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The XPS of Some MoO_3/Al_2O_3 Catalysts and the Distribution of Molybdenum in Catalyst Extrudates following Drying and Calcining

Previous studies have indicated three major differences between unsupported MoO_3 and Mo(VI) supported on alumina (*1*, *2*):

(a) a binding energy shift of 0.5–1.0 eV in Mo(VI) when supported;
(b) an increase in half-width of the Mo(3d) spin states when supported;
(c) a relative decrease in resolution between spin states, a direct corollary of (b) because the Mo(3d) spin states are only 3.0 eV apart.

In this note we describe the X-ray photoelectron spectra (XPS) of MoO_3/Al_2O_3 catalysts, prepared by dry impregnation of both alumina extrudates and powder, and interpret features of the spectra, viz., the binding energy, width, and resolution of the Mo(3d) peaks as well as the peak intensity ratios of Mo($3d_{5/2}$) to Al(2p), in terms of the dispersion and distribution of molybdenum in the catalysts as a function of loading and calcination. The basis for our analysis is qualitative and straightforward. The binding energy shift in Mo(VI) noted above for MoO_3 supported on alumina arises from a unique interaction between MoO_3 and the alumina support (*1*, *3*). It is also associated with a broadening of the Mo(3d) peak width. Consequently, we should be able to differentiate between monolayer MoO_3, with a binding energy and peak width appropriate to MoO_3 interacting with alumina, and multilayer or aggregated MoO_3, with a binding energy and peak width more appropriate to bulk MoO_3. The relative distribution of molybdenum between the surface of an extrudate and its interior can be determined from the Mo($3d_{5/2}$): Al(2p) peak intensity ratio of a pelleted and a powdered sample of a catalyst at a given loading. The ratio will be the same from both samples in a uniformly distributed catalyst. With shell impregnation the ratio from the pellets will be larger.

γ-Alumina (Akzo Chemie, surface area 300 m^2 g^{-1} and water pore volume 0.7 cm^3 g^{-1}) as extrudate (diameter 1.7 mm, length 3.5 mm) or powder (100–200 mesh) was impregnated with an aqueous solution of ammonium heptamolybdate by the dry (or pore-filling) method. The samples were dried at 120°C for 3 h and calcined at 500°C for 24 h in static air. XPS data were obtained using an AEI ES 100 spectrometer. It is our experience that binding energies are repeatable to +0.2 eV. The spectroscopic measurements are summarized in Table 1 and representative spectra are shown in Fig. 1.

Considering the binding energies of the extrudate samples, we note that the average Mo($3d_{5/2}$) value for the dried samples (232.0 eV) is 0.7 eV lower than for the calcined samples (232.7 eV). This suggests that a Mo(VI) multilayer present after drying has become a Mo(VI) monolayer after calcination, but we must ask whether the binding energy of a monolayer of Mo(VI) after drying is equal to the binding energy of the same monolayer after calcination. Powdered samples 2 and 7 answer that question. The binding energy shift after calcination is 1 eV but there is no change in peak width or Mo/Al intensity ratio. The greater peak width of the dried specimen (sample 2) compared with extrudate samples at adjacent loadings (samples 1 and 3) supports the hypothesis of a monolayer. Thus, for the change from multilayer MoO_3 to monolayer MoO_3 to be confirmed we in fact need three experimental observations:

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TABLE 1

XPS of MoO_3/Al_2O_3 Catalysts

Sample number	Physical form	Heat treatment (°C)	Mo (wt%)	B.E.[a] $Mo(3d_{5/2})$ (eV)	Peak width[b] (eV)	$\frac{I(Mo)^c}{I(Al)}$	Resolution[d]
1	Extrudate	120	2	232.0	5.1	0.56	R
2	Powder	120	3	232.0	5.6	0.14	NR
3	Extrudate	120	4	232.0	5.3	0.92	R
4	Extrudate	120	9	232.0	5.1	2.84	R
5	Extrudate	120	15	232.1	5.0	5.81	R
6	Extrudate	550	2	232.7	5.5	0.29	NR
7	Powder	550	3	233.0	5.6	0.16	NR
8	Extrudate	550	4	232.9	5.3	0.47	NR
9	Extrudate	550	9	232.7	5.05	6.35	R
10	Extrudate	550	15	232.5	5.0	4.19	R
11	Crushed extrudate	120	9	232.5	5.9	0.43	NR
12	Crushed extrudate	550	9	232.9	5.6	0.56	NR

[a] Binding energy relative to Al(2p) = 74.5 eV.

[b] Width of *both* Mo(3d) peaks at half-height of $Mo(3d_{5/2})$ peak.

[c] Relative intensity of $Mo(3d_{5/2})$ and Al(2p) peaks.

[d] $Mo(3d_{3/2})$ and $Mo(3d_{5/2})$ peaks: R, resolved; NR, not resolved (cf. Fig. 1).

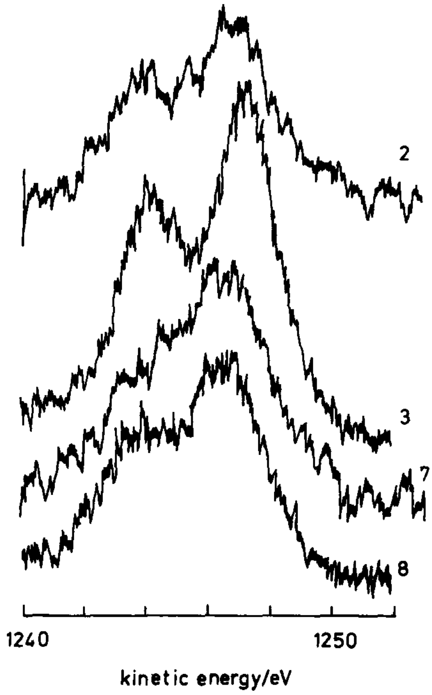

FIG. 1. XPS of MoO_3/Al_2O_3 catalysts showing the Mo(3d) peaks. Numbers on the spectra refer to the samples listed in Table 1.

(a) an increase in binding energy;
(b) an increase in peak width;
(c) a decrease in Mo/Al intensity ratio, either because there is less shielding of the aluminium or because molybdenum moves away from the surface.

The extrudate results at the lower loadings, 2 and 4 wt%, meet all these criteria. The results at 9 and 15 wt% show a lower shift in binding energy, a proportionately smaller shift in intensity ratio (sample 9 is anomalous), and no increase in peak width. Thus, at loadings of 9 and 15 wt% molybdenum the change from multilayer to monolayer cannot be completely accommodated.

The question whether the molybdenum moves from the surface of the extrudate into its interior following calcination can be answered by comparing the whole and the crushed extrudate at the same loading. Samples 4 and 9 should be compared with samples 11 and 12, all at a nominal 9 wt% molybdenum loading. Samples 4 and 11 indicate that the distribution of molybdenum in dried catalysts prepared by dry impregnation is not uniform. Despite the Mo/Al intensity ratio for sample 9 being anomalous, this conclusion must also be valid for the calcined catalysts as we can see by comparing samples 8 and 10. Comparing samples 11 and 12 we see that the Mo/Al ratio is greater in the crushed extrudate following calcination (sample 12) clearly indicating an increase in the bulk level of molybdenum. This conclusion can be extended to lower loadings by comparison of the powdered samples 2 and 7 with adjacent samples.

We conclude that at loadings below 9 wt% molybdenum there is a monolayer dispersion of molybdenum following calcination, but above 9 wt% some multilayers are present. Dry impregnation of alumina extrudate with a molybdenum(VI) solution gives a shell-impregnated catalyst at all loadings. Calcination induces movement of molybdenum from the surface of the extrudate to its interior but does not result in a completely uniform distribution.

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T. EDMONDS

BP Research Centre
Chertsey Road
Sunbury-on-Thames
Middlesex TW16 7LN, England

P. C. H. MITCHELL

Department of Chemistry
University of Reading
Whiteknights
Reading RG6 2AD, England

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