^{31}P MAS NMR Study of $H_3PW_{12}O_{40}$ Supported on Silica: Formation of $(\equiv SiOH_2^+)(H_2PW_{12}O_{40}^-)$

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A series of $H_3PW_{12}O_{40}$–SiO_2 catalysts with various polyanion contents (ranging from 13 to 87 wt%) were studied by ^{31}P MAS NMR spectroscopy; two peaks were detected, one corresponding to the bulk $H_3PW_{12}O_{40}$ and the other to $(\equiv SiOH_2^+)(H_2PW_{12}O_{40}^-)$.

Heteropoly acids in the solid state are strong protonic acid catalysts.[1,2] They absorb polar molecules into the bulk of the solid leading to a pseudo-liquid-phase catalysis.[3] However, apolar molecules react only on the surface, which leads to poor reactivity as the Brunauer–Emmett–Teller (BET) surface area of these compounds is very low.[4] As a consequence, many attempts have been made to support heteropoly acids, using various materials, the most often used being silica.[2,5,6] However, the nature of the polyanion on the surface has been discussed only briefly, and was described as having a slight interaction with the silica surface.[6] As a consequence, we have undertaken the study of $H_3PW_{12}O_{40}$ (denoted HPW) supported on silica in order to determine the nature of the polyanion on the surface.

A series of HPW–SiO_2 catalysts with various polyanion loadings (from 13 to 87 wt%) were prepared by impregnating SiO_2 Aerosil (S = 380 m^2 g^{-1}) with a solution of $H_3PW_{12}O_{40}$. Typically, 0.5 g of silica was used; the desired amount of polyanion was dissolved in 5 ml of distilled water and the solution mixed with the solid. The suspension was then dried at 100 °C for 24 h. The resulting solid was kept in a desiccator in order to avoid rehydration. ^{31}P MAS NMR spectra were recorded on a Bruker MSL-300 spectrometer using a single pulse sequence. A small flip angle (15°) and a long delay between each scan (100 s) were chosen so as to allow observation of quantitative spectra. The number of scans varied between 60 and 500 depending on the phosphorus content of the sample. Chemical shifts are referred to external H_3PO_4 (85 wt%) (precision 0.3 ppm); they are not corrected for magnetic susceptibility.

A typical ^{31}P MAS NMR spectrum of an HPW–SiO_2 catalyst is given in Fig. 1. Clearly, two peaks can be detected at about δ −15 (peak I, linewidth ≈50 Hz) and at about δ −14.5 (peak II, linewidth ≈80 Hz). Such a spectrum is different from that of pure phosphotungstic acid (in the hexahydrate form): However, for the pure polyanion, only one peak at about δ −15 with a small linewidth (depending on the crystallinity of the sample) is observed. For all polyanion loadings, the ^{31}P MAS NMR spectrum of the HPW–SiO_2 catalyst shows the two peaks with only a variation of their relative proportions. The contributing area of these two signals can be obtained by deconvolution and least-squares fitting of the observed envelope, with two component signals. For all catalysts the linewidths, Lorentzian : Gaussian ratio and relative separation of these two peaks were taken as constant, allowing only a modification of their relative proportions and a translation of all of the spectrum (due to the drift of the magnet). The data

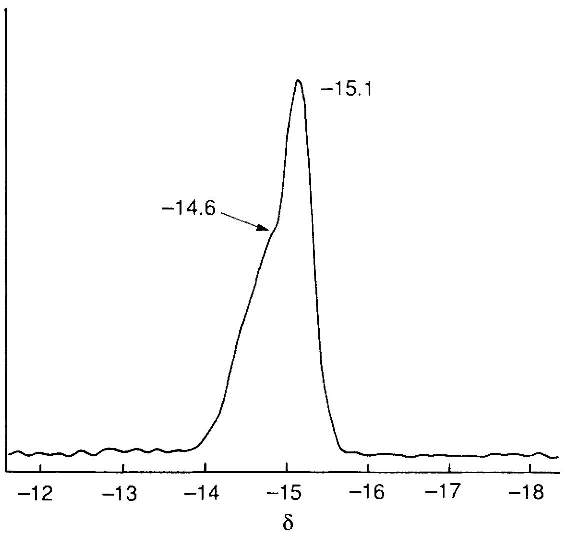

Fig. 1 ^{31}P MAS NMR spectrum of an $H_3PW_{12}O_{40}$–SiO_2 catalyst (50 wt% SiO_2)

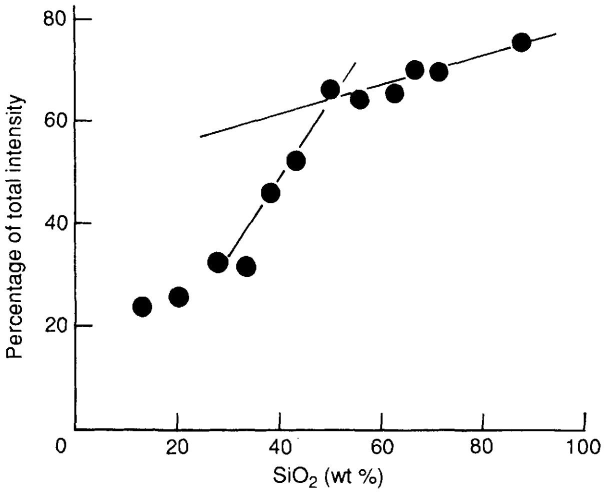

Fig. 2 Variation of the proportion of the peak at about δ −14.5 to the total ^{31}P NMR spectrum intensity as a function of the silica content in the $H_3PW_{12}O_{40}$–SiO_2 catalysts

obtained from the simulations are summarised in Fig. 2, which shows the evolution of the relative amount of the broader peak (at δ −14.5) on the total surface area of the composite signal as a function of the amount of silica in the catalyst.

Such a feature has been observed for 12-molybdosilicic acid supported on silica.[6] Two peaks were observed, one corresponding to a polyanion unperturbed by the impregnation and the other was attributed to a $SiMo_{12}O_{40}^{3-}$ species, which had a slight interaction with the silica surface; the pure polyacid gave only one signal. By analogy with these results and by taking into account Fig. 2 we can propose that the peak at about δ −15, which becomes preponderant at high polyanion content, is due to $H_3PW_{12}O_{40}$ without interaction with the silica surface and which has crystallized near or on the SiO_2 particles (the XRD spectra of the catalysts are similar to those of $H_3PW_{12}O_{40}\cdot 6H_2O$). The polyanion which undergoes a slight interaction with the silica surface should give rise to the other slightly broader NMR peak. However, more information on these species can be obtained from the data for Fig. 2. Indeed, the evolution of the relative amount of HPW in interaction with the silica support is not linear but for a composition of about 50% silica a modification is observed. If we calculate the number of polyanions of type II as a function of the HPW loading for a constant mass of silica and by assuming that there is no other phosphorus compound formed during the impregnation reaction (this hypothesis is probably true as no other NMR peaks were detected even for very high signal-to-noise ratios) it appears that for a polyanion content of lower than 3.5×10^{-4} mol g^{-1} of SiO_2 (52 wt% SiO_2) the amount of species II increases linearly but for higher loadings it is not modified. For very high loadings some discrepancies can be observed but the precision of results is not very good, as it is difficult to evaluate relative proportions that are very different. We can thus estimate the maximum number of polyanions of type II to 2.4×10^{-4} mol g^{-1} of silica. As the silica surface area is 380 m^2 g^{-1} this value corresponds to 3.8 polyanions over 10 nm^2, which is similar to the number of silanol groups on the surface (≈3 for 10 nm^2) as specified by the manufacturer. As a consequence we can propose that each polyanion of type II corresponds to a silanol group. As the OH groups are protonated in acidic medium, we can suppose that one proton of $H_3PW_{12}O_{40}$ will react with the OH of silanol leading to a $SiOH_2^+$ group, which should act as a counter ion for the polyanion. The formula of a polyanion in such an environment can then be written as $(\equiv SiOH_2^+)(H_2PW_{12}O_{40}^-)$, which shows that the reaction of the polyanion with the support cannot be described as an exchange but as an acid–base reaction between the silanol groups, acting as the base, and the polyanion, which acts as a Brønsted acid. This formula also explains why the polyanion can be extracted by acetonitrile,[7] the equilibrium between free and supported polyanions being displaced by the solvent. These results could also explain the different conclusions found by some workers on the stabilization of polyanions by the support, as in all of the catalysts there are two types of phosphotungstic acid. A study of the properties of $(\equiv SiOH_2^+)(H_2PW_{12}O_{40}^-)$ including its preparation in pure form and its thermal behaviour will be published elsewhere. Indeed, the elimination of water in the $(\equiv SiOH_2^+)$ group should involve a direct bonding of the polyanion to the support. Such a feature can be considered as the first step of a chemistry of polyanions anchored on a solid.

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