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Reduction Studies on Supported Metal Oxide Catalysts

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A procedure is described for determining the reduction characteristics of metal oxide-promoted catalysts. The method involves circulating a measured volume of hydrogen in a closed system that includes a suitable tube for the catalyst, an absorption tube for removing the water formed, and a manometer for measuring the consumption of hydrogen. Reductions may be conducted either at a definite temperature or the temperature may be increased on a fixed time schedule. In the latter case, regular temperature and pressure readings provide information necessary to plot "reduction profiles" in which the reduction rate is plotted versus temperature (or time). Characteristic curves are obtained for various promoter–support combinations and the areas below the "reduction profile" curves are proportional to the amount of reduction. However, the latter is obtained more precisely by accurate measurement of the hydrogen consumption.

The procedure was used for studying the reduction characteristics of supported nickel oxide and chromium oxide catalysts as affected by methods of preparation, kinds of support, and the effects of heat treatment, temperature, and promoter concentrations. The results showed that promoter oxide–support oxide interaction increased the difficulty of reducing the promoter metal oxide. This effect was most pronounced for nickel oxide when supported on alumina and for chromium oxide supported on silica. Coprecipitated catalysts were more difficult to reduce than those prepared by impregnation, apparently because of better distribution and therefore better opportunity for interaction. For the same reason, higher temperatures of catalyst heat treatment resulted in increased difficulty of reduction. The interaction between the metal oxide promoter and the support oxide appears to have an important effect on the catalytic properties of metal oxide-promoted catalysts. This is illustrated by results obtained with chromium oxide–silica–alumina catalysts.

I. INTRODUCTION

In studies of supported metal oxide catalysts it is frequently important to have information regarding the reducibility of the metal oxide. Such information can be helpful in establishing the availability of the metal oxide (or metal) on the surface, the extent of interaction with the support, the degree of metal oxide dispersion in the support surface, and the apparent valence of the promoting metal as influenced by the valence characteristics of the supporting oxide. These factors may vary with the method of catalyst preparation and have an important part in determining the catalytic activity of the metal oxide–support combination. Current interest in the reducibility of supported metal oxide catalysts is demonstrated by the fact that several papers (*1–4*) on this particular subject have appeared in recent years.

In the past, reducibility has been a useful means for detecting interaction between the promoter metal oxide and the oxide support in catalyst systems. DeLange and Visser (*5*) observed that nickel oxide supported on silica, was more difficult to reduce than nickel oxide alone and on the basis of this and X-ray work suggested the formation of nickel hydrosilicates. Van Eijk van Voorthuysen and Franzen (*6*) varied the nickel:silica ratio in a series of coprecipitated preparations and were able to show that reduction became more difficult for materials with higher silica contents. Reduction studies by Hill and Selwood (*7*) on nickel

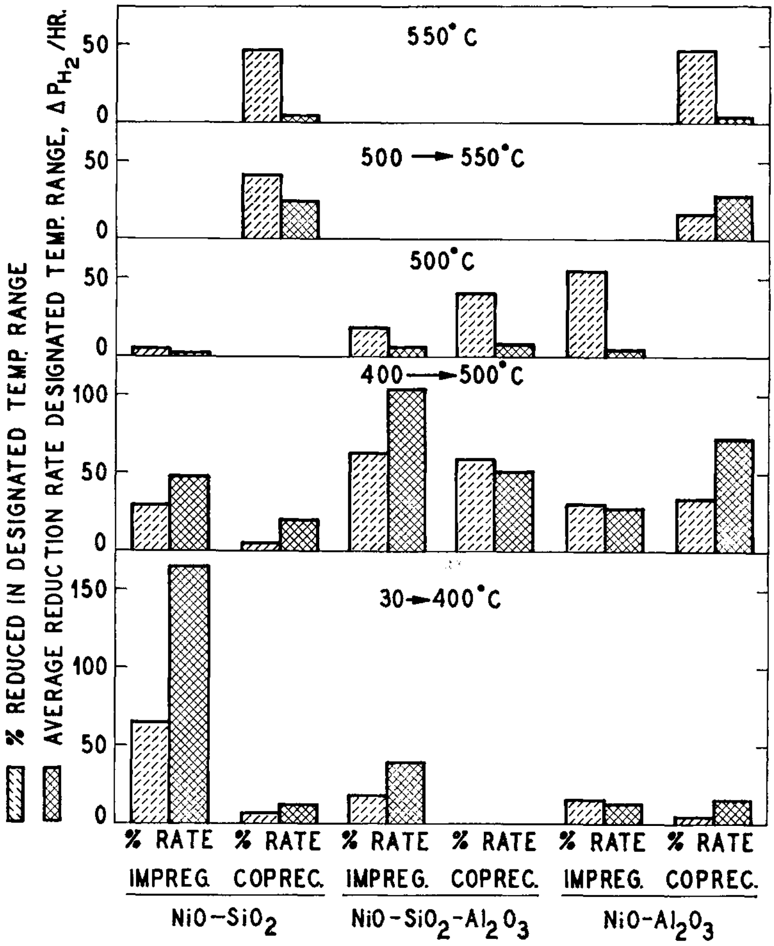

Fig. 1. Effect of support and method of preparation on reducibility in hydrogen for catalysts containing 2.8 to 5.87 Ni as NiO: impregnated $NiO\text{-}SiO_2$ (calculated Ni valence, 2.22); coprecipitated $NiO\text{-}SiO_2$(2.39); impregnated $NiO\text{-}87SiO_2\text{-}13Al_2O_3$ (2.04); coprecipitated $NiO\text{-}SiO_2\text{-}Al_2O_3$ (1.94); impregnated $NiO\text{-}Al_2O_3$ (2.08); coprecipitated $NiO\text{-}Al_2O_3$ (2.65).

oxide–γ-alumina catalysts indicated that at nickel concentrations below 5%, the nickel valence was between 2 and 3. Selwood ascribes this to "valence induction" influenced by the trivalent aluminum in the alumina. Reinen and Selwood (*8*) have reported that the difficulty of reduction of NiO in supported NiO catalysts decreases in the following order: impregnated $NiO\text{-}Al_2O_3$, coprecipitated $NiO\text{-}SiO_2$, and impregnated $NiO\text{-}SiO_2$. The present authors (*9*) presented data showing that the nickel oxide in coprecipitated $NiO\text{-}SiO_2\text{-}Al_2O_3$ was more difficult to reduce than that in a catalyst prepared by impregnation and that nickel oxide alone could be reduced far more readily than either of these. They reported that a coprecipitated catalyst of optimum nickel concentration had higher activity for ethylene polymerization than one prepared by impregnation and attributed this to better dispersion of the promoter oxide. On the other hand Selwood (*10*) found that a reduced $NiO\text{-}Al_2O_3$ catalyst with 10.5% nickel prepared in a one-step impregnation, had almost nine times the activity for benzene hydrogenation of one with the same nickel content but impregnated by a multistep procedure. Here it was assumed that the one-step application of nickel resulted in

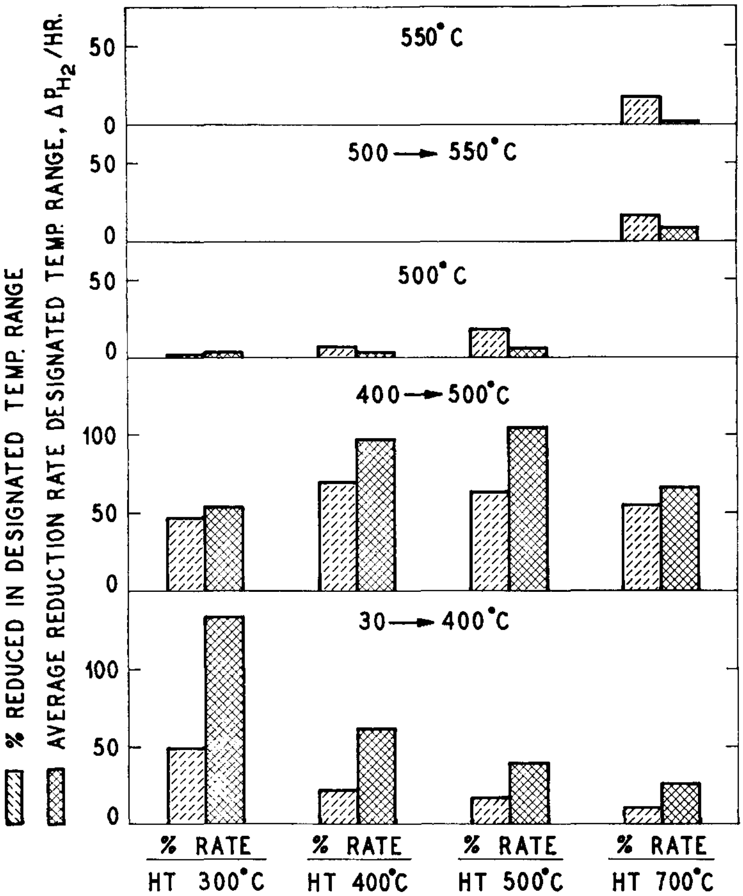

FIG. 2. Effect of heat treatment temperature on reducibility in hydrogen. Impregnated NiO-87 SiO_2-13 Al_2O_3 catalysts with 2.77% Ni, heat-treated 5 hr in air as follows: 300°C (calculated Ni valence 2.55); 400°C (2.14); 500°C (2.04); 700°C (1.91).

The high values for the nickel valences of the impregnated catalysts heat-treated at only 300 or 400°C may be due to simultaneous reduction of undecomposed nickel nitrate. However, abnormally high valences for nickel in impregnated and coprecipitated catalysts heat-treated above 500°C, are considered to be caused by valence induction.

"clumping" of nickel oxide which on reduction produced larger particles of nickel that were considered advantageous in this reaction. Another factor, of course, may be the greater difficulty in completely reducing nickel oxide which has had better opportunity to interact with the alumina support. Thus, the optimum degree of dispersion of a promoter may be different depending on the type of catalytic reaction under consideration.

This report concerns a study of reducibility of supported metal oxides involving a number of different promoter–support combinations, different methods of preparation, and different degrees of heat treatment. The method used involved a measurement of hydrogen consumption in a closed system. This procedure was first reported by Hill and Selwood (*7*) and was used in a modified form in reduction studies in a previous investigation (*9*). Later this procedure was also utilized by Voge and Atkins (*3*) in reductions of supported copper oxide. In the present study, part of the data was obtained by an additional modification of the method which involved performing reduction while increasing the

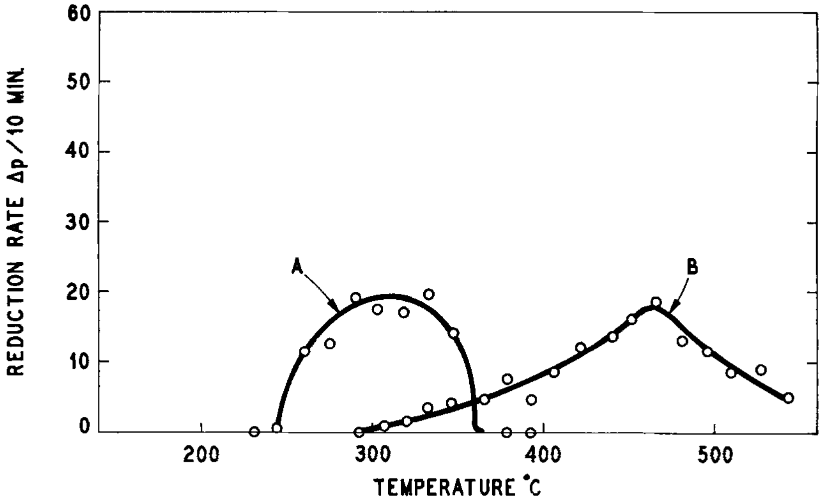

FIG. 3. Reduction profiles for impregnated nickel oxide catalysts. A, NiO on Cabosil SiO_2 with about 2% Ni; B, NiO on 87 SiO_2-13 Al_2O_3 with 2.92% Ni (reduction data showed divalent Ni equivalent to 2.93% Ni).

temperature on a regular time schedule and making corresponding measurements of hydrogen pressure in the system as the reaction proceeded. Finally, the temperature was held at 500° or 550°C until pressure measurements indicated that reduction was complete. The pressure decreases representing reduction for equal increments of temperature (or time), were graphed so that the plots were essentially "reduction profiles" for each catalyst and showed the temperature ranges in which reduction occurred most rapidly. These "reduction profiles" were reproducible and furnished better reducibility information for supported metal oxide catalysts than could be presented in any other way.

II. EXPERIMENTAL

Materials. The impregnated catalysts were prepared by impregnation of a support with a solution of the promoter oxide (usually nitrate) followed by drying and heat treatment, usually for 5 hr in a stream of dry air at 500°C. The coprecipitated catalysts were made by reacting appropriate solutions of the promoter oxide with those of the support oxide and coprecipitating the

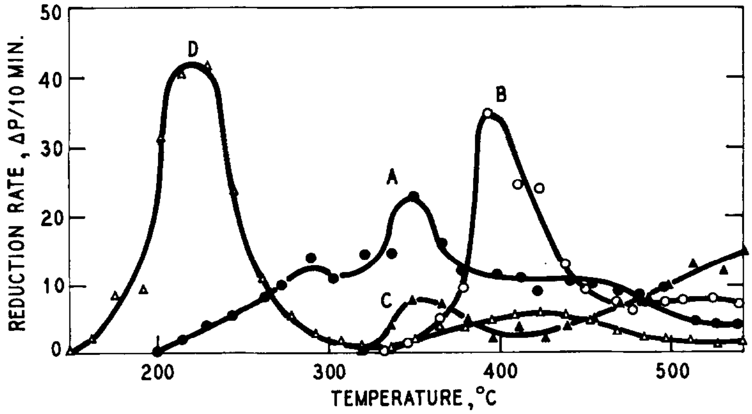

FIG. 4. Reduction profiles for four metal oxide-promoted catalysts. A, FeO on 87SiO_2-13Al_2O_3 with about 3.8% Fe; B, MoO_3 on SiO_2-Al_2O_3 with about 5.4% Mo; C, MoO_3 on Al_2O_3 with about 10% MoO_3; D, CrO_3 on ZrO_2 with about 1% Cr.

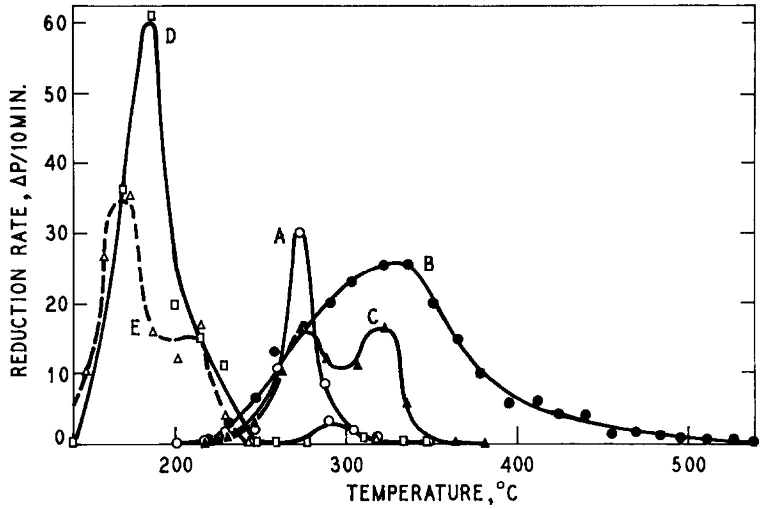

Fig. 5. Reduction profiles for CrO_3. A, CP CrO_3 mixed with CP Cr_2O_3; B, CrO_3 impregnated on porous glass; C, CP CrO_3 mixed with silica sand; D, CrO_3 on Cr_2O_3 gel; E, vacuum-heated Cr_2O_3 gel.

mixed oxides under conditions to produce acceptably high surface areas. If sodium ions were present, these were base-exchanged out by suitable treatment, either of the wet gel or of the material dried at 110°C, with warm ammonium chloride solutions. After washing with distilled water, the product was redried and heat-treated, generally at 550°C for 16 hr in a stream of dry air.

The hydrogen was Matheson prepurified grade, dried with anhydrous magnesium perchlorate.

Apparatus and procedure The apparatus was simply a closed circulating system consisting of a magnetic pump (*11*), a furnace containing a "hairpin" reactor for the catalyst, a tube of anhydrous magnesium perchlorate for water removal, and a full length manometer made of 2-mm ID capillary tubing for measuring pressure changes. The circulating system formed a hydrogen reservoir of about 100-ml capacity at atmospheric pressure and samples of catalysts were taken which required about

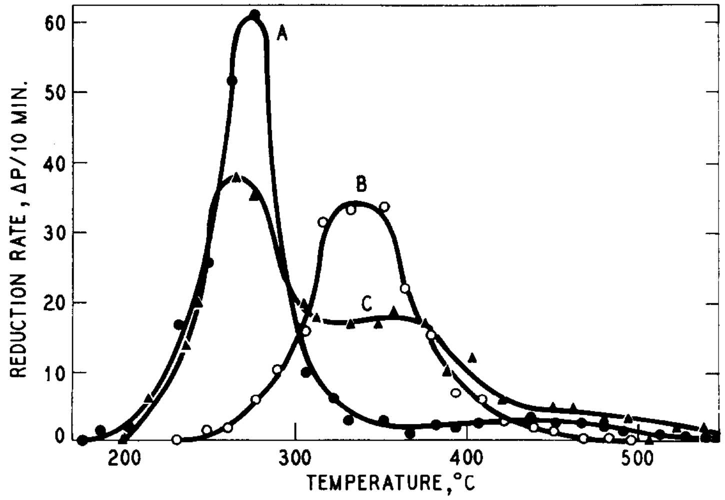

Fig. 6. Reduction profiles of supported CrO_3 catalysts as effected by composition of supports. A, CrO_3-Al_2O_3; B, CrO_3-SiO_2; C, CrO_3-87SiO_2-13Al_2O_3.

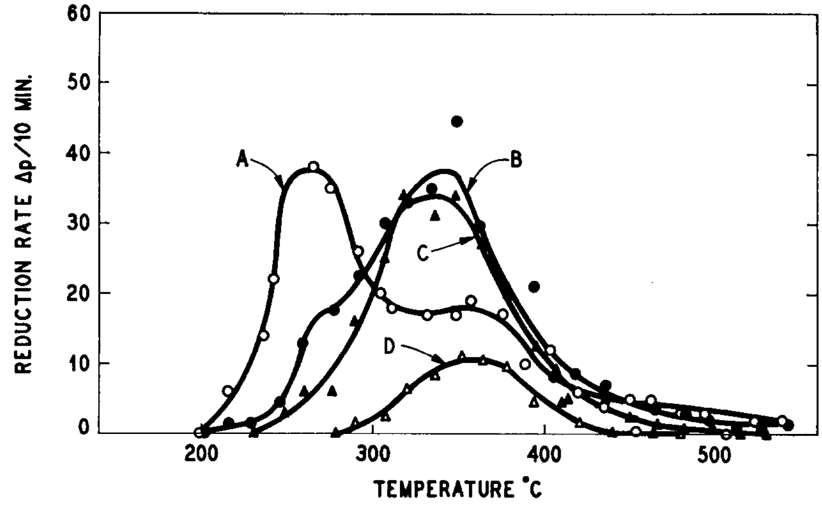

FIG. 7. Reduction profiles for CrO_3-SiO_2-Al_2O_3 catalyst with about 3% Cr, heat-treated at different temperatures. A, 500°C, 5 hr in dry air; B, 600°C; 5 hr in oxygen; C, 700°C, 5 hr in oxygen; D, 900°C, 5 hr in oxygen.

20 to 40 ml of hydrogen for reduction, usually 2 g. A thermocouple bead placed in the furnace with the catalyst tube, was used for temperature measurements. Usually a temperature of 500°C was adequate to obtain complete reduction but for most coprecipitated catalysts and for impregnated NiO-Al_2O_3, it was necessary to go to 550°C. Reduction periods ranged from 5 to 24 hr. In each case the initial hydrogen pressure was about 1 atm.

The performance and calibration of the apparatus were checked by determinations on dried samples of CP nickel oxide (NiO) and cupric oxide (CuO). The reductions indicated valences of 2.01 for nickel and 2.02 for copper in these materials.

When the apparatus was used for obtaining "reduction profiles" the initial temperature setting on the Celectray controller was 100°C and after 10 min, the temperature was advanced 15°. This sched-

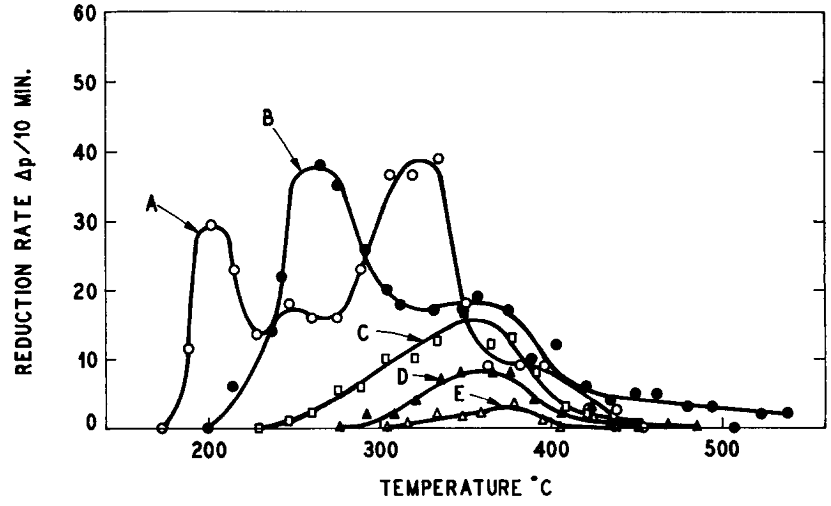

FIG. 8. Reduction profiles for impregnated CrO_3-SiO_2-Al_2O_3 catalysts with varying chromium concentrations. A, 17.6% Cr; B, 2.79% Cr; C, 0.75% Cr; D, 0.48% Cr; E, 0.18% Cr.

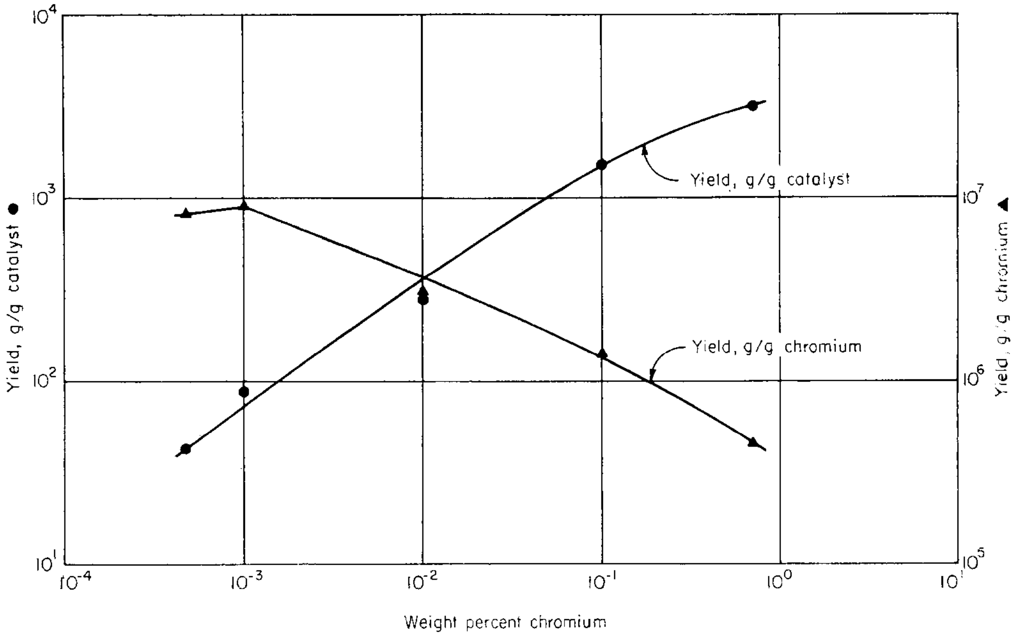

FIG. 9. Effect of chromium concentration on activity.

ule of advancing the temperature was followed up to the maximum temperature and at each level, accurate measurements of reactor temperature and hydrogen pressure were recorded. Plots of decreases in hydrogen pressure for each temperature (time) increment versus the temperature (time) thus indicated the variation of reduction rate with rising temperature. In these "reduction profiles" the areas under a complete curve are proportional to the total hydrogen consumption based on the initial pressure and the volume of the system. Results computed in this manner agreed to within 5% of the more accurate data calculated on the basis of initial and final pressure readings at 25°C.

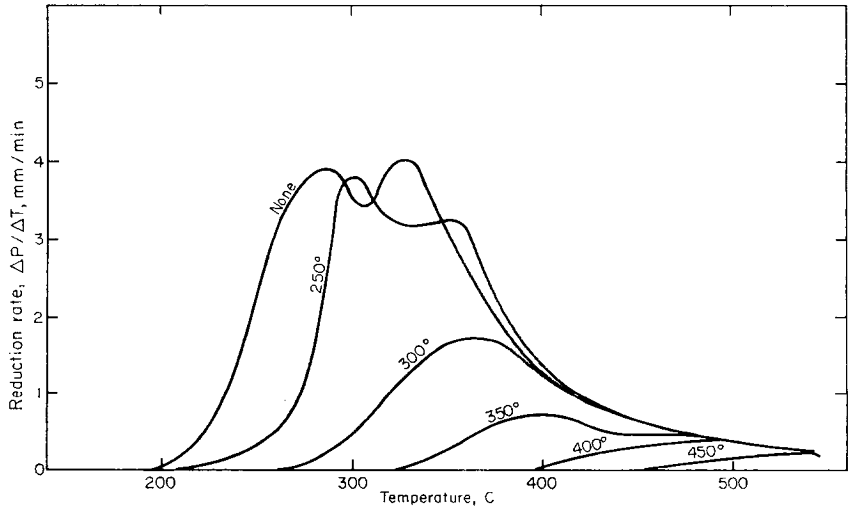

FIG. 10. Reduction profiles for a chromium oxide-silica-alumina catalyst after 1- or 2-hr reductions at the indicated temperatures.

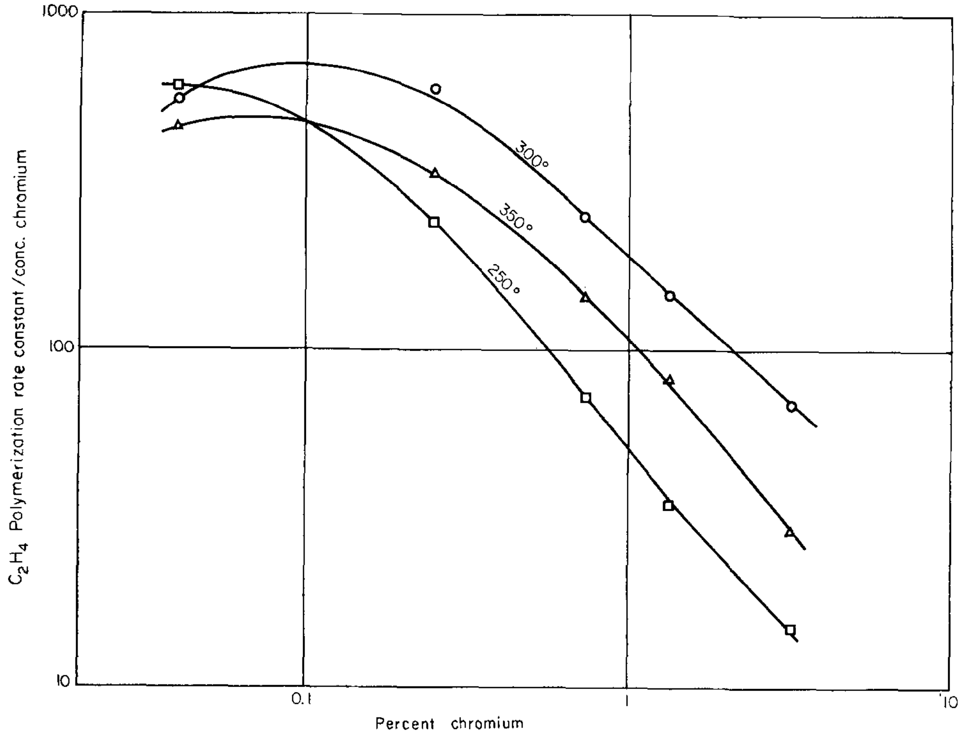

FIG. 11. Variation in ethylene polymerization per gram chromium as a function of chromium concentration for various 1-hr pretreatments with hydrogen.

III. RESULTS AND DISCUSSION

Nickel catalysts. Tests of the effect on reducibility caused by variation in support material, method of preparation, and heat treatment temperature, were performed by the initial procedure in which the following approximate heating schedule was used: 30° to 400°C, ¾ hr; 400° to 500°C, 1¼ hr; and at 500°C, 5 or 20 hr. When it was necessary to use a higher temperature, instead of holding at 500°C, the temperature was increased from 500° to 550°C in about 2½ hr and then leveled at 550°C for about 20 hr. Periodic pressure and temperature readings were made throughout the runs and these provided a means of determining the approximate percentage of the total reduction occurring in each of the above temperature ranges or levels as well as the corresponding approximate rates of reduction.

Runs were made on impregnated and coprecipitated preparations in which nickel oxide was associated with three supports—silica, alumina, and silica-alumina. The results are presented in Fig. 1. It is evident that the impregnated $NiO-SiO_2$ catalyst was most easily reduced, whereas the coprecipitated $NiO-SiO_2$ and $NiO-Al_2O_3$ were the most difficult to reduce, with more oxide in $NiO-SiO_2$ still unreduced at 500°C. Of the impregnated catalysts, the resistance to reduction of NiO increased in the following order on the respective supports: SiO_2, $SiO_2-Al_2O_3$, Al_2O_3. Of the coprecipitated materials, $NiO-SiO_2-Al_2O_3$ was reduced most readily with somewhat more reduction occurring below 500°C than in the case of impregnated $NiO-Al_2O_3$.

Figure 2 shows the effect of heat treatment temperature on the reducibility of nickel oxide in impregnated $NiO-SiO_2-Al_2O_3$. The results show clearly that the difficulty in reduction increases as the heat treatment temperatures were increased from 300° to 700°C. This is in accord with findings of other investigators (*5*, *6*) who attributed the increase in resistance to reduction when

NiO was combined with SiO_2, to interaction resulting in the formation of some form of nickel silicate. Similar observations regarding the effect of heat treatment temperature were reported by Bicek and Kelly (*2*).

"Reduction profiles" for two impregnated catalysts, NiO on Cabosil SiO_2, and NiO on $87SiO_2$–$13Al_2O_3$ are shown in Fig. 3. The "reduction profiles" verify the data in Fig. 1, indicating the greater ease of reduction of NiO on SiO_2 than that for NiO on SiO_2-Al_2O_3.

"Reduction profiles" of various supported metal oxides. Because of convenience and the fact that more specific information could be shown by this procedure, all of the reducibility data for chromium oxide catalysts were obtained so that "reduction profiles" could be plotted. These have the advantage of showing graphically the particular temperature ranges in which reduction occurs. Since time is proportional to temperature the accumulative areas under the reduction peaks are indicative of the degree of reduction at various temperatures and the slopes of the curves indicate how rapidly the reduction rate varies with temperature. Figure 4 presents "reduction profiles" for four different promoter–support combinations to illustrate how this procedure differentiates reduction characteristics for various materials. Iron oxide on silica-alumina (A) is reduced over a wide temperature range with a peak at about 350°C. Evidently promoter–support interaction occurs for both components in the support producing both iron silicates and iron aluminates that reduce rather slowly. Molybdena on silica-alumina prepared by impregnation and heat-treated at 500°C for 5 hr shows rapid reduction for the major portion of the MoO_3 at about 375–400°C (B), whereas the commercial molybdena-alumina catalyst (C) reduces more slowly over a wide temperature range, indicating considerable promoter–support interaction. The calcination conditions used for the latter are not known. The CrO_3-ZrO_2 catalyst (D) shows rapid reduction of most of the CrO_3 occurring at about 225°C, with a small, broad maximum at about 425°C, which is attributed to interaction between the components.

Effect of environment on reducibility of CrO_3. When a run was made with CP CrO_3 mixed with CP Cr_2O_3, reduction occurred in a narrow temperature range, peaking at about 275°C (A, Fig. 5). When it was mixed with silica sand (C), the reduction again occurred over a short temperature interval but the curve showed two peaks, one coinciding with curve A, and the other at about 320°C. The latter is near the peak found for CrO_3-SiO_2 combinations and may indicate the effect of contact of CrO_3 with the surface of the sand grains and rapid interaction between CrO_3 and SiO_2 even at low temperatures. When CrO_3 was impregnated on porous glass and heat-treated at 500°C, the reduction curve (B) peaked at about 340°C, which is typical of CrO_3-SiO_2 catalysts, as will be shown later. The reduction curve for Cr_2O_3 gel impregnated with CrO_3 (D) indicated a sharp maximum at about 170–180°C. This was the lowest temperature peak observed for any of the catalysts studied and it was suspected that the data indicated the possible presence of strongly chemisorbed oxygen. Similar curves were obtained on chromic oxide gel, either as previously heat-treated or after a 2-hr evacuation *in vacuo* at 500°C (E). Evidently some of the oxygen comes from an easily reduced oxidation state that forms on the surface of the gel on exposure to air.

The effect of support composition and conditions of heat treatment. The results for three impregnated catalysts, CrO_3-SiO_2, CrO_3-Al_2O_3, and CrO_3-SiO_2-Al_2O_3 (1.63%, 5.13%, and 2.79% chromium, respectively) are presented in Fig. 6. Most of the reduction for CrO_3-Al_2O_3 (A) occurs in a narrow range between 220° and 320° with a pronounced maximum at about 275°C. The maximum occurs at the same temperature as for CrO_3 mixed with crystalline Cr_2O_3. That only a small amount of interaction occurs between the promoter and support, is indicated by the low flat secondary maximum at around 440°C. When silica is promoted with CrO_3, however, considerable interaction is indicated since the symmetrical "reduction profile" for CrO_3-SiO_2 (B) peaks at 340° instead of at 275°C. The curve for CrO_3-SiO_2-Al_2O_3 (C) has an unsymmetrical form in which the principal peak is at 270°C, at the same point as for pure CrO_3 and CrO_3-Al_2O_3, but there is a hump suggestive of a secondary peak at about 350°C, near the peak for the CrO_3-SiO_2 catalyst. (Heat treatment in each instance was at 500°C for 5 hr in a stream of dry air.) In this case, therefore, one can conclude that part of the CrO_3 has interacted with the support due to the silica content, but the remainder behaves as if it were supported by alumina.

The appearance of the "reduction profiles" depends also on the conditions of heat treatment. This is demonstrated in Fig. 7 for impregnated CrO_3-SiO_2-Al_2O_3 catalysts containing about 3% chromium. The curve A (same as C in Fig. 6) represents heat treatment for 5 hr in air at 500°C. When heat treatment was at 600°C in oxygen, the "reduction profile" is shown by the slightly unsymmetrical curve B, with a maximum at 340°C characteristic of CrO_3-SiO_2 and with a slight hump at 270°C, suggesting a small secondary maximum at the same point as the same point as the principal maximum in curve A. Thus it appears that the effect of the higher temperature was to produce interaction between CrO_3 with SiO_2 for most of the CrO_3 present. After heat treatment of the catalyst at 700°C in oxygen the "reduction profile" becomes completely symmetrical and transformation to the silica-bound CrO_3 is apparently complete. When heat treatment was at 900°C in oxygen, the maximum of the resulting symmetrical curve is shifted to a slightly higher temperature (360° instead of 340°C), but the principal change is in a reduction in the area below the curve, showing that less CrO_3 was available for reduction. This is, without doubt, due to the loss of oxygen by thermal decomposition of the supported CrO_3 at 900°C.

"Reduction profiles" of catalysts with different chromium contents. The effect of variation in chromium content for several impregnated CrO_3–$87SiO_2$–$13Al_2O_3$ catalysts, heat-treated at 500°, is shown in Fig. 8. Here, curve B (same as C in Fig. 6) is for a catalyst containing 2.79% chromium. Curve A (17.6 Cr) indicates three maxima. The largest occurs at about 325°C, slightly lower than the usual maximum for CrO_3-SiO_2 (340°). A small maximum appears at 250°C which is at a little lower temperature than that for CrO_3-Al_2O_3 (270°). A maximum of intermediate height is found at 200°C. This is at about the same temperature as the maximum in the "reduction profile" for CrO_3-impregnated Cr_2O_3 gel (Fig. 6). This again, indicates the presence of a stable, easily reducible state of chromium oxide that is reduced by hydrogen at a lower temperature even than CrO_3, physically mixed with crystalline Cr_2O_3.

When the chromium content is 0.75% (C), most of the CrO_3 seems to be associated with the silica as in the CrO_3-SiO_2 catalysts. This is also the case for the catalysts with still less chromium, 0.48% (D) and 0.18% (E).

Relation between reduction characteristics and catalytic activity. The "reduction profiles" of chromium oxide catalysts are helpful in interpreting variations in activity for ethylene polymerization. This is illustrated by reference to Fig. 9, which shows the variation in yield of ethylene polymers per gram of catalyst and per gram of chromium promoter as functions of the chromium concentration for chromium oxide–silica–alumina catalysts (*12*). It shows that in the range studied, 0.7 to 0.0005% chromium, the yield per gram of catalyst increases with chromium concentration whereas the efficiency per gram of chromium becomes greater as the chromium concentration decreases to less than 0.0001%. The former reflects the advantage of higher chromium contents to reduce the effects of catalyst poisons and to utilize the aggregate contribution of polymerization activity for sites of a wide range of activities. The higher efficiency of chromium utilization at the extremely low concentrations, suggests that the reaction mechanism involves polymer growth on single sites. Competition between sites may lower the specific effectiveness of chromium at higher concentrations where the effective concentration of ethylene available from surrounding "feeder" sites may thus be a factor. Nevertheless, the data show that the maximum specific activity of chromium is obtained at low concentrations, where the chromium is less easily reduced.

Reference to Fig. 8 indicates that at low chromium concentrations, the chromium appears to be associated with silica, which combination likewise represents the highest thermal stability (Fig. 7).

In low-pressure laboratory polymerization tests a microbalance was used to monitor changes in catalyst weight due to polymer formation at 100°C and an initial ethylene pressure of 0.6 mm of mercury. Pretreatment of the catalyst with hydrogen followed by vacuum heating at 380–400°C, greatly increased the activity above that of a catalyst that had merely been vacuum-heated at the indicated temperature. The optimum hydrogen reduction treatment was at 300°C. Figure 10 shows "reduction profiles" of a 3% air-activated chromium oxide–silica–alumina catalyst after 1- or 2-hr reductions at various temperatures. The "profile" for the 300° prereduction shows a maximum at about 350° similar to chromium oxide on silica gel (Fig. 6), chromium oxide–silica–alumina catalysts heat-treated in the range 600–900°C (Fig. 7), as well as catalysts containing from 0.18% to 0.75% chromium, heat-treated at 500°C (Fig. 8).

Reductions at temperatures higher than 300°C cause progressive reductions in polymerization activity, as indicated in Fig. 11. This is a plot of polymerization activity at 100°C and 0.6-mm ethylene pressure, as a function of chromium concentration for prereductions at three different temperatures. It is evident that the 300°C prereduction treatment produced higher activity than treatments at 250° or 350° for all except the lowest concentration of chromium. This is explainable on the basis that for the latter there is little or no chromium in a more easily reducible form which should be removed to eliminate the formation of products with ethylene that can poison or block active sites. The treatment at 350°C is too severe and results in destruction of some of the active chromium oxide–silica component that is not affected by the 300°C prereduction. These observations suggest that the critical active component in these catalysts is a stable combination of chromium oxide plus silica.

Pretreatment with carbon monoxide also enhances the activity of these catalysts for polymerization and results in even higher activity than is produced with hydrogen. The enhancement of activity by CO occurs in two ways. In the first place, CO, like hydrogen, reacts with the easily reducible forms of chromium oxide and thus eliminates their interaction with ethylene to form poisoning debris on the surface. Secondly, CO interacts with the potential polymerization sites and forms a complex (*13*) beginning at temperatures slightly above room temperature, resulting in increased activity. The optimum temperature for CO treatment is around 250°C where chemisorption of CO reaches a maximum value.

In this connection it should be mentioned that "reduction profiles" can be obtained by the use of carbon monoxide instead of hydrogen for catalysts promoted with reducible oxides. The "profiles" obtained with CO reduction resemble those obtained with hydrogen but locations and magnitudes of the maxima may be different for a given catalyst.

Kinetic considerations. The regular and reproducible forms of the "reduction profiles," suggest the possibility of computing values for activation energies. The data obtained are adequate to determine both the instantaneous values of hydrogen pressure and of the amounts of unreduced chromium oxide. However, the reducibility varies continuously throughout the course of a run (in fact the characteristic shape of a "reduction profile" depends upon this variation) and this eliminates computation of meaningful rate constants or energies of activation.

IV. CONCLUSIONS

The results presented illustrate the application of a simple and convenient procedure for studying the reducibility of several metal oxide promoters on various supports. The pressure-metric method, in which the water produced by reduction is taken up continuously by an efficient drying agent, has the advantage that reductions can be conducted over a wide range of temperatures without concern for any retention of water in the catalyst support. The method lends itself readily to the use of a reduction procedure with temperature increasing continuously for which the results may be represented by a "reduction profile." With a modern programming device and automatic pressure and temperature measuring equipment connected to a recorder, the operation could be made practically automatic.

The forms of the "reduction profiles" for various promoter–support combinations, provide useful information concerning the reduction characteristics of a catalyst, which appear to have an important, though complex, bearing on catalytic properties. The application of such information with respect to the nature of a catalyst and its catalytic activity, was illustrated for supported chromium oxide polymerization catalysts.

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