University of Stuttgart

Collaborative Research Center 1333

Molecular Heterogeneous Catalysis in Confined Geometries

New solid-state NMR probe molecules for Noble Metals on porous supports

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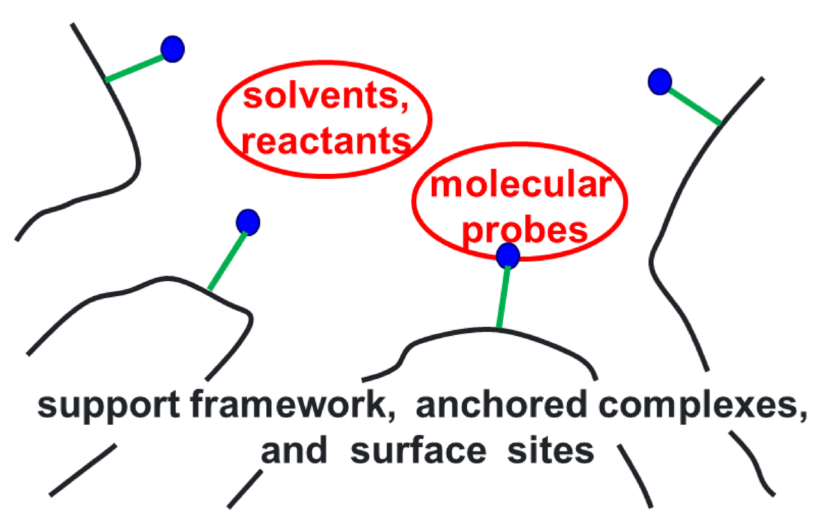
Goals/Vision



Alkyl- and arylphosphines and their corresponding oxides are applied as probe molecules in solid-state NMR spectroscopy.

Scopes are to:

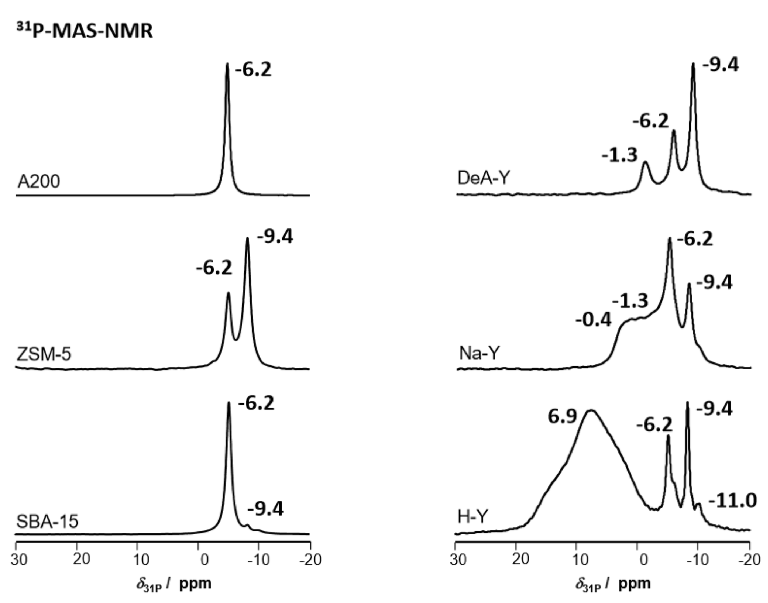
- Characterize Lewis and Brønstedt acid sites in solid acids like zeolites.
- Find suitable phosphines to characterize reactive noble metals and metal ions
- Develop new methods for the sterical localization of active sites

The advantage of ^{31}P is its broad chemical shift range and a natural abundance of 100 %. Also, the relaxation time is quite low and a close location to the metal is attainable.

Results and Discussion

Phosphines as Probe Molecules

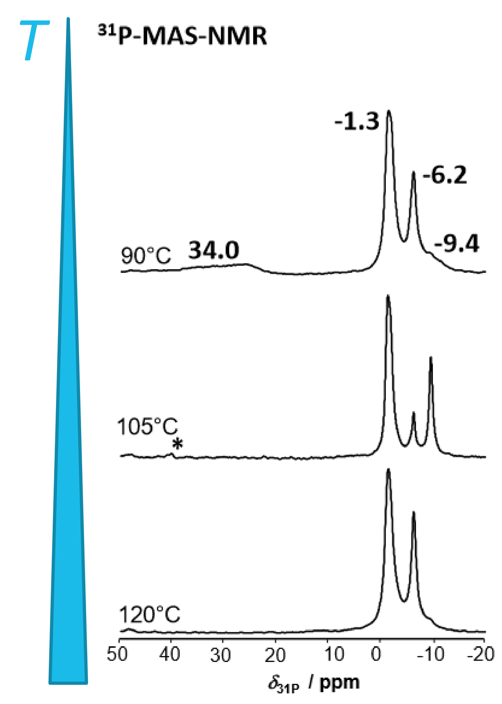
Triphenylphosphine PPh_3



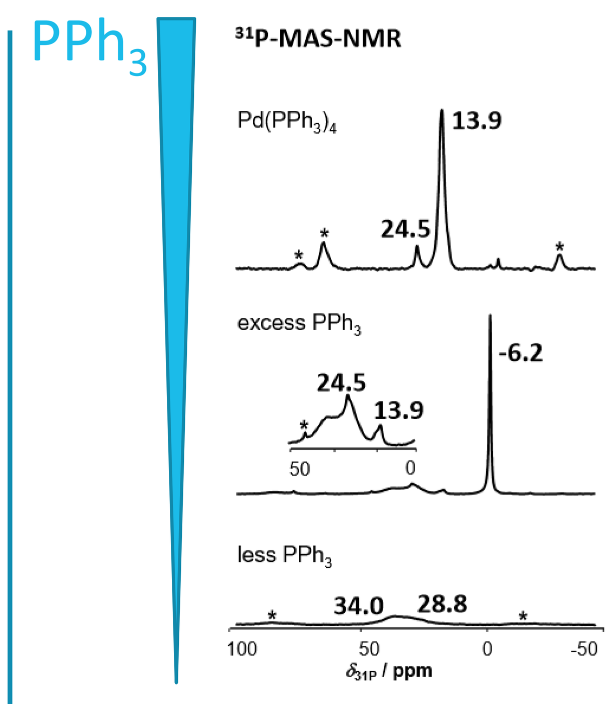
Signals of PPh_3 on various materials. On the left side are depicted silica A200, mesoporous SBA-15 and microporous ZSM-5, on the right side bifunctional Y-zeolites. The signals at δ_{31P}= -6.2 ppm and δ_{31P}= -9.4 ppm can assigned to physisorbed and crystalline PPh_3. The pore size of ZSM-5 is to small for PPh_3 to enter.

PPh_3-Metal Complex Formation

Support: DeA-Y zeolite

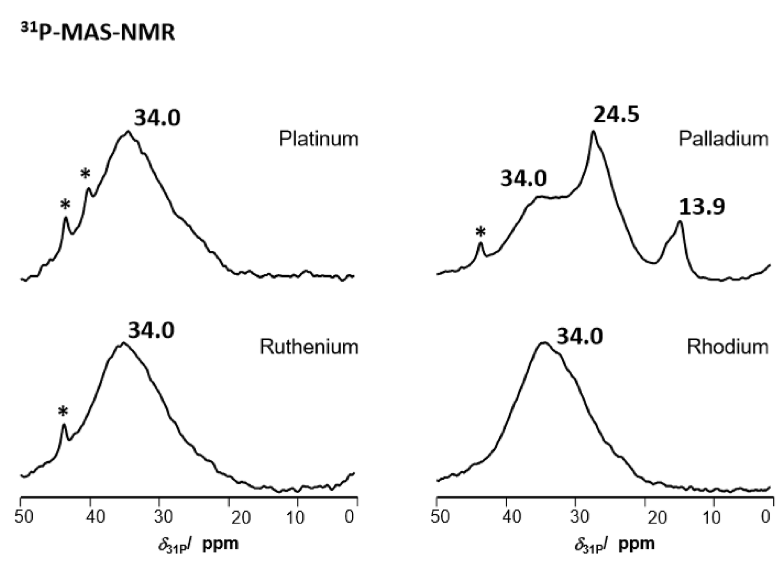


The complex stability is temperature dependent. Here, the formed complex is most stable at 90 °C. The asterisks denote spinning side bands.



Commercial $Pd(PPh_3)_4$ (first row) is compared with Palladium on silica loaded with PPh_3. In the middle spectra are visible the characteristic signals of $Pd(PPh_3)_4$ at δ_{31P}= 13.9 ppm and 24.5 ppm.

Support: Silica A200

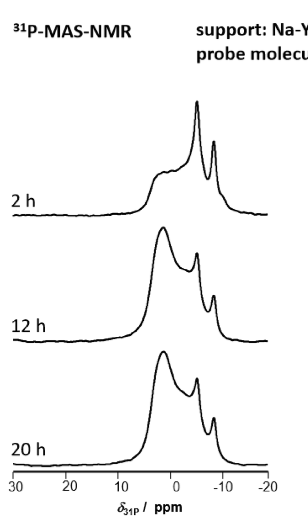


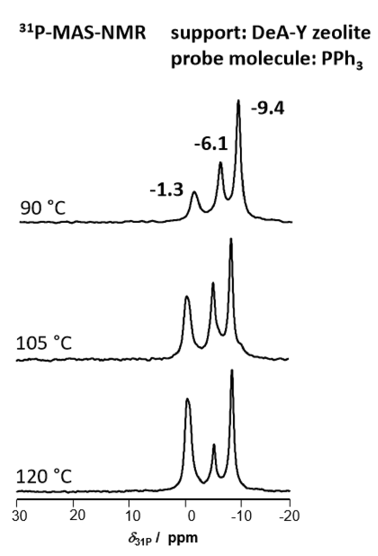
Triphenylphosphine coordinating at Platinum, Palladium, Ruthenium and Rhodium on amorphous silica A200. A new signal at δ_{31P}= 34 ppm occured for each metal caused by binding of PPh_3.[1]

Experimental Section

Loading Procedure

The solid phosphines were layered together with the support material at 90 °C over a variing time.





The left figure shows loading times of PPh_3 on a Na-Y zeolite between 2 and 20 hours, each at 90 °C, slightly higher than the melting point of PPh_3. With increasing time more probe molecule is migrated into the micropores, thereby the equilibrium is reached after 12 hours. The right figure shows the loading procedure at increasing temperatures, each with a loading time of 20 hours. For higher temperature faster migration into the cavities can be observed.

References

[1] X.Lan, W.Zhang, L.Yan, Y.Ding, X.Han, L.Lin and X.Bao, *J Phys Chem* C, 2009, **113**, 6589-6595.