

## EFFECT OF ALKALI METALS ON THE ACTIVITY OF CHROMIA AS A CATALYST FOR DEHYDROGENATION OF ALCOHOLS

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Chromium oxide catalysts containing approx. 3% of Li, Na, K, Rb, Cs resp., and a catalyst without any additive, were tested on the activity for the dehydrogenation of secondary alcohols and the decomposition of hydrogen peroxide and studied by means of reflectance and EPR spectra. Rate measurements with four secondary alcohols allowed to compare the catalysts on the basis of the proportionality constants from the Taft equation and from an other linear free energy relationship. The results show that alkali metals influence chromium oxide as a dehydrogenation catalyst in several ways: They increase the surface concentration of chromate ions which are catalytically inactive and thus decrease the specific activity. Alkali metals change also the interaction of  $\text{Cr}^{3+}$ - $\text{Cr}^{3+}$  in the surface layers and this results in a change of the energy of interaction of the reacting alcohol with the active centres. In contrast, the rate of hydrogen peroxide decomposition is probably related with electron transfer from the bulk of the solid to the substrate as indicated by the correlation of specific activity with the  $D_1$  parameter from EPR spectra.

Alkali metals are usually used as promoters of chromium(III) oxide catalysts. Earlier EPR investigations established the formation of defect structures due to the introduction of alkali ions and  $\text{Cr}^{6+}$  ions in the lattice of the oxide. A relationship between the extent of these defect structures and catalytic activity of samples containing alkali metals was found<sup>1</sup> for dehydrogenation of hydrocarbons. In studying the effect of catalyst preparation variables on catalytic activity of chromium(III) oxide for dehydrogenation of secondary alcohols we were able to correlate<sup>2</sup> the sensitivity of reaction rate to changes in the structure of the reacting alcohol with the Racah parameter calculated from reflectance spectra of the catalyst samples.

In the present paper we have continued these investigations<sup>1,2</sup> with the purpose to bring further insight into the way in which the alkali metals influence chromium(III) oxide as a catalysts for dehydrogenation of secondary alcohols and decomposition of hydrogen peroxide. Similar approach as in the preceding paper<sup>2</sup> has been used.

## EXPERIMENTAL AND RESULTS

The techniques of the measurements of catalytic activity of chromium oxide samples and of their reflectance spectra were the same as in the previous papers<sup>2,3</sup>. The catalysts were prepared by precipitation by ammonia of chromium hydroxide from a solution of chromium nitrate containing chlorides of alkali metals, by drying at 110°C and by calcination at 800°C. The samples contained approx. 3 w. % of alkali metal; a sample without any additive was also prepared. For spectral measurements samples have been used which have previously worked as catalysts in the dehydrogenation of 2-propanol at 350°C and which have attained a steady activity. The rate of hydrogen peroxide decomposition was measured in a static volumetric apparatus and steady state values of gas evolution were recorded. The surface concentration of hydroxyl groups was determined by the pulse method using dimethyl zinc-tetrahydrofuranate as reagent<sup>4</sup>. For the study of the structure effect on the dehydrogenation rate the following alcohols were used: 2-propanol, 2-butanol, 3-methyl-2-butanol and 3,3-dimethyl-2-butanol. The surface area of catalysts was determined by the BET method. The content of chromates in the samples was found by 3 hours extraction of the sample into boiling water and by iodometric titration<sup>1</sup>.

The results of the measurements are summarized in Table I which contains also characteristic parameters obtained from correlation of some experimental data. The weight content of chromates was transformed into surface concentration as only chromate ions from outer layers are extracted<sup>1</sup>. The Racah parameter  $B_{35}$  was calculated by the formula<sup>5</sup>

$$B_{35} = (\delta E/15)(A - \delta E)/(0.8 - \delta E), \quad (1)$$

where  $A$  denotes the position of the first band (corresponding to the transition  ${}^4A_{2g} \rightarrow {}^4T_{2g}$ ) and  $\delta E$  is the difference between the position of the first and second band in the reflectance spectrum (*cf.*<sup>2</sup>).  $B_{35}$  values are proportional to the  $e_g$  and  $t_{2g}$  orbitals Coulomb integrals; the higher value of  $B_{35}$  indicates a decrease in the  $Cr^{3+}-Cr^{3+}$  interaction. The values of the  $D_1$

TABLE I  
Results of Measurements and Correlation of Data

Denotation of the catalyst	O	Li	Na	K	Rb	Cs
Surface area, m <sup>2</sup> /g	2.9	1.6	5.4	14.1	17.1	8.4
Chromates, mmol/m <sup>2</sup> ( <i>c</i> )	0.005	0.44	0.070	0.011	0.034	0.080
OH groups per 100 Å	13.2	7.8	8.0	5.6	9.0	11.6
Specific activity dehydrogenation <sup>a</sup>						
( <i>r</i> ) <sub>b</sub> H <sub>2</sub> O <sub>2</sub> decomposition ( <i>r</i> ) <sub>0</sub>	9.9	0.5	0.5	3.3	1.7	0.6
H <sub>2</sub> O <sub>2</sub> decomposition <sup>b</sup> ( <i>r</i> ) <sub>0</sub>	0.30	0.20	0.46	0.36	0.53	0.50
$B_{35}$	450	496	440	446	456	475
$D_1$ , cm <sup>-1</sup>	0	0.09	1.33	0.98	1.49	1.65
$\varrho^*$	3.0	1.4	3.2	2.1	2.6	1.1
<i>a</i>	1.00 <sup>c</sup>	0.45	0.85	1.20	1.11	0.80

<sup>a</sup> Reaction of 2-propanol at 350°C and 0.5 atm; rate in mol/h m<sup>2</sup>. <sup>b</sup> At 25°C, rate in ml/s m<sup>2</sup>.

<sup>c</sup> By definition.

constant (axial spin Hamiltonian parameter) were obtained from EPR spectra (*cf.*<sup>1</sup>). The parameter  $\rho^*$  was calculated from the dependencies of the initial reaction rates of alcohol dehydrogenation  $r$  at 350°C and at the partial pressure of the alcohol in the feed 0.5 atm on the Taft  $\sigma^*$  constants for the groups R in  $\text{CH}_3\text{—CHOH—R}$ , *i.e.* on the basis of the Taft equation<sup>6</sup>

$$\log r = \rho^* \sigma^* . \quad (2)$$

Examples of these dependencies are given in Fig. 1. The parameter  $a$  was calculated as the slope of the dependencies of  $\log r_M$  vs  $\log r_O$  (where O denotes the catalyst without any additive and M the catalysts with various alkali metals) for four different alcohols, *i.e.* from a linear free energy correlation where unpromoted catalyst serves as a standard; dependencies of similar shape as in Fig. 1 were obtained.

## DISCUSSION

The inspection of Table I reveals immediately the fact that the properties of the catalysts are in no connection with atomic weight of the added alkali metal or any property which changes monotonously with the position of the metal in the periodic table. On the contrary, the values vary quite irregularly in the series and therefore relationships were sought between different characteristics of individual catalysts.

The most pronounced influence on the rate of dehydrogenation seems to have the content of chromates. It is known from the literature<sup>7</sup> that the increase of potassium

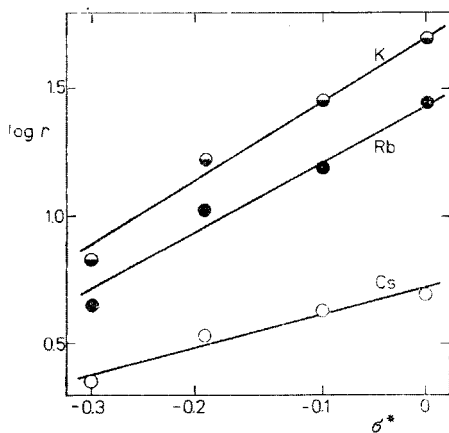


FIG. 1

Correlation of the Rates of the Dehydrogenation of Alcohols  $\text{R—CHOH—CH}_3$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{i-C}_3\text{H}_7$  and  $\text{t-C}_4\text{H}_9$ ) at 350°C in the Coordinates of the Taft Equation (2)

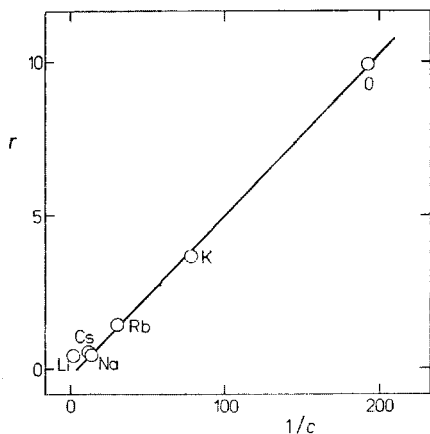


FIG. 2

Correlation of Specific Activity for 2-Propanol Dehydrogenation  $r$  with Reciprocal Surface Concentration of Chromates ( $c$ )

content lowers the catalytic activity of chromium oxide for hydrogenation of ethylene, dehydrogenation of cyclohexane, oxidation of CO and  $H_2-D_2$  exchange. Alkali metals stabilize  $Cr^{6+}$  ions in the lattice and as the chromate phase is catalytically inactive for most reactions, a relationship may be expected between the surface concentration of chromates in various catalysts and their activity for dehydrogenation. This has been confirmed by Fig. 2 which shows a linear dependence of specific activity for the dehydrogenation of 2-propanol on the reciprocal surface concentration of chromates. However, closer examination of the data in Table I indicates a certain residual activity (of about  $0.5 \text{ mol/h m}^2$ ) for chromate concentrations higher than approx.  $0.07 \text{ mmol/m}^2$ . The hydrogen peroxide decomposition exhibits no dependence on chromate content.

In the preceding paper<sup>2</sup> a successful correlation was obtained between the proportionality constant  $a$  from a linear free energy relationship and the parameter  $B_{35}$  calculated from reflectance spectra for chromium oxide catalysts prepared in different ways. Therefore we tried to find similar correlation in the present work and as Fig. 3 shows a clear relationship between this two variables has been established. A slightly worse correlation was obtained when instead of  $a$  the Taft  $\rho^*$  parameter from Fig. 1 and Table I was applied. A comparison reveals that here we have found a negative slope whereas in the previous work<sup>2</sup>, where we have correlated catalysts differing in the extent of surface hydration, a positive slope was observed. The standard catalyst

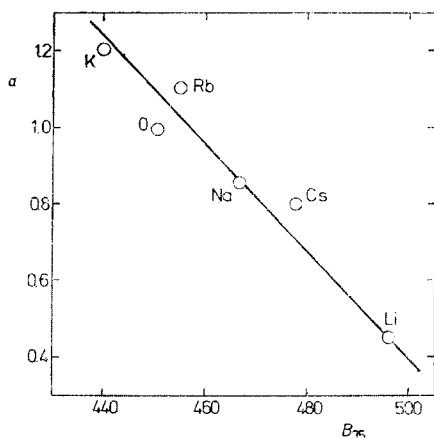


FIG. 3  
Correlation of Racah Parameter  $B_{35}$  with the Parameter  $a$

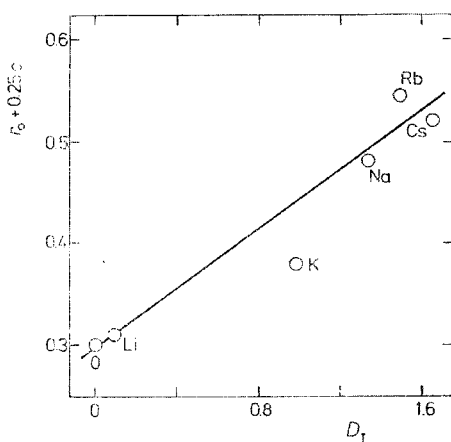


FIG. 4  
Correlation of Corrected Specific Rate of Hydrogen Peroxide Decomposition with the Parameter  $D_1$

in this paper has similar properties as the catalyst B3 from the previous paper<sup>2</sup>; this allows to link the two series of catalysts.

Considering both series we observe that the parameter  $a$  varies in the range of approx. 0.5 to 1.7 (relative values). The lowest value exhibits the catalyst calcined at 800°C and containing Li as the additive. The highest value was obtained<sup>2</sup> for the catalyst calcined at 400°C and without any additive. The parameter  $B_{33}$  varies in the range of 430 to 540 cm<sup>-1</sup> and its value tends to increase with both the extent of surface hydration<sup>2</sup> and the influence of alkali metals. This parameter characterizes mainly the properties of surface Cr<sup>3+</sup> ions which are responsible for the hydrogenating activity; its shift to higher values indicates a decrease in Cr<sup>3+</sup>-Cr<sup>3+</sup> interaction. In this light we may assume that this interaction is weaker when foreign species (water, hydroxyl groups, alkali ions, Cr<sup>6+</sup> ions) are present in the surface layers of chromium oxide lattice. The parameter  $a$  is a relative measure of the interaction between the active centres and the reacting molecule. Its change in the series of the catalysts with alkali metals is probably a manifestation of a change in the mean quality of active centres caused by a change in the ligand field of the surface Cr<sup>3+</sup> ions, whereas in the series of the catalysts with varying degree of surface hydration<sup>2</sup> the change can be attributed to surface inhomogeneity (*cf.*<sup>3</sup>) and blocking of active centres in the order of their strength by adsorbed water.

The data in Table I show a certain parallelism between the value of  $D_1$  and the rate of hydrogen peroxide decomposition. A satisfactory correlation (Fig. 4) has been obtained when the specific rate has been corrected on the specific surface concentration of chromates ( $c$ ); the correction is appreciable for the catalyst containing lithium. The factor 0.25 (Fig. 4) has been found by the try and error procedure. In contrast to  $B_{35}$ , the parameter  $D_1$  from EPR spectra reflects much more the properties of the bulk of the solid phase. The correlation on Fig. 4 may be interpreted as a result of the involvement of an electron transfer from the catalyst in the decomposition of hydrogen peroxide which is hindered by the inactive chromate phase.

The results presented in this paper show that the alkali metals influence the catalytic properties of chromium oxide in several ways. The Cr<sup>6+</sup> ions are stabilized which are catalytically inactive and thus the concentration of the active sites on the surface is very probably lowered. Beside that the energetics of the interactions within the solid and between the catalyst and the substrate is changed as revealed by the observed differences in the parameters of the linear free energy relationships and parameters obtained from spectroscopic data. On the other hand, the differences in the extent of surface hydration which are very important with relatively pure chromium oxide samples<sup>2</sup> are almost insignificant when alkali metals are present. We may conclude that the effect of an alkali metal addition to chromia is complex and not easily predictable on the basis of the knowledge of general properties of a additive.

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