

## Surface and Catalytic Properties of Chromia in Dehydrogenation of Secondary Alcohols

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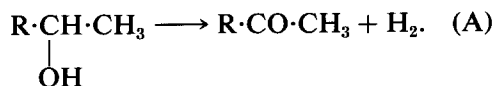
The rates of dehydrogenation of a series of 2-alkanols, the selectivity of the decomposition of 3,3-dimethyl-2-butanol, adsorption heats of diethyl ether by gas chromatographic method, crystallite size, total water content and surface concentration of hydroxyl groups were measured with six samples of chromium(III) oxide differing in the method of preparation. Correlation of the results showed that the catalytic properties of chromium oxide depend mainly on its temperature of calcination which governs the surface concentration of hydroxyl groups and the state of coordination of surface  $\text{Cr}^{3+}$  ions.

### INTRODUCTION

It is a well known fact that the catalytic properties of chromium oxide are very sensitive to its method of preparation. Rode (1) studied this problem with dehydrogenation of cyclohexane as the test reaction but in spite of extensive experimental material she was not able to arrive at conclusive results. Dyne *et al.* (2) have found an increase in activation energy and specific activity for hydrogenolysis and isomerization of cyclopropane after recrystallization of an amorphous sample. They have explained it by an increase in symmetry and by a change in coordination of the active centers. Arias and Selwood (3) have observed a jump in activity for ortho-para hydrogen conversion when crossing over the Néel temperature. Burwell and co-workers (4) using the theory of coordinative chemisorption (5) have stressed the important effect of water bound to the surface of chromium oxide in the form of hydroxyl groups. The influence of water on the catalytic activity of chromium oxide has been, however, observed by a number of authors. Salley *et al.* (6) and Minachev *et al.* (7) found inhibition

of alkane dehydrogenation on chromium oxide by addition of small amounts of water into the feed. Voltz and Weller (8,9) have reported a decrease in the rate of hydrogen-deuterium exchange with increased amount of adsorbed water. An inhibiting effect of water on the dehydrogenation of secondary alcohols has been observed by Nondek and Sedláček (10) who have interpreted it as a result of blocking of the surface coordinatively unsaturated  $\text{Cr}^{3+}$  ions which are part of the active centers.

In this paper we have applied as the test reaction the dehydrogenation of 2-alkanols at 350°C [Eq. (A)] and the obtained rate data were correlated with physical properties and with water content of the catalysts.



### EXPERIMENTAL METHODS

The apparatus and procedure for kinetic measurements was described in the preceding paper (10). Selectivity of the de-

composition of 3,3-dimethyl-2-butanol was studied in an apparatus in which the liquid products were frozen out from the stream at  $-78^{\circ}\text{C}$ ; their gas chromatographic analysis was conducted at  $100^{\circ}\text{C}$  using 2 m column with polyethylene glycol. The selectivity was calculated as the ratio of conversions to ketone and to olefin at standard conditions (partial pressures of the alcohol and of nitrogen in the feed were both 0.5 atm, feed rate 0.1 mol/hr, temperature  $350^{\circ}\text{C}$ ). The adsorption heats were measured by a pulse chromatographic method [e.g. (11)].

**Catalyst N1:** To a solution of chromium nitrate (200 g) in 4 liters of distilled water a 5% solution of ammonium hydroxide was added with mixing at room temperature during 10 min. The precipitate was decanted, filtered off and washed with distilled water. The obtained chromium hydroxide was dried at  $150^{\circ}\text{C}$  for 16 hr in an oven and then calcined at  $400^{\circ}\text{C}$  in a stream of nitrogen for 3 hr.

**Catalyst N2:** Chromium nitrate (60 g) was dissolved in 4 liters of water and the solution was heated to  $90^{\circ}\text{C}$ . Ammonium hydroxide was added to the point when a first precipitate was formed and this was then dissolved by a small amount of nitric acid. Then a hot solution of 10 g of urea in 50 ml of water was added and the mixture was heated to  $90^{\circ}\text{C}$  for a short while. After cooling, the dark-green gel was worked up as in the previous case.

**Catalyst N3** was obtained by calcination of the catalyst N1 at  $700^{\circ}\text{C}$  for 3 hr.

**Catalyst B1** was prepared by thermal decomposition of chromium oxide at  $800^{\circ}\text{C}$  for 2 hr.

**Catalyst B2** was prepared in the same way as N1 but it was dried at  $110^{\circ}\text{C}$  and the calcination at  $400^{\circ}\text{C}$  was shortened to 2 hr.

**Catalyst B3** was obtained by calcination of the catalyst B2 at  $800^{\circ}\text{C}$  for 2 hr.

Catalysts B1, B2 and B3 were prepared in the Institute of Organic Chemistry of

the Bulgarian Academy of Sciences, Sofia by Dr. A. Andreev.

*Properties of the catalysts.* Specific surface areas of the catalysts were measured by the BET method, and their water content was estimated from the weight loss after calcination to  $1100$ – $1200^{\circ}\text{C}$ . The mean crystallite size  $\bar{d}_x$  was calculated from the width of X-ray diffraction lines (12); X-ray diffractograms were obtained on a Chirana apparatus (Cu/Ni, 32 kV/22 mA). As the values of crystallite size calculated from three most intensive lines were practically the same we can assume an approximately spherical form of the crystallites in the region of 200 to 600 Å. This has enabled us to calculate the mean particle size  $\bar{d}_s$  from the specific surface area and density of chromium oxide (1). All these quantities are summarized in Table 1; they show that catalyst particles are formed mostly from single crystallites.

*Purity of the catalysts.* Although analytical grade substances were used for the preparation of the catalysts, all samples contained impurities, as shown by spectrographic analysis. Calcium, sodium, potassium, aluminum and iron were present in the concentrations in the range of 0.1%, calcium being the most abundant impurity.

*Surface concentration of hydroxyl groups.* A newly developed pulse chromatographic method was applied which is based on the reaction of gaseous dimethylzinc tetrahydrofuranate with surface OH groups and on determination of formed methane by means of a thermal conductivity detector (13); the results are given in Table 3.

## RESULTS AND DISCUSSION

The experimental dependences of initial reaction rates  $r^0$  on partial pressures of the alcohols  $p_A^0$  for the dehydrogenation of 2-alkanols were correlated by the same rate equation (1) as in the preceding paper (10).

TABLE 1  
 PREPARATION AND PROPERTIES OF THE CATALYSTS BEFORE USE

Catalyst	N1	N2	N3	B1	B2	B3
Prepared from	Cr(OH) <sub>3</sub>	Cr(OH) <sub>3</sub>	Cr(OH) <sub>3</sub>	CrO <sub>3</sub>	Cr(OH) <sub>3</sub>	Cr(OH) <sub>3</sub>
Calc. temp (°C)	400	400	700	800	400	800
Surface area (m <sup>2</sup> /g)	115	60	5	3	43	15
$\bar{d}_s$ (Å)	100	190	2500	3800	270	790
$\bar{d}_x$ (Å)	— <sup>a</sup>	200	800	— <sup>b</sup>	300	600
Water content (%)	17.2	5.6	0.16	0.09	6.2	0.68

<sup>a</sup> No diffraction lines were found.

<sup>b</sup> Chosen as standard.

Calculated rate constants  $k$  and adsorption coefficients  $K_A$  are given in Table 2.

$$r^0 = kK_{APA}^0 / (1 + K_{APA}^0)^2 \quad (1)$$

The rate constants  $k$  were treated by the method of linear free energy relationships (14,15) in its most simple form. We have correlated the data by the equation

$$\log k_{i,I} = a_I \log k_{i,B1} + b_i \quad (2)$$

where index  $i$  denotes an alcohol and index  $I$  a catalyst. The procedure consisted of plotting  $\log k$  for the reaction of the five alcohols on one catalyst against  $\log k$  for the same alcohols and catalyst B1 chosen as standard. In this way a family of straight lines was obtained whose slope  $a$  is a characteristic of the sensitivity of the catalyst to the change of the structure of the reacting alcohol; two examples of the

 TABLE 2  
 VALUES OF THE CONSTANTS  $k$  (mol/hr kg) AND  $K_A$  (atm<sup>-1</sup>) CALCULATED FOR EQ. (1)

Alcohol		Catalyst					
		N1	N2	N3	B1	B2	B3
2-Propanol	$k$	1319	373.8	145.6	89.8	201.8	386.8
	$K_A$	0.68	2.64	2.08	2.15	1.23	1.15
2-Butanol	$k$	1390	271.7	110.9	73.0	160.9	311.7
	$K_A$	1.86	2.15	2.34	2.54	1.98	2.27
3-Methyl-2-butanol	$k$	418.5	110.3	44.6	34.6	40.3	149.0
	$K_A$	1.17	1.37	4.30	3.02	2.34	3.13
4-Methyl-2-pentanol	$k$	466.8	15.5	39.19	43.0	48.4	170.1
	$K_A$	2.54	1.46	3.32	3.71	2.54	2.93
3,3-Dimethyl-2-butanol	$k$	158.0	49.3	20.30	19.9	14.8	68.3
	$K_A$	0.54	1.56	1.13	3.21	1.27	2.54

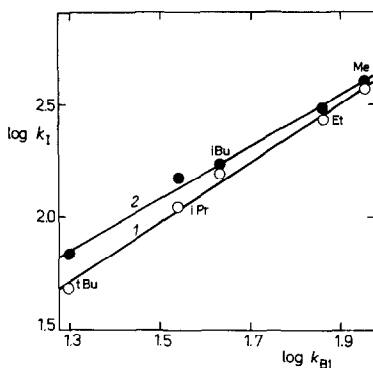


FIG. 1. Correlation of rate constants from Eq. (1) in the coordinates of Eq. (2). (1) Catalyst N2, (2) catalyst B3. Symbols at points denote the group in  $R\cdot\text{CHOH}\cdot\text{CH}_3$ . Me = methyl, Et = ethyl, iBu = isobutyl, iPr = isopropyl, tBu = *tert*-butyl.

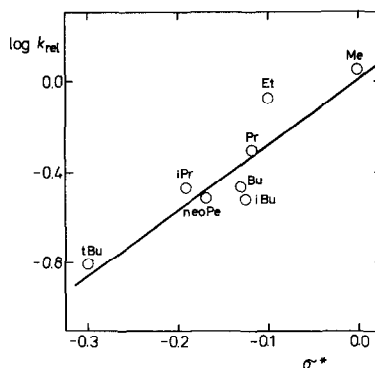


FIG. 2. Correlation of rate constants  $k_{\text{rel}} = k_1/k_2$ -propanol from Eq. (1) for catalyst N<sub>3</sub> in the coordinates of the Taft equation. Slope  $\rho^* = 2.88$ , correlation coefficient 0.902 (critical value on 99% significance level 0.834). Symbols at points have the same meaning as in Fig. 1, and Pr = propyl, Bu = butyl, neoPe = neopentyl.

correlation by Eq. (2) are given in Fig. 1.

In order to establish whether the decrease in  $k$  with the size of the group R in alcohols  $R\cdot\text{CHOH}\cdot\text{CH}_3$  has a steric or electronic reason the kinetics of dehydrogenation of a further three alcohols have been measured with catalyst N3 and the logarithms of the rate constants for all the alcohols have been plotted against Taft inductive  $\rho^*$  and steric  $E_s$  constants [e.g. (14)]. A better correlation was obtained in the former case (Fig. 2) which means that also the constant  $a_1$  from Eq. (2) reflects the difference in strength of the interaction between the active center of the catalyst and the reaction center of the alcohol and not a change in the steric requirements of active centers. Therefore, we can compare our parameter  $a_1$  with other characteristics of the catalyst which have the dimension of energy or are proportional to it.

As has been shown by Kochloeff *et al.* (16) a catalyst is characterized by two distinct types of parameters. Extensive parameters include the concentration of active centers; most typical are reaction rates and rate constants. Intensive parameters are obtained usually from extensive parameters from which the concentration of ac-

tive centers has been eliminated by a suitable procedure. In this group belong activation energies, constants of linear free energy relationships, etc. Our parameter  $a_1$  is clearly of this nature. The selectivity of decomposition of 3,3-dimethyl-2-butanol is an extensive parameter as it is most probable that the dehydrogenation and dehydration proceed on different active centers. Also the heat of adsorption measured by the gas chromatographic technique includes the concentration of active sites [cf. (11)].

As has been stated in the Introduction, many authors (4-10) have drawn attention to the important influence of surface bonded water. Therefore, we have determined it and it is evident that there exists a clear relationship between specific activity and the degree of dehydration of the surface (Table 3). By loss of water surface coordinatively unsaturated  $\text{Cr}^{3+}$  and  $\text{O}^{2-}$  are formed which constitute together the assumed active centers (10). Also the selectivity is changed with surface concentration of hydroxyl groups. Therefore all attempts to correlate the selectivity of an oxide catalyst only with parameters of the

TABLE 3  
 COMPARISON OF SOME PROPERTIES OF THE CATALYSTS

Catalyst	$c(\text{H}_2\text{O})$ ( $\mu\text{mol}/\text{m}^2$ )	Specific activity ( $\text{mol}/\text{nm}^2$ )	Selectivity <sup>a</sup> $x_{\text{ket}}/x_{\text{olef}}$	$a_1^b$	$\Delta H_{\text{ads}}$ ( $\text{kcal}/\text{mol m}^2$ )
B1	10	29.9	2.8	1.00 <sup>c</sup>	-10.5
N3	11	31.6	2.2	1.33	-11.6
B3	13	26.7	2.2	1.13	-10.6
N2	20	6.2	0.9	1.33	-12.2
B2	25	4.7	0.7	1.78	-15.8
N1	23	5.9	0.6	1.49	-17.1

<sup>a</sup>  $x$  denotes conversion.

<sup>b</sup> Slope from Eq. (2).

<sup>c</sup> By definition.

crystal lattice, with diameter and charge of the cation [cf. (17-19)] should be supported by experimental evidence that the selectivity is not dependent on the method of catalyst preparation.

However, not only extensive but also intensive parameters are changed by dehydration of the surface (Table 1 and 3). That means that on the surface of chromium oxide several energetically differing types of active centers co-exist and that their concentrations are changed with surface concentration of hydroxyl groups. If we imagine the (111) plane of crystalline  $\alpha\text{-Cr}_2\text{O}_3$  covered by hydroxyl groups as described by Burwell and co-workers (4) we see that by splitting off two water molecules from one site two different active centers may be formed. One consists of four coordinatively unsaturated  $\text{Cr}^{3+}$  with coordination number 5 and of two oxygen anions  $\text{O}^{2-}$ , the other of two coordinatively unsaturated  $\text{Cr}^{3+}$  with coordination number 5, of one  $\text{Cr}^{3+}$  with coordination number 4 and of two  $\text{O}^{2-}$ . Because the stabilization energy of the crystal field depends on the number and arrangement of the ligands (2,5) the two active centers must be energetically different and also their concentration cannot be the same. Similarly, by splitting off three molecules of water three different active centers can be formed. The same situation can be

found on other crystal planes, on crystal edges, etc. Pak (20) has arrived to similar conclusions on the basis of quantum-chemical analysis. The heating of oxides causes dehydration of their surface and a decrease in the mean coordination number of surface cations. This process is becoming more difficult with increasing dehydration of the surface and therefore the energy of the Me-O bond increases. For  $\text{Al}_2\text{O}_3$  Pak (20) came to the conclusion that also the acid strength of surface OH groups is changed with the degree of dehydration. According to Voltz and Weller (8,9) one molecule of water requires an area of  $10.8 \text{ \AA}^2$  of the surface of chromium oxide. Taking the value of  $10 \text{ \AA}^2$  we find that the concentration of dissociatively adsorbed water on fully covered surface is approximately  $17 \mu\text{mol}/\text{m}^2$ . Table 3 shows experimental concentrations around this value.

The results presented here show a strong dependence of the catalytic activity of chromium oxide on the structure of the catalysts which in turn is mostly influenced by the temperature of calcination. In our series of catalysts the specific area, size of crystallites, water content and surface concentration of water (or hydroxyl groups) are the properties which vary significantly and in the same order as activity. Also the intensive parameters which are

not dependent on the surface density of active sites exhibit a similar trend. This is in accord with findings of Dyne *et al.* (2) who report a change of activation energy of hydrogenolysis on chromium oxide after recrystallization of amorphous samples. All these variations can be explained qualitatively on the basis of changes of the number of surface  $\text{Cr}^{3+}$  ions and their state of coordination due to decrease of surface hydration. This conclusion has been supported by the results of spectroscopic studies of the catalysts which are presented in the following paper (21).

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