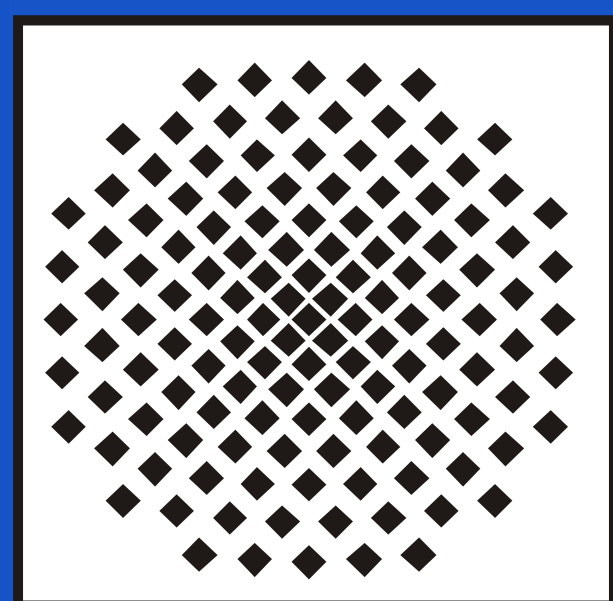
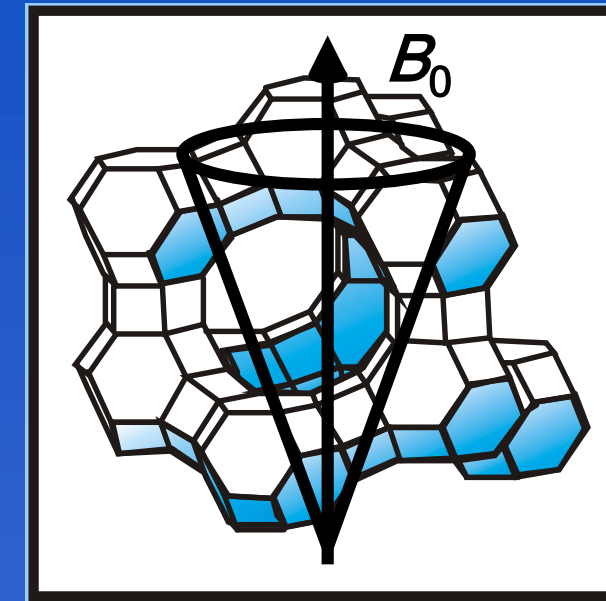




Brønsted acidity of noble metal-containing zeolite catalysts studied by solid-state NMR upon adsorption of probe molecules

U. Obenaus, S. Lang, M. Hunger

Institute of Chemical Technology, University of Stuttgart, 70569 Stuttgart, Germany



INTRODUCTION

Noble metal-containing zeolites are important catalysts for a number of reactions, such as the hydrogenation/dehydrogenation, hydrocracking, isomerization, and hydrogenolysis of hydrocarbons. Upon reduction of the noble metal atoms introduced into zeolites by exchange with noble metal complexes, bridging OH groups (SiOHAl) acting as Brønsted acid sites are formed. Due to these surface sites, noble metal-containing zeolites are bifunctional catalysts. Solid-state NMR spectroscopy combined with application of probe molecules gives insight into the formation mechanism and properties of Brønsted acid sites in bifunctional zeolites, which significantly influence the catalytic performance of these materials. Via these methods, the amount, strength, and distribution of Brønsted acid sites can be clarified.

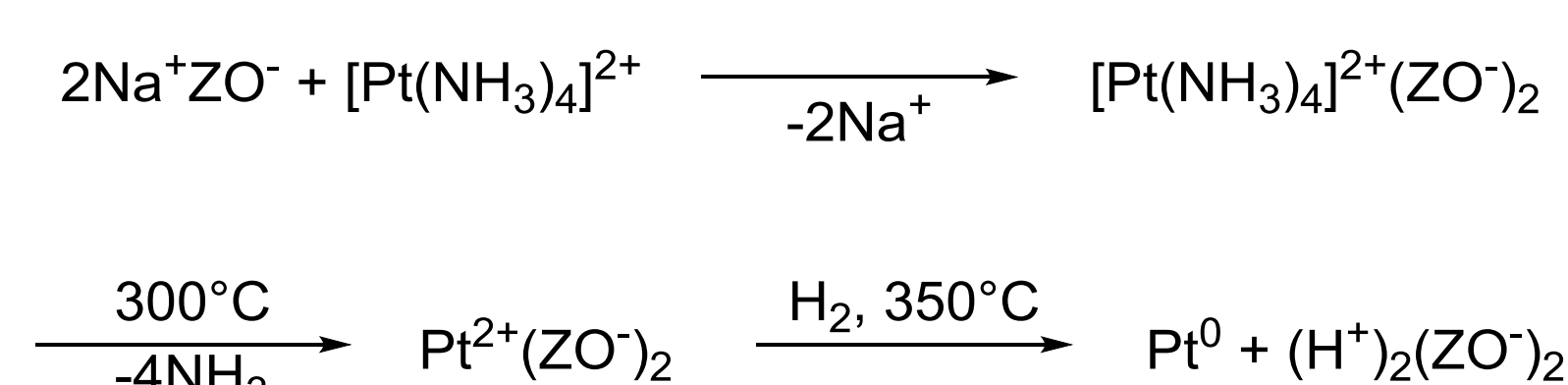
EXPERIMENTAL SECTION

Commercial zeolite Na-Y (Degussa AG, Germany) was either exchanged with NH_4NO_3 to get zeolites H,Na-Y or loaded with different amounts of $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ or $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ via ion exchange in aqueous suspension to get the noble metal-containing catalysts. The noble metal-containing catalysts were calcined in synthetic air for 3 h (1.0 bar, 300 °C) and subsequently reduced in H_2 for 2 h (1.0 bar, 350 °C) in a fixed-bed reactor. Assuming a stoichiometric factor of 1 : 1 (H / metal), the noble metals on all above-mentioned zeolites reached a dispersion of 19 to 121 % (Tab. 2). The Brønsted acid sites (SiOHAl) were characterized by ^1H MAS NMR spectroscopy via an evaluation of the integral intensity of the ammonium signals upon loading with NH_3 (density of Brønsted acid sites, Fig. 1) and via the low-field shift, $\Delta\delta_{\text{H}}$, of the SiOHAl signal, observed upon adsorption of acetonitrile- d_3 (strength of Brønsted acid sites, Fig. 2). Furthermore, the samples were loaded with trimethylphosphine oxide under nitrogen and heated (2 h, 160 °C) before the ^{31}P CPMAS NMR experiments.

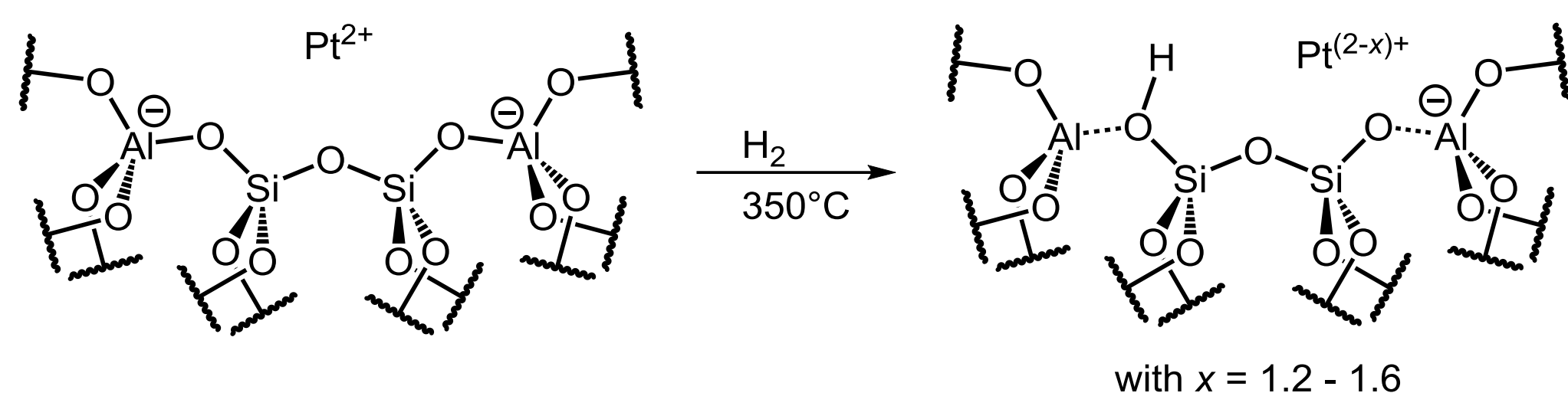
RESULTS AND DISCUSSION

Generation of Brønsted acid sites

The theoretical number of generated Brønsted acid sites per noble metal atom corresponds to the charge number of the noble metal atom, e.g. 2 for Pt^{2+} :



Experimental analysis shows much lower numbers of generated Brønsted acid sites per noble metal atom:



Even in aluminum-rich zeolites, like Na-Y with $n_{\text{Si}}/n_{\text{Al}} = 2.7$, the experimental number of generated Brønsted acid sites (acOH) is significantly lower and depends on the type and amount of noble metal (NM) loading (Tab. 1).

Determination of the number of Brønsted acid sites using NH_3 as probe molecule:

- Brønsted acid sites (SiOHAl) cause ^1H MAS NMR signals at 3.5 ppm (Fig. 1, left)
- Loading of the acidic catalyst with NH_3 cause a signal at 6.4 ppm due to NH_4^+ (Fig. 1, right)
- Integration of the signal at 6.4 ppm gives the SiOHAl density (see Tab. 2, 3rd column)
- Numbers of SiOHAl groups in the noble metal-containing catalysts under study are lower or similar to a 10 % decationized zeolite Y (0.1H,Na-Y)

Metal type	Theoretical acOH/NM ratio	Experimental acOH/NM ratio
Rh	3	0.3 - 1.1
Ir	3	0.5 - 1.3
Pd	2	0.3 - 0.7
Pt	2	0.4 - 0.8

Tab. 1 Theoretical and experimental ratios of Brønsted acid sites per noble metal atom for the zeolites Y under study.

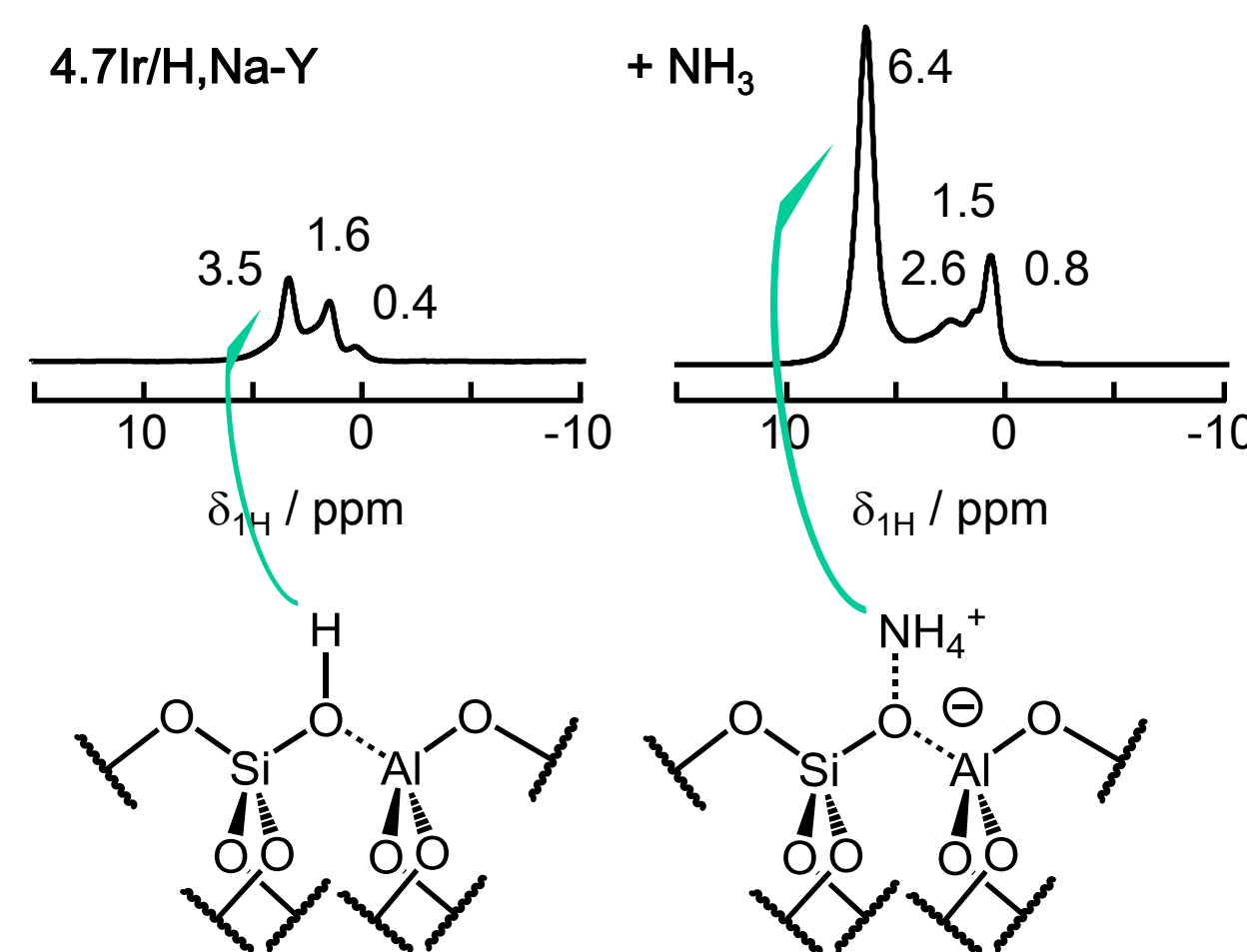


Fig. 1 ^1H MAS NMR spectra of zeolite 4.7Ir/H,Na-Y before (left) and after (right) loading with NH_3 .

Strength of Brønsted acid sites

Determination of the strength of Brønsted acid sites using CD_3CN as probe molecule (Fig. 2):

- ^1H MAS NMR signal of Brønsted acid sites (SiOHAl) at 3.5 ppm
- Loading of zeolite 4.7Ir/H,Na-Y with CD_3CN shifts the SiOHAl signal from 3.5 ppm to 8.7 ppm ($\Delta\delta_{\text{H}} = 5.2$ ppm)
- Shift $\Delta\delta_{\text{H}}$ correlates with the strength of the SiOHAl groups (Tab. 2, last column)
- Strength of SiOHAl groups in zeolites with low noble metal loadings is significantly weaker than in H,Na-Y zeolite, but increases with the metal loading (not shown)

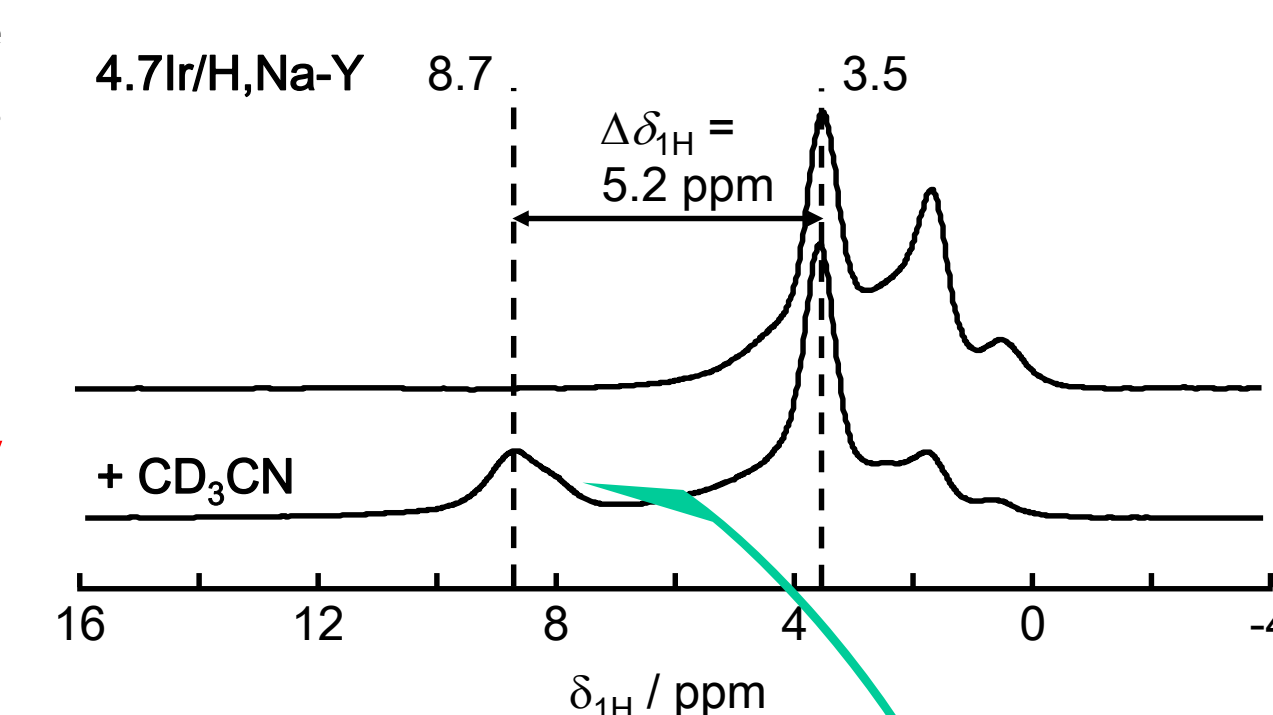


Fig. 2 ^1H MAS NMR spectra of zeolite 4.7Ir/H,Na-Y before (top) and after (bottom) loading with CD_3CN . The signal of Brønsted acid sites shifts from 3.5 ppm to 8.7 ppm.

Catalyst	Dispersion in %	Acid site density in SiOHAl/u.c.	$\Delta\delta_{\text{H}}$ in ppm
0.1H,Na-Y	-	2.8	5.0
0.2H,Na-Y	-	6.2	5.2
0.8H,Na-Y	-	35.6	5.3
0.4Rh/H,Na-Y	54	0.3	4.4
0.8Ir/H,Na-Y	121	0.5	4.4
0.4Pd/H,Na-Y	19	0.3	4.7
0.8Pt/H,Na-Y	73	0.4	4.3

Tab. 2 Properties of the zeolites Y under study.

Distribution of Brønsted acid sites studied with trimethylphosphine oxide (TMPO) as probe molecule

Different types of Brønsted acid sites in zeolites H,Na-Y (Fig. 3):

- ^{31}P MAS NMR signals at 42 ppm and 48 ppm are due to crystalline and physisorbed TMPO, respectively
- Loading of noble metal-containing zeolites Y with TMPO causes two signals of TMPO at different Brønsted acid sites with a shift difference of ca. 10 ppm
 - Brønsted acid sites in sodalite cages and supercages
- Exchange of Na^+ by H^+ in zeolite Na-Y: At first, exchange of Na^+ in the supercages before their exchange in the sodalite cages [1]
- With increasing degree of proton exchange, two raising signals of TMPO interacting with SiOHAl groups occur in the spectra of zeolites H,Na-Y
- At first, a signal at 65-66 ppm appears, which is assigned to TMPO interacting with Brønsted acid sites in the supercages (Fig. 3 a-d)
- Then, an additional signal at 56 ppm is observed, which is caused by TMPO interacting with Brønsted acid sites in the sodalite cages (Fig. 3 c-d)
- Ratio of Brønsted acid sites in supercages and sodalite cages decreases from ca. 300 for zeolite 0.1H,Na-Y to 1.6 for zeolite 0.8H,Na-Y

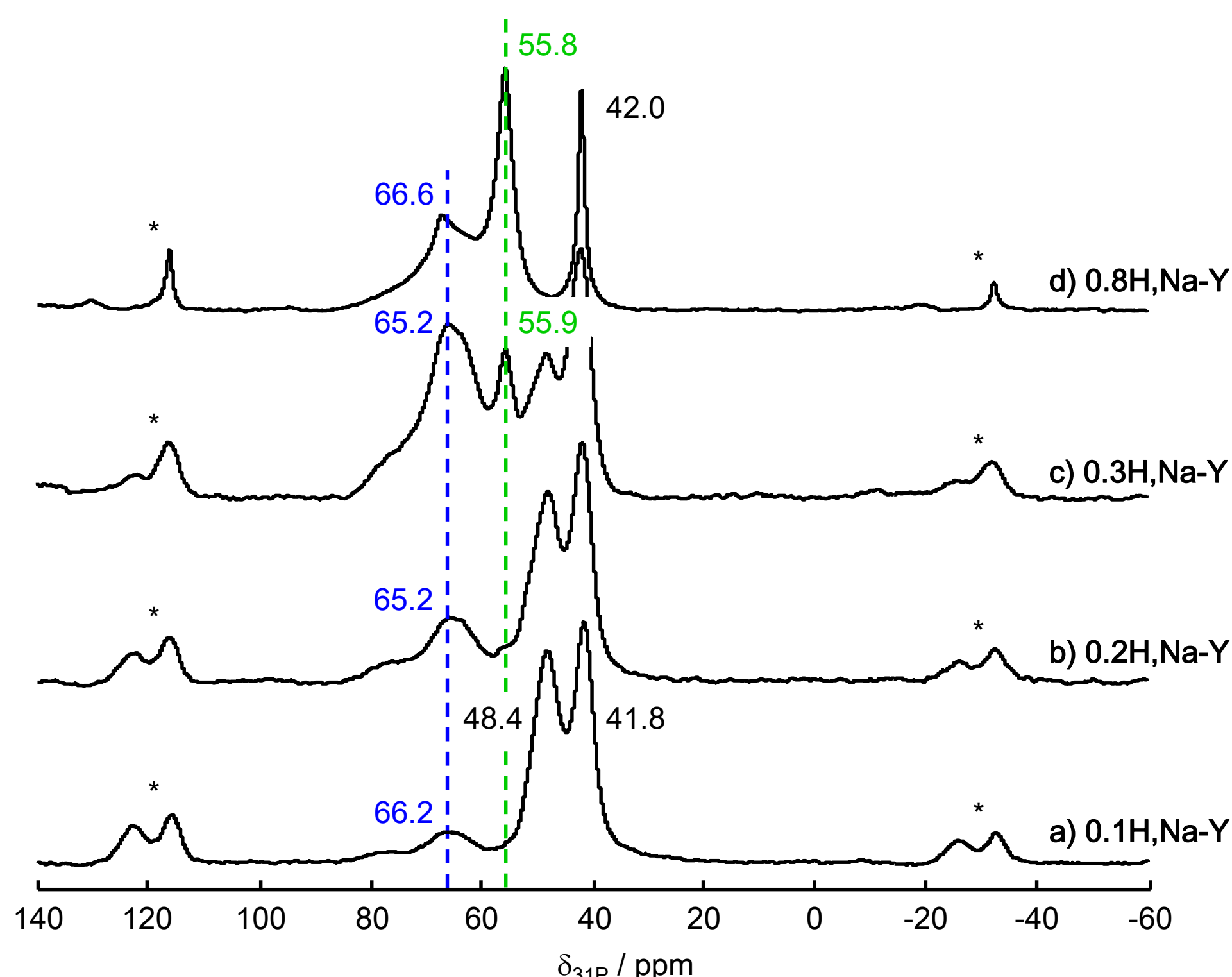


Fig. 3 ^{31}P MAS NMR spectra of zeolites 0.1H,Na-Y (a), 0.2H,Na-Y (b), 0.3H,Na-Y (c), and 0.8H,Na-Y (d), loaded with trimethylphosphine oxide (TMPO). Asterisks assign spinning sidebands.

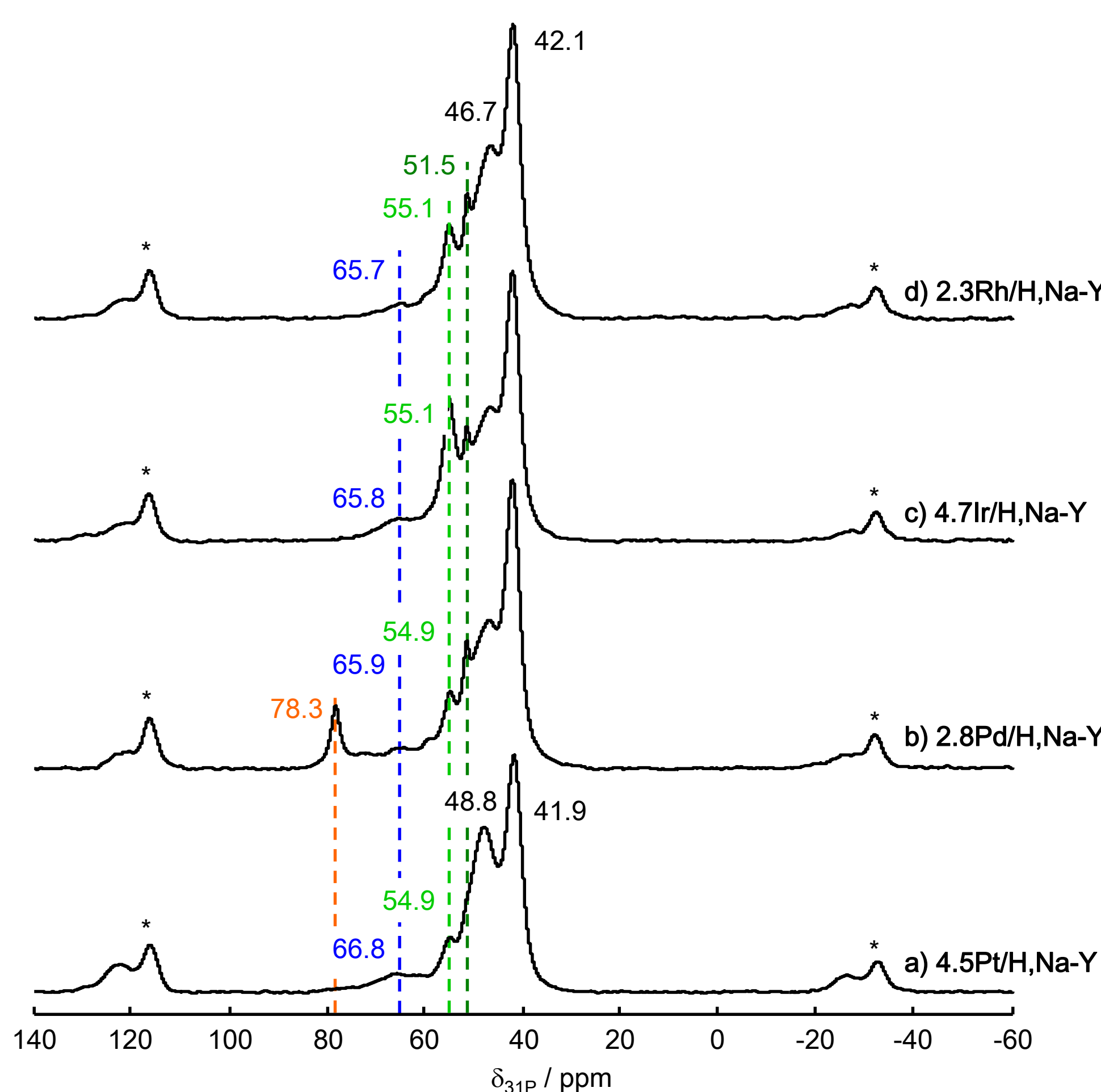


Fig. 4 ^{31}P MAS NMR spectra of reduced zeolites 4.5Pt/H,Na-Y (a), 2.8Pd/H,Na-Y (b), 4.7Ir/H,Na-Y (c), and 2.3Rh/H,Na-Y (d), loaded with trimethylphosphine oxide (TMPO). Asterisks assign spinning sidebands.

Different types of acid sites in noble metal-loaded zeolites Y (Fig. 4):

- ^{31}P MAS NMR signals at 66 ppm: Brønsted acid sites in supercages
- ^{31}P MAS NMR signals at 55 ppm: Brønsted acid sites in sodalite cages
- Ratios of the numbers of Brønsted acid sites in supercages and sodalite cages are in the range of 0.3 to 0.5
 - Distribution of Brønsted acid sites different to that in zeolites H,Na-Y
 - Higher percentage of Brønsted acid sites in sodalite cages
- ^{31}P MAS NMR signals at 51 ppm: TMPO at cationic metal species
- ^{31}P MAS NMR signal at 78 ppm: may hint at the interaction of TMPO with very strong Brønsted acid sites, formed by a partial dealumination of zeolite 2.8Pd/H,Na-Y (Fig. 6)

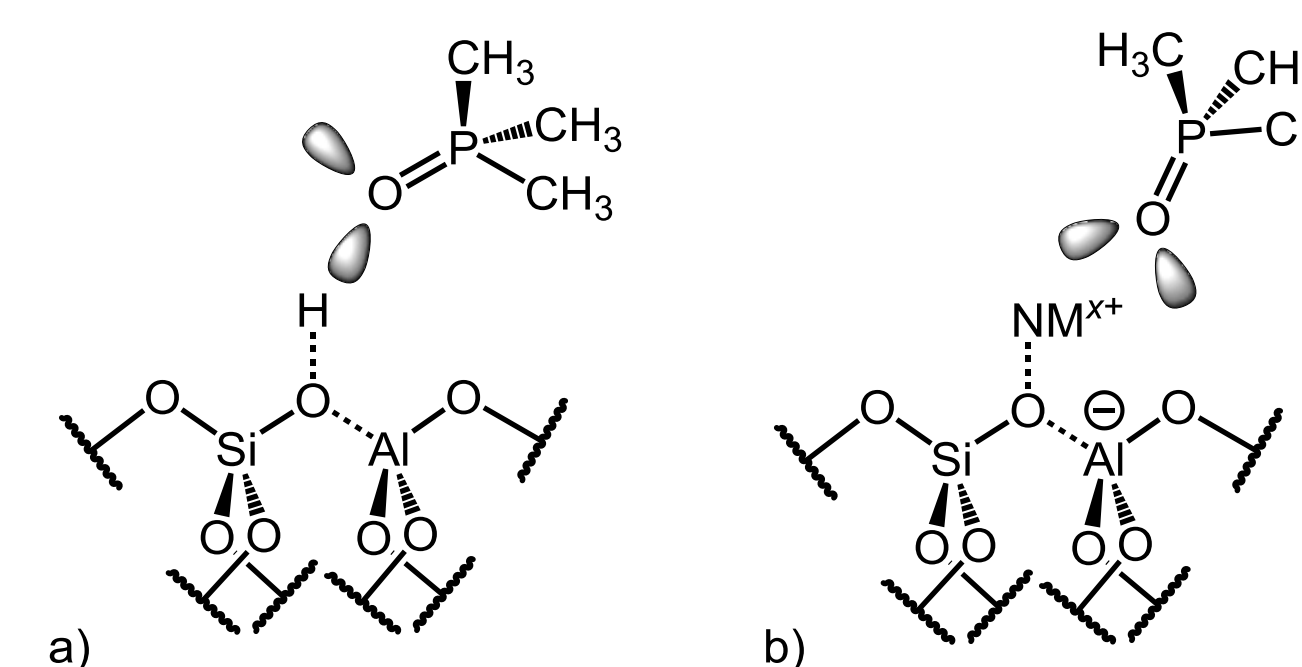
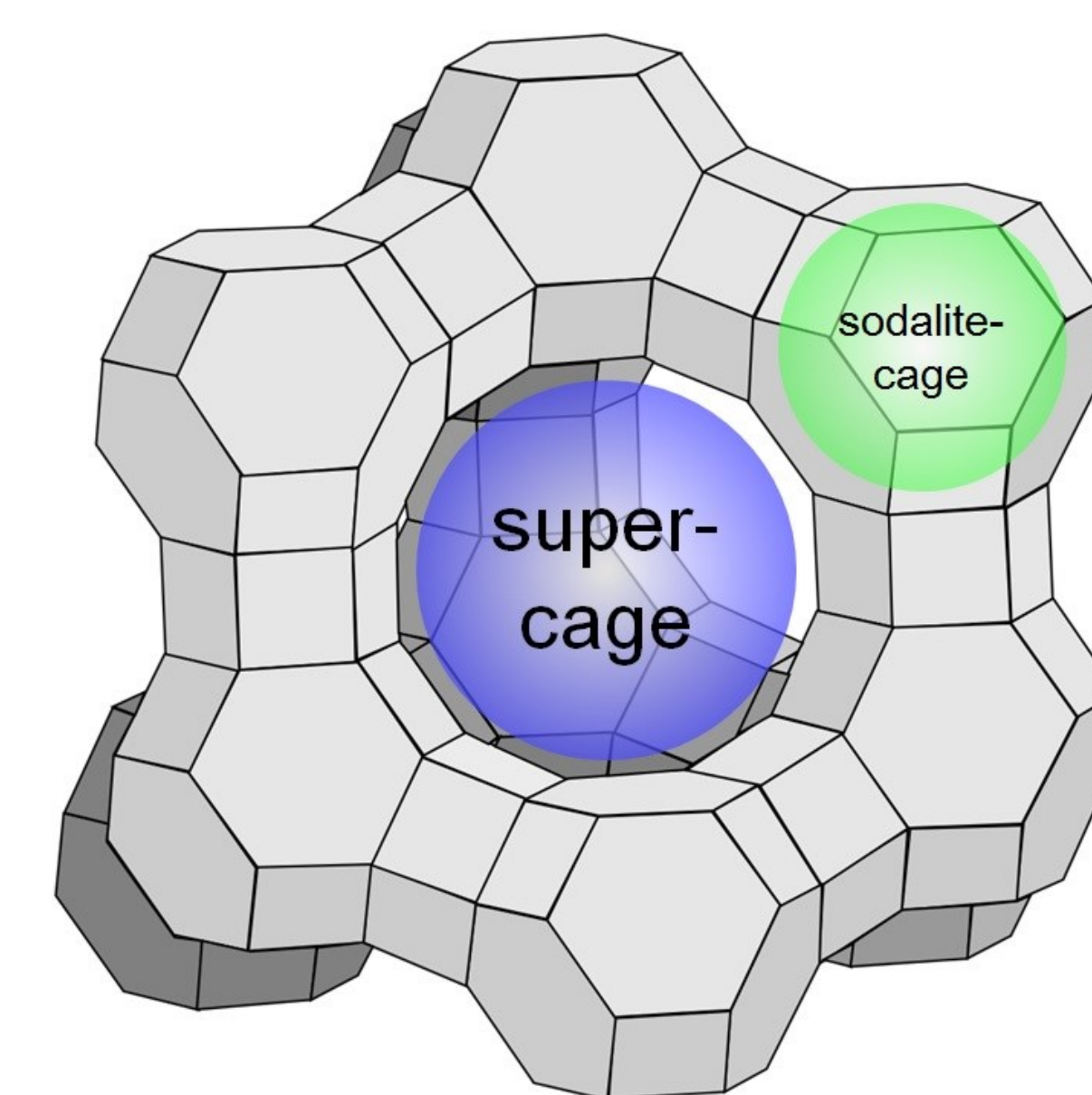


Fig. 5 Coordination of TMPO at a Brønsted acid site (a). Model of TMPO coordinating at cationic metal species (b).

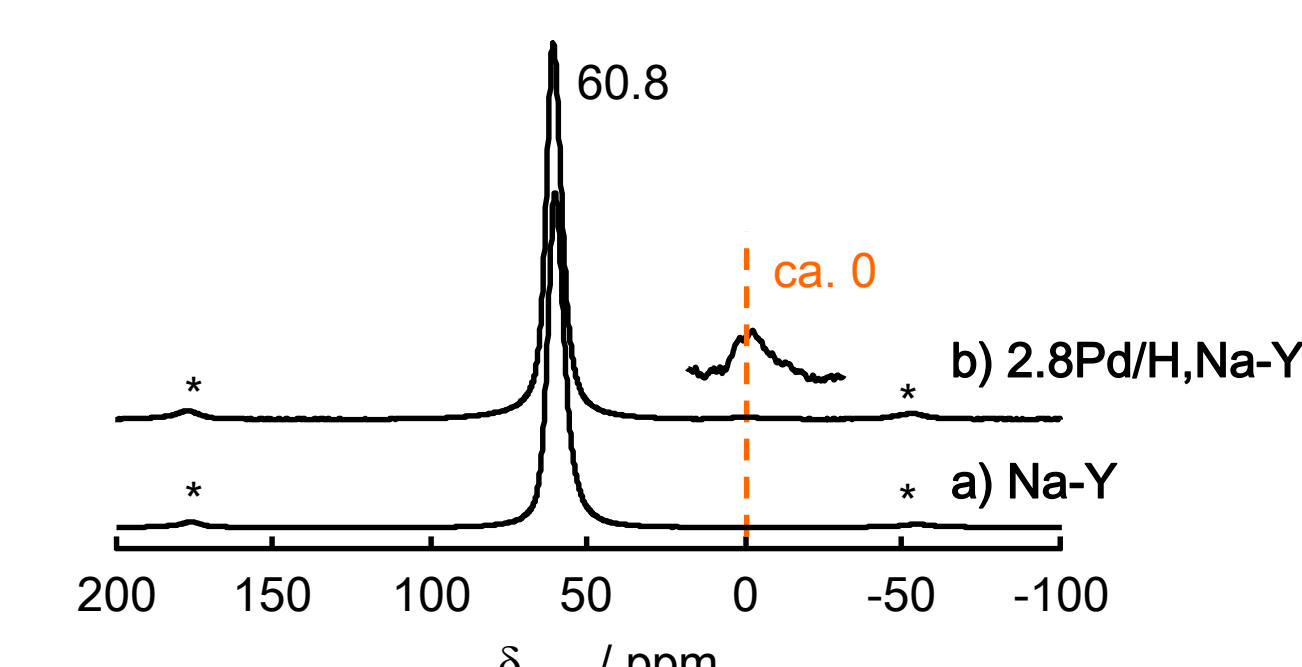


Fig. 6 ^{27}Al MAS NMR spectrum of parent zeolite Na-Y (a) and zeolite 2.8Pd/H,Na-Y (b), rehydrated after reduction. The signal at 0 ppm is caused by extra-framework aluminum. Asterisks assign spinning sidebands.