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Supported Chromium Oxide Catalysts for Propene Polymerization

III. Magnetic Properties and Dispersion State of the Chromium Oxide

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Measurements of the magnetic susceptibility of chromium oxide on silica-alumina polymerization catalysts, carried out in the range 4–300°K, show the character of superantiferromagnetism of the chromium oxide domains. These measurements allow us to determine more precisely the dispersion state of the oxide upon its support and give some indications about the distribution of the size of the single domains of the oxide.

INTRODUCTION

In the first paper of this series (*1*) two linear relationships have been shown to be valid between the catalytic activity in propene polymerization and the area covered by the chromium oxide for two sets of activated catalysts obtained after impregnation of a silica-alumina with chromic acid; in the first set the chromium content, and in the second set the average oxidation degree of a fixed amount of chromium, were varied. A more general statement was established in the second paper (*2*): For a variety of catalysts differing either by their composition, the conditions of activation, or the nature of the supporting material, the polymerization activity is maximum when the average number of chromium oxide layers is about 2 or 3, but becomes nul if this number is 1 (maximum dispersion) or is greater than about 5. In the present study magnetic measurements have been performed in order to define more precisely the dispersion state of the chromium oxide on its support.

As early as 1947, Eischens and Selwood (*3*) suggested the use of the special magnetic properties of chromia on alumina to estimate this dispersion state. They have shown actually, that the atomic susceptibility of the supported oxide is much greater than that of the bulk oxide, chiefly when the chromium content is low; besides, the susceptibility follows a Curie-Weiss law between −190° and +100°C, so that the solid possesses a paramagnetic behavior. The Weiss constants so obtained depend on the chromium content, and this effect was attributed to the change of the number of neighboring chromium ions on the surface. The authors have concluded that the surface of the support is incompletely covered with chromium oxide clusters, which involve several layers of chromium atoms. The paramagnetic character of the chromium oxide, which is normally antiferromagnetic, was not fully explained.

In 1961, Néel (*4*) showed that highly dispersed antiferromagnetic materials must have special magnetic properties such as the "superantiferromagnetism" and also, at temperatures low enough, a weak ferrimagnetism. An antiferromagnetic material must have two sublattices of ions with antiparallel spins. If the material is crystalline, the two sublattices are regularly built and cancel mutually, except, possibly at the edges of the crystal. If the material is dispersed, the contribution of the edges is not negligible when the crystal size is small. The resulting moment μ of a single-domain particle, the value of which is fixed by the

difference in population of the two sublattices, does not possess a fixed orientation, at least if the energy change associated with its rotation is small relative to kT. Then its orientation in a magnetic field follows a Langevin law (*5*). There results a strong paramagnetism named superantiferromagnetism by Néel (*4*), by analogy with a similar phenomenon observed with dispersed ferromagnetic material which, more generally, is known as "collective paramagnetism." Then when the ratio $\mu H/kT$ is low enough, the material follows well a Curie-Weiss law.

It appears that the results described by Selwood (*3*) are well explained by the Néel theory. He has observed also that the value of the apparent atomic moment, as resulting from the measurement of the Curie constant, is lower than the calculated value for trivalent chromium with three unpaired electrons (*3, 6*). This anomaly is also explained by the Néel's theory. Néel has shown indeed that for ultrafine particles, the observed Curie constant C_A differs from the calculated one C_p. The ratio is

$$\frac{C_A}{C_p} = \frac{p^2}{N}\frac{j}{j+1}$$

where N is the number of antiferromagnetic atoms in the single-domain particle; p, the difference in population of the two sublattices; and j, the spin quantum number (*7*).

Néel considers essentially two cases. The first is concerned with the ultrafine particles where the position of the unpaired electrons is random; in this case one has $p^2 = N$. In the second case, the size of the particles is great enough to allow the existence of well-defined crystallites. Then the ratio $p^2 = N$ is greater or lower than 1 (*5*).

Finally, Néel has foreseen the phenomenon of thermal blocking of the orientation of the moments at very low temperatures, and also the possibility of a thermoremanent magnetization if the particles are fines rather than ultrafines.

The theory of Néel was fully confirmed by the experiments carried at low temperature with dispersed nickel oxide (*8, 10*). A few results concerning chromium oxide were also published chiefly by Srivastava (*7*), who studied several samples in the range 20–2000 Å.

At the present time, measurements of the magnetic susceptibility of the supported chromium oxide polymerization catalysts, activated in oxidizing atmosphere, have been carried out only at room temperature and related to the average oxidation degree of the chromium (*11, 12*). In these catalysts, indeed, the chromium is distributed in two main species, the hexavalent chromium, which shows a constant weak paramagnetism (*13*), negligible at low temperature; and the trivalent chromium, which is antiferromagnetic. The present study was undertaken in a broad range of temperature (4° to 300°K). For some typical catalysts, the character of superantiferromagnetism was clearly shown, and the data confirm and refine the results obtained in our preceding studies (*1, 2*) from selective chemisorption of oxygen measurements. Carrying out the measurement before and then after reduction in situ with hydrogen and taking into account the results of chemical titration, it was possible to calculate the atomic susceptibility of trivalent chromium, and that of chromium initially hexavalent.

Experimental Methods

The preparation and characterization of the catalysts concerned here were described previously (*1*). The catalysts are stored in sealed glass ampoules under a pressure of helium just sufficient to assure an adequate thermal contact. (Possibly this condition was not fully satisfied in the case of Catalysts 2 and 3, Table 1, before reduction, and then the corresponding results below 20°K may be doubtful.)

The magnetic measurements are carried out following the method of Faraday with a Ugine-Eyraud B 60 recording balance. The power supply of the electromagnet is controlled within 0.01%. The magnetic fields obtained are in the range 3000–6000 oersted. The cryostat used for the measurements is built of Pyrex and has a nonsilvered window in order to allow verification of the correct centering of the sample

and the absence of any solid friction. Because the Pyrex does not exclude any diffusion of the helium, the insulating jacket is evacuated before each experiment. Temperature is measured with a cobalt-doped gold-copper thermocouple located near the sample; the thermocouple was calibrated using a platinum resistance thermometer. A preliminary experiment was carried out using chrome alum as a sample, the susceptibility of which follows exactly the Curie law; it showed the existence of a difference of about 5°K on heating, between the temperature of the sample and that of the thermocouple; this experiment allows an adequate correction of temperatures.

The sample ampoule being in place, the laboratory tube is evacuated overnight up to a pressure of 2×10^{-5} torr, in order to exclude any further condensation. Then pure helium (99.999%) is introduced up to a pressure of 20 torr, in order to ensure a good thermal contact without making necessary any correction for buoyancy. The two Dewar vessels of the cryostat are filled with liquid nitrogen, and after purging the inner Dewar, liquid helium is transferred. The magnetic force increases rapidly and levels off after a few minutes and then, the temperature is 4°K; it remains constant during about 10 hr and, when all the liquid helium is vaporized, it increases slowly up to 77°K. The magnetic force, which decreases very much, is recorded at the same time as the temperature.

Because of the possible occurrence of thermal blocking, it is necessary to make measurements above 77°K in order to determine correct values of the Curie and Weiss constants of the sample. Then a simpler Dewar is used; it permits use of poles designed following Rimet (*14*) which cause a greater field gradient; the magnetic force is consequently greater and measured more easily. A vacuum jacket between the laboratory tube and the Dewar full of liquid nitrogen allows us to obtain slow temperature changes; then the thermal hysteresis is reduced. The calibration is made after each experiment, at room temperature, using Mohr's salt, and correcting for the diamagnetism of the cell and of the silica-alumina. Mohr's salt is a convenient standard; it was checked by measurement of the susceptibility of manganese pyrophosphate, $Mn_2P_2O_7$, and cobalt mercurithiocyanate, $CoHg(SCN)_4$, at 20°C. The values published in the literature (*15, 16*) have been reproduced within 1%.

Results

For comparison with the data of Srivastava (*7*), we have carried out measurements of the magnetic susceptibility of a chromia prepared by ammonium bichromate decomposition under air atmosphere. The particle size of this sample may be estimated using the electron micrograph in Fig. 1. The grains are irregular in shape and their size ranges between 100 and 1000 Å. Figure 2 shows the curve of its atomic susceptibility versus temperature. The Néel point of the chromia appears normally at about 330°K.

At elevated temperatures, the atomic susceptibility of the sample is greater than that of the bulk chromia, which is 980×10^{-6} at room temperature (*17*). The phenomenon of superantiferromagnetism is clearly shown by the increase of the susceptibility below 150°K. Finally the thermal blocking occurs at 20° and 30°K. A plot of the reciprocal of the difference between the susceptibility of the sample and that of the bulk product versus the temperature between 40° and 250°K gives a straight line which does not go through the origin; the Weiss constant which is obtained is —64°K and the molecular Curie constant is 0.4. The corresponding value of p^2/N is 0.09, much less than unity. However the superantiferromagnetism involves probably only a part of the sample, because, as shown by Fig. 1, only a small fraction of the grains has a size smaller than 100 Å. Then the true value of p^2/N is probably higher and should not be very different from the values of 0.36 and 0.31 observed by Srivastava for two samples with sizes of 20 and 50 Å, respectively; further, these two samples do not show thermal blocking above 4°K. Anyway, this value suggests a certain degree of order in the sample, although its particle size is

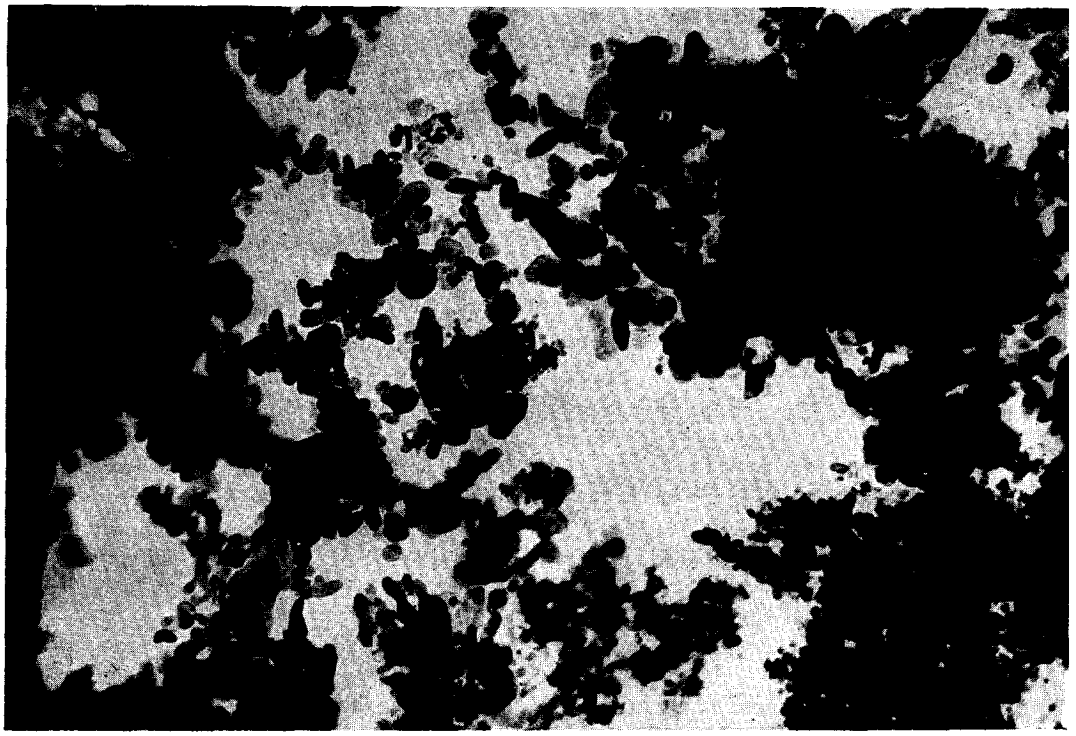

FIG. 1. Electron micrograph of a chromia sample. 100 000×.

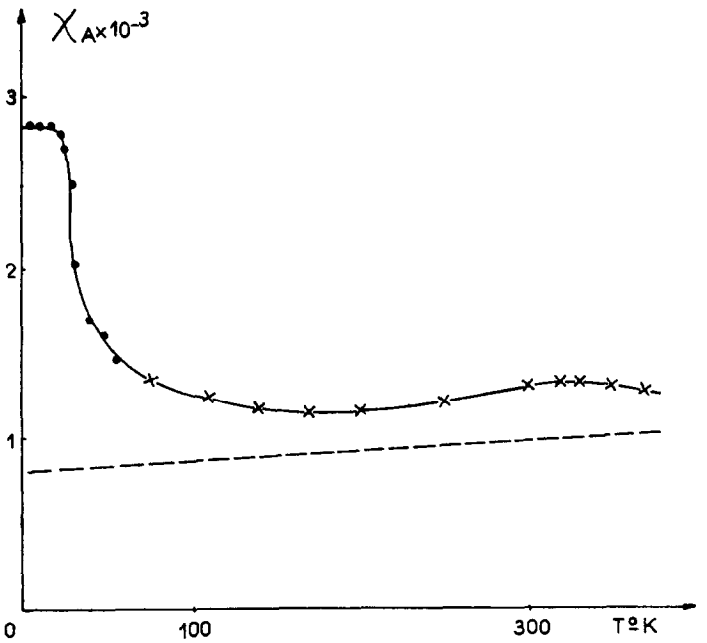

FIG. 2. Atomic susceptibility of a fine chromia sample versus temperature.

TABLE 1
CHARACTERISTICS OF THE FOUR CATALYSTS[a]

Catalyst	% Cr	% Cr$_I$	S_{Cr} (m^2/g)	S_{Cr}^{III} (m^2/g)	N_{III}	N_{VI}	$k \times 10^6$ (sec^{-1}g^{-1})
1	12.65	8.40	20.4	20.9	2.5	5.0	0.1
2	2.9	2.52	24.3	2.9	1.6	1.25	14.0
3	3.18	0.20	5.9	4.9	6.3	(I)	0.0
4	3.18	2.89	21.4	1.27	2.75	1.62	13.0

[a] S_{Cr}, area covered with hexavalent chromium oxide; S_{Cr}^{III}, area covered with trivalent chromium oxide; N_{III}, average number of trivalent chromium layers; N_{VI}, average number of hexavalent chromium layers; k, catalytic activity in propene polymerization.

rather small. The X-ray crystallographic data show that the Cr^{3+} ions of the chromia are located in a planar configuration at the apexes of regular hexagons. A main direction of coupling of the antiparallel spins of the ions of the two sublattices may be shown to occur by neutron diffraction (*18*) along one of the three directions of the hexagonal edges. As the values of p^2/N are less than 1, it is possible that the crystallites possess an elongated shape in this direction of spin coupling.

Four polymerization catalysts, obtained after impregnation of a silica-alumina with 13.5% alumina, were studied. The main properties together with the activity in propene polymerization are gathered in Table 1, which shows especially the results

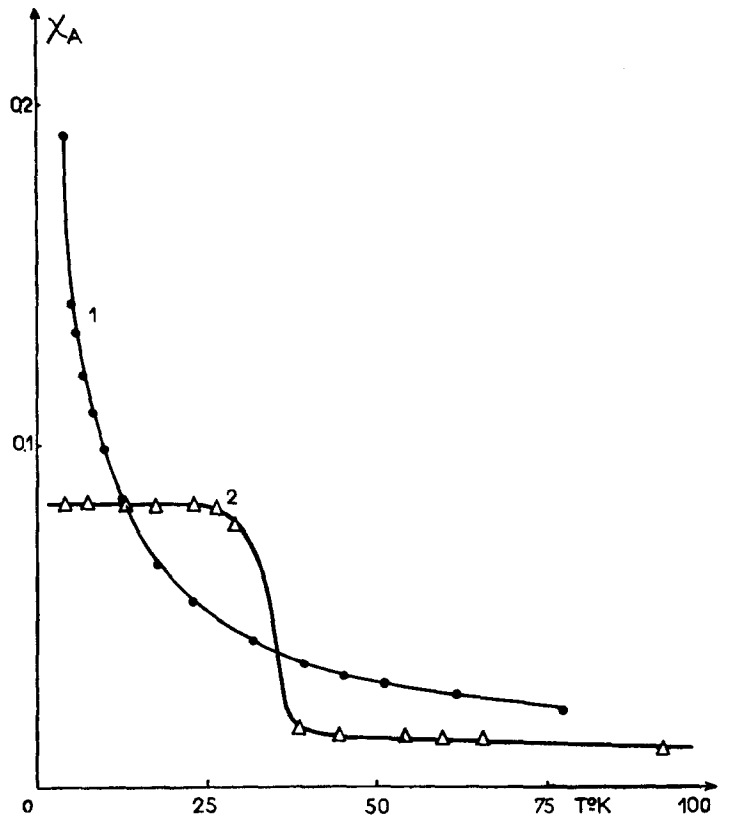

FIG. 3. Atomic susceptibility of Catalyst 1 extracted (curve 1) and reduced (curve 2) versus temperature.

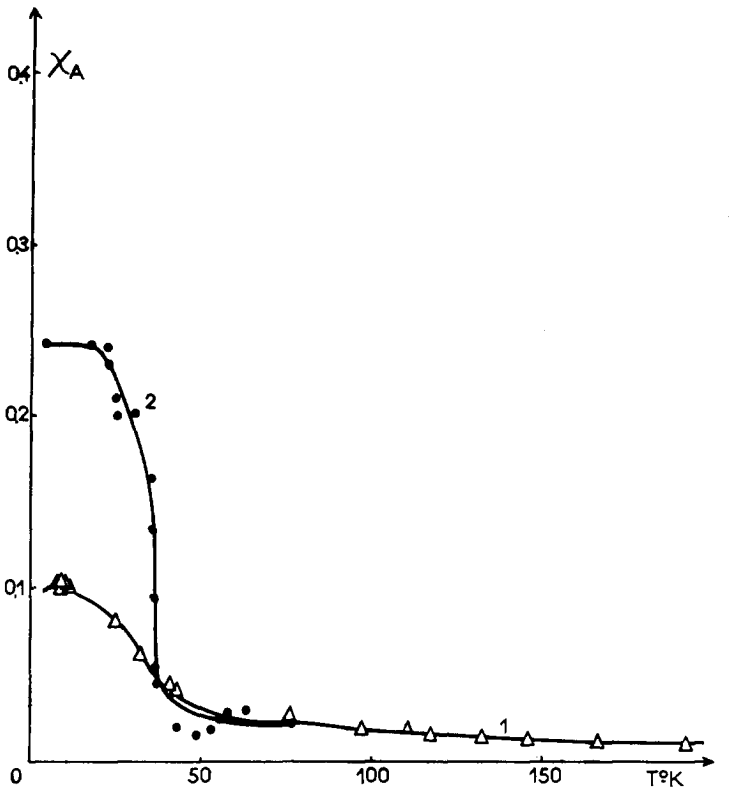

FIG. 4. Atomic susceptibility of Catalyst 2, before (curve 1) and after (curve 2) reduction, versus temperature.

of measurements by selective oxygen chemisorption of the area covered by chromium, before and after extraction of the hexavalent oxide by water. From the measurements are calculated the average number N_{III} and N_{VI} of the layers of trivalent and hexavalent chromium oxide. For the last number, it was assumed that the soluble oxide accounts for all the covered area, except in the case of Catalyst 2, which was activated and stored under nitrogen atmosphere.

The part played by the chromium oxides other than the trivalent one in the observed magnetic force is, a priori, small. Indeed the hexavalent oxide, present in rather high amount, does have a low paramagnetism independent of temperature (*13*); its contribution becomes more nearly negligible when the temperature is lower. A possible contribution could arise from the pentavalent oxide; its paramagnetism may be estimated from the intensity of its narrow ESR signal; our measurements show that the content of the catalysts in pentavalent chromium never exceeds 0.03%. Its contribution to the magnetic force cannot account for more than 4% of that of the trivalent oxide. Under these conditions, the extraction of the water-soluble oxide is not expected to change the magnetic force. As shown on Fig. 8 (curves 1 and 3) this assumption is verified between 4° and 77°K with Catalyst 4, which has the lowest content of trivalent chromium. The results may be safely expressed as the atomic susceptibility of one gram-atom of trivalent chromium oxide present in the sample. In this manner, the Curves 1 of Figs. 3, 4, 5, and 6 illustrate the atomic susceptibility of the four catalysts as a function of the temperature.

The Curves 2 of Figs. 3–6 present the results obtained with the catalysts which

have undergone a reduction treatment by hydrogen at 450°C during 15 hr under a pressure of 500 torr. This treatment induces the higher valence state oxides to be highly paramagnetic. All the curves of the four figures show clearly that all the catalysts studied possess the behavior anticipated by Néel for the antiferromagnetic material as highly dispersed to be superantiferromagnetic. Besides, for Catalysts 2, 4, and especially 1, the thermal blocking is apparent up to about 25°K, after the reduction treatment. Such a phenomenon is expected to be accompanied by a thermoremanent magnetization; actually the curve of magnetization versus magnetic field goes through the origin; probably, it should be measured at lower temperatures in order to observe the phenomenon clearly; also it would be better to use the extraction method (*18*), which would allow making measurements even without external field.

Discussion

Because the superantiferromagnetism is associated with fine or ultrafine single-domain particles, it should allow an estimation of the dispersion state of the antiferromagnetic material onto its diamagnetic support. It is interesting to compare such an estimation with that which was deduced from the measurements of oxygen-selective chemisorption; the last measurements give the area covered with chromium oxide and the number average of the number of oxide layers (Table 1). The area measurements of the surface covered by chromium in the water-extracted catalysts correspond to the measurements of the magnetic susceptibility of the catalysts, extracted or not, but not reduced, and are relative to the trivalent chromium oxide; on the other hand, the area measurements of the fresh catalysts may be compared with the susceptibil-

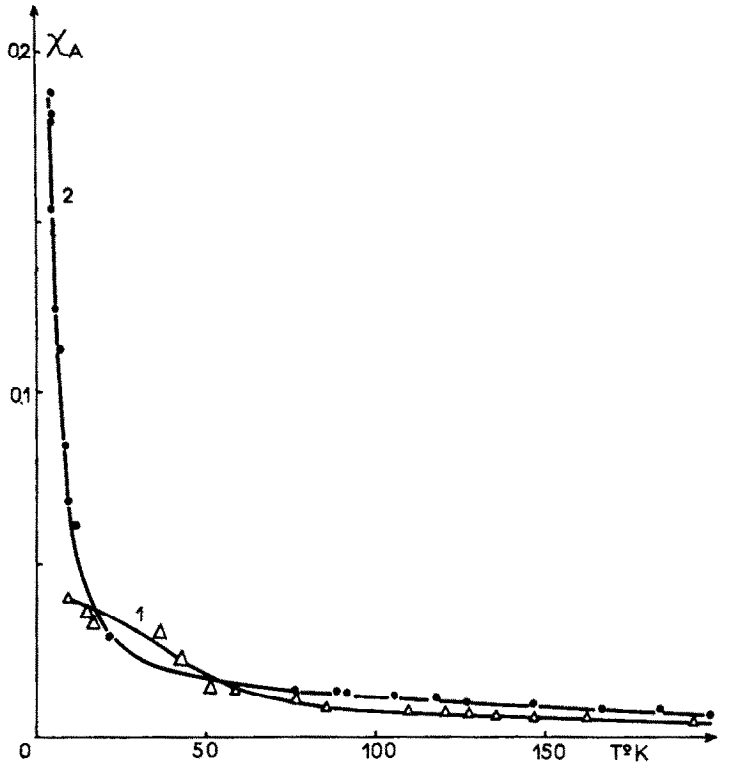

Fig. 5. Atomic susceptibility of Catalyst 3, before (curve 1) and after (curve 2) reduction, versus temperature.

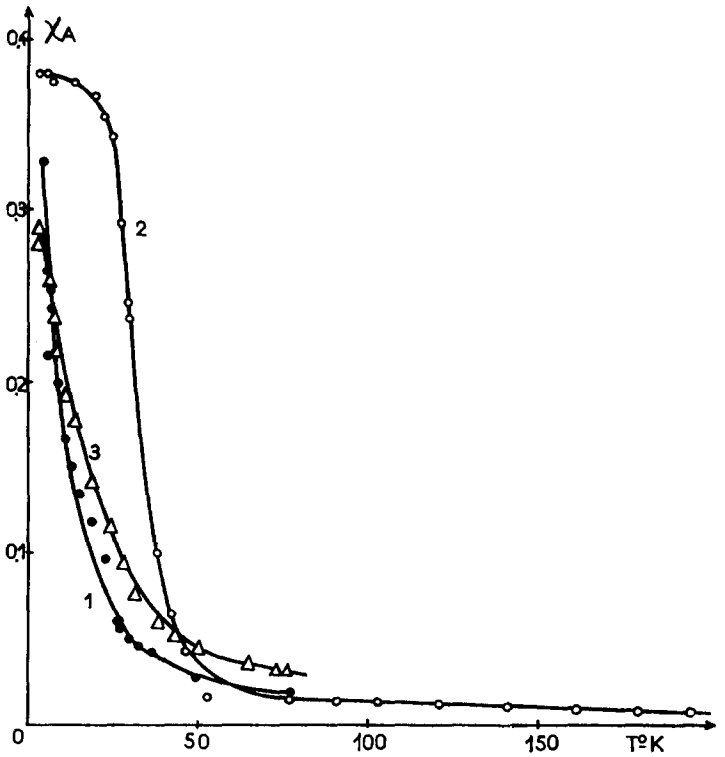

FIG. 6. Atomic susceptibility of Catalyst 4 versus temperature: curve 1, fresh catalyst; curve 2, reduced catalyst; curve 3, extracted catalyst.

ity data for the reduced catalysts, which accounts for the hexavalent chromium.

With Catalyst 1, extracted (Fig. 3), there is no thermal blocking anywhere in the low-temperature range; thus the major part of the magnetic force is caused by very fine single-domain particles. The high dispersion state thus confirms the rather high value of the area covered after extraction of the water-soluble chromium oxide. When the hexavalent chromium is reduced, the size of the domains is greatly increased; above 40°K, the atomic susceptibility is divided by two; below 40°K, the thermal blocking is obvious. Such a blocking is more pronounced when the fine superantiferromagnetic particles are larger (*8*). These results are consistent with the fact that the area covered with the chromium oxide is not reduced by the extraction of the hexavalent oxide. The last one is thus located upon the trivalent oxide and its reduction causes an increase in the size of the trivalent chromium domains.

With Catalyst 2, reduced (Fig. 4), which contains a lesser amount of chromium, the thermal blocking is observed at a higher level, and the concerned domains are, on the average, smaller; this result is consistent with the value obtained for the average number of chromium oxide layers. Catalyst 3 contains essentially trivalent chromium, the content of which is only slightly increased by the reduction treatment. However, the increase of the atomic susceptibility is rather large; it is due only to the reduction of the part of the hexavalent chromium oxide which is not deposited upon the trivalent oxide and which covers here only 1 m^2/g. The small amount of hexavalent chromium oxide deposited upon the trivalent cannot change significantly the size of its domains and consequently the magnetic force. With Catalyst 4 a moderate thermal blocking indicates the occurrence of rather big domains in the reduced catalyst. But the atomic susceptibility of this last is greater than that of the

fresh catalyst which, consequently, contains some highly dispersed hexavalent chromium. The major part of the hexavalent chromium is most probably agglomerated in clusters which are likely deposited upon the trivalent chromium, which is in small amount and highly dispersed.

In a broad range of temperatures above those where the thermal blocking is possible, the different solids follow a Curie-Weiss law; the corresponding Curie and Weiss constants, which are the only quantitative data which can be obtained, are reported in Table 2, together with the calculated values of p^2/N.

TABLE 2
MAGNETIC PROPERTIES OF FRESH AND REDUCED CATALYSTS[a]

Catalyst	% Cr^{III}	C_A (e.m.u.)	Δ (°K)	p^2/N
1 extracted	4.25	1.15	−27°	1.03
1 reduced	12.65	1.4	−45°	1.25
2	0.41	2.3	−20°	2.06
2 reduced	2.90	1.6	−20°	1.43
3	2.98	1.1	−50°	0.98
3 reduced	3.18	2.0	−60°	1.85
4	0.29	3.3	0	3.02
4 reduced	3.18	1.5	−18°	1.37

[a] C_A, Curie constant (atomic); Δ, Weiss constant.

Most Weiss constants are found negative, in agreement with the result $\Delta = -50°K$ reported by Eischens and Selwood (*3*) for a catalyst with 3.2% of chromium. We have previously suggested a possible correlation between the dimensions of the single domains and the value of the ratio p^2/N. Here, these values are rather dispersed but almost always greater than 1; as a rule, they are higher when the trivalent chromium content is lower. We suggest that the domains have shapes elongated in a direction perpendicular to that of spin coupling. This suggestion is in agreement with the model proposed by Topchieva *et al.* (*20*) for silica-alumina; this solid is not homogeneous but composed essentially of silica spheres and alumina spheres assembled together by co-oxide zones where the alumino-siloxane bonds are located along the intersection circles. Some results obtained in our preceding studies (*1, 2*) suggest an interaction of the chromic acid and the silica-alumina, located on selected sites, and followed during the activation treatment by the reduction of the concerned chromium atoms. Obviously these sites are the alumino-siloxane bonds and then the trivalent chromium domains are located at first along the intersection circles. The extra amount of chromium is deposited preferentially at the same place and is reduced more or less depending on the activation conditions. It appears from Table 1 that unreduced hexavalent chromium oxide is easily dispersed and because the two oxides Cr_2O_3 and Al_2O_3 can form solid solutions, upon reduction, these more nearly isolated chromium ions are expected to give chromium ions inserted at the surface of an alumina lattice and free from any coupling. A small number of such ions might account for a high paramagnetism without any possible blocking in the whole range of temperature used here.

CONCLUSIONS

It appears that the theory of superantiferromagnetism elaborated by Néel, if applied to a catalyst prepared by impregnating a diamagnetic support with an antiferromagnetic oxide, allows at least a qualitative estimation of the interaction modes between the catalyst and its support, and also of the dispersion state of the oxide. In this connection, the magnetic measurements are a good complement to the measurements of selective chemisorption. These last give only an average value of the number of the oxide layers, but do not allow determination of the distribution of these layers. The atomic susceptibility is also an average value, but the kind of average is different and the contribution of the finest particles is more important. The study of the magnetization as a function of the field strength and of the temperature is now a classical way to quantitatively determine the size distribution of the single domains in the simpler case of ferromagnetic catalysts such as Raney nickel (*21*). One uses the remanent magnetization. This suggests the use of the thermal blocking in

the case of antiferromagnetic materials. Most probably, more sophisticated experiments might allow one to obtain such results, and such work is in progress in our laboratory.

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