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Reduction Studies on Supported Chromic Anhydride Catalysts

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Hydrogen and carbon monoxide reduction of chromic anhydride (CrO_3) supported on SiO_2, Al_2O_3, and $SiO_2 \cdot Al_2O_3$ has been studied using a closed circulation system operated under rising temperature conditions. The data have been rationalized using a simple kinetic model. The results show that the reduction characteristics of the CrO_3 are affected by the kind of support, the combination of supports in different concentrations, calcination temperature of the catalyst, and the concentration of the metal oxide. Results with both H_2 and CO indicate that the effect of increasing the calcination temperature, particularly above 500°C, is to decompose more CrO_3 on the surface. For both Al_2O_3 and $SiO_2 \cdot Al_2O_3$ an increase in calcination temperature increases the interaction between the promoter and the support. The data show that the order of thermal stability afforded by the supports for the promoter are: $SiO_2 > SiO_2 \cdot Al_2O_3 > Al_2O_3$. This is also the order reported for the efficacy of the supports for CrO_3 in the polymerization reaction. The relative activation energy per unit of Cr reduced on $CrO_3 \cdot SiO_2$ is nearly constant for all calcination temperature studied. This ratio varies with calcination temperature for both Al_2O_3 and $SiO_2 \cdot Al_2O_3$. Collectively, these data indicate that there exists a distribution of binding energies for CrO_3 over the surface of the supports. This implies that any activation energy calculated for the reduction is an average for the different Cr species present on the catalyst.

I. INTRODUCTION

Reduction studies of supported metal oxide catalysts give information about the properties of the metal oxide under the influence of the support surface. This information can be used to establish the availability of the metal oxide on the surface, the degree of interaction between the metal oxide and the support, and the extent of the reduction. The extent of reduction is used to infer the apparent valence of the promoting metal under the influence of the support. Under certain conditions the reduction studies reveal interactions of the metal oxide with different components of the support and the presence of the promoter species in various stages of reduction. These characteristics are affected by the method of catalyst preparation, the composition of the support, calcination temperature, and the metal oxide concentration. Holm and Clark (*1*) and Hogan (*2*) have demonstrated that the reduction of supported chromatic anhydride (CrO_3) can be studied effectively in a circulating system under rising temperature conditions. In this technique the pressure of the reducing gas is monitored while the temperature of the catalyst is increased linearly with time. An effective adsorbent removes the gaseous oxidation products from the reducing gas that is circulated over the catalyst. The data are usually presented in form of a "reduction profile" which is obtained by plotting the rate of pressure decrease against temperature. Interactions involving the promoter and different components of the support and the presence of different valence states in the surface should appear in the reduction profile as peaks. However, if the variation in the rate of reduction with respect to temperature is small for two different promoter–support interactions or two different-valence states then the peaks will not be resolved and the profile will be the envelope of all the peaks.

The present paper reports the results of the study of the reducibility of supported CrO_3 involving a number of promoter–support combinations and different calcination temperatures. Reduction profiles were obtained using both H_2 and CO as reducing gases. The data are rationalized using a simple kinetic model which, under rising temperature conditions, permits calculation of the ratio of the activation energy to reaction order (E_i/n) from a single reduction profile.

II. EXPERIMENTAL METHODS

A. Catalyst Preparation

The impregnated catalysts were prepared by treating 30–60 mesh supports with CrO_3 solution. Sufficient solution containing the appropriate metal content was used to just fill the pore volume of the catalyst. The majority of the studies involved three supports: Harshaw alumina AL 1404; Davison SiO_2 Grade A, Type 3; and Houdry M46 $SiO_2 \cdot Al_2O_3$ containing 87% SiO_2 and 13% Al_2O_3. The surface areas were 181, 605, and 260 m^2/g, respectively. Other commercial supports used were Harshaw AL 1802 containing 94% Al_2O_3 and 6% SiO_2, and an American Cyanamid product containing 75% Al_2O_3 and 25% SiO_2. Silica–aluminas of other compositions were prepared by the usual coprecipitation methods. One catalyst was prepared by coprecipitation to contain 3% Cr on a support having the SiO_2 to Al_2O_3 ratio of 87:13.

B. Apparatus and Procedures

The apparatus was similar to those used by Holm and Clark (*1*) and by Hogan (*2*). The apparatus was a closed circulating system consisting of a magnetic pump, a furnace containing a "hairpin" reactor for the catalyst, a tube of adsorbent for product removal, anhydrous magnesium perchlorate [$Mg(ClO_4)_2$] for water or Ascarite for CO_2, and a manometer of 1 mm i.d. tubing. The latter was used to calibrate a Whittaker digital manometer, Model Pace DM1, which was utilized for pressure measurement during the experiment. A 50 cm^3 bulb attached to the system was used as a gas reservoir and as a means of determining the volume of the system. The volume of the circulating system excluding the reactor was 79 cm^3. This volume was determined with the adsorbent in place. Two different reactors designed to give equivalent bed heights for 2 and 7 g catalyst samples were used in the study. The reactors with catalyst in place added 26 and 38 cm^3, respectively, to the system. Three thermocouples distributed along the length of the catalyst bed were used to monitor the catalyst temperature. The temperature of the middle couple was used in plotting the data. A Hewlett-Packard temperature programmer, Model 240, was modified to advance the catalyst temperature linearly at 1.5°C/min from 25 to 550°C.

The catalysts, both the 2 and 7 g samples, were calcined *in situ* under a stream of dry air at the desired temperature for 16 hr. The catalysts were then evacuated, cooled to about 100°C and isolated from the system. The reducing gases, Matheson prepurified H_2 and pure grade CO, charged to the system at room temperature were then admitted to the catalyst and the pressure monitored as the temperature increased linearly to 550°C. Appropriate corrections were made for the contribution of the heated section of the apparatus to the observed pressures. Pressure recordings made initially at 10 min intervals were increased to 5 min intervals during the period of reduction. Thus, the reduction profile, $\Delta P/10$ min plotted against T, was based on two different 10 min intervals to better define the curve. Reducing gas consumption calculated from the area under the profile curve agreed well with that calculated from the volume of the system and the corrected initial and final pressure.

C. Treatment of the Data

The rate of reduction of supported CrO_3 shows little if any dependence on the pressure of the reducing gas above 200 mm. Thus, changes in the pressure of the reducing gas are directly related to changes in the amount of reducible Cr. If a is a constant relating pressure and reducible Cr for reductions to a constant oxidation number, P_0 and C_{Cr_0} are the pressure and reducible Cr concentration initially, and P and C_{Cr} are the same quantities at some time t; then we can write

$$a(P_0 - P) = (C_{Cr_0} - C_{Cr}). \qquad (1)$$

If P_f is the final pressure, then $C_{Cr_0} = a(P_0 - P_f)$. When this expression is substituted into Eq. (1), we obtain the concentration of reducible CrO_3 at time t in terms of pressure:

$$a(P_0 - P) = [a(P_0 - P_f) - C_{Cr}]$$

or

$$C_{Cr} = a(P - P_f). \qquad (2)$$

The general rate equation for the reduction using these quantities is

$$-adP/dt = k[a(P - P_f)]^n. \qquad (3)$$

Introducing the Arrhenius dependence, $k = Ae^{-E/RT}$, the equation becomes

$$+adP/dt = -Ae^{-E/RT}[a(P - P_f)]^n. \qquad (4)$$

Now at the rate maximum with temperature in the reduction profile (point of inflection in a pressure–temperature curve), the derivative of the rate equation is zero. Differentiating Eq. (4) and setting d^2P/dT^2 to zero, we obtain

$$E_i = \frac{-nRT_i^2(dP_i/dt)}{(dT/dt)(P_i - P_f)}, \qquad (5)$$

where the subscript i means that the quantity is measured at the rate maximum in the profile. The quantity dT/dt is simply the heating rate, 1.5°C/min in our case. The only quantity not readily determined from a single profile is the reaction order, n. Hence, the ratio E_i/n is calculated and used for comparison purposes.

Taking the logarithm of both sides of Eq. (4) and simplifying gives

$$2.3 \log \frac{(-dP/dt)}{(P - P_f)^n} = 2.3 \log Aa^{n-1} - E/RT. \qquad (6)$$

Plots of the left member of Eq. (6) against $1/T$ should give a straight line with a slope of E/R. A number of profiles were plotted for assumed values of n to obtain the best straight line. The activation energies calculated from the slopes of these lines were compared for consistency with the E_i/n values determined with Eq. (5).

When little CrO_3 has been reduced at the beginning of the reaction, i.e., $(P - P_f)^n$ is nearly constant, Eq. (6) can be written

$$2.3 \log (-dP/dt) = 2.3 \log Aa^{n-1}(P - P_f)^n - \frac{E}{R}\frac{1}{T} \equiv \text{constant} - \frac{E}{R}\frac{1}{T}. \qquad (7)$$

This provides a method for estimating the activation energy at the very beginning of the reaction without knowledge of n.

III. RESULTS AND DISCUSSION

A. Study of the Effect of Pressure of the Reducing Gas on the Reduction of Supported CrO_3

The reduction profiles for three equivalent samples of $CrO_3 \cdot SiO_2 \cdot Al_2O_3$, 2 g containing 2.5% Cr, were recorded using different initial H_2 pressures. The initial pressures were selected such that the pressure observed at the rate maximum (P_i at T_i) varied from 302 mm to 666 mm. This represents changing the pressure by

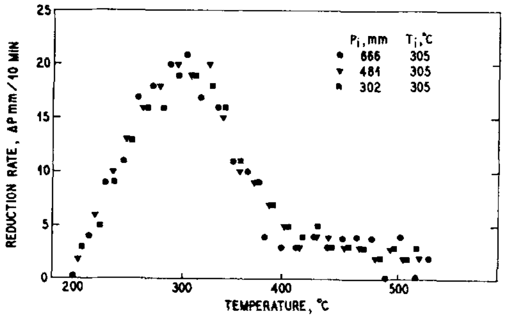

FIG. 1. H_2 reduction of $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ 2.5% Cr on 87% SiO_2–13% Al_2O_3 (2 g); calcined at 500°C; reaction vol, 155 cm^3.

a factor greater than 2. Within experimental error the profiles shown in Fig. 1 are indistinguishable—the same shape with the rate maximum occurring at the same temperature. All three specimens consumed the same amount of H_2, 36 cm^3 STP.

A similar study was made using 7 g samples of $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ prepared from the same support to contain 0.15% Cr. Initial pressures were selected such that the pressure observed at the rate maxima varied from 57 to 527 mm. Only when the pressures observed at the rate maxima fell below 200 mm did the rate maxima shift to higher temperatures. The H_2 consumption remained the same for all samples.

Pressure dependence studies using CO as a reducing gas were made on $CrO_3 \cdot Al_2O_3 \cdot SiO_2$, 3% Cr on 87% $SiO_2 \cdot 13\%$ Al_2O_3. The profiles which are plotted in Fig. 2 show no significant differences in shape or position of rate maximum with temperature for three different pressures. Somewhat less CO was consumed by the catalyst reduced at the lowest pressure.

Since the reduction profiles for supported CrO_3 show no significant dependence on the pressure of the reducing gas, particularly for gas pressures above 200 mm, then the rates of reduction are also independent of pressure. Admittedly the data for CO show more dependence on pressure than do the data for H_2. Verhoeven and Delman (*3*) have reported that the reduction of ZnO shows no pressure dependence. We believe our results justify using a rate equation of the form of Eq. (4) to rationalize our data.

B. Apparent Reaction Order of the Reduction of Supported CrO_3

An advantage in using the rising temperature principle to study reactions is that the activation energy can be computed from a single experiment when the reaction order is known. The constant temperature experiments on the H_2 reduction of $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ (3% Cr) conducted to determine whether the reaction followed some integral order gave inconsistent results. For example, the data for reductions at 255 and 368°C obeyed third order kinetics. In contrast the data for the H_2 reduction at 303°C followed neither the second or third order law. The results for the reduction of the catalyst with CO at 200°C suggest that initially the reaction follows third order kinetics and then declines to second order.

In selected cases the rising temperature data for the reduction of $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ with H_2 obeys Eq. (6) for $n = 3$. The activation energies calculated using Eqs. (5) and (7) are consistent with the third order dependence. The reduction behavior of a $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ catalyst (3% Cr) which was calcined at 500°C illustrates this point. The activation energy calculated from the slope of the straight line obtained by plotting the data using Eq. (6) with $n = 3$ is 24.9 kcal. The activation energy calculated

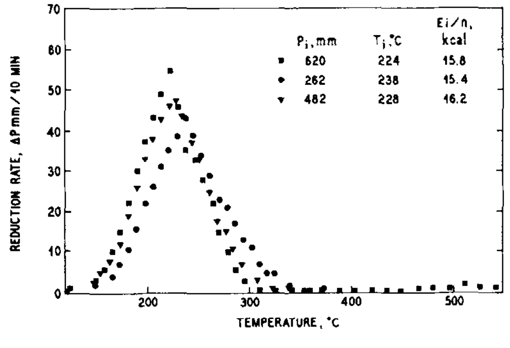

FIG. 2. Pressure dependence study for the CO reduction of $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ (3% Cr); reaction vol, 155 cm^3; calcined at 500°C.

from the reduction profile by setting $n = 3$ in Eq. (5) is 21.9 kcal. Finally the activation energy obtained by applying Eq. (7) to the data collected early in the reduction is about 28 kcal. This value is significant because reaction order is not involved in its calculation. Some catalysts failed to obey Eq. (6) when n was set equal to 3 by giving a variety of curve shapes or two intersecting lines with one of the lines associated with the increasing rates and the other with the declining rates of the profile. The $CrO_3 \cdot SiO_2$ catalyst (3% Cr) showed similar behavior with H_2 for different calcination temperatures—some profiles could be resolved by setting $n = 3$ in Eq. (6) and others could not be resolved for any integral reaction order. The $CrO_3 \cdot Al_2O_3$ system, although giving symmetrical profiles, afforded few examples obeying Eq. (6) for any integral reaction order. Application of Eqs. (5), (6) and (7) to the data for the CO of $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ (3% Cr) calcined at 500°C gave activation energies of 35, 28 and 26 kcal, respectively, for $n = 3$. In general the reduction studies with CO provided fewer cases following third order kinetics than did H_2 reduction.

These results indicate the complexity of the reduction of CrO_3 on different supports and with different reducing gases. It is reasonable to expect both activation energy and reaction order to be functions of the variety of environments in which the Cr is present on the surface. Any measurement would be an average reflecting these various environments. The present data suggest that the apparent reaction order lies between 2 and 3. The mechanistic significance of the high reaction order observed is not understood. It may be that the reaction proceeds on the surface by several reaction orders. However, it seems more likely that there is a broad spectrum of activation energies for CrO_3 reduction on the surface and that the reaction proceeds by some single mechanism. In this case the ratio, E_i/n, is probably the best criterion for comparing results of one experiment with those of another.

C. Study of H_2 Reduction of Supported CrO_3 as a Function of Catalyst Calcination Temperature

Calcination temperature controls the water content of the catalyst, affects the degree of metal oxide–support interaction and influences the amount of thermal reduction occurring on a given support. The effect of the pretreatment temperature on these factors was investigated for the reduction of CrO_3 supported on SiO_2, Al_2O_3, and $SiO_3 \cdot Al_2O_3$ (87% $SiO_2 \cdot$ 13% Al_2O_3) and calcined at 100°C intervals in the 200–800°C range. In all cases the reduction profile, the plot of $\Delta P/10$ min vs temperature of reaction, consisted of a single peak. If different oxide species and different metal oxide–support interactions give individual peaks, then the energy separations of these peaks must be too small to be resolved by this technique. This suggests that the observed profiles are envelopes of the profiles of the different metal oxides present in a variety of environments on the surface of the support. The results of the study along with the calculated ratio, E_i/n, are listed for all three supports in Table 1.

An activation energy calculated from Eq. (5) varies with the square of the temperature of the rate maximum, T_i. Consequently, the E_i/n ratios listed in Table 1 reflect in part changes in the temperature of the rate maximum. The data show that T_i and E_i/n for $CrO_3 \cdot SiO_2$ remain relatively constant for all the calcination temperatures studied. Both T_i and E_i/n for $CrO_3 \cdot Al_2O_3$ decrease as the calcination temperatures are increased from 200 to 500°C. As the calcinations are increased from 500 to 800°C, T_i increases while E_i/n remains constant. The data for $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ show that E_i/n decreases while T_i remains constant as calcinations are increased from 200 to 500°C and then both

TABLE 1

Hydrogen Reduction of: (A) $CrO_3 \cdot SiO_2$, (B) $CrO_3 \cdot Al_2O_3$, and (C) $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ All Containing 3.0% Cr[a]

Calcination temp (°C)	Rate maximum temp (T_i) (°C)			H_2 consumed (cm^3 STP)			E_i/n (kcal)		
	A	B	C	A	B	C	A	B	C
200	310[b]	305	286	48.0[b]	39.3	46.4	24.3[b]	30.1	17.1
	320	305	284	55.9	39.5	46.4	13.1	29.4	16.5
300	292[b]	267	281	52.0[b]	39.0	46.7	18.6	14.8	9.83
	320	280	280	57.6	39.8	47.5	14.8	16.7	10.8
400	324[b]	251	278	50.5[b]	41.2	47.2	21.6[b]	16.5	7.88
	312[b]	250	284	52.0[b]	40.4	47.3	17.2[b]	17.2	8.30
	321			58.6			14.2		
500	320[b]	235	290	50.0[b]	35.5	47.0	18.5[b]	15.0	7.16
	328	240	293	57.2	41.3	46.4	15.1	14.9	7.80
	326			57.6			13.6		
600	322	229	316	53.4	35.4	36.2	14.6	13.6	10.0
	322	233	320	53.3	36.1	34.8	13.6	12.8	10.9
700	326	238	330	50.0	26.9	26.1	13.0	12.6	11.3
	320	238	325	45.5	27.5	28.0	12.0	13.1	11.3
800	326	254	340	40.6	15.5	13.5	12.0	12.7	15.2
	326	251	338	38.7	14.6	13.9	12.8	12.4	15.2

[a] Sample wt = 2.0 g.

[b] These reductions were conducted in a volume of 155 cm^3 instead of the usual 105 cm^3.

E_i/n and T_i increase as the calcinations are increased from 500 to 800°C.

The data in Table 1 show that the total amount of H_2 consumed in reduction is nearly constant for a given support for catalysts calcined up to 500°C. At calcination temperatures above 500°C, H_2 consumption declines, the decline being most severe for CrO_3 supported on Al_2O_3 and $SiO_2 \cdot Al_2O_3$. Figure 3 is a plot of the number of gram-equivalents of H_2 consumed divided by the number of gram-atoms of Cr originally present against the calcination temperature of the catalysts. These data indicate that the order of the supports imparting greater thermal stability to CrO_3 for calcinations up to 500°C is $SiO_2 > SiO_2 \cdot Al_2O_3 > Al_2O_3$. Above 500°C there is little difference in the stabilizing effect of $SiO_2 \cdot Al_2O_3$ and Al_2O_3. This is also the order reported for the efficacy of the supports for CrO_3 in the polymerization reaction (*4*, *5*).

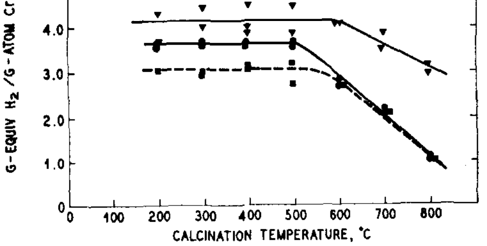

FIG. 3. H_2 reduction of supported CrO_3 (3% Cr).

The ratios, gram-equivalents H_2 consumed per gram-atom Cr orginally present, represent average changes in oxidation number of the metal oxide. The final oxidation state for the metal oxide under the reducing conditions employed here is probably Cr(II). Thus the change in oxidation number of 4 observed for $CrO_3 \cdot SiO_2$ calcined in the 200 to 600°C range indicates that the oxide was stabilized at Cr(VI). For higher calcination temperatures the changes in oxidation number indicate that the oxide was stabilized at average oxidation states ranging between 5 and 6. The results for the reduction of $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ calcined in 200 to 500°C range point to an average oxidation state of approximately 5.6. For the same temperature range the metal oxide in $CrO_3 \cdot Al_2O_3$ is stabilized at an oxidation state averaging about 5. These average oxidation states probably consist of contributions from all possible species ranging from Cr(II) to Cr(IV). At higher calcination temperatures both $SiO_2 \cdot Al_2O_3$ and Al_2O_3 provide less and less stabilization to Cr(VI) until at 800°C the principle species present on the supports is Cr(III).

The variation in the amount of reducible Cr with catalyst calcination treatment suggests that E_i/n should be expressed on the basis of the amount of reducing gas consumed. Figure 4 shows the plot for E_i/n per gram-equivalent H_2 consumed against the calcination temperature. As would be expected, the data for the reduction of $CrO_3 \cdot SiO_2$ give a straight line. The data for CrO_3 supported by Al_2O_3 and $SiO_2 \cdot Al_2O_3$ give similar curves showing that the activation energy per gram-equivalent of H_2 consumed is minimum for catalysts calcined at about 500°C. The increase in this parameter on increasing the calcination temperature from 500 to 800°C is due to the reduction of metal oxides in the lower oxidation states formed by increasingly severe thermal treatment. Part of the increase in E_i/n per gram-equivalent H_2 consumed may be due to the metal oxides undergoing greater interaction with the support. The decrease in E_i/n per gram-equivalent H_2 consumed on increasing the calcination temperature from 200 to 500°C is due in part to a manifestation of H_2O. In this region the reduction is carried out over catalysts undergoing dehydration. The H_2O content of this $SiO_2 \cdot Al_2O_3$ declines from 1.9% at 200°C to 0.64% at 500°C. The presence of excess moisture in the reducing gas is known to convert part of the CrO_3 to the difficulty reducible Cr_2O_3 (*2*). Additional H_2O is formed during the course of the reduction. Based on H_2 consumption the quantity of H_2O formed during the reduction of $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ varies from 0.5 to 1.9% of the catalyst weight.

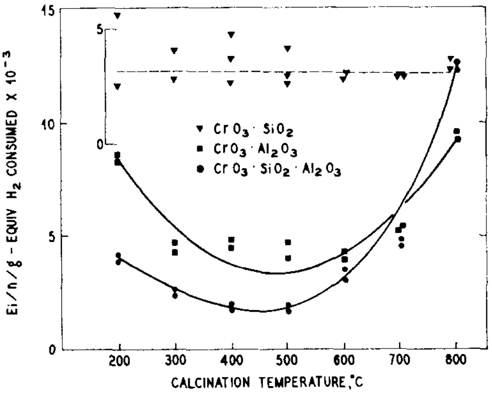

FIG. 4. H_2 reduction of supported CrO_3 (3% Cr).

The nature of the initial interaction of CrO_3 with the various supports may influence the thermal stability and reducibility of the metal oxide for a given calcination temperature. For example, coordination of CrO_3 to SiO_2 through the oxygen atoms of the metal oxide and the protons of the hydroxyl groups of the support would give structures having thermal stability and consequently, uniform reducibility. On the other hand CrO_3 reacts with hydroxyl groups on Al_2O_3 to form aluminum chromate-type compounds which would be more difficultly reducible than the oxide itself. This would account for the high value of E_i/n per gram-equivalent H_2 shown in Fig. 4 for $CrO_3 \cdot Al_2O_3$ calcined at

TABLE 2

Hydrogen Reduction of $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ (87% SiO_2–13% Al_2O_3) with Variable Cr Content[a]

Sample wt (g)	Wt% Cr	Rate maximum temp (T_i) (°C)	E_i/n (kcal)
2.0	3.0	290	7.2
	3.0	293	7.8
7.0	1.0	330	9.8
	1.0	330	10.2
	0.5	350	15.2
	0.5	345	13.0
	0.75	338	11.9
	0.75	340	12.0
	0.25	354	17.3
	0.25	354	16.3
	0.15	365	20.1
	0.15	360	17.7
	0.10	370	16.6
	0.10	365	16.3
	0.05	375	(14.4)
	0.05	370	(11.5)

[a] Activation at 500°C.

200°C. At higher calcination temperatures the hydroxyl content of the Al_2O_3 would decline and smaller amounts of the difficultly reducible surface compound would be formed. The increases in the value of E_i/n per gram-equivalent H_2 for catalyst calcinations above 500°C would be due to formation of increasing amounts of Cr_2O_3 under the severe thermal conditions. On $SiO_2 \cdot Al_2O_3$ the stabilization of CrO_3 against thermal decomposition probably occurs by formation of coordinate bonds of the oxygen atoms of CrO_3 and the isolated aluminum atoms of the support. Formation of these structures would be favored by the decline in H_2O content of $SiO_2 \cdot Al_2O_3$ which accompanies an increase in calcination temperature from 200 to 500°C. Calcinations above 500°C would decompose increasing amounts of the coordinated CrO_3 to the difficultly reducible Cr_2O_3. Thus the data for CrO_3 supported on $SiO_2 \cdot Al_2O_3$ resembles the data for $CrO_3 \cdot SiO_2$ and $CrO_3 \cdot Al_2O_3$. The interactions proposed here are similar to those used by Miesserov (*6*) to explain differences in "oxidative power" of CrO_3 on different supports.

D. Study of the H_2 Reduction of $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ as a Function of Cr Concentration

The H_2 reduction of CrO_3 supported on 87% $SiO_2 \cdot$13% Al_2O_3 was investigated for Cr contents ranging from 3.0 to 0.05%. All samples were calcined *in situ* at 500°C. The sample size was increased to 7 g for Cr concentrations of 1% and lower in order to get significant pressure changes in the system. Accuracy and repeatability became problems at the lower Cr concentrations. The H_2 pressure in the system was maintained above the level required to make the data independent of that variable. The results are summarized in Table 2. In Fig. 5 the logarithm of the percentage of Cr has been plotted against the temperature of the rate maximum, T_i. The plot shows that the temperature of the rate maximum increases with decreasing Cr contents. The temperature increase is small, however, for Cr concentrations below 0.5%. These data suggest that up to a certain point the lower the Cr concentration the more firmly it is bound to the surface. The ratios, E_i/n, also

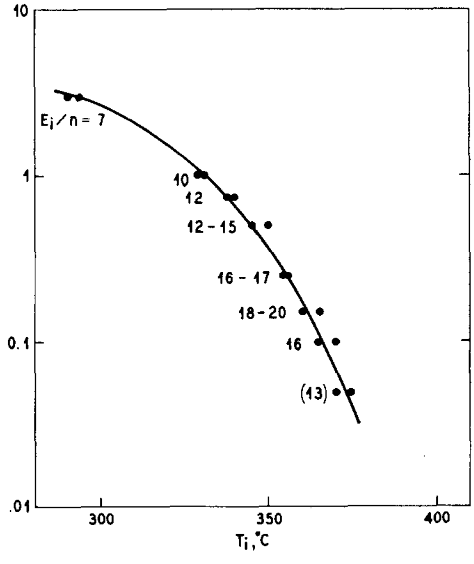

FIG. 5. H_2 reduction of $CrO_3 \cdot SiO_2 \cdot Al_2O_3$; variation in rate maximum, T_i, with Cr content.

support this view. This probably means that there is a continuous range of Cr binding energies present on the surface.

Further evidence of the heterogeneity of the Cr on the surface was given by partially reducing the $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ containing 3% Cr. In these experiments the catalyst was treated with H_2 under rising temperature conditions until one-fourth, one-half, or three-fourths of the CrO_3 had been reduced. A second profile shows that the effect of the partial reduction is to decrease the rate maximum and to displace it to a higher temperature. The new rate maximum and the temperature where it occurs are consistent with those for a virgin catalyst having the same reducible Cr concentration as the partially reduced material.

E. The Effect of the Composition of the Support on the H_2 Reduction of $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ (3% Cr)

The temperatures of the rate maxima for the H_2 reduction of $CrO_2 \cdot Al_2O_3$ and $CrO_3 \cdot SiO_2$ both calcined at 500°C are separated by 80°C. This observation prompted the study of the effect of different $SiO_2 \cdot Al_2O_3$ compositions on the hydrogen reduction of supported CrO_3. One objective was to find a support combination having more than one rate maximum with temperature. This was never realized. Catalysts ranging in support composition from 6% $SiO_2 \cdot$94% Al_2O_3 to 87% $SiO_2 \cdot$13% Al_2O_3, all impregnated to contain 3% Cr, gave a single rate maximum with temperature during reduction. Figure 6 shows the temperatures of these maxima for the support combinations studied. The relative activation energies, E_i/n, for each support combination are listed on the graph.

The temperatures for the rate maxima shown in Fig. 6 vary little for support compositions up to 70 to 80% SiO_2. These data suggest that the CrO_3 is associated with the Al_2O_3 and the isolated Al^{3+} ions of the $SiO_2 \cdot Al_2O_3$ solid solution which are the two phases present in $SiO_2 \cdot Al_2O_3$ containing more than 25% Al_2O_3. Compositions containing more than 75% SiO_2 consist of only one phase, $SiO_2 \cdot Al_2O_3$ solid solution, and possess only isolated Al^{3+} ions for reaction with CrO_3. Consequently with further decline in Al_2O_3 content the CrO_3 becomes coordinated with the protons of the SiO_2 and the temperature of the maximum rate approaches that of pure SiO_2.

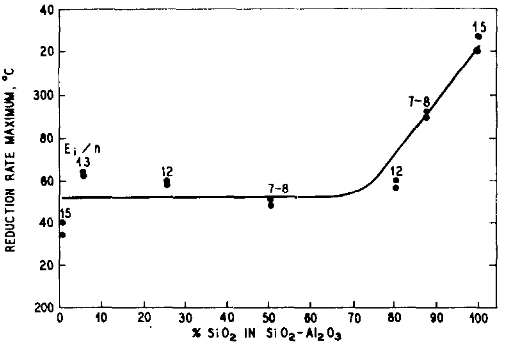

Fig. 6. H_2 reduction of $CrO_3 \cdot SiO_2 \cdot Al_2O_3$: variation of reduction rate maximum (°C) with support composition; calcination temp, 500°C.

F. Carbon Monoxide Reduction of Supported CrO_3 as a Function of Calcination Temperature

The use of CO instead of H_2 to reduce supported CrO_3 avoids the formation of water. Water has been shown to alter the future course of the reaction (*2*). There is no evidence that CO_2 influences the course of the reduction of CrO_3. The reduction of CrO_3 supported on SiO_2, Al_2O_3 and $SiO_2 \cdot Al_2O_3$ (87% $SiO_2 \cdot$13% Al_2O_3) was investigated for calcinations at 100°C intervals in the 200 to 800°C range. The reduction profiles, $\Delta P/10$ min vs reaction temperature, for all catalysts consisted of a single relatively symmetrical band. In particular, the symmetry of the reduction profile for $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ was improved over that found for the catalyst using H_2. The data for the study are summarized in Table 3.

The reduction of supported CrO_3 occurs at much lower temperatures for CO than for H_2. Data listed in Table 3 for SiO_2,

TABLE 3

Carbon Monoxide Reduction of: (A) $CrO_3 \cdot SiO_2$, (B) $CrO_3 \cdot Al_2O_3$, and (C) $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ All Containing 3.0% Cr[a]

Calcination temp (°C)	Rate maximum temp (T_i) (°C)			CO consumed (cm^3 STP)			E_i/n (kcal)		
	A	B	C	A	B	C	A	B	C
200	234	240	230	53.3	43.3	52.2	12.8	21.2	11.7
300	234	230	224	63.6	45.3	53.7	12.7	16.7	9.25
400	232	232	220	64.5	47.8	54.2	12.1	12.3	9.17
500	233	218	228	65.5	46.8	54.7	12.6	12.5	11.4
	234			63.9			12.9		
600	232	218	240	65.3	43.1	41.5	12.8	15.7	13.9
700	233	214	252	58.7	32.0	28.8	13.3	10.0	17.4
800	239	235	260	53.3	16.0	17.9	14.1	8.4	22.5

[a] Sample wt = 2.0 g.

Al_2O_3 and $SiO_2 \cdot Al_2O_3$ calcined at 500°C show that with CO the temperature of the maximum rate occurs at 233, 220, and 228°C for the respective supports. Data for H_2 reduction listed in Table 1 show that the temperatures associated with the maximum rate for SiO_2, Al_2O_3, and $SiO_2 \cdot Al_2O_3$ calcined at 500°C occur near 330, 230, and 300°C, respectively. It is surprising how constant the temperature of the rate maximum, T_i, for CO reduction is for all calcination temperatures and all supports studied. With the exception of $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ calcined at 700 and 800°C, all the values for T_i lie between 220 and 240°C. This contrasts with the data for reduction of $CrO_3 \cdot Al_2O_3$ and $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ obtained with H_2 where T_i changes 72 and 62°C, respectively, over the range of calcination temperatures studied. The narrow range of T_i and the more symmetrical profiles observed for CO reduction of CrO_3 on all three supports is consistent with the concept that product H_2O does alter reductions with H_2.

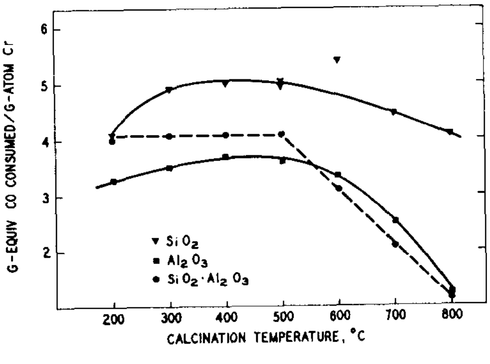

FIG. 7. CO reduction of supported CrO_3 (3% Cr).

Figure 7 shows a plot of the number of gram-equivalents of CO consumed per gram-atom Cr originally present against the calcination temperature of the supports studied. Our data indicate that the average change in oxidation number determined with CO is greater than that determined with H_2 for calcinations in the 200–500°C range. This difference is probably due to some conversion of CO to CO_2 over the supports and to some CO forming thermally stable complexes with the metal oxide. We believe that the final oxidation state of the Cr is 2 and that the average oxidation state of Cr on all of these supports calcined in the 200 and 500°C range lines between 5 and 6. Again the order of stability afforded by the supports to CrO_3 against thermal decomposition in 200–500°C range is: $SiO_2 > SiO_2 \cdot Al_2O_3 > Al_2O_3$. At higher calcination temperatures SiO_2 affords CrO_3 much greater stability against decomposition than either $SiO_2 \cdot Al_2O_3$ or Al_2O_3. When calcined at 800°C both promoted $SiO_2 \cdot Al_2O_3$ and Al_2O_3 stabilize Cr(III) against further decomposition.

Figure 8 shows changes in the relative activation energy per unit of CO consumed, i.e., gram-atoms Cr reduced, with changes in calcination temperature. As in the case for reduction with H_2 the relative activation energy per unit of Cr reduced with CO is nearly constant for all calcination temperatures. For calcinations between 200 and 500°C the data for reduction of $CrO_3 \cdot SiO_2$ and $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ with CO are nearly identical. After calcination above 500°C the calculated parameter is greater for $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ than either $CrO_3 \cdot SiO_2$ or $CrO_3 \cdot Al_2O_3$. The metal oxide that is so difficult to reduce on the dehydrated surface is probably Cr_2O_3 strongly interacted with $SiO_2 \cdot Al_2O_3$.

G. *Investigation of CO Reduction of* $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ *as a Function of Cr Content*

The study was carried out using the 87% $SiO_2 \cdot 13\%$ Al_2O_3 support. All specimens were calcined at 500°C. The Cr concentration varied from 3.0 to 0.15%. Even with 7 g-samples the pressure changes after appropriate corrections were not sufficient for accurate measurements at Cr concentrations less than 0.15%. The results tabulated in Table 4 show that as the Cr concentration decreases the temperature associated with the rate maximum increases. This is consistent with the view that there is a distribution of Cr binding energies on the surface and that the metal oxide is more firmly bound to the surface at the lower concentrations. The values for E_i/n reflect this trend.

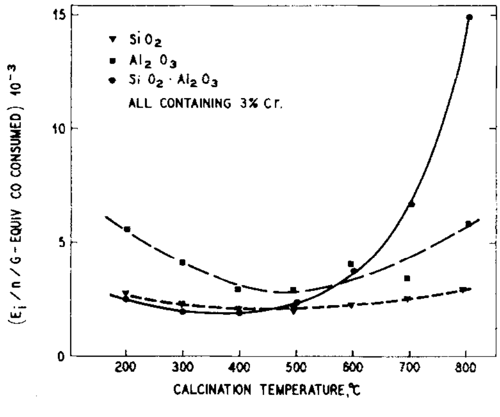

FIG. 8. CO reduction of supported CrO_3.

TABLE 4

Carbon Monoxide Reduction of $CrO_3 \cdot SiO_2 \cdot Al_2O_3$ (87% SiO_2–13% Al_2O_3) with Variable Cr Content[a]

Sample wt (g)	Wt% Cr	Rate maximum temp (T_i) (°C)	E_i/n (kcal)
2.0	3.0	228	11.4
	1.0	255	16.1
7.0	0.75	260	13.8
	0.50	260	13.4
	0.25	268	17.9
	0.15	273	(16.2)

[a] Calcination at 500°C.

A specimen containing 3% Cr was reduced with CO in absence of adsorbent, i.e., no Ascarite in the system. No pressure change occurred during the reduction indicating that the reaction $2\ CO \rightarrow C + CO_2$ did not take place. A coprecipitated catalyst prepared to contain 3% Cr on an 87% $SiO_2 \cdot 13\%$ Al_2O_3 base gave a reduction profile almost identical to that of an impregnated catalyst of the same composition.

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