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Temperature-programmed decomposition of $[Mo(CO)_6]$: indication of surface reactions and cluster formation

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The influence of the extent of hydroxylation on the surface-mediated decarbonylation of $[Mo(CO)_6]$ has been studied using temperature-programmed decomposition (TPDE). Different CO-evolution spectra were obtained on silica and γ-alumina supports, which can be explained based on the density of the OH groups and the strength of Lewis-acid sites on the surface of the supports. The TPDE spectra changed dramatically with the extent of surface dehydroxylation. The desorption signal can be deconvoluted into individual signals which correspond to the stepwise elimination of one CO group after the other from the carbonyl complex. Intermediate subcarbonyl species are stable on hydroxylated surfaces, whereas evidence for the formation of multinuclear clusters has been obtained on dehydroxylated surfaces. Increasing dehydroxylation of the support lowered the temperature for the first elimination of CO, but the temperature for complete decarbonylation became higher. The reaction mechanism changed from nucleophilic ligand exchange on hydroxylated surfaces to Lewis-acid-assisted decarbonylation on severely dehydroxylated surfaces. Owing to its surface sensitivity, the decomposition of $[Mo(CO)_6]$ can be used as a probe for surface acid–base properties. Besides evolution of CO, variable amounts of H_2 were also observed. Hydrogen is formed in a redox reaction between the metal and surface OH groups. The amount and temperature of hydrogen evolution depended on the chemical nature and the pretreatment of the support. Even on thoroughly dehydroxylated supports, thermal decomposition of $[Mo(CO)_6]$ did not lead to zerovalent metal, but to a slightly oxidized species.

Supported transition-metal carbonyl complexes have catalytic properties which are attracting increasing interest. For example, the system $[Mo(CO)_6]$–alumina is highly active in reactions such as olefin metathesis,[1] hydrogenation[2,3] and hydrogenolysis.[3–5] However, in most catalytic reactions the exact identity of the active site is unknown. It has been shown[6] that heating the adsorbed complex to different temperatures greatly influences the activity. Different species are formed which catalyse different reactions. Hydrogenation of propylene, H/D exchange on alkanes, and the hydrogenolysis of alkanes are generally assumed to indicate a metallic species,[7] whereas a partially oxidized subcarbonyl $[Mo(CO)_2O_2]$ has been identified as the most active species for metathesis.[8] Proper characterization of the catalyst with respect to the nature of the active site is essential for predicting the path of catalytic reactions, and to optimize the activity.

The thermal decomposition of complexes containing zerovalent metal species, notably of metal carbonyls, has been proposed as a method to obtain highly dispersed metal.[9] However, it has been observed that, on heat treatment, many carbonyl complexes do not decompose to the metal, but react with residual surface OH groups with evolution of hydrogen and concomitant oxidation of the metal. Reduction of the resulting oxides with hydrogen at elevated temperature leads to sintering of the metal particles, so that the final dispersion is not considerably higher than that obtained in the conventional method. In order to obtain metal particles of high dispersion it is therefore necessary to prevent oxidation. The surfaces of metal oxides are normally terminated with hydroxyl groups. Heat treatment can remove these. The density of the OH groups as a function of treatment temperature has been determined for a number of supports.[10] Treatment temperatures above 1000 °C are necessary to eliminate the surface hydroxyl groups. However, most studies of the decomposition of supported metal carbonyls have been performed in Pyrex apparatus. They were therefore restricted to temperatures below 550 °C and consequently deal mostly with hydroxylated or partially dehydroxylated supports.[9]

Brenner and Burwell[8,11,12] investigated the decomposition of $[Mo(CO)_6]$ on partially dehydroxylated supports (γ-Al_2O_3, SiO_2) in detail and characterized the subcarbonyls and oxidation state of the molybdenum species upon activation to different temperatures. Thermal decomposition of $[Mo(CO)_6]$ on partially dehydroxylated supports leads to a catalyst with high activity for metathesis, where the active site is believed to be a co-ordinatively unsaturated and partially oxidized molybdenum species (probably Mo^{2+}).[13]

The presence of a support thus greatly affects the thermal decomposition of the complex. Pure $[Mo(CO)_6]$ is not sensitive to air and is stable at room temperature. It can be sublimed but decomposes above 150 °C; the decomposition process is autocatalytic and appears to be a single-step reaction. When deposited onto a support, however, $[Mo(CO)_6]$ can interact with surface Lewis-acid and Bronsted-base sites, rendering it more reactive and unstable. The system $[Mo(CO)_6]$–alumina is not only air sensitive, but starts to decompose at a much lower temperature. Moreover, the decarbonylation process occurs over a wide temperature range. On partially dehydroxylated alumina decarbonylation up to a temperature of 100 °C gives the isolable subcarbonyl species $[Mo(CO)_5]$(ads), $[Mo(CO)_4]$(ads) and $[Mo(CO)_3]$(ads).[11] Each of these initial decarbonylation steps is reversible.[14,15] Further heating of the tricarbonyl is accompanied by evolution of hydrogen together with the loss of the remaining CO groups. By 270 °C about 2 H per Mo have been produced in this reaction, increasing to more than 4 H by 725 °C. Thus, decarbonylation beyond the tricarbonyl species is accompanied by oxidation of the Mo^0. Hydrogen is obviously produced in a redox reaction between surface OH groups and the molybdenum subcarbonyl. Complete decarbonylation is irreversible. On a highly dehydroxylated alumina support, however, stable intermediate subcarbonyls are not formed, and even after heating to 500 °C the average oxidation state of Mo is only about 0.3. Obviously, the decarbonylation pathway depends on the extent of surface hydroxylation.

In this paper, we report the influence of support pretreatment on the decomposition pathway of adsorbed $[Mo(CO)_6]$. In par-

ticular, the effect of increasing surface dehydroxylation has been addressed. Evidence for the formation of multinuclear cluster species on fully dehydroxylated surfaces is presented.

Calculations

Temperature-programmed desorption (TPD) or decomposition (TPDE) can be used to study the kinetics of desorption and decomposition, surface-catalysed reactions of adsorbates with a reactive gas as well as reactions between co-adsorbates.[16] The technique is frequently applied in surface science and catalysis to measure surface coverages and to determine adsorption energies.[17]

Thermal desorption is the removal of adsorbed species from a surface by heating. The time and temperature dependence of the surface coverage θ under desorption conditions is described by the Polanyi–Wigner equation (1)[16] where $r(\theta)$ is the rate of

$$r(\theta) = -\mathrm{d}\theta/\mathrm{d}t = \nu(\theta)\theta^n \exp[-E(\theta)/RT] \quad (1)$$

desorption, $\nu(\theta)$ is the pre-exponential factor of desorption, $E(\theta)$ is the (coverage-dependent) activation energy of desorption, t is time, n is the order of desorption, R is the gas constant and T the temperature; for a linear temperature ramp $T = T_0 + \beta t$ where β is the heating rate and T_0 the initial temperature.

Quantitative evaluation of thermal desorption spectra is normally only possible when the surface is uniform and provides only a limited number of well defined adsorption sites. For coverage-independent desorption parameters and first-order kinetics, differentiation of the Polanyi–Wigner equation gives (2). Redhead[18] showed that, with some approximations,

$$E/RT_m^2 = (\nu/\beta)\exp(-E/RT_m) \quad (2)$$

one obtains a simple linear relation (3) between the temperature

$$E = RT_m[\ln(\nu T_m/\beta) - 3.64] \quad (3)$$

at the peak maximum, T_m, and the desorption energy E. This equation is frequently applied to determine E from a single TPD spectrum. One has to assume a value for ν. Following common practice, we choose $\nu = 10^{13}$ s^{-1}.

We show in this work that the elimination of CO from the metal carbonyl complex can be treated with the same formalism as the thermal desorption of an adsorbate from a surface. Since the initial surface coverage with metal carbonyl complexes is low, it is unlikely that the stability of the complex is influenced by other adsorbed molecules. It was assumed that the desorption steps follow (pseudo-) first-order kinetics. The observed signal was interpreted as the result of successive CO-elimination steps rather than as desorption from energetically different states. This interpretation is justified by the observation that on some supports, *e.g.* partially dehydroxylated silica, the desorption signal is very narrow. In this case the influence of surface heterogeneities on the bond energies within the complex is obviously negligible. The observed desorption profile is indeed even narrower than predicted by the Polanyi–Wigner equation for a single-step reaction. However, we have shown that sharper signals are the consequence of consecutive reactions with very similar rate constants.[19] The observed desorption spectra were deconvoluted into individual CO-dissociation signals with the assumption that the reaction proceeds through the successive elimination of one CO molecule after the other from the complex. For the deconvolution, a number of Gaussian functions was summed in order to obtain a good fit to the observed desorption profile. The area of each Gaussian contribution has to correspond to one CO. The minimum width is given by the 'natural linewidth' of a first-order reaction. Computer simulation shows that the linewidth is related to the temperature of the peak maximum, $\Delta T = fT_m$ where the parameter f depends on the heating rate. At the heating rate used, f has a value of approximately 0.064. Broader lines indicate heterogeneity with desorption from states with a distribution of energies. The Redhead expression was then used to obtain activation energies for each rate-determining reaction step.

Experimental

The supports used were fumed aluminium oxide (Degussa aluminium oxide C) and silica gel (Merck). The alumina was pelletized before use by mixing with water and drying overnight in an oven at 100 °C, after which it was ground and sieved. The surface area of the pelletized alumina was only marginally reduced by this treatment. All surface areas were determined by single-point nitrogen adsorption (Micromeritics Flowsorb 2300). The values for the various supports after pretreatment at different temperatures are given in Table 1. The support (0.5 g) was placed in a quartz reactor and pretreated at 500, 800 and 1000 °C for 2–3 h before impregnating with $[Mo(CO)_6]$. The support pretreatment, impregnation with $[Mo(CO)_6]$, and TPDE were all carried out *in situ* in a continuous flow of helium gas. The experimental set-up for TPDE has been previously described.[19] Its main components are the quartz reaction cell (volume 25 cm^3), which is placed inside a temperature-programmed clam-shell oven. A continuous sweep of helium gas is passed over the sample to remove all desorbed species. The evolved gases are analysed in a quadrupole mass spectrometer (Hiden Analytical) which is coupled to the reactor by a differentially pumped interface. For impregnation, $[Mo(CO)_6]$ (*ca.* 5 mg) was dissolved in freshly distilled pentane (5 cm^3) and 4 cm^3 of the solution were injected through a septum onto the pretreated support. All operations were done under flowing helium. The slurry was kept at 0 °C, and the pentane was slowly purged off by the helium flow over about 2–3 h. The solvent is recovered from a cold trap placed downstream of the reactor. The amount of $[Mo(CO)_6]$ sublimed with the solvent can be quantified by measuring the UV absorption of the contents of the cold trap at 290 nm. After the sample is completely dry, the cold trap is exchanged with a U-tube of lesser volume to reduce peak broadening and the time lag between desorption in the reaction cell and detection in the mass spectrometer. The cold trap removes all condensable components from the gas stream and allows only the gases hydrogen and CO into the detector. Most of the measurements were done with a linear ramp of 20 °C min^{-1}. In order to quantify the amount of gas evolved, the instrument was calibrated by injecting a known volume of the gas into the reactor, using a six-port Valco valve with a 250 μl sample loop.

For experiments with fully dehydroxylated supports, strict exclusion of moisture is essential otherwise the support may be rehydroxylated during cooling from the pretreatment temperature or during impregnation. High-purity helium was further dried by passing it through a column with freshly activated molecular sieve placed just upstream of the reactor. The composition of the carrier gas was monitored with the quadrupole mass spectrometer which was tuned for m/z 18. The water signal decreased by a factor of 3 to a value indistinguishable from the background signal in the mass spectrometer [2×10^{-11} mbar (2×10^{-9} Pa)]. Immersing the molecular sieve in liquid nitrogen did not lower the signal any further. Hence, it is concluded that the molecular-sieve trap is sufficient to ensure a moisture-free carrier flow through the set-up.

Despite thorough drying of the carrier gas, the TPDE of $[Mo(CO)_6]$ on fully dehydroxylated alumina pretreated at 1000 °C still showed a hydrogen signal at <500 °C. In order to ensure that this hydrogen did indeed result from a reaction between the $[Mo(CO)_6]$ and residual surface OH groups, and was not caused by other sources like moisture getting into the system when the $[Mo(CO)_6]$ solution was injected, or from a reaction between the hydrocarbon solvent with the highly acti-

Table 1 Surface area, loading and coverage of Mo on different supports

Code	Sample	Pretreatment temperature/°C	Surface area/m^2 g^{-1}	Loading, % w/w Mo	Coverage, Mo nm^{-2}
A500	Alumina	500	101	0.24	0.16
A800	Alumina	800	95.8	0.30	0.21
A1000	Alumina	1000	93.4	0.21	0.15
S200	Silica	200	470	0.14	0.020
S500	Silica	500	450	0.24	0.034
S800	Silica	800	395	0.31	0.049
S1000	Silica	1000	277	0.35	0.078

Table 2 Oxidation state of Mo at 500 °C and OH : Mo ratio on different supports

Code	Oxidation state of Mo at 500 °C	Ratio OH : Mo [a]	H_2 Evolution [b]/ μmol	No. OH per nm^2 reacting with Mo [c]	Dehydroxylation extent, [d] OH per nm^2 [d]
A500	5.4	19.3	27.9	0.69	3.1
A800	0.6	2.86	3.5	0.12	0.6
A1000	0.3	0.67	1.66	0.04	0.1
S200	0.54	224	1.93	0.011	4.48
S500	0.52	57	2.97	0.017	1.94
S800	0.38	11	2.79	0.018	0.55
S1000	0.21	1.8	1.76	0.017	0.14

[a] Calculated from the extent of dehydroxylation and molybdenum coverage. [b] Up to 500 °C. [c] Obtained from the integrated hydrogen evolution signal (assuming that 1 H_2 comes from two OH groups). [d] Data from ref. 10.

vated surface, some blank runs were performed. For these the alumina support was pretreated as before, pure distilled pentane was injected and purged dry. Thereafter, a TPDE was run with the mass spectrometer set to detect *m/z* 2 and 28 for hydrogen and CO respectively. In these experiments neither CO nor hydrogen was detected. In another experiment the cool bath was removed from the trap, the support was pretreated in a similar manner, and *m/z* 18 was observed. No increase in the water signal was recorded during reheating of the support. It has therefore to be concluded that the small amount of hydrogen evolved stems indeed from the reaction of the decarbonylated molybdenum with residual surface OH groups.

In the following, a code M*xxx* will be used to describe the samples, where M = A for alumina and S for silica support, and *xxx* represents the temperature to which the support has been pretreated. Hence, $[Mo(CO)_6]$ adsorbed on alumina which had been pretreated to 500 °C is referred to as A500.

Results

The surface areas of the supports after pretreatment are shown in Table 1. For alumina the surface area did not change with activation up to 500 °C. Upon heating to 800 and 1000 °C the surface area fell marginally by 5 and 7.5% respectively. Silica had a higher loss in surface area, especially upon heating to 1000 °C.

After impregnation with $[Mo(CO)_6]$ and thermal treatment in helium, the product appears greyish. The loading of $[Mo(CO)_6]$ was determined from the integrated CO-desorption signal, assuming that six CO are evolved for each adsorbed Mo. In addition, the molybdenum loading of the thermally treated material was determined by X-ray fluorescence (Link 2000) and inductively coupled plasma atomic emission. The results from the different methods were in good agreement. They also agreed well with the amount calculated from the mass balance of $[Mo(CO)_6]$ introduced into the sample and that recovered from the cold trap. The amount of $[Mo(CO)_6]$ determined in this way corresponds to the strongly chemisorbed species, as physically bound $[Mo(CO)_6]$ will sublime intact from the surface before the decomposition temperature is reached, and therefore does not undergo decomposition. Surface areas were determined on all samples after TPDE. The values were within the reproducibility of the instrument identical with those measured on the pure support material subjected to an identical temperature treatment. The surface coverage with $[Mo(CO)_6]$ can then be expressed in terms of Mo atoms per nm^2. The loading and surface coverage are listed in Table 1 as a function of pretreatment temperature.

Alumina-supported molybdenum hexacarbonyl

Values for the number of OH groups on the surface as a function of pretreatment temperature were taken from Iwasawa.[10] This number decreases from 3.1 nm^{-2} for alumina calcined at 500 °C to less than 0.1 nm^{-2} after heating to 1000 °C (Table 2). However, the surface coverage of Mo was found to be about 0.2 Mo nm^{-2}, independent of the extent of hydroxylation of the alumina support.

The maximum number of $[Mo(CO)_6]$ which can be adsorbed in a monolayer can be calculated from simple geometrical considerations. Taking $[Mo(CO)_6]$ as a spherical particle with a radius of 0.43 nm gives a coverage of 1.5 Mo nm^{-2} for the closely packed surface layer. The experimentally determined coverage of 0.2 Mo nm^{-2} thus corresponds to about 13% of a monolayer. This number can also be compared with the number of defect sites on the alumina surface, which has been reported to be about 0.6% of the surface cations,[20,21] or about 0.12 nm^{-2}. It is therefore possible that the binding sites on dehydroxylated alumina are Al^{3+} cations in a co-ordinatively unsaturated environment, *e.g.* at steps and edges. Such Lewis-acid sites are only formed at very high temperatures.

Typical TPDE spectra of $[Mo(CO)_6]$ on alumina pretreated at 500, 800 and 1000 °C are shown in Fig 1. The CO-desorption spectrum for A500 shows two peaks in the ratio of 1 : 1. This is consistent with the findings of Brenner and Hucul[15,22] who showed that decomposition of $[Mo(CO)_6]$ proceeds to a stable tricarbonyl, $[Mo(CO)_3]$(ads), which decomposes only above 200 °C. On alumina supports which had been dehydroxylated at 800 °C and higher the CO-evolution profile changes, and the spectrum consists of a series of overlapping peaks.

Fig. 2 shows the deconvolution of the signal of CO into its components. Each individual peak has to correspond to an integral number of CO molecules, and the total signal has to correspond to a multiple of 6. For supports dehydrated at >500 °C, integer values for all peaks are obtained only by using a total number of 24 CO, indicating that 4 $[Mo(CO)_6]$ are involved in the reaction. The elimination of one CO molecule

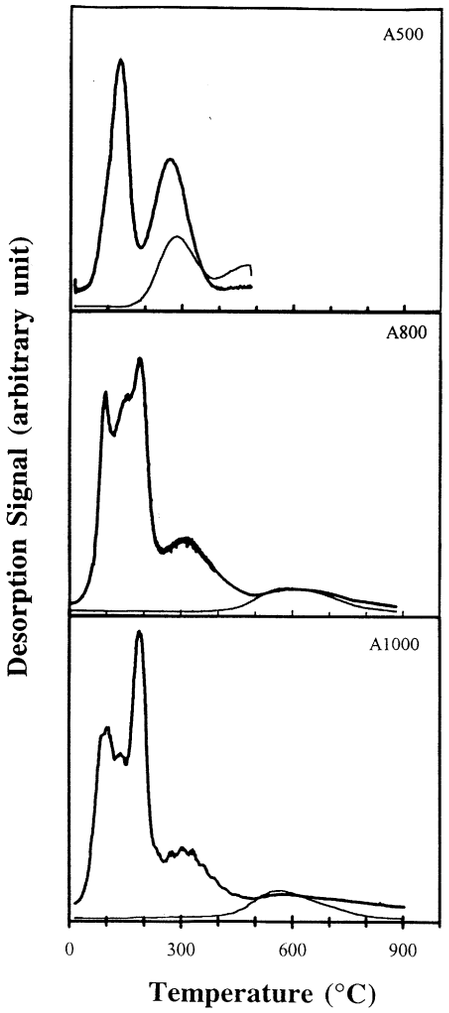

Fig. 1 The TPDE spectra of $[Mo(CO)_6]$ on alumina pretreated at different temperatures; heating rate = 20 °C min^{-1}. Thick lines, CO; thin lines, H_2

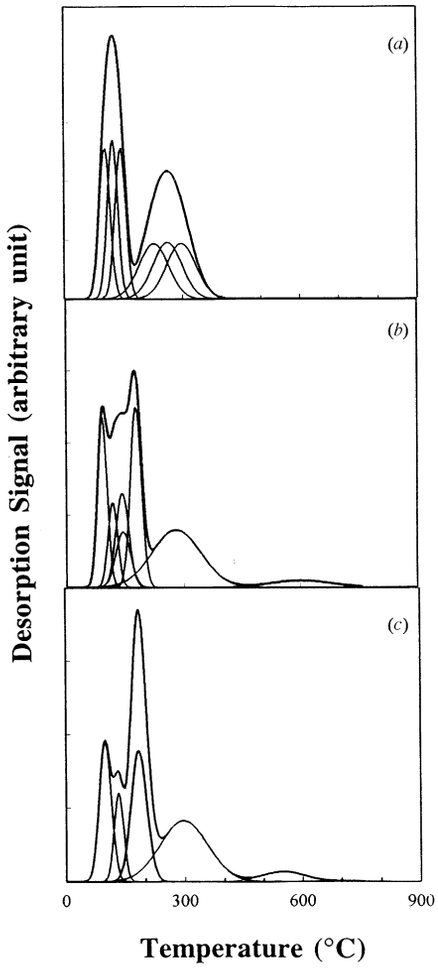

Fig. 2 Deconvolution of the TPDE signal of $[Mo(CO)_6]$ on alumina pretreated at (*a*) 500, (*b*) 800 and (*c*) 1000 °C

for every two Mo atoms is taken as evidence that dimer formation occurs. Since the decomposition of $[Mo(CO)_6]$ finally leads to finely dispersed metal particles on the surface, such clustering appears to be a necessary step in a reaction sequence that leads from the mononuclear complex to the metallic particles. The deconvolution of the spectra for A800 and A1000 gives a series of narrow features followed by two very much broader peaks at higher temperature. Narrow bands arise from the decomposition of well defined surface species, whereas the broad features are typical of desorption from states with a wide distribution of binding energies. The first four bands indicate the loss of 4, then 2, 5, and another 5 CO for every 4 Mo atoms. This is then followed by the evolution of another 7 and finally 1 CO in two broad bands. These broad bands indicate the formation of larger entities, possibly metallic aggregates which are still covered with CO.

The surface-assisted decomposition of metal carbonyls does not in all cases proceed directly to a metal. Rather, it is observed that hydrogen evolves during the temperature ramp, especially at higher temperature. This hydrogen evolution takes place simultaneously with elimination of CO from the complex. The amount of hydrogen evolved depends strongly on the pretreatment temperature. In the case of A500, two hydrogen desorption peaks were observed. The first coincides with the second CO-desorption signal, and a second one has a maximum above 500 °C. Up to 150 °C oxidation of the metal does not take place and the decarbonylation is reversible. However, if the complex is heated to a higher temperature, then not only are the remaining CO removed from the $[Mo(CO)_3]$(ads) complex, but one observes also the evolution of hydrogen. This indicates that the metal becomes oxidized. A second hydrogen-evolution peak is observed above 400 °C, with a maximum at about 525 °C. The final oxidation state of Mo, calculated from the amount of hydrogen evolved, is 5.4 (Table 2). A higher pretreatment temperature leads to a much reduced hydrogen signal as most of the surface OH groups have been removed.

The thermal bond dissociation does not involve an additional activation energy. The activation energies as determined from the desorption temperature using the Redhead equation are therefore identical with the Mo–CO bond energies in the surface-bound complex. The results (Table 3) show that on more highly dehydroxylated alumina the temperature for the first evolution of CO is lowered. The temperature of the onset of evolution of CO seems to be correlated with the extent of surface hydroxylation. Obviously, the interaction of $[Mo(CO)_6]$ with a more highly dehydroxylated alumina surface weakens the Mo–CO bond.

Silica-supported molybdenum hexacarbonyl

The results for the TPDE of $[Mo(CO)_6]$ on silica are different from those on alumina. The surface coverage on silica is lower than that on alumina by a factor of seven or more (Table 1). However, increasing dehydroxylation of the silica surface leads to an increase in the surface coverage, whereas on alumina the amount chemisorbed was essentially independent of the density of surface OH groups.

The TPDE spectra for $[Mo(CO)_6]$ on silica are characterized by a single peak. Evolution of CO starts at a substantially higher temperature than on alumina. Typical TPDE spectra of

Table 3 Temperature of evolution of CO and H_2 during TPDE

Code	First CO peak, °C	Subsequent CO peaks (deconvoluted), °C	H_2 Evolution, °C	Activation energy E_A for first decarbonylation/kJ mol^{-1}
A500	105	263	200–500	105.3
A800	103	141, 184, 190, 299, 560	300–800	104.7
A1000	99	133, 183, 184, 297, 560	400–800	103.6
S200	182	—	120–350	127.5
S500	178	—	120–350	126.3
S800	163	196 (main peak)	140–320	122.0
S1000	163	204 (main peak)	200–250	122.0

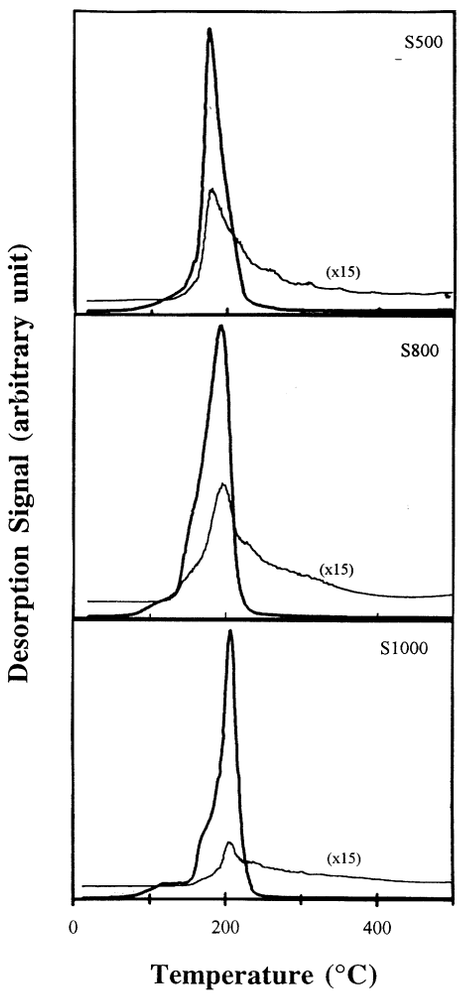

Fig. 3 The TPDE spectra of $[Mo(CO)_6]$ on silica pretreated at different temperatures; sensitivity of detector for H_2 is about 15 times higher than for CO. Other details as in Fig. 1

$[Mo(CO)_6]$ on silica pretreated at 500, 800 and 1000 °C are shown in Fig 3. Partially dehydroxylated silica supports were previously investigated by Brenner *et al.*[23] We confirm their findings of a single very narrow decomposition signal. The sharpness of this signal indicates that it arises from a single species, and surface heterogeneity does not play a role. On more highly dehydroxylated material, S800 and S1000, the onset of decarbonylation begins earlier. A small broad shoulder develops on the low-temperature side of the main peak. Simultaneously, the maximum of the peak shifts to higher temperature. Thus, as in the case of alumina, the temperature range over which decarbonylation takes place increases with increasing extent of dehydroxylation. As discussed for alumina, more complete dehydroxylation will create Lewis-acid centres (metal ions in a co-ordinatively unsaturated environment) accessible on the surface. The shift to lower temperatures of the onset of evolution of CO may be explained by the interaction of the hexacarbonyl complex with the increasing number of Lewis-acid sites. Nevertheless, the decomposition profile for CO remains narrow, and no evidence of clustering is detected even on the fully dehydroxylated silica surface.

The amount of hydrogen produced during the TPDE of $[Mo(CO)_6]$ on silica is much less than that on alumina. The resulting oxidation state of Mo after activation to 500 °C is below 0.6. Thus, the different nature of the supports affects the decomposition reaction of adsorbed carbonyl complexes.

Discussion

After exposure to air at room temperature the surfaces of most oxidic materials are terminated with OH groups and physisorbed water. The latter can be removed by heating to about 100 °C but much more drastic treatment is necessary to remove the residual OH groups. In fact, even at temperatures as high as 1000 °C, there are still some OH groups present at the surfaces of refractive oxides as is evident from IR and Raman spectra and high-temperature TGA. However, the OH groups of different materials differ widely in their nucleophility, that is in the ability of the oxygen to donate electrons from its lone pair and act as a ligand. The compound $[Mo(CO)_6]$ is a relatively large molecule of high symmetry. It will therefore be quite polarizable, and will bind to a surface by dispersive forces. Such a physisorbed nearly spherical molecule is expected to possess high mobility on the surface. When the temperature is increased the physisorbed $[Mo(CO)_6]$ can react with surface OH to form a chemisorbed complex. This complex in turn can become further stabilized by loss of a CO and formation of a bond to the oxygen. The temperature at which this reaction sets in depends very much on the chemical nature of the support. We have earlier reported that the loss of the first CO from the hexacarbonyl complex is a function of the surface nucleophility. Small cations polarize the metal–oxygen bond and reduce the ability of the oxygen to act as an electron donor. Experimentally, it was found that for a large number of different supports the charge density at the metal cation correlates well with the observed desorption temperature.[19]

The present study concentrates on the influence of dehydroxylation on the reactivity of alumina and silica surfaces. The surface-assisted decarbonylation of $[Mo(CO)_6]$ can follow either of two mechanisms depending on the extent of hydroxylation of the surface. (*i*) The $[Mo(CO)_6]$ binds to the surface by ligand exchange with one or more surface OH groups. More nucleophilic OH groups react at a lower temperature. The molybdenum binds as a formally zerovalent subcarbonyl, with three CO ligands being replaced by surface OH groups to form the stable subcarbonyl $[Mo(CO)_3]$ as observed in the case of A500. Since this species is anchored by three bonds to the surface it is not mobile. On increasing the reaction temperature the remaining CO is lost, the metal atom becomes oxidized, and hydrogen evolves. This mechanism will be dominant if the number of surface OH groups is much larger than that of the physisorbed complex.

(*ii*) On a dehydroxylated surface, the density of OH groups is much reduced, and the probability of finding two or more OH

groups sufficiently close to bind to the same molybdenum carbonyl becomes very small. The decrease in the surface density of OH leads to an increase in the number of Lewis-acid sites. This has been confirmed by measurements of the adsorption of CO on dehydroxylated alumina.[24] These Lewis-acid sites form when surface OH groups are removed as water, leading to exposed cations in co-ordinatively unsaturated sites on the surface. The compound $[Mo(CO)_6]$ chemisorbs at these Lewis-acid sites since they are strong electron-pair acceptors whereas the CO ligand is a soft base, its oxygen acting as an electron-pair donor. Such complexes have been identified by IR spectroscopy.[25] The chemisorbed $[Mo(CO)_6]$ has considerable mobility[26] since the surface bond is relatively weak, and a large number of Lewis-acid sites provide almost identical adsorption sites. At the same time, the binding interaction between the complex and the Lewis-acid site leads to charge transfer to the co-ordinatively unsaturated site, resulting in a weakening of the *trans*-CO bond in the complex. The adsorbed carbonyl may move over the surface until it finds a site next to an OH group (s-OH) where the ligand substitution can take place. The resulting $Mo(CO)_5$(OH-s) subcarbonyl is less strongly bound to the surface than the three-fold anchored species formed on the hydroxylated surface, and has therefore still some mobility. This leads to encounters between adsorbed subcarbonyl entities, which react to form surface-adsorbed clusters of higher nuclearity. The accuracy of our measurement is not sufficient to monitor the formation of larger clusters, but we have clear evidence for the formation of dimers and possibly of tetramers on the alumina surface.

The analysis of the evolution of CO from A800 and A1000 shows a series of narrow features corresponding to 4, 2, 5 and 5 CO, followed by much broader bands the area of which corresponds to another 7 and finally 1 CO. The following model is proposed to describe the decomposition of $[Mo(CO)_6]$ on dehydroxylated alumina. In the first step, the $[Mo(CO)_6]$ chemisorbs at a Lewis-acid site L*, equation (4). This species is mobile

$$[Mo(CO)_6]\,(\text{physisorbed}) + L^* \longrightarrow [(OC)_5Mo{-}CO{-}L^*] \quad (4)$$

and can 'hop' from one Lewis-acid site to the next until it encounters a surface OH or O^{2-} group, where it can undergo ligand replacement, equation (5). These chemisorbed sub-

$$[(OC)_5Mo{-}CO{-}L^*] + \text{O-s} \longrightarrow [(OC)_4Mo(\text{O-s})(CO{-}L^*)] + CO \quad (5)$$

carbonyls are still sufficiently mobile on the surface to move towards each other as the temperature is raised. The evolution of one CO for every two Mo atoms may indicate the reaction (6) where for simplicity the binding site is no longer explicitly

$$2\,[(OC)_4Mo(\text{O-s})(CO{-}L^*)] \longrightarrow [Mo_2(CO)_9]\,(\text{chemisorbed}) + CO \quad (6)$$

indicated. Subsequently, about 10 more CO are lost for every four Mo in two rapid reaction steps, leading to a species of the composition $[Mo_2(CO)_4]$ or perhaps $[Mo_4(CO)_8]$, equation (7).

$$2\,[Mo_2(CO)_9] \longrightarrow [Mo_4(CO)_8] + 10\,CO \quad (7)$$

Further loss of CO takes place over a considerable temperature range. The broad feature corresponding to seven CO is probably not the result of a single decomposition step from a well defined cluster species, but the signal is more likely the envelope of many desorption/decomposition processes with slightly different bond energies. The broad feature is thus indicative of the formation of larger metal particles, where the coverage of CO decreases with temperature from two CO per molybdenum atom to a composition of approximately one CO for four Mo, equations (8) and (9).

$$[Mo_4(CO)_8] \longrightarrow [Mo_4(CO)] + 7\,CO \quad (8)$$

$$[Mo_4(CO)] \longrightarrow Mo_4 + CO \quad (9)$$

However, it is unlikely that this remaining CO is bound in a four-co-ordinated (B4) state on a metallic cluster. More likely, it is desorbed as the product of recombination between a carbidic carbon and lattice oxygen, similar to the reaction which has been proposed to explain the high-temperature signal observed during TPD of CO from metallic single-crystal tungsten and molybdenum.[27,28] This interpretation is made all the more plausible by the fact that the last desorption signal is separated from the other broad feature by more than 200 °C. The existence of carbidic carbon can also be inferred from Bowman and Burwell's observation of methane, which is evolved alongside hydrogen during activation of $[Mo(CO)_6]$ on dehydroxylated alumina.[29] Recent extended X-ray absorption fine structure work by Lee and Boudard[30] also confirmed the existence of a carbidic species and the formation of clusters with an average Mo–Mo co-ordination number of four during the thermal decomposition of $[Mo(CO)_6]$ on alumina which had been dehydroxylated at 883 °C.

For the silica support, the molybdenum coverage is found to increase with dehydroxylation. The surface of silica is terminated by silanol and siloxane groups. The silanol groups, Si–OH, are fairly acidic. Owing to the strong polarization of the Si^{4+}–OH bond, they are not as good a nucleophile for ligand substitution of CO as is the Al–OH group. Thus substitution of CO by OH on partially dehydroxylated silica does not occur until a much higher temperature is reached (175–190 °C). Under the conditions of the experiment (continuous helium sweep) sublimation occurs as a parallel reaction channel. This explains why the observed loading on silica is about one order of magnitude lower than that on alumina. If $[Mo(CO)_6]$ cannot become anchored to the surface *via* ligand substitution or Lewis acid–base interaction, it will eventually sublime away, resulting in a very low coverage with subcarbonyl species.

When silica is dehydroxylated surface OH groups are removed, exposing Si^{4+} ions in the surface. These species are good Lewis-acid sites which can aid in anchoring the $[Mo(CO)_6]$. Hence, the loading of Mo increases progressively with increasing dehydroxylation (Table 1). A *trans*-CO labilization can occur in the chemisorbed species, so that decarbonylation sets in at a slightly lower temperature. Since the OH groups on silica are poor nucleophiles, it is postulated that the removal of the first CO is unassisted by substitution of OH. This leads to the species $L^*{-}OC{-}Mo(CO)_4$, which however cannot be isolated but decomposes further at a slightly higher temperature without any cluster formation. The magnitude of the *trans* labilization will depend on the strength of the interaction with the surface. Lewis acids of different strength exist at the surface. This heterogeneity is reflected in the width of the initial desorption feature which consists of a plateau about 50 °C wide.

The final oxidation state of the molybdenum depends on the ratio of surface OH to deposited Mo. Lowering the hydroxide concentration by pretreating the support at a higher temperature reduces the extent of oxidation of Mo. Likewise, increasing the loading of Mo at constant surface hydroxylation should also reduce the extent of oxidation. The first factor is well illustrated by the TPDE of $[Mo(CO)_6]$ on alumina. Both factors are seen at work in the case of silica.

The number of OH groups which react with the molybdenum complex is only a fraction of the totally available OH groups. On alumina the oxidation of molybdenum is significantly reduced at OH : Mo ratios less than 3 : 1 (Table 2). For the silica support, OH : Mo ratios are as big as 300 : 1. Nevertheless, the extent of oxidation is much less than on alumina and decreases with increasing dehydroxylation of the support.

In recent spectroscopic studies[21,25] of $[Mo(CO)_6]$ on hydroxy-

lated (treated at 200 °C) and partially dehydroxylated alumina several of the postulated species have indeed been observed: the physisorbed hexacarbonyl, a chemisorbed species identified as $[Mo(CO)_6]$ bound to surface-exposed aluminium ions, a $[Mo(CO)_5(OH\text{-}s)]$ species, as well as a pentacarbonyl species, $[Mo(CO)_5]$. Reddy and Brown[25] postulate that, on partially dehydroxylated alumina, chemisorption of $[Mo(CO)_6]$ occurs at Lewis-acid sites. This leads to weakening of the bond to the *trans*-CO group, which is lost forming the $[Mo(CO)_5](ads)$ complex. The loss of this CO is proposed to be the rate-determining step. Such a mechanism seems to describe the $[Mo(CO)_6]$–silica system where the surface silanol groups have little tendency to act as ligands and to stabilize subcarbonyls. The initial decomposition of the hexacarbonyl occurs at a high temperature of 178 °C, and is facilitated by increasing Lewis acidity of the binding site so that on more highly dehydroxylated surfaces the evolution of CO sets in at a somewhat lower temperature. However, our results for alumina do not agree with the observations of Reddy and Brown. On partially dehydroxylated alumina there are still sufficient OH groups at the surface so that an S_N2 type of nucleophilic ligand-replacement reaction can take place. On supports dehydroxylated at 800 and 1000 °C the onset of desorption of CO shifts gradually to lower temperatures. There is no change in the mechanism of nucleophilic substitution. On partially and fully dehydroxylated alumina surfaces the decomposition of $[Mo(CO)_6]$ is assisted by OH groups. However, the presence of Lewis-acid sites decreases the strength of the Mo–CO bond and accelerates the ligand-replacement reaction.

Reddy and Brown[25] were able to follow the reaction from the physisorbed to the chemisorbed state, and further to the first subcarbonyl species, $[Mo(CO)_5]$, by observing the changes in UV absorption at 410 nm. They reported a rate constant for the first process $k_1 = 2.3 \times 10^{-3}$ s^{-1} at 25 °C, while the decomposition reaction has a rate constant $k_2 = 1.8 \times 10^{-4}$ s^{-1}. From the TPDE spectra we calculate values for k_2 between 6.8×10^{-6} and 2.1×10^{-7} s^{-1} at 25 °C, depending on the extent of surface hydroxylation. Our values are more than three orders of magnitude smaller than the rate constant reported by Reddy and Brown. The higher value applies obviously to a photoassisted reaction since the spectroscopic experiments were done under white light illumination in a diode-array spectrophotometer. In our measurements the sample was kept in the dark, and the rate constants are more likely to represent the intrinsic kinetics of the process.

Conclusion

Molybdenum hexacarbonyl adsorbed on partially dehydroxylated alumina forms a highly dispersed subcarbonyl species, $[Mo(CO)_3](ads)$, upon thermal decomposition at 100 °C in flowing gas. Heating this material further to a temperature of 500 °C results in complete decarbonylation, but produces Mo in a higher oxidation state (>5), which seems to be highly dispersed. On more severely dehydroxylated alumina (dried at 1000 °C), Mo with an oxidation number near zero (≈0.3) can be obtained after heating to 500 °C. Higher heating leads to further oxidation of the metal. The TPD profile gives evidence for the formation of bi- and perhaps tetra-nuclear molybdenum subcarbonyls adsorbed at the surface which are intermediates on the way to the formation of metallic particles. The decomposition on silica supports follows a different reaction mechanism. On partially dehydroxylated SiO_2 surfaces the tricarbonyl does not form as a stable intermediate. Instead, complete decarbonylation takes place in a single step once a sufficiently high temperature is reached. On more highly dehydroxylated silica the presence of Lewis-acid sites seems to stabilize the subcarbonyl $[Mo(CO)_5]$, but it loses the remaining 5 CO at a slightly higher temperature simultaneously, resulting in Mo of near zerovalent state. Metallic Mo of very high dispersion is formed but the maximum loading which can be achieved is low due to the poor ability of silica to chemisorb $[Mo(CO)_6]$.

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