Organometallic Complexes of Molybdenum and Tungsten as Catalyst Precursors in the Disproportionation of Propene

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Organometallic complexes of molybdenum and tungsten have been supported on silica or alumina and activated at temperatures at or above 373 K; the activities of the resulting substances as propene-disproportionation catalysts have been determined at ambient temperatures. Catalysts derived from alkyl and acetato-complexes show activities of the same order as catalysts made from supported $Mo(CO)_6$. Tungsten-based catalysts have activities of the same order as molybdenum-derived catalysts, and catalysts derived from less thermally stable complexes are the more active. No propene disproportionation has been observed for chromium-based catalysts.

CATALYSTS prepared from supported molybdenum hexacarbonyl for olefin disproportionation[1] have been studied previously in these laboratories.[2,3] Investigations into the nature of the catalyst have suggested[4,5] that the active species is non-carbonyl containing, and that the complex $Mo(CO)_6$ merely acts as a convenient source of molybdenum in a form which will readily interact with the support to produce, *inter alia*, the catalytically active species. Other main classes of heterogeneous disproportionation catalysts are derived from a variety of supported metal oxides, sulphides, and halides,[6] and operate at temperatures of 323 K and above. However, there seems to be no reason why other organometallic complexes should not exhibit disproportionation activity when supported, particularly if they can readily interact with the support, as is the case with $Mo(CO)_6$.

In the present study, binary alkyls and acetates of molybdenum and tungsten have been supported on silica and alumina using, where possible, the air-free

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wet-mix impregnation technique previously found to give reproducible catalytic activities with $Mo(CO)_6$ catalysts;[3-5] $W(CO)_6$ and some non-organometallic tungsten complexes were also supported and their activities measured for comparison. A preliminary report of the hexamethyltungsten–silica catalyst has been published.[7]

EXPERIMENTAL

The complexes $W(CO)_6$ and WCl_6 were obtained commercially and sublimed prior to use; the following were prepared as in the literature: $M_2(CH_2SiMe_3)_6$ (M = Mo and W);[8] $Mo_2(CH_2CMe_3)_6$;[9] $Mo_2(CO_2R)_4$ (R = Me[10] or CF_3[11]); WMe_6;[12] $[WMe_4\{ON{\cdot}N(Me)O\}_2]$;[12] $W(OPh)_6$;[13] $W(OPh)_5$;[14] and $Cr(CH_2CMe_3)_4$.[15] The complex $W_2(CH_2CMe_3)_6$ was not isolated pure; neopentyl-lithium was treated with WCl_6 in the same manner as for the molybdenum analogue and a cyclohexane extract of the reaction mixture was used.

The catalyst supports used were Peter Spence type A alumina and silica gel (Fisher Scientific Company). They were calcined in air at 923 K for 18 h before use. The surface areas of the supports after calcination, determined by adsorption of nitrogen at 77 K, were: alumina, $1{\cdot}8 \times 10^5$; silica, $4{\cdot}71 \times 10^5$ m^2 kg^{-1}. Propene (Matheson C.P. grade) was degassed and distilled under vacuum before use, the middle-third fraction being retained.

Catalyst samples were prepared in a silica reaction vessel of volume $2{\cdot}54 \times 10^{-4}$ m^3, attached to a conventional gas-handling line through a water-cooled grease-free joint. The catalyst support (10^{-4} kg) was outgassed *in vacuo* in the reaction vessel at the desired temperature for 1 h, cooled to room temperature, and 1 atm dry oxygen-free nitrogen admitted. A degassed solution of the complex was prepared in cyclohexane under a nitrogen atmosphere; WCl_6 was dissolved in diethyl ether and $W(OPh)_5$ in acetone for reasons of solubility. The solution was introduced into the apparatus by a syringe through a serum cap and 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 was then removed by careful pumping, and the catalyst activated at the desired temperature *in vacuo*. Prior admission of nitrogen was necessary to avoid deposition of the complexes on the walls of the reaction vessel. The amount of each complex dissolved was calculated such that the same molar quantity (halved in the case of the dimers) was available to the support in each case; 4×10^{-5}M was equivalent to the amount of $Mo(CO)_6$ used in the ‘ 10% by weight $Mo(CO)_6$ catalysts ’,[2-5] and thus allowed direct comparison of results. In most cases, excess of complex sublimed off the support on activation *in vacuo*. Where sublimation did not occur, the complexes were also supported on charcoal and tested to ensure that there was no contribution to the catalytic activities from ‘ non-interacted ’ involatile thermal-decomposition products. It has been shown[16] that when charcoal is used as a support for the complex $Mo(CO)_6$ an active catalyst is not obtained.

Provided all traces of air were excluded, catalysts prepared in the above manner gave activities which were reproducible to better than ±20%. Catalyst activities were determined by admitting $3{\cdot}33$ kN m^{-2} propene into the reaction vessel at 298 K and measuring the initial rate of disproportionation to ethylene and butenes at this temperature. The reaction vessel was connected through a sampling valve to a Perkin-Elmer F11 gas chromatograph; details of the analysis of the disproportionation products have been given previously.[2] For low activities (initial rate less than 1% min^{-1}), 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 in ref. 2. The uncertainty in the initial rates, and hence the activities, determined by either of these methods was less than ±10%. For the most active catalysts, the rate of disproportionation was probably diffusion limited, which imposes an upper limit on the measured activities. The activities are expressed as initial rates of propene disproportionation at $3{\cdot}33$ kN m^{-2} and 298 K.

RESULTS

The activities of the catalysts are shown in Tables 1 and 2, together with corresponding data for $Mo(CO)_6$. The best catalysts were clearly derived from the organometallic complexes, *i.e.* alkyls, acetates, or carbonyls. Activities of molybdenum-based catalysts were of the same order as their tungsten analogues, where these exist, but the best catalysts were, in fact, derived from hexamethyltungsten. In general, the better catalysts were those obtained from less thermally stable precursors, but the very stable acetate complexes did yield particularly efficient catalysts once they had been activated at 573 K.

The complexes $Mo_2(CH_2SiMe_3)_6$ and $Mo_2(CH_2CMe_3)_6$ are moderately stable but air sensitive. On impregnation and activation at 373 K, light brown catalysts were obtained, the excess of complex being cleanly sublimed off. The complex WMe_6 is an air-sensitive volatile liquid, extremely unstable in its pure form at temperatures above 233 K, but decomposing only slowly at room temperature in cyclohexane solution. The unstable nature of the complex led to problems in estimatimg the amounts impregnated on the support. Handling difficulties were overcome by treating an aliquot portion of the solution with nitric oxide. This quantitatively yielded $[WMe_4\{ON{\cdot}N(Me)O\}_2]$,[7] a considerably more stable crystalline complex which could be weighed to allow estimation of WMe_6 in the original solution. The complex $Cr(CH_2CMe_3)_4$ supported on silica yielded a green species which failed to show any disproportionation activity after exposure to propene for 24 h. Chromium hexacarbonyl was also supported with the same negative results.

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TABLE 1

Heterogeneous molybdenum catalysts for propene disproportionation

Complex	Support	Activation temperature/K	Activity[a] at 293 K/% min^{-1}	Remarks
$Mo(CO)_6$	SiO_2[b]	373	4·0	From ref. 3
	SiO_2[b]	473	5·8	
	SiO_2[b]	573	1·3	
	Al_2O_3[c]	373	0·4	
	Al_2O_3[c]	473	1·3	
	Al_2O_3[c]	573	0·3	
$Mo_2(O_2CCH_3)_4$	SiO_2	373	$<10^{-3}$	These complexes were dry-mixed (because of insolubility in suitable solvents) by grinding under a dry-nitrogen atmosphere
	SiO_2	473	$8·7 \times 10^{-2}$	
	SiO_2	573	4·8	
	Al_2O_3	373	$<10^{-3}$	
	Al_2O_3	473	$6·0 \times 10^{-2}$	
	Al_2O_2	573	$8·0 \times 10^{-2}$	
$Mo_2(O_2CCF_3)_4$	SiO_2	373	$<10^{-3}$	
	SiO_2	473	0·6	
	SiO_2	573	6·7	
	Al_2O_3	373	$3·0 \times 10^{-2}$	
	Al_2O_3	473	0·2	
	Al_2O_3	573	0·2	
$Mo_2(CH_2SiMe_3)_6$	SiO_2	373	0·8	
	SiO_2	473	4·2	
	Al_2O_3	373	1·8	
	Al_2O_3	473	1·4	
$Mo_2(CH_2CMe_3)_6$	SiO_2	373	3·5	
	SiO_2	473	6·4	
	Al_2O_3	373	1·8	
	Al_2O_3	473	1·2	

[a] Given as initial rates of disappearance of propene at 3·33 kN m^{-2}. [b] Surface area = $4·71 \times 10^5$ m^2 kg^{-1}. [c] Surface area = $1·81 \times 10^5$ m^2 kg^{-1}.

TABLE 2

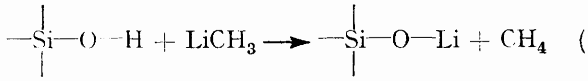
Heterogeneous tungsten catalysts for propene disproportionation

Complex	Support	Activation temperature/K	Activity at 293 K/% min^{-1}	Remarks
$W(CO)_6$	Al_2O_3	373	$1·3 \times 10^{-2}$	Dry-mix method, ref. 11
	SiO_2	373	0·4	
	SiO_2	473	0·4	
	Al_2O_3	373	0·3	
	Al_2O_3	473	0·3	
$W_2(CH_2SiMe_3)_6$	SiO_2	373	0·5	
	SiO_2	473		
	Al_2O_3	373	1·4	
	Al_2O_3	473	3·6	
$W_2(CH_2CMe_3)_6$	SiO_2	373	3·8	The pure complex was not isolated. Solutions were prepared in the same manner as for the molybdenum analogue
	SiO_2	473	$<10^{-3}$	
	Al_2O_3	373	4·2	
	Al_2O_3	473	0·8	
WMe_6	SiO_2	293	$5·0 \times 10^{-2}$	
	SiO_2	373	5·2	
	SiO_2	473	9·0	
	SiO_2	573	9·0	
	Al_2O_3	373	3·6	
	Al_2O_3	473	3·1	
$[WMe_4\{ON{\cdot}N(Me)O\}_2]$	SiO_2	373	$<10^{-3}$	
	SiO_2	473	$5·0 \times 10^{-3}$	
$W(OPh)_6$	SiO_2	373	$<10^{-3}$	
	SiO_2	473	$5·0 \times 10^{-3}$	
$W(OPh)_6$	SiO_2	373	$<10^{-3}$	
	SiO_2	473	$<10^{-3}$	
	SiO_2	573	$9·0 \times 10^{-3}$	
$W(OPh)_5$	SiO_2	473	$<10^{-3}$	The solvent used was acetone
	SiO_2	573	$<10^{-3}$	
WCl_6	SiO_2	373	$<10^{-3}$	The solvent used was diethyl ether
	SiO_2	473	$2·4 \times 10^{-3}$	
	SiO_2	573	$4·4 \times 10^{-3}$	

DISCUSSION

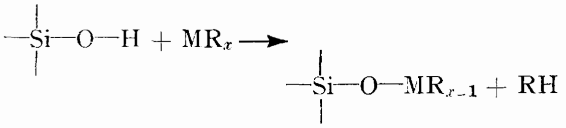
The reason for the high activity of the complex $Mo(CO)_6$ compared with MoO_3 as a precursor for heterogeneous disproportionation is thought to be[4,5] that it provides a more labile source of molybdenum to interact with the support. The formal oxidation states of $Mo(CO)_6$ and MoO_3 are 0 and VI respectively, so it is clear that oxidation to the catalytically active species is considerably more efficient than reduction from Mo^{IV}. Thus the preferred oxidation state of the complex should be low rather than high, but if the ligands can readily be replaced by sites on the support, or can thermally dissociate from the metal atom, it might be expected that active species similar to those formed with known catalysts could be produced.

When $Mo(CO)_6$ is supported on silica or alumina, it has been shown that carbonyl groups are sequentially displaced as carbon monoxide[4] and it seems probable that this also happens to arene and olefin ligands in substituted molybdenum carbonyl complexes, which also yield active catalysts.[16] The initial linking of the molybdenum carbonyl species to the support has been postulated as involving hydrogen bonding with surface hydroxo-groups,[4] but the nature of the subsequent full-bonding step is unknown. Initial bonding of molybdenum or tungsten alkyl complexes to the support is easier to visualise, as the interaction of alkyl-lithium and Grignard reagents with silica has been studied.[17,18] Methyl-lithium reacts as in equation (1). Molybdenum and tungsten alkyl complexes are susceptible


(1)

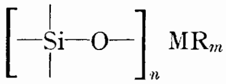
$$-\overset{|}{\underset{|}{Si}}-O-H + LiCH_3 \longrightarrow -\overset{|}{\underset{|}{Si}}-O-Li + CH_4 \qquad (1)$$

to hydrolysis with evolution of alkane,[8,9,12] and reaction (1) is expected to occur readily, providing the initial linkage of the transition metal to the support [equation (2)]. Allyl complexes have been reported


(2)

$$-\overset{|}{\underset{|}{Si}}-O-H + MR_x \longrightarrow -\overset{|}{\underset{|}{Si}}-O-MR_{x-1} + RH \qquad (2)$$

to interact with silica–alumina supports in a similar way, yielding propene.[19] When tetra-allyltungsten is supported, a catalyst is obtained which will disproportionate hex-1-ene.[19] Reaction (2) probably occurs with more than one alkyl group leading to a complex of the form (3), with n unlikely to initially exceed 3 in


(3)

$$\left[-\overset{|}{\underset{|}{Si}}-O-\right]_n MR_m \qquad (3)$$

monomers like WMe_6 for steric reasons. In dimeric species (the other alkyl complexes and acetates), reaction (2) can occur at either one or both of the metal centres, and cleavage of the metal–metal bond is also possible. In order to account for Mo^V signals observed in e.s.r. spectra of $Mo(CO)_6$ catalysts,[5] and also in molybdenum alkyl and acetate catalysts,[20] oxidation must take place on the support. The nature of this oxidation is unknown, but may involve the interaction of co-ordinatively unsaturated molybdenum with further hydroxo-groups.

When the WMe_6–SiO_2 catalyst was exposed to vacuum for several hours to remove excess of WMe_6 and organic products, but without any thermal activation, its i.r. spectrum showed weak C–H stretches in the 3 000—2 900 cm^{-1} region arising from methyl groups still probably attached to tungsten. Furthermore the e.s.r. spectrum of this catalyst[21] shows, on exposure to vacuum at 293 K and at temperatures up to 573 K, signals due to methyl radicals, which may be produced during reductive elimination of methyl ligands bonded to tungsten. This latter evidence illustrates how the intermediate oxidation state of the catalytic species (probably IV or V[5]) may be attained from a precursor of oxidation state VI. Reductive-elimination reactions of this type have been shown for transition-metal alkyl complexes,[21] but they are by no means a common decomposition path.

The acetates, alkoxides, and halides would be expected to interact with the supports in a similar way to the alkyl complexes, producing acetic acid, alcohols, and hydrogen chloride respectively. These compounds are all considerably more stable than the alkyls, and in the case of the acetates activation at 573 K is required to produce a catalyst of high activity. With the tungsten(VI) complexes, the reduction step is expected to be considerably less easy than for WMe_6, and it is no surprise that these complexes yield only poor disproportionation catalysts under these conditions.

The Molybdenum Complexes.—On silica, the complex $Mo_2(CH_2SiMe_3)_6$ yields a catalyst of lower activity than the neopentyl derivative, a reflection of its marginally higher thermal stability. The neopentyl complex shows the same support–activity relation as $Mo(CO)_6$, *i.e.* silica gives a catalyst about twice as active as that with alumina. This trend is reversed with the trimethylsilylmethyl complexes, both with molybdenum and tungsten, and such unexpected behaviour is not easily explained. However, since this behaviour was only observed with the silicon-containing complexes, it is possible that there is some kind of silylation reaction occurring on the alumina support. Such reactions have been observed on surfaces using compounds such as Me_3SiCl[22] and Me_3SiOEt,[23] but in order to silylate with less-active compounds, *e.g.* tetramethylsilane,[24] relatively high temperatures are required.

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The presence of the transition metal atom will undoubtedly have an effect on the reactivity of the trimethylsilylmethyl ligand, and this could account for any enhanced interaction with the support. No further investigations have been carried out which might confirm that silylation does indeed take place.

Molybdenum acetate and trifluoroacetate both yield catalysts similar to the alkyl complexes, but their higher thermal stability ensures that activation temperatures of *ca.* 573 K are required to produce catalysts of high activity. The trifluoroacetate complex produces a better catalyst than the acetate, and it is interesting to note that organofluorine compounds have been shown to enhance activities of supported $Mo(CO)_6$ catalysts,[25] although the reasons for this are not clear.

The Tungsten Complexes.—Tungsten hexacarbonyl supported on alumina has been shown to give an active catalyst,[1,26] but was reinvestigated for this work using the solution impregnation technique and displayed activities around a factor of ten less than the $Mo(CO)_6$ catalysts. While the activities and reproducibility of the catalysts were considerably improved as compared to dry-mix catalysts, they were still a factor of *ca.* 10 less active, and noticeably more sensitive to traces of air, than the molybdenum analogues.

The supported $W_2(CH_2SiMe_3)_6$ catalysts were not significantly less active than the molybdenum catalysts, and showed the same support behaviour. The tungsten neopentyl complex decomposed on the support with no sublimation and, as with the molybdenum catalysts, it was a better precursor than the trimethylsilylmethyl complex. The hexamethyltungsten catalysts were the most active of those examined. On silica in particular, the disproportionation rates were highest, with equilibrium being approached in some cases after less than 15 min.[7] This was also the only catalyst to show measurable activity without any thermal activation. After impregnation at room temperature for 45 min, any excess of WMe_6 is likely to have decomposed, even before activation at higher temperatures. The reason for these particularly high activities is probably a combination of the thermal instability of the precursor and its simplicity as a complex, *i.e.* there are no metal–metal bonds and very volatile decomposition products.

The very poor activity of the catalyst derived from the complex $[WMe_4\{ON{\cdot}N(Me)O\}_2]$ is, in part, a reflection of its high thermal stability, but the presence of the nitroso-containing ligands would be likely to poison any potential catalyst, as nitric oxide has been shown to poison $Mo(CO)_6$ catalysts.[27]

Chromium Complexes.—The usefulness of the molybdenum and tungsten alkyl complexes as catalyst precursors prompted a study of $Cr(CH_2CMe_3)_4$ supported on silica. No heterogeneous disproportionation catalysts of chromium have yet been reported, and the homogeneous catalysts[28] have much lower activities than their Mo or W analogues.

Conclusion.—The catalysts obtained here show that molybdenum or tungsten complexes may provide efficient catalysts if there is a suitable means of interaction with the support. Formal oxidation state is not important, provided that high oxidation-state precursors can be reduced at some stage during catalyst preparation. The active catalysts in this work have been derived from only molybdenum or tungsten. Chromium-based catalysts do not appear to be very active in olefin disproportionation, but Re_2O_7 and $Re_2(CO)_{10}$ are known to provide extremely efficient catalysts at 373 K and higher temperatures.[8,29,30] If suitable organometallic rhenium complexes could be supported, catalysts might be obtained which were even more efficient at 293 K than those reported here. Furthermore, ref. 8 mentions disproportionation activity associated with other transition metals, but under very high temperature conditions. Use of suitable organometallic complexes could improve the conditions required for catalysts based on these metals.

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