^{31}P NMR MAS Spin-lattice Relaxation as a Dispersion Probe: an Easy Access to Active-site Concentration in Silica-supported Dodecamolybdophosphoric Acid

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Solid-state ^{31}P spin-lattice relaxation of silica-supported dodecamolybdophosphoric acid dramatically depends on the polyanion : SiO_2 ratio for concentrations above that required for the saturation of the adsorption sites on the silica surface; this dependence allows the density of the active sites at the silica surface to be determined.

Catalysis by silica-supported polyoxometallates is now well developed[1] but access to the optimal polyoxometallate : silica ratio requires relatively tedious measurements of catalytic activities.[2,3] It was recently reported that solid-state ^{29}Si spin-lattice relaxation in silica-supported $H_4SiMo_{12}O_{40}$ decreases with increasing polyanion dilution and could be therefore a measure of the polyoxometallate dispersion over silica.[4] This study has been extended to solid-state ^{31}P spin-lattice relaxation of silica-supported $H_3PMo_{12}O_{40}$ and it is shown that these measurements can give a good estimation of the coverage of the silica support.

The Keggin dodecamolybdophosphoric acid was supported by the impregnation method on a macroporous silica (Rhône-Poulenc Spherosil XOA-400), for different polyanion : silica ratios: the molar ratio n'/n (n' = number of moles of SiO_2; n = number of moles of $H_3PMo_{12}O_{40}$) varies from 20 to 1000 (Mo mass% from 35 to 2).

Solid-state magic-angle-spinning (MAS) spin-lattice relax-

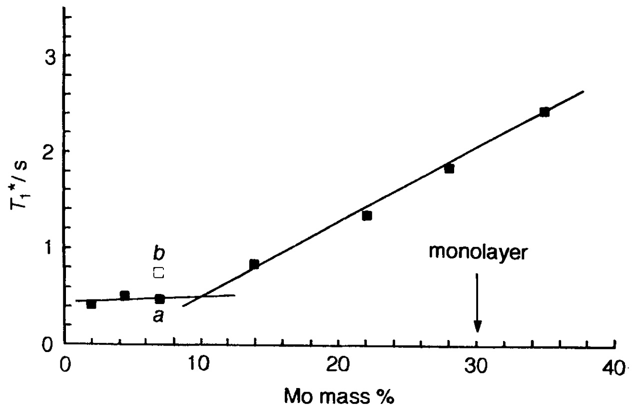

Fig. 1 Plot of the solid-state ^{31}P mean relaxation time T_1* (see text for the definition) of silica-supported $H_3PMo_{12}O_{40}$ as a function of the Mo mass%. The points *a* and *b* correspond to the same sample (Mo 7% in mass) before and after thermal treatment at 500 °C (6 h) followed by exposure to water vapour (more than 3 days).

ation measurements have been performed at 162 MHz (Bruker MSL 400) for the ^{31}P resonance of the central PO_4 tetrahedron of the Keggin anion. A mean relaxation time value T_1* was determined by the null-method in the inversion-recovery Fourier transform (IRFT) experiment.[5]

For unsupported $H_3PMo_{12}O_{40}\cdot13\ H_2O$, T_1* amounts to 20 s, but, as shown in Fig. 1, T_1* dramatically decreases by dilution, from about 2.5 s for the most concentrated sample (Mo mass% = 35; *n'*/*n ca.* 20) to about 430 ms (Mo mass% = 2; *n'*/*n ca.* 1000). The high sensitivity of ^{31}P ($I = \frac{1}{2}$; natural abundance 100%; receptivity with respect to $^1H = 6.6 \times 10^{-2}$) and the favourable relaxation rates allow these measurements to be made at a very low concentration level (less than 6×10^{17} ^{31}P nuclei in the resonant coil of the MAS probe). As can be seen in Fig. 1, the mean relaxation time T_1* reaches a minimum for a Mo mass concentration of about 10% (*n'*/*n ca.* 160) and does not decrease further with increasing dilution. This can be interpreted on the following basis, derived from similar observations made on the $H_4SiMo_{12}O_{40}$–SiO_2 system:[4] supported samples contain two kinds of $[PMo_{12}O_{40}]^{3-}$ anions, characterized by different ^{31}P NMR properties. There are anions in $H_3PMo_{12}O_{40}\cdot13H_2O$ microcrystals, just deposited on the silica surface, which do not differ from macroscopic $H_3PMo_{12}O_{40}\cdot13H_2O$ (species **1**), and $[PMo_{12}O_{40}]^{3-}$ anions directly in interaction with hydroxy groups at the silica surface (species **2**). The former exhibits the NMR parameters of pure $H_3PMo_{12}O_{40}\cdot13H_2O$, *i.e.* δ −4.1 (ref. 85% phosphoric acid) and a relaxation time of about 20 s, whereas the latter experiences a short relaxation time (the origin of this short T_1 has been tentatively explained in the case of ^{29}Si for the analogous $H_4SiMo_{12}O_{40}$–SiO_2 system[4]). In contrast to what was observed for ^{29}Si, the relative broadness of the ^{31}P resonance ($\Delta\nu_{1/2} \approx 50$ Hz, *i.e.* about 0.3 ppm at 162 MHz) does not allow an eventual chemical shift difference between species **1** and **2** to be observed. For high polyanion concentrations, the supported material should contain both species and the preparation conditions (impregnation method) ensures that the available silica surface sites are fully saturated by the polyanions: the relaxation rate for the unique resonance line then depends on the relative proportion n_1 and n_2 ($n_1 + n_2 = n$) of the species **1** and **2**, *i.e.* on the excess of polyanion with respect to the amount $n_2{}^s$ required to 'saturate' the silica surface. The relaxation rate consistently increases with polyanion dilution when the molar fraction x_1 of the species **1** [$x_1 = n_1/(n_1 + n_2{}^s)$] decreases. When the polyanion amount reaches the value $n_2{}^s$ just sufficient to 'saturate' the silica, the species **1** is no longer present ($x_1 = n_1 = 0$) and the observed relaxation rate should be that of the species **2**; further polyanion dilution only results in decrease of the concentration of the unique species **2** ($n_2 < n_2{}^s$), *i.e.* some of the accessible silica surface sites are now unoccupied. The ^{31}P resonance line decreases in intensity but the relaxation time remains unchanged.

It appears then that the singularity observed for the plot of T_1* *vs.* polyanion concentration should correspond to the exact 'saturation' of the silica surface by the $[PMo_{12}O_{40}]^{3-}$ anions. In the present case this saturation is reached for Mo mass% about 10, corresponding to about 1 mole of $H_3PMo_{12}O_{40}$ for 160 moles of SiO_2. The surface area of the macroporous Spherosil silica is given to be 376 m^2 g^{-1}; conversion at the microscopic level leads to 3.8×10^{-2} nm^2 for one SiO_2 'molecule' and then a surface of 6.1 nm^2 is available with 160 SiO_2 'molecules'. For the quasi-spherical $[PMo_{12}O_{40}]^{3-}$ anion we can define a 'radius' of about 0.52 nm,[6] such as the centres (phosphorus atoms) of two anions in close contact would be distant from 1.04 nm (apparent area of a polyanion unit = 1.1 nm^2). It appears then that 'saturation' of the silica surface by the polyanion is reached with only 1:5.5 (0.18) of the amount expected from the surface area in the 'monolayer approximation' (Mo mass% = 30). The reason for that could be explained as follows: (*i*) the surface area generally determined by Brunauer–Emmett–Teller (BET) methods (from nitrogen physisorption) does not give information about site accessibility: this could give strong discrepancies in the case of a microporous support and relatively large adsorbed species; (*ii*) the 'monolayer approximation' is based on a close contact of the adsorbed species: this approximation could be well-founded for non-polar, neutral molecules, implying only van der Waals interactions but certainly does not hold in the case of highly-charged polyanions where repulsive electrostatic forces are to be considered; (*iii*) finally, the surface area does not take into account the heterogeneity of the surface which presents both favourable and unfavourable sites for the fixation of the charged species. Therefore the 'saturation rate' determined by NMR spectroscopy must certainly be more useful for catalytic applications than the 'covering rate' calculated in the 'monolayer approximation' from the surface area: in fact catalytic tests performed at different polyanion concentrations on the $H_4SiMo_{12}O_{40}$–SiO_2 system with the same silica had shown that alterations of the catalytic behaviour (inversion of the character of the catalysis) precisely occur between 0.2 and 0.1 'monolayer coverage'.[2]

The NMR method could then give information about the exact amount of species in interaction with the support, just those species usually expected to be the active ones in the catalytic process. Offering the possibility to determine the effective surface occupancy as well as the site accessibility (eventual dependence on the size, the form and the surface properties of the supported species) it can be used to rationalize the preparation of supported catalysts (introduction of the optimal amount of supported species with respect to the support) and also to check an eventual alteration of the support surface during the catalytic process.

The potential of the method is illustrated by the following example: a silica-supported $H_3PMo_{12}O_{40}$ sample (Mo 7% in mass, *i.e.* *n'*/*n* ≈ 240) was submitted to thermal treatment (6 h at 500 °C) which resulted in the nearly complete destruction of the polyanion framework, evidenced by a 95% decrease of the $[PMo_{12}O_{40}]^{3-}$ anion resonance; the exposure to water vapour at room temperature (more than 3 days) restores the initial polyanion as shown by the recovery of the ^{31}P resonance intensity, but the mean relaxation time T_1* (≈780 ms) exceeds by about two-fold that of the initial sample (points *b* and *a* respectively in Fig. 1); such an observation could be the consequence of either the collapse of the silica during the thermal treatment with a concomitant loss of porosity, or the segregation of the molybdate fragments during the rebuilding phase with the help of water molecules (spillover). Whatever the interpretation, the resulting material would likely be less efficient in the catalytic process than the initial material. Such an observation could help us to understand the progressive loss of catalytic activity of some polyoxometallate systems during the course of the reaction.

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