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ESR Studies on ZnO-Cr_2O_3 Catalysts

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The effects of the conditions of preparation of ZnO-Cr_2O_3 catalysts on their ESR spectra have been investigated by means of a Q-band spectrometer. The linewidths of oxides prepared by a low-temperature decomposition of the respective hydroxides in nitrogen flow are large and exhibit concentration dependence. As contrasted, the samples of oxides prepared by hydroxide decomposition in hydrogen flow, as well as the samples prepared by impregnation of ZnO, give relatively narrow absorption lines even at low temperatures of activation. The linewidths of samples prepared by decomposition in nitrogen flow decrease under the influence of the reaction products of the catalytic decomposition of methanol. An explanation of the found linewidth dependence is suggested, based on considerations of the distance functions of the competitive interaction forces. From the results it can be concluded that a stabilization of chromium in the spinel form takes place.

INTRODUCTION

In recent years, the method of ESR has proved to be successful in investigations of mixed catalysts, especially of oxide systems (*1*, *2*). Among the mixed oxides containing chromium, the system Cr_2O_3-Al_2O_3 has been frequently studied, in polycrystalline samples (*3*, *4*) as well as in monocrystals (*5*) with various chromium contents. Again, catalysts prepared by impregnation of γ-Al_2O_3 in aqueous CrO_3 solution were studied (*6*). The purpose of the investigations was to clarify the bonding and valence of the surface atoms and the nature of the active centers in the oxide catalysts. The ESR method gave, in the case of the system Cr_2O_3-Al_2O_3, important results, which have complemented conductivity and susceptibility measurements as well as X-ray structure analysis.

The study of the ESR spectra yields, besides the Lande splitting factor, also a basis for conclusions on the electronic structure of the paramagnetic ions. The study of the linewidth gives valuable information about the magnetic dipole–dipole interaction and the quantum mechanical exchange coupling. As these, partially competitive factors do not exhibit the same concentration dependence, a study of the concentration dependence of the ESR linewidth of oxide catalysts helps to elucidate the kind and strength of the operating interaction forces. Furthermore, changes of absorption lines, which can be observed after catalytic reactions, allow some conclusions regarding paramagnetic centers participating in the reaction process.

It suggests itself to extend these investigations to mixed oxides of bivalent and trivalent transition metals. Thus, ESR signals of the NiO-Cr_2O_3 system have been studied in connection with catalytic experiments (*7*). Thereby, the question of the existence of the so-called intermediate states ("active oxides") arose, already discussed by Hüttig and co-workers (*8*). In this respect, the conditions in the system ZnO-Cr_2O_3, essential for hydrogenation of CO to methanol, are of special interest. Pure zinc oxide itself is a good catalyst for methanol synthesis. However, the zinc oxide loses its catalytic activity in the methanol synthesis at about 350°C in a short time, due to a decrease of the active surface. The activity is strongly dependent on the preparation conditions as well as on the initial material used. The recrystallization processes are suppressed by addition of chromium oxide, so that the mixed oxide catalysts maintain their catalytic activity. The chromium concentration in the mixed catalysts, favorable for an optimal catalytic activity, strongly depends on the method of preparation and can be found in the range of concentration between 10 and 30 wt % of Cr_2O_3. The detailed mechanism of the chromium oxide action is not quite clear, however. The catalysts prepared at low temperatures by thermal decomposition of the mixed hydroxides or of the basic mixed carbonates are found to be amorphous with respect to X-rays, if the chromium contents are high. Only after calcination at a temperature exceeding 350°C, is a very broad diffraction line formed, belonging to the spinel $ZnOCr_2O_3$. There is no catalytic activity of the spinel in the pure state.

By measuring the magnetic susceptibility and especially by extended ESR investigations, the physical properties of the system $ZnO\text{-}Cr_2O_3$ have been studied with respect to their dependence on the conditions of preparation, on the pretreatment atmosphere, and on the influence of the reaction components of the methanol synthesis.

The ESR investigations have been made at a wavelength of 8 mm (frequency about 32 Gc/sec). Other investigations (*9*) have shown that especially in the case of chromium catalysts, characteristic differences between the spectra taken at a wavelength of 8 mm (Q band) and at the usual 3-cm wavelength (X band) occur. With the 8-mm wavelength asymmetrical line forms, indicating an anisotropy of the splitting factor, are found.

EXPERIMENTAL

a. Preparation of catalyst samples. The $ZnO\text{-}Cr_2O_3$ catalysts were prepared either by thermal decomposition of mixed hydroxides in nitrogen and hydrogen atmospheres, or by reduction of zinc oxide impregnated by chromium acid, H_2CrO_4. Mixed hydroxides were precipitated at room temperature from mixtures of $0.5\,M$ chromium (III) nitrate and zinc nitrate solutions by diluted NH_3 solution (pH = 7.6–9). After removal of the nitrates by frequent decanting with distilled water, mixed hydroxides were dried at 125°C and decomposed at various temperatures in the range 260–800°C by a 6-hr calcination at 125°, 800°, and 900°C in purified nitrogen and hydrogen flow.

Initial material for impregnated catalysts was pure zinc oxide (Merck Co., Darmstadt, Germany) of the specific surface about 5 m^2/g. The dried ZnO was moistened with chromium acid solution, the material dried for 6 hr at 125°C, and thereafter reduced by 6-hr heating in a hydrogen flow at 350° or 500°C.

In addition, the spinel $ZnOCr_2O_3$ for comparative tests was prepared. As initial material an equimolar mixture of the two oxides was used; it was calcinated and homogenized for 10 hr at 900°C.

In the catalysts prepared from the mixed hydroxides, the zinc contents were deter-

TABLE 1
CR-CONTENT AND METHOD OF PREPARATION OF DIFFERENT SAMPLES

Catalyst No.	$\frac{Cr}{Cr + Zn}$	Preparation of sample
1	0	Precipitation
2	0.026	Precipitation
3	0.063	Precipitation
4	0.118	Precipitation
5	0.160	Precipitation
6	0.211	Precipitation
7	0.269	Precipitation
8	0.401	Precipitation
9	0.488	Precipitation
10	0.601	Precipitation
11	1	Chromium oxide hydrate
12	0.025	Impregnation
13	0.061	Impregnation
14	0.115	Impregnation
15	0.207	Impregnation
16	0.395	Impregnation
17	0.67	Spinel $ZnO \cdot Cr_2O_3$

mined by complexometric and the chromium contents by iodometric analysis. The composition of the impregnated catalysts was calculated from the volume of the added chromium acid. The chemical composition of the different samples is shown in Table 1, referred to the molar relation Cr/(Cr + Zn).

b. Determination of surfaces. The specific surfaces of Catalysts 1, 5, 7, and 9, prepared by decomposition in nitrogen, were determined by the heat desorption method (*10*). TiO_2 (area of 7.2 m^2/g) was used as the reference substance. A mixture of hydrogen and nitrogen (10 vol % H_2, 90 vol % N_2) at the boiling point of liquid nitrogen was taken as adsorbate. Furthermore, the areas of six samples determined by the heat desorption method were checked with the standard BET method, the differences in resulting area values being lower than 4%.

c. Determination of the magnetic susceptibility. With Catalysts 7 and 9, prepared by thermal decomposition of the mixed hydroxides in nitrogen flow, the magnetic mass susceptibility χ_g was determined according to the field difference method of Knappwost (*11*) applying magnetic field strengths H_1 up to 14.000 Oe. Because of possible ferromagnetic contamination, corrections had to be made by graphical extrapolation of the measured χ_g values up to $1/(H_1 + H_2) \rightarrow 0$.

d. Differential thermal analysis. The Catalysts 1, 5, 7, and 9 were tested by means of DTA equipment of the usual type. The velocity of the rise in temperature was 20°/min.

e. ESR measurements. The ESR spectra were recorded at room temperature by Q-band equipment ($\nu = 32$ Gc/sec) described in detail earlier (*12*). The spectrometer used was equipped with a T bridge with frequency stabilization and magnetic field modulation. The differentiated absorption curve dI/dH was recorded in dependence on the magnetic field strength H. For measurement of magnetic field strength, a nuclear magnetic resonance magnetometer constructed by Gunsser and Hille (*13*) was used.

f. The influence of the products of methanol decomposition on mixed catalysts. The influence of the reaction products on the linewidth of the mixed oxides prepared by decomposition of the respective hydroxides in nitrogen flow at 400°C (Catalyst 7) has been observed in a Schwab reactor, in which the decomposition of methanol occurred at 350°C. In certain time intervals the catalytic reaction was interrupted and the linewidth of the ESR absorption checked. At the same time the quantity of gas formed per unit time during the catalytic reaction was determined. From these measurements it was possible to calculate changes in the catalytic activity.

To avoid contamination of methanol by liquid reaction products, the cooled vapors were not recycled into the Schwab reactor after the reaction.

RESULTS AND DISCUSSION

The Surface Area and DTA Measurements

The dependence of the specific surface area on the decomposition temperature is shown in Fig. 1. It can be noted that the specific surface areas rise with increasing chromium content in the sample.

Figure 2 shows the results of the DTA measurements. Pure zinc oxide produces two very weak waves at temperatures above 200°C. However, the samples of mixed hydroxides Nos. 5, 7, and 9 show endothermal waves of high intensity between 200° and 400°C. With increasing chromium content the peaks are shifted to lower temperatures.

The ESR and the Susceptibility Measurements

The ESR patterns of all tested samples contained only one absorption line, the width of which (measured from peak to peak) was dependent on the kind of chemical activation of the respective sample. The splitting factor of most of the samples covered the interval between 1.97 and 1.98 (the Cr^{3+} ions in the compound $CrCl_3$ have a splitting value of 1.98). Only in the case of very broad lines, where the accuracy of the

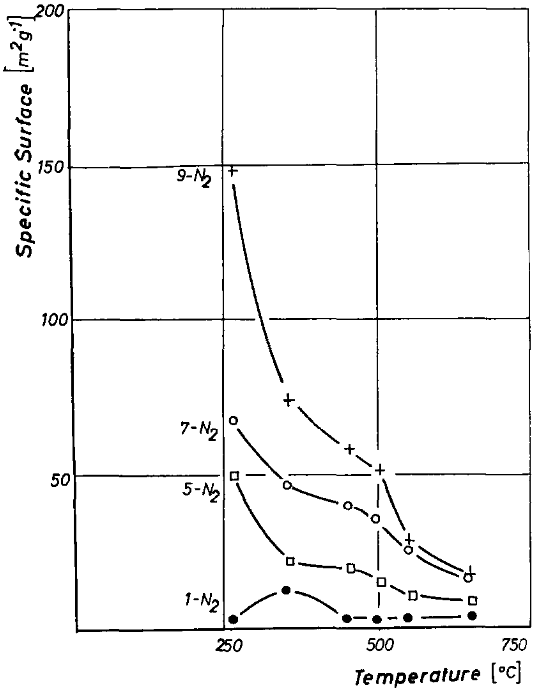

FIG. 1. Dependence of the specific surface on the activation temperature.

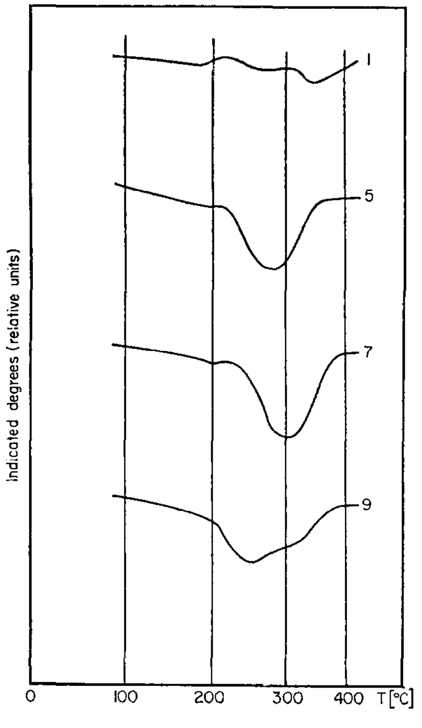

FIG. 2. Results of DTA measurements.

splitting factor determination is limited, were the values found between 1.95 and 1.99.

The linewidth of the ESR absorption was determined from the differentiated absorption curves. The form of the lines was not examined in detail. However, by comparison with other published work it can be assumed that the curves have a form between the Gaussian and the Lorentzian type, depending on the preparation procedure. By this reason, the measured linewidths ΔH_{diff} are in all cases smaller by the factor 1.18 to 1.73 than the linewidths $\Delta H_{1/2}$ discussed in theoretical works.

Figure 3 illustrates the linewidth dependence of the ESR lines on the activation temperature for Catalyst 11 (pure chromium oxide hydrate) prepared by decomposition of the hydroxide in pure nitrogen flow. The resonance absorption completely vanishes when the sample is calcined above 500°C. This temperature being attained, Cr_2O_3 appears to have been formed. It is antiferromagnetic with a Neél temperature of 45°C (*3*). Absorption occurs only above this Neél temperature. In Fig. 4a the linewidth of initial mixed hydroxides dehydrated at 125°C in air and then heated at 800°C in nitrogen flow is plotted as a function of the ratio $Cr/(Cr + Zn)$. Figure 4b demonstrates the same for the impregnated samples after reduction. The pure zinc oxide (Catalyst 1) heated either in hydrogen or in nitrogen, exhibited no resonance with the spectrometer used.

Figure 5 shows the dependence of the resonance linewidths of the activated mixed hydroxides prepared in nitrogen or hydrogen, respectively (Nos. 5, 7, and 9) on the activation temperature.

When comparing Figs. 4 and 5, the following can be noted: The linewidths of the initial mixed hydroxides are independent of the concentration at low chromium contents. However, for powders heated at high temperatures, the linewidths are completely independent of the chromium contents in the whole concentration range. Samples heated in nitrogen flow exhibit a linewidth broadening with increased activation temperatures which is independent on the chromium contents above 500°C. With a further tempera-

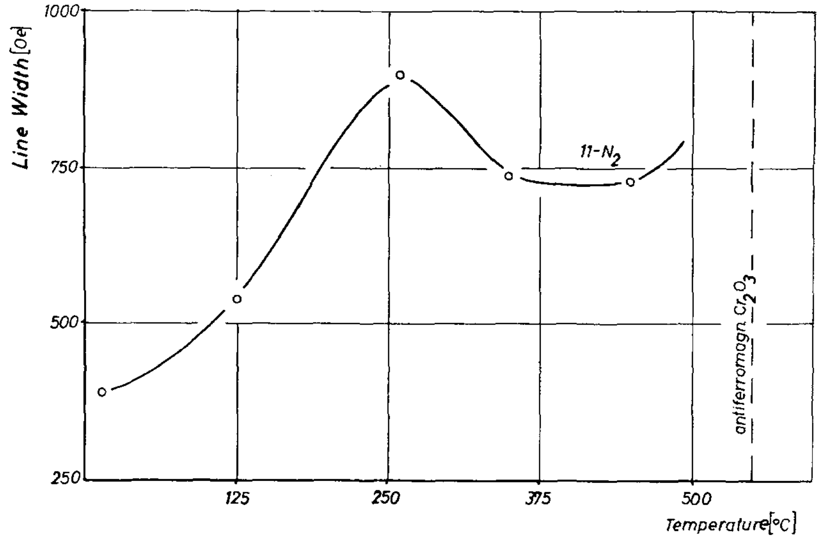

FIG. 3. Dependence of ESR linewidth on the activation temperature for chromium oxide hydrate.

ture increase, the linewidths drop and finally reach a limit corresponding to the width of the spinel ZnOCr$_2$O$_3$. Samples prepared in hydrogen flow show no initial broadening of the line, and the resonance curves are already comparatively narrow at low activation temperatures.

It is furthermore obvious that the linewidths of the samples prepared in nitrogen are lowered by subsequent exposure to a hydrogen atmosphere. Again, decrease of the half-value of the linewidth of the mixed oxides prepared in nitrogen was encountered in a catalytic decomposition of methanol which gives rise to CO and H$_2$. Along with the said decrease of the linewidth, a decrease of the activity of the mixed catalysts takes place.

Figure 6 shows the dependence of the magnetic susceptibilities of the mixed oxides on the decomposition temperature of the initial composition of the hydroxides. The values of susceptibility drop steeply up to about 260°C. With a further increase of the decomposition temperature the susceptibility increases again and approaches a limit.

In order to find an interpretation for the obtained results, the measured linewidth dependences were compared with the linewidth dependences theoretically expected as well as with the results obtained by different methods. To this end, the possible exchange and coupling mechanisms of the chromium ions in the mixed oxides, their effects on the linewidths, and the dependence of the said different mechanisms from various parameters had to be considered.

The orbital singlet ground state of the Cr^{3+}($^4A_{2g}$) in the exterior magnetic field splits into four Zeeman terms which are equidistant in a crystal field of cubic symmetry (spinel) and, therefore, only one ESR line results.

With crystal fields of lower symmetry (e.g., Cr$_2$O$_3$), several fine-structure lines should appear. However, at chromium contents of about 8 mole %, the fine structure vanishes due to the line-broadening by spin–spin interactions. The narrow absorption line frequently encountered with other catalytically active chromium compounds, the coordination of which has remained a matter of discussion for a long time, was not observed.

For the linewidth in paramagnetic compounds in which an exchange interaction occurs, there holds by the theory of Anderson and Weiss (*14*) the relation

$$\Delta H_{1/2} = 3.3(H_p^2/H_e) \qquad (\omega_e \gg \omega_0) \tag{1}$$

where

$$H_p^2 = 5.1(g\mu_B n)^2 S(S+1) \tag{2}$$

$$H_e = 2.83(J/g\mu_B)[S(S+1)]^{1/2} \tag{3}$$

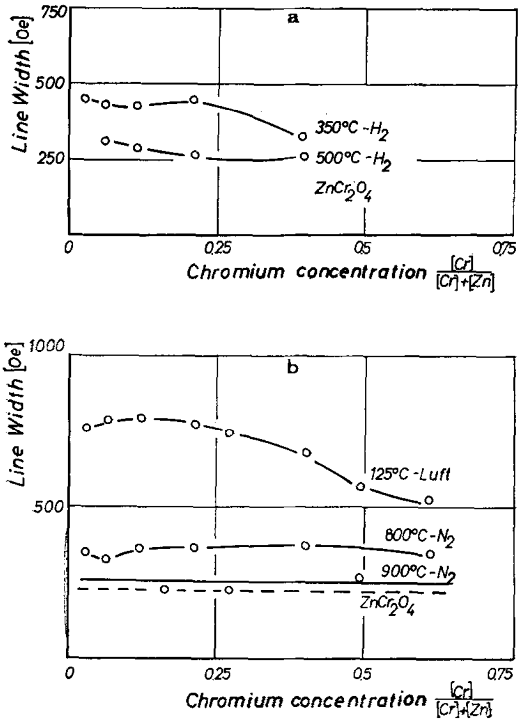

FIG. 4. (a) ESR linewidths for different compositions of mixed oxides; (b) ESR linewidths of samples of ZnO impregnated with different amounts of Cr_2O_3.

and where μ_B is the Bohr magneton; S, the spin; J, the exchange integral of $\Theta = 2JzS(S + 1)/3k$ (z, number of nearest neighbors); n, the density of spins (spins/cc); Θ, the Weiss constant; ω_e, the exchange frequency; and ω_0, the resonance frequency. In Eq. (1), H_p is the dipole broadening and H_e the exchange narrowing of the respective line.

Chromium oxide hydrate has a composition dependent on the activation temperature. The upper limit of the spin density in completely dehydrated chromium hydroxide $[Cr(OH)_3]$ is estimated from the composition of the volumes of the respective ions to be 65% of the value found with $HCrO_2$ (*15*). This is equal to 0.029 spins/Å^3 (*16*).

For estimation of the expected linewidth due to dipole–dipole interaction in a chromium hydroxide which was nondehydrated, as well as in mixed hydroxides in which the paramagnetic components are homogeneously distributed, the linewidths for the different spin densities have been calculated from Eq. (2), neglecting a possible zero-field splitting (Table 2). The value $n = 18.8 \times 10^{21}$ spin/cc^{-1} denoted as 100% in the first line of Table 2, belongs to chromium oxide hydrate in the dehydrated state. The measured linewidth for pure chromium oxide hydrate dried at room temperature, amounts to about 400 Oe. No sign of a line-narrowing below 100 Oe was found, at variance with Slinkin (*7*), who explained this line by the exchange interaction of the neighboring Cr ions via OH groups.

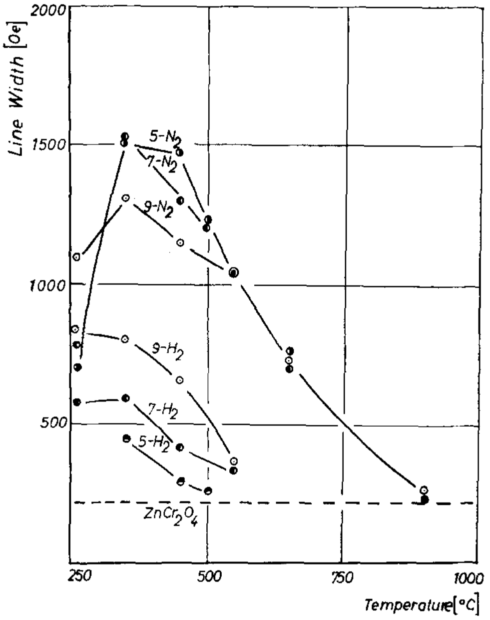

FIG. 5. Dependence of the linewidths of the mixed oxide catalysts on the activation temperature.

TABLE 2

LINEWIDTH CALCULATED FROM THE SPIN DENSITY

Spin density (%)	H_p (Oe)
100	1500
20	300
10	150
5	75

As the ESR investigations have been made at room temperature only, it could not be established whether the said indirect exchange interaction takes place or whether the linewidths originate from the dipole–dipole broadening.

The diluted mixed hydroxides should show narrow lines provided that the paramagnetic species are distributed homogenously. It

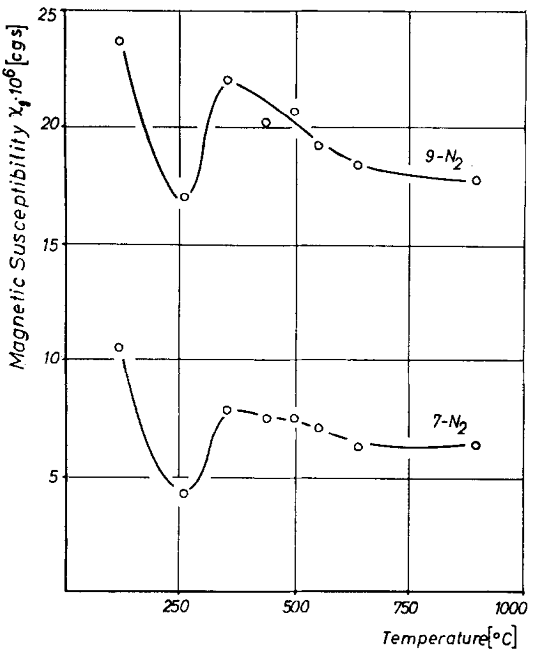

FIG. 6. Dependence of magnetic susceptibility on the activation temperature.

follows from Fig. 4a that the linewidth is independent of the composition in a concentration range between 0 and 20 mole % of the chromium contents. Only with larger chromium concentrations, the linewidth drops to a value equalling that of the chromium hydrate.

A dependence of the linewidth on the concentration deduced by Kittel and Abrahams (*16*) for "diluted" paramagnetism was not observed. Hence it may be inferred that the respective mixed hydroxides were not homogeneous and that chromium is present in the mentioned system in clusters.

Thermal Activation

In pure chromium oxide hydrate the same linewidth was observed as that found earlier by Slinkin (*7*). He states that the Weiss constant Θ takes a negative value during the thermal activation of the chromium oxide hydrates. For activation temperatures 200°, 300°, and 350°C, the values of Θ are −300°, −320°, and −500°K, respectively. Also from the temperature dependence of the linewidths it can be noted that spins must be partially coupled in the heat-treated samples (*7*, *19*).

The thermal activation of pure chromium hydroxides and mixed hydroxides calls forth a volume contraction which results in an increase of the spin density in different clusters and of the dipole–dipole exchange, too. At the same time, however, the exchange interaction also increases. Thus, the measured linewidth can be regarded as a result of superposition of both these factors which are, according to Eq. (2), opposite. Also the observed decrease of susceptibility values up to 260°C can be explained by an increasing exchange interaction in the chromium hydroxide clusters (*6*). Due to volume contraction, the constant Θ in the Curie-Weiss equation $\chi = C/(T + \Theta)$ increases, as the number of nearest neighbors and the values of the exchange integrals increase.

The values of susceptibilities, surfaces, and linewidths of the mixed oxides prepared by decomposition at 260°C (Figs. 1, 5, and 6) indicate that the two hydroxide phases at first decompose in an almost independent way. Chromium oxide hydrate clusters dissolved in a diamagnetic matrix result in this decomposition. The process reaches a maximum value at temperatures of about 300°C and stops at about 400°C (Fig. 5).

In the temperature range up to 350°C, the susceptibility values rise and at the same time the ESR lines broaden. Therefrom it can be concluded that the exchange interaction diminishes owing to the formation of a disarranged transition structure, whereby the dipole–dipole exchange plays an important role. This disordered structure probably corresponds to the so-called "active states" described by Hüttig *et al.* (*20*), and others, in which the different physical properties rapidly change. Furthermore, beginning with temperatures of about 350°C, the solid state reaction $ZnO + Cr_2O_3 \rightarrow ZnCr_2O_4$ takes place. Formation of the spinel structure at these low temperatures was also observed by Natta (*21*).

The narrowing of the absorption lines at temperatures exceeding 350°C indicates that in the transition structure of the mixed oxides, which was initially disordered, an exchange interaction occurs, the intensity of which increases with rising activation temperature. A dependence of the linewidth on chromium concentration was not found.

From this it can be concluded that chromium was not dissolved in the zinc oxide excess but that it formed the stable spinel phase $ZnCr_2O_4$.

With the impregnated samples, zinc chromate is found on the surfaces after the reaction of zinc oxide with chromium acid. This zinc chromate is deoxidized to spinel at relatively low temperatures. The ESR linewidth is therefore comparatively small and a further lowering of the linewidth at higher temperatures can be explained by structure ordering.

The experiments on mixed hydroxides show the following:

(1) Even when carefully precipitated, no completely mixed hydroxides result, but rather an unmixing occurs. This effect can be explained as follows: The precipitation of both pure chromium and zinc hydroxides, respectively, occurs in a complex way via several transition states. The ϵ-zinc hydroxide described consists of $Zn(OH)_4^{2-}$ tetrahedrons bound by OH groups between which hydrogen bonds exist (*17*, *18*). The microstructure of the chromium hydrate is unknown. However, it can be assumed that it is similar to the structure of ρ-$Al(OH)_3$. In this structure, the Al^{3+} ions coordinate six OH groups and each OH group is bound to three Al^{3+} ions. This difference in structure causes a limitation of solubility of the mixed hydroxides. Furthermore, an unmixing occurs during precipitation and aging within an aqueous suspension. It is not yet known whether the unmixing process occurs in one or two phases.

(2) During the thermal activation of mixed hydroxides, a solid state reaction takes place above a certain temperature, leading at first to a disordered transition structure.

(3) As a reaction product a spinel phase results, in which the chromium ions are stabilized. The formation of the spinel phase can be explained as follows: $ZnCr_2O_4$ belongs to the group of normal spinels (*22*) in which the chromium ions occupy octahedral positions. The configuration of the electrons of these chromium ions present in the octahedral oxygen ligand field, is t_{2g}^3. In case the energy difference between t_{2g} and e_g orbitals is 10 *Dq* for stabilization energy of the octahedral chromium complex, a value of 12 *Dq* will be reached. In case of the chromium complex mentioned before, this stabilization energy as a contribution to the whole lattice energy, amounts to 53.7 kcal/mole. It has been calculated from the *Dq* values obtained on the basis of spectroscopic data for Cr_2O_3 and indicates that the chromium ions occupy primarily the octahedral positions in the spinel. The energy difference reaches 37.7 kcal/mole (*23*) compared with the tetrahedral positions. During the transition process of the chromium ions into the wurtzit-type lattice of the zinc oxide, the chromium ions should occupy the positions of the zinc ions and form here oxygen ion complexes with the tetrahedron structure. This transition would lead to their energetic destabilization. Moreover, it can be supposed that the solution of chromium in the lattice of zinc oxide would be diminished by the partial covalent character of the bonds. As a further support for the assumption that formation of a stable form during the solid state reaction in the system $ZnOCr_2O_3$ takes place, results of conductivity measurements may serve. The conductivity of ZnO is not strongly dependent on the Cr_2O_3 contents. In the concentration range between 0.2 and 3 mole % Cr_2O_3, it turns out to be completely independent (*24*). Conductivity of chromium oxides is also but little influenced by addition of zinc oxide (*25*). Should chromium oxide be dissolved in zinc oxide, conductivity in this system would be strongly influenced by addition of chromium oxide. As an example for this the analogous system ZnO-Al_2O_3 can serve. Aluminum ions are here not stabilized by the crystal field and therefore dissolve more easily in the excess of zinc oxide. This doping of zinc oxide with trivalent Al^{3+} ions leads to an increase of conductivity, as substitution of Zn^{2+} ions by Al^{3+} ions in zinc oxide results in a formation of the Zn^{1+} ions with a freely separable electron. Hereby, the trivalent Al^{3+} ions will be electrostatically compensated by univalent zinc ions.

(4) This process is strongly influenced by hydrogen as well as by the reaction components of the methanol synthesis. If it is assumed that the narrowing of the linewidth

results from the spinel structure formation, the above-mentioned influence of the hydrogen atmosphere can be explained as follows: In the zinc oxide a larger amount of zinc atoms in interstitial positions is formed. For these zinc atoms a lower separation energy has to be applied, and therefore they are more reactive (*26*). During the reduction, also in the samples impregnated with chromium a formation of the spinel phase easily takes place.

From the results obtained it can be deduced that in the studied system the intercrystalline promoters described by Natta (*21*) are represented by the spinel phase.

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