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# Formation of Tungsten Carbide during Carbon Monoxide Activation of Tungsten Oxide on Silica Disproportionation Catalysts

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Tungsten carbide is formed during the carbon monoxide activation of tungsten oxide on silica gel disproportionation catalysts. A study of the catalyst activation in $H_2$, $H_2 + H_2O$, CO, and $CO + CO_2$ has shown that the catalyst can be selectively reduced to the substoichiometric oxides $WO_{2.84}$ and $WO_{2.72}$, $WO_2$, and WC. Reduction in CO only or $H_2$ followed by CO did not produce a uniform reduction along the length of the catalyst bed due to the inhibiting effect of $CO_2$ on the reduction. The pure binary oxide forms were not highly active for the disproportionation reaction. Minor amounts of tungsten carbide in a matrix of $WO_{2.72}$ or pure tungsten carbide on silica gel are highly active for the disproportionation reaction.

## INTRODUCTION

Several authors have reported the existence of long induction or "break-in" periods during the catalytic disproportionation of olefins over tungsten oxide supported on silica gel (*1–6*). During this break-in period the color of the catalyst changes from yellow, characteristic of $WO_3$, to blue, the color ascribed to the various substoichiometric oxides of tungsten. The blue form can also be produced by prior activation of the catalyst in hydrogen; however, this did not eliminate the induction period (*3, 5*). Another reported feature of the catalyst was the unexpected mass transfer limitations, which has been explained as being due to a small number of very active sites widely separated on the catalyst surface (*1*).

The catalytic disproportionation of stilbene with ethylene (*6–7*)

$$C_6H_5\text{–}CH{=}CH\text{–}C_6H_5 + C_2H_4 \rightleftharpoons 2\ C_6H_5\text{–}CH{=}CH_2$$

is an equilibrium controlled reaction, with an equilibrium constant of ca. 3.6 at 500°C. The selectivity of the reaction is greater than 99% for styrene at temperatures up to about 480°C. The tungsten oxide catalyst used for studying this reaction exhibited the same long break-in periods as reported with other olefin systems, with equilibrium conversion being approached after 4–6 hr on stream at 450–500°C if the catalyst had been activated in air or reduced in hydrogen for varied periods of time at temperatures up to 600°C. Immediate equilibrium conversions were achieved at contact times as low as 0.25 sec if the catalyst was activated in CO at 550°C and higher. A detailed study of the catalyst activation in $H_2$, $H_2 + H_2O$, CO, $CO + CO_2$ blends, and series combinations of these gases has shown that (a) the catalyst can be uniformly and selectively reduced to $WO_{2.84}$, $WO_{2.72}$, or $WO_2$, none of which is the most highly active form for disproportionation, (b) activation of the catalyst in CO only or in CO after reducing in $H_2$ does not give uniform reduction of the catalyst along the length of the catalyst bed due to the inhibiting effect of $CO_2$ on the CO reduction, and (c) the ulti-

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mate product from the exhaustive reduction in CO is tungsten carbide supported on silica gel.

## EXPERIMENTAL

Samples of the tungsten oxide on silica catalysts were reduced in $H_2$, CO, or CO–$CO_2$ blends at different temperatures. The reactor effluent during CO reduction was analyzed at regular intervals for $CO_2$. Graphical or computer integration of the $CO_2$–time curve was used to determine the millimoles of $CO_2$ produced during the reduction. The reduced samples were titrated with $O_2$ using dilute (2–4 mole%) blends of $O_2$ in helium. The effluent from the reactor was sampled at regular intervals and analyzed by gas chromatography (GC) to determine millimoles of $O_2$ reacted. For those samples reduced in CO, $CO_2$ was evolved during the reoxidation. The periodic sampling and analysis of the effluent permitted the determination of the millimoles of $CO_2$ produced and the millimoles of $O_2$ reacted during the reoxidation. The millimoles of $O_2$ and $CO_2$ could be related to the reactions occurring during the oxidation step.

### *A. Catalyst Preparation*

The catalyst samples were prepared by impregnation of Davison Grade 59 silica gel (previously calcined at 600°C in air) with aqueous ammoniacal solutions of ammonium metatungstate (Sylvania) using the minimum solution technique. After air drying the impregnated gel was calcined in air at 600°C to convert the salt to $WO_3$ (*8*). Potassium salts (0.1–0.2% as $K_2O$) were added to some of the samples to neutralize the acidic sites on the support. The weight percent loading on the catalyst was calculated from the weights of support, ammonium metatungstate, and calcined catalyst.

The tungsten oxide level used for the work reported here was 20%. Although this level was higher than was ultimately found necessary for optimum performance of the catalyst, the catalyst pellets were completely and uniformly coated (see below), with no evidence of uncoated surface area. Catalyst loadings from 7.5 to 30% $WO_3$ gave the same results, as did samples containing no added potassium salts. Other silica gels and macroporous silica beads produced the same results. The surface area of the catalysts after calcination was ca. 200 $m^2/g$ and did not change significantly with the various reduction and oxidation cycles.

Portions of each preparation were reduced in hydrogen at 500–550°C to the blue form in order to observe the distribution of $WO_3$ on the support. The reduced catalyst particles were uniformly colored, both on the surface and the interior of the particles.

The catalysts were tested for disproportionation activity in a type 309 stainless steel reactor; details of these studies will be reported separately.

### *B. Apparatus*

A schematic flow diagram of the apparatus used is shown in Fig. 1. The gas control system provided regulated supplies of helium, air, CO, and various blends used in the catalyst reduction and oxygen titration/carbon burnoff steps. Flow rates were in the range 90–160 scc/min. Brooks flowmeters with R-2-15-AA tubes and glass and stainless steel floats were found suitable in the flow ranges used. Four-port rotary valves (Whitey 43Y series) provided the ability to direct the feed gases to the reactor or vent. Lines connecting the gas control system to the reactor were 1/16 in. o.d. × 0.03 in. i.d.

Figure 2 is a drawing of the three-zone quartz reactor used for the catalyst reduction studies and for the determination of the carbon content and oxygen consumption of the samples. The feed gas was preheated to reaction temperature in the first zone filled with quartz chips. When the reactor was used for the reduction studies, the catalyst was placed in the third zone and the center zone was filled with quartz beads to reduce the void space. When used for carbon/oxygen analyses, the catalyst was placed in the

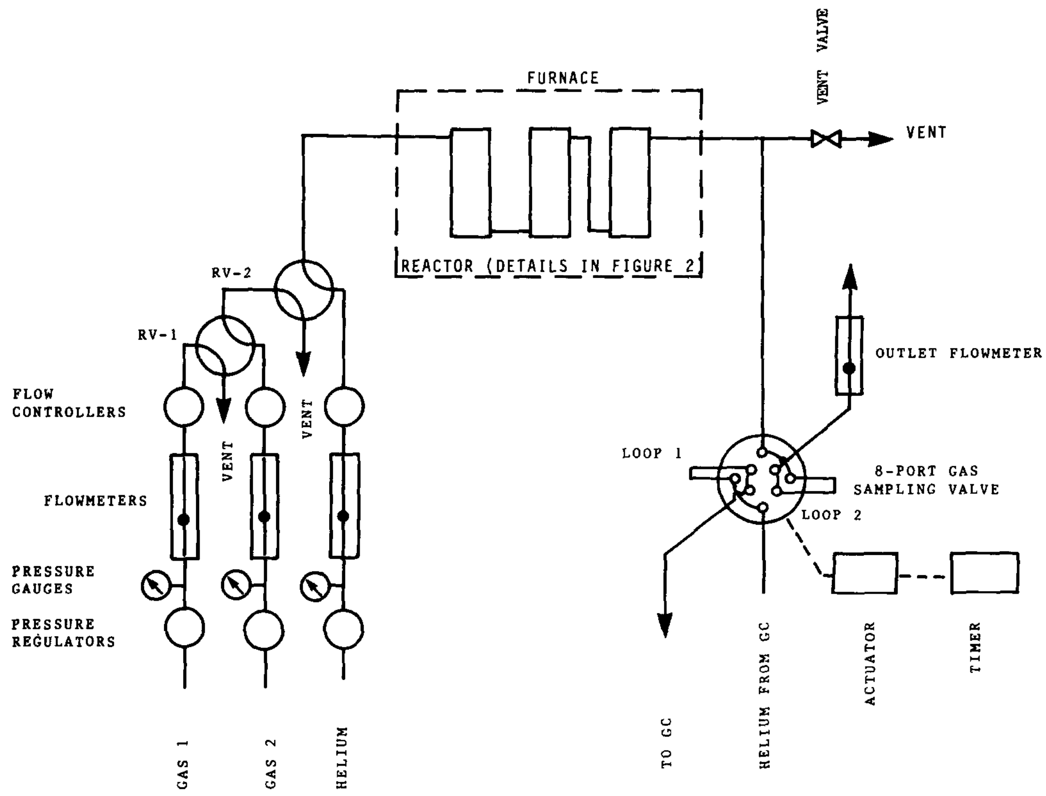

FIG. 1. Flow diagram of experimental apparatus.

center zone and the third (right) zone was filled with wire-form copper oxide.

Both standard taper and ball and socket joints were used for the seals on zones 2 and 3. The extended plugs on the joints terminated just above the connecting tubes and were only slightly smaller than the internal diameter of the zones so as to minimize diffusion of the gases into the space above the ends of the plugs.

The reactor was mounted in a radiantly heated low mass furnace made from 1-in.-thick Marinite insulation with batts of Fiberfrax on the inside of the furnace. The heater coils were wound from Nichrome wire. The temperature of the reactor was regulated by a power-proportioning controller of local design. The tops of zones 2 and 3 extended through the upper surface of the furnace so that the joints were at ambient temperature.

Samples of the catalyst were removed from the reaction zones using the vacuum sample receiver shown in Fig. 3. By applying vacuum to the bottom fitting, all or fractional portions of the catalyst were removed from the reaction tubes even at elevated temperatures, if desired. Use of a polymeric sleeve on the standard taper joint rather than lubricant permitted quantitative recovery of the catalyst.

The effluent from the reactor was sampled at regular intervals and analyzed on a 6-ft × 1/8-in. Porapak Q column operated at 60°C with a helium flow of 30 ml per minute. The chromatograph was an F and M Model 720. The thermal conductivity detector was operated at a bridge current of 250 mA and the detector response displayed on a 1-mV Honeywell Model 16 recorder, 1-sec full scale response. A Carle Instruments Company Model 2014 eight-port gas

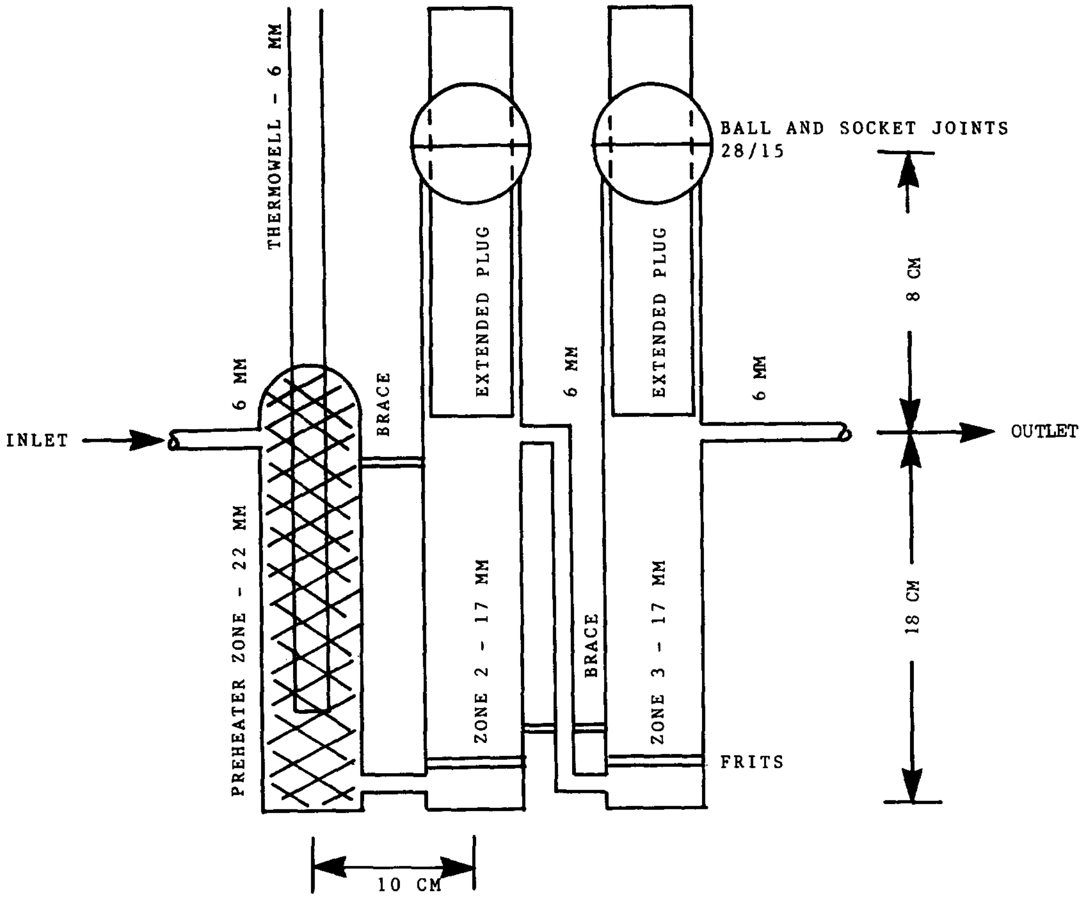

FIG. 2. Three-zone quartz reactor.

sampling valve was used. The valve had two sample loops, a gas sample being taken each time the valve was actuated. The sample loop size was nominally 250 μl. The volumes of the loops were matched to less than 1.0% by inserting lengths of fine wire into the loop initially giving the greater response. The valve was pneumatically operated using a Carle Model 2050 actuator controlled by a Flexopulse variable interval timer. When used only for the detection of $O_2$ for oxygen titrations after reduction in $H_2$, a sampling interval of 15 sec was used. For CO reductions or oxygen titrations in which $CO_2$ was evolved, a 30-sec interval (minimum) was possible. The sampling intervals were determined only by the width of the peak(s), not by the overall retention time.

To provide a relatively constant flow of the effluent to the gas sampling valve at varied reactor flows, a tee arrangement in the effluent line directed only a portion of the effluent to the valve, the balance going to vent. This arrangement also reduced the back-pressure on the reactor caused by the sampling valve. The outlet flow was adjusted to give the same flow to the sampling valve, as indicated by the outlet flowmeter, regardless of the total flow through the system.

Blends of the components were prepared on a high vacuum gas blending apparatus, using instrument or C. P. grade gases from Matheson for all blends.

Cylinder carbon monoxide used for the reduction studies was found to contain variable levels of iron and nickel carbonyls (9).

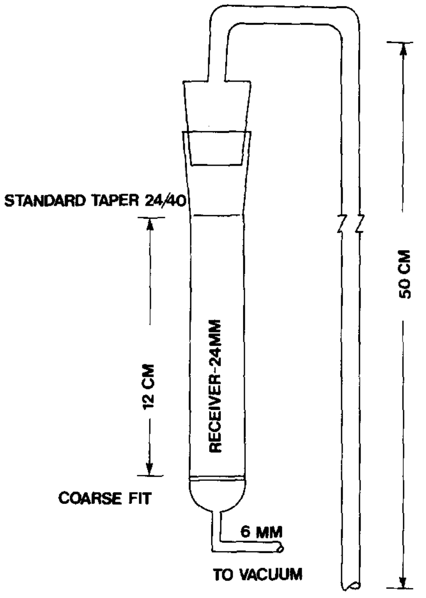

FIG. 3. Vacuum receiver for sample removal.

At a reaction temperature of 500°C and higher, the metal carbonyls decomposed in the inlet tube and the preheater section with the production of low levels of CO and $CO_2$ and the deposition of metallic residues. The metal carbonyls were removed by passing the CO through a column of activated charcoal. The amount of $CO_2$ produced by the disproportionation of CO in the flow and temperature ranges of this study was negligible after removal of the metal carbonyls. At 700°C less than 0.02 mol% $CO_2$ was detected in the effluent from an empty reactor.

## C. *Procedures*

(*a*) *Reduction in hydrogen.* A weighed amount (2–10 g) of the calcined catalyst was placed in reactor zone 3 with the reactor at a temperature below which any reaction might occur. The reactor and catalyst were purged with helium and heated to the desired operating temperature. While purging the reactor with helium, the hydrogen flow was set to the desired value. After the temperature stabilized, valve RV-2 was rotated to feed hydrogen to the reactor. After the desired reduction period, the reactor was flushed with helium. The flow of the oxidizing blend (2 or 4 mole% oxygen in helium) was adjusted and fed to RV-2 through RV-1. The timer on the sampling valve actuator was set for a 15-sec interval and the timer started. With only helium flowing through the system and the outlet flow control valve adjusted to give the proper flow of sample through the gas sampling valve, no response was obtained for samples taken during this period. At the same time that a gas sample was taken, valve RV-2 was rotated to feed the oxidizing blend to the reactor and the start time was marked on the recorder by momentarily blocking one of the exit ports of the detector. The oxidation was continued until the oxygen reached a steady-state level (constant GC peak height). Without changing any flows, valve RV-2 was rotated back to feed helium to the reactor with the sampling timer left on. After the system was cleared of oxygen (no GC response for samples), the oxidation step was repeated with the fully oxidized catalyst to obtain the blank value for oxygen breakthrough. Since the times were read directly from the recorder chart measured at the oxygen peak, the blank value takes into account both the dead volume of the reactor system and the retention time of the oxygen peak. Typically the oxygen peak height was over 90% of the steady-state value for the sample taken at 30 sec for a fully oxidized catalyst. Blank values were generally in the range 0.5–0.7 min. The oxygen titration times for reduced samples were typically greater than 10 min. The millimoles of oxygen consumed were then calculated from the net time (sample–blank), the oxidizer blend concentration and flow rate. After cooling, the catalyst was removed with the vacuum receiver and reweighed to determine the millimoles of $WO_3$.

(*b*) *Reduction in CO or CO–$CO_2$ blends.* Reduction of the catalyst with CO or gas blends followed basically the same procedure as used for hydrogen reduction (above), except that the reactor effluent was sampled at 30-sec intervals during the reduction period to determine the number of millimoles of $CO_2$ produced.

Reoxidation of the catalyst after CO reduction was found to produce a mixture of CO and $CO_2$ in a variable ratio before $O_2$ breakthrough. Analysis of the mixture for the three components could not be done with sufficient frequency and accuracy to obtain reliable data for calculation of the millimoles of $O_2$ consumed and CO + $CO_2$ evolved. In addition it was also desirable to divide the reduced catalyst into several portions due to the nonuniformity of reduction, as will be discussed later. The reduced catalyst was cooled under helium flow and removed in several weighed fractions.

The third zone was then loaded with wire-form copper oxide, the reactor heated to 550°C and burned off in air. The reactor was then flushed with helium, cooled, and the second zone loaded with all or a portion of the catalyst fractions removed. After flushing for several minutes with helium, the reactor was heated to 550°C during which time the flow rate of the oxidizer blend was adjusted to the desired value. The reoxidation was carried out as given before except that the effluent was sampled every 30 sec. The oxidation was continued several minutes past oxygen breakthrough. During the initial portion of the oxidation, the chromatographic samples show only a series of $CO_2$ peaks of nearly constant peak height. As the oxidation neared completion, the $CO_2$ concentration decreased as the $O_2$ concentration increased to a steady-state level. The pattern of peaks is shown in bar-graph form in Fig. 4.

The blank value and millimoles of $O_2$ were determined as given above. The millimoles of $CO_2$ were determined by graphical or computer integration of the area under the $CO_2$–time curve. The $CO_2$–blank time was determined by adding the difference in retention times for $O_2$ and $CO_2$ to the $O_2$–blank value. In many cases the concentration of $CO_2$ in the effluent was constant, within experimental measurement, for most of the titration and then decreased rapidly and essentially linearly to zero. The integration in this case was based on the times $T(CO_2)$ and $T'(CO_2)$ shown on the figure.

No corrections to the flows were necessary based on the reactions found to be occurring. At the $O_2$ concentrations used in the oxidizer blends (2–4 mole%), the change in flow during oxidation was small and the inlet and outlet flows were the same at the $O_2$ titration endpoint. The change in flow rate during reduction was within the experimental error of setting the flow as the concentration of the $CO_2$ in the effluent was less than 5 mole% and the amount of the CO reacting to WC relative to the total amount reacting was less than 0.25: for example, for the reaction

$$WO_{2.72} + 4.72\ CO = WC + 3.72\ CO_2$$

mmole CO to WC/mmole CO reacted = 1/4.72 = 0.21.

## RESULTS AND DISCUSSION

### *A. Reduction in Hydrogen*

Tungsten oxide supported on silica was rapidly reduced in hydrogen to $WO_{2.84}$ at temperatures below 575°C (Fig. 5). After the initial rapid reduction, the value of $x$ in $WOx$ decreased slowly at longer reduction times. According to the thermogravimetric studies of Ogata *et al.* (*10*), $WO_{2.72}$ is not formed by hydrogen reduction in this temperature range. An apparent value of $x$ = 2.80 would be composed of a mixture of 95% $WO_{2.84}$ and 5% $WO_2$. The reduction in hydrogen only was not studied extensively as it was determined early, consistent with other reports, that hydrogen reduction was not effective in reducing the induction or break-in period. The data did, however, indicate that $WO_{2.84}$ could be reproducibly formed within 10 min at 550°C under the experimental conditions used.

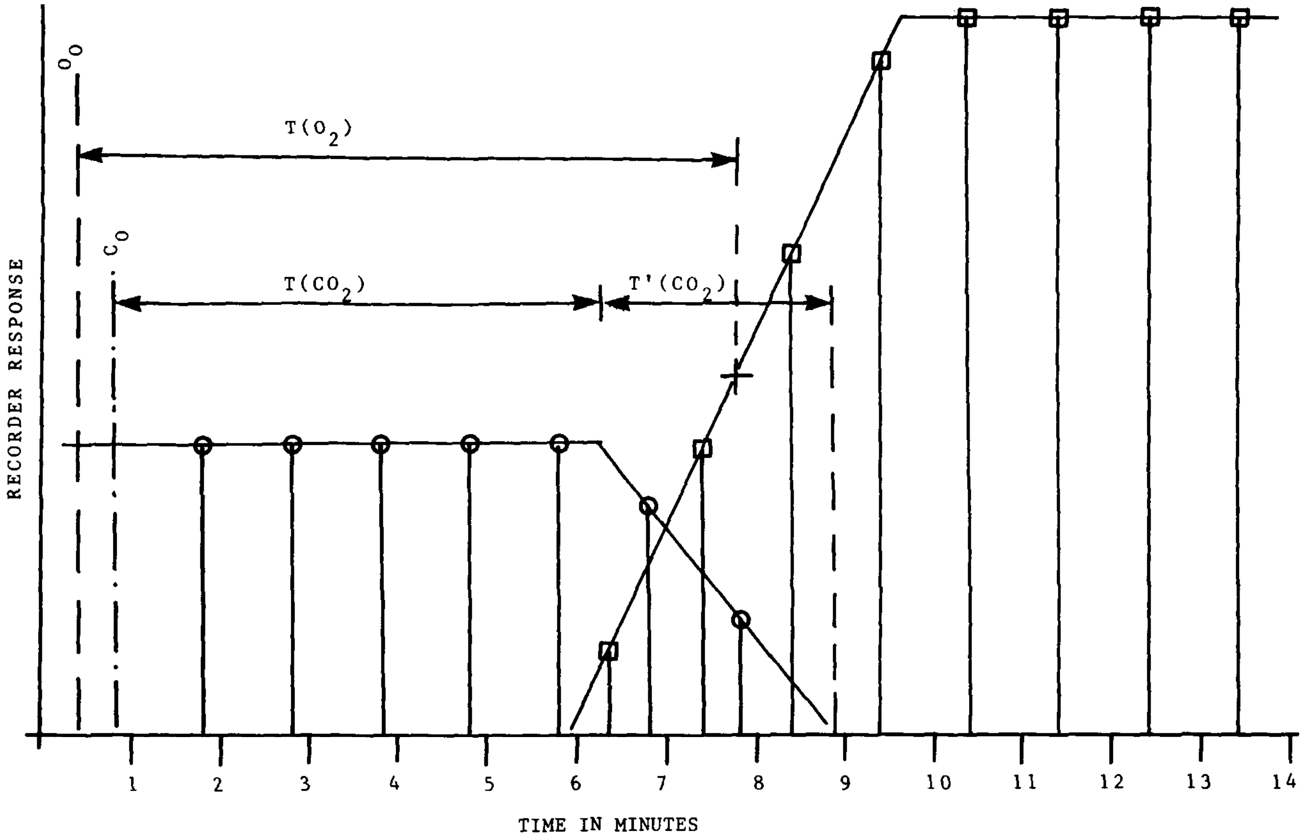

FIG. 4. Bar-graph representation of $O_2$–$CO_2$ analysis. Bars with circles represent $CO_2$ peaks and bars with squares represent $O_2$ peaks. $O_0$ and $C_0$ are times for $O_2$ and $CO_2$ peaks from blank run. For illustration purposes sampling interval of 1 min shown; actual sampling interval was 30 sec.

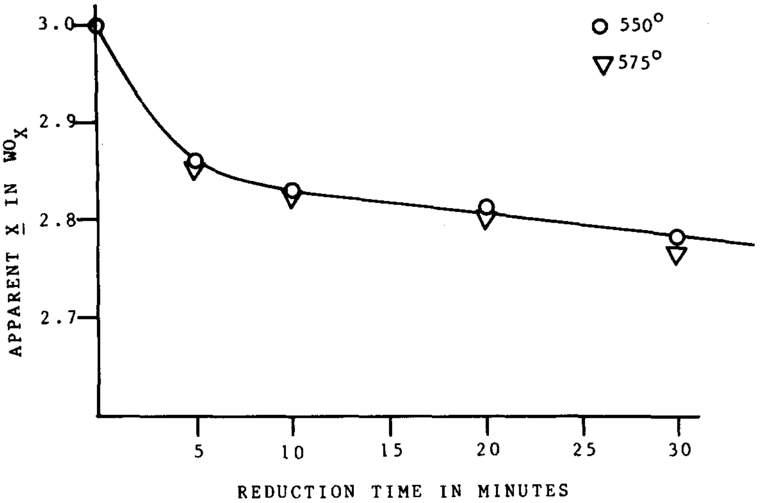

FIG. 5. Apparent composition of $WO_x$ vs time for $WO_3$ reduction with $H_2$: ○ reduction at 550°C; ▽ reduction at 575°C.

The $WO_{2.84}$ form was also produced by $CO_2$ oxidation of samples which had first been reduced in hydrogen. After reducing catalyst samples for varied periods of time in hydrogen at 550°C to compositions corresponding to average values of $x$ less than 2.84, treatment of the catalyst with $CO_2$ in helium produced CO. After treatment with $CO_2$ to the extinction of CO, oxygen titration of the samples consistently gave average compositions of $WO_{2.82-2.84}$ through the length of the catalyst bed.

Complete reduction of $WO_3$ to the brown oxide $WO_2$ was achieved by reduction at 700° in hydrogen saturated with water (*11*, *12*). Duplicate reduction–oxygen titration cycles gave values of $WO_{2.03}$ and $WO_{1.96}$ after 1.5 to 2 hr reduction in $H_2$–$H_2O$. The observed weight loss was in exact agreement with the theoretical value for com-

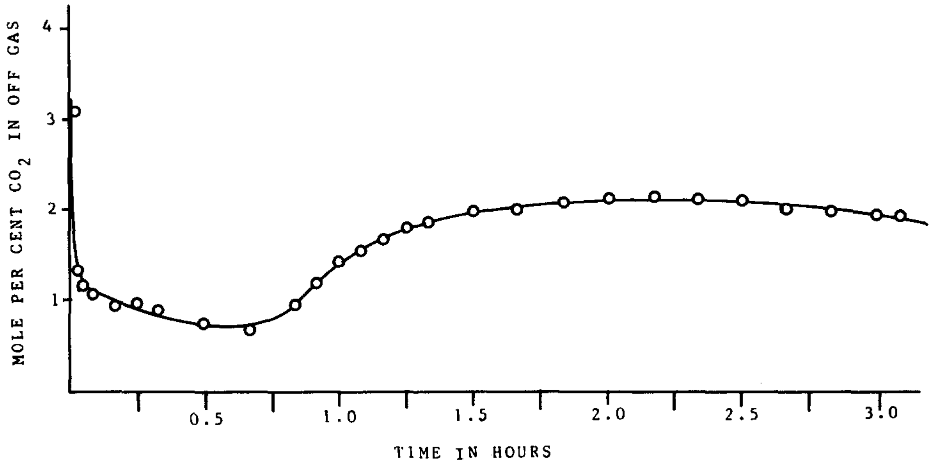

FIG. 6. Mole percent $CO_2$ in reactor effluent vs time for CO. Reduction without initial hydrogen reduction. Temperature: 600°C; 2-sec contact time.

plete reduction to $WO_2$. In the absence of water, reduction at 700°C resulted in at least partial reduction to W metal. Reduction to $WO_2$ did not eliminate the break-in period for the disproportionation reaction, a result consistent with other studies (*3*).

### *B. Reduction in Carbon Monoxide*

Figure 6 is a plot of the mole per cent $CO_2$ in the reactor effluent during the CO reduction of supported $WO_3$ at 600°C. The reduction apparently occurred in three distinct stages as indicated by the initially high but declining $CO_2$ concentration (0–10 min), a plateau region with evolution of about 1% $CO_2$ (10–40 min), and finally after about 45 min the $CO_2$ production increased and remained at about the 2% level for the remainder of the experiment. The three steps appear to correspond to the initial reduction to $WO_{2.9}$, then $WO_{2.84}$ and/or $WO_{2.72}$, and finally to WC and oxidation states lower than $WO_{2.72}$. As will be shown in the next section, $CO_2$ production at the final (ca. 2%) level may continue for many hours at this temperature as the catalyst was ultimately completely reduced to WC.

### *C. Reduction in Hydrogen followed by Carbon Monoxide*

Reduction of the catalyst with hydrogen to the $WO_{2.84}$ form before reduction with CO shifted the region of increasing and plateau formation of $CO_2$ to significantly shorter times than observed in Fig. 6. Figure 7 is a similar plot for CO reduction at 575 and 600°C after initially reducing in hydrogen at 550°C for 10 min. Before introduction of the CO, the reactor was flushed with helium. Within the first 5 min the sample was reduced from $WO_{2.84}$ to $WO_{2.72}$, with the increase in $CO_2$ production occurring after 5–6 min. Evolution of $CO_2$ reached a maximum at 45–60 min then decreased slowly for the duration of the experiment.

When catalyst reduced in this manner

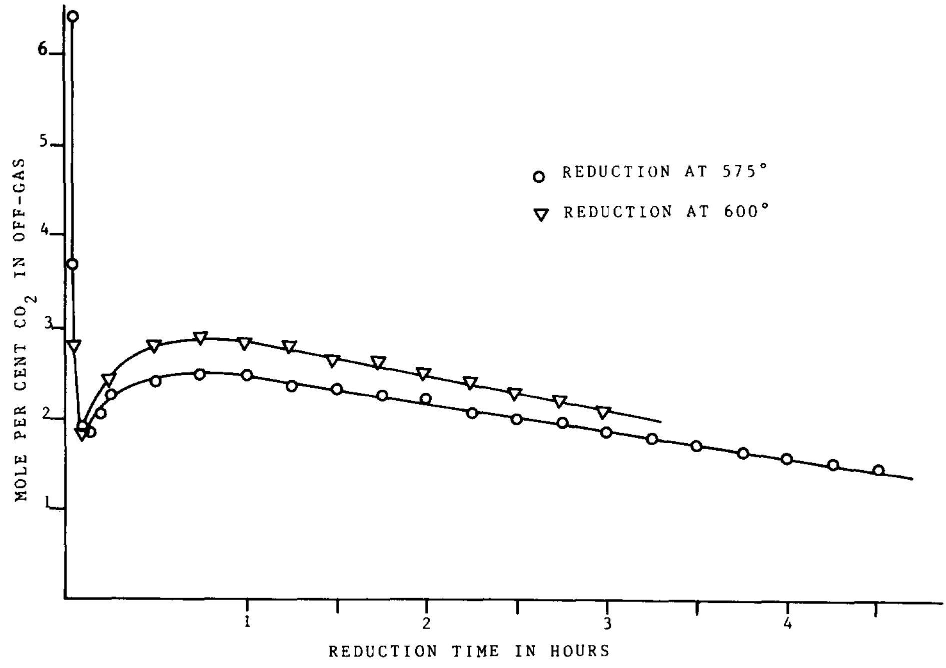

FIG. 7. Mole percent $CO_2$ in reactor effluent vs time for CO. Reduction after initial hydrogen reduction: ○ CO reduction at 575°C; ▽ CO reduction at 600°C.

were titrated with oxygen, it was observed that the blue-yellow interface between the reduced and oxidized forms moved slowly through the inlet portion of the catalyst then rapidly through the remainder of the bed. This observation was in contrast to the samples which had been reduced only in hydrogen, in which case the interface moved uniformly through the length of the catalyst bed. Low levels of C and $CO_2$ were produced during the reoxidation.

Following a reduction similar to that illustrated in Fig. 7, the catalyst was purged with helium, cooled, and then removed in several weighed fractions. Carbon analyses on each portion produced the results shown in Fig. 8. The percent carbon and the $CO_2$/W ratio both decreased linearly from inlet to exit of the reactor. The percent carbon and the $CO_2$/W ratio suggested the possible formation of WC, while the decrease in these values through the bed suggested that the formation of WC was inhibited by the $CO_2$ formed in the reduction process. Both of these possibilities were verified by subsequent experiments.

Complete reduction to supported WC was achieved at 650–700°C within 4–6 hr (Fig. 9). Carbon analyses on samples which had been exhaustively reduced in CO were in excellent agreement with theory:

% C (theory) = 1.069 (for initial 20% $WO_3$)

% C (found) = 1.078.

Oxygen titration of the samples also confirmed the reduction to WC:

| | $\frac{\text{mmole } O_2}{\text{mmol W}}$ | $\frac{(O_2 - CO_2)\text{ mmole}}{\text{mmol W}}$ |
|---|---|---|
| Theory* | 2.50 | 1.50 |
| Found | 2.53 | 1.53 |

* For the reaction $WC + 2.5\ O_2 = WO_3 + CO_2$.

XRD examination of the samples demonstrated that WC was the primary crystalline

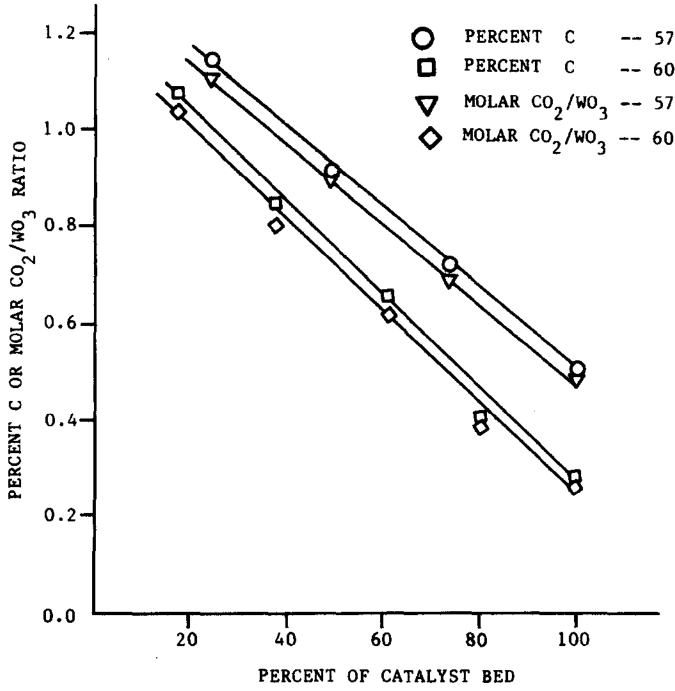

FIG. 8. Percent carbon and molar $CO_2$/W ratio through catalyst bed. Samples taken after reduction as shown in Fig. 7.

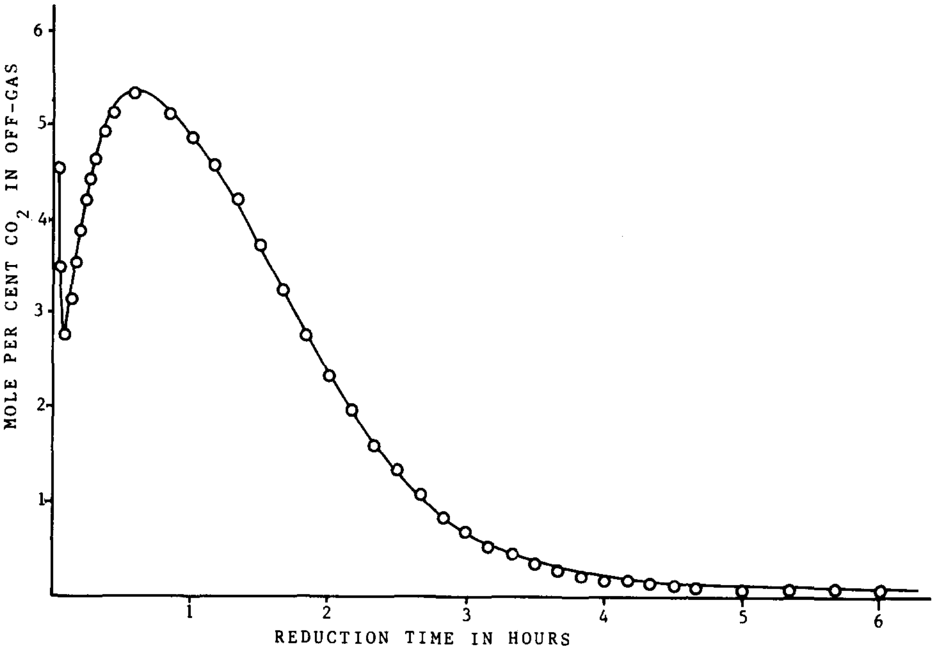

FIG. 9. Mole percent $CO_2$ in reactor effluent vs time for exhaustive reduction in CO at 700°C. Initial reduction in $H_2$ at 550°C.

phase, having a crystallite size of about 50 Å.

The amount of carbon on the reduced catalyst did not increase on continued reduction as expected, since there was no corresponding production of $CO_2$.

Carbon monoxide reduction of catalysts which had first been reduced to $WO_2$ in $H_2$–$H_2O$ did not produce the pattern of $CO_2$ evolution shown in Figs. 7 and 9. The level of $CO_2$ started at an initially constant level, then decreased continuously for the duration of the reduction.

### *D. Reduction in Carbon Monoxide–Carbon Dioxide Blends*

Selective reduction to $WO_{2.72}$ and virtual elimination of the formation of WC was achieved by reduction in CO containing 5 mole% $CO_2$ (Fig. 10). After reduction in hydrogen to $WO_{2.84}$, reduction in the CO–$CO_2$ blend resulted in the gradual decrease in the $CO_2$ evolution to the level found in the absence of the catalyst. The metal carbonyls in the CO–$CO_2$ blend could not be removed by use of the activated charcoal column as $CO_2$ would also be removed. There was no increase in the $CO_2$ level even after 2.5 hr. The net millimoles of $CO_2$ after 100-min reduction gave a C/W ratio of 0.12, consistent with the reduction to $WO_{2.72}$. The catalyst was cooled and removed in four portions. The inlet portion gave a C/W ratio of 0.079, indicating some reduction to WC. The average C/W ratio for the other three portions was 0.008, corresponding to only 0.8% reduction to WC. The average ($O_2$ − $CO_2$)/W ratio was 0.145, consistent with reduction to $WO_{2.71}$. Reduction in pure CO after reducing in the 5% $CO_2$–CO mixture resulted in the expected increase in $CO_2$ evolution.

Reduction in CO with 2.5% $CO_2$ was not as effective in preventing the formation of WC. An increase in $CO_2$ was observed after about 60 min. The level of carbon in the samples was higher than found in the reduction with 5% $CO_2$ in CO.

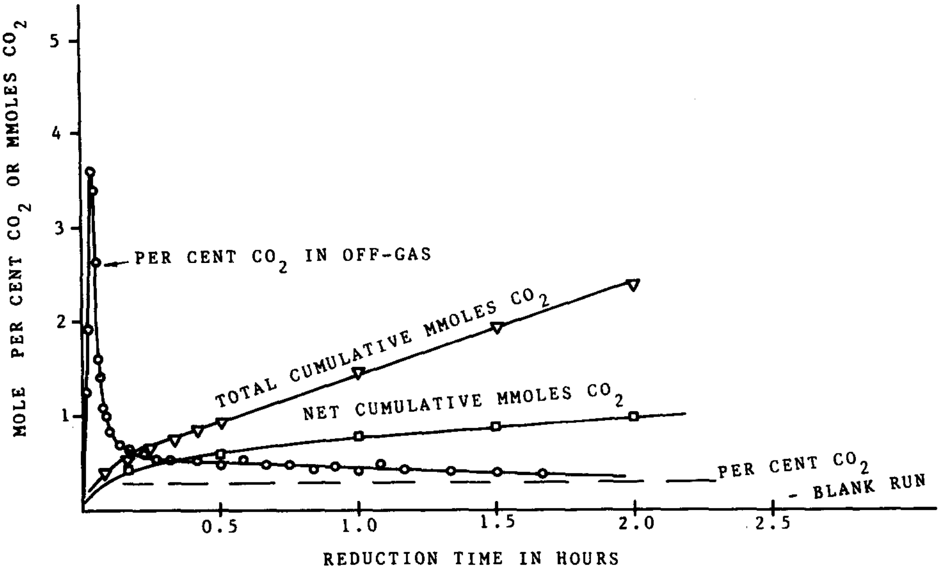

FIG. 10. Mole percent $CO_2$ in reactor effluent vs time for reduction with 5% $CO_2$ in CO. Initial reduction in $H_2$ at 550°C. Temperature: 600°C. Percent $CO_2$ is net over 5% in the blend.

### *E. Effect of Reduction Procedure on Disproportionation Activity*

Catalyst samples were tested for disproportionation activity after reduction to $WO_{2.84}$ (with hydrogen or hydrogen followed by $CO_2$), to $WO_{2.72}$ ($H_2$ followed by $CO_2$ in CO), and to $WO_2$ ($H_2$–$H_2O$). None of the "pure oxide" forms gave immediate high activity. Only when the catalyst had been activated in CO was the catalyst immediately highly active. The most stable performance was achieved when the catalyst was first reduced in $H_2$ followed by CO for 1 hr or longer at 575°C and higher. Short periods of CO treatment gave initial high activity, but the catalyst did not remain active, possibly due to minor amounts of oxygenated impurities in the feed or those formed by oxidation of the feed olefin(s) by the unreduced catalyst. The most active form appeared to be minor amounts of WC dispersed in a matrix of $WO_{2.72}$. Supported WC on silica gel (produced by exhaustive reduction in CO) was also found to give immediate equilibrium conversion.

Testing of the disproportionation activity of catalysts reduced in $H_2$ then CO indicated that equilibrium conversions could be achieved at contact times as low as 0.25 sec (equivalent to a total flow of 540 scc/min over 6.7 g of catalyst at 490°C). Recognizing that the reduction process does not give a uniform composition along the length of the catalyst bed and that at least part of the catalyst still existed in a less active oxide form, the minor amounts of WC formed in the first (inlet) part of the catalyst bed must be extremely active for disproportionation.

### *F. Other Observations*

One attempt was made to activate the catalyst in syn gas ($H_2$–CO). Extensive deposition of carbon without the production of significant amounts of $CO_2$ with or without the catalyst present in the quartz reactor indicated that the reverse water gas reaction was occurring.

This paper was intended to present the experimental observations from the reductive activation of the tungsten oxide on silica catalyst and was not intended to explore any mechanistic implications of WC as the active catalytic form. Tungsten carbide as a highly active disproportionation site is consistent with other studies where it was postulated that disproportionation takes place on active centers containing tungsten with an unusually low degree of oxidation (*13*) and that activity is promoted by the formation of vacant coordination sites on tungsten (*4*).

The reactor system and techniques described in the experimental section were originally designed for the rapid determination of coke deposits on used catalyst samples. Table 1 shows that the results obtained by this method of analysis are comparable to those obtained by conventional methods of carbon analysis at low levels. When the used catalyst samples were found to contain carbon at levels greater than that possible for WC formation, the millimoles of $O_2$ consumed could not be related to the catalyst composition due to the presence of coke in the form of $CH_x$ ($x$ less than 1).

Treatment of catalysts with hydrogen at 500°C and higher following reduction in carbon monoxide resulted in the formation of methane. Decarburization of WC in hydrogen has been reported (*14*), but at significantly higher temperatures than used in this study. The higher dispersion of WC in the present study is presumed to be responsible for methane formation at the lower temperatures.

TABLE 1

Comparison of Coke Analyses by Technique Described and Microgravimetric Method

| Sample number | Weight percent C | |
|---|---|---|
| | Combustion | Gravimetric |
| 730-73-1 | 1.40 | 1.38 |
| -3 | 1.86 | 1.38 |
| -5 | 2.70 | 2.73 |
| 756-82-1 | 1.23 | 1.18 |
| -2 | 4.07 ± 0.12 | 4.46 ± 0.08 |
| -3 | 4.06 ± 0.23 | 4.23 ± 0.08 |
| -4 | 4.94 ± 0.08 | 4.64 ± 0.10 |
| -5 | 6.81 ± 0.03 | 6.10 ± 0.03 |
| 770-49-1 | 0.60 | 0.50 |
| -2 | 0.56 | 0.54 |
| -3 | 0.62 | 0.59 |
| -4 | 0.607 | 0.605 |
| -5 | 0.72 | 0.67 |
| 770-45-1 | 0.610 | 0.625 |
| -2 | 0.598 | 0.575 |
| -3 | 0.656 | 0.585 |
| -4 | 0.692 | 0.73 |

All of the results reported here were obtained in the quartz reactor. Except for the minor amounts of carbon oxides formed from the decomposition of the metal carbonyl impurities in the carbon monoxide when the activated charcoal pretreatment was not used, very little disproportionation of CO was observed at any temperature studied. This may not be the case if the reduction is carried out in metal (stainless steel) reactors (*6*).

### *G. Summary of Reductions to the Various Tungsten Forms*

(a) $WO_{2.84}$ was produced by reduction in hydrogen at 550–575°C. Continued reduction at these temperatures produced a mixture of several oxide forms. Treatment of the reduced catalyst with $CO_2$ after hydrogen reduction resulted in the uniform formation of $WO_{2.84}$.

(b) $WO_{2.72}$ was produced by reduction in CO containing 5% or greater $CO_2$ after an initial reduction in $H_2$.

(c) $WO_2$ was produced by reduction at 700°C in hydrogen saturated with water (*11, 12*).

(d) WC was produced by reduction in CO only or CO after $H_2$ reduction. Several hours reduction was necessary to completely reduce all the tungsten to WC.

## CONCLUSIONS

Tungsten oxide on silica gel disproportionation catalysts were selectively reduced to the various stoichiometric and substoichiometric oxides by reaction with $H_2$, $H_2 + H_2O$, CO, or CO blended with $CO_2$. Reduction with CO, particularly after an initial reduction for a short period of time in $H_2$, produced a nonuniform reduction along the length of the catalyst bed due to the inhibiting (oxidizing) effect of $CO_2$ produced by reduction of the inlet portion of the catalyst bed. Reduction of fractional amounts of the tungsten to tungsten carbide occurs early in the reduction cycle. All of the tungsten can be reduced to the carbide form by exhaustive treatment at 650°C and higher. Tungsten carbide is a highly active species for olefin disproportionation.

## REFERENCES

1. Moffatt, A. J., Clark, A., and Johnson, M. M., *J. Catal.* **22,** 379 (1971).
2. Luckner, R. C., McConchie, G. E., and Wills, G. B., *J. Catal.* **28,** 63 (1973).
3. Luckner, R. C., and Wills, G. B., *J. Catal.* **28,** 83 (1973).
4. Pennella, F., and Banks, R. L., *J. Catal.* **31,** 304 (1973).
5. Banks, R. L., and Heckelsberg, L. F., *Ind. Eng. Chem. Prod. Res. Dev.* **14,** 33 (1975).
6. Innes, R. A., Sabourin, E. T., and Swift, H. E., Reprints of the Symposium on Selective Oxidation and Aromatic Chemistry, Division of Petroleum Chemistry, ACS meeting, September, 1979.
7. Montgomery, P. D., Moore, R. N., and Knox, W. R., U.S. Patent 3,965,206 (to Monsanto Co.), June 22, 1976.
8. Technical Information Bulletin, "Ammonium Metatungstate," Sylvania Chemical and Metallurgical Division, Towanda, Pa.
9. Harris, L. A., and Yakel, H. L., *Chem. Eng. News,* June 12, 1972.
10. Ogata, E., Kamiya, Y., and Ohta, N., *J. Catal.* **29,** 296 (1973).
11. Griffis, R. D., *J. Electrochem. Soc.* **105,** 398 (1958).
12. Hougen, J. O., Reeves, R. R., and Mannella, G. G., *Ind. Eng. Chem.* **46,** 318 (1956).
13. Fel'dblyum, V. Sh., Baranova, T. I., and Karpov, O. I., *Neftekhimiya* **16,** (3), 435 (1976).
14. Newkirk, A. E., and Aliferis, I., *J. Amer. Chem. Soc.* **79,** 4629 (1957).