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The Activity of Supported Molybdenum Hexacarbonyl Catalysts for the Disproportionation of Propene

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The disproportionation of propene has been investigated over catalysts prepared from molybdenum hexacarbonyl supported on silica, alumina, silica–alumina and magnesium oxide. The activity of these catalysts is found to depend markedly on the temperature at which the support is outgassed before the molybdenum hexacarbonyl is added and on the temperature of activation after addition of the hexacarbonyl. These variations in activity are discussed in terms of the sites on the supports which are available for interaction with the molybdenum hexacarbonyl, and the possible state of the molybdenum in active catalysts.

INTRODUCTION

The catalytic disproportionation of olefins to yield homologues of longer and shorter chain length has recently been the subject of several reviews (*1, 2*). A wide range of supported transition metal compounds shows catalytic activity for disproportionation, including oxides (*3–8*), sulfides (*4*), and carbonyls (*3, 9, 10*), but a quantitative comparison of the relative activities of the various catalysts has not been possible because of wide variations in the experimental conditions used.

As part of a general investigation of the catalytic properties of supported organometallic compounds we have developed a reproducible method of catalyst preparation by which to compare directly the relative activities of different catalysts for olefin disproportionation. We report here an investigation of the activity of molybdenum hexacarbonyl on several different supports. Supported molybdenum hexacarbonyl catalysts have been examined by infrared (*11*) and EPR (*12*) spectroscopy, and it has been shown that activation of the catalysts by mild heating *in vacuo* causes decomposition of the hexacarbonyl and oxidation of the molybdenum on the support. We considered that a detailed study of the variations in catalyst activity from one support to another, as a function of the temperature at which the supports were outgassed before adding the molybdenum hexacarbonyl and the temperature of activation, might provide further information about the nature of the interaction between molybdenum and the support and on the generation of the catalytically active species.

EXPERIMENTAL METHODS

Molybdenum hexacarbonyl supplied by B.D.H. Ltd. was used without further purification. The catalyst supports used were γ-alumina (Peter Spence, type A), silica gel (Fisher Scientific Co.), magnesium oxide [prepared by hydrolysis of the methylate and subsequent calcination (*13*)], and silica–alumina (I.C.I. Ltd.) containing 45% alumina. All supports were calcined in air at 923 K for 18 hr before use. The surface areas of the supports after calcination, determined by adsorption of nitrogen at 77 K, were: alumina, 1.81×10^5 m^2 kg^{-1}; silica, 4.71×10^5 m^2 kg^{-1}; silica–alumina, 2.08×10^5 m^2 kg^{-1}; magnesium oxide, 4.9×10^4 m^2 kg^{-1}. Propene (Matheson CP grade) was degassed and distilled under vacuum before use, the middle third being retained.

Catalyst samples were prepared in a silica reaction vessel of volume 2.54×10^{-4} m^3, attached to a conventional gas handling line through a water-cooled grease-free joint. The catalyst support (usually 10^{-4} kg) was outgassed *in vacuo* in the reaction vessel at the desired temperature for 1 hr, cooled to room temperature, and about 20 kN m^{-2} of dry oxygen-free nitrogen were admitted. A degassed solution of molybdenum hexacarbonyl in cyclohexane under nitrogen (sufficient to give a 10% by weight molybdenum hexacarbonyl to support ratio) was then slowly run onto the support through a greaseless stopcock at the top of the reaction vessel, and allowed to remain in contact with the support for a period of at least 45 min. The solvent and any excess molybdenum hexacarbonyl were then removed by careful pumping, and the catalyst was activated at the desired temperature *in vacuo*. The prior admission of nitrogen was necessary to avoid deposition of molybdenum hexacarbonyl on the walls of the reaction vessel. Provided all traces of air were excluded, catalysts prepared in this manner gave activities which were reproducible to within better than ±20%.

Catalyst activities were determined by admitting propene into the reaction vessel at 298 K to a pressure of 3.33 kN m^{-2} and measuring the initial rate of disproportionation to ethene and butenes at this temperature. The reaction vessel was connected through a sampling valve to a Perkin-Elmer F 11 gas chromatograph; details of the analysis of the disproportionation products have been given previously (*10*). For low activities (initial rate less than 1% min^{-1}) the initial rates were determined directly from plots of propene concentration against time extrapolated to zero time. Where the activity was high, the initial rate was calculated from the second order rate constant, evaluated as before (*10*). The uncertainty in the initial rates and hence the activities determined by either of these methods is less than ±10%. The activities are expressed as initial rates of propene disproportionation at 3.33 kN m^{-2} and 298 K per unit surface area of support, for convenience of presentation and comparison.

Spent catalyst samples were analyzed for molybdenum by X-ray fluorescence (alumina-supported catalysts) or atomic absorption spectrophotometry (silica–alumina-supported catalysts). Spent catalyst samples were also examined by X-ray diffraction, but no evidence was found for the existence of any new phase.

Results

Effect of Support Pretreatment

The activities of silica-, alumina-, silica–alumina- and magnesium oxide-supported catalysts were determined as a function of the temperature at which the support was outgassed *in vacuo* before adding the molybdenum hexacarbonyl. The results are summarized in Fig. 1. In all cases the supported catalysts were activated *in vacuo* for 1 hr at 373 K after preparation. Any excess

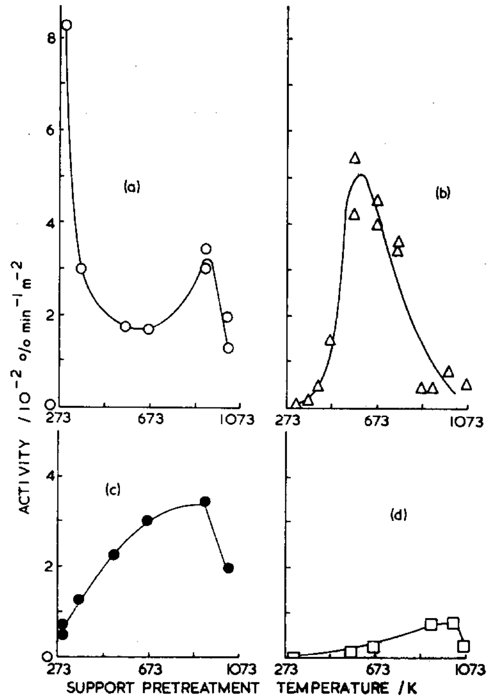

FIG. 1. Variations in catalyst activity with pretreatment temperature of support. (a) SiO_2 support; (b) Al_2O_3 support; (c) SiO_2–Al_2O_3 support; (d) MgO support.

molybdenum hexacarbonyl was removed from the support during activation. In order to determine whether the catalyst activity was directly related to the amount of molybdenum retained by the support, the percentage of molybdenum in spent catalyst samples was measured as a function of the support pretreatment temperature for a series of γ-alumina- and silica-alumina-supported catalysts; the results are given in Fig. 2.

Blank experiments were carried out with the supports alone after outgassing at 973 K, but these showed no activity for propene disproportionation at 298 K.

Catalyst Activation

The variations in activity with the temperature at which the catalysts were activated after addition of molybdenum hexacarbonyl to the support have also been investigated. For each support two series of experiments were performed; one with the support pretreated at 298 K, and one with the support pretreated at the temperature found to give maximum activity (i.e., 573 K for γ-alumina, 923 K for silica-alumina, and 1023 K for magnesium oxide). In the case of silica-supported catalysts maximum activity was obtained on a support pretreated at 298 K, so a second series of experiments was carried out with a silica support pretreated at 1023 K. Catalysts were activated *in vacuo* initially at 373 K for 1 hr, and then for 1 hr at each successive temperature, the activity being measured after each activation step. The results are summarized in Fig. 3. The conditions necessary for obtaining the maximum activity for propene disproportionation from the four catalysts studied are summarized in Table 1.

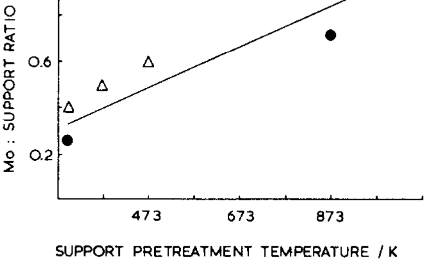

FIG. 2. Variations in amount of molybdenum retained by support after addition of excess $Mo(CO)_6$ with support pretreatment temperature. (●) SiO_2–Al_2O_3 support; (△) Al_2O_3 support.

DISCUSSION

The variations in activity on the different supports indicate clearly the importance of a support-molybdenum interaction in the formation of the active catalyst. The support pretreatment temperatures cover the range from room temperature, where all of the supports are fully hydroxylated, through to 1000 K, which is high enough to

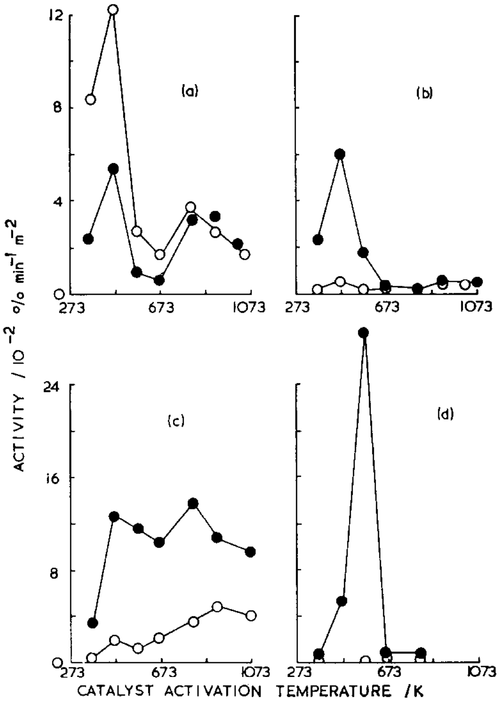

FIG. 3. Variations in catalyst activity with catalyst activation temperature. (a) SiO_2 support, (○) pretreated at 298 K, (●) pretreated at 1023 K; (b) Al_2O_3 support, (○) pretreated at 298 K, (●) pretreated at 573 K; (c) SiO_2–Al_2O_3 support, (○) pretreated at 298 K, (●) pretreated at 923 K; (d) MgO support, (○) pretreated at 298 K, (●) pretreated at 1023 K.

TABLE 1
MAXIMUM RATES OF PROPENE DISPROPORTIONATION

Support	Support pretreatment temp (K)	Catalyst activation temp (K)	Initial rate[a]/ % min^{-1} m^{-2}
γ-Al_2O_3	573	473	0.06
SiO_2	298	473	0.12
SiO_2-Al_2O_3	923	823	0.14
MgO	1023	573	0.29

[a] Propene pressure = 3.33 kN m^{-2}, T = 298 K.

cause complete removal of surface hydroxyl groups. All of the catalysts tested showed some activity on fully dehydroxylated supports. There are, however, marked differences between the four supports when pretreated at lower temperatures (Fig. 1).

Infrared studies (*11*) of molybdenum hexacarbonyl on fully hydroxylated supports showed that the initial interaction between the hexacarbonyl and the support may be envisaged as involving replacement of one carbonyl ligand in the coordination sphere of the molybdenum by a surface hydroxyl group to form a pentacarbonyl species which then decomposes further. If this is the case, maximum dispersion of molybdenum hexacarbonyl will be achieved on a support containing a monolayer of hydroxyl groups. For silica, the maximum in catalytic activity can thus be correlated with the presence of a maximum concentration of hydroxyl groups on the support outgassed at room temperature. For alumina, a similar correlation may be made if it is accepted that alumina surfaces are dehydroxylated less readily than silica (*14, 15*), so that the pretreatment temperature for maximum activity is higher with an alumina support, and that complete removal of physically adsorbed water from the support is required before a maximum concentration of catalytically active molybdenum species can be formed. The amount of molybdenum retained by the alumina support is not reduced when the support is dehydroxylated (Fig. 2); the reduction in activity may occur because the molybdenum is less well dispersed on the dehydroxylated support.

The behavior of silica–alumina-supported catalysts is intermediate between those of silica- and alumina-supported catalysts in that although there is a significant activity on the support pretreated at room temperature, complete removal of adsorbed water by pretreatment at higher temperatures (*16*) leads to enhanced activity, and the activity falls on an extensively dehydroxylated support. This behavior is not unexpected, since the silica–alumina with an alumina content of 45% is likely to contain conglomerates of the pure alumina phase. In contrast, the activity of magnesium oxide-supported catalysts is extremely low unless the support is pretreated above 673 K. This anomalous behavior is probably due to the greater basicity of hydroxyl groups on magnesium oxide compared with silica or alumina. The infrared studies have shown that the hydroxyl groups on magnesium oxide hinder the decomposition of molybdenum hexacarbonyl by stabilizing intermediate subcarbonyl species to a greater extent than on silica or alumina (*11*). EPR measurements indicate that decomposition of molybdenum hexacarbonyl during activation is followed by oxidation of the molybdenum (*12*). While alumina and silica–alumina have surface sites capable of oxidizing aromatic hydrocarbons, for example (*17*), such sites are generated only on outgassing at high temperatures, and have not been observed on silica or magnesium oxide. The reproducibility of catalyst activities and the wide variations in the behavior of different supports seems to rule out the possibility of oxidation being caused by residual adsorbed oxygen (*18*). However, an oxidation mechanism involving electron transfer from molybdenum to support hydroxyl groups would account for the observed pattern of catalytic activities on the hydroxylated supports, particularly the low activity on hydroxylated magnesium oxide.

The variations in activity with the temperature of activation after addition of molybdenum hexacarbonyl to the support (Fig. 3) may also be accounted for in terms of oxidation of molybdenum on the support. One feature common to all catalysts is the occurrence of a maximum in the activity for an activation temperature of 473 K (on silica, alumina and silica–alumina supports) or 573 K (on magnesium oxide). We attribute this maximum to the formation of a maximum concentration of the catalytically active molybdenum species by oxidation from molybdenum(0), assuming that the active species is further oxidized at higher temperatures. It has been suggested that the active species may be molybdenum(IV); while this identification is tentative, the EPR results (*12*) have shown clearly that high concentrations of molybdenum(V) are formed only after activation at temperatures above the temperature for maximum catalytic activity. There is some suggestion in Fig. 3 of a secondary maximum in the activity at high activation temperatures, which is particularly pronounced for silica- and silica–alumina-supported catalysts. High temperature activation *in vacuo* of supported molybdenum trioxide catalysts causes loss of oxygen and reduction from molybdenum(VI) to lower oxidation states (*19, 20*). In view of the demonstrated similarity (*12*) between supported molybdenum trioxide and supported molybdenum hexacarbonyl after high temperature activation, the secondary maxima in Fig. 3 may be attributed to further formation of the active molybdenum species by reduction from higher oxidation states.

In conclusion, it appears that the role of the support in supported molybdenum hexacarbonyl catalysts is twofold, initially to disperse the molybdenum hexacarbonyl, and then to assist oxidation of the molybdenum to form the active species. Maximum activity on any particular support is achieved when both of these conditions are optimized. We can largely account for the results presented here in terms of the model of the active catalyst deduced from spectroscopic studies, although definite identification of the active species is still not possible.

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