Photoreduction of Silica Supported MoO_3

By Pio Forzatti* and Claudio Attardo
(*Istituto di Chimica Industriale del Politecnico, Piazza Leonardo da Vinci* 32, 20133 *Milano, Italy*)
and Ferruccio Trifirò
(*Istituto di Technologie Chimiche Speciali, Facoltà di Chimica Industriale, Viale Risorgimento* 4, 40136 *Bologna, Italy*)

Summary Silica supported MoO_3 is photoreduced on irradiation at *ca.* 350 nm provided that water vapour is present during thermal treatment carried out at high temperature prior to irradiation.

Photoreduction occurs upon irradiation, at *ca.* 350 nm, of silica supported MoO_3 (5·5% by wt. MoO_3 on Ketjen FV SiO_2). No vacuum pre-treatment was applied and irradiation was carried out at atmospheric pressure in air. That reduction had occurred was indicated by a change of colour to blue, causing a broad absorption band at λ *ca.* 700 nm, and by appearance of an unsymmetrical signal in the e.s.r. spectrum with two g factors, $g_{\perp} = 1{\cdot}93$ and $g_{\parallel} = 1{\cdot}87$. The absorption in the visible region arises from intervalence charge transfer transition $Mo^{V} \rightarrow Mo^{VI}$.[1] The e.s.r. signal is attributed to Mo^{V} $4d^1$ ions.[2]

The behaviour upon irradiation depends on whether MoO_3–SiO_2 was calcined in humid air or in dry oxygen. The samples fired in dry oxygen were insensitive to the u.v. light while those calcined in humid air were photoreduced on irradiation. It was possible to bleach the induced colouration by means of thermal treatment in humid air or in dry oxygen at high temperature (500 °C), which finally resulted in the re-oxidation of the samples. The bleached samples did not show the absorption band in the visible region (Figure, curves c and e) or the e.s.r. signal. Again, different behaviours were observed on further irradiation: the u.v. light did not affect the sample bleached in dry oxygen while the sample bleached in humid air was photoreduced.

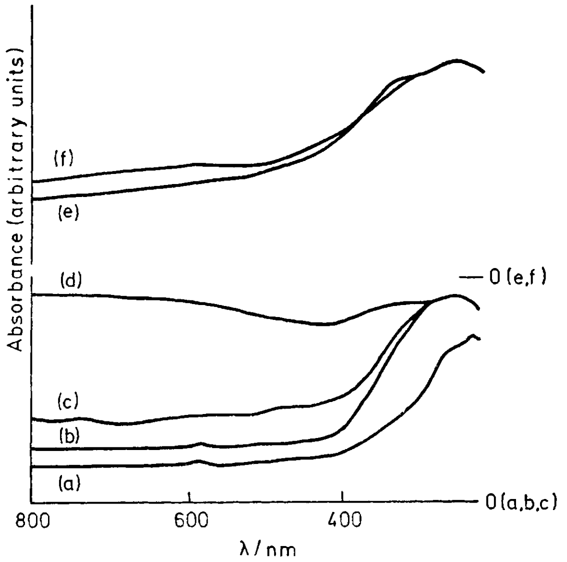

FIGURE. Diffuse reflectance spectra of: (a) SiO_2; (b) MoO_3–SiO_2 calcined in humid air; (c) MoO_3–SiO_2 after bleaching in humid air; (d) MoO_3–SiO_2 after irradiation with u.v. light; (e) MoO_3–SiO_2 after bleaching in dry oxygen; and (f) MoO_3–SiO_2 calcined in dry oxygen.

The above colouration process appears to be different from that already reported in the literature for vacuum evaporated MoO_3 layers.[3,4] These layers would be expected to be deficient in oxygen because of vacuum pre-treatment, a property believed to be responsible for the formation of colour centres. Indeed freshly evaporated MoO_3 layers exhibit an e.s.r. signal associated with the Mo^{5+} state which increases slightly as a result of colouration by u.v. irradiation.[3] However in the cases of the MoO_3 systems we investigated there is no reason to assume that they are deficient in oxygen since no vacuum pre-treatment was applied and in fact no e.s.r. signal was observed in the fresh specimen. Therefore in these systems, the change of colour may be attributed to photoreduction.

Information on the presence of surface hydroxy groups which might be of relevance to the observed process was obtained from electronic spectra. All the spectra exhibited an absorption edge at 400 nm due to the charge transfer process $O^{2-} \rightarrow Mo^{6+}$ (Figure).[5] However, a shift to slightly shorter wavelengths could be observed in the samples calcined or bleached in humid air (curves b and c), relative to the samples fired in dry oxygen (curves e and f). The shift can be explained in terms of an erosion of low co-ordination surface features similar to that reported for CaO and MgO owing to the process $O^{2-} + H_2O \rightarrow 2\,OH^-$.[6] The spectra are therefore consistent with the presence of surface hydroxy groups only in the MoO_3–SiO_2 samples calcined or bleached in humid air. This is further substantiated by the results of low temperature but-1-ene isomerization given in the Table. Indeed only the systems calcined or bleached in humid air were found to be active in the isomerization suggesting that reactive acid sites (presumably hydroxy groups) are present at the surface.

TABLE. Isomerization of but-1-ene (4% by volume in N_2) at 60 °C.

Catalyst	Isomer yield (%) after reaction for 6 h
MoO_3–SiO_2 Calcined in humid air	7·4
MoO_3–SiO_2 Calcined in dry oxygen	—
MoO_3–SiO_2 After bleaching in humid air	27
MoO_3–SiO_2 After bleaching in dry oxygen	—
SiO_2 Calcined in air	—

It is noteworthy that models for hydrated surfaces, with hydroxy groups generated by dissociative chemisorption of water, have been proposed in the case of TiO_2[7] and that several observations in the literature indicate that the presence of water or water vapour enhances the ability of TiO_2 and of other materials to participate in photoprocesses.[8]

The mechanism of generation of the hydroxy groups in the photoreduction of MoO_3–SiO_2 could involve formation of vacant sites by release of hydroxy groups on irradiation with u.v. light which would also produce free electrons as a result of band-to-band transitions; these are finally trapped in the vacant sites. A similar explanation has been given in the case of vacuum evaporated thin films of MoO_3 where the vacant sites are believed to form during vacuum pre-treatment.[3] The trapping results in the formation of Mo^{5+} species which result in stable e.s.r. signal and colour centre absorption. Further work is required to clarify this point in order to obtain a suitable model which would account for the observed behaviour.

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