “method 27”), is not able to enter the supercages of zeolite Y and to interact with the Brønsted acidic bridging OH groups ( $\text{Si(OH)Al}$ ) located in these cages.



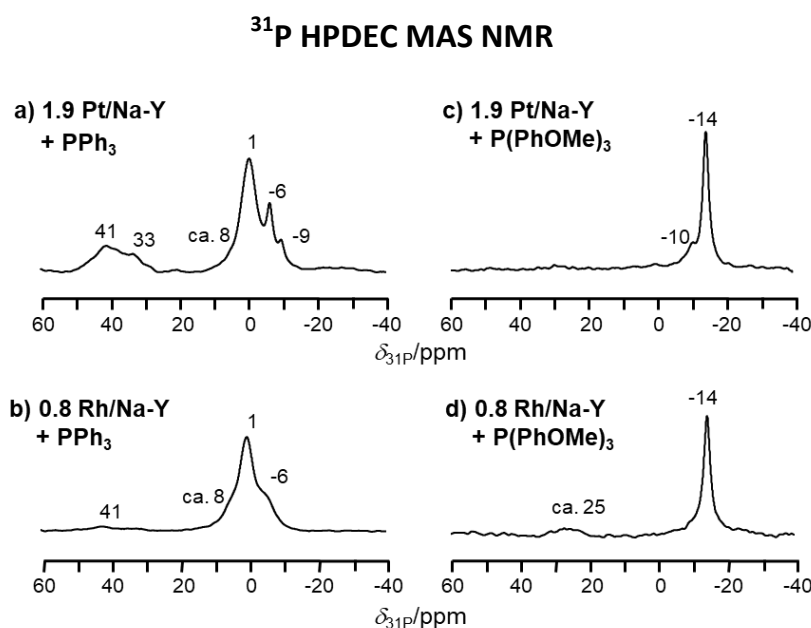
**Fig. 2**

For studying the complex formation of  $\text{P(PhOMe)}_3$  with noble metals,  $\text{H}_2$ -reduced Pt-, Rh-, Pd-, and Ru-loaded meso- and microporous support materials were prepared as described in Refs. [1-5]. In their  $\text{H}_2$ -reduced state, these catalysts demonstrated a high activity in the hydrogenation of propene and the dehydrogenation of propane [4, 5]. The complex formation of  $\text{P(PhOMe)}_3$  with noble metals, such as **platinum and rhodium, on silica A200 and mesoporous SBA-15** with well accessible surfaces leads to broad  $^{31}\text{P}$  MAS NMR signals at  $\delta_{^{31}\text{P}}$  **ca. 35 ppm**, which is a similar chemical shift range as observed for complexes formed by adsorption of  $\text{PPh}_3$  (compare left- and right-hand side of **Fig. 3** and Fig. 2 in Ref. [1]).



**Fig. 3**

In contrast, upon adsorption of  $\text{P(PhOMe)}_3$  on platinum- and rhodium-loaded zeolites Na-Y, no  $^{31}\text{P}$  MAS NMR signals of complexes occur at  $\delta_{31\text{P}}$  ca. 35 ppm, while complex formation with  $\text{PPh}_3$  is indicated by signals at  $\delta_{31\text{P}}$  ca. 33 and 41 (compare left- and right-hand side of **Fig. 4** and Fig. 3 in Ref. [1]). This observation additionally evidences that  $\text{P(PhOMe)}_3$  is too large for a complex formation with noble metal atoms located in the pores and cages of zeolite Y. Since the pore and cage system of zeolite Y is characterized by 12-ring windows with a diameter of 0.74 nm, which is one of the largest of common microporous zeolites, also the complex formation of  $\text{P(PhOMe)}_3$  with noble metal inside the pores and cages of other zeolites can be excluded.



**Fig. 4**

**Table 1** gives a summary of the above-mentioned  $^{31}\text{P}$  chemical shift values of bulk and physisorbed  $\text{P(PhOMe)}_3$  as well as of complexes of  $\text{P(PhOMe)}_3$  with noble metals. Considering these values, the **location of noble metals on the outer surface of zeolites** can be determined by formation of complexes with  $\text{P(PhOMe)}_3$  leading to **signals at  $\delta_{31\text{P}}$  ca. 35 ppm**. Contact of  $\text{H}_2$ -reduced noble metal-containing catalysts under study with oxygen (e.g. air) must be strictly avoided. Otherwise, oxidation of  $\text{P(PhOMe)}_3$  may occur, leading to  $^{31}\text{P}$  MAS NMR signals with chemical shifts near the chemical shift range of signals caused by complex formation with noble metals (line 4 of **Table 1**).

$\delta_{31\text{P}}$ / ppm	Assignment of $\text{P(PhOMe)}_3$ species
-14	bulk $\text{P(PhOMe)}_3$
-10	physisorbed $\text{P(PhOMe)}_3$ on open surfaces and in mesopores
ca. 25	decomposed oxidation products of $\text{P(PhOMe)}_3$
ca. 35	$[\text{P(PhOMe)}]_n\text{NM}$ complexes on open surfaces and in mesopores

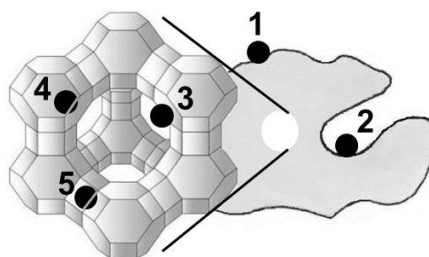
**Table 1**

For the quantitative evaluation of the  $^{31}\text{P}$  MAS NMR signal intensities of noble metal complexes with phosphines, the procedure described by Eq. (3) in Section “method 1” is utilized. As an intensity standard, a well-known aluminosilicate-type zeolite, such as VPI-5, is suitable. In this case, the repetition times  $t_{\text{rep}}$  of the  $^{31}\text{P}$  MAS NMR measurements can be optimized by evaluating the  $^{31}\text{P}$  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  $T_1$  relaxation times compared with phosphines involved in complex formation with noble metals.

If  $\text{P(PhOMe)}_3$  is applied together with  $\text{PPh}_3$  (see Section “method 27”) 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. [1]) and visualized in **Fig. 5** can be distinguished by their complex formation with phosphines. Ref. [6] gives a survey on the above-mentioned topics.

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

**Table 2**



**Fig. 5**

**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 to 4, loading of the  $H_2$ -reduced catalysts with tris(methoxyphenyl)phosphine ( $P(PhOMe)_3$ ) of Sigma-Aldrich was performed by mixing of ca. 50 mg catalyst with ca. 10 mg  $P(PhOMe)_3$  inside a rotor using 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  $P(PhOMe)_3$  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  $\nu_0 = 161.9$  MHz using a 4 mm MAS NMR probe with a sample spinning rate of  $\nu_{rot} = 10$  kHz. The spectra of the  $P(PhOMe)_3$ -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  $\text{H}_3\text{PO}_4$  ( $\delta_{31\text{P}} = 0$  ppm).

### References:

- [1] 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.
- [2] 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.
- [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.