Role of Excess of MoO_3 in Fe_2O_3–MoO_3 Methanol Oxidation Catalysts Studied by *X*-Ray Photoelectron Spectroscopy

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Summary The essential role played by excess of MoO_3 in Fe_2O_3–MoO_3 catalysts with the respect to bulk composition Mo/Fe = 1·50 was found on the basis of an *X*-ray photoelectron study to be the production of stoicheiometric iron(III) molybdate at the catalyst surface; this is the active phase for the oxidation of methanol to formaldehyde.

Fe_2O_3–MoO_3 mixed oxides are the most widely used industrial catalysts for the oxidation of methanol to formaldehyde.[1] Although the active phase is generally considered to be iron(III) molybdate, $Fe_2(MoO_4)_3$,[2–4] Fe_2O_3–MoO_3 catalysts show the highest performance only when they contain excess of MoO_3 (Mo/Fe > 1·50) with respect to the iron(III) molybdate.[1] The role played by excess of MoO_3 is still controversial, however. Boreskov *et al.*[2] showed that the highest specific activity (conversion/m^2) for methanol oxidation was attained at Mo/Fe = 1·7 and suggested that excess of MoO_3 was needed to convert iron(III) oxide into iron(III) molybdate. On the other hand, Pernicone *et al.*[5] proposed, on the basis of *X*-ray diffraction analyses, Fe-defective iron(III) molybdate in which two Fe^{3+} ions were replaced by two Mo^{6+} ions, accompanying the insertion of three O^{2-} ions. However, Trifiro *et al.*[3,6] found only one kind of Fe atom in MoO_3–$Fe_2(MoO_4)_3$ catalysts from Mössbauer spectroscopic studies. They concluded that excess of MoO_3 did not affect bulk reduction and re-oxidation processes nor the specific activity for the reaction and that excess of MoO_3 was related only to the textural properties of the catalysts. Taking into consideration the fact that the segregation of excess of MoO_3 inside the catalyst pellets relates to the deactivation of the catalysts,[7] it is important to determine the role of excess of MoO_3 in the oxidation of methanol and to minimize the amount required if its presence is in fact essential for the reaction.

We report here *X*-ray photoelectron spectroscopic (XPS) results on the surface composition and surface structure of Fe_2O_3–MoO_3 catalysts having various compositions. These results lead us to the conclusion that excess of MoO_3 is essential for the formation of stoicheiometric $Fe_2(MoO_4)_3$ at the catalyst surface.

Fe_2O_3–MoO_3 catalysts having various compositions were prepared by adding the required amount of aqueous $Fe(NO_3)_3.9H_2O$ to vigorously stirred aqueous $(NH_4)_6Mo_7O_{24}.4H_2O$ at room temperature, followed by evaporation at 90 °C, drying at 110 °C, grinding in a mortar, and finally calcination at 410 or 600 °C for 5 h in air. The XP spectra of the catalysts were measured on a Hitachi 507 photoelectron spectrometer[8] using Al-*K*α radiation. Binding energies were referenced to the C 1s level (285·0 eV) due to the carbon contaminant. The reproducibility of the binding energies was ±0·2 eV. The XP spectra were also analysed in terms of the relative peak areas of the Fe 2p, Fe 3p, and Mo 3d levels. The effects of carbon contamination on the relative intensities were neglected here, since the C 1s intensities were nearly invariant among the catalysts. Mechanical mixtures of the pure MoO_3 and Fe_2O_3 catalysts were used to obtain the relative atomic sensitivities of the Fe 2p, Fe 3p, and Mo 3d bands. From linear correlations between the Fe 2p/Mo 3d and Fe 3p/Mo 3d intensity ratios and the Fe/Mo atomic ratio, the relative atomic sensitivities were determined to be 0·68 ± 0·02 for the Fe 2p/Mo 3d ratio and 0·15 ± 0·01 for the Fe 3p/Mo 3d ratio. The reproducibility of the surface composition [S_{Mo} = Mo/(Mo + Fe)] thus obtained from the Fe 2p or Fe 3p level was ± 0·015.

The oxidation of methanol over the Fe_2O_3–MoO_3 catalysts was carried out by using a conventional fixed-bed flow reactor in the differential mode at 230—300 °C (O_2/methanol = 1·2). The reaction gas was analysed by gas chromatography.

The binding energies of the Fe $2p_{3/2}$ and Fe 3p levels for the catalysts seemed to be dependent on the composition, with values of 711·4 and 56·2 eV, respectively, at low Mo content [B_{Mo} = Mo/(Mo + Fe) $\leqslant$ 0·6 or Mo/Fe $\leqslant$ 1·5] and slightly but consistently higher values of 711·7 and 56·5 eV, respectively, at $B_{Mo} \geqslant 0{\cdot}62$ (Mo/Fe = 1·63), whereas the Mo $3d_{5/2}$ binding energy was 232·9 eV irrespective of the composition. The Fe $2p_{3/2}$ and Fe 3p binding energies at $B_{Mo} \leqslant 0{\cdot}6$ were in agreement with those for Fe_2O_3, although *X*-ray diffraction analyses showed the presence of iron(III) molybdate alone at moderate Mo concentration. It is considered that the Fe binding energies observed at $B_{Mo} \geqslant 0{\cdot}62$ may be assigned to $Fe_2(MoO_4)_3$.

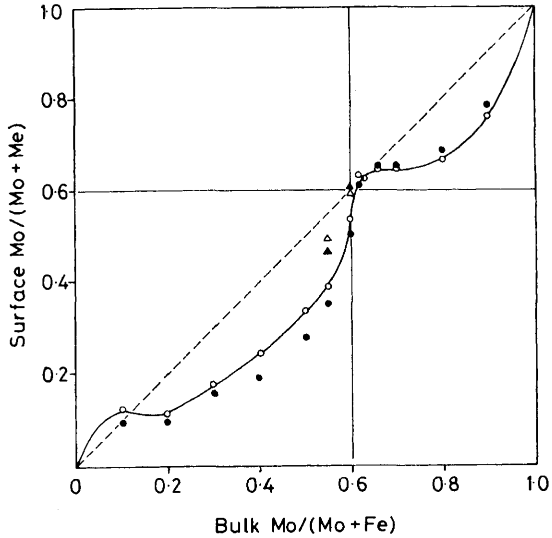

Figure. Surface composition of Fe_2O_3–MoO_3 catalysts as a function of bulk composition. ○, ●: calcined at 410 °C; △, ▲: calcined at 600 °C; filled symbols obtained from the Fe 2p level, and open symbols from the Fe 3p level. The reproducibility of the surface composition was ±0·015 (the corresponding error bars are slightly larger than the sizes of the circles or triangles).

The surface composition of the Fe_2O_3–MoO_3 catalysts calcined at 410 °C is shown in the Figure as a function of the bulk composition [B_{Mo} = Mo/(Mo + Fe)]. In order to obtain information on the surface structure of the catalysts,[9] S_{Mo} values were calculated by using two Fe levels having significantly different binding energies: the Fe 2p (escape depth λ_{2p} = *ca.* 1 nm[10]) and Fe 3p (λ_{3p} = *ca.* 2 nm) levels. With the catalysts calcined at 410 °C, two important conclusions can be drawn from the Figure. (i) At $B_{Mo} = 0{\cdot}60$ or Mo/Fe = 1·50, the surface concentration of Mo is significantly lower than the bulk concentration. S_{Mo} reaches 0·60 only when about 3 wt% excess of MoO_3 is present ($B_{Mo} = 0{\cdot}61$ or Mo/Fe = 1·56). Accordingly, the presence of excess of MoO_3 is essential to produce stoicheiometric iron(III) molybdate at the catalyst surface. This is substantiated by the binding energy shifts of the Fe levels. (ii) Comparison of the surface compositions of the catalysts obtained from the Fe 2p and Fe 3p levels leads to the conclusion that at $B_{Mo} \leqslant 0{\cdot}60$ the catalyst surface is enriched in iron oxide, forming a core structure (S_{Mo} obtained from the Fe 2p level is lower than that from the Fe 3p level), in which iron oxide covers the iron(III) molybdate, whereas at $B_{Mo} \geqslant 0{\cdot}7$, a considerable segregation of Mo occurs over iron(III) molybdate. These findings are consistent with the XP binding energies mentioned above. The agreement of the surface compositions obtained from both Fe levels at $0{\cdot}61 < B_{Mo} < 0{\cdot}7$ substantiates unambiguously the formation of an iron(III) molybdate layer at the catalyst surface.

When the Fe_2O_3–MoO_3 catalysts were calcined at 600 °C, the surface concentration of Mo increased considerably, compared with the catalysts calcined at 410 °C. The catalyst with $B_{Mo} = 0{\cdot}60$ showed a surface composition very similar to that for $Fe_2(MoO_4)_3$, as illustrated in the Figure, although the surface area of the catalyst decreased markedly.

The activity of the catalyst calcined at 410 or 600 °C for the oxidation of methanol was measured and compared with S_{Mo} values. The highest specific activity was obtained exactly at $S_{Mo} = 0{\cdot}60$ which corresponds to stoicheiometric $Fe_2(MoO_4)_3$ formation at the surface, and in both composition ranges $S_{Mo} < 0{\cdot}60$ and $> 0{\cdot}60$ the activity decreased significantly with decreasing or increasing the Mo concentration at the surface. In addition, the XPS study on the reduction behaviour of the catalyst surface with methanol at 300 °C demonstrated that iron(III) molybdate was easily reduced, while the remaining MoO_3 was not. These facts clearly indicate that the active phase is iron(III) molybdate, in conformity with other workers.[2–4]

In summary, it is concluded that the presence of excess of MoO_3 in Fe_2O_3–MoO_3 catalysts is essential to produce stoicheiometric iron(III) molybdate at the catalyst surface; this is the active species for the oxidation of methanol. The surface of the catalyst has a core structure, excess of Fe_2O_3 and unchanged excess of MoO_3 covering the iron(III) molybdate and reducing the catalyst performance.

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