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Studies of surfaces through molecular probe adsorption and solid-state NMR

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The interaction between the basic probe trimethylphosphine oxide and the Brønsted acid sites of a silica-alumina has been spectroscopically resolved for the first time using a new solid-state NMR approach that opens the possibilities for the investigation of surfaces.

Trialkylphosphine oxides have been proposed as molecular probes for investigating surface acidity in oxide materials sixteen years ago.[1] These probes were shown to give a good distinction between ^{31}P NMR signals associated to their interactions with Lewis and Brønsted acid sites. Afterwards, new experimental data showed the feasibility of site content quantification, but also the existence of various ^{31}P signals for each type of site depending on their relative acidic strength.[2] Recently, a more global argument arose: ^{31}P chemical shifts of the trialkylphosphine oxide probes are effectively dependent on the acidic strength of the sites but not directly on their nature, Lewis or Brønsted.[3] If such an argument is valid it makes it more difficult to assign directly ^{31}P signals to acid sites of known nature without a deeper NMR characterisation.

The general aim of our approach is to characterise, at different length scales, the chemical environment of specific sites at the boundary of oxide domains. This combines three complementary steps: (i) high resolution solid-state NMR spectra. These would allow a clear distinction between chemical sites. In the case of ^{1}H spectra, new methodological developments like the Phase Modulated Lee–Golburg decoupling scheme (PMLG)[4] are used for this purpose; (ii) precise selection of ^{1}H and X neighbouring nuclei. In ^{1}H coupled systems, this is successfully obtained using cross-polarisation under ^{1}H Lee–Golburg decoupling (CPLG)[5] instead of classical cross-polarisation (CP). Effectively, the use ^{1}H pulses under Lee-Golburg conditions (proton irradiation is shifted in frequency so as to average to zero the ^{1}H homonuclear dipolar interaction at the first order[6]) eliminates most of the ^{1}H spin diffusion process that takes place during classical CP; (iii) exploration of distances between ^{1}H and X nuclei from some Å up to 200 nm. This can be achieved by the additional introduction of the ^{1}H spin diffusion process during an appropriate mixing time τ_m.[7]

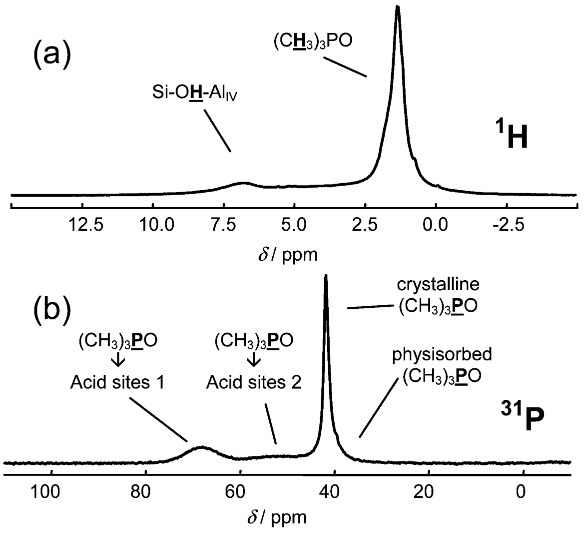

Fig. 1 ^{1}H MAS (a) and ^{31}P{^{1}H} CP MAS (b) NMR spectra of the TMPO loaded silica-alumina.

Here, we propose to apply this NMR approach to identify clearly ^{31}P signals of trimethylphosphine oxide (TMPO) probes in interaction with Brønsted acid sites. The material used for our work was a precipitated silica-alumina (5% weight of alumina) from Rhodia (France). After dehydration (5 days under primary vacuum at 25 °C), the material (0.16 g) was loaded with TMPO (by addition of 2.5 ml of 0.2 M TMPO in CH_2Cl_2, followed by solvent extraction under vacuum). Solid-state NMR experiments were carried on a Bruker Advance 400 MHz spectrometer with radio-frequency pulse fields of *ca.* 50 kHz. The zirconia 4 mm MAS rotors spinning at 12 kHz were filled in a glove-box under inert atmosphere. In the ^{1}H NMR spectrum (Fig. 1(a)), it has been possible to identify in particular an intense signal at *ca.* 1.5 ppm, and a broad signal located at 7 ppm. From literature data[8] and other NMR experiments run in parallel† these particular signals are assigned to TMPO methyl groups (no differentiation between them was observed) and Si–OH–Al_{IV} Brønsted acid sites, respectively. 2D ^{1}H–^{1}H PMLG exchange experiments[9] (not shown) were carried out at moderate and long mixing times τ_m (20 and 100 ms). At moderate mixing time, it was possible to observe off-diagonal correlation peaks between Si–OH–Al_{IV} and methyl signals while all ^{1}H signals exchange at long mixing times. We thus conclude that some TMPO molecules are located in the vicinity of Brønsted acid sites.

1D ^{31}P NMR spectra obtained through simple pulse or

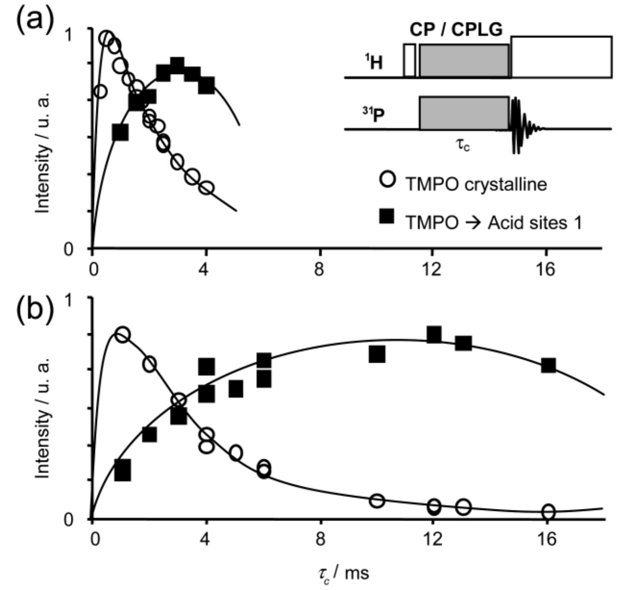

Fig. 2 Variations of ^{31}P signal intensities of the loaded silica-alumina as a function of the contact time τ_c for crystalline TMPO (○) and for TMPO in interaction with acid sites 1 (○): (a) using CP; (b) using CPLG. Lines are purely indicative.

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through $^{31}P\{^1H\}$ CP pulse sequences present four signals (Fig. 1(b)): an intense Lorentzian like signal at 42 ppm with a large spinning side-bands pattern associated to phase-separated TMPO, a smaller signal at 41 ppm due to physisorbed TMPO, and two Gaussian like signals at 64 and 58 ppm ascribed to TMPO in interaction with acid sites 1 and 2, respectively. From comparison with literature data,[1] site 1 could be of Brønsted type, and site 2 of Lewis type. When increasing CP contact times τ_c in $^{31}P\{^1H\}$ CP or CPLG experiments, intensity variations differ for ^{31}P signals (Fig. 2). This behaviour is much clearer for the CPLG experiment that avoids ^1H spin diffusion during cross-polarisation. In this case, it becomes possible by adjusting τ_c to favour the observation of signals assigned to phase separated TMPO ($\tau_c \approx 1$ ms) or to TMPO interacting with acid sites 1 or 2 ($\tau_c \approx 12$ ms).

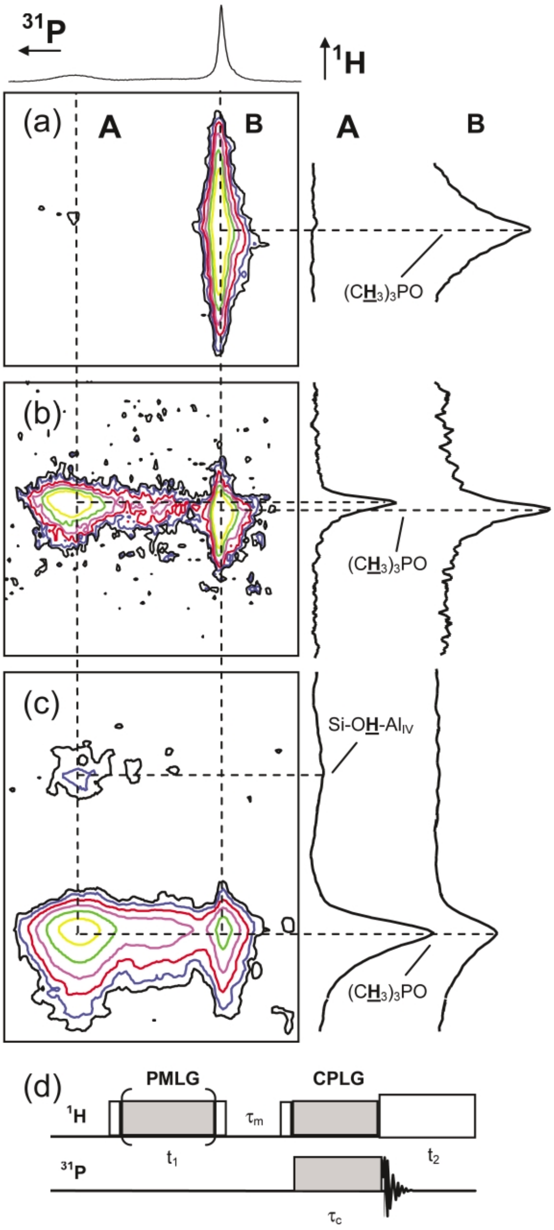

Fig. 3 2D contour plots of the ^1H–^{31}P heteronuclear correlation experiments (1024×128 data points) using the pulse sequence depicted in (d). Contact and mixing times vary as follow: (a) $\tau_c = 0.5$ ms, $\tau_m = 0$ ms, 384 scans; (b) $\tau_c = 12$ ms, $\tau_m = 0$ ms, 384 scans; (c) $\tau_c = 12$ ms, $\tau_m = 50$ ms, 2048 scans. ^1H vertical spectra shown here correspond to TMPO in interaction with acid sites 1 (A) and crystalline TMPO (B) and were obtained from a multi-step fitting procedure of all rows (F1 dimension) using the four ^{31}P signals.

2D ^1H–^{31}P heteronuclear correlation experiments with ^1H homonuclear decoupling during t_1 evolution (PMLG) and during τ_c (CPLG), and with a variable mixing time τ_m (Fig. 3(d)) were recorded. By choosing appropriate values for τ_c and τ_m, it is possible to explore the chemical environment of the TMPO molecules and of the proton sites. Main results are presented in Fig. 3. At low contact time ($\tau_c = 0.5$ ms) and zero mixing time, a single correlation peak is observed between the ^{31}P signal of phase separated TMPO and the ^1H signal of methyl groups (Fig. 3(a)). Increasing the contact time ($\tau_c = 12$ ms) allows identification of new correlation peaks between all ^{31}P signals and methyl ^1H signals (Fig. 3(b)). In particular, a difference of *ca.* 0.5 ppm could be estimated between the chemical shifts of ^1H signals associated to the methyl groups of phase separated TMPO and those associated to methyl groups of TMPO in interaction with acid sites 1. When allowing ^1H spin diffusion to proceed, a new peak starts to be observed at moderate mixing times (here $\tau_m = 50$ ms). This correlates the ^{31}P signal of TMPO in interaction with acid sites 1 at 68 ppm, and the ^1H signal of Si–OH–Al$_{IV}$ at 7 ppm (Fig. 3(c)). Under these conditions we clearly resolve the interaction between the TMPO probe and the Brønsted acid sites.

By quenching or introducing the ^1H spin diffusion process in these 2D ^1H–^{31}P NMR experiments, we determine precisely the chemical environment of the TMPO molecular probe and thus justify the attribution of ^{31}P signals to probes in interaction with Brønsted or Lewis acid sites on an oxide surface. This approach can be extended to other molecular probes of different size and nature, or to various NMR sensitive nuclei (^{13}C, ^{19}F, ^{27}Al, *etc.*), for the characterisation of properties such as the accessibility and the reactivity of specific sites.

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Notes and references

† Identification and assigment of ^1H signals was done using ^1H MAS spectra (at 12 and 30 kHz spinning rates), $^1H\{^{27}Al\}$ Redor and CP experiments, and also treating the samples in various ways: dehydration, rehydration and deuteration. Chemical shifts (δ) were observed at 1.5 ppm ($(CH_3)_3PO$); 3–1 ppm (Si–OH); ≈ 3 ppm (Al$_{VI}$–OH); 4.8 ppm (residual H_2O); 7.0 ppm (Si–OH–Al$_{IV}$).

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