# Spectroscopic Study of Chromia Catalysts for Dehydrogenation of Secondary Alcohols

L. NONDEK, D. MIHAJLOVA, A. ANDREEV,
A. PALAZOV, M. KRAUS, AND D. SHOPOV

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences,
165 02 Prague 6-Suchdol, Czechoslovakia[1],
and Institute of Organic Chemistry,
Bulgarian Academy of Sciences, Sofia 13, Bulgaria[2]*

Infrared, EPR and reflectance spectra in the uv and visible region were measured for six different chromium(III) oxide preparations. With some samples also the changes of spectra caused by the use of the catalysts for dehydrogenation of isopropanol to acetone at 350°C were studied. The results are interpreted in terms of the change of coordination of surface $Cr^{3+}$ atoms and interaction between them due to preparation variables, surface hydration and influence of the reactants. A linear correlation was found between the Racah parameter calculated from the reflectance spectra and sensitivity of the reaction rate of dehydrogenation of secondary alcohols $R \cdot CHOH \cdot CH_3$ to the change in the structure of the group R.

## INTRODUCTION

Catalytic properties of chromium oxide in dehydrogenation of secondary alcohols are dependent on its method of preparation. The most important properties from this point of view are the size of crystallites, surface concentration of hydroxyl groups and the arrangement of coordinatively unsaturated surface $Cr^{3+}$ atoms (1). The catalytic activity of the sample also depends on the presence of $Cr^{6+}$ ions on the surface (2).

Spectroscopic methods have been used for the study of chromium oxide in several papers. Infrared spectroscopy yields qualitative information about the crystal structure (3–5). In the range of 400–700 cm$^{-1}$ amorphous samples show a broad band which separates into several narrow bands (410, 450, 540 and 620 cm$^{-1}$) with crystalline $Cr_2O_3$. Stretching vibrations of O–H bonds of surface hydroxyl groups can be found in the range of 3500–3800 cm$^{-1}$. Electronic reflectance spectra have been used to study $Cr^{3+}$-containing systems by Reinen (6); the spectra of $Cr^{3+}$ in an octahedral ligand field show three main bands which correspond to the transfer of d-electrons from the ground state $^4A_{2g}$ to the levels $^4T_{2g}$, $^4_aT_{1g}$ and $^4_bT_{1g}$. From the electronic spectra the empirical parameters $\Delta$ and $B_{35}$ may be calculated which characterize bonding in $Cr_2O_3$. According to the MO theory, the Racah parameter ($B_{35}$) is inversely proportional to the $Cr^{3+}$–$Cr^{3+}$ interaction and the parameter $\Delta$ is related to the distance Cr–O (6).

Another suitable method for the investigation of chromium catalysts is EPR spectroscopy (7). EPR shows that the $Cr^{3+}$ cations exist in polycrystalline samples as various phases; the resulting form and temperature dependence of the EPR signal is then a superposition of the signals of individual phases. The particle size strongly influences the EPR spectrum line shape.

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[1] L. N. and M. K.

[2] D. M., A. A., A. P. and D. S.

Nondek and Kraus (1) and Nondek and Sedláček (8) assume on the basis of rate measurements of the dehydrogenation of secondary alcohols, of estimation of surface hydration and its effect on activity and of quantum-chemical calculations that the catalytic activity of chromium oxide is determined mainly by the concentration of coordinatively unsaturated $Cr^{3+}$ cations on its surface. In the present paper we seek further confirmation of this hypothesis using ir, EPR and reflectance spectroscopy in the uv and visible region. The influence of the $Cr^{3+}-Cr^{3+}$ exchange interaction on the catalytic activity of the $Cr_2O_3$ samples was also studied.

## EXPERIMENTAL METHODS

The preparation of the catalysts and their properties were described in previous papers (1,8). The catalysts described further as used ones were employed for 1 hr at 350°C for dehydrogenation of 2-propanol (partial pressure, 0.5 atm; feed rate, 0.1 mol/hr $kg_{cat}$).

Infrared spectra were measured on a UR-10 spectrometer (Carl Zeiss, Jena); the catalyst samples were suspended in Nujol.

Reflectance spectra were obtained in the range 250–650 nm using a VSU-2p spectrometer (Carl Zeiss, Jena); magnesium oxide was used as a standard.

EPR spectra were measured on a JEOL-3BS spectrometer at 9.240 MHz and 20–25°C; for the determination of line width and value of the $g$-factor a $Mn^{2+}$ standard was used.

## RESULTS AND DISCUSSION

The ir spectra of the fresh catalysts N1, N2, B1, B2 and B3 and of the catalyst N2 after reaction are shown in Fig. 1. The spectra of N1 and N2 are typical for amorphous samples. During its use in the catalytic reactor, catalyst N2 very probably suffered partial recrystallization as indicated by the splitting of the broad band
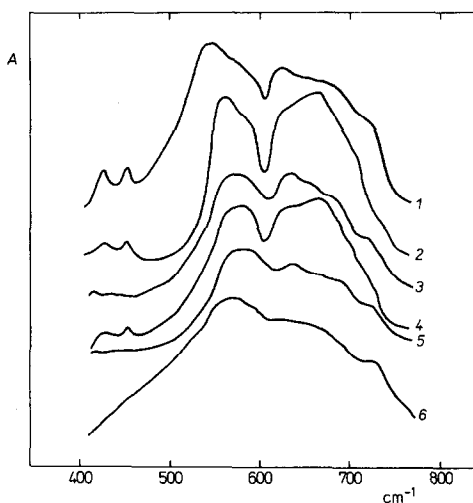


FIG. 1. Infrared spectra of the catalysts in the range 400–800 cm$^{-1}$. (1) Catalyst B1, (2) B3, (3) B2, (4) N2 used, (5) fresh N2, (6) N1.

into two bands at 540 and 620 cm$^{-1}$ and by bands 410 and 450 cm$^{-1}$. The spectra of B1 and B3 reflect the macrocrystallinity of the preparations. Catalyst B2 is again amorphous. The sequence of the catalysts according to the relative amount of crystalline phases and size of the crystallites following from the ir spectra is the same as from X-ray diffraction (1). However, as the form of the spectrum of materials like chromium oxide depends also on the method of adjustment of the sample before measurement (9) no precise conclusions about the size of crystallites can be made.

The spectra in the region of wavelength 250–700 nm were measured with fresh and used catalysts N2, B1, B2 and B3. The amorphous samples N2 and B2 show changes caused by their use as catalysts (for example see Fig. 2). The broad band at 300–1000 nm was split into three bands corresponding to the transitions $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}_a^4T_{1g}$ and $^4A_{2g} \rightarrow {}_b^4T_{1g}$, respectively. For comparison, the spectrum of the crystalline sample B1 is given on Fig. 3; with this catalyst the intensity of the bands was increased as the result of its use as catalyst. Because these bands correspond to $d$-electron transitions of $Cr^{3+}$ in
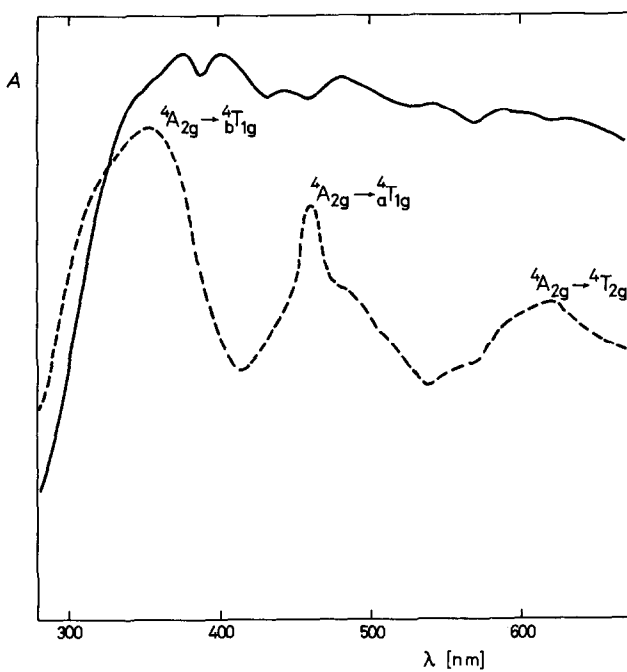
FIG. 2. Reflectance spectra in the region 250–700 nm of the catalyst B2 in fresh (—) and used (---).
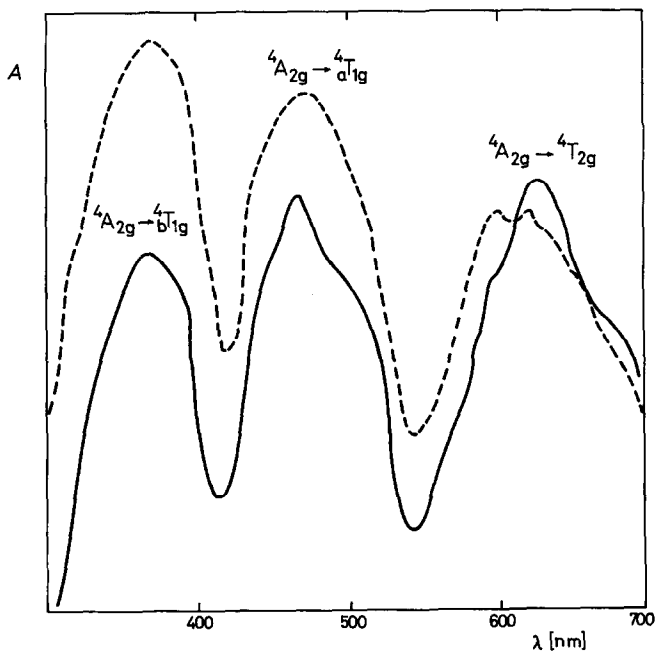


FIG. 3. Reflectance spectra in the region 250–700 nm of the catalyst B1 in fresh (—) and used (---).

an octahedral ligand field (6) the observed changes in spectra can be interpreted as evidence of the change in the number of coordinatively unsaturated surface $Cr^{3+}$; with amorphous catalyst B2 it could be surface recrystallization, with B1 reduction of surface chromate groups.

The reflectance spectra provide information concerning mainly the surface layers of the particles in a polycrystalline sample; therefore the present results describe to a great extent the changes in the surface of the chromium oxide. From the reflectance spectra the parameters $\Delta$ and $B_{35}$ based on crystal field theory were calculated. For $B_{35}$ the following formula was used (6):

$$B_{35} = (\delta E/15)[(\Delta - \delta E)/(0.8 - \delta E)],$$

where $\Delta$ denotes the position of the first band $({}^4A_{2g} \rightarrow {}^4T_{2g})$ and $\delta E$ is the difference between the position of the first and second band. Interpretation of the $B_{35}$

value according to molecular orbital theory shows that it is proportional to the Coulomb integral of the $e_g$ and $t_{2g}$ orbitals. A high value of $B_{35}$ shows a decrease in the $Cr^{3+}-Cr^{3+}$ interaction. Thus well crystallized $\alpha$-$Cr_2O_3$ will exhibit a small $B_{35}$ value compared with that of the small or defective crystals in which the exchange interaction is decreased.

Table 1 shows that with catalysts B1 and B3 the value of $B_{35}$ decreased after its use in the reactor and the value of $\Delta$ increased in the same time. This fact again supports the assumption about the change of average coordination number of surface $Cr^{3+}$ during the catalytic work. The processes of recrystallization must also be considered.

The parameter $B_{35}$ which is more sensitive to the change of the structure than parameter $\Delta$ (see Table 1) is proportional to energy and may be classified as an in-

TABLE 1

PROPERTIES OF THE CATALYSTS

| Property | Catalyst | | | |
|---|---|---|---|---|
| | B1 | B3 | N2 | B2 |
| Reflectance spectroscopy data | | | | |
| Fresh catalyst, $\Delta^a$ | 16,100 | 16,400 | —[b] | —[b] |
| $B_{35}{}^c$ | 520 | 480 | —[b] | —[b] |
| Used catalyst, $\Delta^a$ | 16,500 | 16,500 | 16,300 | 16,200 |
| $B_{35}{}^c$ | 430 | 440 | 480 | 540 |
| Sensitivity parameter, $a$[see (1)] | 1.00 | 1.13 | 1.33 | 1.78 |
| OH/100 Å² [see (1)] | 12 | 16 | 24 | 30 |
| $d_s(\text{Å}^2)^d$ | 3880 | 790 | 190 | 270 |
| $d_x$ (hkl) (Å²)[e] (110) | —[f] | 600 | 200 | 300 |
| (211) | —[f] | 650 | 230 | 320 |
| (321) | —[f] | 570 | 170 | 240 |

[a] $\Delta$ denotes the energy of the ${}^4A_{2g}-{}^4T_{2g}$ transition (cm⁻¹).
[b] The positions of maxima were not clear (cf. Fig. 2).
[c] Racah parameter $B_{35}$ (cm⁻¹).
[d] $d_s = 6/\rho S$, $\rho = 5.25$ g/cm³ [see (11)], for specific surface area $S$ (BET) [see (1)].
[e] Crystallite size from X-ray diffraction [see (1)]. Notation of crystal planes after (12).
[f] The sample was used as macrocrystalline standard for the correction of line width.

tensive property. Another intensive property of the catalysts is the relative sensitivity of the catalysts $a$ to the change of the structure of the reacting alcohol (i.e., the proportionality factor of a linear free energy relationship). This was ascertained by following the kinetics of dehydrogenation of a series of secondary alcohols $R \cdot CHOH \cdot CH_3$ (where R denotes various alkyl groups) and by correlation of the observed log $k$ for various catalysts against log $k$ for one of them chosen as standard (*1*). Besides that, Table 1 contains also data on surface hydration of catalysts (given as the concentration of OH groups) and on the size of the catalyst crystallites.

A linear relationship was found between the Racah parameter $B_{35}$ and the sensitivity parameter $a$; as both of them are proportional to energy this correlation can be again classified as a linear free energy relationship (Fig. 4). Our interpretation of it is that it reflects the change in coordination of surface $Cr^{3+}$ cations. The reasons for this change are the differences in surface hydration and in crystallinity which influence not only the number of active sites
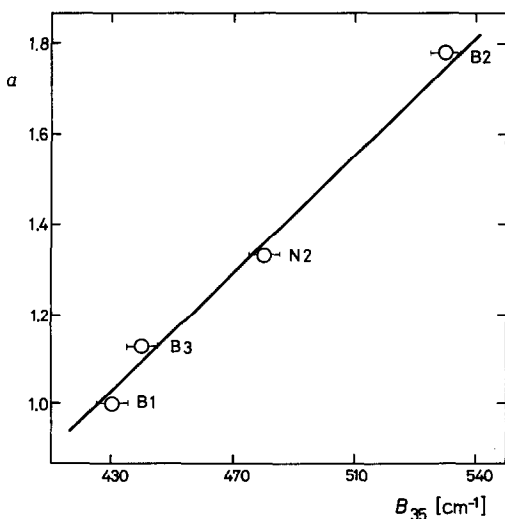
but also their energetics by changing their neighborhood.

Further information about the structure of the samples was obtained by means of EPR spectroscopy. Figure 5 shows the EPR spectra of catalyst B2 before and after catalytic work. In the EPR spectrum two bands appeared at about $g = 4$ and $g = 1.98$. The second one has a complex character and it is composed at least of two bands. One of these components is due to the small particles of chromium oxide which exhibit ferromagnetic properties. Spin decoupling caused by $Cr^{6+}$ ions embedded mainly on the surface layers of the chromium oxide is also the reason for the appearance of the EPR signal at $g = 1.98$ (*13*). After the catalytic dehydrogenation over the sample this signal disappeared and the spectrum changed its shape (Fig. 5, curve 2).

The absorption observed at $g = 4$ has been in the spectrum of samples which have contained some chromium hydroxide (*14*). Consequently, this line can be considered as a component of the pure resolved fine structure by $Cr^{3+}$ ions partially isolated from the crystal due to a hydrate surrounding which remains a result of the incomplete chromium hydroxide decomposition during the sample preparation.



FIG. 4. Linear correlation of the parameter $B_{35}$ for used catalysts and parameter $a$. Correlation coefficient 0.9954, critical value for 99% confidence level 0.9900.
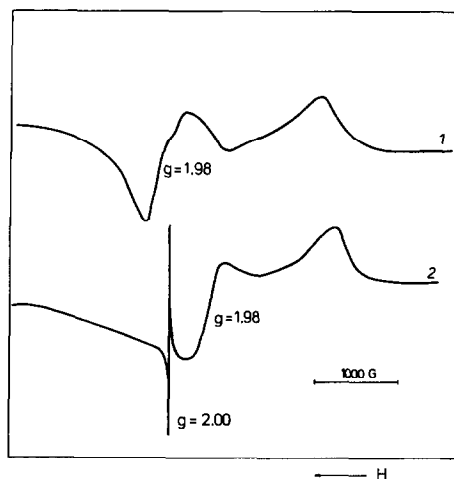


FIG. 5. EPR spectra of the catalyst B2 in fresh (1) and used (2) state.

The narrow signal in the EPR spectrum of used B1 corresponds to free carbon; similar but not such intense signals were also observed in catalysts B2 and B3 after the catalytic work. In the spectrum of used N2 no signal of free carbon appeared. The decrease of activity of a chromium oxide catalyst during dehydrogenation of secondary alcohols is partially reversible (10). The reversible part is due to water formed by competitive dehydration, the irreversible part very probably due to cracking of the alcohols and formation of coke. The highest concentration of coke deposits were found on the most active catalyst B1.

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