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Physical Properties of Coprecipitated Chromia-Alumina Catalysts

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Coprecipitated chromia-alumina catalysts containing from 0.3 to 44 mole % chromia, and calcined at temperatures ranging from 500 to 1400°C were investigated by means of electron spin resonance (ESR), X-ray diffraction, and gas adsorption. All samples except those calcined at 1400°C were found by X-ray diffraction to be inhomogeneous and to contain various mixtures of gamma-Al_2O_3, theta-Al_2O_3, alpha-Cr_2O_3, and both gamma- and alpha-phase chromia-alumina solid solutions. At low chromia concentrations the ESR spectra indicated two principal chromium resonances, a so-called δ-resonance attributed to electronically isolated Cr^{3+} ions and a resonance due to Cr^{5+} ions. At higher chromia concentrations an additional resonance was observed which was attributed to electronically coupled Cr^{3+} ions. This resonance, designated as the β-resonance, appeared to be associated with the presence of chromia-rich alpha-phase chromia-alumina solid solutions. The Cr^{5+} resonance seemed to be related to the chromia surface area as determined by gas adsorption, the intensity increasing, up to a point, with increasing chromia area.

INTRODUCTION

Chromia-alumina has been widely employed as a catalyst for such reactions as the dehydrocyclization of paraffins, and considerable interest exists in its physical and chemical properties. Previous publications (*1*) have discussed the electron spin resonance (ESR) spectra of impregnated chromia on alumina catalysts at X-band (9.5 kmc/sec) and K-band (23.9 kmc/sec). The samples so studied contained between 0.08 and 10 mole % chromia, and were examined in both their oxidized and reduced states. The three types of resonance observed were attributed to three "phases" of chromium. At low chromia concentrations, isolated Cr^{3+} ions (δ-phase Cr) were found to predominate, and at high chromia concentrations, clumped, strongly coupled Cr^{3+} ions (β-phase Cr) predominated. Low concentration, oxidized samples also produced a sharp electron spin resonance signal which was attributed to Cr^{5+} ions (γ-phase Cr).

In the present investigation, a series of coprecipitated chromia-alumina catalysts was examined by ESR, x-ray diffraction, and gas adsorption techniques. The magnetic resonance results were compared with the results from the impregnated catalysts and correlated with the x-ray diffraction and gas adsorption data.

EXPERIMENTAL

The chromia-alumina samples used in the present work were prepared by mixing aqueous $Al(NO_3)_3$ and $Cr(NO_3)_3$ solutions and then forming a gel by slowly pouring the mixture into aqueous NH_4OH in such a fashion that the pH was always greater than 8. The liquid phase was removed by filtration and the gel dried at 110°C. Three sets of samples were calcined for 24 hr at 500°, 750°, and 900°C respectively, and several samples were calcined at 1400°C. All samples were studied by ESR in this oxidized state. Several were reduced by heating at 500°C in contact with hydrogen and then examined again by ESR, without subsequent exposure to oxygen. The chromia concentrations ranged from 0.32 to 43.7 mole % Cr_2O_3. The color of the oxidized samples was found to vary with increasing Cr_2O_3 concentration in the following manner as a function of calcination temperature:

500°C—yellow to brown to green
750°C—yellow to green
900°C—yellow to green
1400°C—pink to green

The electron spin resonance spectrometer and associated equipment were the same as employed previously (*1*).

The structural studies were made on these catalysts by x-ray diffraction, using nickel-filtered CuK_α radiation, a Norelco diffractometer, and a xenon-filled, gas proportional counter detector. The high background due to the fluorescence excited in the chromium by the CuK_α radiation was eliminated by means of a pulse amplitude discriminator. The instrumentation and method have been described elsewhere (*2*).

The adsorption data were obtained using a standard volumetric gas adsorption system (*3*). The tube containing the adsorbent was provided with both an inlet and an outlet line so that the sample could be pretreated in a flowing gas stream. Elevated temperatures were obtained with a small ceramic furnace regulated by a Foxboro Potentiometer Controller and low temperatures were provided by either a liquid nitrogen or Dry Ice-acetone bath. The total BET surface areas were measured with argon at −195°C and specific chromia surface areas were obtained from oxygen adsorption (*4*) at −195°C.

RESULTS

Electron Spin Resonance

The δ-phase Cr resonance was observed with all oxidized samples containing from 0.87 to 9.2 mole % Cr_2O_3. For a given Cr_2O_3 concentration the strength of the δ-phase signal generally increased with calcining temperature. The calcination appeared to produce ordering of isolated Cr^{3+} ions in axially symmetric sites, and the spectrum indicated $|D| > 0.2$ cm^{-1}. The δ-phase did not appear in the lowest concentration (0.3 mole % Cr_2O_3) 500° and 750°C samples, while in the corresponding 900°C sample it appeared superposed on a ruby spectrum. This spectrum of ruby characterized the two low concentration samples which were examined after calcination at 1400°C, namely the 0.87 and 1.80 mole % Cr_2O_3 samples. The experimental spectral line produced by isolated Cr^{3+} ions (δ-phase) is illustrated in Figs. 1 and 2.

The low Cr_2O_3 concentration samples (0.3 to 5.3 mole % Cr_2O_3) in the oxidized state showed a sharp ESR singlet at $g = 1.968 \pm 0.004$, originating from γ-phase chromium as indicated in Figs. 1 and 2. The width between points of maximum slope was about 55 gauss for the 500° and the 750°C samples containing from 0.3 to 1.8 mole % Cr_2O_3. The width was increased by 10 to 20% for the 900°C samples and for the 750°C samples containing from 3 to 9.2 mole % Cr_2O_3. In all cases, the γ-phase ESR intensity was proportional to the square root of the microwave power from 10 to 110 mw, indicating the absence of saturation of the spin system. Following the previous publication (*1*), this phase is identified with Cr^{5+} ions. The number of spins in this γ-phase as a function of chromia concentration is shown in Fig. 3. From this graph it may be observed that for each calcination temperature there was a concentration where the number of spins in the γ-phase reached a maximum, and the concentration where this maximum occurred decreased with increasing calcination temperature. For a given chromia concentration, the number of spins in the γ-phase decreased with increasing calcination temperature, and it was not present at all in the samples calcined at 1400°C. None of the samples reduced in hydrogen produced a γ-phase, indicating that hydrogen reduces Cr^{5+}, perhaps to Cr^{3+}.

The high Cr_2O_3 concentration samples (5.3 to 43.7 mole % Cr_2O_3) produced spectra containing a broad line referred to as the β_w phase resonance, a narrower line referred to as the β_n phase resonance, or a superposition of both as exemplified in Fig. 4. The β_w resonance had a $g = 1.98 \pm 0.02$ and a peak to peak line width of

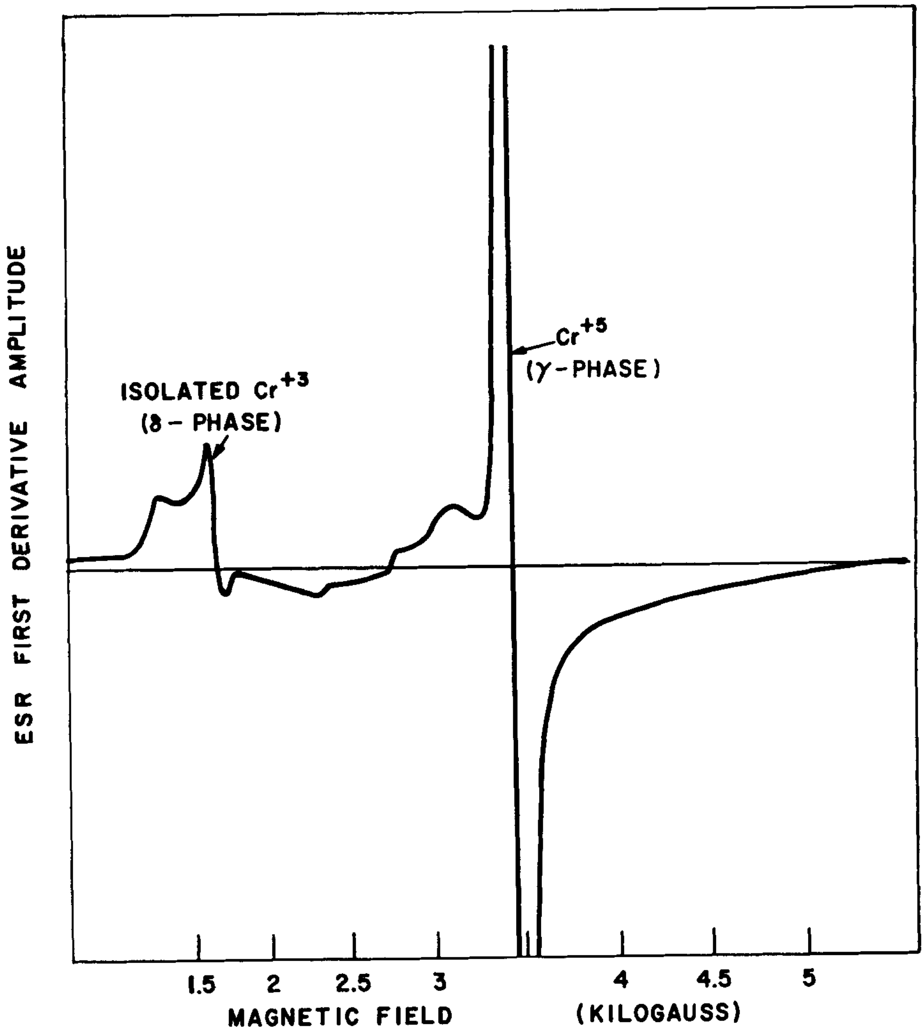

FIG. 1. Observed ESR spectrum for 0.87 mole % Cr_2O_3 sample calcined at 750°C.

~1300 gauss while the β_n resonance had a $g = 1.975 \pm 0.01$ and a width that varied between 200 and 750 gauss as shown on Fig. 5. These two lines were approximately Lorentzian in shape, and the process of decomposing a spectrum into β_w and β_n phases, illustrated in Fig. 4, renders the resulting line widths and spin concentrations less precise than those obtained from a single line.

Figure 6 shows that in a high Cr_2O_3 concentration range the β_w phase alone appeared at 5.3 mole % Cr_2O_3, the β_n phase alone at 43.7 mole % Cr_2O_3, and both phases at the two intermediate concentrations for the 500°, 750°, and 900°C samples. Only the β_n phase appeared in the samples calcined at 1400°C.

X-Ray Diffraction Results

The only structure observed for samples containing 19.6 mole % or less of Cr_2O_3 and calcined at 500°C was that of gamma-Al_2O_3[*] and the x-ray lines were quite broad, even for the pure alumina sample. As the chromia content increased from 0

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[*] In order to avoid confusion, the use of Greek letters will be confined to designating ESR spectra (i.e. γ-phase chromium, δ-phase chromium, etc.); crystalline phases (i.e. γ-Al_2O_3, α-Cr_2O_3 etc.) will be designated by the equivalent letter names (i.e. gamma-Al_2O_3, alpha-Cr_2O_3, etc.).

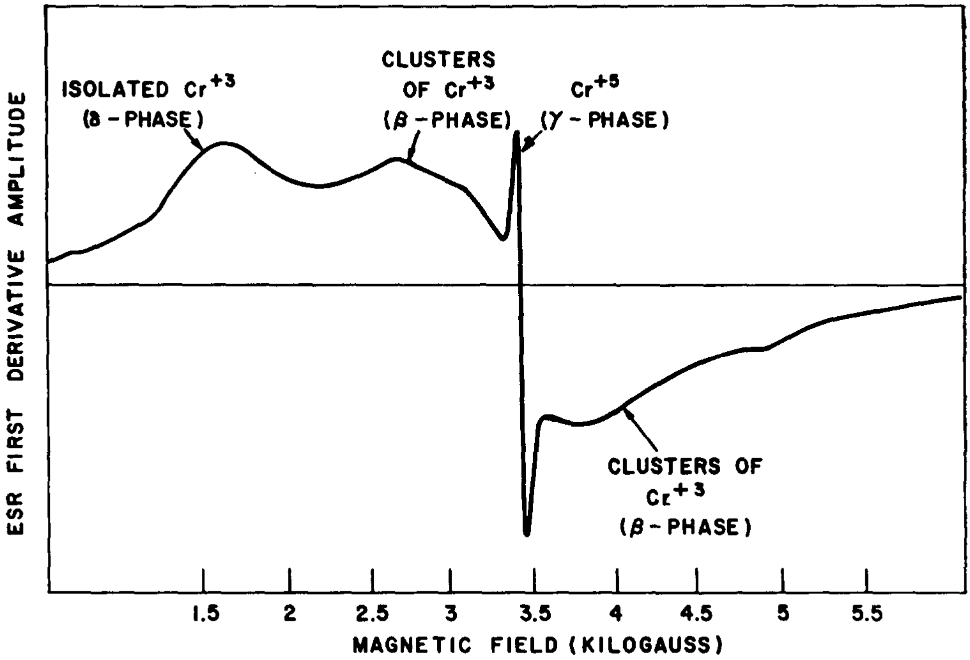


Fig. 2. Observed ESR spectrum for 5.3 mole % Cr_2O_3 sample calcined at 750°C.

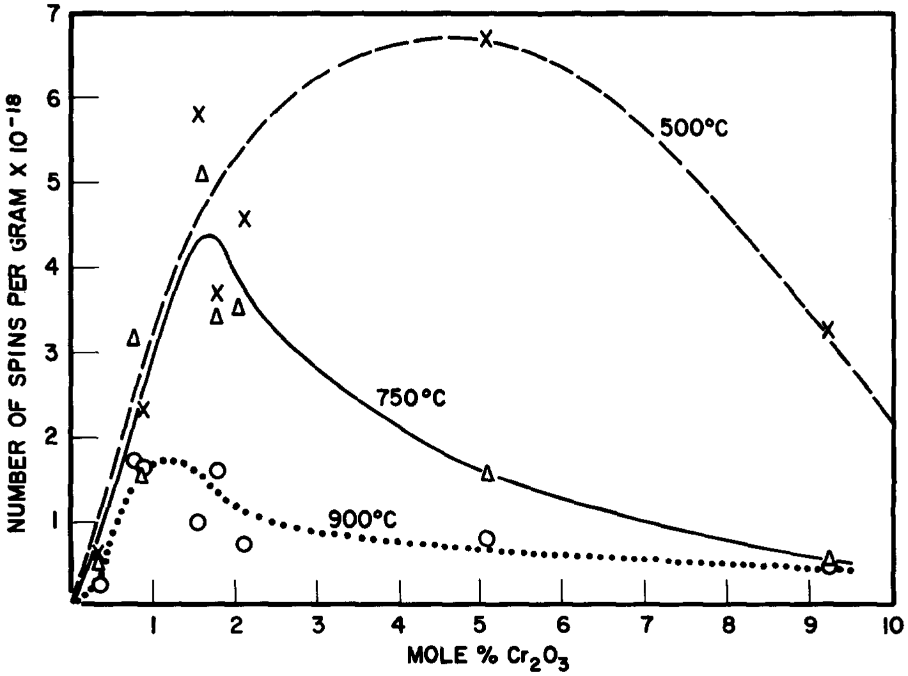


Fig. 3. Intensity of Cr^{5+} (γ-phase chromium) as a function of chromium concentration.

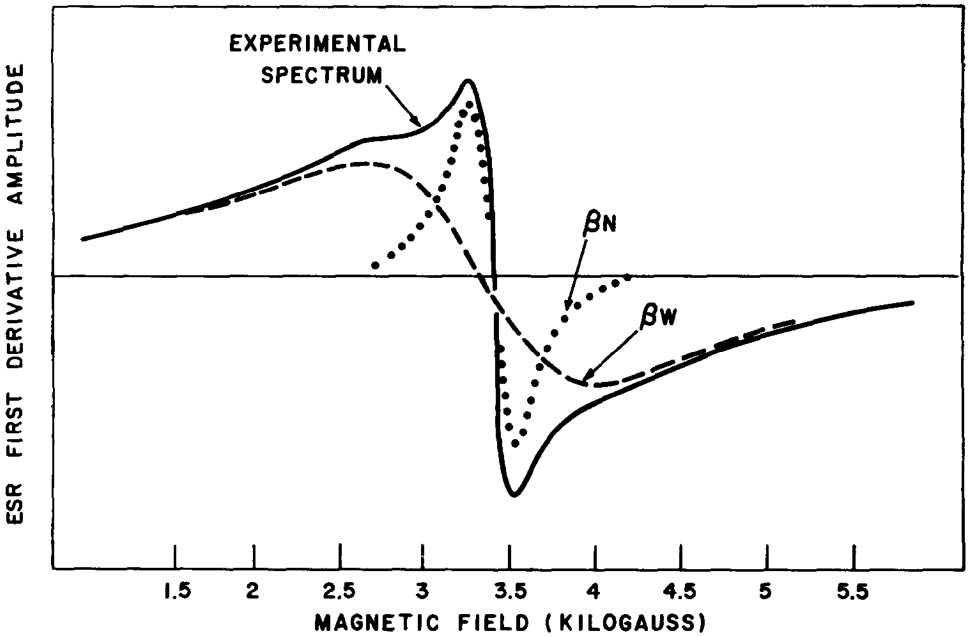


FIG. 4. Observed spectrum for 9.2 mole % Cr_2O_3 sample calcined at 900°C. The spectrum is shown decomposed into its two component lines.

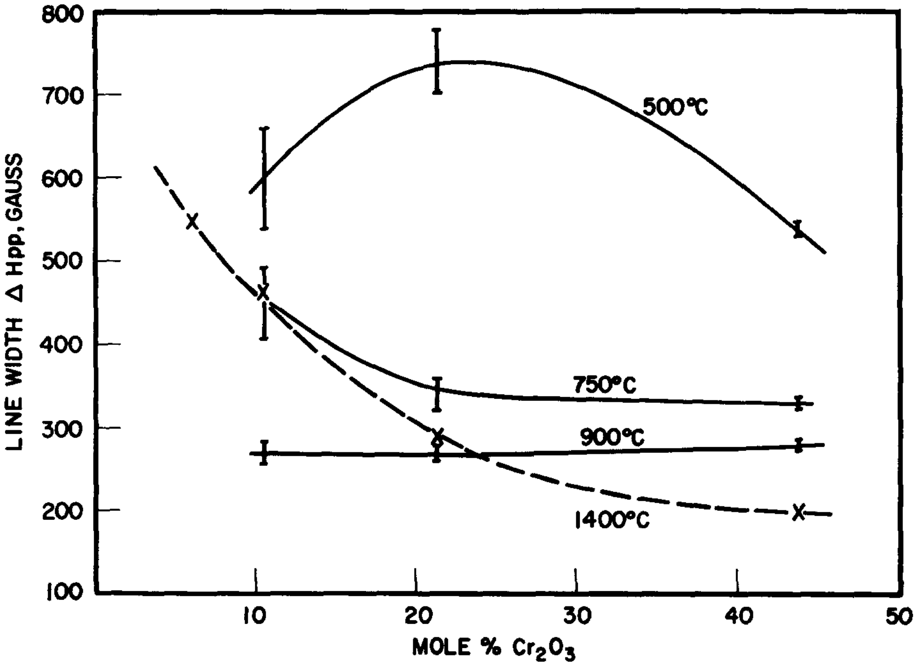


FIG. 5. The variation of the β_n-phase line width as a function of chromium concentration.

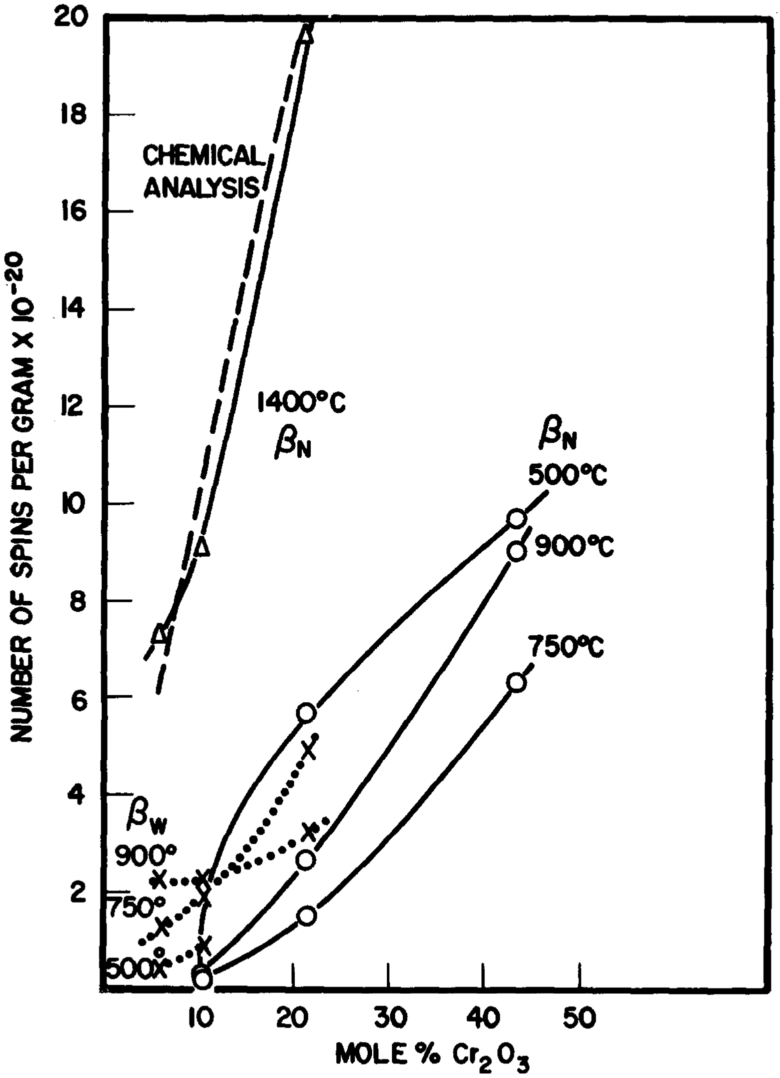


FIG. 6. The variation in the number of chromium ions in the high concentration phases β_n and β_w as a function of chromium concentration.

through 19.6 mole %, the gamma-Al_2O_3 pattern became gradually weaker, but there was no clear evidence of lattice expansion which would indicate solid solution of gamma-Cr_2O_3 in the gamma-Al_2O_3 lattice. An amorphous phase was apparently formed at 500°C between the Cr_2O_3 and the Al_2O_3 at these lower Cr_2O_3 concentrations. However, in the sample containing 43.7 mole % Cr_2O_3 an alpha-phase solid solution was observed with the approximate molar composition 70% Cr_2O_3–30% Al_2O_3. A small amount of alpha-Cr_2O_3 was also found. The remaining Al_2O_3 was apparently amorphous in this inhomogeneous sample.

Calcination at 750°C produced a better crystallized gamma-Al_2O_3 structure in the pure alumina and in samples containing small amounts of chromia. The lower chromia concentrations, up to and including 1.8 mole %, caused some line broadening and a reduction in the intensity of the gamma-Al_2O_3 pattern but again there was no measurable lattice expansion which would indicate solid solution of gamma-Cr_2O_3 in the gamma-Al_2O_3 lattice. Apparently the chromia-alumina phase was amorphous in these samples. A gamma-phase solid solution was first observed in the sample containing 5.3 mole % chromia, and the lattice expansion indicated a Cr_2O_3 concentration of approximately 4 mole %. A gamma-phase solid solution with a Cr_2O_3 concentration of approximately 7 mole % was also observed in the sample containing 9.2 mole % Cr_2O_3. The bulk of the sample containing 19.6 mole % Cr_2O_3 was amorphous to x-rays, but the three crystalline phases, alpha-Cr_2O_3, a gamma-phase solid solution containing approximately 60 mole % Cr_2O_3, and a small amount of alpha-phase Cr_2O_3–Al_2O_3 were observed. The sample containing 43.7 mole % Cr_2O_3 consisted of an alpha-phase solid solution with a molar concentration of 70% Cr_2O_3 as the principal crystalline component along with a small amount of alpha-Cr_2O_3. No phase was observed which would account for the remaining alumina.

Calcination at 900°C transformed the pure alumina to poorly crystallized theta-Al_2O_3. The sample containing 0.3 mole % Cr_2O_3 consisted of some alpha-Al_2O_3 in addition to the poorly crystallized theta-Al_2O_3. Only this theta-Al_2O_3 phase was observed in the samples containing 0.87 to 9.2 mole % Cr_2O_3, but the diffraction lines were further broadened with increasing Cr_2O_3 concentration. The pattern for the sample containing 19.6 mole % Cr_2O_3 was quite weak, but three phases were observed, namely an alpha-phase solid solution containing approximately 60 mole % Cr_2O_3, alpha-Cr_2O_3, and a small amount of theta-Al_2O_3. An unexpected result for the sample containing 43.7 mole % Cr_2O_3 was the observation of two alpha-phase solid solutions containing approximately 70 and 35 mole % Cr_2O_3, respectively, as determined from lattice parameter measurements.

All of the samples were also heated at 1400°C to produce homogeneous alpha-phase solid solutions, and the lattice parameters were measured from the x-ray diffraction patterns. A plot of lattice parameter vs. chromia concentration resulted in a curve convex upward rather than a straight line corresponding to Vegard's rule. This is in agreement with the results obtained by Graham (*5*) and differs from the results reported by Thilo, Jander, and Seemann (*6*), who found no change in the lattice parameter until a concentration of 8 mole % Cr_2O_3 in Al_2O_3 was reached.

Davis, Griffith, and Marsh (*7*) determined the structure of coprecipitated chromia-alumina catalysts which were calcined at 500°C in air. The results described above are in general agreement with their findings. Some differences were noted in phase compositions, and in the Cr_2O_3 concentrations at which gamma-phase solid solutions were observed. These can probably be attributed to differences in sample preparation methods and in the experimental techniques used to obtain the x-ray diffraction patterns.

Results of Surface Area Determinations

Both the total BET surface areas and the specific chromia surface areas were determined for several of the samples, and they are listed in Table 1. As indicated earlier, the chromia surface areas were determined by the method of Bridges, MacIver, and Tobin (*4*). This method involves a measurement of the amount of oxygen chemisorbed by a reduced chromia-alumina surface at −195°C; the amount of oxygen so chemisorbed provides an approximate indication of the portion of the total surface which consists of chromia. The fifth

TABLE 1
SURFACE AREA DATA

Chromia concentration (Mole %)	Calcination temperature (°C)	BET area (m^2/g)	Cr_2O_3 area (m^2/g)	Surface coverage (θ)[a]
0.3	500	212	2	0.009
0.9	500	235	8	0.034
1.8	500	241	18	0.075
5.3	500	257	34	0.132
9.2	500	254	35	0.138
19.6	500	213	32	0.150
43.7	500	158	28	0.190
1.8	750	173	12	0.069
5.3	750	158	25	0.158
1.8	900	111	6	0.054
5.3	900	102	12	0.117

[a] θ = fraction of total surface consisting of chromia.

column of Table 1 gives the fraction of the surface covered with Cr_2O_3 (i.e. Cr_2O_3 area divided by BET area). Up to 1.8 mole % Cr_2O_3 both the Cr_2O_3 area and the fractional surface coverage increase almost linearly with the mole % Cr_2O_3, while above 5.3 mole % Cr_2O_3 both quantities decrease slowly with increasing chromia content.

Discussion

At low chromia concentrations the specific chromia surface area measurements indicate that over half of the chromium ions are on the surface. The δ-phase detected by ESR is due to isolated Cr^{3+} ions in strong axial crystalline electric fields, and it is attributed to isolated Cr^{3+} ions both on and beneath the alumina surface. Thin surface layers of poorly crystallized material are not detectable by x-ray diffraction, and so the x-ray data on the low concentration samples showed only the presence of alumina.

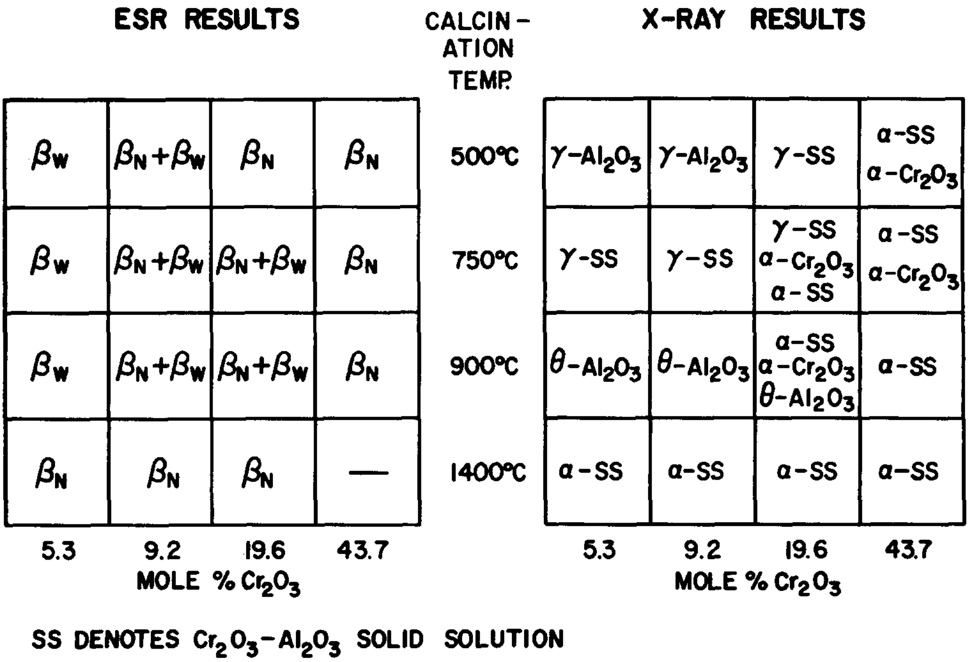
As mentioned earlier the γ-phase resonance is due to Cr^{5+} ions, and the disappearance of the γ-phase signal in reduced samples indicates that these Cr^{5+} ions are also on the surface. Since the isolated Cr^{3+} ions of the δ-phase are insensitive to reduction, the γ-phase resonance is believed to arise from Cr^{5+} ions in small chromia clusters on the alumina surface.

If the chromium ions are assumed to occupy surface sites randomly, then at extremely low concentrations most of them will be isolated, that is, without nearest neighbor chromium ions. As the chromium concentration increases, small clusters of chromium ions will form, and further increases in chromium concentration will cause these small clusters to grow in size. Thus the number of small clusters at first increases with increasing chromium concentration, and then at high concentration it decreases with the growing preponderance of very large chromia clusters. The number of spins in the γ-phase increases linearly with the specific chromia area up to 5.3 mole % Cr_2O_3 for the 500°C samples, and then it decreases for higher chromia concentrations. As mentioned above, the chromia area data indicate extensive "clumping" of chromia for samples with more than 5.32 mole % Cr_2O_3, in support of the contention that the γ-phase arises from Cr^{5+} in small Cr_2O_3 clusters.

At high chromia concentrations, the x-ray diffraction data indicate the presence of chromia, alumina, and solid solutions of chromia in alumina while the ESR spectra showed the presence of the broad resonance line (β_w phase) and a narrow resonance line (β_n phase). In Fig. 7 the ESR and x-ray diffraction data are compared for the high chromium content samples. The presence of the β_n phase appears to correlate with the solid solutions of chromia in alumina, while the β_w phase seems to correlate with the amorphous phase which is not directly detected by x-ray diffraction.

Both the formation of solid solutions and the formation of bulk chromia entail a reduction in the number of surface chromium atoms, and the constancy of the chromia surface area for high chromia concentrations indicates that one or both of these mechanisms is operative. The x-ray diffraction data indicate the presence of solid solutions and also some bulk chromia in the high chromium content samples.

A comparison of the results obtained from the study of the impregnated chromia-on-alumina catalysts (*1,4*) with the present results indicate that there are several similarities in the properties of catalysts prepared by the two methods when the catalysts are calcined at 500°C. For example, when the specific chromia areas of both sets of samples are plotted against the chromia content they follow a smooth curve. The same is true of the surface coverage (θ) up to 5 mole % Cr_2O_3, although above this value the impregnated coverages are 30% higher. The electron spin resonance results for these two series of catalysts are similar except that the high chromium concentration, coprecipitated samples showed two β-phase resonances instead of one. Because of the poorly crystallized nature of the samples of both sets calcined at 500°C, the structures of these materials are not known in sufficient detail to permit further comparison.



ESR RESULTS				CALCINATION TEMP.	X-RAY RESULTS			
β_W	$\beta_N+\beta_W$	β_N	β_N	500°C	γ-Al_2O_3	γ-Al_2O_3	γ-SS	α-SS α-Cr_2O_3
β_W	$\beta_N+\beta_W$	$\beta_N+\beta_W$	β_N	750°C	γ-SS	γ-SS	γ-SS α-Cr_2O_3 α-SS	α-SS α-Cr_2O_3
β_W	$\beta_N+\beta_W$	$\beta_N+\beta_W$	β_N	900°C	θ-Al_2O_3	θ-Al_2O_3	α-SS α-Cr_2O_3 θ-Al_2O_3	α-SS
β_N	β_N	β_N	—	1400°C	α-SS	α-SS	α-SS	α-SS
5.3	9.2	19.6	43.7		5.3	9.2	19.6	43.7

MOLE % Cr_2O_3 MOLE % Cr_2O_3

SS DENOTES Cr_2O_3-Al_2O_3 SOLID SOLUTION

FIG. 7. Comparison of X-ray diffraction and ESR data. The symbols γ-SS and α-SS denote gamma- and alpha-phase solid solutions.

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