

Short Communication

On the Dehydrogenation of Isopropanol over a Zinc Oxide Catalyst

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From mechanistic studies on the dehydrogenation of isopropanol on a $ZnO-Al_2O_3$ coprecipitated catalyst it has been concluded that the rate determining step is the desorption of acetone¹. Literature data^{2–5} on the dehydrogenation of this alcohol over ZnO are also in agreement with this view. However, a recent paper by VISWANATHAN, SASTRI and SRINIVASAN⁶ on the dehydrogenation of isopropanol on ZnO throws some doubt on this mechanism. An attempt is made here to clarify this point.

A ZnO catalyst was prepared as described by VISWANATHAN et al.⁶ and the dehydrogenation of isopropanol on it was studied in a flow reactor functioning at atmospheric pressure as described previously¹. The influence of hydrogen, nitrogen and acetone on the catalyst was studied at 330 °C and at a contact time of 0.89 seconds. Products were analysed by the vapour phase chromatographic technique using a carbowax column.

Fig. 1 shows the extent of dehydrogenation of isopropanol over ZnO at various partial pressures, the dilution being effected by either nitrogen or the products of the reaction. Hydrogen has no effect on the catalytic activity and acetone increases the dehydrogenation at low

¹ R. UMA and J. C. KURIAKOSE, Indian J. Chem. **10** (1972) 69.

² E. WICKE, Z. Elektrochem. angew. physik. Chem. **53** (1949) 279.

³ A. EUCKEN, Naturwissenschaften **36** (1949) 48.

⁴ G. M. ZHABROVA, Chem. Tech. [Berlin] **15** (1963) 193.

⁵ K. HAUFFE, Advances in Catalysis **7** (1955) 213.

⁶ B. VISWANATHAN, M. V. C. SASTRI and V. SRINIVASAN, Z. physik. Chem. Neue Folge **79** (1972) 216.

partial pressures but inhibits it at higher pressures. Electrical resistance measurements of the catalyst in the presence of different reagents using a Keithley Electrometer reveal that acetone, hydrogen and isopropanol, all get adsorbed by donating electrons to the catalyst surface. The increase and decrease in electrical resistance of *p*-type *NiO* and *n*-type *ZnO* respectively, on adsorption of acetone, prove that

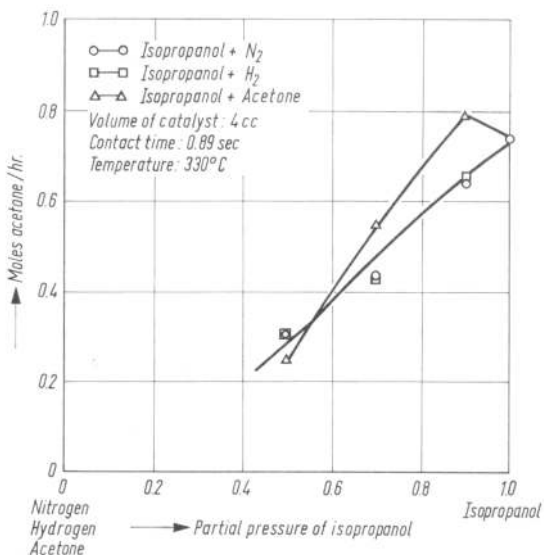
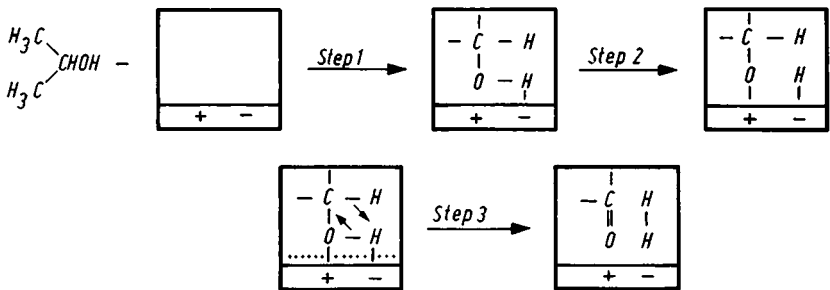


Fig. 1. Effect of nitrogen, hydrogen and acetone on the rate of decomposition of isopropanol over *ZnO*

the electrical resistance measured is a result of an interaction between the solid and the reactant and not due to other causes like surface film formation or liquefaction in the pores.

WICKE², EUCKEN³, ZHABROVA⁴ and HAUFFE⁵ have concluded that desorption of acetone is the rate determining step for the dehydrogenation of isopropanol on *ZnO*. BIELANSKI et al.⁷ have also arrived at a similar conclusion regarding the rate determining step for the same reaction over *NiO* which unlike *ZnO* is a *p*-type semiconductor. However, VISWANATHAN et al.⁶ suggest the following mechanism:

⁷ A. BIELANSKI, J. DEREN and J. HABER, Bull. Acad. polon. Sci. **7** (1959) 345.



and conclude that "it is more likely that either step 2 involving the adsorption of alcohol through oxygen of the $O-H$ group or the subsequent rearrangements and desorption, step 3, might be rate determining on these catalysts."

Since both hydrogen and acetone inhibit the activity to the same extent, VISWANATHAN et al.⁶ conclude that isopropanol is attached to the surface at two points through the hydrogen and oxygen atoms of the $O-H$ group. If such were the case, the effect of adsorption of isopropanol on the electrical conductivity should be small since the adsorption of the H and the O of the alcohol would practically neutralise the alterations their adsorption will produce in the electrical conductivity of ZnO , unless the adsorption through the hydrogen is very strong compared to that through oxygen.

The inhibition by hydrogen as well as acetone observed by VISWANATHAN et al.⁶ could be explained if the adsorption of isopropanol can be considered the rate determining step. Isopropanol as well as hydrogen being adsorbed by a donor process there will be mutual inhibition of the adsorption of each other. So, the rate of the reaction can be decreased by hydrogen. The facilitation of the desorption of hydrogen due to the increased n -typeness of the catalyst will prevent desorption of hydrogen becoming rate determining. Adsorption of acetone on the other hand, being an acceptor process, should increase the adsorption of isopropanol. But the sizes of isopropanol and acetone being comparable, it is possible that the surface available for isopropanol is being considerably reduced by the acetone leading to a decrease in rate. The desorption of the product, acetone, must be facilitated by the preadsorption of acetone and so desorption of acetone cannot be the rate determining step under these conditions. Incidentally, the acceptor adsorption of acetone observed by VISWANATHAN et al.⁶ is

contrary to the observations of previous workers^{8,9} as well as our own observations.

We have found that hydrogen has no effect on the dehydrogenation activity while low concentrations of acetone enhance the rate and high concentrations decrease the rate, a behaviour similar to that observed on a $ZnO-Al_2O_3$ coprecipitated catalyst¹. These results suggest that adsorption of isopropanol cannot be the rate determining step because (i) hydrogen and isopropanol, both get adsorbed by a donor process and yet hydrogen has no effect on the dehydrogenation activity even at high concentrations and (ii) at low concentrations of acetone, in spite of the increase in n -typeness of the surface brought about by the adsorption of acetone which should actually retard the adsorption of isopropanol, there is an increase in rate. The activity trend can, however, be easily explained assuming desorption of acetone to be the rate determining step. Hydrogen being a small molecule may not affect the adsorption of isopropanol to any considerable extent through coverage of the surface. Further, as in the case of $ZnO-Al_2O_3$ catalysts¹, the strength of adsorption of hydrogen may be less than that of isopropanol and so its competitive effect may not be much when mixed with isopropanol and passed over the catalyst. Acetone desorption involves acceptance of electrons from the surface. So, increase in the electron concentration of the surface brought about by acetone adsorption increases the rate of dehydrogenation when the acetone concentration is small. At high acetone concentration, while the electronic effect is still beneficial, the surface coverage by the large acetone molecules deprives isopropanol of access to the surface. The consequent low adsorption of isopropanol makes its adsorption rate determining under these conditions. Thus the rate of dehydrogenation is depressed. In the presence of high concentrations of acetone there is therefore a change in the rate determining step.

VISWANATHAN et al.⁶ have also drawn a correlation between reaction rate, the energy of activation for the dehydrogenation reaction and the concentration of charge carriers for ZnO and ZnO doped with Ga and Li oxides. The charge carrier concentration decreases in the order Ga doped oxide $>$ ZnO $>$ Li doped oxide. The energy of activation for the dehydrogenation reaction as well as the rate show a similar

⁸ A. BIELANSKI, "Catalysis and Chemical Kinetics", Academic Press Inc., 1964, p. 93.

⁹ J. F. GARCIA DE LA BANDA, Actes Congr. Int. Catal. II, Editions Technip, Paris 1961, vol. 2, p. 1763.

trend. If the same mechanism with the same rate determining step is operative on all these three catalysts and the effect is only due to the electron concentration, then, the energy of activation should not change from one catalyst to another. It is to be inferred therefore that even if the overall mechanism is the same on the three catalysts, the rate determining steps might be different. Hence their results do not permit drawing any conclusions as to the mechanism of dehydrogenation on pure ZnO .

Our results confirm the accepted view that the desorption of acetone is the rate determining step in the dehydrogenation of isopropanol on a ZnO catalyst.

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