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The Remarkable Decarbonylation of Chromium, Molybdenum, and Tungsten Hexacarbonyls Supported on Silica and the Nature of These Materials as Heterogeneous Catalysts

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The temperature-programmed decomposition (TPDE) of the hexacarbonyls supported on SiO_2 gives rise to a single, narrow peak which is quite uncharacteristic of high surface area supports. Unlike Al_2O_3, SiO_2 does not sufficiently stabilize zerovalent subcarbonyl species during TPDE to allow for their ready isolation. Nonetheless, such species exist during the initial stages of TPDE and at least some of them are reversibly formed as was found for all of the subcarbonyl species identified on alumina. Thus, the hexacarbonyls provide a route to low-valent, supported Cr, Mo, and W which cannot be achieved by the traditional methods of catalyst synthesis. Contrary to published reports, the metals undergo partial oxidation by reaction with the support during TPDE and the complete decompositions are irreversible. The nature of the active sites for the metathesis of propylene is reinterpreted in light of this surface chemistry and it is suggested that the activity is due to both a subcarbonyl species which is formed near 100 °C and mildly oxidized and decarbonylated species which are formed at higher temperatures. It is reported that these materials are also slightly active for propylene hydrogenation, and the surface chemistry and activity of the catalysts are compared to those of the hexacarbonyls supported on Al_2O_3.

Introduction

The chemistry of molecular complexes has been at the forefront of catalytic research during the last decade. Most of this work has been directed at homogeneous catalysts or their close cousins, immobilized homogeneous catalysts. A significant feature of this last class of catalysts is that the active site is known to exist in solution and in grafting the complex to a support, usually a polymer, considerable effort is made to prevent the support from modifying the active site. Relatively few results have been published on another class of catalysts which might be considered to bridge the gap between traditional heterogeneous catalysts of supported metals and homogeneous catalysts: molecular complexes directly deposited on refractory oxides. Such catalysts have the advantages of a large choice of catalyst precursors (as in homogeneous catalysis) and thermal stability of the support (characteristic of traditional heterogeneous catalysts). Since the metal is not shielded from the support by a chain of ligands, it is expected that the activity of these catalysts will be strongly influenced by the nature of the support.

$Mo(CO)_6$ and $W(CO)_6$ supported on Al_2O_3 were among the first catalysts reported for the metathesis of olefins[2] and this prompted detailed studies of $Mo(CO)_6/Al_2O_3$.[3-15] Some salient features of this system are that activation in flowing He near 100 °C gives quantitative formation of $Mo(CO)_3$ads[11] and recent work suggests that this species is probably an active site for the metathesis of propylene.[10] Temperatures above 300 °C are necessary to remove the remaining ligands at a reasonable rate and the complete decarbonylation is accompanied by a reaction of the Mo with the hydroxyl groups of the support (σ-OH) which causes the Mo to become oxidized.[9] Both $Mo(CO)_3$ads and the active site for metathesis of this catalyst are reversibly formed, but the complete decomposition of $Mo(CO)_6/Al_2O_3$ is not reversible.[10] Mild oxidation (to $\sim Mo^{2+}$) also produced an active catalyst.

The hexacarbonyls supported on SiO_2 have been studied by IR[5,15] and in addition $Mo(CO)_6/SiO_2$ has been characterized by ESR[6] and its activity for the metathesis of propylene measured.[7] The primary conclusions of these works are as follows: (1) The hexacarbonyls undergo complete decarbonylation near room temperature to yield zerovalent metals.[15] (2) No subcarbonyl species are formed during the decompositions.[15] (3) The complete decompositions are reversible (by exposure to ≥50 torr of CO at 45 °C).[15] (4) The support can oxidize the hexacarbonyls at temperatures ≥20 °C.[6] (5) The active site of $Mo(CO)_6/SiO_2$ for the metathesis of propylene is a completely decarbonylated species in which the metal is partially oxidized (perhaps Mo^{4+}).[5-7] Most of these conclusions are quite different from what was found in the case of $Mo(CO)_6/Al_2O_3$. In this paper we apply the recently developed technique of temperature programmed decomposition (TPDE)[14] to further examine the surface chemistry of the hexacarbonyls supported on SiO_2. We also introduce the "activity spectrum" as a complementary technique which provides information on the nature of the active sites for a catalytic reaction.

Experimental Section

A 0.500-g sample of SiO_2 (Davison Grade 62, a_s = 340 m^2/g, average pore diameter = 14 nm, and in one experiment Cabot Corporation Grade EH-5 Cab-O-Sil, a_s = 390 m^2/g, nonporous) was cleaned in a flow of oxygen for 45 min at 500 °C and then evacuated at this temperature for 45 min to a final pressure of $\sim 10^{-6}$ torr by using a two-stage oil diffusion pump. The pump is separated from the Pyrex system by a cold trap at −196 °C. The system is free of grease and mercury. The SiO_2 was then cooled in a flow of He to room temperature. Traces of oxygen and water vapor were removed from the He by passage through a trap of Cr^{2+}/SiO_2 and then 5A molecular sieve at −196 °C.[16] A solution of hexacarbonyl (Pressure Chemical Co.) in pentane (MCB Spectroquality) was degassed on the vacuum system and then added to the support under an atmosphere of He. The pentane was evaporated in a flow of helium and collected along with any sublimed hexacarbonyl in a cold trap at −196 °C downstream of the reactor. When the catalyst was dry, the flow of He was set at 10 cm^3/min and the temperature of the reactor raised at a linear rate with a proportional temperature programmer. One thermocouple (type K) outside of the reactor was used to control power to the oven, and a second 30-gauge, bare thermocouple (type K) was immersed in the catalyst bed. This arrangement gives a perfectly linear increase in temperature and correctly measures the true temperature of the catalyst.

Gases evolved during TPDE first pass through a cold trap at −196 °C and then a catharometer. Since the quantity of CH_4 formed is very small and H_2 has a very low response in a He carrier (about 3% of the response of CO), this detector is essentially specific for the rate of CO evolution. The effluent from the first detector is then passed through SiO_2 at −196 °C leaving only H_2 in the He carrier. The H_2 is diffused through a thin tube of Pd alloy into a stream of nitrogen.[14] A second detector (which has nitrogen as its reference gas) monitors the concentration of H_2. The data are presented on a two-pen recorder and with minor corrections for the dead times give a continuous plot of the rates of CO and H_2 evolutions. At the completion of the TPDE the SiO_2 trap is warmed to room temperature and the gases are back-flushed through a column of Spherocarb (Analabs, Inc) and then back through the first detector. This allows accurate quantization of CO and CH_4. The cold trap is then warmed to −78 °C and CO_2 and light hydrocarbons (up through C_3) are analyzed in a similar fashion by using temperature programming. Sublimed hexacarbonyl is analyzed by UV to yield the correct catalyst loading. The system can detect gas evolutions of 2×10^{-11} mol/s of CO, 6×10^{-10} mol/s of H_2, and 3×10^{-10} mol of hydrocarbons. At the usual loading of 0.02% hexacarbonyl (0.1 mg) this corresponds to being able to detect the evolution of 1 molecule of CO/(2×10^4 complexes per s).

In two experiments the average oxidation number (ON) of $W(CO)_6/SiO_2$ after TPDE was determined by titration with small pulses of O_2 at 500 °C to form W^{6+}.[9] Correction was made for any CO_2 formed during the titrations and in one of the runs the $W(CO)_6$ was sublimed onto the support to avoid possible complications from solvent.

Separate analyses show that the O_2 leak into the system upstream of the reactor is too small to significantly affect the results. The leak is about 1×10^{-6} cm^3 of O_2/min, corresponding to 0.007 O_2/complex over a 2-h experiment.

ESR measurements were performed at −196 °C, 1-mW power level, 9.0 GHz, and 100-kHz modulation with a Varian E109E spectrometer. The number of spins and g values were obtained by comparison to 10^{-5} M *N*-(2,3,6,6-tetramethyl-4-piperidinyl-1-oxy)maleimide. For these experiments $Mo(CO)_6$ was sublimed onto SiO_2 and activated in vacuo in a reactor which was equipped with a Spectrosil side arm and which allowed the ESR spectra to be obtained with the rigorous exclusion of air. Due to the weak signals, the spin concentrations are only accurate to a factor of 2, but the relative values are accurate to ±10%.

Reversibility of the decomposition of the hexacarbonyls was assessed by passing a roughly equimolar mixture of H_2 and CO (both purified by passage through Cr^{2+}/SiO_2 and then 5A sieve) over the catalysts at various elevated temperatures. Hexacarbonyl which has re-formed will sublime out of the reactor and is trapped at −196 °C for UV analysis. At a loading of 0.02% hexacarbonyl the reversible formation of about 0.05% of surface complex can be detected.

Kinetic parameters for the decomposition of $Cr(CO)_6/SiO_2$ were determined by isothermal measurements of the rate of CO evolution at temperatures corresponding to the leading edge of the peak in the TPDE chromatogram (IIIS technique[17]). By operating in this temperature range only a few percent of the surface species undergo decomposition at each temperature, thereby maintaining pseudo-zero-order kinetics. At the end of the run the catalysts were heated to 600 °C to determine the total CO evolution. By use of this information the rate data were then corrected for the slight differences in surface coverage at the various temperatures.

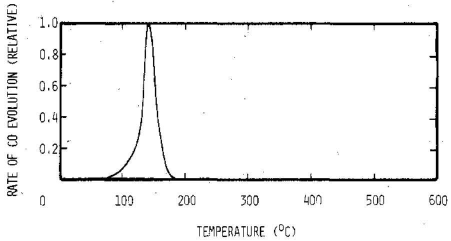

Figure 1. TPDE of $Cr(CO)_6/SiO_2$.

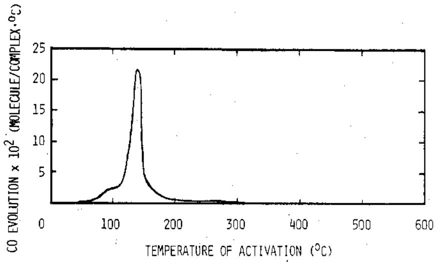

Figure 2. TPDE of $Mo(CO)_6/SiO_2$.

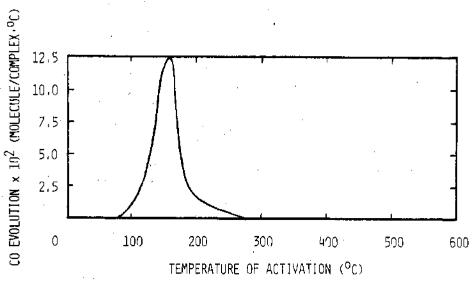

Figure 3. TPDE of $W(CO)_6/SiO_2$.

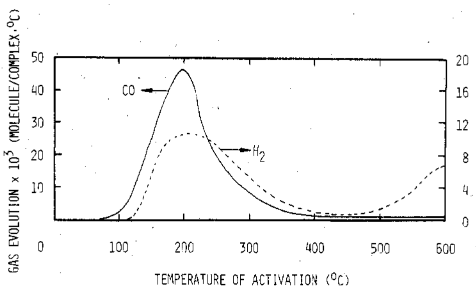

Figure 4. TPDE of $Mo(CO)_6/SiO_2$ at a heating rate of 30 °C/min.

Catalyst activity was measured by using 0.500 g of catalyst in a flow system both by standard, isothermal experiments and by the "activity spectrum" technique. A flow of H_2 and C_3H_6 was passed through the reactor at a total flow = 30 cm^3/min, $H_2/C_3H_6 = 4$, and $P = 1$ atm. The C_3H_6 (CP grade, Union Carbide, Corp.) was analyzed by gas chromatography as 99.4% C_3H_6, 0.6% C_3H_8, and <10 ppm air. The H_2 was purified in the same manner as the He. The effluent was sampled at 2-min intervals with a gas sampling valve and analyzed by gas chromatography by using a column of *n*-octane/Porasil C (Waters Associates) and Spectra-Physics System I Computing Integrator. An activity spectrum is produced in an experiment similar to TPDE except that a flow of reactant gases is used in place of He. The heating rate was 5 °C/min so the effluent was sampled at intervals of 10 °C.

Results

Figures 1, 2, and 3 show the TPDE at a heating rate of 5 °C/min of the hexacarbonyls supported on silica. A small amount of H_2 is also detected, but the concentration is too low for accurate measurements in these experiments. Since the concentration of H_2 is proportional to the heating rate, separate runs were done at 30 °C/min to more accurately establish the stoichiometry of the decompositions. This is illustrated for

Table I. Gas Evolutions during TPDE to 600 °C

hexacarbonyl	final loading (mg of complex)	% sublimation during activation	CO evolved/ complex	H_2 evolved/ complex	CH_4 evolved/ complex	CO_2 evolved/ complex	ON[c] by gas evolution	ON[c] by O_2 titration
$Cr(CO)_6$	0.13	49	5.69	1.6 ± 0.6	0.13	0.54	4.0 ± 1.2	
$Mo(CO)_6$	0.16	28	5.50	2.3 ± 0.5	0.054	0.31	4.9 ± 1.0	
$Mo(CO)_6$[a]	0.098	54	5.71	1.9 ± 0.8	0.070	0.19	4.2 ± 1.6	
$W(CO)_6$	0.086	57	5.04	1.7 ± 0.7	0.15	0.81	4.3 ± 1.4	4.3 ± 0.3
$W(CO)_6$[b]	0.20	56	5.70	1.9 ± 0.4	0.16	0.24	4.7 ± 0.8	4.6 ± 0.3

[a] Supported on Cab-O-Sil. [b] Solventless run. [c] ON = oxidation number.

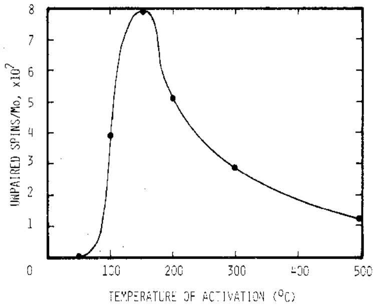

Figure 5. ESR signal of Mo(V) during the activation of Mo$(CO)_6/SiO_2$. The catalyst was activated for 15 min at each of the indicated temperatures.

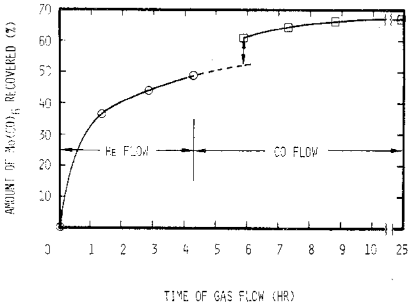

Figure 6. Recovery of $Mo(CO)_6$ from $Mo(CO)_6/SiO_2$ after activation at 65 °C. The discontinuity in the graph represents the amount of reversibly formed subcarbonyl species.

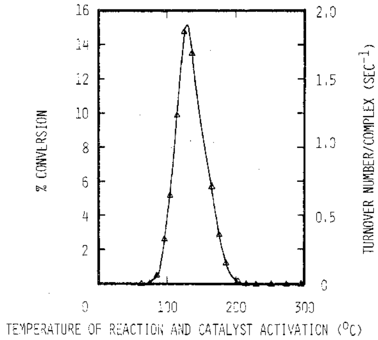

Figure 7. Activity spectrum of $Mo(CO)_6/SiO_2$ for the metathesis of propylene.

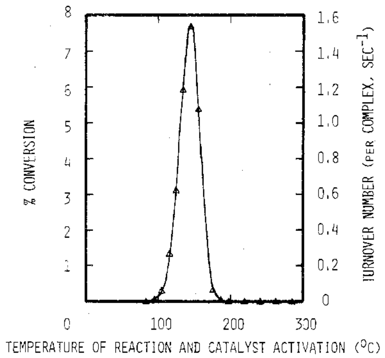

Figure 8. Activity spectrum of $W(CO)_6/SiO_2$ for the metathesis of propylene.

the case of $Mo(CO)_6$, Figure 4. The TPDE at 30 °C/min of $Mo(CO)_6$/Cab-O-Sil is very similar to Figure 4. Increasing the heating rate will also shift the peaks to a higher temperature,[18] but in addition in our system it causes an artificial broadening of the peaks which is largely due to the effect of the −196 °C trap on the CO peak and the effect of the time for H_2 transfer through the Pd alloy tube on the H_2 peak. Stoichiometry and ON data based on these runs are shown in Table I. Very small quantities of C_2H_4 and C_2H_6 were also observed, but blank (no carbonyl) and solventless runs established that most of this was derived from the pentane, the corrected evolutions being ~0.003 molecule/complex.

Activation of $Mo(CO)_6/SiO_2$ at $T \gtrsim 100$ °C results in the appearance of the ESR signal of Mo(V), Figure 5, with $g = 1.941 \pm 0.002$ and a peak to peak width of 40 G. After activation at 50 °C the catalyst was white, after activation at 100 °C it was faintly yellow, and at higher temperatures the catalyst was again white.

Reversibility of the *complete* decomposition of the hexacarbonyls was examined in several ways. After TPDE to 600 °C, an equimolar mixture of CO and H_2 was flowed at about 80 cm^3/min over $W(CO)_6$ and $Mo(CO)_6$ catalysts for 1 h at 130 °C. The recovery of hexacarbonyl was <0.06% in both cases. Raising of the temperature to 350 °C for 1 h increased the recovery of $Mo(CO)_6$ to 0.2% but did not increase the recovery of $W(CO)_6$. $Cr(CO)_6/SiO_2$ was activated for 35 min at 250 °C. A 50-cm^3 flow of CO and H_2 for 30 min at 125 °C resulted in <0.03% recovery of $Cr(CO)_6$. After activation at 170 °C for 2 h, $Mo(CO)_6/SiO_2$ was exposed to 100 cm^3/min of CO and H_2 at 170 °C for 2.5 h. The recovery of $Mo(CO)_6$ was 2.8% in the first 0.5 h and <0.01% in the remaining time.

The presence of reversibly formed *subcarbonyl* species was checked by first activating $Mo(CO)_6/SiO_2$ in flowing He for 65 min at 65 °C. The temperature was then lowered to 45 °C, the He flow set at 150 cm^3/min, and the recovery of residual, physisorbed $Mo(CO)_6$ was monitored. After 4.5 h the gas was suddenly changed to CO at the same flow and temperature and again the recovery of $Mo(CO)_6$ measured, Figure 6.

The activation energy (E_d) and the preexponential factor (A) for the initial loss of CO during the TPDE of $Cr(CO)_6/SiO_2$ were determined in the temperature range 69–84 °C. Good Arrhenius plots were obtained, the average of four separate determinations being $E_d = 33 \pm 2$ kcal/mol and $A = 6 \times 10^{15}$ s^{-1}.

Figures 7 and 8[19] show the activity spectra of $Mo(CO)_6/SiO_2$ and $W(CO)_6/SiO_2$ for the metathesis of propylene. $Cr(CO)_6/SiO_2$ was inactive. In a separate run (dry mix) analysis was made for the CO evolution during the activity spectrum of $Mo(CO)_6/SiO_2$. The results were identical in form with Figures 2 and 7 except that the peak maxima for

Table II. Activity of $Mo(CO)_6/SiO_2$ for the Metathesis of Propylene

T of activation, °C	initial conversion, %	conversion after 500 turnovers, %
25	0.0	
100[a]	19.0	15.1
200	16.1	4.4
250	9.6	0.8
300	3.2	0.1
400	$\lesssim 0.2$	
550	0.0	

[a] Activated for only 15 min.

metathesis and CO evolution were shifted down by ~20 °C. Table II contains the isothermal activities for metathesis by $Mo(CO)_6/SiO_2$, measured after activation for 30 min in flowing He at various temperatures and cooling in He to the reaction temperature of 70 °C. The activity spectra of $Mo(CO)_6/SiO_2$ and $W(CO)_6/SiO_2$ also revealed a low activity for the hydrogenation of propylene which began developing at about 100 °C. At 150 °C the conversions were about 1 and 0.1%, respectively (above 250 °C the SiO_2 alone begins to develop a similar level of activity). In the isothermal experiments the maximum hydrogenation was 1.8% after activation at 200 °C.

Discussion

Surface Chemistry. The presence of a single narrow peak for the TPDE of the hexacarbonyls supported on SiO_2 is quite remarkable since it requires that all *six* of the carbonyl ligands are lost in rapid succession. Either the evolution of the first CO ligands is rate determining or all six ligands have nearly the same activation energy for bond cleavage (assuming that the preexponential factor does not drastically change during the decomposition).[20] In either case the result is unexpected. It is a tenet of inorganic chemistry that as the CO ligands of a complex are replaced with weaker π-bonding ligands the metal to carbon bond strength increases and the remaining carbonyl ligands become progressively harder to remove.[21] In practice it is difficult to replace more than three of the ligands of a hexacarbonyl complex by thermal means, photochemical activation being the method of choice for more demanding reactions.[22] In our system it is likely that as decomposition proceeds some of the coordination sites around the metal are filled by surface ligands, such as hydroxyl groups,[9] but we do not have detailed information on this subject due to the difficulties of studying a system at such low loadings. It is noteworthy that Atwood and Brown have recently shown that various ligands can induce a cis-labilizing effect on the dissociation of CO ligands from hexacarbonyls.[23] The effect spans about 8 orders of magnitude and the ordering of ligands is the reverse of that found for the trans effect in the substitution of Pt(II) complexes. Thus, the inclusion of σ-OH ligands into the coordination sphere may partly explain the facile decarbonylation (OH^- is a very weak trans-directing ligand[21]). However, $Mo(CO)_3$ads (on γ-Al_2O_3) is stable and the three coordination positions vacated by CO are probably also filled by surface ligands, including σ-OH.[9]

Due to the very low capacity of SiO_2 to bind hexacarbonyl (especially compared to the capacity of Al_2O_3[9]), the possibility of adsorption at impurity sites was considered. The Davison SiO_2 is 99.7% pure, with 530 ppm of Al as the main impurity.[36] At a typical loading of 0.02% complex and with the assumption that all of the Al is on the surface, the limiting value of Al/complex is 26. Cab-O-Sil has 8 ppm Al and 30 ppm Na with all other impurities below the limit of detection,[36] yielding a limiting value of Al/complex = 0.4. Since both the peak shape and stoichiometry of the TPDE of $Mo(CO)_6$/Cab-O-Sil are similar to the results with the Davison SiO_2, it may be concluded that bonding at impurity sites does not significantly affect the data.

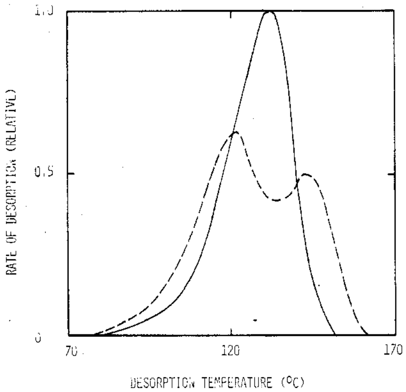

Figure 9. Effect of heterogeneity on desorption peak shape. The solid curve is for E_d = 33 and the dashed curve is for a 50% mixture of sites having E_d = 32 and E_d = 34 kcal/mol $A = 6 \times 10^{15}$ s^{-1} and β = 5 °C/min.

Temperature-programmed desorption (TPD) of gases adsorbed on practical heterogeneous catalysts (supports are high surface area, inorganic oxides) is a widely used technique for characterizing the nature of the adsorbate–surface interaction. Both TPD and TPDE peaks can be analyzed by the same mathematical expression for the case of first-order desorption.[24] This is equivalent to a unimolecular process being the rate-limiting step in each case: desorption in the former and ligand dissociation in the latter. The desorption peaks produced by TPD from such catalysts are almost always quite broad indicating considerable heterogeneity of the surface. Furthermore, the preexponential factors which are obtained are usually many orders of magnitude too low for a unimolecular process.[17] For a unimolecular reaction the preexponential factor is given by

$$A = (kT/h)(Q^*/Q)$$

where k is Boltzmann's constant, T is the temperature, h is Planck's constant, Q is the partition function for the initial complex, and Q^* is the partition function for the transition state. The value of kT/h is about 10^{13} s^{-1}. Normally $Q^*/Q > 1$ since there are more degrees of freedom available to the products than the initial, bound state. Rate constants for gas-phase (noncatalytic) unimolecular decompositions agree well with these considerations, most values being in the range 10^{12}–10^{16} s^{-1}.[25] Kinetic analysis of the TPDE of $Cr(CO)_6/SiO_2$ yielded the values E_d = 33 kcal/mol and $A = 6 \times 10^{15}$ s^{-1}. The latter value implies that $Q^*/Q = 7 \times 10^2$.

At a heating rate of 5 °C/min (under these conditions experimental artifacts should not affect the peak shape) the observed peak width at half-maximum for $Cr(CO)_6/SiO_2$ is 24 °C, compared to a theoretical value of 23 °C. It must be stressed that the theoretical model corresponds to the unimolecular desorption (dissociation) of a *single* species (no spread in the kinetic parameters) from a *homogeneous* surface. A more quantitative evaluation of the effect of site heterogeneity on the TPDE spectrum is shown in Figure 9. It is clear that a spread of 2 kcal/mol in the activation energy for breaking the various metal to ligand bonds is sufficient to produce a significant broadening of the peak. Thus, the reasonable values of A and peak width suggest that the system is self-consistent with the model. Hence, we find that the TPDE of $Cr(CO)_6/SiO_2$ is remarkable in several respects: (1) It is the only practical heterogeneous catalyst for which the preexponential factor and peak width are consistent with theory for a first-order process. (2) The activation energy for breaking the M–CO bonds does not significantly increase during successive bond breakings. (3) The surface of the SiO_2 appears homogeneous to the $Cr(CO)_6$ads. The similarity of the TPDE of the hexacarbonyls suggests that the energetics of the decompositions of $Mo(CO)_6$ and W(CO) are similar to that for $Cr(CO)_6$. Assuming the same value for Q^*/Q, we find E_d = 33 and E_d = 34 kcal/mol, respectively.

CO is not the only gas evolved during the TPDE of these complexes, Table I. For complexes supported on γ-Al_2O_3, the H_2 has been shown to arise from a redox reaction between surface hydroxyl groups (σ-OH) and the metal, which can be approximated as[9,14]

$$M(CO)_6\text{ads} + n(\sigma\text{-OH}) \xrightarrow{\Delta} (\sigma\text{-O}^-)_nM^{n+} + (n/2)H_2 + 6CO$$

Thus, the evolution of H_2 indicates an oxidation of the originally zerovalent metal. Some CH_4 is also formed. Since the quantity was the same in a solventless run, the hydrogen in the CH_4 must also be derived from σ-OH, thus implying additional oxidation of the metal. The final average ON for the complexes can be computed on the basis of the metals undergoing an amount of oxidation equivalent to the amount of H^+ (in σ-OH) which was reduced, Table I. The ON are of mediocre accuracy due to the extremely low loadings, but the values computed for $W(CO)_6/SiO_2$ agree with the values found independently by titration with O_2. Agreement between the two methods has also been found for various carbonyls supported on γ-Al_2O_3,[9,17] systems which afford better precision due to higher loadings. Consistent with this model, decomposition of $Mo(CO)_6$ supported on highly dehydroxylated Al_2O_3[9] or SiO_2[35] results in much less oxidation. Thus, it is clear that the main products of the decomposition of the initially zerovalent complexes are oxidized metals.

Although the spectra are too weak to merit detailed analysis, the results of the ESR study, Figure 5, are also consistent with the model requiring oxidation of the complexes at $T \gtrsim 100$ °C. The development of a yellow color which then disappeared at higher temperatures of activation is also significant. Such coloration is observed with both unsupported[37] and supported,[9] zerovalent subcarbonyl species. The g value of the Mo(V) signal is nearly the same as that found for $Mo(CO)_6/Al_2O_3$,[9] although the peak width is considerably less. Howe and Leith[6] observed the ESR signal of Mo(V) after preparing $Mo(CO)_6/SiO_2$ (at a loading of ~5%) by mixing in air at 20 °C. However, their catalyst developed a pale blue color characteristic of hydrated Mo(V) (molybdenum blue), indicating reaction with O_2 and H_2O in addition to any interaction with the support. No blue color was observed for $Mo(CO)_6$ supported on either SiO_2 or Al_2O_3[9] prepared under air-free conditions.

The complete decomposition of the hexacarbonyls is clearly irreversible after heating to 600 °C. Since the work of Howe[15] was done at lower temperatures, reversibility was also checked after heating to only 250 °C to minimize the possibility that some undetected process occurring at higher temperatures could be responsible for the lack of reversibility. The decomposition was again completely irreversible. As a final check, $Mo(CO)_6/SiO_2$ was activated at only 170 °C. Figure 2 shows that this is a minimal temperature for ensuring complete decomposition. Still, the decomposition was 97% irreversible. The inability to form $M(CO)_6$ by exposing the decomposed catalysts to CO at low temperatures and pressures is also consistent with the inefficiency of even severe reaction conditions to synthesize the hexacarbonyls by direct reaction of metal powders with CO.[26]

The existence of a single peak in the TPDE does not require a concerted removal of all six carbonyl ligands. In the case of $Mo(CO)_6/Al_2O_3$, the low-temperature peak in the TPDE corresponds to the loss of 3 CO/complex and hence the formation of $Mo(CO)_3$ads,[14] but under different conditions it is possible to isolate the intermediate species $Mo(CO)_5$ads and $Mo(CO)_4$ads.[12] Figure 6 portrays an experiment to detect the existence of reversibly formed subcarbonyl species on $Mo(CO)_6/SiO_2$. Because the catalyst was only activated at 65 °C, undecomposed $Mo(CO)_6$ continues to slowly sublime from the surface in a flow of He at 45 °C. However, when the gas flow is suddenly switched to CO there is a discontinuity in the rate of recovery of $Mo(CO)_6$. Since complete decomposition has been shown to be irreversible, it is assumed that the only difference between the two gases is the possibility that the CO could reverse the decomposition of a surface subcarbonyl species. Therefore, Figure 6 shows that subcarbonyl species exist and at least 21% of them are reversibly formed.

The surface chemistry of the group 6B hexacarbonyls supported on SiO_2 may now be summarized: (1) Temperatures close to 200 °C are necessary for complete decarbonylation. (2) The complete decompositions are irreversible. (3) CO is not the only gas formed during the decompositions; H_2, CO_2, and CH_4 are also evolved. (4) The main product of the decompositions is a substantially oxidized metal. In particular, the decomposition of these zerovalent complexes yields little, if any, zerovalent metal on the support. (5) Subcarbonyl species are formed during the decomposition and at least some of them are reversibly formed. (6) The TPDE peaks are in good agreement with what is expected for a unimolecular decomposition on a homogeneous surface. It should also be noted that TPDE defines the conditions required for the formation of low-valent supported Cr, Mo, and W and due to the incomplete reducibility of the supported oxides,[16,28,29] such catalysts cannot be synthesized by the traditional techniques.

The chemistry of hexacarbonyls supported on SiO_2 is now more consistent with their behavior when supported on alumina and their bulk chemistry. On both supports we find that complete decarbonylation is accompanied by a synchronous H_2 evolution indicating oxidation of the metal. The amounts of oxidation are similar[34] suggesting that the acidity[27] of a support is not an important parameter. On both supports subcarbonyl species exist which are reversibly formed and in neither case are the complete decompositions reversible.

A difference between the two supports is that γ-alumina stabilizes the existence of $M(CO)_3$ads which results in the TPDE displaying two peaks.[14] Shifting the high-temperature CO peak and its concurrent H_2 peak down to overlap with the low-temperature (and H_2 free) CO peak would make the TPDE of the Al_2O_3 supported hexacarbonyls look very similar to the SiO_2 systems. A second difference between the two supports is that the capacity of Al_2O_3 to bind hexacarbonyls is much greater than that of SiO_2. It is fairly easy to support 6% $Mo(CO)_6$ on Al_2O_3,[9] but SiO_2 only holds about 0.1% $Mo(CO)_6$, corresponding to 1 complex/1.5×10^2 nm^2. Attempts to support larger amounts of complex can result in close to 100% sublimation of unreacted complex during catalyst preparation. The high sublimation and very dilute nature of the true catalyst (fractional surface coverage $\simeq 3 \times 10^{-4}$) may be reasons for the conflicting conclusions concerning the surface chemistry of these complexes as found by IR studies.[15]

Catalytic Activity for Metathesis. There are a large number of variables which can affect the activity of catalysts. Therefore, in synthesizing new types of catalysts it can be of value to develop efficient techniques of monitoring *patterns* of activity in order to avoid a nearly endless quagmire of experiments. Minor changes in activity are less important in this viewpoint. To this end a technique called the "activity spectrum" has been developed. The activity spectrum is performed in the same manner as TPDE, except in place of a sweep gas of helium the appropriate reaction gases are continually passed over the catalyst and the activity is monitored by sampling the effluent. Thus, as the temperature is raised, two important variables are continuously changing: surface composition, as previously revealed by TPDE, and reaction temperature which will affect the activity in the normal manner (Arrhenius activation energy). The task, then, is to deconvolute these two effects.

The activity spectra, Figures 7 and 8, show a remarkable resemblance to the corresponding TPDE spectra, Figures 2 and 3. Since the Arrhenius effect requires that an increase in temperature also increases the rate of reaction (side reactions are negligible in this temperature range), it is clear that the rapid decline in activity that occurs above roughly 130 °C must be due to the destruction of active sites. Furthermore, catalysts activated in He at 400 or 550 °C also gave zero activity indicating that some type of high-temperature poisoning by the reactants is not the cause of the deactivation. The decline in activity is apparently related to the changes in surface composition as shown by TPDE. The most likely culprit is the destruction of catalytically active subcarbonyl species and oxidation of the metal. It is important to note that H_2 (in the feedstock) cannot reduce the metals to the zerovalent state after they have become oxidized by reaction with σ-OH[16,28,29] and the feedstock does not significantly affect the evolution of CO. If the increase in activity which is observed to start at about 100 °C were only due to the Arrhenius effect, then cooling of the catalyst should retrace the curve and yield zero activity at 70 °C. However, a catalyst activated in He at 100 °C had substantial activity at 70 °C. The inactivity of the undecomposed hexacarbonyls is reasonable, since they are stable, 18-electron, coordinatively, saturated complexes (exchange with CO(g) is very slow below 100 °C[21]). Thus, the leading edge of these activity spectra primarily reflects the generation of active sites. Therefore, the very important result follows that *the activity spectrum can provide a direct mapping of the creation and destruction of catalytically active sites.* It is clear that the activities measured by the activity spectrum are not steady-state activities and that only qualitative comparisons can be made between the activities measured at different temperatures. Nonetheless, because obtaining information on the generation of active sites is normally very difficult and is certainly at the heart of catalysis, it is felt that the technique of coupling the activity spectrum with TPDE will be a very general and valuable technique for characterizing patterns of catalytic activity. It should further be stressed that the activity spectrum also defines those regions of catalyst activation which merit more detailed study by standard, isothermal techniques.

Although not studied in as much detail, the active sites for $W(CO)_6$ are probably of the same nature as those derived from $Mo(CO)_6$. $Cr(CO)_6$ is not known to form a catalyst for metathesis.[30]

The isothermal activity data measured after 500 turnovers, Table II, supports the conclusions drawn from the activity spectrum of $Mo(CO)_6/SiO_2$, but the initial isothermal activities do not. It appears that in the temperature range 200–300 °C there are some active species formed which have a much shorter lifetime than the active sites formed at lower temperature. Since the presence of subcarbonyl species is unlikely above 200 °C, these additional active sites are probably due to some mildly oxidized and completely decarbonylated Mo. The total amount of oxidation of $Mo(CO)_6/SiO_2$ and $W(CO)_6/SiO_2$ after activation at 600 °C is about 4.6 units and such catalysts are inactive, so the ON of this active site is probably less than 4. For $Mo(CO)_6/Al_2O_3$ it was found that a subcarbonyl species was active for metathesis and had a long lifetime, and mildly oxidized species, probably Mo^{2+}, were also active but quickly deactivated.[10] Mo of ON ≥4 were inactive.[10] The parallels between the two systems suggest that M^{2+} may also be the high-temperature active site for the SiO_2 supported systems.

Smith et al.[7] have also studied the effect of the temperature of activation of $Mo(CO)_6/SiO_2$ on the activity for the metathesis of propylene at 25 °C. These workers found maximal activity was developed by pretreatment at 200 °C and there was a local maximum for activation at 550 °C. Howe et al.[5] used IR data to claim that the active site is a partially oxidized and completely decarbonylated species and ESR data to suggest that Mo^{4+} may be the active site. It was suggested that the low-temperature maximum was due to decarbonylation and partial oxidation, and the high-temperature maximum was due to a rereduction of the Mo (as by evolution of O_2 from MoO_3ads).[7] In their study Smith et al. used a single catalyst which was activated at successively higher temperatures (increments of 100 °C) and it is possible that exposure of residual, adsorbed hydrocarbons to elevated temperatures could affect the activities as has been shown for $Mo(CO)_6/Al_2O_3$.[10] We did not observe the high-temperature maximum and our ON results with both the SiO_2 and Al_2O_3 supported systems require *increasing* oxidation of the metal as the temperature of activation is increased. The conclusion of these workers that decarbonylated Mo^{4+} is the only active site seems inconsistent with the activity spectrum since it would require that the activity develops in precisely the region in which it is rapidly declining. However, it is well-known that a variety of oxidation states are apparently active for olefin metathesis[30] and in one case a supported Mo(IV) complex was more active ($N = 0.03\ s^{-1}$ at 90 °C) than a reduced (Mo(II)) form of the catalyst.[38] The system is clearly very complex and some form of mildly oxidized and decarbonylated Mo is probably active.

Catalytic Activity for Hydrogenation. Even though the hydrogenation activities of $Mo(CO)_6/SiO_2$ and $W(CO)_6/SiO_2$ have not been previously reported, they were not studied in detail due to the low conversions. Wrighton et al.[31] have reported that photolysis of the hexacarbonyls in solution yields catalysts which have slight activity for the hydrogenation of conjugated dienes (but not monoolefins) at 25 °C (turnover number, $N \simeq 10^{-4}\ s^{-1}$). The much lower activity of the homogeneous catalysts is probably due to the dimerization of the active species (presumedly subcarbonyl species) which is inhibited by a support.

$Mo(CO)_6/SiO_2$ is more active than $W(CO)_6/SiO_2$, which is also the ordering for the hydrogenation of ethylene by films of these metals: Mo $\gg$ W $\sim$ Cr.[32,33] The interesting feature of the hydrogenation activities is that the turnover numbers are much lower than found for the alumina-supported catalysts, in contrast to the results for metathesis.[10] Activity spectra ($H_2 + C_3H_6$) of the alumina-supported catalysts show the hydrogenation activity developing rapidly at roughly 100 °C.[35] The activity of $Cr(CO)_6/Al_2O_3$ peaks at 195 °C ($N = 0.8\ s^{-1}$), $W(CO)_6/Al_2O_3$ peaks at 260 °C ($N = 0.4\ s^{-1}$), and $Mo(CO)_6/Al_2O_3$ gives 100% conversion in this temperature range.[34] Activation at 200 °C in flowing He of $Mo(CO)_6/Al_2O_3$ gave $N = 5\ s^{-1}$ for reaction at 25 °C. The activities again drop precipitously when the metals become oxidized. Since by appropriate activation procedures it is possible to have nearly exclusively either the metathesis or hydrogenation reaction,[34] it is unlikely that the same sites are responsible for both reactions.

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Registry No. $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; SiO_2, 7631-86-9.

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A Versatile Starting Material: Substitution Reactions of Bis(acetato)bis(diethyl sulfide)platinum with Phosphines, Thiols, *o*-Hydroquinones and Dihydroxybenzoquinones

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The new compound *cis*-$Pt(OAc)_2(Et_2S)_2$ has been prepared, and its use as a starting material in the synthesis of new complexes of platinum has been investigated. Substitution reactions with HO–OH or HO_2–O_2H (HO–OH = substituted catechol, HO_2–O_2H = substituted 2,5-dihydroxy-1,4-benzoquinone) gave the corresponding *cis*-$Pt(O{-}O)(Et_2S)_2$ and *cis*-$Pt(O_2{-}O_2)(Et_2S)_2$ compounds. In the case of O_2–O_2 = 2,5-dioxy-1,4-benzoquinone, a slow conversion to a yellow isomer formulated as *trans*-$Pt_2(\mu\text{-}(O_2{-}O_2))_2(Et_2S)_4$ was observed. Reaction of $K_4[Pt_2(\mu\text{-}(O_2{-}O_2))_2Cl_4]$ (O_2–O_2 = 3,6-dichloro-2,5-dioxy-1,4-benzoquinone) with Et_2S also gave *trans*-$Pt_2(\mu\text{-}(O_2{-}O_2))_2(Et_2S)_4$. Reactions with ArSH (Ar = 4-MePh, 4-ClPh) first gave $Pt(SAr)_2(Et_2S)_2$, which then slowly reacted further to form $[Pt(SAr)_2]_n$. Reactions with phosphines (PPh_3, $PPhMe_2$) led to displacement of the diethyl sulfide group(s) giving mono- and bis-substituted phosphine compounds. Iodine oxidation of the 1,2-quinone complexes $Pt(O{-}O)(Et_2S)_2$ resulted in the rapid formation of the free 1,2-quinone, whereas $Pt(SPhMe\text{-}4)_2(Et_2S)_2$ gave with iodine the free disulfide (4-MePhS–$)_2$. In both cases $PtI_2(Et_2S)_2$ was also formed. The configurations of the compounds described were derived from ^1H NMR and IR data.

Introduction

The preparation of many transition-metal compounds is often achieved by ligand-substitution reactions in which a weaker coordinating ligand is replaced by a stronger one. Therefore, compounds which can act as useful and versatile starting materials in the preparation of a variety of other compounds are of great interest, particularly when they are readily synthesized from commercially available starting materials and are stable on handling and storing over prolonged periods. In addition, such compounds should undergo selective substitutions with other ligands.

Our interest in platinum chemistry led us to investigate which starting materials met these criteria. This study resulted in the preparation of $Pt(OAc)_2(Et_2S)_2$, a compound which has all the properties mentioned above. Both the acetato or sulfide groups can be readily substituted simultaneously or separately in high yield. To demonstrate the important role that such a compound can play in the preparation of interesting new complexes, we studied several reactions with $Pt(OAc)_2(Et_2S)_2$. Substitutions with *o*-hydroquinones (catechols) were chosen because of the recent interest in the transition-metal chemistry of these ligands,[1,2] which play an important role in biochemistry.[3,4]

Compounds of dioxybenzoquinones with transition metals are mostly polymers.[5-7] They have been of considerable interest, as it was expected that due to the easily polarizable dioxybenzoquinone ligands, the compounds could have unusual magnetic and electrical properties.[6,7] Nonpolymeric transition-metal compounds, however, are not very common,[8] and therefore substitution reactions of 2,5-dihydroxybenzoquinone with, e.g., $Pt(OAc)_2(Et_2S)_2$ were studied.

Many thiol complexes of the nickel triad were prepared by fission of the sulfur bridges of the polymeric metal thiolates.[9] In this paper it is shown that platinum thiolates can easily be prepared by substitution of acetato groups.

Experimental Section

The substituted catechols, 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone, K_2PtCl_4, (4-methylphenyl)thiol, and (4-chloro-

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