Electronic Factor in Catalysis

I. Decomposition of Isopropyl Alcohol

By

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With 4 figures

The dehydrogenation of isopropyl alcohol on ZnO catalysts doped with Li_2O or Ga_2O_3 has been studied in the temperature range of 370—445°C at various contact times. Seebeck potential measurements were used to determine the nature and relative concentration of charge carriers in the catalysts. Conductivity-changes during reaction and also on adsorption of hydrogen and acetone have been studied. The mechanism of the dehydrogenation of isopropyl alcohol on n-type catalysts is discussed.

Introduction

Recent studies[1] have shown that the catalytic activity of zinc oxide for the dehydrogenation of primary and secondary alcohols is markedly affected by the incorporation of minute amounts of mono- and tri-valent cations (e.g. Li^+ and Ga^{3+}) and by pretreatment with hydrogen and oxygen[2]. The addition of "altervalent" cations ("doping") has also been shown to alter the Fermi level of this oxide in opposite ways. Ga^{3+} raises it, while Li^+ lowers it so remarkably that at Li_2O concentrations greater than 1 mole per cent the conduction is reported to change from n- to p-type[1]. Hauffe[3] and Wolkenstein[4]

[1] J. Deren, B. Crzybowska and B. Russer, Bull. Polish. Akad. Sci. Ser. Sci. Chem. 15 (1967) 491.

[2] R. L. Moss, Chem. Engng. 199 (1966) 114.

[3] K. Hauffe, Angew. Chem. 7 (1955) 189.

[4] Th. Wolkenstein, Advances in Catalysis 12 (1960) 189; "The Electronic Theory of Catalysis on Semiconductors", Pergamon Press, Oxford 1963, p. 66.

have attempted to relate selectivity for dehydrogenation to the position of the Fermi level of electrons in the oxides, but their theories lead to mutually contradictory correlations between changes in Fermi level and catalyst-selectivity. The present paper reports a comparative study of the catalytic activities of ZnO, $ZnO + 1\%$ Li_2O and $ZnO + 1\%$ Ga_2O_3 for the decomposition of isopropyl alcohol combined with electrical measurements with a view to elucidate the rôle of the electronic factor in this type of catalysis.

Experimental

Zinc oxide was obtained by the decomposition of zinc oxalate in air at 500 °C for 16 hours. Pure zinc oxalate was prepared by the addition of the required amount of zinc nitrate to a hot solution of ammonium oxalate. The contents were heated to about 100 °C and kept at that temperature for one hour to ensure complete precipitation. The precipitate of the oxalate was filtered, washed and dried at 100 °C. Zinc oxide doped with Li_2O or Ga_2O_3 was prepared by mixing the aqueous slurry of ZnO with required amounts of the respective nitrate solutions, evaporating to dryness and subsequently calcining the residue in air for 16 hours at 500 °C. All chemicals used were of purest analytical reagent quality.

The reaction studies were carried out in a flow type reactor similar to the one described by UPRETI et al.[5]. The liquid products (unreacted alcohol, acetone and water) were analysed gas chromatographically and propylene in the gas product estimated by Orsat analysis.

The changes in conductivity during reaction were measured *in situ* using the technique of BIELANSKI et al.[6]. One of the pellets of the catalyst was held tightly between two platinum discs and the leads from these electrodes were connected to a potentiometer (used as a variable e.m.f. source) and a sensitive micro-ammeter (Hewlett-Packard Model 425 A). From the e.m.f. applied and the current-reading, the resistance of the sample was deduced at various time intervals while the reaction was occurring over the catalyst.

Changes in conductivity arising from adsorption of hydrogen and acetone were ascertained on powdered samples placed in a conductivity cell attached to a volumetric adsorption apparatus. The oxide powder

[5] M. C. UPRETI, J. C. KURIACOSE and M. V. C. SASTRI, Bull. Polish. Akad. Sci. Ser. Sci. Chem. **11** (1963) 651.

[6] A. BIELANSKI, J. DEREN, J. HABER and J. NEDOMA, Przemys. chem. **12** (1956) 642.

was placed in a small cup between two platinum foils, the upper foil being kept pressed against the sample with the help of a glass disc which was surmounted by a container loaded with lead shots.

The thermoelectric potentials of these oxide samples were measured by the method described by Dunlap[7]. The nature and the relative concentrations of charge-carriers were deduced from the direction and magnitude of the current passing between the hot and cold junctions.

Results

Thermoelectric potential measurements showed that all the three catalysts were n-type semiconductors and that the concentrations of charge-carriers (electrons) in ZnO doped with Li^+, ZnO and ZnO doped with Ga^{3+} were in the ratio of $2:3:4$. In an atmosphere of oxygen the n-type semiconductivity of zinc oxide decreased, without however showing the charge reversal reported by Cimino et al.[8]. The adsorption of hydrogen increased the conductivity of zinc oxide above 100°C and, in accordance with earlier observations with ZnO[9], the conductivity isobar showed a maximum around 180°C. The conductivity of zinc oxide decreased when acetone was adsorbed indicating the decrease in the number of current carriers.

All the three catalysts behaved predominantly as dehydrogenation catalysts, the dehydration being less than 10 mole per cent. The dehydrogenation reaction was studied in the temperature range of 370—445°C at various contact times. The plots of activity vs temperature at fixed contact time, are shown in Fig. 1. From the graphs of contact time vs concentration at various temperatures, the initial

Table 1. *Apparent activation energies for the dehydrogenation of isopropyl alcohol*

Catalyst	Activation energy kcal/mole
Zinc oxide	11.6
Zinc oxide + 1% Li_2O	16.8
Zinc oxide + 1% Ga_2O_3	8.7

[7] W. C. Dunlap, "An Introduction to Semiconductors", John Wiley and Sons, Inc., New York 1960, pp. 189—194.

[8] A. Cimino, F. Molinari and F. Cramarossa, J. Catalysis 2 (1963) 315.

[9] T. S. Nagarjunan, M. V. C. Sastri and J. C. Kuriacose, Proc. Nat. Inst. Sci. India 27 (1961) 496.

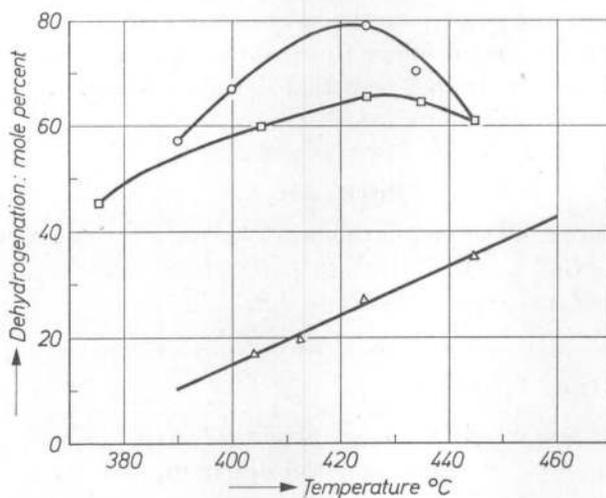Fig. 1. Variation of dehydrogenation reaction as a function of temperature.
□ ZnO (contact time = 1.9 sec); ○ $ZnO + 1\%\ Ga_2O_3$ (c. t. = 1 sec); △ $ZnO + 1\%\ Li_2O$ (c. t. = 2.25 sec)

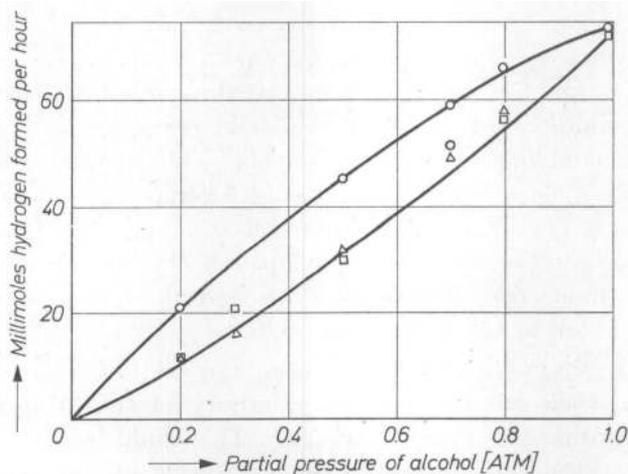Fig. 2. Effect of partial pressure of nitrogen, hydrogen and acetone on the dehydrogenation of isopropyl alcohol on ZnO. ○ Nitrogen, △ Acetone, □ Hydrogen

rates were deduced and these were used for the calculation of the apparent activation energies given in Table 1.

The individual effects of the reaction products, hydrogen and acetone, on the dehydrogenation of isopropyl alcohol on ZnO were

studied at 425 °C and at a contact time of one second. For comparison, the activity was evaluated under the same conditions, using nitrogen as diluent. It is seen from Fig. 2 that both hydrogen and acetone inhibit the dehydrogenation reaction almost to the same extent.

Discussion

Two correlations observed in this work between electrical measurements and reaction-kinetics data are particularly noteworthy. These are the linear relationships:

a) between conductivity-change ($\Delta \log \sigma$) during reaction and the reaction yield (Fig. 3), and

b) between the relative charge-carrier concentrations (from Seebeck potential measurements) and the apparent activation energies (Fig. 4).

The observed effects of Ga^{3+} and Li^+ on the Fermi level of the zinc oxide are thus closely paralleled by their effects on the dehydrogenating activity of the oxide, in accordance with the views of Wolkenstein[4].

The maxima observed in the temperature-concentration plots (Fig. 1) for ZnO and ZnO doped with Ga reveal that these two catalysts, being predominantly n-type semiconductors, promote the backward reaction, thus enabling rapid attainment of equilibrium on the surface. Earlier studies[10] on the hydrogenation of acetone have shown that this reaction is favoured by electron-rich surfaces. The absence of any such maximum in the case of Li-doped ZnO might be because it behaves as an electron-deficient surface and does not favour the backward reaction to any appreciable extent.

It is interesting to note that hydrogen and acetone which behave differently in their effect on the conductivity of the sample, have the same retarding effect on the reaction. This could be due to competition by acetone and hydrogen for adsorption on the same pair of sites as are required for the dehydrogenation of the alcohol.

Since the adsorption of alcohol, like that of hydrogen, increases the conductivity of the oxide, it is inferred that the alcohol molecule is attached to the surface through the H-atom of the OH-group. The observation that acetone and hydrogen (which affect the conductivity

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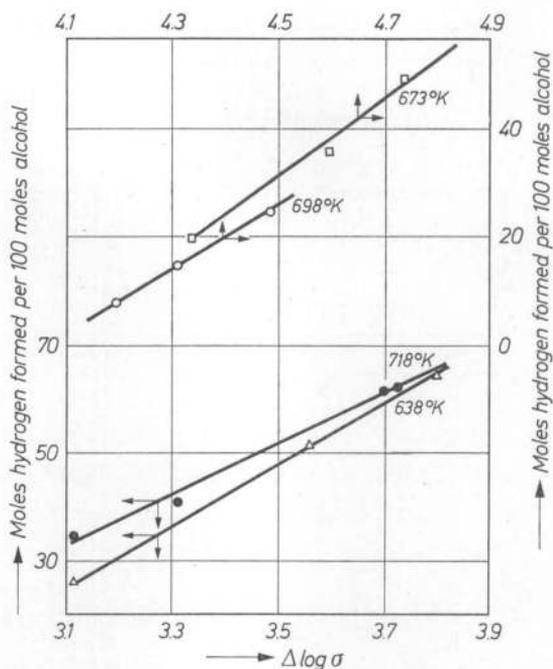[10] C. Daniel and J. C. Kuriacose, Indian J. Chem. 6 (1968) 645.

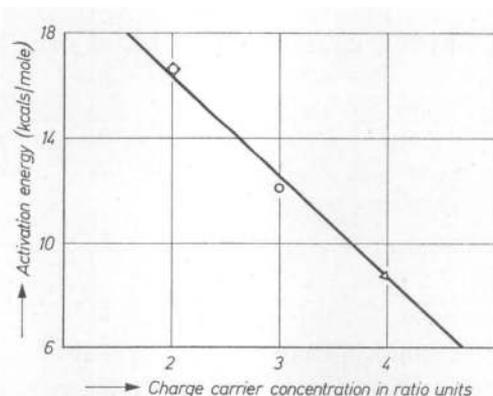Fig. 3. Relationship between conductivity change and reactivity for dehydro-
genation

Fig. 4. Variation of activation energy with charge carrier concentration. △ Zinc
oxide doped with *Ga*, ○ Pure *ZnO*; ◈ *ZnO* doped with *Li*

of the oxide oppositely) equally inhibit the dehydrogenation, suggests
a second point of attachment which, like the adsorption of acetone,
is presumably through the oxygen atom.

To sum up, the overall mechanism of the dehydrogenation of isopropanol on zinc oxide may be represented as follows:
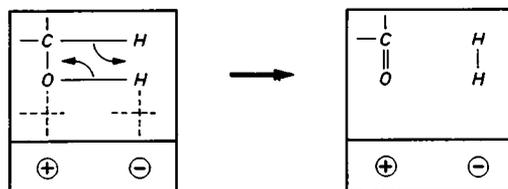
1. Initial adsorption of the alcohol through the hydrogen of the hydroxyl group.

$C_3H_7OH +$
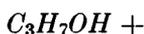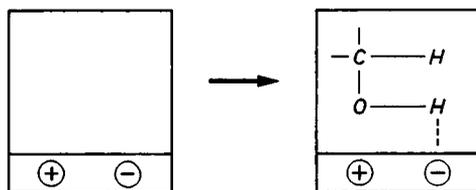
2. The primary adsorption state transforms into a two point adsorption involving both hydrogen and oxygen of the hydroxyl group.
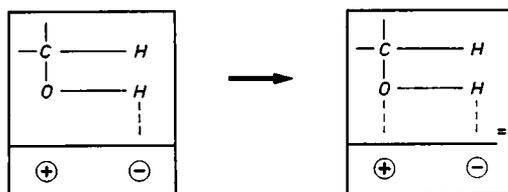
3. Acetone and hydrogen are desorbed leaving the surface in its original state.

In the above reaction sequence, the desorption of acetone cannot be the rate determining step, as claimed by HAUFFE, since hydrogen and acetone inhibit the reaction to the same extent. According to WOLKENSTEIN, the initial adsorption of the alcohol (step 1) is the rate determining step in the dehydrogenation reaction. This is also unlikely, since the initial step is an electron-transfer process, analogous to the adsorption of hydrogen, which has been observed to be fast. It is more likely that either step (2), involving the adsorption of

alcohol through oxygen of the hydroxyl group, or the subsequent rearrangements and desorption (step 3), might be rate determining on these catalysts.

Acknowledgements