

## ACTIVE CENTRES ON CHROMIUM OXIDE-ZINC OXIDE CATALYSTS FOR DEHYDROGENATION

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Five catalysts ( $\text{Cr}_2\text{O}_3$ ,  $\text{ZnO}$  and three  $\text{Cr}_2\text{O}_3$ - $\text{ZnO}$  of varying composition) were studied from the point of view of the nature of the active centres for dehydrogenation of secondary alcohols. The experimental measurements included kinetics, deuterium isotope effects, influence on rate of added hydrogen, ketone, carbon monoxide and oxygen, resp., and IR, EPR and electronic reflectance spectra. It was concluded that the specific activity of the catalysts is given by relative densities of Cr and Zn sites on the surface and has only indirect connection to the bulk composition; the surface concentration of  $\text{Cr}^{3+}$  ions seems to be higher than the corresponding bulk concentration.

A number of proven industrial catalysts is prepared by mixing of two oxides or their precursors. As these species can often form one or more compounds the question arises which are the active components of the particular catalyst and which function have the others. One of such well-known composite catalysts is made from chromium(III) oxide and zinc oxide; preparations containing around 30% of  $\text{Cr}_2\text{O}_3$  are used for methanol synthesis. Catalysts of any composition are also active for dehydrogenation of alcohols as well as the pure components but maximum activity per unit mass of the catalyst is observed in the range of 30–50 mol% of  $\text{Cr}_2\text{O}_3$ . Because zinc chromite  $\text{ZnCr}_2\text{O}_4$  is formed when the mixture of oxides is calcined there might be a tendency to declare this compound for the most active component. However, if the activity is related to unit surface area a continuous decrease of activity from pure zinc oxide to chromium oxide is found<sup>1,2</sup>. This and other findings led to the conclusion<sup>2</sup> that zinc chromite is quite inactive for the dehydrogenation of 2-propanol and that the activity per unit mass of the preparations is proportional to the surface area of the free zinc oxide component which was estimated by electron microscopy.

The purpose of this work was to study the effect of composition of  $\text{Cr}_2\text{O}_3$ - $\text{ZnO}$  catalysts for the dehydrogenation of secondary alcohols using various methods for their characterization some of which were not available to the previous authors<sup>1,2</sup>.

TABLE I  
Properties of the Catalysts and Calculated Characteristics

Catalyst	1	2	3	4	5
Values	Structure and texture				
Cr <sub>2</sub> O <sub>3</sub> , w.%	100	78	54	28	0
Cr <sub>2</sub> O <sub>3</sub> , mol.%	100	65	38	18	0
Cr/(Cr + Zn), mol.%	100	79	56	30	0
Diffractogram	Cr <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub> ZnCr <sub>2</sub> O <sub>4</sub>	ZnCr <sub>2</sub> O <sub>4</sub>	ZnCr <sub>2</sub> O <sub>4</sub> ZnO	ZnO
Surface area (BET, m <sup>2</sup> /g)	23	44	46	33	3·2
	Spectral properties				
IR bands, cm <sup>-1</sup>	410	415	—	—	—
	—	515	515	515	—
	585	585	—	—	—
	—	630	630	630	—
	660	—	—	—	—
	—	940	940	940	—
Reflectance spectroscopy, B <sub>35</sub> , cm <sup>-1</sup>	450	470	630	660	—
EPR spectroscopy					
g-value	1·98	1·98	1·99	~ 1·98	~ 1·99
line width, Gauss	~600	480	1 400	~1 700	~1 100
	Kinetic parameters				
k (310°C), mol/h kg <sub>cat</sub>	23	62	596	364	130
k <sup>spec</sup> (310°C), mol/h m <sup>2</sup>	1·0	1·4	12·8	11·9	40·6
E, kJ/mol	141	143	131	132	140
Kinetic isotope effect, α	1·7	1·8	1·5	1·8	1·8
K <sub>R</sub> /K <sub>A</sub> (310°C)	2·8	3·9	3·1	3·1	2·9
K <sub>CO</sub> /K <sub>A</sub> (310°C)	0·0	0·33	1·00	1·07	1·53
K <sub>O<sub>2</sub></sub> /K <sub>A</sub> (310°C)	—	—	—	—	9·4
Kinetic isotope effect at p(O <sub>2</sub> ) = 6·9 kPa	1·0	1·2	1·4	1·6	2·5
r <sub>O</sub> <sup>spec</sup> (310°C), mol/h m <sup>2</sup> at p <sub>A</sub> = 50 kPa + + p(O <sub>2</sub> ) = 4 kPa	2·1	4·3	12·3	9·2	32·2
+ p(O <sub>2</sub> ) = 1·25 kPa	1·3	2·2	13·8	9·7	37·8
	Calculated fraction of Cr surface (b)				
from k <sup>spec</sup> (310°C)	1	0·99	0·70	0·73	0
from CO influence	1	0·99	0·64	0·71	0
from O <sub>2</sub> influence at p(O <sub>2</sub> ) = 4 kPa	1	0·93	0·66	0·76	0
at p(O <sub>2</sub> ) = 1·25 kPa	1	0·98	0·66	0·77	0

## EXPERIMENTAL

*Catalysts.* From an approx. 4% solution of chromium and/or zinc nitrates in water the hydroxides were precipitated by the addition of 3% solution of  $\text{NH}_3$  at room temperature under mixing. The precipitate was washed with water, filtered off and dried at  $120^\circ\text{C}$ . The solid was calcined at  $600^\circ\text{C}$  in air, crushed and the fraction of 0.1–0.25 mm was sieved out. The composition of the catalysts is given in Table I.

*Activity measurements.* An all-glass flow reactor was used with catalyst samples amounting from 0.1 to 0.5 g. Nitrogen was used as diluent of alcohol vapours in most experiments. The change of catalyst activity with time was tested; no decrease was observed in the range of 300 to  $380^\circ\text{C}$  where all measurements were made. For kinetic study the reactor was operated as a pseudo-differential one, i.e. the conditions were chosen in such a way as to keep the conversion under 10%. The initial rates were calculated as the ratio of conversion to reciprocal space velocity. The independence of the rate on the partial pressure of the alcohol in the feed has shown that the reaction is of zero order at all temperature levels. Alcohols used for kinetic measurements and estimation of deuterium isotope effect were the same as in previous papers<sup>3,4</sup>.

*Spectral measurements.* Infrared spectra were recorded using a UR-20 spectrometer (Zeiss, Jena) with the catalyst samples suspended in Nujol. Reflection spectra were measured on a VSU-2p spectrometer (Zeiss, Jena) in the range of 250–650 nm using magnesium oxide as a standard. EPR spectra were recorded on a JEOL-3BS spectrometer at an X-band frequency and a manganese standard was used for the determination of the  $g$ -value and line-width.

## RESULTS AND DISCUSSION

The measured properties of the catalysts are summarized in Table I. The X-ray analysis of the samples gave information about their phase composition and showed that with the exception of pure ZnO all preparations were microcrystalline. The surface area of the ZnO catalyst was by one order lower than that of other catalysts. All this is in accord with findings of other authors<sup>1,2,5,6</sup>. The results obtained by IR spectroscopy confirm the X-ray data. Spectrum of the sample 1 (Table I) contains absorption bands at 410, 585 and  $660\text{ cm}^{-1}$ , characteristic for microcrystalline  $\text{Cr}_2\text{O}_3$  (ref.<sup>7,8</sup>). In addition to these bands some new ones appeared in the spectrum of the sample 2 due to the  $\text{ZnCr}_2\text{O}_4$  spinel phase<sup>9</sup>. Spectra of the samples 3 and 4 exhibited only bands of the  $\text{ZnCr}_2\text{O}_4$  phase. Samples 2, 3 and 4 contained traces of zinc chromate as indicated by the absorption at  $940\text{ cm}^{-1}$  (cf.<sup>10</sup>).

It has been found in a preceding paper<sup>8</sup> that the Racah parameter<sup>11</sup>  $B_{35}$  is a valuable characteristics of chromia catalysts. Therefore the values of  $B_{35}$  were calculated from the reflectance spectra of the present samples 1–4 (Table I). The  $B_{35}$  values of the samples 1 and 2 are characteristic for  $\text{Cr}_2\text{O}_3$  ( $450$  and  $470\text{ cm}^{-1}$ ) but for the samples 3 and 4 ( $630$  and  $660\text{ cm}^{-1}$ ) values typical for the spinel structure<sup>11</sup> were obtained. This is an evidence of close similarity in the surrounding of  $\text{Cr}^{3+}$  ions in sample 1 and 2 or 3 and 4, resp.

The results from EPR measurements are summarized also in Table I. Spectrum of the sample 1 is typical for chromia and its nature has been already discussed<sup>8</sup>.

The strong symmetrical signal present in the spectrum of the sample 3 with a  $g$ -value of 1.99 is very close to that reported in the literature for a similar system<sup>1,2</sup>. In the spectrum of the sample 2 line narrowing was observed due probably to the  $\text{Cr}_2\text{O}_3$  particle size homogenation under the influence of zinc oxide. The dilution of the  $\text{ZnCr}_2\text{O}_4$  phase with  $\text{ZnO}$  in the sample 4 increases the dipole-dipole interaction between the particles with non-uniform structure and as a result of it the line-width also increases. The EPR signal from zinc oxide (our sample 5) was assigned to conduction electrons; no connection of this signal with catalytic activity has been detected<sup>1,3</sup>. Results from the EPR investigation emphasize the role of chromium oxide as a textural promotor which has been discovered by Germain and coworkers<sup>2-5</sup>.

The activity of the catalysts was compared using 2-propanol as the reactant. Kinetics of its dehydrogenation was measured with each catalyst in the temperature range of 30°C between 280 to 350°C according to the activity of the sample. The interpolated values of the rate constants for 310°C were read from Arrhenius diagrams and are given in Table I together with calculated activation energies. Maximum activity per unit weight of catalyst was found with sample 3; however, the specific rate constant (per unit surface area) increased from pure chromium oxide to pure zinc oxide by approx. one and half order of magnitude. This again corresponds well with reports of the previous authors<sup>1,2</sup>.

The found zero order kinetics agrees with observations of García de la Banda and coworkers<sup>1</sup>. However, the activation energies (131–143 kJ/mol, *i.e.* 31–34 kcal/mol) are higher than those found by these authors (8–10 kcal/mol) but are the same as reported by Germain and coworkers<sup>2</sup> who on the other hand observed non-zero, low-order kinetics (0.1 to 0.4). In spite of these minor differences we can conclude that our preparations were closely related to those used by the mentioned authors<sup>1,2</sup>.

The basic kinetic measurements were expanded in order to obtain further information about the reaction and catalysts. Acetone, *i.e.* one of the reaction products, was added to the feed and a decrease of rate was observed with all catalysts. The rate data were evaluated under the assumption that the zero order observed with pure isopropanol feed develops from a Langmuir-Hinshelwood rate equation for initial conditions

$$r = kK_A p_A / (1 + K_A p_A), \quad (1)$$

if  $K_A p_A \gg 1$ .  $r$  denotes initial reaction rate,  $k$  rate constant,  $p_A$  partial pressure of 2-propanol in the feed and  $K_A$  adsorption coefficient of the alcohol. Germain and coworkers<sup>2</sup> have estimated  $K_A$  values in the range of 3 to 12  $\text{MPa}^{-1}$  which support our assumption. When the product (R) is present in the feed Eq. (1) changes to

$$r_R = k_A p_A / (1 + K_R p_R + K_A p_A). \quad (2)$$

The ratio of the initial reaction rates without and with acetone in the feed, other conditions being the same, does not contain the rate constant  $k$ :

$$r/r_R = (1 + K_A p_A + K_R p_R)/(1 + K_A p_A). \quad (3)$$

Omitting 1 in both the numerator and denominator we obtain after rearrangement

$$r/r_R - 1 = (K_R/K_A) (p_R/p_A). \quad (4)$$

This expression allowed us to evaluate the relative adsorption coefficient of acetone ( $K_R/K_A$ ). The mean values calculated from experimental results obtained with two different partial pressures of acetone in the feed ( $p_R = 25$  and  $50$  kPa) are given in Table I. Considering the relatively low accuracy of these measurements we can say that the values are practically the same for all catalysts. When hydrogen was used instead of nitrogen as the diluent no change of rate was observed; this shows that the adsorption of the second product is quite low.

In the next series of experiments the kinetic isotope effect of deuterium placed on the  $\alpha$ -carbon atom was studied. The initial reaction rates of  $\text{CH}_3\text{-CHOH}\cdot\text{CH}_3$  and  $\text{CH}_3\text{-CDOH}\cdot\text{CH}_3$  were put into the ratio  $\alpha = k_H/k_D$  with the results summarized in Table I. Again, the effect is the same for all catalysts; its value shows that the splitting of the  $\text{C}_\alpha\text{-H}$  bond takes part in the rate determining step.

The constancy of values of activation energy, of kinetic isotope effect and of relative adsorption coefficient of acetone in the series of catalysts suggests the same reaction mechanism of dehydrogenation on all catalysts. This is rather surprising in view of the varying chemical and phase composition. However, no other explanation seems to be adequate. Germain and coworkers<sup>2</sup> confronted with a similar situation suggested that the reaction takes place only on Zn sites chromium being completely bound in the inactive spinel  $\text{ZnCr}_2\text{O}_4$ . However, their series of catalysts included only mixtures from 50 to 100% of ZnO. Our series contains also samples with excess of  $\text{Cr}_2\text{O}_3$  and therefore their explanation can not be accepted here.

If we assume the same reaction mechanism on all catalysts including pure ZnO and pure  $\text{Cr}_2\text{O}_3$  the question arises what causes the differences in specific activities. In this connection it was interesting to calculate the site densities from parameters of the Arrhenius equation because the observed zero order corresponding to a high coverage of the surface allows to use a simple procedure<sup>14</sup>. For pure  $\text{Cr}_2\text{O}_3$  the site density was estimated to approx.  $10^{15}$  sites per  $\text{cm}^2$ , for pure ZnO approx.  $10^{16}$  sites per  $\text{cm}^2$ . However, neither the data nor the method are accurate enough for declaring this difference as a significant one.

Further measurements were made with the goal to bring some light onto the quality of active sites on different catalysts. A series of experiments was conducted with

carbon monoxide substituting nitrogen as a diluent of isopropanol ( $p_A = 50$  kPa,  $p_{CO} = 50$  kPa,  $350^\circ\text{C}$ ). Practically no change in rate was found with chromia and a decrease appeared with the presence of ZnO and increased with its content. The results were evaluated as relative adsorption coefficients of carbon monoxide using Eq. (4) ( $R = \text{CO}$ ). Table I shows the calculated values of  $K_{CO}/K_A$ . The observed trend agrees with the literature<sup>15</sup> which reports adsorption of CO on  $\text{Cr}_2\text{O}_3$  about one order smaller than on ZnO under comparable conditions.

For quantitative interpretation of the observed changes in the rate and in the influence of CO with the composition of the catalysts the assumption was accepted that the surface consists of active centres containing either  $\text{Cr}^{3+}$  or  $\text{Zn}^{2+}$  atoms which work independently. Both types of centres act in the same way, *i.e.* they attack the  $\text{C}_\alpha\text{—H}$  bond in the rate determining step<sup>5</sup> but they differ in their density on different catalysts. Then the observed specific rates (per unit of surface area) on mixed catalysts can be separated into a linear combination of specific rates on pure components,

$$k^{\text{spec}} = b k_{\text{Cr}}^{\text{spec}} + (1 - b) k_{\text{Zn}}^{\text{spec}}, \quad (5)$$

where  $b$  denotes the fraction of the surface formed by the chromium component. The results of the calculation of  $b$  using  $k^{\text{spec}}$  values for  $310^\circ\text{C}$  are given in the last section of Table I. They indicate preferential occurrence of chromium on the surface of mixed catalysts.

Quite recently, Rozovskij and coworkers<sup>16</sup> measured the fraction of Zn sites on  $\text{ZnO—Cr}_2\text{O}_3$  mixtures (1 : 1 by weight, roughly corresponding to our sample 3) calcinated at  $550^\circ\text{C}$ , by selective chemisorption of  $\text{CO}_2$ . Their samples had a low surface area and the fraction of Zn sites was approx. 0.1, even smaller than in our case.

The assumption about independent action of two types of active centres was checked by calculation of  $b$  from the decrease of the rate in the presence of CO. Supposing that CO is not adsorbed on chromium centres (*cf.*<sup>15</sup>;  $K_{\text{CO}}^{\text{Cr}}/K_A^{\text{Cr}} = 0$  for  $\text{Cr}_2\text{O}_3$ , see Table I) and that Eq. (2) without 1 in the denominator is valid, the formula

$$r^{\text{spec}} = b k_{\text{Cr}}^{\text{spec}} + (1 - b) \frac{k_{\text{Zn}}^{\text{spec}}}{1 + K_{\text{CO}}^{\text{Zn}} p_{\text{CO}}/K_A^{\text{Zn}} p_A} \quad (6)$$

has been derived. The ratio  $K_{\text{CO}}^{\text{Zn}}/K_A^{\text{Zn}}$  was taken from Table I (1.53). The calculated values of  $b$  for  $p_A = 50$  kPa,  $p_{CO} = 50$  kPa and for  $350^\circ\text{C}$  are given in the last section of Table I. They agree fairly well with the  $b$  values calculated by Eq. (5).

Germain and coworkers<sup>2</sup> have found a reversible poisoning of the  $\text{Cr}_2\text{O}_3\text{—ZnO}$  catalysts by oxygen. Our experiments with oxygen (Table I and Fig. 1) showed similar

decrease of rate of acetone formation with catalysts 3 to 5 (which correspond to Germain's preparations) and a steep increase with catalysts 1 and 2 where chromium predominates. The effect was so dramatic (see Fig. 1) that a change of mechanism from simple dehydrogenation to oxidative dehydrogenation was suspected. Therefore the kinetic isotope effect was measured at the presence of oxygen with the results summarized in Table I. With pure chromium(III) oxide the isotope effect was absent and the value of  $\alpha$  increased with the content of ZnO confirming a change of mechanism. The differences in behaviour of chromium-rich and zinc-rich catalysts could again be explained on the basis of literature data on oxygen adsorption<sup>15</sup> which is by one order larger on  $\text{Cr}_2\text{O}_3$ .

The experiments with oxygen gave opportunity to test further the assumption on two independent types of active centres. Supposing that in the presence of  $\text{O}_2$  on zinc centres only the simple dehydrogenation and on chromium centres only the oxidative dehydrogenation proceeds, the rates on mixed catalysts can be again written as a linear combination of rates on chromium and on zinc fraction of the surface

$$r_{\text{O}}^{\text{spec}} = b r_{\text{Cr,O}}^{\text{spec}} + (1 - b) r_{\text{Zn,O}}^{\text{spec}}, \quad (7)$$

$r_{\text{O}}^{\text{spec}}$  denotes rate values obtained in the presence of oxygen (see third section of Table I). The values of  $b$  found by means of Eq. (7) for two oxygen partial pressures are given in the bottom section of Table I and they show the same trend as the results of previous calculations.

The question may arise why the additivity of contributions of Zn and Cr surface fractions holds over the whole composition range. However,  $\text{Cr}^{3+}$  ions have a very high preference for octahedral and  $\text{Zn}^{2+}$  ions for tetrahedral coordination<sup>17,18</sup>. It follows that in all samples studied (in spite of they containing various mixtures

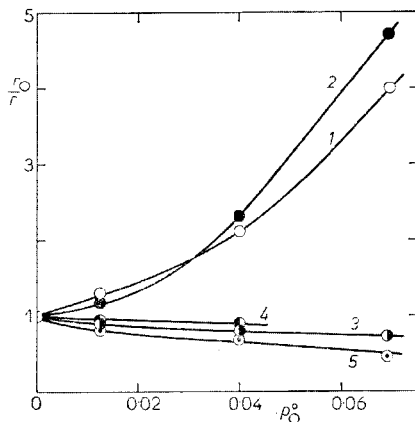


FIG. 1  
Relative Change in Rate of Dehydrogenation  
of 2-Propanol in Dependence on Addition  
of Oxygen

of  $\text{Cr}_2\text{O}_3$ ,  $\text{ZnO}$  and  $\text{ZnCr}_2\text{O}_4$ ) we may assume that  $\text{Cr}^{3+}$  ions always occupy octahedral and  $\text{Zn}^{2+}$  tetrahedral sites in the lattice and therefore exhibit similar catalytic properties at any composition.

The agreement of calculation of  $b$  from various data indicate that the simple model of surface consisting of independently acting chromium and zinc dehydrogenation centres is very probably not far from reality. The relative concentrations of these two types of centres will depend on preparation procedure and calcination temperature of the catalysts. Further on, one may expect a certain heterogeneity within each type of centres given by the position of an atom in a certain type of crystal plane of a catalyst component ( $\text{Cr}_2\text{O}_3$ ,  $\text{ZnCr}_2\text{O}_4$ ,  $\text{ZnO}$ ). This may explain minor differences in properties observed by various authors and also some irregularities found in the present work which were not considered in the discussion in order not to obscure the general picture. Such a discrepancy is the high value of the isotope effect with pure  $\text{ZnO}$  in the presence of oxygen. Surface heterogeneity and preferential poisoning of a certain fraction of centres might result in a change of the observed mean value of  $\alpha$  from 1.8 to 2.5.

Another distinction between the catalysts 1 and 2 with the surface formed entirely or almost entirely by chromium atoms and catalysts 3 to 5 with partial or full employment of zinc atoms was obtained by measuring the rates of dehydrogenation of a series of alcohols  $\text{CH}_3\text{CHOH.R}$  at  $310^\circ\text{C}$ . The groups R were methyl, ethyl, isopropyl, isobutyl and tert-butyl. An attempt was made to correlate linearly the found rate constants for the series of alcohols on a single catalyst in the coordinates of the Taft equation<sup>19</sup> using either polar  $\sigma^*$  or steric  $E_s$  constants for the group R. With data for the catalysts 1 and 2 a better correlation was obtained with  $\sigma^*$  constants whereas for the catalysts 3 to 5  $E_s$  constants seemed to be more suitable. However, the data were not sufficiently precise in order to discriminate the correlations with certainty. Therefore the approach which has been applied with success previously<sup>4</sup> was adopted here, *i.e.* the rate data for the series of the alcohols on catalyst 1 were used as the standard set and the data for other catalysts were linearly correlated against it. The slope  $a$  of this linear free energy relationship<sup>4</sup> is a measure of the sensitivity of the reaction rate to structural changes and its values express the relative changes of the energy of the transition state in the series of the compared catalysts. For the catalysts 1 and 2 the value of  $a = 1$  was found, the catalysts 3 and 4 gave  $a = 0.3$  and for the catalyst 5 also a low value of 0.5 was obtained. Thus the catalysts with the surface formed entirely by chromium sites are characterized by higher values of  $a$ . The reason for it is not clear; in the light of our experience with the Taft correlations we suspect that it might be connected with different steric requirements of the Cr and Zn centres. It is of interest that the same distinction between sample pairs 1, 2 and 3, 4 was obtained by reflectance spectroscopy.

It can be concluded that in the system  $\text{Cr}_2\text{O}_3\text{—ZnO}$  as a dehydrogenating catalyst the activity per unit mass is mostly determined by the occurrence of zinc component



on the surface. Chromium component contributes only little to the activity but its main function is to increase the surface area as also the spectroscopical investigation have pointed out. This textural promotion effect has been declared by Germain and coworkers<sup>2</sup> for the only function of chromium oxide which according to their interpretation has the unfavourable influence of binding a part of ZnO in the inactive compound  $\text{ZnCr}_2\text{O}_4$ . However, our results indicate that irrespectively of the phase composition of the bulk, the specific activity is given by relative densities of zinc and chromium sites on the surface. As chromium tends to have higher surface concentration than corresponding to the bulk concentration the change of specific activity with change of composition might be quite complicated. The activity per unit mass which is important for practical catalysis is further dependent on surface area which also changes appreciably with composition. Thus the quality of  $\text{Cr}_2\text{O}_3$ —ZnO catalysts might be very sensitive to conditions of preparation.

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