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ESR Study of the Chromium Oxide–Alkali Metal Oxide Systems

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An ESR investigation of chromium oxide samples containing lithium, sodium, potassium, rubidium and cesium oxides has been carried out. Two kinds of defect structures attributed to Cr^{3+} vacancies connected with occluded alkali metal ions and Cr^{6+} ions in the α-Cr_2O_3 lattice are discussed. The observed fine structure is interpreted by means of axially symmetric spin Hamiltonian and two different values for parameter D. The possibility for ACr_3O_8 structure formation is also considered. The connection between these defect structures and the catalytic properties of the chromium catalyst is considered.

Alkali metal ions are commonly used as promoters in chromium-containing catalysts but little is known about the mechanism of their action.

In a previous paper (*1*), we reported the results from an investigation of the Cr_2O_3-K_2O system. The fine structure observed in the ESR spectrum of the samples was interpreted by means of an axially symmetric spin Hamiltonian for two different values of D. The observed fine structure was asiqued to defects which can be represented as K^+O^{2-}-Cr^{3+}-O^{2-}-$\square$-O^{2-}, formed when K^+ ions are introduced in the α-Cr_2O_3 lattice. The evidence obtained supported the assumption that these defects affect the catalytic activity of chromium catalysts in the hydrocarbon conversion reactions.

The present investigation aims at studying similar defects formed when Li^+, Na^+, Rb^+, and Cs^+ ions are introduced in the α-Cr_2O_3 lattice. The correlation between ESR spectra parameters and the catalytic activity of the chromium catalysts or chromium oxide containing as promotors alkali metal ions is also discussed.

EXPERIMENTAL METHODS

The samples studied were prepared by two different methods: (a) a wet mixture of CrO_3 and LiCl, NaCl, KCl, RbCl or CsCl in appropriate ratios was dried and then calcinated in air at 800°C; and (b) chromium hydroxide precipitated from chromium nitrate with ammonia, was dried at 100°C, LiOH, NaOH or KOH was added, and the dried mixture was calcined in air at 800°C. Analytical grade reagents were used. The samples studied contained 2% alkali oxide and are characterized in Table 1.

The amount of surface Cr^{6+} ions was estimated by water extraction as CrO_4^{2-} and titration. The surface area of the samples was determined by low-temperature adsorption of air. The catalytic activity of the samples was determined for hydrogen peroxide decomposition by volumetric measurements.

The spectra were recorded on a JEOL-3BS spectrometer at an X-band frequency and a manganese standard was employed for the determination of the *g*-value and linewidth.

RESULTS

The ESR spectra of the samples 2, 3, 4, 5, and 6 of Cr_2O_3 containing 2% Li_2O, Na_2O, K_2O, Rb_2O, or Cs_2O, respectively, are shown in Figs. 1–5. A fine structure is observed in all recorded spectra at room temperature. Sample 1 (without alkali

TABLE 1

Designation	Alkali metal oxide in the sample (2 wt %)	Mode of preparation	Surface area (m^2/g)	Surface Cr^{6+} concentration (mg/g sample)	Catalytic activity for H_2O_2 decomposition, W (cm^3/m^2 sec)
1	pure Cr_2O_3	from CrO_3	2.3	0.01	0.30
2	Li_2O	from CrO_3 and LiCl	0.3	0.06	0.15
3	Na_2O	from CrO_3 and NaCl	2.5	1.60	0.36
4	K_2O	from CrO_3 and KCl	1.1	1.36	0.46
5	Rb_2O	from CrO_3 and RbCl	1.6	0.66	0.53
6	Cs_2O	from CrO_3 and CsCl	1.4	0.80	0.50
7	Li_2O	from chromium hydroxide and LiOH	—	0.60	0.13
8	Na_2O	from chromium hydroxide and NaOH	—	6.00	—
9	K_2O	from chromium hydroxide and KOH	—	4.70	—

metal) did not give rise to an ESR signal. Most of the alkali in samples 7, 8, and 9 remain because of the preparative procedure on the α-Cr_2O_3 surface and are mainly consumed for chromate phase formation. The ESR spectra of the samples 8 (Na_2O) and 9 (K_2O) exhibit the same fine structure as for samples 3 and 4 but with lower intensity and poor resolution. The Li_2O containing sample 7 gave only the signal at $g = 1,91$.

Table 1 shows, that the samples studied contained a considerable amount of Cr^{6+} ions removable as CrO_4^{2-} ions by water

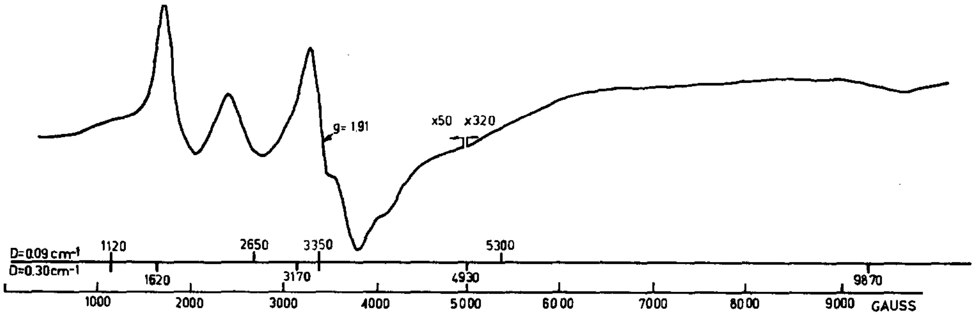

FIG. 1. ESR spectrum of sample 2 at room temperature.

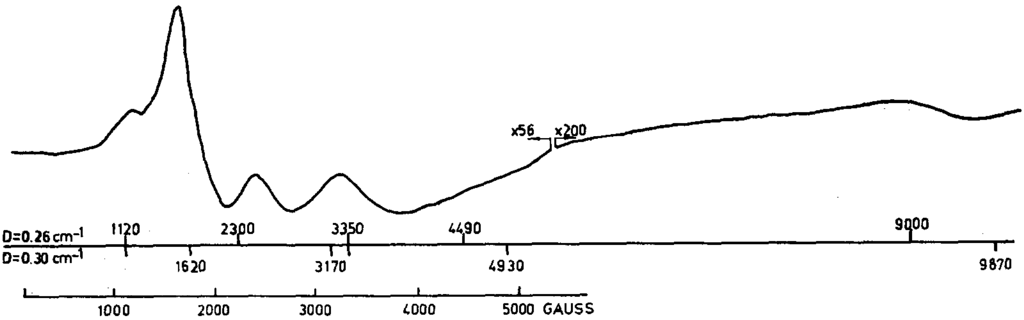

FIG. 2. ESR spectrum of sample 3 at room temperature.

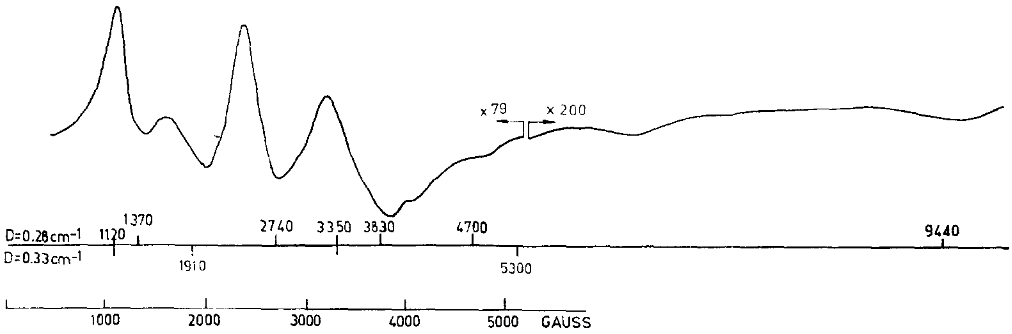

FIG. 3. ESR spectrum of sample 4 at room temperature.

extraction. Samples 7, 8, and 9 prepared under the conditions favorable for concentration of alkali on the surface contain more Cr^{6+} ions, than samples 2, 3, and 4 respectively. Surface chromate phase formation was also established by means of the optical remission spectra bands at 25600 and 39000 cm^{-1} (*2*).

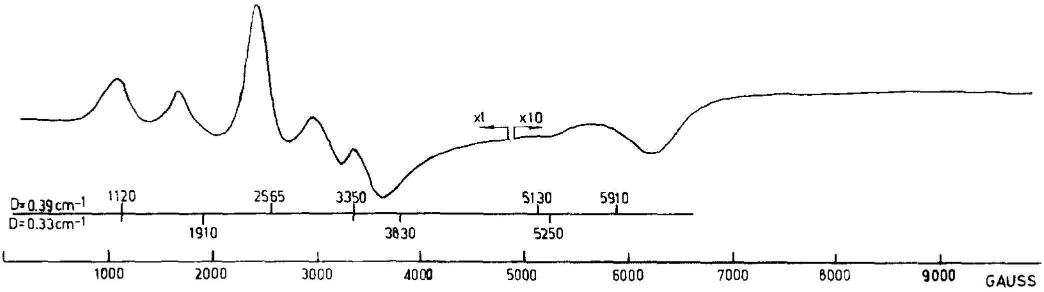

FIG. 4. ESR spectrum of sample 5 at room temperature.

After careful chromate phase water extraction no change in the shape and intensity of the fine structure in the ESR spectra was observed but the chromate band in the optical spectra disappeared.

Catalytic activity for the hydrogen peroxide decomposition of the water-treated samples was determined in the region of conditions where the reaction obeys zero-order kinetics and is not influenced by diffusion. The catalytic activity was evaluated by the volume of oxygen evolved from 1 m^2 of the catalyst surface per second at 60°C.

DISCUSSION

The fine structure in spectra of the α-Cr_2O_3 samples containing potassium ions was explained (*1*) by defect structures

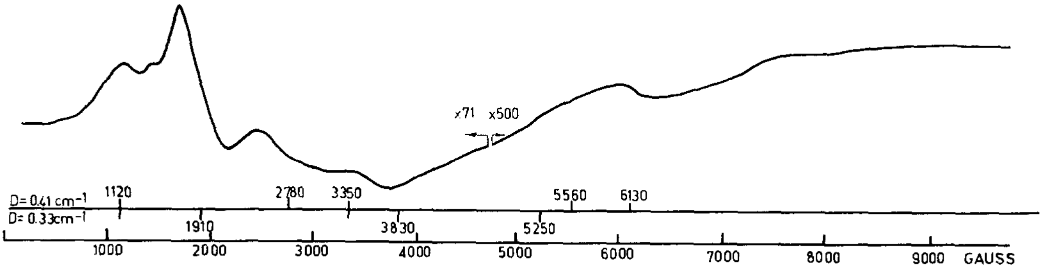

FIG. 5. ESR spectrum of sample 6 at room temperature.

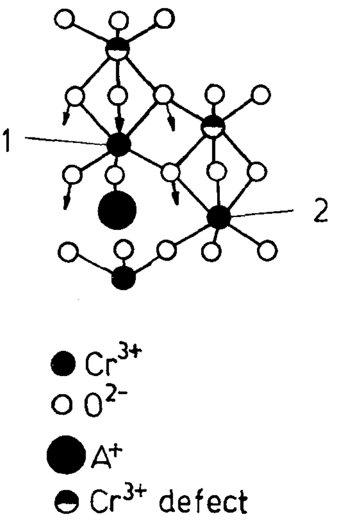

FIG. 6. Defects representation in the corundum type lattice (projection on the (210) plane).

which can be represented as Cr^{3+} vacancies connected with alkali ions (see Fig. 6). If the ionic radii of the alkali are taken into account it becomes evident that the only possible positions for them are the octahedral holes in the α-Cr_2O_3 lattice. Magnetic dilution of the antiferromagnetic phase of α-Cr_2O_3 by Cr^{6+} ions creates favorable conditions for the appearance of an ESR signal. A fine structure in the ESR spectrum of Cr_2O_3 samples containing Li_2O was observed by Slinkin and Fedorovskaja (*3*).

The spectra observed (Figs. 1–5) could be interpreted with an axially symmetric spin Hamiltonian of the form:

$$\mathcal{H} = g\beta H_z\hat{S}_z + D(\hat{S}_z^2 - 5/4)$$

In this study as in the previous one (*1*), the method discussed by van Reijen (*4*) for approximate evaluation of the D constant for powdered samples was used. The polycrystalline samples will exhibit resonance adsorption at values of the magnetic field H for which $\partial H/\partial \cos\theta$ is small (θ is the angle between the symmetry axis in the crystal and the direction of the field). From the theoretically calculated relations H_{res}/θ the D terms for the experimental spectra were approximately evaluated. Similarly to the Cr_2O_3–K_2O system (*1*), for all samples studied two different values for D were obtained (Table 2). The resonance adsorption positions when $\theta = 0$ for the corresponding D_1 and D_2 values are given in Figs. 1–5. D_1 corresponds to a Cr^{3+} ion in positions 1 and D_2 to the same ion in position 2 on Fig. 6. The crystal field around the Cr^{3+} ion in position 1 is more strongly influenced by alkali metal ions than that of Cr^{3+} in position 2. The direction of the axial distortion is shown by arrows in Fig. 6.

A ACr_3O_8 structure formation renders another possibility for interpretation of the ESR spectra of alkali containing Cr_2O_3 samples. It is known (*5*) that the compounds $NaCr_3O_8$, KCr_3O_8, $RbCr_3O_8$, and $CsCr_3O_8$ with a monoclinic crystal lattice contain Cr^{3+} ions in an octahedral field and Cr^{6+} ions in tetrahedral environment. Similar type of Cr^{3+} and Cr^{6+} distribution is achieved in the orthorhombic $LiCr_3O_8$ (*6*). Cr^{3+} and alkali ions are randomly distributed in the octahedral holes so it is quite possible that in these compounds the structures shown in Fig. 6 are likely to exist and Cr^{6+} ions can also serve as magnetic diluents.

There are, however, many facts inconsistent with the above mentioned hypothesis for ACr_3O_8 phase formation. It is well known, that ACr_3O_8 compounds can be readily obtained by reduction of alkali chromate and bichromate with hydrogen at 300–700°C (*6*). Specially planned experiments showed that under the above-

TABLE 2

EXPERIMENTAL D_1 AND D_2 VALUES OF STUDIED SAMPLES

Designation	2(Li^+)	3(Na^+)	4(K^+)	5(Rb^+)	6(Cs^+)
D_1, cm^{-1} ($g = 1.98$)	0.09	0.26	0.28	0.39	0.41
D_2, cm^{-1} ($g = 1.98$)	0.30	0.30	0.33	0.33	0.33
Ionic radius, Å	0.76	0.98	1.33	1.49	1.65

mentioned conditions it was impossible to obtain samples which would give a fine structure in the ESR spectrum. ACr_3O_8 compounds are stable in the temperature range of 250–350°C and decompose completely above 400°C. In our case it was only possible to obtain a fine structure by means of a temperature treatment above 400°C. Another evidence against ACr_3O_8 phase formation is the fact that this structure can not explain the appearance of two different D values in the ESR spectra. Fine structure spectra depend on the alkali concentration (*1*) which is also difficult to explain from the view point of discreet phase formation.

All these facts confirm the above conclusion that the introduction of alkali metal ions into the α-Cr_2O_3 lattice is a much more plausible cause for the appearance of a fine structure in the ESR spectra of the systems studied.

It is known, that as a result of Cr_2O_3 interaction with lithium salts at high temperatures $LiCrO_2$ is formed (*7*). Slinkin and Fedorovskaja (*3*) ascribed the singlet in the ESR spectrum of Cr_2O_3 with a high content of Li_2O to the $LiCrO_2$ phase formed. Such a type of ESR signal is characteristic for Cr^{3+} ions in the cubic field of $LiCrO_2$ (NaCl-type lattice) and the small linewidth observed corresponds to the exchange interaction between Cr^{3+} ions in the $LiCrO_2$ lattice (*8*). Accordingly we assigned signal at $g = 1.91$ with a line width of 160 G in the spectra of samples 2 and 7 to $LiCrO_2$ formation. The preparative procedure of sample 7 is very unfavorable for introducing Li^+ in the Cr_2O_3 lattice and defect structure formation, thus only the signal due to $LiCrO_2$ phase is observed. The quantity of the chromate phase in the Li-containing samples is very small (Table 1) therefore most of the Li^+ ions should be fixed in the insoluble $LiCrO_2$ phase.

It is previously established (*1*) that the defect structures and their changes under the working conditions of the chromium catalysts are linked with the catalytic activity in dehydrogenation and dehydrocyclization reactions of hydrocarbons. In Fig. 7 the correlation is given between experimental values for D_1 and the catalytic activity of samples 2, 3, 4, 5, and 6 for hydrogen peroxide decomposition. The same figure shows also the dependence between D_1 and the dehydrogenation of *n*-butane over the chromium catalysts containing 2% of Li_2O, Na_2O, K_2O, Rb_2O or Cs_2O at 565°C according to Fridshtein and Zimina (*9*). The correlation observed between the D_1 value and the catalytic activity (Fig. 7) is in favor of the already mentioned considerations regarding the impotance of defect structures for the catalytic activity of the chromia catalysts. It is reasonable to assume that the extent of crystal field distortion is one of the most important factors determining the catalytic activity of the metal ion. The gradual change of the catalytic activity with the extent of the crystal field distortion corroborates this assumption.

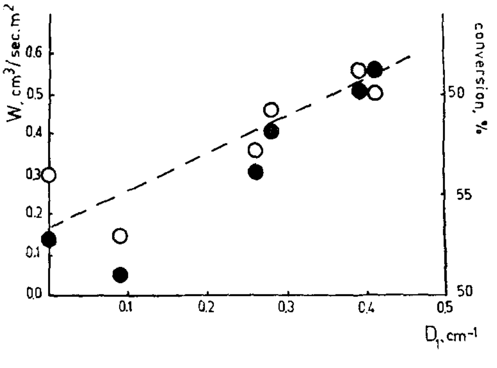

FIG. 7. Dependence between catalytic activity for hydrogen peroxide decomposition (W) of the sample studied and appropriate D_1 values (open circles). Dependence between *n*-butane conversion over alumina-chromia catalysts containing 2% of Li_2O, Na_2O, K_2O, Rb_2O or $Cs_2O^{(9)}$ and D_1 values found in this work (filled circles).

The following conclusion can be drawn: the presence of defect structures arising from the introduction of alkali and Cr^{6+} ions in the Cr_2O_3 lattice plays an important role in the catalytic activity. The same is true for some other corund type structures, for instance Al_2O_3–Cr_2O_3 solid solution however the identification of defect structures by ESR is difficult because of the intense "β-phase" signal (*10*). The role of the crystal field distortion should be emphasized.

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