X-ray Photoelectron Spectra of a Supported Molybdenum Hexacarbonyl Olefin Disproportionation Catalyst

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Summary X-ray photoelectron spectra for a catalyst prepared by condensing molybdenum hexacarbonyl on to γ-alumina indicate that the molybdenum in an activated disproportionation catalyst does not exist as hexacarbonyl but is displaced to higher binding energies; the loss of activity on exposure of such a catalyst to air is shown to be accompanied by oxidation of the molybdenum.

MOLYBDENUM hexacarbonyl supported on alumina is known to be a catalyst for the disproportionation of olefins.[1] Catalysts of this type have only minimal activity until they are subjected to mild thermal activation under vacuum for about one hour.[2] Such activated catalysts can cause the disproportionation of propylene at 298 K.

Spectra were obtained[3] on an A.E.I. ES100 electron spectrometer under the control of a DS 100 data system using Al-K_α radiation. Binding energies were measured by using the known[4] value for the carbon 1*s* level of Group VI metal carbonyls to determine the binding energy of the aluminium 2*p* electrons in the alumina: this in turn was used as a calibrating point for other spectra.

The figure illustrates the molybdenum 3*d* region of the spectrum for a sample treated consecutively as follows: (A) molybdenum hexacarbonyl condensed at 173 K on to γ-alumina which had previously been heated to 573 K for 1 h at 10^{-3} Nm^{-2} in the spectrometer; (B) the system was allowed to attain room temperature for 1 h; (C) was heated to 373 K for 45 min; (D) was exposed to air at room temperature for 10 min.

Spectrum (A) together with the carbon 1*s* and oxygen 1*s* regions which are not illustrated, is in agreement with published work[4] and confirms that the alumina surface is covered with bulk molybdenum hexacarbonyl. Warming to room temperature (B) causes removal by sublimation of molybdenum hexacarbonyl from the system but there remain on the surface molybdenum species in which the molybdenum 3*d* binding energy is *ca.* 1 eV higher than that

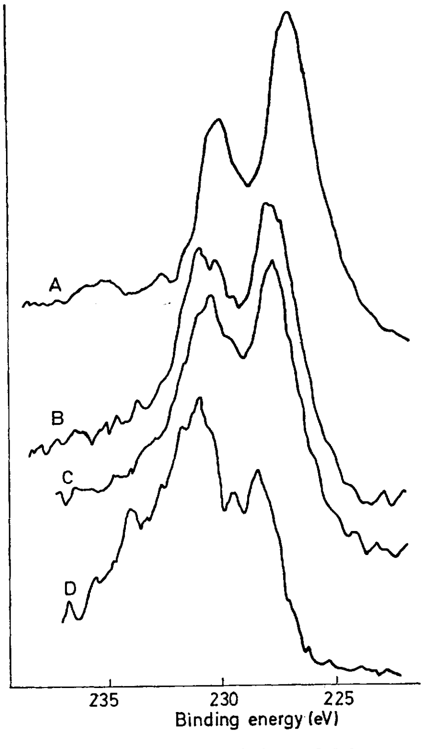

FIGURE. *Photoelectron spectra of the molybdenum* 3d *region of a supported molybdenum hexacarbonyl catalyst.*

of the hexacarbonyl. Loss of the hexacarbonyl is confirmed by the absence of the characteristic[4] carbon and oxygen 1*s* high energy satellite peaks at room temperature. Furthermore the shape of the molybdenum signal, with significantly decreased valley between the 5/2 and the 3/2 levels, suggests that more than one molybdenum species is involved. Similar broad molybdenum signals have been observed[5] for molybdates supported on alumina and have been attributed to association with electron withdrawing sites of differing strengths on the alumina: it is reasonable to suppose that a similar explanation is applicable to the present spectra. The major shift, of the order of 1 eV, seems to be too large and too discrete to be due to support acidity and could result from a change in the oxidation state of the molybdenum.

The spectra of (B) and (C) show no significant difference in agreement with the suggestion[2] that activation of the catalyst by heating to 373 K is likely to be accompanied by loss of carbon monoxide ligands from the molybdenum. There is evidence[6] that carbonyl ligands around a central metal atom have a small net electron withdrawing effect. The chemical shift observed for molybdenum on removal of carbon monoxide ligands is thus likely to be small and the fact that spectra (B) and (C) show no significant difference is not surprising. A comparison of the carbon 1*s* levels in spectra corresponding to (B) and (C) reveals that the signal attributable to the carbonyl carbon is reduced in intensity on heating to 373 K which confirms the loss of carbon monoxide.

The exposure of the catalyst to air, spectrum (D), causes a striking change. As well as a considerable overall shift to higher binding energy, presumably due to further oxidation of the molybdenum, the shape of the peak shows that it is composed of several different species or molybdenum in several different chemical environments.

We conclude that the active species in disproportionation catalysts of this type are molybdenum entities which have an oxidation number probably greater than zero and certainly less than six attached to electron withdrawing sites on the alumina.

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