Specific interaction of bare Pd^{2+} with highly basic sites in calcined PdNaX

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The interaction of bare Pd^{2+} ions with framework oxygen in PdNaX calcined at 500 °C results in an unusual ^{29}Si MAS NMR band at δ −79.5; line intensities indicate that bare Pd^{2+} ions are located preferentially close to highly basic sites exhibiting the Al richest environments; the strong Pd^{2+}–framework interaction is reversibly released upon hydration/dehydration.

The hydration state and nature of the cation in faujasites are known to influence the ^{29}Si MAS NMR chemical shifts.[1–5] Most literature data deal with zeolite Y and few with zeolite X which has a richer Al content. Moreover, no ^{29}Si MAS NMR data are available in the presence of Pd^{2+} cations. The present ^{29}Si MAS NMR study of dehydrated PdNaX demonstrates for the first time that Pd^{2+} in NaX interacts preferentially with highly basic sites. This finding is of high interest since the preparation of metal-supported PdNaX catalysts most often involves a calcination step to favour dispersion.[6] The nature of the interactions between the framework and metal cation after calcination have to be considered to optimize the catalyst.

Three $Pd(NH_3)_4$–NaX samples with different Pd contents were prepared by exchange of a parent NaX (Union Carbide) with a $Pd(NH_3)_4Cl_2$ solution as previously described.[7] Table 1 gives the chemical composition (Pd, Na, Si and Al) of the parent and exchanged samples. The ^{29}Si MAS NMR spectra (reference $SiMe_4$) were recorded at 79.5 MHz on a Bruker MSL-400 spectrometer using a single pulse type measurement (π/3 pulses and 5 s delays). All spectra were identical and they exhibited the usual bands[1–5] assigned to Si(*n*Al) environments, with $0 \leqslant n \leqslant 4$, as illustrated in Fig. 1(*a*) (NaX) and 1(*c*) ($Pd_{6.4}NaX$). The relative intensities of bands, estimated by fitting the curves with Gaussian lineshapes (Win NMR software) were 47, 31, 14, 5 and 3% for Si(4Al), Si(3Al), Si(2Al), Si(1Al) and Si(0Al) environments respectively. The framework Si/Al atomic ratio of 1.3 calculated from these intensities[3] was identical to the global Si/Al ratio deduced from chemical analysis. This shows that no framework dealumination took place during exchange.

The parent and exchanged zeolites were calcined in a fixed-bed reactor (100 ml min^{-1} O_2, 1 °C min^{-1}) up to 500 °C. The preservation of their crystallinity was confirmed by XRD. After calcination at 500 °C under the above conditions palladium is known to be in the form of bare Pd^{2+} ions,[7–13] interacting with framework oxygens and located mostly in I′ sites in the sodalite cages.[8,10,12,13] The calcined samples were transferred from the reactor into the NMR rotor in a dry atmosphere and the ^{29}Si MAS NMR spectra were recorded. Figs. 1(*b*) and (*d*) show the spectra thus obtained for samples NaX (Pd free) and $Pd_{6.4}NaX$ (highest Pd content) respectively.

Table 1 Chemical composition of the samples and number [per unit cell (u.c.) and per Pd] of Si(4Al) atoms with chemical shift at δ −79.5 in the dehydrated calcined samples

	Chemical composition[a]		Si(4Al) from NMR band at δ −79.5	
Sample	Atoms/u.c.	Pd/u.c.	Si/u.c.	Si/Pd
NaX	$Na_{83}Al_{83}Si_{109}$	0	0	—
$Pd_{1.5}NaX$	$Pd_{1.5}Na_{74}H_{8.0}Al_{85}Si_{107}$	1.5	4.3	2.9
$Pd_{2.9}NaX$	$Pd_{2.9}Na_{76}H_{1.2}Al_{83}Si_{109}$	2.9	8.7	3.0
$Pd_{6.4}NaX$	$Pd_{6.4}Na_{63}H_{6.2}Al_{82}Si_{110}$	6.4	18.7	2.9

[a] H/u.c. calculated difference between Al content and total equivalent cations.

The ^{29}Si MAS NMR spectrum of calcined NaX [Fig. 1(*b*)] was similar to that of the hydrated parent sample [Fig. 1(*a*)] except for an upfield shift of all peaks by *ca.* 2 ppm and a broadening of the Si(4Al) band centred at δ *ca.* −86.6. This band moreover exhibits a shoulder at δ *ca.* −84.5. Such changes, also observed in the spectra of the calcined Pd-containing samples, may be attributed to Na^+ ions in stronger interaction with the framework oxygen in the dehydrated state.[1–4] Apart from above effects, important modifications were observed for all calcined samples when Pd^{2+} was present and the trends were identical for all solids. The spectrum of calcined $Pd_{6.4}NaX$ is given as an illustration [Fig. 1(*d*)].

The most important feature in the calcined Pd-containing samples was a decrease in intensity of the band at δ −86.6 related to Si(4Al) environments and the appearance of a new band at δ −79.5. The ^{29}Si CP-MAS NMR (cross-polarisation $^1H/^{29}Si$ experiment) spectrum of calcined $Pd_{6.4}NaX$ [Fig. 1(*g*)] established that the new band at δ −79.5 does not result from the formation of Q^i species[3] ($i \leqslant 3$) during calcination since this band is not significantly enlarged when cross polarisation is

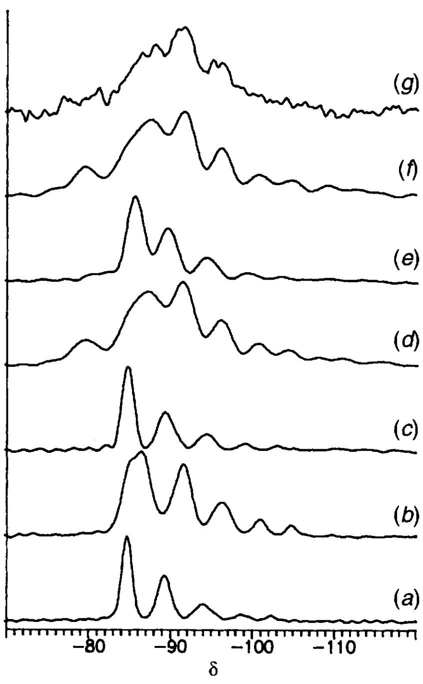

Fig. 1 ^{29}Si MAS NMR spectra of samples (*a*) NaX, (*b*) NaX calcined at 500 °C, (*c*) $Pd_{6.4}NaX$ and (*d*) $Pd_{6.4}NaX$ calcined at 500 °C then (*e*) hydrated in room atmosphere for 3 h then (*f*) dehydrated at 150 °C *in vacuo* for 3 h; (*g*) ^{29}Si CP-MAS NMR spectrum of sample (*d*)

performed. Moreover the band at δ −79.5 disappeared after simple hydration under ambient atmosphere over at least 3 h [Fig. 1(*e*)] and was recovered after dehydration for 3 h in vacuum at 150 °C [Fig. 1(*f*)]. Furthermore, the relative intensity of this band (4, 8 and 17% for $Pd_{1.5}NaX$, $Pd_{2.9}NaX$ and $Pd_{6.4}NaX$ respectively) was always equal to the intensity loss of the band of the Si(4Al) at δ −86.6. The intensities of all other bands were constant in all experiments. The above data clearly indicate that the band at δ −79.5 results from Si(4Al) atoms with bare Pd^{2+} ions in their environment.

^{29}Si chemical shifts in the range δ −76 to −80 have already been reported for zeolitic materials containing sodalite cages and those values were correlated to average $Si(-O-Al)_4$ angles ranging from *ca.* 126 to 131°.[3,14–16] However, a chemical shift of δ −79.5 is highly unusual for faujasites. Moreover, small average angles in the range indicated above are highly unlikely in this structure.[17]

The effect of alkali-metal or rare-earth cations on the ^{29}Si MAS NMR signals in dehydrated NaY is usually an upfield shift by *ca.* 2–5 ppm.[1,3–5] However, downfield shifts were also found for strongly polarising cations such as Li^+[14,15] or Ca^{2+}.[2] In dehydrated CaNaY, this shift was found to be as high as 8.8 ppm.[2] It was then concluded that the deshielding effect of Ca^{2+} on the ^{29}Si is higher than that created by framework Al atoms and it was postulated that suitably located Ca^{2+} ions are able to distort the SiO_4 tetrahedra.[2] Structural distortions are also known to occur in Pd zeolites. In particular, short Pd–O distances were observed in zeolite X[8,12] and it was proposed that the Pd–O bond is partially covalent.[8] The strong deshielding effect found in the presence of bare Pd^{2+} suggests that the ^{29}Si chemical shift of δ −79.5 in PdNaX results not only from the distortions of tetrahedra in presence of bare Pd^{2+} but also from possible overlapping of atomic orbitals of Pd^{2+} and framework oxygens belonging to SiO_4 tetrahedra. The strong Pd–oxygen interaction is weakened when water is adsorbed as evidenced by the disappearance of the band at δ −79.5 in rehydrated samples [Fig. 1(*e*)].

The relative intensities of the ^{29}Si MAS NMR bands at δ −79.5 in the dehydrated calcined samples were used to evaluate the number of Si per unit cell affected by the presence of bare Pd^{2+} ions. Comparison of these values with the number of palladium ions per unit cell indicates that the number of Si affected is three times the number of Pd^{2+} ions in the solid (Table 1). In other words, one bare Pd^{2+} would affect three Si(4Al) atoms. Moreover, those Si(4Al) atoms are equally affected (same chemical shift) which points to a symmetrical location with regard to the Pd^{2+} ion. These observations strongly suggest that the Pd^{2+} ion interacts with oxygen atoms of a six-membered ring containing three Si and consequently three Al atoms as tetrahedra, Pd^{2+} being located on the C_6 axis of the ring. This fits well with the proposed location of bare Pd^{2+} mostly in I′ sites[8,10,12,13] and supports the hypothesis of a tetragonal $Pd^{2+}(O_{zeol})_3$ unsaturated complex being formed[8,9] where O_{zeol} are the framework oxygens.

Owing to the lower electronegativity of Al compared to Si, the framework oxygens close to Al atoms are the more basic.[18,19] An important conclusion of the present work is that Pd^{2+} ions are located in close proximity to Si(4Al) atoms which correspond to highly basic environments. In zeolite Y, such strongly basic sites are virtually absent[18,19] and the cations are found to influence all the ^{29}Si MAS NMR component bands which results in poorly resolved spectra.[1,2,4,5] By contrast, the Pd^{2+} effect is unambiguous in NaX since only one band is affected and is transformed to a single isolated band.

In conclusion, the present work clearly shows that bare Pd^{2+} ions in dehydrated NaX are located preferentially in strongly basic sites where they are stabilised. The strong interaction of Pd^{2+} with the framework is reversibly released upon hydration/dehydration cycles.

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