JOURNAL OF CATALYSIS **118**, 360–370 (1989)

Synthesis, Characterization, and Catalytic Activity of Group VIB Metal Carbonyls Supported on Titania

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Received October 6, 1987; revised December 23, 1988

Group VIB metal carbonyls supported on titania which had been partially dehydroxylated at 250 and 500°C were characterized by temperature-programmed decomposition, chemisorption of carbon monoxide, and activity for ethylene hydrogenation. Decomposition profiles on titania dehydroxylated at 500°C showed very little evolution of hydrogen resulting in low-valent catalysts. Chemisorption of CO showed that the metal is well dispersed after decomposition at temperatures between 100 and 200°C. Decomposition on titania dehydroxylated at 250°C resulted in more oxidation of the metal. All catalysts were active for the hydrogenation of ethylene. Activity increased in the order Cr < W < Mo. A Mo catalyst had a formal turnover frequency of 10.4 s^{-1} at 0°C, which is one of the most active Mo catalysts reported. © 1989 Academic Press, Inc.

INTRODUCTION

In the past decade there has been much interest in the study of transition metal complexes, especially carbonyls, supported on high-surface-area refractory supports such as alumina, silica, and molecular sieves. Titania displays strong metal–support interaction (SMSI) effects with some metals (*1*), so it is an interesting support to study to see if it gives rise to different behavior with supported carbonyls than the other supports. However, there have been only a few studies of metal carbonyls supported on titania and only one Group VIB metal carbonyl has been studied. Masuyama and co-workers reported the catalytic activity of $Mo(CO)_6/TiO_2$ for allylic alkylation (*2*). A temperature-programmed decomposition (TPDE) experiment was described but no quantitative data were given. The only other carbonyls of base metals studied were iron and cobalt. Lisitsyn *et al.* (*3*) decomposed $Co_2(CO)_8$ on TiO_2 at 528 K and hydrogenated carbon monoxide over this material. Santos and co-workers (*4*) used Mössbauer spectroscopy to study the interaction of iron and titania during the decomposition of $Fe(CO)_5$. Neither of these studies reported quantitative data for the decomposition of the metal carbonyls. A few studies of carbonyls of noble metals supported on titania have also been made, although none gave quantitative data for the bonding of the complex to the support. Ichikawa (*5*) investigated $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ supported on titania as a catalyst for Fischer–Tropsch synthesis. Beeba and Gates (*6*) used infrared spectroscopy to study the decomposition of $Os_3(CO)_{12}$ supported on titania. Collier *et al.* (*7*) used temperature-programmed decomposition to 250°C and chemisorption of carbon monoxide and oxygen to characterize $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$ supported on titania.

It has been demonstrated that Group VIB metal carbonyl complexes can yield well-dispersed and low-valent catalysts (*8–10*). These catalysts can be much more active for olefin hydrogenation (*11–17*), Fischer–Tropsch synthesis (*18, 19*), hydrogenolysis (*12, 17*), and the hydrogenation of benzene (*20*) than their traditional counterparts (supported salts reduced near 500°C). It has also been shown that the extent of hydroxylation of a support is an important parameter in determining the surface species

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0021-9517/89 $3.00

formed (*21*) and activity (*15*) of supported carbonyls.

In this paper we report the first quantitative study of the interaction of the Group VIB metal carbonyls with titania of varying levels of hydroxylation. Quantitative measurements of TPDE, chemisorption, and the activity for ethylene hydrogenation are reported.

EXPERIMENTAL

The reaction/gas manifold is constructed of metal tubing and bellows valves (Nupro) with a vacuum capability of $<10^{-7}$ Torr and a leak rate under vacuum of $<2 \times 10^{-7}$ cc/s. All catalyst activations were done in a reactor of fused quartz. Typically, a 0.100-g sample of titania (anatase, Degussa P-25) was calcined in flowing dry oxygen at 250 or 500°C, evacuated at temperature, and then cooled in flowing He to room temperature. The BET surface areas of TiO_2 after calcination at 250 and 500°C were 57.1 and 55.0 m^2/g, respectively. Catalysts were prepared by dispersing a carbonyl complex on titania by sublimation at about 65°C. Catalyst activation was usually monitored by TPDE. Briefly, TPDE involves raising the temperature at a linear rate of 10°C/min as helium (C.P. grade, highly purified by passage through a General Electric Go-Getter) is swept through the reactor and the evolution of gases (primarily CO and H_2) is continuously monitored with a pair of thermal conductivity detectors. Other gases formed during TPDE (primarily CH_4 and CO_2) are analyzed separately after TPDE by backflushing through a trap of silica gel which was held at −196°C during the run. After each backflush, pure gas samples were injected for calibration. Accuracy for the gases evolved during TPDE is ±1%. Details of the method of catalyst synthesis, the high-purity reaction system, and the TPDE technique have been previously published (*22, 23*).

Metal dispersion was measured by CO chemisorption at 23°C using an electronic pressure transducer (Sundstrand, Model 314D) after activation in helium at the given temperature for 30 min. After the first isotherm the catalyst was evacuated for 5 min. and the second isotherm obtained. The dispersions are based on the amount of chemisorption (the difference between the two isotherms) at about 200 Torr and assume a 1 : 1 CO to metal adsorption stoichiometry. Details of the chemisorption methodology have been published elsewhere (*8*).

Activity measurements for the hydrogenation of ethylene were done with a flow system immediately after catalyst activation and without removing the catalyst from the reaction line. The hydrogen (C.P. grade, purified by passage first through a Matheson Deoxo purifier and then through molecular sieves) to ethylene (C.P. grade) ratio was 4 : 1 with a total flow of 30 cc/min at a total pressure of 1 atm. Flows were controlled and monitored with an electronic mass flow controller (Brooks Instrument, 5850 and 5815 Series). The reaction products were sampled at 3-min intervals with a gas sampling valve (Carle) and analyzed by gas chromatography using a column ($\frac{1}{8}$ in. o.d. × 12 in. long) packed with silica gel (Davison Chemical, Grade 62) at room temperature. The peak areas were integrated by a Hewlett–Packard Model 3388A digital integrator. Activities are expressed in terms of the formal turnover frequency, N_f, which is the number of molecules reacting per unit time per metal atom in a catalyst (regardless of the dispersion).

Isothermal catalyst activation in helium was done at the given temperature for 30 min. Oxidations were done for 30 min. at 500°C in flowing oxygen (C.P. grade, dried over molecular sieves). Reductions were done at 500°C in a flow of hydrogen for 1 h. A "redox" treatment consists of oxidation followed by evacuation and then reduction at 500°C.

Temperature-programmed reduction (TPR) was done using a heating rate of 15°C/min in a flow of 5% H_2/Ar with a thermal conductivity detector. Data are corrected for the background consumption of

H_2 by the titania (Fig. 8). Details of the TPR procedure have been separately published (*24*). Thermal gravimetric analysis (TGA) was done using a Cahn 2000 microbalance enclosed in a thermostated and vibration-damped glass bottle with a fused quartz hangdown tube. After evacuation of the sample (8.654 mg), TGA was done under an He flow of 75 cc/min. Weight changes are accurate to 0.3 μg.

RESULTS AND DISCUSSION

Stoichiometry of Decomposition

The color of the catalysts was sandy white before TPDE and gray afterward. The TPDE chromatograms of the Group VIB carbonyls supported on titania dehydroxylated at 500 and 250°C are shown in Figs. 1–6. Table 1 gives the gas evolutions during TPDE. The main feature of these chromatograms is the appearance of a single and usually nonsymmetrical peak for CO evolution with peak maxima between 160 and 200°C. Similar behavior has been observed for the Group VIB metal carbonyls on SiO_2 (*22*), HY, and ultrastable-HY zeolites (*25*) in which stable subcarbonyl species were not observed (not isolated). In contrast, well-separated peaks indicating the formation of a stable metal tricarbonyl species were observed on alumina (*14*, *21*), magnesia (*25*), and 13X and NaY zeolites (*25*). Reasons for the difference in behavior are unknown.

In addition to CO, H_2 and traces of CH_4 and CO_2 are evolved during TPDE (Table 1). It has been shown that H_2 evolution arises from a redox reaction between surface hydroxyl groups (σ-OH) and the metal (*14*, *23*, *26*, *27*):

$$M(\mathrm{CO})_6(\mathrm{ads}) + n(\sigma\text{-OH}) \xrightarrow{\Delta} n(\sigma\text{-O}^-)_n\mathrm{M}^{n+} + (n/2)\mathrm{H}_2 + 6\mathrm{CO}. \quad (1)$$

Thus, H_2 evolution indicates an oxidation of the originally zero-valent metal. The small amount of CH_4 evolved represents additional reduction of H^+ and therefore oxidation of the metal. The average oxidation number, O.N., at any point during TPDE can be calculated by the equation

$$\mathrm{O.N.} = 2[\mathrm{H_2}] + 6[\mathrm{CH_4}], \quad (2)$$

where the quantities in brackets are the molecules of gas evolved per metal atom (integrated up to the temperature of interest). For the group VIB carbonyls supported on alumina and silica, these values have been shown to agree within ±0.2 O.N. with the values determined by oxygen titration on the same catalyst sample (*21*, *22*). After TPDE to 600°C of 0.900% Mo/TiO_2 (dehydroxylated at 500°C), the catalyst was studied by TPR to 600°C followed by isothermal reduction for 25 min. The H_2 con-

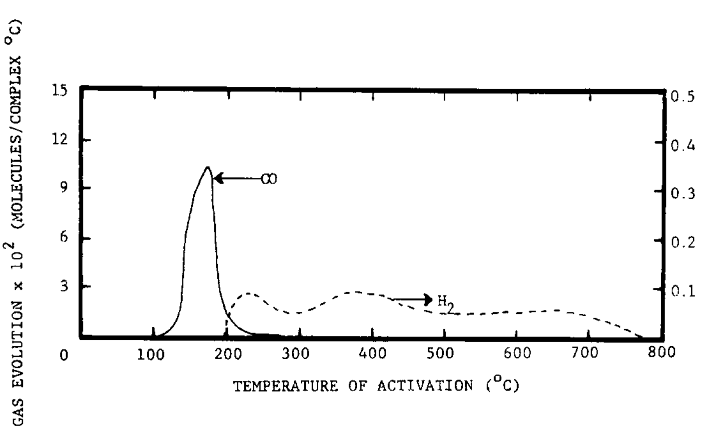

FIG. 1. TPDE of $Cr(CO)_6/TiO_2$, dehydroxylated at 500°C, 0.585% Cr.

TABLE 1

Gas Evolutions during TPDE to 800°C

Catalyst	Loading % metal	Gas evolved/metal				%C recovered	O.N.[a] by gas evolution
		CO	H_2	CH_4	CO_2		
TiO_2 (dehydroxylated at 250°C)							
$Cr(CO)_6$	0.598	5.29	0.67	0.022	0.002	89	1.5
$Mo(CO)_6$	1.234	5.39	0.88	0.041	0.027	91	2.0
$W(CO)_6$	1.086	5.49	1.41	0.106	0.011	93	3.5
TiO_2 (dehydroxylated at 500°C)							
$Cr(CO)_6$	0.585	5.41	0.30	0.008	—	90	0.7
$Mo(CO)_6$	1.492	6.06	0.10	0.011	0.034	101	0.3
$W(CO)_6$	1.362	5.90	0.01	0.051	0.003	99	0.3

[a] O.N., oxidation number.

sumption (corrected for the background due to titania Fig. 8) indicated that after TPDE the average valency of the catalyst was O.N. = 1.0 ± 0.1, in reasonable agreement with the result of Table 1 (for a different catalyst after TPDE to 800°C).

The effect of the degree of dehydroxylation of titania on the extent of oxidation is indicated by the data of Table 1. Titania dehydroxylated at 500°C caused very small amounts of oxidation (primarily due to hydrogen evolution) compared to titania dehydroxylated at 250°C. A substantial amount of the Cr, Mo, and W produced must be zero-valent, since O.N. < 1. Figures 1 through 3 indicate that activation at 200 to 250°C would result in complete decarbonylation and the nearly quantitative formation of zero-valent metal. The low temperature of synthesis would also be expected to yield well-dispersed and, it is hoped, highly active catalysts for reduction reactions. Low-valent Cr, Mo, and W have also been prepared from carbonyls supported on dehydroxylated alumina, but a higher temperature (~400°C) is required for complete decarbonylation (*14, 15, 21*).

The lower amount of oxidation on titania calcined at 500°C can be attributed to the facile dehydroxylation of titania. TGA studies by Che and co-workers (*28*) and Munvera and Stone (*29*) showed that TiO_2

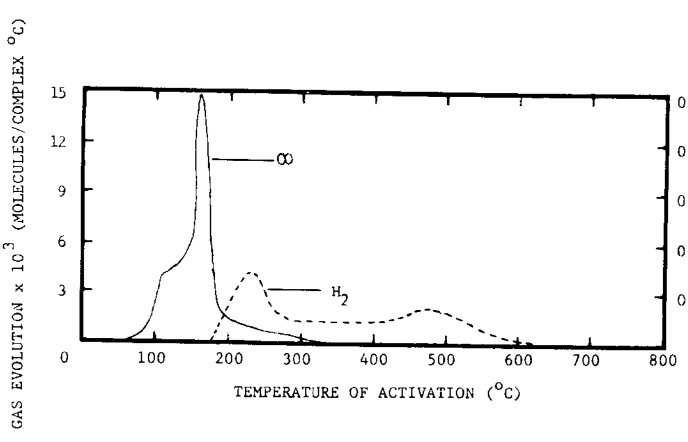

FIG. 2. TPDE of $Mo(CO)_6/TiO_2$, dehydroxylated at 500°C, 1.492% Mo.

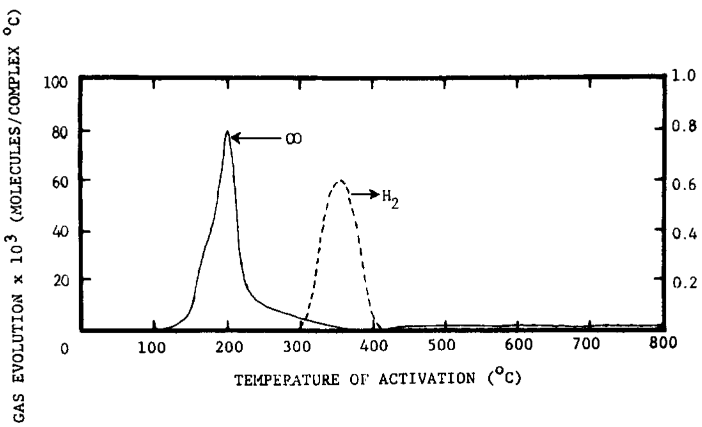

FIG. 3. TPDE of $W(CO)_6/TiO_2$, dehydroxylated at 500°C, 1.362% W.

starts becoming dehydroxylated when heated above about 300°C. Anderson (*30*) states that fully hydroxylated titania (anatase) has 4–5 OH/nm^2, but the adsorption of molecular water can increase this value to the equivalent of ~11 OH/nm^2. We also used TGA to investigate the dehydroxylation of titania. Due to the adsorption of water, it is difficult to directly establish a weight corresponding to 100% hydroxylation. Therefore, the hydroxyl content was based on the increase in weight relative to the weight after dehydroxylation at 800°C for which the hydroxyl content is assumed to be zero. This resulted in site densities of 17.8, 9.1, 4.0, 2.6, and 0.0 OH/nm^2 after dehydroxylation for 2 h (to achieve constant weight) at 23, 150, 250, 500, and 800°C, respectively.

CO Adsorption

The effect of temperature of activation on the adsorption of carbon monoxide for 1.746% molybdenum on titania (dehydroxylated at 500°C) is shown in Fig. 7. Prior to CO chemisorption, the average stoichiometries of the catalysts were 3.32, 1.40, and 0.72 CO/Mo after isothermal activation in flowing He at 100, 150, and 200°C, respectively (not measured at 300 and 400°C). A blank experiment (no complex) showed a background chemisorption of

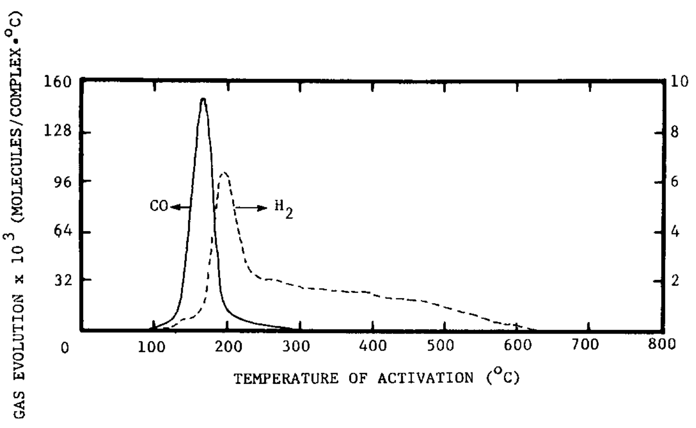

FIG. 4. TPDE of $Cr(CO)_6/TiO_2$, dehydroxylated at 250°C, 0.598% Cr.

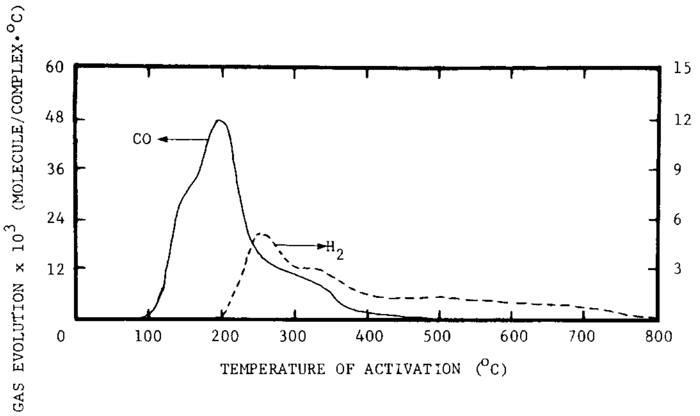

FIG. 5. TPDE of $Mo(CO)_6/TiO_2$, dehydroxylated at 250°C, 1.234% Mo.

0.208 cc CO/g TiO_2 (corresponding to 0.052 cc for this sample). However, experiments on other carbonyl systems suggest that a complex adsorbs on many of the same sites which adsorb CO, so the actual background will be less, roughly by a factor of 2. The dotted curve of Fig. 7 corresponds to the assumption of 0.052 cc background adsorption. Masuyama and co-workers (*2*) have suggested that $Mo(CO)_3$(ads) is formed after activation at 100°C. The stoichiometry, chemisorption capacity, and analogy to $Mo(CO)_3$(ads) intermediates on other supports (*21, 25*) bolster this argument. However, the TPDE chromatograms indicate that the tricarbonyl is unstable and readily undergoes additional decarbonylation which prevents preparing it quantitatively. This catalyst gave the maximum chemisorption, 1.15 CO/Mo. This indicates that the subcarbonyl species is highly dispersed and readily adsorbs CO. Highly dispersed species with stoichiometry close to tricarbonyl metal have also been reported for $Mo(CO)_6$ supported on alumina (*21*) and NaY and 13X zeolites (*25*). A separate, fresh catalyst (1.09% Mo) decomposed in helium at 400°C gave a dispersion of 18%.

Activation at higher temperatures results in substantial decarbonylation, the evolution of very small amounts of H_2 (Fig. 2), and a rapid drop in CO chemisorption. The oxidation states (calculated by Eq. (2)) of this catalyst are 0.0 and 0.2 after activation

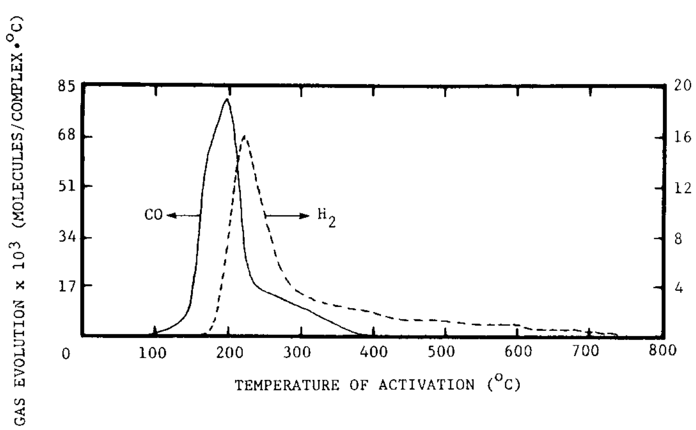

FIG. 6. TPDE of $W(CO)_6/TiO_2$, dehydroxylated at 250°C, 1.086% W.

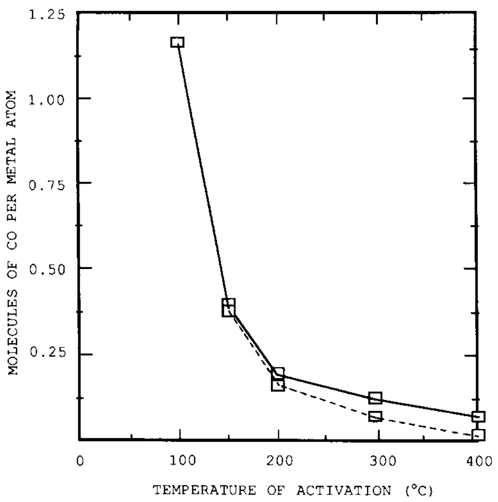

FIG. 7. CO chemisorption as a function of activation temperature for 0.25 g of 1.746% Mo/TiO_2 (dehydroxylated at 500°C). The dotted line assumes a background chemisorption of 0.052 cc CO.

at 200 and 400°C, respectively. Thus, the sudden drop in chemisorption capacity cannot be attributed to the loss of zero-valent metal. Possible explanations are agglomeration or a drop in the capacity to chemisorb CO when >3 CO/Mo are evolved. The latter explanation is more probable for several reasons. First, the drop in chemisorption capability corresponds to the temperature at which there is substantial additional CO evolution. Similar sudden drops in chemisorption capability when >3 CO/metal are evolved have been found for $Mo(CO)_6$ supported on NaY and 13X zeolites (*25*) and for $Mo(CO)_6$ and $W(CO)_6$ supported on highly dehydroxylated alumina (*31*). It is also found that the dispersion of base metal catalysts prepared on a dehydroxylated support is higher than that when a partially hydroxylated support is used. Hence, it is expected that the use of TiO_2 calcined at 250°C would also show a large drop in CO chemisorption. Second, the temperature seems too low for the massive sintering which would be required to generate such a low dispersion. In fact, noble metal catalysts prepared from carbonyls on alumina actually show increasing dispersion up to an activation temperature of about 600°C (*31*). Third, the catalytic activity can be high (vide infra), suggesting that extensive sintering has not occurred. Fourth, Guglielminotti and Zecchina (*32*) using infrared spectroscopy observed that adsorption of CO after decarbonylation of $Mo(CO)_6$ on dehydroxylated MgO at 523 K resulted in very weak bands at 2100–1700 cm^{-1}. This suggested that the Mo(0) adsorbs only very small amounts of carbon monoxide at pressures less than 1 atm. We have also found that CO chemisorption on bulk Mo(0) is weak and only about one in eight of the *surface* Mo atoms chemisorbs CO (*33*).

Chemisorption of CO on Cr and W catalysts was not studied since they are less interesting catalytically. However, studies of the three carbonyls on alumina showed that chemisorption on W was very similar to the result for Mo, and chemisorption on Cr was always low (*12, 17*).

Catalytic Activity for Ethylene Hydrogenation

The activities for the hydrogenation of ethylene as a function of the degree of hydroxylation of titania and the temperature of activation of a supported carbonyl are shown on Tables 2–5. Unless noted otherwise, activities refer to N_f at 0°C. Activation energies are found to be roughly 4 kcal/mol. Literature values are usually about 8 to 10 kcal/mol for supported metals and unsupported metal films (*34, 35*). However,

TABLE 2

Activity of $Cr(CO)_6/TiO_2$ (0.551% Cr, TiO_2 Dehydroxylated at 500°C) for the Hydrogenation of Ethylene

Activation *T* (°C)	Reaction *T* (°C)	Conversion (%)	N_f (s^{-1}) at reaction *T*	E_a (kcal/mol)	N_f (s^{-1}) at 0°C
150, He	24	0.62	2.6×10^{-3}	7.0	2.2×10^{-3}
200, He	23	0.03	1.2×10^{-4}		4.3×10^{-5a}
500, H_2	23	0.36	1.5×10^{-3}	6.7	5.8×10^{-4}
500, O_2	24	4.21	1.8×10^{-2}	15.0	1.4×10^{-3}
500, redox	25	0.32	1.3×10^{-3}	2.8	6.0×10^{-4}

[a] Extrapolated to 0°C assuming E_a = 7.0 kcal/mol.

TABLE 3

Activity of $Mo(CO)_6/TiO_2$ (Dehydroxylated at 500°C) for the Hydrogenation of Ethylene

Activation T (°C)	% Loading	Reaction T (°C)	Conv. (%)	N_f (s^{-1}) at reaction T	E_a (kcal/mol)	N_f (s^{-1}) at 0°C
100, He	0.978	25	1.21	4.9×10^{-3}	4.7	2.4×10^{-3}
150, He	0.978	25	7.42	3.0×10^{-2}	4.8	1.4×10^{-2}
200, He	0.978	25	2.35	9.5×10^{-3}	3.3	5.7×10^{-3}
300, He	0.978	50	0.07	2.9×10^{-4}	3.3	1.1×10^{-4}
500, He	0.978	100	0.07	2.9×10^{-4}	8.6	4.1×10^{-6}
500, redox	0.978	−78	86.34	3.4×10^{-1}	4.2	7.4
500, redox[a]	0.978	−78	0.07	2.9×10^{-4}	5.6	1.8×10^{-2}
200, He	0.481	−74	26.17	7.8×10^{-2}	3.6	9.2×10^{-1}
400, He	0.772	−78	88.45	3.9×10^{-1}	2.4	2.3
500, H_2	0.772	−78	93.90[b]	4.2×10^{-1}	2.5	10.4

[a] Reaction after CO chemisorption. %D = 7.8%.

[b] Reaction mixture diluted in He (total flow = 123 cc/min).

values of 5 kcal/mol have also been reported for metal films (*36*), catalysts for which diffusion limitations are not expected. In view of the range of conversions observed, it is clear that the rates are not mass transport limited. However, it is possible that internal diffusion has affected the rates and hence lowered the observed values of E_a. Table 3 gives data for $Mo(CO)_6$ supported on titania dehydroxylated at 500°C. Increasing the temperature of activation from 100 to 150°C increased the activity since more CO ligands were lost. However, as the temperature of activation increased from 150 to 300°C, the activity dropped by two orders of magnitude, from $N_f = 1.4 \times 10^{-2}$ to 1.1×10^{-4} s^{-1}. A redox treatment yielded a very active catalyst, $N_f = 7.4$ s^{-1}. Also, *fresh* catalysts activated at 200 and 400°C in helium showed high activities, $N_f = 9.2 \times 10^{-1}$ and 2.3 s^{-1}, respectively. These catalysts will be completely decarbonylated (Fig. 2). The highest activity ($N_f = 10.4$ s^{-1}) was achieved after exposure to H_2 at 500°C (unlike He, H_2 will help clean the surface by hydrogenolysis and hydrogenation of adsorbed hydrocarbons). This catalyst will be completely decarbonylated and mainly zero-valent (O.N. ≅ 0.2, Table 1 and Fig. 2). Thus, sintering is not the reason for the decrease in activity when the temperature of activation is increased from 150 to 300°C. It is probably caused by the adsorption of hydrocarbons (resulting

TABLE 4

Activity of $W(CO)_6/TiO_2$ (Dehydroxylated at 500°C) for the Hydrogenation of Ethylene

Activation T (°C)	% Loading	Reaction T (°C)	Conv. (%)	N_f (s^{-1}) at reaction T	E_a (kcal/mol)	N_f (s^{-1}) at 0°C
150, He	1.005	−74	29.53	4.2×10^{-2}	2.5	2.3×10^{-1}
200, He	0.962	−78	16.11	2.4×10^{-2}	2.2	1.1×10^{-1}
300, He	0.962	25	2.28	3.4×10^{-3}	1.3	2.8×10^{-3}
500, H_2	0.962	25	3.83	5.7×10^{-3}	1.5	2.6×10^{-3}
500, O_2	0.962	25	0.06	9.6×10^{-5}	—	6.7×10^{-5}[a]
500, redox	0.962	25	11.41	1.7×10^{-2}	3.8	9.4×10^{-3}

[a] Assumes E_a = 2.3 kcal/mol.

TABLE 5

Activity (N_f, s^{-1}) at 0°C of Group VIB Metal Carbonyls on Titania (Dehydroxylated at 250°C) for the Hydrogenation of Ethylene

Complex	Loading (% metal)	Activation		
		200°C, He	500°C, H_2	Redox
$Cr(CO)_6$	0.483	1.9×10^{-4}	1.0×10^{-3}	1.4×10^{-3}
$Mo(CO)_6$	0.976	2.5×10^{-1}		
$Mo(CO)_6$	0.081	6.0×10^{-2}	1.1	1.0
$W(CO)_6$	0.452	1.9×10^{-1}	4.0×10^{-4}	2.0×10^{-2}

from the reaction) which poison the catalyst as the temperature is raised. Oxidation at 500°C converts the Mo to Mo(VI) which is nearly inactive, $N_f = 4.1 \times 10^{-6}$ s^{-1}. As the oxidation state of the Mo increases from 0 to 6, the activity of the catalyst drops by a factor of 10^6.

Supported MoO_3 is inactive, MoO_2 is of low activity, and Mo(0) is highly active for the hydrogenation of ethylene. Mo(0) supported on dehydroxylated alumina gave $N_f = 27$ s^{-1} and a Mo film gave a turnover frequency (N, not N_f) of $N = 0.9$ s^{-1} under the conditions used here (*15*). The high activities of some of the Mo/TiO_2 catalysts are consistent with the Mo being well dispersed and primarily zero-valent. As noted in the previous section, after the loss of >3 CO/Mo, CO chemisorption probably significantly underestimates the true dispersion, so, if calculated, turnover frequencies (N, not N_f) would be anomalously high. The TPR (Fig. 8) of MoO_3/TiO_2 (prepared by oxidizing $Mo(CO)_6$) showed that Mo^{6+} can be reduced to below Mo^{1+} (after correction for the blank, Fig. 8, average O.N. = 0.9 ± 0.5) at approximately 800°C (isothermal reduction can be achieved at lower temperature). This is about 200°C lower than that for MoO_3/Al_2O_3 (*33*) and MoO_3/SiO_2 (*37*). Tanaka et al. (*38*) found that MoO_3/TiO_2 with less than 5% Mo can be completely reduced to Mo(0) in hydrogen at 500°C in 1 h. This result is unusual in both that the supported MoO_3 is easier to reduce than bulk MoO_3 and that the reducibility increases as the loading is decreased. The high activity after redox treatment suggests that our MoO_3/TiO_2 is also reduced to Mo(0) by H_2 at 500°C in 1 h.

CO poisons the activity of the catalyst. This can be seen by the 400-fold drop in activity of the 0.978% Mo catalyst after redox treatment and then CO chemisorption. These data also indicate that ≤7.8% of the Mo is active. Residual CO ligands also poison a catalyst. This is shown by the first two entries in Table 3. Stoichiometry measurements referred to earlier indicate that after activation at 100°C the first catalyst had about 3.3 residual CO/Mo, whereas after activation at 150°C only 1.4 CO/Mo is left. The latter catalyst is sixfold more active, and probably would be much more active if it were a fresh catalyst (vide supra).

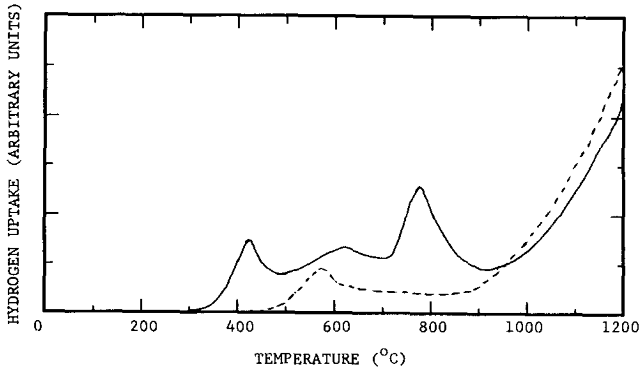

FIG. 8. TPR of MoO_3/TiO_2 (dehydroxylated at 500°C), 0.900% Mo. Dotted line represents the TPR of bare TiO_2.

Table 5 shows the effect of using titania of different levels of hydroxylation. It is normally found that carbonyls are more active when deposited on a dehydroxylated support since reaction (1) is suppressed and this results in a lower valent catalyst (*15*, *39*). However, Figs. 4–6 and Table 1 indicate that on titania, activation of a carbonyl at only 200°C does not result in much oxidation. By comparison of equivalent activations from Tables 3 and 5 (the 0.481% Mo catalyst of Table 3 should be used for comparison of activations at 200°C, since it is a fresh catalyst), it is seen that in each case titania dehydroxylated at 500°C resulted in about tenfold higher activity.

Data for Cr are shown in Table 2. The first catalyst had a modest activity, $N_f = 2.2 \times 10^{-3}$ s^{-1}, which may be compared to the value for decarbonylated Cr(0) supported on dehydroxylated alumina, $N_f = 0.9$ s^{-1} (*15*). The lower activity is probably due to residual CO ligands. Activation at 200°C lowered the activity, probably due to poisoning by adsorbed hydrocarbons (vide supra). Treatment with H_2 at 500°C only partially restored the activity. This material will be completely decarbonylated, but unlike the case with Mo, H_2 may fail to clean the surface due to the very low activity of Cr for hydrogenolysis. Oxidation and a redox treatment give improved and similar activities. The effects of O_2 and H_2 at 500°C on Cr supported on titania are not known. However, TPR and temperature-programmed oxidation experiments (*33*) show that CrO_3/Al_2O_3 is reduced to an average oxidation number of 2.7 ± 0.3, reoxidation of this material yields O.N. = 3.3 ± 0.3, and repeated reduction again yields O.N. = 2.7. Thus, the series of catalysts in Table 2 effectively spans the oxidation states 0 through 3. Partly for this reason, the activities vary by only fourfold (excepting the poisoned catalyst in the second line). The use of titania dehydroxylated at 250°C (Table 5) sometimes gives higher and sometimes lower activity than titania calcined at 500°C.

$W(CO)_6$ activated at 150°C in He gave $N_f = 0.23$ s^{-1} and activation of a fresh catalyst at 200°C gave about the same activity, $N_f = 0.11$ s^{-1} (Table 4). It is unexpected that the more decarbonylated catalyst did not give higher activity. The activities are similar to the value ($N_f = 0.9$ s^{-1}) for decarbonylated W(0) supported on dehydroxylated alumina (*15*). Treatment at 300°C lowers the activity, probably due to poisoning by hydrocarbons. Activation in H_2 at 500°C does not regenerate the activity, again probably due to the low activity of W for hydrogenolysis. Oxidation converts the catalyst into nearly inactive W(VI) and a redox treatment yields modest activity. This suggests that the WO_3 is not fully reduced. Thermodynamics for the reduction of bulk MoO_3 and WO_3 are similar, but when supported on alumina and silica, WO_3 is harder to reduce (*33*, *40*). As the oxidation state of the W increased from 0 to 6, the activity dropped by a factor of 10^3. Data in Tables 4 and 5 indicate similar activities for the two types of titania.

The order of activities is Mo > W > Cr. This is the same order found for the complexes supported on alumina for the hydrogenations of ethylene (*15*) and benzene (*20*), methanation (*12*), Fischer–Tropsch synthesis (*18*, *19*), the hydrogenolysis of ethane (*17*) and for ethylene hydrogenation over metal films (*41*, *42*).

ACKNOWLEDGMENT

Support of this research by the Department of Energy, Office of Basic Energy Sciences, is gratefully acknowledged.

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