Evidence of β-MoO_3 Formation during Thermal Treatment of Silica-supported 12-Molybdophosphoric Acid Catalysts

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Unsupported and silica-supported $H_3PMo_{12}O_{40}$ catalysts show a wide temperature range for decomposition on thermal treatment allowing the formation of monoclinic β-MoO_3 (characterized by Raman spectroscopy and X-ray powder diffraction); this new supported phase leads specifically to dimethoxymethane in the methanol oxidation reaction.

Silica-supported heteropolyacid catalysts are widely used in fundamental and applied research.[1] In the case of 12-molybdosilicic acid ($H_4SiMo_{12}O_{40}$), a correlation between the catalytic behaviour in the methanol oxidation reaction and the dispersion on the silica surface was established (acidic catalysis at high Mo loading, redox catalysis at low Mo loading) in the temperature range of 12-molybdosilicic acid stability.[2] However the true nature of the active species strongly depends on the thermal treatment, and, at low loadings, on the dispersion. It was clearly shown that, in the case of $H_4SiMo_{12}O_{40}$, the supported samples are destroyed over a larger temperature range than the unsupported parent, because of the destabilizing interaction between the heteropolyacid and the protonated hydroxy groups on the support.[3] Moreover, it was claimed that 12-molybdophosphoric acid, $H_3PMo_{12}O_{40}$, is a more efficient catalyst than $H_4SiMo_{12}O_{40}$ because of its more positive redox potential and its higher thermal stability. It is well known that phosphorus heteropolyacids are less stable in aqueous solution than silicon heteropolyacids, with formation of lacunary anions such as $HPMo_{11}O_{39}{}^{6-}$ or $H_6PMo_9O_{34}{}^{3-}$, depending on the pH and the concentration.[4] As a consequence, silica-supported $H_3PMo_{12}O_{40}$ catalysts, giving eventually mixture of oxo-species, are expected to have thermal behaviour more complex than that of the related silicon compounds.

We report here results obtained with unsupported and silica-supported 12-molybdophosphoric acid catalysts. The preparation of $H_3PMo_{12}O_{40}$ has been reported previously.[5] The silica support (Rhône-Poulenc XOA 400, surface area 376 $m^2\ g^{-1}$) was impregnated by the incipient wetness method with aqueous solutions of $H_3PMo_{12}O_{40}$. The catalysts were dried at 100 °C *in vacuo*. Oxidation of methanol in the presence of oxygen was used as the test reaction. Activities and selectivities were measured with a continuous-flow fixed-bed reactor under atmospheric pressure. Pretreatments were for 2 h at different temperatures between 140 and 500 °C. The reaction was conducted at 240 °C, and the flow composition He–O_2–MeOH was 85.2, 10.3, 4.5 mol%. Reaction products were analysed on line by gas-phase chromatography. IR, Raman and X-ray diffraction techniques were used to characterize the samples before and after the catalytic reaction.

The catalytic behaviour of unsupported $H_3PMo_{12}O_{40}$ is roughly similar to that of unsupported $H_4SiMo_{12}O_{40}$: acidic catalysis giving essentially dimethyl ether for treatment temperatures under 240 °C, redox catalysis giving mainly formaldehyde for treatment temperatures higher than 400 °C, according to the decomposition scheme of the heteropolyacid. It appears however from the reactivity results, and unexpected from thermogravimetric measurements, that the $H_3PMo_{12}O_{40}$ decomposition does not occur so abruptly as that of $H_4SiMo_{12}O_{40}$: the transition between acidic and redox catalysis occurs progressively over the range 280–400 °C.

For the silica-supported samples, the catalytic character depends on the Mo loading and on the temperature of the thermal treatment. For treatment temperatures under 240 °C, the samples have a behaviour similar to that of the supported $H_4SiMo_{12}O_{40}$ catalysts; the acidic catalysis predominant for high Mo loadings (> 8% *m*/*m*) tends toward redox catalysis for low Mo loadings (disappearance of dimethyl ether for Mo loadings $\leqslant$ 2%). In this temperature range, the conversion of methanol is due only to the heteropolyacid, and the change in the catalysis character is caused by the proton-trapping increasing with the dispersion (only the typical $H_3PMo_{12}O_{40}$ Raman pattern[5] is observed at least down to 2% Mo).

Considering now the treatment temperatures higher than 240 °C, important modifications occur. After treatment at 500 °C, only orthorhombic α-MoO_3[6] is apparent from X-ray powder diffraction and Raman spectroscopy, and the catalysis is mainly redox (formaldehyde and methyl formate production). For intermediate treatment temperatures (in the range 250–450 °C), Raman spectroscopy and XRD give evidence for mixtures of species. The major fact is the formation of an unexpected form of molybdenum trioxide, the monoclinic phase, *i.e.* β-MoO_3 already reported as an analogue of WO_3 (type ReO_3).[7] The formation of the monoclinic β-MoO_3 on the silica surface of our samples is shown by Raman spectroscopy even after thermal treatment at 250 °C [in this case the spectrum is that of a mixture of $H_3PMo_{12}O_{40}$ and β-MoO_3; see Fig. 1(*c*)]. After treatment at 350 °C, $H_3PMo_{12}O_{40}$ completely disappears, leading essentially to β-MoO_3; the orthorhombic α-MoO_3 is only seen in small amounts for the highest loading (16.2% Mo), and at low loadings β-MoO_3 is the only oxomolybdenum species observed on the support. Spectra in Fig. 1 show these transformations. β-MoO_3 is no longer observed after exposure of the calcined catalysts to saturated water vapour, and $H_3PMo_{12}O_{40}$ is easily rebuilt on the silica surface, as in the case of α-MoO_3. Reactivity studies at 240 °C after thermal treatment at different temperatures between 240 and 500 °C show a remarkable behaviour of these supported materials. First, when the heteropolyacid is not destroyed, acidic reactivity giving dimethyl ether is observed, together with

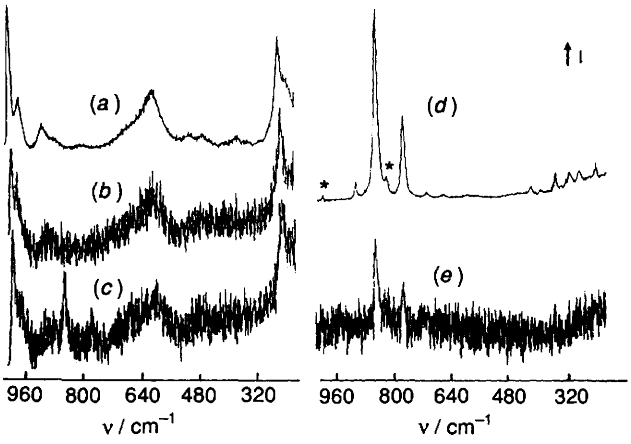

Fig. 1 Raman spectra of (*a*) unsupported $H_3PMo_{12}O_{40}$ and (*b*–*e*) silica-supported $H_3PMo_{12}O_{40}$ catalysts: 16% Mo (*b*) before any thermal treatment; (*c*) after treatment at 250 °C; (*d*) after treatment at 350 °C (the presence of α-MoO_3 is denoted by asterisks); (*e*) 5.75% Mo after treatment at 350 °C (powdered samples pressed in a matrix and rotated at 1000 rpm)

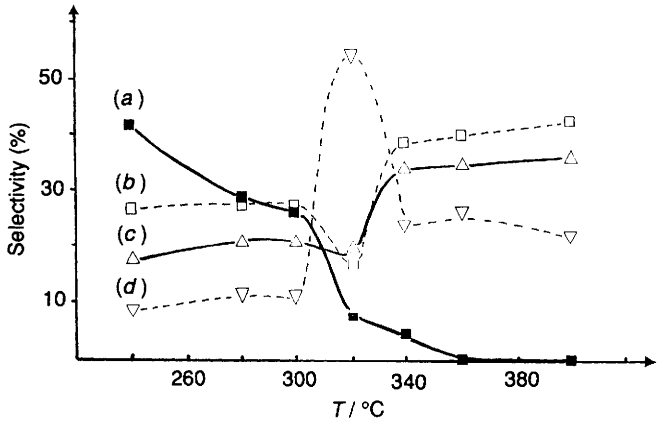

Fig. 2 Selectivities (%) for methanol oxidation at 240 °C *vs.* temperature of thermal pretreatment for a silica-supported $H_3PMo_{12}O_{40}$ catalyst (5.75% Mo): (*a*) dimethyl ether; (*b*) formaldehyde; (*c*) methyl formate; (*d*) dimethoxymethane. The reproducibility of the point at 320 °C in (*d*) has been tested.

significant production of formaldehyde, due to the greater oxidising power of phosphorus compounds than that of silicon compounds. Then, when β-MoO_3 becomes the main species (treatment temperatures about 300–350 °C), the selectivity for dimethyl ether decreases strongly, and a simultaneous increase in selectivity for dimethoxymethane is observed. At higher temperatures, β-MoO_3 transforms gradually into α-MoO_3, and the classical redox behaviour occurs (formaldehyde and methyl formate production; see Fig. 2). This is a noteworthy result. β-MoO_3 could favour dimethoxymethane formation, and α-MoO_3 methyl formate formation. Taking into account the structural differences between these trioxomolybdenum phases, it could be concluded that, when the initial oxidation step occurs (formation of formaldehyde), the secondary evolution of the formaldehyde by reaction with other adsorbed methanol molecules implies two different kinds of oxygen atoms (terminal for methyl formate production, and bridging for dimethoxymethane production).

It appears then that, in contrast with the assumed behaviour, the transformation of unsupported $H_3PMo_{12}O_{40}$ into oxides is carried out over a wider range of temperatures than for the parent silicon compound. It is known that the Keggin phosphomolybdic acid in solution gives rise easily to equilibria, which are evident from ^{31}P NMR spectroscopy. This is also valid in the solid state (the solid samples have to be stored in a deepfreeze to avoid partial or even complete degradation). This behaviour could be due to the fact that the bonds between the central tetrahedron and the trimolybdic groups through the oxygen atoms could be weaker for P compounds than for Si compounds. As for the supported $H_4SiMo_{12}O_{40}$ catalysts, supporting $H_3PMo_{12}O_{40}$ on a silica surface enhances the width of the temperature range. However, for the phosphorus compounds, the width of the range is so large that it favours the formation of β-MoO_3 (partial degradation of $H_3PMo_{12}O_{40}$ can occur in the thermal stability range of β-MoO_3). This could explain the interest of using supported $H_3PMo_{12}O_{40}$ as a precursor of supported oxide. This work shows that β-MoO_3 is easily obtained on a silica support, by a simple mild calcination of silica-supported $H_3PMo_{12}O_{40}$ catalysts, and the results obtained could suggest that it could play a determinant role in catalytic processes. Further investigations are in progress to get better understanding of the kinetic mechanism of the action of supported β-MoO_3.

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