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Volatility of MoO_3 in the Presence of Water Vapor: Highly Dispersed MoO_3/Silica Catalysts Prepared from MoO_3 and Silica by Steam Deposition

In recently published work (*1, 2*) a comparison has been made between MoO_3/silica catalysts prepared by the grafting technique of reacting $MoCl_5$ with surface Si–OH groups and those prepared by conventional impregnation techniques using a molybdenum-containing salt, ammonium paramolybdate; for both preparations fumed silica was employed (Rhône-Poulenc Spherosil XOA 400). It was claimed that grafted catalysts were characterized by better molybdenum dispersion and stronger molybdenum–silica interactions (*1*) and there was evidence to suggest that molybdenum ions were isolated from one another. Furthermore, the coordination of the molybdenum species, revealed by ESR spectroscopy of the hydrogen-reduced material, showed important differences (*2*). In the case of grafted catalysts an ESR signal attributed to a four-coordinated species was detected in addition to those from six-coordinated octahedral and five-coordinated square pyramidal forms of Mo^{5+}. Only the latter two forms were observed in the impregnated catalyst. An examination of the adsorption of N_2O and the formation of O^- on reduced catalysts led Che *et al.* to conclude (*2*) that the presence of the four-coordinate Mo^{5+} species was essential for the decomposition of N_2O to O^- on MoO_3/silica catalysts.

These results are of topical relevance because of the current interest in the oxidation of methane to methanol on impregnated MoO_3/silica catalysts by N_2O in the presence of water vapor as reported by Liu *et al.* (*3, 4*) and others (*5, 6*).

We report the preparation of MoO_3/silica catalysts by the simple process of treating silica at elevated temperatures with wet air preexposed to MoO_3 at 540°C, after the method used by Buiten to adsorb Mo on SnO_2 (*7*) and by Sonnemans and Mars (*8*) to prepare MoO_3/alumina catalysts. MoO_3/silica catalysts prepared in this manner yield, after hydrogen reduction, ESR spectra which closely resemble those obtained from catalysts prepared by the $MoCl_5$ grafting procedure: four-, five-, and six-coordinated Mo^{5+} species can be distinguished in each case.

In a 8-mm-i.d. quartz tube, a 20-mm-long bed of MoO_3 powder (Analar grade, BDH Chemicals Ltd., Poole, England) and a 15-mm-long bed of 150- to 425-μm granules of fumed silica (Cab-O-Sil M-5, Cabot Corp., Tuscola, IL, Aerosil 200, Degussa AG, Frankfurt, FRG) were lightly compressed between plugs of quartz wool (10 mm long) and separated by a 40-mm air gap. The tube was placed inside a long tubular furnace with a supplementary internally concentric heater surrounding the silica bed to provide a (variable) temperature difference between the two beds. Air was saturated with water to give a partial pressure of water vapor of 107 Torr before passing, at a flow rate of 60 ml/mm, through the bed of MoO_3 maintained at 540°C and then through the silica bed at 702°C. After 24 h of such treatment, the silica contained 5.7% (w/w) MoO_3 and possessed a very pale lemon color which, after several weeks, had changed to very faint blue.

As a control, air dried by passage through P_2O_5 and molecular sieve beds was used instead of wet air. Under the same ex-

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perimental conditions, no transfer of molybdenum to silica could be detected; that is, no visible alteration in the colorless state of the silica was observed even after hydrogen reduction and no Mo^{5+} signal could be detected by ESR. However, when the temperature was raised to about 600°C throughout, crystals of sublimed MoO_3 were clearly visible in the interspace and silica bed. For comparison, a 0.29% (w/w) MoO_3/silica catalyst was made by grafting Cab-O-Sil M-5 with $MoCl_5$ following Che's technique (*9*) employing cyclohexane as the refluxing medium. After calcination at 600°C grafted catalysts were colorless and remained thus on prolonged standing.

Steam-deposited catalysts were also prepared with silica-bed temperatures of 655 and 750°C while maintaining other conditions intact. In both cases the same MoO_3 content of 5.6% was obtained. Short deposition periods (2–6 h) revealed that a band of color moved up through the silica bed, suggesting a strong interaction between the silica and the vapor-borne molybdenum. This view was supported when a sample of Aerosil 200 was exposed to the same treatment for 248 h at 630°C. In this extended treatment long needle crystals of MoO_3 accumulated downstream from the silica bed where the reactor tube emerged from the major furnace. No MoO_3 crystals were observed in the immediate region of the silica bed. The amount of molybdenum deposited on the silica in this exposure was also 5.6% (w/w) MoO_3. That this value was the same as that obtained after a 24-h exposure suggests a high sticking efficiency of the vapor-borne molybdenum to the silica surface and, possibly, the formation of a surface molybdate. It is interesting to note that 5.6% corresponds to 1.2×10^{14} Mo atoms/cm^2 of silica surface (assuming the manufacturer's quoted surface area of 200 m^2/g for Aerosil), a value close to that of the surface hydroxyl group concentration, $3–4 \times 10^{14}/cm^2$, originally present on fumed silicas (*10*). Although surface dehydration would be rapid at ~700°C, the transient formation of Si–OH centers in the wet reactant stream would permit the attachment of molybdenum hydroxyoxide molecules via elimination of water to form surface molybdate.

When reduced with 60 Torr hydrogen at 600°C for 90 min, the steam-deposited catalysts were a uniform black color; under an optical microscope granules had a homogeneous appearance similar to smoked glass. The same uniformity of dispersion was observed in the grafted catalysts but at a much reduced color density.

The ESR spectra of both materials were recorded on a Varian E-4 ESR spectrometer at −195°C and as is shown in Fig. 1 were very similar; *g* values, measured with respect to DPPH, for the three identifiable components of the Mo^{5+} peak corresponded closely in each case and agreed with values found by Che *et al.* (*1*) for grafted catalysts and which were assigned to four-, five-, and six-coordinate centers. Spectra similar to that in Fig. 1b were ob-

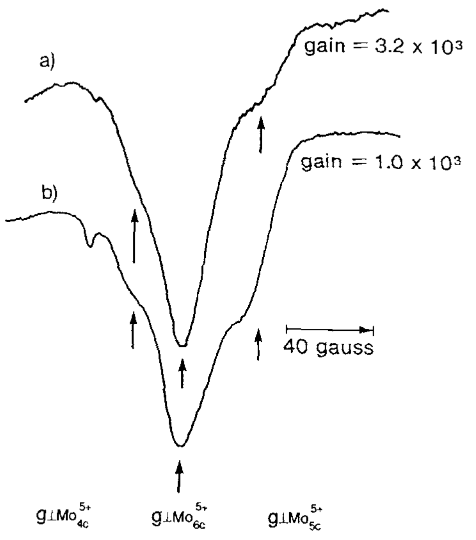

FIG. 1. ESR spectra of Mo^{5+} centers in hydrogen-reduced MoO_3/silica catalysts recorded at −195°C: (a) A 0.29% (w/w) grafted catalyst; $g_\perp Mo^{5+}_{4c} = 1.958$, $g_\perp Mo^{5+}_{6c} = 1.945$, $g_\perp Mo^{5+}_{5c} = 1.924$. (b) A 5.7% (w/w) steam-deposited catalyst prepared at 704°C; $g_\perp Mo^{5+}_{4c} = 1.959$, $g_\perp Mo^{5+}_{6c} = 1.945$, $g_\perp Mo^{5+}_{5c} = 1.927$ ($g_\perp$ values assigned by Che *et al.* (*1*) to Mo^{5+}_{4c}, Mo^{5+}_{6c}, and Mo^{5+}_{5c} are 1.957, 1.944 and 1.926, respectively.)

tained with steam-deposited catalysts prepared at 655 and 750°C.

The steam-deposited catalyst when reduced as described above was active for the formation of O_2^- from oxygen and O^- from N_2O, giving rise to characteristic spectra for these radical ions (*11*).

These results demonstrate that the formation of volatile molybdenum hydroxyoxides, while leading to undesirable molybdenum loss in some cases such as the iron molybdate methanol-oxidation catalyst, can also be used as a means of preparing MoO_3/silica catalysts where the metal oxide is highly dispersed in a homogeneous manner. Indeed, the method could have practical advantages over grafting techniques requiring stringent operating conditions such as a water or oxygen-free environment. Steam-deposited MoO_3/silica catalysts may have useful properties in hydrocarbon oxidation or olefin disproportionation. Certainly these preliminary results show that the coordination of the Mo^{5+} ions in the hydrogen-reduced catalysts is similar in steam-deposited and $MoCl_5$ grafted catalysts as is, approximately, the activity for the formation of O^- and O_2^- radical ions.

In recent publications dealing with the oxidation of methane to methanol with N_2O on MoO_3/silica catalysts (*3–5*) the reported conditions existing in the catalyst bed, namely temperatures of 500–600°C with water vapor in the feed stream at ca. 250 Torr, imply that molybdenum will be rendered volatile due to the formation of the hydroxyoxide, $MoO_2(OH)_2$, as has been pointed out by Pitchai and Klier (*6*). While it is not inconceivable that molybdenum could be lost from the catalyst bed by this process the results reported here indicate that a redistribution of molybdenum on the silica surface will be a more likely occurrence. Indeed, recent reports have emphasized the importance of water to the dispersion of MoO_3 in physical admixture with Al_2O_3 (*12*).

Enhanced molybdenum dispersion may result in changes in catalytic activity for methane oxidation. The effects of molybdenum redistribution therefore could perhaps contribute to an explanation of difficulties experienced in reproducing methanol yields on MoO_3/silica catalysts (*4, 6*).

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