JOURNAL OF CATALYSIS 61, 216–222 (1980)

The Synthesis and Nature of Heterogeneous Catalysts of Low-Valent Tungsten Supported on Alumina

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Received February 5, 1979; revised August 21, 1979

Temperature-programmed decomposition has been used to study the nature of the bonding to Al_2O_3 of the zero-valent catalyst precursor $W(CO)_6$. The pretreatment conditions and activation temperatures which lead to the formation of supported, low-valent W (which cannot be prepared by the standard techniques of catalyst synthesis) have been identified. At temperatures below 200°C highly dispersed, zero-valent, subcarbonyl species are formed. $W(CO)_3$ads is readily isolated and the decomposition can be reversed by exposure to a flow of CO. This is only the second system for which the stoichiometry of supported subcarbonyl species has been identified. Decomposition at high temperatures is sensitive to the ratio of hydroxyl groups on the alumina divided by the number of complexes on the surface. At high ratios the primary product of the complete decarbonylation is W(VI), whereas at low ratios W(0) is the primary product. Both of these products are also well dispersed and the complete decomposition is not reversible.

INTRODUCTION

Catalysts of supported tungsten are normally made by impregnating a support of high surface area, such as alumina, with an aqueous solution of a hexavalent salt of tungsten, such as ammonium tungstate. It has recently been shown that the supported WO_3 which is formed during the calcination of these catalysts cannot be appreciably reduced by treatment with hydrogen at 550°C even though bulk WO_3 can be reduced to tungsten metal at these conditions (*1*). Consequently, it is of interest to investigate the interaction of $W(CO)_6$, a zero-valent complex of tungsten, with alumina as a possible means of preparing supported tungsten in low oxidation states.

The surface reactions between $W(CO)_6$ and alumina have been briefly investigated using infrared spectroscopy (*2, 3*). One report (*2*) claims that on γ-Al_2O_3 the hexacarbonyl undergoes complete decarbonylation near room temperature without the formation of any isolatable subcarbonyl species, that the product of the decomposition is W(0), and that the decomposition can be reversed by exposure to 50 Torr of CO at 45°C. In another infrared spectroscopic study Bilhou *et al.* (*3*) found tha on η-Al_2O_3 the decarbonylation of $W(CO)_6$ was complete at 120°C and no carbonyl species were regenerated by exposure to CO. Brenner and Hucul (*4*) have reported preliminary studies of $W(CO)_6/\gamma$-Al_2O_3 using the technique of temperature-programmed decomposition (TPDE). It was here claimed that reversibly formed subcarbonyl species may exist and that the complete decarbonylation requires high temperatures, is probably not reversible, and does not yield W(0) as the primary product. In this paper we attempt to resolve these differences by presenting a more detailed and quantitative study of the decomposition and bonding of $W(CO)_6/Al_2O_3$.

EXPERIMENTAL

The details of the rigorously air-free catalyst preparation, the high-purity vacuum system, and the TPDE technique have been recently published (*5, 6*). For these experiments 0.500 g of γ-Al_2O_3 (Conoco Catapal SB, 60–80 mesh, a_s = 250 m^2/g, average pore diameter = 7 nm and in one experiment η-Al_2O_3 prepared from β-trihydrate, a_s = 150 m^2/g) was calcined for ~1 hr in flowing O_2 at the pretreatment temperature (for catalysts I, L, M, and N the oxidation was done at 500°C) followed by evacuation

0021-9517/80/010216-07$02.00/0

at that temperature for about another 1 hr. The TPDE were done at $\beta = 5$ K/min unless stated otherwise. Carbonyl which sublimed from the reactor during catalyst activation was condensed in a cold trap downstream from the reactor and analyzed by uv spectroscopy to allow the calculation of the true catalyst loading. In two experiments the average oxidation number (O.N.) of the catalysts was determined after TPDE by titration with small pulses of O_2 at 500°C to form W(VI). With correction for the small amount of CO_2 formed, determination of the amount of O_2 consumed allows a trivial calculation of what the O.N. had been. In one experiment the reactor effluent was sampled and analyzed (Spherocarb column) at intervals of 12°C to determine the temperature at which the CH_4 was formed.

RESULTS

Table 1 summarizes the characteristics of each catalyst and Table 2 contains the stoichiometries of the TPDE. For some of the earlier runs the values of the H_2 evolution are low, but the forms of the TPDE spectra are otherwise correct. Additional analyses using a type C catalyst revealed that the CH_4 is formed in a single peak coincident with the high temperature CO (and H_2) peak, but displaced 20°C higher in temperature. Not included in Table 2 are very small evolutions of C_2 hydrocarbons, about 0.01 C_2H_4 and 0.03 C_2H_6 per W, which were observed in runs for which the alumina was calcined below 600°C (no C_3 were detected). Blank experiments indicated that roughly half of this material (but a negligible part of the other gases evolved) was derived from the pentane.

Unless stated otherwise, the TPDE commenced at 25°C and were terminated at 600°C. Prior to TPDE the catalysts were white except catalysts prepared by sublimation at 60°C which were light yellow. After TPDE catalysts pretrated below 700°C were light, sandy brown. The other catalysts were progressively darker after heating, catalyst L being dark brown and catalyst M being black. Figures 1 through 4 illustrate the TPDE of $W(CO)_6/\gamma\text{-}Al_2O_3$ after various temperatures of pretreatment. The TPDE of catalyst D (prepared on $\eta\text{-}Al_2O_3$) was nearly identical to that of catalyst C.

Integration of the low-temerature TPDE peak for all of the catalysts pretreated between 350 and 750°C yielded 3.0 ± 0.1 CO/W. Figure 5 shows the evolution of CO from a catalyst which was activated

TABLE 1

Catalysts

Catalyst designation	Pretreatment (°C)	Type impregnation	Sublimation (%)	Loading (%W)	Hydroxylation of Al_2O_3 (%)	$\frac{\sigma - OH}{W}$
A	350	Pentane	42	0.206	52	181
B	350	Pentane	31	0.212	52	175
C	500	Pentane	30	0.228	28	88
D ($\eta\text{-}Al_2O_3$)	500	Pentane	29	0.373	28	54
E	500	Pentane	32	0.200	28	100
F	500	Dry mix	1	0.335	28	60
G	530	Pentane	17	0.108	25	166
H	625	Pentane	27	0.183	14	55
I	750	Dry mix	3.1	0.361	5	10
J	750	Pentane	23	0.218	5	16
K	900	Pentane	30	0.432	~1.5	3
L	950	Dry mix	2.2	0.324	~1	2
M	950	Dry mix	25	1.212	~1	0.5
N	1000	Dry mix	49	1.16	~0.6	0.4

TABLE 2

Gas Evolutions during TPDE[a]

Catalyst designation	Gas evolution per W				Peak maxima (°C)			E_a (kcal/mol)		O.N. by gas evolution	O.N. by O_2 titration
	CO	CH_4	CO_2	H_2	Low T CO	High T		Low T CO	High T CO		
						CO	H_2				
A	5.35	0.12	0.33	2.4	150	257	256	31	40	5.5	
B	5.48	0.21	0.25	—	153	270	270	31	41	—	
C	5.40	0.22	0.11	2.07	131	287	284	30	42	5.7	
D (η-Al_2O_3)	5.11	0.25	0.17	1.8	129	278	274	30	41	5.1	
E	5.42	0.24	0.02	—	130	302	302	30	43	—	
F	5.39	0.33	0.09	1.71	137	293	293	30	42	5.8	5.8
G	5.46	0.23	0.27	—	130	342	343	30	46	—	
H	4.87	0.30	0.45	—	124	355	355	29	47	—	
I	4.39	0.30	0.001	0.80	116	360	418	29	48	3.4	
J[b]	5.28	0.25	0.17	—	115	362	421	28	48	—	
K[b]	6.08	0.08	0.006	—	110	317	730	28	44	—	
L[c]	4.65	0.06	0.000	0.32	172	~400	>600	31		1.0	
M	4.97	0.006	0.002	0.19	136	See discussion		30		0.4	
N[b]	5.20	0.007	0.002	0.51	138	~750	~750	30		1.1	1.0

[a] Dashes indicate early runs for which H_2 data were not accurate.

[b] For runs J, K, and N the TPDE was continued up to 750, 900, and 950°C, respectively.

[c] $\beta = 30$ K/min, this will shift the peaks upscale relative to runs at $\beta = 5$ K/min.

isothermally at 135°C in flowing He. After 1 hr the rate of CO evolution had decreased by a factor of 5×10^3, the cumulative evolution of CO was 2.96 CO/W (no CH_4 was detected), and the catalyst was gold colored. Flowing CO over this material at 135°C led to the recovery of 46, 56, and 68% of the $W(CO)_6$ after 15, 30, and 180 min, respectively. Raising the temperature to 175°C increased the recovery to 73% after 1 hr and 75% after 2.5 hr. Flowing an equimolar mixture of H_2 and CO at 130 or 350°C for 1 hr over a type C catalyst after TPDE to 600°C failed to recover any of the supported $W(CO)_6$ in a cold trap downstream of the reactor (<0.03%).

DISCUSSION

As noted in the introduction, catalysts of supported W are usually made by impregnation with salts of W(VI) and are resistant to reduction, even at quite high temperatures. The technique of catalyst synthesis utilized here is quite different: (i) No water is present. (ii) The catalyst precursor is a zero-valent, molecular complex. (iii) The comlex may be decomposed at comparatively low temperatures. (iv) The synthesis is sufficiently free of extraneous components to allow the stoichiometry of the individual surface reactions accompanying catalyst activation to be analyzed and

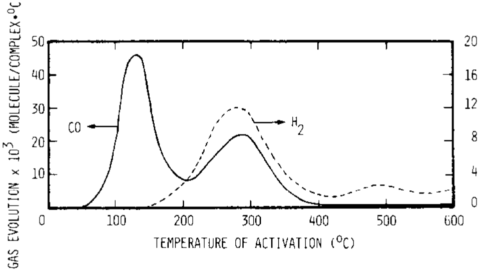

FIG. 1. The TPDE of catalyst C.

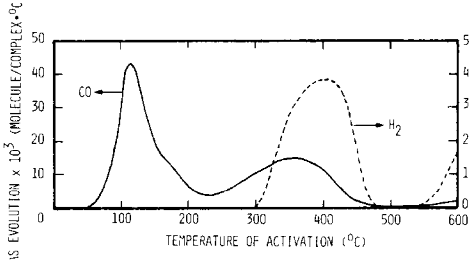

FIG. 2. The TPDE of catalyst J.

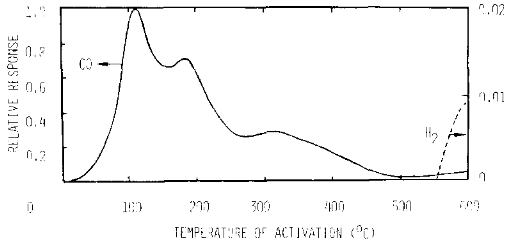

FIG. 3. The TPDE of catalyst K.

quantified *as they occur*. These changes should encourage the synthesis and characterization of catalysts containing highly dispersed, low-valent, supported W.

Low-Temperature Decomposition

Table 1 indicates that there can be substantial sublimation of $W(CO)_6$ from the alumina during catalyst activation. Sublimation of $Mo(CO)_6$ under similar conditions is several fold less (*9*). Experiments with other supported carbonyls suggest that one parameter important in determining the amount of sublimation is the volatility of the carbonyl. For example, sublimation of highly volatile $Fe(CO)_5$ is much larger than for $Fe_3(CO)_{12}$ (*6*). However, the vapor pressure of $W(CO)_6$ is about threefold less than that of $Mo(CO)_6$. Also important is the temperature required to achieve initial decarbonylation of the complex, since higher temperatures enhance the ability of the complex to sublime from the support prior to binding to it. $W(CO)_6$ decomposes about 30°C higher than does $Mo(CO)_6$ (*14*), and correction for this temperature difference gives $W(CO)_6$ an effective vapor pressure twice that of $Mo(CO)_6$ (*10*). Sublimation from SiO_2 is much higher for both carbonyls, and the peak for CO evolution comes at about 150°C (*5*).

The TPDE spectra of all but the most dehydroxylated catalysts display two peaks with the first peak containing 3.0 CO/W. This suggests the formation of a relatively stable $W(CO)_3$ ads intermediate. The existence of this species is further confirmed by a highly accurate isothermal activation at 135°C (Fig. 5). It is very unlikely that in each of these experiments a mixture of subcarbonyl species fortuitously provided an integral average for the amount of CO evolved per W (*7*). The only other such subcarbonyl species unambiguously identified are $Mo(CO)_n$ads, $n = 3, 4, 5$, on Al_2O_3 (*8*). The TPDE spectra of $W(CO)_6$ and $Mo(CO)_6$ on Al_2O_3 are very similar and the latter system has been studied in great detail (*9*). Thus, by analogy it is likely that $W(CO)_3$ads is formed by the stepwise decomposition of $W(CO)_6$ads, $W(CO)_5$ads, and $W(CO)_4$ads each of which can probably be isolated in high yield under the appropriate conditions (*8*), but is unstable under these reaction conditions.

The formation of $W(CO)_3$ads is reversible since $W(CO)_6$ is recovered in moderately high yield upon exposure to CO at 135°C. $W(CO)_6$ is not formed by reaction of CO with finely divided W metal at these mild conditions (*10*). It is unclear why the recovery of $W(CO)_6$ is not quantitative, however, it is noteworthy that some $W(CO)_6$ was still being recovered when the experiment was

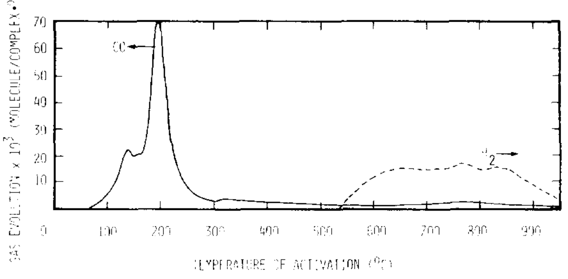

FIG. 4. The TPDE of catalyst N.

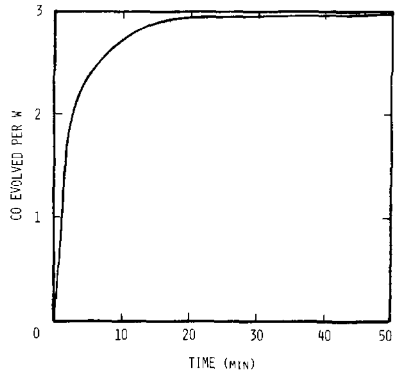

FIG. 5. The evolution of CO in flowing He from a type G catalyst at 135°C.

terminated. The $W(CO)_3$ads is zero-valent since neither H_2 nor CH_4 was evolved during its formation (vide infra). Furthermore, it is likely that most of the $W(CO)_3$ads is *molecularly dispersed* on the surface since the three CO ligands will tend to isolate each of the W atoms (*9*).

It has been shown (*5, 11*) that the kinetics of the decomposition of the hexacarbonyls supported on SiO_2 can be described by a semiempirical technique in which the preexponential factor in the rate constant is set equal to $10kT_m/h$ and the position of the peak maximum, T_m, then determines the activation energy, E_a, for M–CO bond scission (k is Boltzmann's constant and h is Planck's constant). Although the CO peaks for the Al_2O_3-supported system are broader than the theoretical value for a unimolecular decomposition on a homogeneous surface (for which the peak width at half maximum is ~25°C) at least the low-temperature peaks are still much narrower than usually observed during the temperature-programmed desorption of gases adsorbed on high surface area materials. A heterogeneity inducing a spread of about 3 and 8 kcal/mol in the low- and high-temperature peaks, respectively, would account for the observed peak broadening. The E_a determined in this manner are shown in Table 2.

High-Temperature Decomposition

The data in Table 2 and Figs. 1 to 4 clearly indicate that moderately high temperatures are required for the complete decomposition of $W(CO)_6/Al_2O_3$. A carbon balance using the data in Table 2 also indicates that except for the experiments involving highly dehydroxylated Al_2O_3 no more than a few percent of the products of decomposition could have escaped detection. The poorer carbon balance in the latter cases is partly due to a small amount of decomposition (or possibly slow desorption from these highly activated supports) occurring above 600°C as evidenced by Fig. 4. Thus, runs H, I, L, and M which were terminated at 600°C have a poorer carbon balance than runs J, K, and N. Comparing runs J and I one also sees the expected passivation of the surface caused by pentane.

Extensive H_2 evolution accompanies the second CO peak of all except the most dehydroxylated catalysts. For a variety of systems including $Mo(CO)_6$ (*9*) and the Fe carbonyls (*6*) on Al_2O_3 and the hexacarbonyls on SiO_2 (*5*), this H_2 evolution has been shown to result from a redox reaction between surface hydroxyl groups (σ-OH) and the initially zero-valent metal in a reaction which may be approximated as:

$$W(CO)_6 + n(\sigma - OH) \xrightarrow{\Delta} (\sigma - O^-)_n W^{n+} + (n/2)H_2 + 6CO \quad (1)$$

The small amount of CH_4 which is evolved represents additional reduction of H^+ and therefore oxidation of the W. Hence, by measuring these gas evolutions an accurate measure is obtained of the average O.N. of the W at any time during TPDE. For example, for catalyst N the average O.N. after TPDE is 2(0.51) + 6(0.007) = 1.06. Note that the H_2 evolution (which is continuously monitored during TPDE) primarily determines the amount of oxidation. As shown in the figures and Table 2, oxidized W is usually the product of the complete decomposition, but $W(CO)_3$ads is zero valent.

Since the recovery of CO is not 100%, it is possible that other reactions are occurring which effect the O.N. of the W. It has already been noted that tiny amounts of C_2 hydrocarbons are formed which also represent additional oxidation of the W. Due to the uncertain level of the background this has been neglected for the catalysts prepared by impregnation, but this can only cause the values of O.N. shown in Table 2 to be low by about 0.2 unit. The mechanism by which CO_2 is formed during TPDE is unknown, but we feel that the Boudouard reaction

$$2CO \rightarrow C + CO_2 \qquad (2)$$

(which does not effect the O.N. of the W) is the most likely candidate. (We find that TPDE of some of the group 8B metals (which have substantial evolutions of CO_2) yields negative values for the O.N. if one assumes that CO_2 implies reduction of the metal. Also, except on highly dehydroxylated supports, the amount of missing carbon is often similar to the amount of CO_2 formed which is consistent with the stoichiometry of reaction (2). If this is also the case for $W(CO)_6/Al_2O_3$, then the carbon balances of Table 2 are also improved.) In any case, titration with O_2 allows an independent check on the O.N. of the W which is without the preceding qualifications. As shown in Table 2, there is excellent agreement between the two methods, even for catalyst N for which the carbon balance is comparatively poor. Similar agreement between the two techniques has also been demonstrated for other catalysts of supported carbonyls (*5*, *6*, *9*) which include both cases of excellent and poor carbon balance.

The critical parameter in determining the amount of oxidation during activation at high temperature is the ratio σ-OH/W. Thus, runs F and L show that lowering the concentration of σ-OH lowers the amount of oxidation, and runs L and M show that increasing the loading lowers the amount of oxidation. Only if σ-OH/W $\lesssim 20$ is the amount of oxidation reduced. (It should be pointed out that the values for the level of hydroxylation of alumina in Table 1 are very approximate for pretreatment temperatures above 750°C (*13*).) This suggests mobility of the σ-OH at $T \gtrsim 300°C$ since the probability is very low of there being sufficient clumps of σ-OH (the stoichiometric requirement to form W(V) is 5 σ-OH) at this level of dehydroxylation (*12*). Infrared spectroscopic studies suggested mobility above 400°C (*13*). Consistent with these observations, reducing σ-OH/W to a very low value can shift the decomposition product from primarily W(VI) to primarily W(0) (Table 2). In comparing runs M and N it may appear that the O.N. for catalyst N is anomalously high, but this is due to the TPDE of run N being continued to 950°C (Fig. 4). Hence, $W(CO)_6$ can be used to provide two types of supported, low-valent W: highly dispersed subcarbonyl species after decomposition at low temperatures and W(0) after decomposition at high temperatures on a support with σ-OH/W $\lesssim 1$. Although direct proof is lacking, it is also likely that the high-temperature forms of the catalyst are highly dispersed since Eq. (1) effectively requires that all of the W be accessible for reaction with σ-OH. Presumedly, the absence of σ-OH would not substantially increase the surface mobility of the W species causing a low dispersion of W(0). It is likely that other supports lacking oxidation ability could also be used to synthesize highly dispersed, low-valent W.

The complete decomposition of $W(CO)_6/Al_2O_3$ is irreversible. The lack of reversibility for the oxidized decomposition products but the existence of reversibility for the subcarbonyl species was also found for other supported carbonyls (*5*, *6*, *8*). By inference from the similar chemistry of $Mo(CO)_6/Al_2O_3$ (*9*), it is also unlikely that significant quantities of $W(CO)_2$ads or $W(CO)$ads accumulate during the decarbonylation and oxidation of $W(CO)_3$ads.

As shown in Table 2, the peak positions depend on the temperature of pretreatment of the Al_2O_3. At higher temperatures of pretreatment, the first CO peak develops a pronounced shoulder and then splits into two peaks and the high temperature CO peak flattens (Figs. 2–4). The H_2 peak is shifted to higher temperatures. Run M was distinct from all other TPDE of $W(CO)_6$ and $Mo(CO)_6$ on Al_2O_3 in that about half of the H_2 was evolved during the low-temperature CO peak, the remainder being evolved above 520°C. As the pretreatment temperature is lowered, the separation between the high and low temperature CO peaks decreases in a roughly linear manner. The reason for these effects is unknown at this time, but it is interesting to note that on SiO_2 the ultimate coalescence occurs with a single peak ($CO + H_2$) being observed at 160°C (*5*).

In general, the TPDE of dry mix runs are very similar to the results from runs in which the complex was supported by impregnation. However, during the dispersion of solid $W(CO)_6$ (done at 60°C) prior to TPDE, ~0.7 CO/W is evolved and this causes the peak height of the lowest temperature CO peak to be ~40% lower than it is in wet mix runs.

The amount of CH_4 formed first increases and then decreases as the temperature of pretreatment of the alumina is increased (Table 2). Since the CH_4 is formed simultaneously with the second CO peak, the initial increase in CH_4 formation is probably related to the second CO peak being shifted to higher temperatures and therefore allowing a more efficient hydrogenation of the carbonyl ligands (Arrhenius effect). At very high temperatures of pretreatment, the decrease in σ-OH/W limits CH_4 formation.

In studying the surface chemistry of $W(CO)_6/Al_2O_3$ by highly quantitative techniques, some discrepancies have been revealed with the results of the infrared spectroscopic studies. The reasons for the differences are unknown. However, it should be pointed out that the interaction of carbonyls with a support results in a complex mixture of sublimed carbonyl, subcarbonyl species, gas evolutions, and oxidation. Hence, unless the experimental conditions are carefully chosen it would be very difficult to separate clearly the various phenomena using infrared spectroscopy. It appears that TPDE data coupled with infrared spectroscopic studies would be especially valuable.

ACKNOWLEDGMENTS

Support of this work by the AMAX Foundation, Research Corporation, and donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We are also grateful to Wayne State University for a Faculty Research Award and E. Kugler (Exxon) for providing the sample of η-Al_2O_3.

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