Catalytic Oxidation of Methanol by 12-Molybdosilicic Acid Supported on Silica: Dispersion Effect

Jean-Michel Tatibouët,[a] Michel Che,[a] Mohamed Amirouche,[b] Michel Fournier,[b] and Claude Rocchiccioli-Deltcheff[b]

[a] *Laboratoire de Réactivité de Surface et Structure (UA-CNRS 1106), and*
[b] *Laboratoire de Physicochimie Inorganique (UA-CNRS 419), Université Pierre et Marie Curie (UPMC), 4, place Jussieu, 75252 Paris Cedex 05, France*

The acidity of silicomolybdic acid supported on silica, measured by its activity in the dehydration of methanol, is dramatically decreased at a support coverage of less than 0.25 monolayer.

The sensitivity of the mild oxidation of alcohols by oxides to oxide structure is now well documented.[1—3] Another important parameter for catalytic reactions on supported oxides is the dispersion of the active phase. We have recently shown[4] that methanol oxidation is very sensitive to the dispersion of molybdenum oxide on silica: isolated molybdenum ions from grafted samples selectively produce methyl formate, whereas associated ions from impregnated samples produce mainly formaldehyde.

Increasing dispersion is generally obtained by decreasing the concentration of active species on the support, without real control of the nuclearity of the deposit. The supported oxide can exist as clusters, heaps, or isolated ions.[5]

The nuclearity of the deposit can be controlled by the use of polyoxometalates, which can be considered as simplified oxide models. These anionic oxide clusters have the advantage of a known nuclearity. Moreover, since generally they are soluble in various solvents without structure change, they can be used directly, which makes deposition easier.

On this basis, and as a part of studies with silica-supported polyoxomolybdates, we report here results obtained with 12-molybdosilicic acid, $H_4SiMo_{12}O_{40}$ (denoted $SiMo_{12}H$). The crystal structure of this compound[6] shows that the $SiMo_{12}O_{40}{}^{4-}$ anion (denoted $SiMo_{12}$) is of the Keggin type, consisting of 12 MoO_6 octahedra surrounding a SiO_4 tetrahedron. Moreover, cohesion between the Keggin units is achieved by means of hydrated protons and water molecules.

The preparation of $SiMo_{12}H$ has been previously reported.[7] The silica support was dried under vacuum at 150 °C, and then impregnated by the incipient wetness method with aqueous solutions of $SiMo_{12}H$. Excess of water was removed by drying the samples at 100 °C under vacuum.

Samples with various contents of molybdenum have been prepared by this method (SiMoH series, from 1.2 to 30.7 weight % of Mo or, in the approximation of close packing of anions on the silica surface, from 0.02 to 1 monolayer) (see Figure 1).

Oxidation of methanol was used as test reaction. The catalytic activity was measured by using a conventional flow reactor at atmospheric pressure. The reaction temperature was 250 °C and the flow composition (He/O_2/MeOH) was 76.1/16.2/7.7 (mol %). The conversion rate of methanol was always kept lower than 10%. Reaction products were analysed by gas chromatography.

The results are shown in Figure 1. The selectivites for the various products remain essentially constant for samples with coverages larger than 0.25 monolayer (6.7% Mo). Dimethyl ether produced by methanol dehydration is the main product (about 80%), showing the acidic character of the catalyst. The dimethyl ether selectivity rapidly decreases for coverages

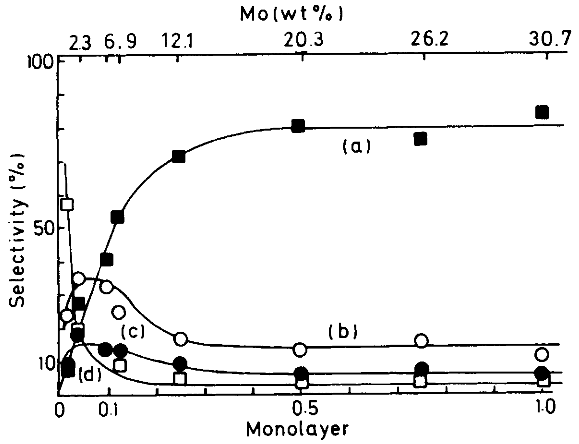

Figure 1. Selectivities in methanol oxidation *versus* surface coverage (and Mo weight %) for the SiMoH series; (a) Me_2O; (b) HCHO; (c) $(MeO)_2CH_2$; (d) HCO_2Me.

below 0.25 monolayer, showing a lowering of the acidic character. At the lowest coverages (less than 0.1 monolayer), almost all the acidic character has disappeared. A strong increase in methyl formate selectivity is observed for the least covered sample (0.02 monolayer).

We have confirmed by i.r. and Raman spectroscopy that the Keggin unit $SiMo_{12}$ is preserved for coverages down to 0.1 monolayer (5% Mo). For lower contents, i.r. and Raman data are not reliable enough to prove unambiguously the presence of $SiMo_{12}$ on the support. Nevertheless, we can state on the basis of Raman data that all the samples are free of organized MoO_3.

It seems possible to correlate the catalytic data to the dispersion of silicomolybdic acid, since, generally, the lower the coverage, the higher the dispersion. If this is true, the results show that high dispersion may be connected with low acidity. This low acidity could arise from a strong interaction of silica and silicomolybdic acid by means of the OH surface groups and the acidic protons, respectively, to form OH_2^+ groups. This interaction resembles the solvation of H^+ by H_2O in solid heteropolyacids.[6,8]

If the aggregates of silicomolybdic acid are large and multilayered, only protons in contact with silica can interact with OH groups, the others being available for the reaction as in the solid compound. The reaction is mainly acidic in character, and essentially produces dimethyl ether by dehydration of methanol.

If silicomolybdic acid is completely isolated on silica, or if only some units are aggregated in two-dimensional rafts, almost all the protons are trapped in the interaction between the polyanion and the support, and the acidic character is low. The catalytic reaction is then mainly of the redox type, and very little dimethyl ether is produced.

The high selectivity for methyl formate at very low coverages (less than 0.1 monolayer) is not clearly understood. I.r. and Raman data in the high-frequency region are consistent with two possible interpretations: (i) a low concentration on the support leads to isolated $SiMo_{12}$ anions;[7] and (ii) high dispersion induces partial degradation of the Keggin units in constitutive fragments,[9] in interaction with silica.

In both cases, the important parameter is the dispersion on the support. Further investigations are in progress to probe these possibilities.

Moreover, the results obtained in this work and with silica-grafted molybdenum catalysts[4] suggest that selectivity for methyl formate could be used as a dispersion-sensitive probe.

In conclusion, it appears that a silica support can interact strongly with catalytic species and modify their catalytic behaviour. In the case of $SiMo_{12}H$, the silica surface could act as a solvent, probably by complexing acidic protons with surface OH groups.

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