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Fig. 1. EPR spectra of the mixture $\text{CrO}_3 + \text{K}_2\text{Cr}_2\text{O}_7$ calcined at different temperatures: a–450° ($\chi = 17.5 \cdot 10^{-6}$); b–600° ($\chi = 24.4 \cdot 10^{-6}$); c–700° ($\chi = 39.4 \cdot 10^{-6}$); d–850° ($\chi = 45.0 \cdot 10^{-6}$)

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Abstract

Full Text

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EPR SPECTRA OF PRODUCTS OF THE HIGH-TEMPERATURE INTERACTION OF CrO_3 WITH $\text{K}_2\text{Cr}_2\text{O}_7$, K_2CrO_4 , K_2CO_3 , KCl , AND KOH

(Presented by Academician A. A. Balandin, January 29, 1963)

Topochemical reactions occurring in the preparation of multicomponent catalysts ultimately determine their chemical composition and catalytic properties. Therefore, the study of chemical reactions in the solid state is of considerable theoretical and practical interest. We have studied the EPR spectra of the products of the interaction of CrO_3 with $\text{K}_2\text{Cr}_2\text{O}_7$ at high temperature, since both components are used jointly to obtain alumopotassium chromia catalysts.

Fig. 1. EPR spectra of the mixture $\text{CrO}_3 + \text{K}_2\text{Cr}_2\text{O}_7$ calcined at different temperatures:

a–450° ($\chi = 17.5 \cdot 10^{-6}$); b–600° ($\chi = 24.4 \cdot 10^{-6}$); c–700° ($\chi = 39.4 \cdot 10^{-6}$); d–850° ($\chi = 45.0 \cdot 10^{-6}$)

The reaction of CrO_3 with K_2CrO_4 at 208–220° was investigated by V. I. Spitsyn and co-workers⁽¹⁾, who showed that it begins in the melt and proceeds with the formation of $\text{K}_2\text{Cr}_2\text{O}_7$. Zukhov et al.⁽²⁾ found that treatment of $\text{K}_2\text{Cr}_2\text{O}_7$ and K_2CrO_4 with hydrogen at 300–700° forms a black product of composition KCr_3O_8 , in which the authors assumed the presence of Cr^{5+} ions. However, a magnetochemical study carried out by Klemm⁽³⁾ showed that in this compound only Cr^{3+} and Cr^{6+} ions are present. Rohde, Kazanskii, and Pecherskaya⁽⁴⁾ investigated the EPR spectra of the decomposition products of CrO_3 (chromium bichromate, chromium dichromate, chromium monochromate) and the EPR spectrum of CrO_2 . For all compounds, one line with $\Delta H = 130\text{--}150$ Oe and

Fig. 2. Dependence of the form of the EPR spectrum for a mixture of $\text{CrO}_3 + \text{K}_2\text{Cr}_2\text{O}_7$, calcined at 859° , on the measurement temperature: $a -25^\circ$; $b -43^\circ$; $v -54^\circ$; $g -80^\circ$.

Figure 2: Fig. 2. Dependence of the form of the EPR spectrum for a mixture of $\text{CrO}_3 + \text{K}_2\text{Cr}_2\text{O}_7$, calcined at 859° , on the measurement temperature: $a -25^\circ$; $b -43^\circ$; $v -54^\circ$; $g -80^\circ$.

$g \simeq 1.97$ was found. Thus, in all these compounds only Cr^{3+} and Cr^{6+} ions are present.

The reaction of CrO_3 with $\text{K}_2\text{Cr}_2\text{O}_7$, K_2CrO_4 , K_2CO_3 , KCl , and KOH was carried out by us in the solid phase by heating in air at a rate of ~ 7 deg/min and holding at constant temperature for 6 hr. The products of the interaction of CrO_3 with $\text{K}_2\text{Cr}_2\text{O}_7$ obtained at 450 , 600 , 700 , and 850° were examined, and with the remaining salts at 600° . The ratio of components in the initial mixture corresponded to a content of $\sim 10\%$ K_2O in the final mixture.

The EPR spectra were recorded on an RE-1301 spectrometer at a frequency of 9326 MHz at room temperature and at temperatures of 43 , 54 , and 80° , produced by blowing hot air through the resonator. Magnetic susceptibility was measured by the Faraday method in the field-strength interval $H = 1300-4500$ Oe. Figure 1 presents the EPR spectra of the products of heating the mixture $\text{CrO}_3 + \text{K}_2\text{Cr}_2\text{O}_7$. As is seen from the figure, the mixture heated at 600° shows an absorption spectrum sharply different from the spectrum of Cr_2O_3 and the spectra of various chromium chromates (⁴), which have one li-

line with $g \approx 1.97$. The spectra obtained have a distinct fine structure, the resolution of which improves as the calcination temperature of the mixture is increased. It should be noted that these mixtures are strongly paramagnetic, and the paramagnetism* increases with increasing calcination temperature. Figure 2 shows how the EPR spectrum of a mixture calcined at 850° changes depending on the temperature at which it was recorded. Increasing the temperature leads to the contraction of the fine-structure components into a single line, while lowering the temperature again leads to the original spectrum. Figure 3 gives the spectra of the products of the interaction of CrO_3 with K_2CrO_4 , K_3CO_2 , KCl , and KOH at 600° . They also display a distinct fine structure and differ sharply from the spectra of ordinary Cr_3O_2 .

Fig. 2. Dependence of the form of the EPR spectrum for a mixture of $\text{CrO}_3 + \text{K}_2\text{Cr}_2\text{O}_7$, calcined at 859° , on the measurement temperature: $a -25^\circ$; $b -43^\circ$; $v -54^\circ$; $g -80^\circ$.

Apparently, there are two explanations for these spectra:

1. The observed spectra are associated with hyperfine structure (h.f.s.) due to interaction with the nuclear spin of the isotope Cr^{53} .
2. The observed spectra are due to the fine structure (f.s.) of the Cr^{3+} ion,

Fig. 3. EPR spectra of mixtures of CrO_3 with various substances, calcined at 600° : *a* $-\text{CrO}_3 + \text{K}_2\text{CO}_3$; *b* $-\text{CrO}_3 + \text{KOH}$; *v* $-\text{CrO}_3 + \text{K}_2\text{CrO}_4$; *g* $-\text{CrO}_3 + \text{KCl}$.

Figure 3: Fig. 3. EPR spectra of mixtures of CrO_3 with various substances, calcined at 600° : *a* $-\text{CrO}_3 + \text{K}_2\text{CO}_3$; *b* $-\text{CrO}_3 + \text{KOH}$; *v* $-\text{CrO}_3 + \text{K}_2\text{CrO}_4$; *g* $-\text{CrO}_3 + \text{KCl}$.

Fig. 4. E.p.r. spectrum of chrome-potassium alum: *a* –starting alum, *b* –heated at 200°

Figure 4: Fig. 4. E.p.r. spectrum of chrome-potassium alum: *a* –starting alum, *b* –heated at 200°

analogous to that which exists in chrome alum.

The first assumption is unlikely, since in ordinary chromium compounds there is little Cr^{53} isotope, and h.f.s. is observed only when compounds are enriched with the isotope Cr^{53} .

Fig. 3. EPR spectra of mixtures of CrO_3 with various substances, calcined at 600° : *a* $-\text{CrO}_3 + \text{K}_2\text{CO}_3$; *b* $-\text{CrO}_3 + \text{KOH}$; *v* $-\text{CrO}_3 + \text{K}_2\text{CrO}_4$; *g* $-\text{CrO}_3 + \text{KCl}$.

To test the second assumption, the EPR spectrum of powdered chrome-potassium alum, $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, shown in Fig. 4a, was recorded. It can be seen that this spectrum is very similar to the spectra obtained in the work. Apparently, topochemical reactions in the solid phase between CrO_3 and the substances considered lead to the formation of substances of the chrome-potassium alum type, for example, $\text{KCr}(\text{CrO}_4)_2$. As already mentioned, this compound was synthesized in work (2). The proposed assumption encounters one substantial difficulty. In the investigated compounds, $\text{KCr}(\text{CrO}_4)_2$ is found in a strongly paramagnetic ($\alpha = \text{Cr}_2\text{O}_3$) and even ferromagnetic matrix, therefore—

* Mixtures calcined at 700 and 850° are ferromagnetic with $\sigma = 0.14$ and $\sigma = 0.16$, respectively. The figure gives data corresponding to $H = 3500$ oersted.

the fine structure of the Cr^{3+} ion should not have been observed because of strong dipole-dipole interaction, as indeed occurs upon decomposition of chrome-potassium alum (Fig. 4b). If the spectra observed in the work are in fact associated with the fine structure of the Cr^{3+} ion, then there must exist an effective mechanism for shielding the Cr^{3+} ion in $\text{KCr}(\text{CrO}_4)_2$ from magnetic interaction with the Cr^{3+} ions of chromium oxide.

Fig. 4. E.p.r. spectrum of chrome-potassium alum:
a –starting alum,
b –heated at 200°

The reactions studied also have very interesting topochemical features. The in-

teraction of CrO_3 with $\text{K}_2\text{Cr}_2\text{O}_7$ at low temperatures (up to 350°) leads to products that were found in work (4) and described in detail in the monograph (5). In the e.p.r. spectra of these substances we also found narrow (100–130 oersted) e.p.r. lines and ferromagnetic properties. When a mixture of $\text{CrO}_3 + \text{K}_2\text{Cr}_2\text{O}_7$ is heated to 450° , the e.p.r. signal disappears (Fig. 1a) and appears only at higher calcination temperatures (Fig. 1b, c, d). Since $\text{K}_2\text{Cr}_2\text{O}_7$ melts at about 400° , it could be assumed that the products giving the e.p.r. spectra are obtained by reaction of Cr_2O_3 , formed during decomposition of CrO_3 , with molten $\text{K}_2\text{Cr}_2\text{O}_7$. However, special experiments on the interaction of Cr_2O_3 with $\text{K}_2\text{Cr}_2\text{O}_7$ showed that this does not yield substances giving the spectra shown in Fig. 1. Moreover, the interaction of CrO_3 with K_2CrO_4 , K_2CO_3 , KCl , which do not melt at all under the experimental conditions, leads to spectra (Fig. 3) analogous to those shown in Fig. 1. The interaction in these systems, leading to products of the KCr_3O_8 type, is probably due to the reaction of active products formed in the initial stages of decomposition of CrO_3 (chromium chromates) with $\text{K}_2\text{Cr}_2\text{O}_7$ and other salts. In this process compounds are formed which at high temperatures give products of the $\text{KCr}(\text{CrO}_4)_2$ type.

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