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The Oxidation and Leaching of Some Chromia-Alumina and Chromia-Silica-Alumina Preparations

ALCUIN F. GREMILLION AND WALTER R. KNOX

From the Hydrocarbons Division, Monsanto Chemical Company, St. Louis, Missouri

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The oxidation and leaching of some chromia-alumina and chromia-silica-alumina preparations have been studied. A correlation has been found between ionic potential of a number of ions used as promoters on a chromia-alumina, and the amount of equivalent CrO_3 leached from these preparations after oxidation at 500°. The correlation is good for ions having inert gas electron configurations. Those ions having pseudo-inert gas configurations fit the correlation as well. A study of extended oxidation and leaching shows that a limit of oxidizability of chromia on alumina can be reached. However, this limit is closely approached while much of the clump chromia is still present. This is shown by electron spin resonance spectra. The presence of dispersed phase chromia is also shown. The loss of oxidizability is related to activity in dehydrocyclization of *n*-hexane and is explained in terms of accumulated surface acidity. The effect of potassium promotion on oxidizability and dehydrocyclization activity has also been studied.

INTRODUCTION

The review paper of Hansch (*1*) shows that chromia or chromia on alumina has been the most widely used catalyst for dehydrogenation and dehydrocyclization. The literature since 1953 indicates the same trend. Chromia-alumina has been used as a catalyst for other reactions and has a long history, but it was not until the work of Eischens and Selwood (*2*) that an understanding of the nature and structure of the catalyst began to evolve. These workers used magnetic susceptibility measurements to show that the chromia on alumina exists as chromia clumps and as a more highly dispersed form as well. From their measurements, they showed that as the chromia content of the preparation increases, percentage of the chromia in the dispersed phase decreases. Recently, O'Reilly and MacIver (*3*) have given support to this interpretation with electron spin resonance studies of chromia-alumina. Cossee and VanReijen (*4*) have confirmed the results of O'Reilly and MacIver and have also studied various mild reductions of CrO_3 on a number of supports. Voltz and Weller have published a series of papers reporting on the surface oxidation of chromia and chromia-alumina as related to electrical conductivity (*5*), water adsorption and hydrogen-deuterium exchange (*6*), activity to hydrogen peroxide decomposition (*7*), adsorption of hydrogen and oxygen (*8–9*), carbon monoxide oxidation (*10*), potassium promotion (*11*), and acidities (*12*). They used an iodometric titration method to determine the extent of surface oxidation while Givaudon (*13*) and co-workers used a Soxhlet extraction followed by iodometric titration. This latter method has been used in this work.

Matsunaga (*14*) has studied the oxidation of chromia on α- and γ-alumina by magnetic susceptibility methods and iodometric titration. The methods agreed in showing that as the chromia content decreases the average oxidation number of the chromia, after exposure to air at various temperatures from room temperature to 450°, increases. These results were interpreted as indicating an increasing fraction of Cr^{3+} exposed on the surface as chromia content decreases and that in the limit of infinite dilution all chromia would be exposed for oxidation. As O'Reilly and MacIver (*3*) have pointed out, this is contrary to their observation that the dispersed phase chromia fraction increases as the chromia content decreases and that this phase is passive to oxidation at 500°.

The potassium promotion of chromia-alumina is well known as a means of improving dehydrocyclization activity (*15*) and its effect on the activity in other reactions has been studied (*11*). Chen, Haag, and Pines (*16*) have shifted the attention away from the chromia and have shown the effect of potassium in the alumina and the method of alumina preparation on dehydrocyclization and its mechanism.

Bridges *et al.* (*17*) have also studied chromia-alumina and have concluded that acid sites on bare alumina are responsible for formation of species which poison dehydrogenation sites on the chromia surface. Neutralization of acid sites and increased chromia clump size are given as results of potassium promotion.

The literature cited here in no way constitutes a complete listing of recent studies on chromia catalysts, but it is a good sampling of those more pertinent to the present study.

The work reported here was undertaken principally to obtain more knowledge of factors bearing on the oxidation of supported chromia and to isolate and study one of the known phases of a supported chromia. This latter goal has not been achieved, but interesting results have come from the attempt to isolate the dispersed chromia phase.

EXPERIMENTAL

Materials. The alumina used was a Bayer process alumina in ⅛ × ⅛ inch cylindrical form. X-ray diffraction showed it to be a γ-alumina. It contained 0.4% sodium, 0.05% iron, had a specific surface area of ca. 125 m^2/g and an average pore diameter of 160 Å. The silica-alumina was the Houdry S-36 cracking catalyst containing 86% SiO_2, 0.1% sodium and 0.07% iron. Its specific surface area was 190 m^2/g, and the average pore diameter was 118 Å.

Baker Analyzed Reagent grade chromium trioxide was the source of chromia.

Catalyst preparation. The supported chromias were made by calcining the support to be used at 550° for 15 hours and impregnating the support at room temperature with an aqueous solution of CrO_3. The solution volume was such as to completely wet the support pellets without leaving excess solution. The amount of CrO_3 was such as to give the desired level of Cr_2O_3. The preparation was then dried at 120° for several hours, calcined in air at 550° for 15 hours, reduced in hydrogen at 500° for 1 hour and cooled to room temperature in hydrogen.

In cases where other metal oxides were added to chromia-alumina, finished chromia-alumina samples were put through the above procedure using solutions of the desired metal nitrates in place of CrO_3.

Oxidations and leachings. Various samples were oxidized at room temperature or 500°. Except where stated, exposure to air or oxygen was for 1 hour duration. All leachings were with water in a Soxhlet apparatus for one or more 20 hour periods. After each 20 hours of leaching, the oxidized chromia removed from the sample was determined iodometrically and is expressed as milligrams of equivalent CrO_3. Except in dehydrocyclization runs and where stated, samples were 30 g. In cases where a sample was subjected to more than one 500° oxidation, each oxidation was followed by leaching and drying. The drying was at 100° for 5 to 8 hours in a container under house vacuum. In cases where more than one oxidation at room temperature was conducted, each oxidation was followed by leaching and drying. The drying was the same as above with an additional drying under 10^{-3} mm Hg pressure to 350° and then in hydrogen from 350° to 500° and down to room temperature.

Dehydrocyclizations. In syntheses from *n*-hexane, the feed composition was 97.4 wt % *n*-hexane and 2.6 wt % methylcyclopentane. Runs were of 2 hours duration with a liquid feed rate of 0.033 ml/min and an LHSV of 0.5 ml/hr/ml of catalyst. Catalyst bed volume was 4 ml, and it was in a reactor tube of 12 mm diameter. The reaction was performed at 540°. The catalyst was always brought up to temperature in hydrogen and remained in hydrogen for 1 hour before starting the feed. The effluent from the reactor was passed through a cold trap at 0°. The liquid product was weighed and then analyzed by gas chromatography.

Electron spin resonance spectra. The spin resonance spectra were taken with a Varian dual purpose V-4300-2 NMR spectrometer equipped with a Varian K-3510 EPR conversion unit. A Varian V4500-30 room temperature cavity was used.

Instrument conditions were the following: magnet gap, 2.75 inches; cavity frequency, 9.53 kmc/sec; modulation frequency, 400 c/sec; peak to peak modulation amplitude, 1.75 gauss; leakage, ca. 100 μamp; and bridge attenuation of 5 db. The spectra were obtained by a continuous scan of the magnet field strength range of ca. 0 to 6 kilogauss.

RESULTS AND DISCUSSION

Several batches of 10% chromia-alumina were prepared in this work. One batch was used entirely for experiments in which various promoters were put on the 10% chromia-alumina. The ratio of gram atoms of promoter element to moles of Cr_2O_3 was 0.09 in all cases. After final reduction of each of these preparations, a sample of each was oxidized with air at 500° for 1 hour. Each sample was cooled to room temperature and leached 15 hours. In Table 1 are listed the ions used to promote the chromia-alumina, the mg of equivalent CrO_3 leached in 15 hours per gram of catalyst (Q values) and the charge to radius ratio, or ionic potential, of each promoter ion. The charge to radius ratios were calculated from Moeller's (*18*) empirical ionic radii.

The oxidation states of a few promoters warrant some discussion. The 4+ oxidation state was taken for thorium because Th^{2+} and Th^{3+} are oxidized by water. In all oxidations and reductions of chromia-alumina, water is formed in large amounts. The lead promoted chromia-alumina sample became yellow upon exposure to air at 500°. Lead monoxide is yellow. Some of the iron in the iron promoted sample was probably present as Fe^{3+} which has a charge-to-radius ratio of about 4.5. The 2+ state of manganese is stabilized by a $3d^5$ configuration so that some Mn^{2+} is expected. The instability of a lone $4f$ electron makes the presence of some Ce^{4+} probable in the case of the cerium promoted sample. In these last three cases, multiple oxidation states are expected.

Figure 1 is a plot of the data of Table 1 for the ions having inert and pseudo-inert gas electronic configurations and for which multiple oxidation states are not expected. A similar plot using charge-to-radius ratios of Cartledge (*19*) gives essentially the same result although with fewer points. These points fit the curve in view of several experimental errors and in particular the probability that the distribution of promoter ions between bare alumina surface and chromia clump surface was not identical from case to case. We are assuming that the promoter distributions were largely the same in all cases.

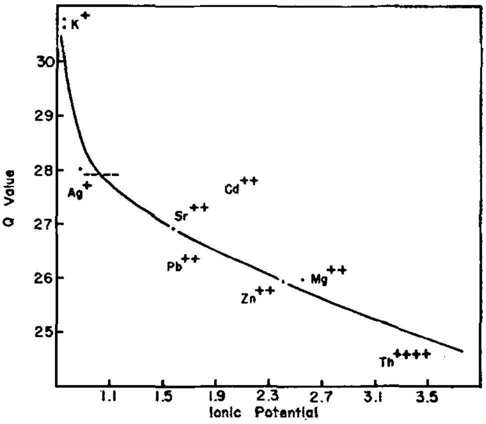

FIG. 1. Oxidizability at 500° as a function of ionic potential.

Increasing charge-to-radius ratio results in increasing power to polarize anions and increasing acidity. As the charge-to-radius

TABLE 1

PROMOTER IONS AND PROPERTIES AND EFFECT ON 500° OXIDIZABILITY OF A 10% CHROMIA-ALUMINA

Ion	Electronic config.	Charge/radius	Q Values (mg CrO_3/g cat.)
K^+	Inert gas	0.75	30.6 (30.7)
Mg^{2+}	Inert gas	2.56	26.0
Sr^{2+}	Inert gas	1.58	26.9
Ce^{3+}	Inert gas	2.54	26.4
Th^{4+}	Inert gas	3.64	24.4
Ag^+	Pseudo-inert gas	0.88	28.1
Zn^{2+}	Pseudo-inert gas	2.41	25.9
Cd^{2+}	Pseudo-inert gas	1.94	27.8
Pb^{2+}	Pseudo-inert gas	1.51	26.5
Mn^{2+}	Unfilled 3*d* shell	2.20	26.9
Cu^{2+}	Unfilled 3*d* shell	2.50[a]	25.8
Fe^{3+}	Unfilled 3*d* shell	4.5	24.8

[a] An ionic radius of 0.80 Å was used. This value was obtained from the spinel unit cell edge data of reference (*20*).

ratio of promoter ions increases, the environment of the chromia surface may become more acidic, and chromia becomes more difficult to oxidize. This is reminiscent of the situation in solution chemistry where Cr^{3+} is difficult to oxidize in an acid medium. The acidity referred to here is difficult to specify. It is used only to imply capability to neutralize base. Acidity is referred to later where the sense of the acid again cannot be specified. However, in this latter instance, Bransted acidity seems to be preferred if one were specific.

The dotted line of Fig. 1 indicates the level of oxidizability of the unpromoted chromia-alumina batch from which the samples of Fig. 1 were prepared.

A second batch of 10% chromia-alumina was used to study the oxidation of chromia-alumina at room temperature and 500°. A chromia-alumina that has had only hydrogen contact after reduction is partially oxidized when it contacts air at room temperature. If air contact at room temperature is not allowed before leaching, no oxidized chromia is leached in 20 hours. Air contact at room temperature of the second batch of 10% chromia-alumina results in 3.6 to 4.5 mg of equivalent CrO_3 per g of catalyst being leached in 20 hours. Numerous examples of this confirm the range 3.6 to 4.5 mg as long as air contact is in excess of a few minutes. Other experiments have shown that once an unoxidized sample, or one from which oxidized chromia has been leached, is thoroughly wet by water oxygen contact at room temperature does not result in further oxidation. Furthermore, oxidizability at room temperature is restored if the sample is heated to 500° in a reducing or inert gas. The room temperature oxidation has been observed by others (*3, 14*). The restoration of oxidizability by heating to 500° is to be expected from the results of Voltz and Weller (*6*).

Several room temperature oxidations of a 10% chromia-alumina were carried out. After each oxidation, the sample was leached for 80 hours. The equivalent CrO_3 leached in each 20 hour period was determined. After each 80 hour leach, the sample was dried by the method previously described. Restoration of room temperature oxidizability requires heating to 500°. Each exposure to air at room temperature was for 1 hour. The results of these experiments are given in Fig. 2. The point was eventually reached where oxidation at room temperature would not take place after the sample had been dried in a vacuum up to 350° and in hydrogen from 350 to 500°. The same experiments were performed in which helium was substituted for hydrogen during the 350 to 500° temperature treatment. The same results were obtained. In the two cases totals of 335.0 and 343.5 mg equivalent CrO_3, respectively, were removed from the two 30 g samples.

It is interesting to compare chromia on alumina with chromia on silica-alumina. At the concentration of 10% chromia, the chromia-alumina has a dull grey-green color while the chromia-silica-alumina has a bright, well developed, light green color. The alumina supported sample is oxidized at room temperature to the extent that leaching 20 hrs gives 3.6 to 4.5 mg equivalent CrO_3/g of sample. The silica-alumina supported sample gives only 10 mg equivalent CrO_3/30 g of sample or ca. one-third mg/g of sample.

A similar difference between these two is seen in their oxidizabilities at 500°. Several 500° oxidations of a 10% chromia-alumina were carried out in a manner similar to that described for the room temperature oxidation. Each oxidation was carried out with oxygen and was followed by leaching a number of 20 hour periods until one 20 hour period netted not more than 1–2 mg equivalent CrO_3. Drying followed each leaching. The drying is described above. The results of this type of experiment are shown in Fig. 3. Results from the same type of experiment on a 10% chromia-silica-alumina are given in Fig. 4. In the case of chromia-alumina, the oxidation of the chromia becomes more difficult with each succeeding oxidation. Eventually oxidation proceeds to an approximately constant but much reduced level. The chromia-alumina shows the same effect, but this material is oxidized to a smaller degree and reaches the lower level of oxidizability more rapidly than does chromia-alumina. In all of these cases of multiple oxidations, the chromia becomes more difficult to oxidize. It is suspected that this is due to the accumulation of acidic sites on the chromia clump surface as successive oxidations and leachings occur. However, there are other possible explanations. Among these is the possibility that a

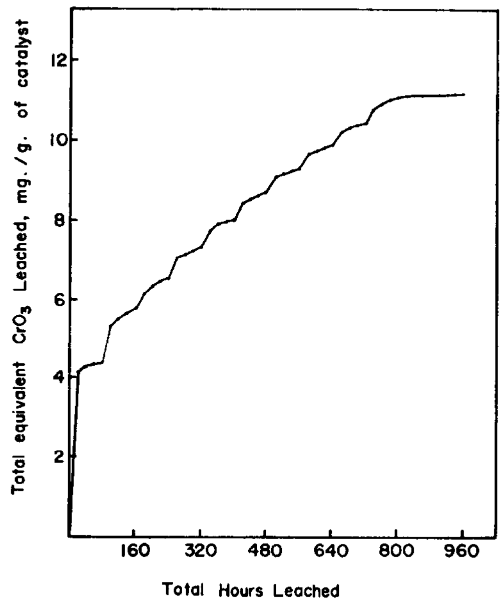

FIG. 2. CrO_3 leached from 10% Cr_2O_3–Al_2O_3 after room temperature oxidation following H_2 treatment at 500°.

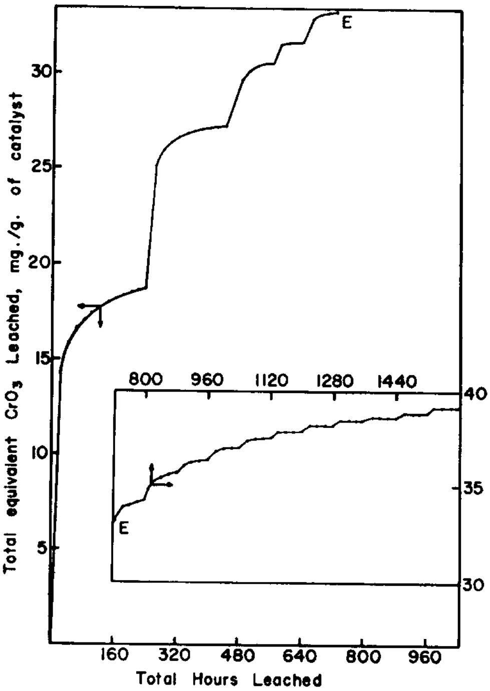

FIG. 3. CrO_3 leached from 10% Cr_2O_3–Al_2O_3 after O_2 oxidation at 500°.

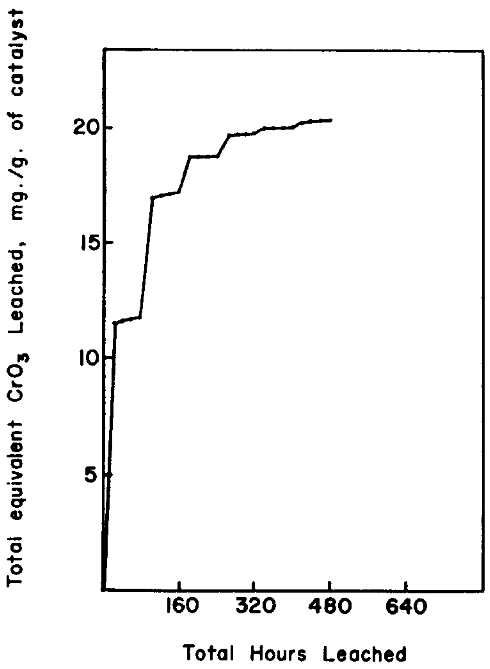

FIG. 4. CrO_3 leached from 10% Cr_2O_3-SiO_2-Al_2O_3 after oxidation at 500°.

geometrical influence on surface oxidation causes preferred oxidation along a crystallographic direction with the result that clump chromia would be revealed as having an easily oxidized portion and a less readily oxidized portion. Assuming the formation of acidic sites on the chromia surface, as oxidized chromia is removed, their type is difficult to specify. However, Bronsted sites seem more likely than other types. Experiments with a third batch of 10% chromia-alumina have given more evidence concerning the loss of chromia oxidizability. A 30 g sample of this gave 554.7 mg equivalent CrO_3 when leached 20 hr after 500° oxidation for one hour. Another 30 g sample was heated to 500° and then cooled to room temperature in hydrogen. This sample was leached 20 hr without air contact. No oxidized chromia was removed. The sample was then dried and oxidized at 500° for 1 hr. A 20 hr leach followed in which 550.9 mg equivalent, CrO_3 were obtained. Exposure to water alone is not responsible for the decrease in the oxidizability of the chromia. Leaching removes some of the sodium from the bare alumina surface. This is also not responsible for the decrease in chromia oxidizability.

The removal of sodium from alumina was assessed by determining the equivalent base obtained during each of several 20 hr leaches of an alumina sample. The results are shown in Fig. 5. In less than 40 hr, the leachable sodium was removed, and 88.5% was removed in 20 hr. After 80 hr of leaching, the sample was dried at 120° for 5 hr then transferred to a furnace at 550°. It remained there for 15 hr. It was then leached again. A small additional amount was removed in less than 20 hr of leaching.

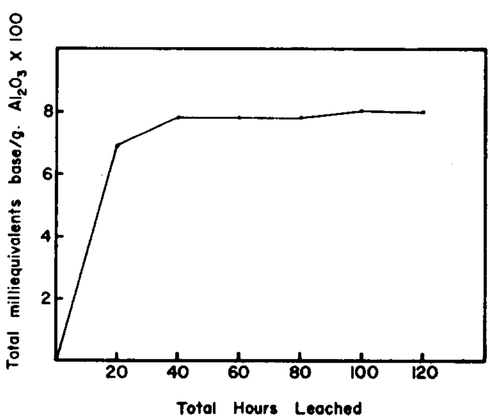

FIG. 5. Leaching of base from alumina.

Figures 6 and 7 show the benzene from n-hexane yields based upon hydrocarbon charged and consumed as a function of

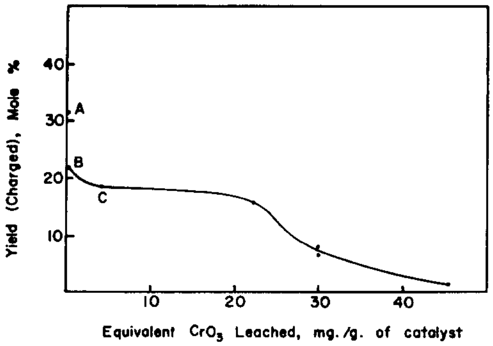

FIG. 6. Benzene from n-hexane on leached 10% Cr_2O_3-Al_2O_3. Based on hydrocarbon charged.

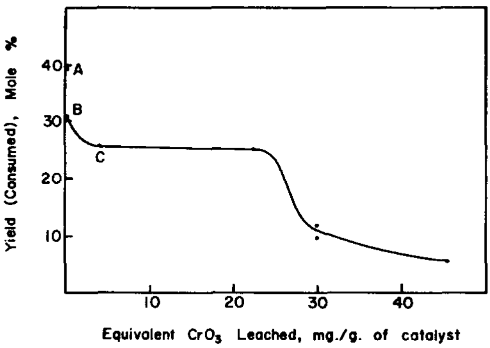

FIG. 7. Benzene from *n*-hexane on leached 10% Cr_2O_3–Al_2O_3. Based on hydrocarbon consumed.

equivalent CrO_3 removed from a 10% chromia-alumina. All catalysts from which oxidized chromia had been removed were leached 20 or more hours. Points A on these figures are for a chromia-alumina from which no oxidized chromia had been removed and which did not come into contact with water. Points B are for the same catalyst after being leached with water for 20 hr but without removal of chromia. Points C are from a catalyst from which the equivalent CrO_3 was removed in a single 20 hr leach.

The break near the middle of Fig. 6 and 7 is pronounced and comes between ca. 700 and 900 mg equivalent CrO_3 leached. There is also a tailing off to about 1000 mg CrO_3. This break and the tailing off correspond to the knee of the Fig. 3 curve, i.e., that portion of Fig. 3 where the oxidizability is diminishing most rapidly. It is suspected that the region of low oxidizability of Fig. 3 and the tails of Figs. 6 and 7 correspond to chromia-aluminas having chromia clump surfaces nearly loaded to capacity with acid sites. Potassium promotion of such a sample to a level of ca. 1% K_2O restored the benzene charged yield to 33 mole %. It also restored the oxidizability at 500° to a high level such that a 20 hr leach after 1 hr of oxidation gave 20.3 mg equivalent CrO_3 per g of sample.

The large drop in activity following leaching with no removal of chromia may be connected with the removal of base from the surface of bare alumina. There is probably an additional influence. It has been found that whereas water contact without removal of chromia (i.e., in an inert or reducing atmosphere) does not affect oxidizability at 500°, under the same conditions it decreases room temperature oxidizability to ca. one-tenth its normal value of 3.6 to 4.5 mg CrO_3/g of catalyst. The decrease in activity represented by the drop in yields from the levels of Points A to Points C is not due to the lower level of chromia achieved by leaching ca. 4.5 mg CrO_3/g of catalyst. This is indicated by yields from a benzene synthesis on a 1% chromia-alumina that was not oxidized or leached. The yields based on hydrocarbon charged and consumed were 18.5 and 28.7 mole %, respectively.

Table 2 indicates the fraction of *n*-hexane recovered in the liquid product from each benzene synthesis. The last column indicates the fraction of *n*-hexane feed accounted for by conversion to benzene plus that which remained unreacted. The data indicate that up to ca. 23 mg CrO_3/g of catalyst the decreased dehydrocyclization activity does not result from increased side-reaction but is compensated for by increased *n*-hexane recovery. Beyond this point, further decrease in dehydrocyclization is accompanied by an increase in side-reaction. However, at some point (below ca. 45.2 mg CrO_3/g of catalyst) an increase in dehydrocyclization activity relative to side-reactions occurs but with both at their lowest levels.

Figure 3 accounts for the removal of ca.

TABLE 2

n-HEXANE RECOVERY

Mg CrO_3/g catalyst leached	% *n*-Hexane recovered	% *n*-Hexane recovered + % *n*-hexane to benzene
0[a]	20.5	51.7
0[b]	29.7	51.8
4.5	34.5	52.3
22.4	36.7	52.5
29.8	28.9 and 30.3	36.8 and 37.0
45.2	65.5	67.3

[a] No water contact.

[b] Contacted water 20 hr.

one-third the chromia originally placed on the alumina. The remainder is not dispersed phase chromia but is largely clump chromia. We have shown this by spin resonance spectra of several samples.

Oxidizability at 500° is greatly increased after potassium promotion is carried out. The oxidizability at 500° of the second batch of chromia-alumina was increased by a factor greater than two. However, the effect on room temperature oxidizability is complicated and is indicated in Table 3. Here an unpromoted chromia-alumina is contrasted with one that has been potassium promoted. In agreement with Voltz and Weller (*11*), it appears that potassium promotion has a small tendency to stabilize the oxidized chromia. However, under the conditions used here it greatly delays oxidation at room temperature of about two-thirds of the chromia oxidizable at that temperature. Equally interesting is the fact that the level of oxidation of the unpromoted chromia-alumina is eventually attained and not exceeded. That the potassium promotion retards room temperature oxidation seems to indicate that partial blocking of chromia clumps is being accomplished.

TABLE 3
EFFECT OF POTASSIUM PROMOTION ON ROOM TEMPERATURE OXIDATION

Catalyst	Mg. equivalent CrO_3 leached in 20 hr, per g of reduced catalyst			
	No air contact	After air contact 1 hr to 5 days	After air contact for 95 days	After air contact for 162 days
10% Cr_2O_3–Al_2O_3	0	3.6–4.5	3.6–4.5	3.6–4.5
10% Cr_2O_3–Al_2O_3 (K_2O)	ca. 0.1	1.3	4.1, 4.3	3.9

This effect is not restricted to potassium promotion nor is it a universal result of promotion. Table 4 confirms this. These data were taken on the samples from which the Table 1 data were obtained. The majority of the promoters have decreased the room temperature oxidation to about the same extent, but Ce, Mg, and Zn have changed it very little.

TABLE 4
ROOM TEMPERATURE OXIDIZABILITIES OF PROMOTED 10% CHROMIA-ALUMINAS

Promoter element	Mg equiv. CrO_3 per g of catalyst leached in 15 hr after room temp. oxidation
K	1.4, 1.5
Ag	1.8
Cd	2.0
Mn	1.6
Sr	1.3
Pb	1.4
Ce	3.2
Mg	2.9
Zn	3.1
Cu	1.4
Fe	1.4
Th	1.4
None	3.6 to 4.5

It has been possible to prepare a chromia-alumina which does not respond to potassium promotion. The preparation of previous 10% chromia-aluminas included impregnation of the support, drying, calcination in air at 550° and reduction at 500°. Promotion of such a preparation with potassium has the well-known effect of increasing oxidizability at elevated temperatures and increasing dehydrocyclization activity. When the preparation procedure is altered by replacing calcination in air at 550° with calcination in vacuum from room temperature to 550°, the ability of the catalyst to respond to potassium promotion is lost.

A sample of 10% chromia-alumina was prepared in which vacuum calcination was used. The pressure was kept below 10^{-3} mm Hg, and the temperature was raised slowly. From 5 to 8 hr have been required in heating to 550° in order to maintain the pressure below the 10^{-3} mm limit. Observation of the apparatus clearly indicated in several such experiments that some chromia was being volatilized although the amount finally removed from the catalyst was small. Volatilization started at ca. 220°. In all other respects the preparation was the same as in other cases. However, this catalyst was the same green color as other preparations while in hydrogen but turned grey upon contacting air. It was black after potassium promotion and calcination in air but turned green upon reduction and grey again when contacted with air at room temperature. Dehydrocyclization on such a catalyst without potassium gave the same yields as 10% chromia-alumina prepared with calcination in air. Unlike the "normal" preparation, potassium promotion to a 1 wt % level did not result in improved dehydrocyclization yields nor were they decreased.

The EPR spectrum of a 10% chromia-alumina is given in Fig. 8. It was in reduced form except for exposure to air at room temperature. It was taken with an instrument signal attenuation greater than the other spectra by a factor of ten. When the spectrum was taken with the signal attenuation used with the other samples, the main resonance went off scale, but it was then possible to discern a faint shoulder on the positive phase of the signal where dispersed phase resonance is expected to appear. Although exposed to air at room temperature, no paramagnetic oxidized chromia resonance was seen in spectra of this sample. O'Reilly (*3*) reported such an absorption near the crossover point after exposure of samples to air at room temperature. These were for samples containing less than 0.8% Cr_2O_3. At a chromia level of 10%, the agglomerate phase resonance may mask the resonance of paramagnetic oxidized chromia formed at room temperature.

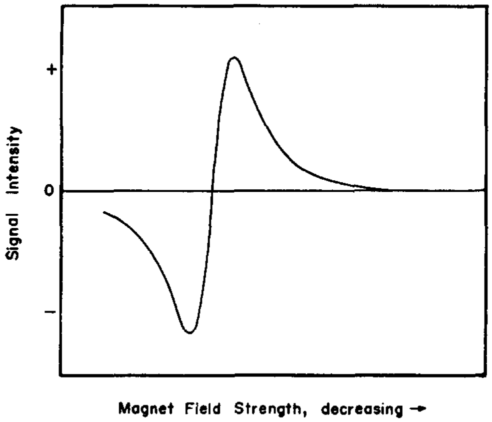

FIG. 8. EPR spectrum of 10% Cr_2O_3-Al_2O_3.

Figure 9 shows that oxidation at 500° produces some paramagnetic oxidized chromia, and Fig. 10 indicates that 20 hrs of leaching removes most, if not all of it. In that leaching, ca. 14 mg equivalent CrO_3 were removed per g of sample.

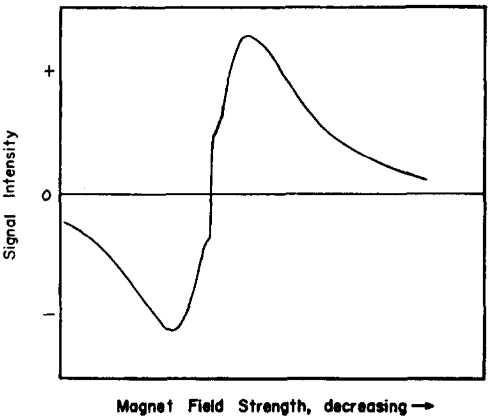

FIG. 9. EPR spectrum of 10% chromia-alumina after oxidation at 500°.

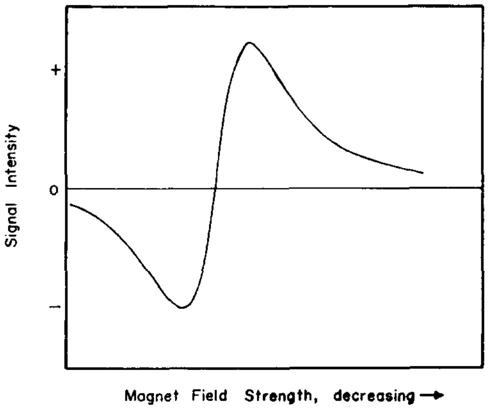

FIG. 10. EPR spectrum of 10% Cr_2O_3-Al_2O_3 oxidized at 500° and leached once for 20 hours.

Sample A of Fig. 11 was obtained by cyclic oxidation at 500°, leaching and drying 25 times. About 30% of the chromia was removed. The dispersed phase resonance is now quite clear. It can be seen that when cyclic oxidation, leaching, and drying reduces the oxidizability to a very low level, there remains appreciable agglomerate phase chromia. The absence of a paramagnetic oxidized chromia resonance is due to two factors. The last 6 of the 25 leaches were of 80 hr duration. This represents a very efficient leaching. In addition, the dryings following each leaching were at 100° under house vacuum and not at 500° as has been found necessary to restore room temperature oxidation after water contact.

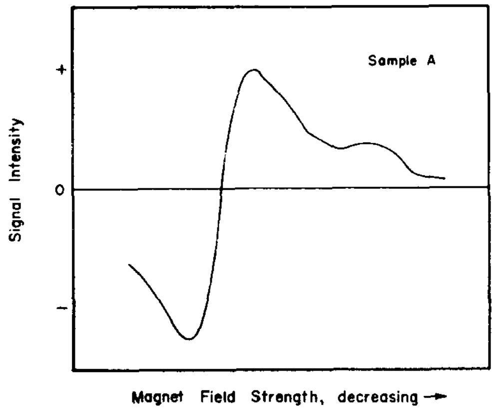

FIG. 11. EPR spectrum of 10% Cr_2O_3–Al_2O_3 oxidized at 500°, leached, and dried cyclicly 25 times.

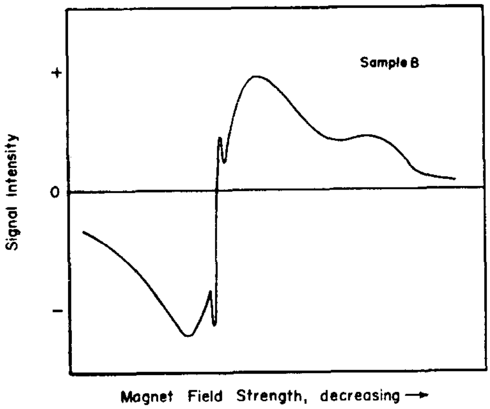

FIG. 12. EPR spectrum of sample A after potassium impregnation, reduction, oxidation at 500°, 20 hour leaching and drying.

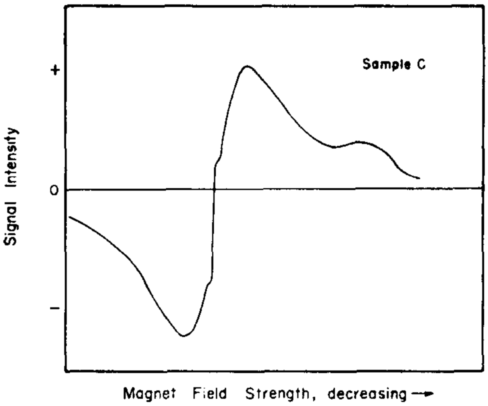

FIG. 13. EPR spectrum of sample B after reduction at 500°.

Sample B of Fig. 12 was prepared from Sample A by potassium promotion, oxidation at 500°, a 20 hr leach and drying. In the leach 20.3 mg equivalent CrO_3 per g of sample and more than 99% of the potassium was removed. Some of the paramagnetic oxidized chromia remained. By reducing Sample B at 500° for 1 hr, Sample C of Fig. 13 was obtained. The sample contacted air at room temperature which may have caused the oxidized chromia resonance seen in Fig. 13.

Sample D of Fig. 14 was prepared from

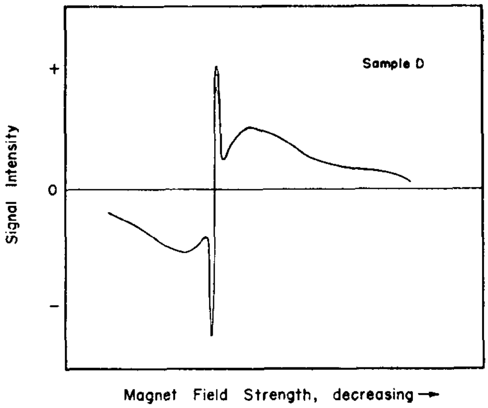

FIG. 14. EPR spectrum of 10% Cr_2O_3–Al_2O_3 oxidized at 500°, leached, and dried cyclicly 10 times.

a 10% chromia-alumina by cyclic oxidation, leaching and drying ten times. However, each leach was of 20 hr duration resulting in inefficient chromia removal. When this sample was reduced at 500° for 1 hour and then sealed in a quartz tube without air contact, the oxidized chromia absorption disappeared. When Sample D was potassium promoted and reduced at 500°, it gave the spectrum of Fig. 15 although after reduction it contacted air at room temperature.

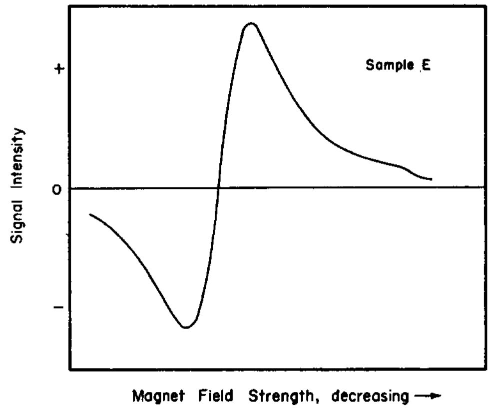

FIG. 15. EPR spectrum of sample D after potassium promotion and reduction.

The data reported here have not been thoroughly interpreted. For example, it remains to be shown why potassium promotion does not permanently decrease or increase the extent of oxidation at room temperature. Perhaps at some future date a complete interpretation of the influences on catalytic activity shown here can be given.

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