

Influence of the Method of Preparation on the Activity of ZnO-Al₂O₃ Catalysts

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ZnO-Al₂O₃ catalysts prepared by impregnation as well as coprecipitation have been investigated for the decomposition of isopropanol. Coprecipitated catalysts have better dehydrogenation properties while the impregnated catalysts exhibit better dehydration properties. In both the preparations, depending upon the composition, the seat of dehydrogenation activity is the ZnO-ZnAl₂O₄ or ZnO-Al₂O₃ interface. The micropores in the catalysts influence the dehydration activity considerably.

THE catalytic activity of a solid depends upon its physical and chemical properties. These in turn are dependent on the method of preparation of the catalyst. The present paper deals with the influence of the mode of preparation of a ZnO-Al₂O₃ catalyst on its activity for the decomposition of isopropanol.

Experimental :

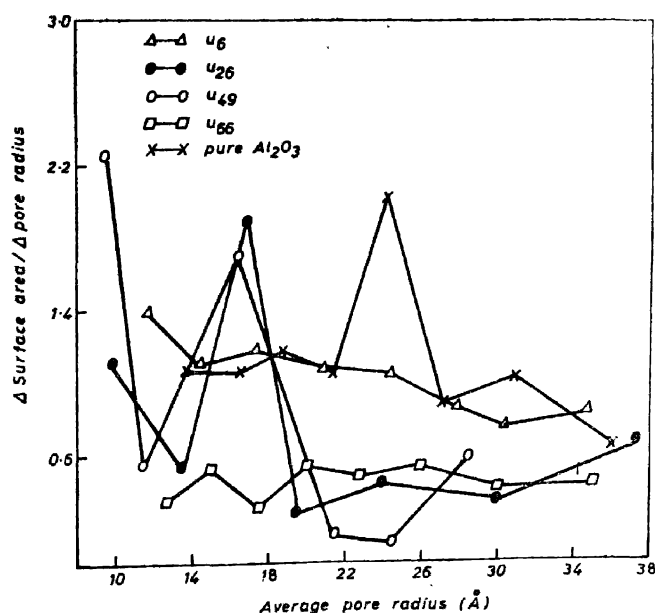
ZnO-Al₂O₃ catalysts prepared by two different methods namely impregnation and coprecipitation were used for the study of the decomposition of isopropanol. The preparation of the impregnated catalysts is described in an earlier paper¹. The impregnated samples obtained by using unsintered Al₂O₃ are labelled U. When sintered Al₂O₃ is used for the preparation, the catalyst is labelled S. The effect of high-temperature treatment of the catalyst on its activity was studied by sintering both the U and the S catalysts at 840° for 12 hr. They are labelled US and SS respectively. Coprecipitated catalysts were prepared by precipitating the respective hydroxides simultaneously from a mixture of the nitrate solution by the addition of ammonia. The precipitate was filtered, washed free of nitrate, dried at 110° and then heated at 400° for 6 hr. This catalyst is labelled C. In each series, catalysts containing different proportions of ZnO were prepared to study the effect of composition on the catalytic activity. The ZnO

content in them were estimated by dissolving the sample in sulphuric acid and titrating the ZnSO₄ formed against standardised ferrocyanide². The percentage of ZnO in each catalyst is indicated by a suffix eg. U₅₀. This denotes a catalyst prepared by using unsintered Al₂O₃ and contains 50% by weight of ZnO.

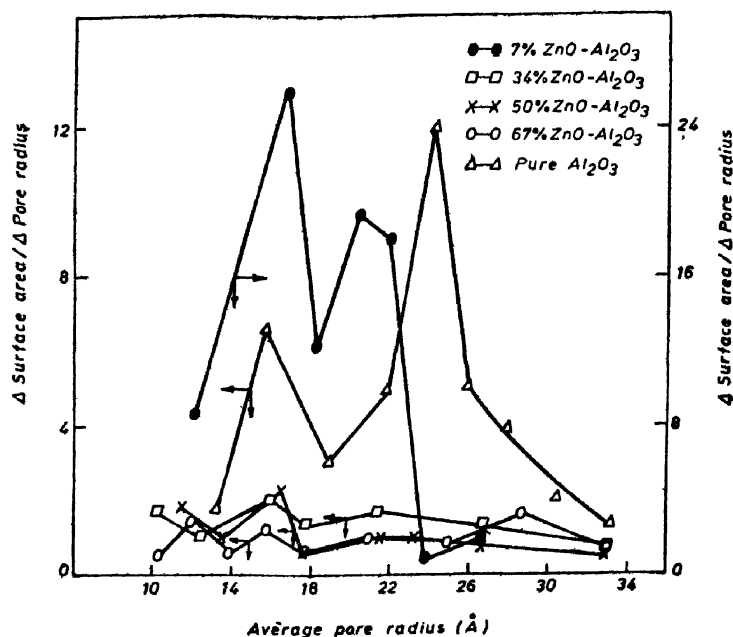
Reactions were carried out in a flow type reactor at atmospheric pressure¹. The liquid products were analysed by the vapour phase chromatographic technique using a carbowax column. The surface area and pore-size distribution were estimated from an analysis of the nitrogen adsorption and desorption isotherms at liquid nitrogen temperature. Electrical resistance of the powder catalysts were measured by a two probe technique using a Keithley Electrometer (610 B). The ohmic nature of the contact was checked by measuring the current for various small DC voltages applied between the electrodes. The solid phases in the catalyst samples were identified by the x-ray diffraction technique.

Results :

The variation in the surface area of the impregnated and coprecipitated catalysts with composition is given in Table I. The pore-size distribution in the U and C series of catalysts obtained by plotting $\Delta S/\Delta R_C$ against average R_C are given in figs. 1 and 2. S represents the total surface area in the pores having radius greater than R_C , the pore radius.



Fig—1 Pore Size Distribution of the 'U' Series of Catalysts.

Fig—2 Pore Size Distribution of ZnO-Al₂O₃ Coprecipitated Catalysts.

The results for the dehydrogenation and dehydration activities per 4 ml of the catalyst are given in Table I. The U and S series of catalysts exhibit dehydrogenation activity for all the compositions studied while the catalysts US and SS show dehydrogenation activity only for the compositions containing about 50% ZnO and above. In the coprecipitated series excepting C₇, all the other catalysts exhibit only dehydrogenation activity. Dehydration activity is exhibited by all the catalysts of the U, S, US and SS series and catalyst C₇ of the coprecipitated series.

U₆₆ and C₅₀ were chosen as representative catalysts to make a more detailed study of the substrate-surface interaction. Fig. 3 shows the relative changes in the electrical resistance of these two catalysts in different reagent atmospheres at 350°. On adsorption of isopropanol the relative change in the electrical resistance $\Delta R/R^\circ$ reaches a limiting value at almost the same partial pressure of isopropanol (~0.5 atm.) on both the catalysts. (ΔR =resistance in an atmosphere of nitrogen-resistance in an atmosphere of reagent). However the relative change brought about by isopropanol adsorption on C₅₀ is greater than that on U₆₆. On adsorption of acetone, the value of $\Delta R/R^\circ$ reaches a maximum at a partial pressure of about 0.5 atm. in the case of C₅₀ while a much higher pressure namely about 0.8 atm. is required in the case of U₆₆.

Discussion :

The surface area trends in the catalyst series U, S and C are similar though their magnitudes are different. The cause for the rise and fall observed in the U and S series of catalysts has been discussed previously³. The initial fall is attributed to the filling of pores, the ZnAl₂O₄ formed on the surface being insufficient to compensate for the reduction in area due to the filling of the pores. Increase in the ZnO content enhances the formation of ZnAl₂O₄ thus causing a rise in the

surface area until a maximum is reached at about 26% ZnO after which it decreases due to the covering up of the ZnAl₂O₄ surface by ZnO. The surface area trend in the C series also may be explained along the same lines. These results show that the interaction between the component oxides is of the same type irrespective of the mode of preparation. However the extent of interaction differs from one preparation to another. Except US₄₉, the surface area of the catalysts of the US and SS series are less than the corresponding unsintered catalysts U and S. Heating to 840° which can help the formation of ZnAl₂O₄ at the same time reduced the surface area of the catalysts presumably by agglomeration.

In the U series of catalysts, dehydrogenation takes place at the interface between ZnO and ZnAl₂O₄ in catalysts containing large amounts of Al₂O₃ (Al₂O₃ > 50%)⁴. Considering the inactivity of the ZnO deposited from zinc nitrate on kieselguhr and the activity per gram of ZnO in the 49-66% ZnO region, it can be concluded that the ZnO-Al₂O₃ interface is the seat of activity in catalysts containing high proportions of ZnO. The ZnO-Al₂O₃ interface may also contribute to some extent in the Al₂O₃ rich catalysts. Taking into account the manner in which the surface area of the catalysts varies with composition, the phases detected in catalysts of different compositions and their activities (Table 1), the seat of dehydrogenation in the S and C series of catalysts can also be considered to be the same as mentioned above. In the US and SS series of catalysts dehydrogenation is observed only in catalysts containing more than 50% ZnO. This is because free ZnO which is essential for the reaction is not present in catalysts containing less than 50% ZnO even though large amounts of ZnAl₂O₄ are present. The dehydrogenation activity in all these catalysts can thus be attributed to the same cause irrespective of the mode of preparation.

A comparison of the dehydrogenation activity of the impregnated and coprecipitated catalysts shows that the latter exhibit better dehydrogenation activity. This can be attributed to the more efficient mixing of the component oxides leading to an increase in the extent of active interface.

Electrical resistance measurements throw some light on the reason for the differences in activity of the two types of preparations. With the experimental set up employed in these studies it is found that on adsorption of acetone, the electrical resistance of p -type NiO increases while that of n -type ZnO decreases. These two observations prove that the electrical resistance measured is the 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. The partial pressure of the reagent required to saturate the surface of a catalyst is an indication of the strength of its adsorbability on the surface. It is seen from fig. 3 that the strength of adsorption of acetone on C_{50} is greater than that on U_{66} because the partial pressure of acetone required to saturate the surface of the former is much lower than for the latter. The desorption of acetone is suggested to be the rate determining step for the decomposition of isopropanol on catalyst C_{50} .

If acetone desorption is assumed to be the rate determining step in U_{66} also, the dehydrogenation activity per unit area of U_{66} should be greater than that of C_{50} . But it is found to be otherwise. As the relative changes produced in the electrical resistance by the adsorption of isopropanol on U_{66} is less than that on C_{50} , the surface concentration of isopropanol should be less on U_{66} than on C_{50} . The higher surface con-

centration may be the reason for the higher dehydrogenation activity on the coprecipitated catalysts. Moreover the impregnated catalysts cause considerable dehydration and water which is a product of reaction, is strongly adsorbed on the surface (Fig. 3). This will retard the reaction on the impregnated catalyst contributing yet another reason for U_{66} having less activity than C_{50} . So the mode of preparation influences the catalytic activity by affecting the extent of adsorption of the reagents on the catalyst surface.

X-ray diffraction data show that the form in which Al_2O_3 is present is different in the two preparations. It exists as "chi" Al_2O_3 in the impregnated catalyst and as the "eta" form in the coprecipitated catalyst. The higher dehydrogenation activity of the coprecipitated catalysts can also be attributed to the presence of "eta" Al_2O_3 in them.

In keeping with earlier suggestions⁶ the dehydration activity of both the impregnated and coprecipitated catalysts bear a relationship to the micropore content in them. The adsorption-desorption isotherm of U_6 shows a hysteresis loop revealing the presence of micropores while catalyst U_{19} exhibits no such hysteresis. If the presence of micropores is an important factor contributing to dehydration, the activity of U_6 should be greater than that of U_{19} . This is so as can be seen from Table 1. In catalysts U_{26} and U_{49} there is an increase in the amount of micropores accompanied by an increase in the dehydration activity. In catalyst U_{66} there are no micropores and dehydration correspondingly decreases. The dehydration pattern in the S, US and SS series of catalysts can also be explained in a similar manner.

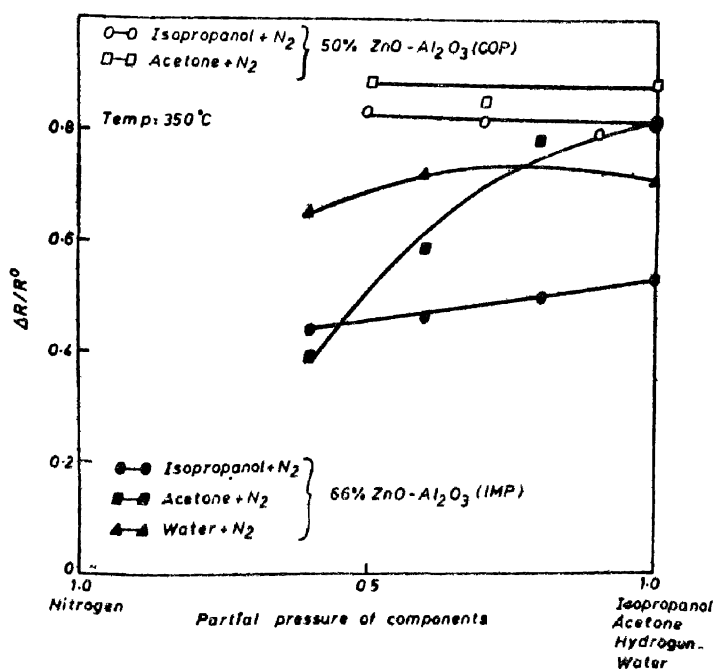


Fig-3 The Relative Electrical Resistance of $\text{ZnO-Al}_2\text{O}_3$ Catalysts as a Function of the Ambient Atmosphere.

In the C series of catalysts, C₇ has a large proportion of micropores while the catalysts of other compositions have fewer micropores. So the fact that dehydration is found only in C₇ while it is absent in the others is similarly explained.

U₆ and C₇ were chosen as representative catalysts to compare the dehydration activities on the two types of preparations namely impregnation and coprecipitation because C₇ was the only catalyst which exhibited dehydration activity in the coprecipitated series of catalysts and U₆ had a composition similar to that of C₇. A comparison of the dehydration activities of these two catalysts shows that U₆ has a higher dehydration activity. One of the reasons for this may be the smaller concentration of free Al₂O₃ in the coprecipitated catalyst. A large amount of Al₂O₃ is used up for the formation of ZnAl₂O₄ in the coprecipitated catalyst while in the impregnated catalyst the solid-solid interaction may not be much.

The impregnated and coprecipitated catalysts do not behave in a similar manner towards the decomposition of isopropanol though the nature of interaction between ZnO and Al₂O₃, their surface area patterns and the cause of activity either for dehydrogenation or dehydration appear to be the same. The impregnated catalysts exhibit both dehydrogenation and dehydration for all the compositions studied. In the coprecipitated series of catalysts C₇ is purely dehydrating while the catalysts of other compositions are purely dehydrogenating. So the mode of preparation affects the selectivity of the catalysts.

The maximum in the dehydrogenation and the dehydration activity in all these catalysts is found to occur at different ZnO contents. The positions of the activity maximum for each series of catalysts are not exact as only a limited number of compositions have been studied. But still they give an idea as to the composition at which the highest activity is manifested.

Sintering, as expected, brings about a reduction in surface area of the catalysts. Except US_{4.9}, all the sintered catalysts have a surface area less than the corresponding unsintered catalyst. The heat treatment also affects the activity of the catalyst. The dehydrogenation activity of the U & S series of catalysts is higher than the corresponding sintered catalysts i. e. US and SS. So on sintering the dehydrogenation activity is decreased. This decrease in activity can be attributed to the clustering of active centres upon high-temperature treatment. The reduction in surface area observed in all the sintered catalysts except US_{4.9} confirms the above reasoning.

The dehydration activity on the other hand is enhanced. Except SS_{2.7} and SS_{6.4} all the other sintered catalysts show increased dehydration activity. In the case of the coprecipitated catalyst also the sintered C₇

catalyst exhibited higher dehydration activity. Qualitative tests were done to determine the relative acidities of the unsintered and sintered C₇ catalysts. The colour of *p*-ethoxy chrysoidin indicator is red in an acid medium and yellow in a basic medium. When a solution of the above indicator in benzene was added to these two catalysts, the sintered catalyst was coloured red while the colour of the unsintered catalyst was not so intense thereby showing that sintered C₇ is more acidic than the corresponding unsintered one. So the increase in activity could be due to the increase in the acidity of the catalyst as reported by previous workers.⁷ This can be the reason for the increased dehydration activity observed on the impregnated sintered catalysts also. On sintering, new active sites with higher dehydration activity are created which more than compensate for the loss in activity due to the destruction of micropores.

TABLE—I DECOMPOSITION OF ISOPROPANOL ON ZnO-Al₂O₃ CATALYSTS VOL. OF CAT. 4 ML; C. T. 1 SEC.

Catalyst series	% ZnO	Acetone (moles/hr)	Water (moles/hr)	Surface area (m ² /g)	Phases detected
U (350°)	6	.020	.152	48.3	—
	19	.031	.039	39.0	Z, A, X
	26	.044	.090	68.5	Z, A, X
	49	.025	.139	17.5	Z, X
	66	.061	.057	16.7	Z
S (350°)	6	.021	.036	44.2	—
	15	.020	.112	36.8	Z, A, X
	27	.016	.242	50.1	Z, A, X
	48	.036	.117	19.4	—
	64	.067	.061	15.3	Z
US (350°)	6	—	.182	20.3	—
	19	—	.173	33.0	—
	26	—	.190	26.6	A, X
	49	.006	.227	43.2	—
	66	.028	.142	10.6	Z, X
SS (350°)	6	—	.176	10.6	—
	15	—	.158	31.6	—
	27	—	.192	21.7	A, X
	48	.001	.188	7.8	—
	64	.031	.037	6.1	Z, X
C (320°)	7	—	.062	12.0	A, X
	34	.119	—	42.9	—
	50	.106	—	25.4	Z, A, X
	67	.099	—	24.1	Z

Where, Z denotes Zinc oxide
A denotes Alumina
X denotes Zinc aluminate

Conclusion :

The activity and selectivity of ZnO-Al₂O₃ catalysts depend upon the mode of preparation. The impregnated catalysts have better dehydrating properties while the coprecipitated catalysts exhibit better dehydrogenation activity. However, the seat of activity in both the preparations is the same. Depending upon the composition the ZnO-ZnAl₂O₄ or ZnO-Al₂O₃ interface functions as the seat of action for the dehydrogenation reaction. Dehydration activity appears to depend to a considerable extent on the presence of micropores. Sintering increases the dehydration activity but decreases the dehydrogenation activity.

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References :

1. R. UMA, and J. C. KURIACOSE, *Indian J. Chem.*, 1971, **9**, 322.
2. A.I. VOGEL, *A text-book of Quantitative Inorganic Analysis*. Longmans Green 1962, p. 401.
3. R. UMA, Thesis submitted for the Ph. D. degree (Indian Institute of Technology, Madras, 1972).
4. R. UMA, R. VENKATACHALAM and J. C. KURIACOSE, Paper presented at the 5th International Congress in Catalysis held at Miami Florida, U. S. A., 1972.
5. R. UMA and J. C. KURIACOSE, *Indian J. Chem.*, 1972, **10**, 69.
6. G. M. SCHWAB and Elly Schwab Agallidis, *J. Amer. Chem. Soc.*, 1949, **71**, 1806.
7. M. W. TAMELE, *Disc. Faraday Soc.*, 1950, **8**, 270.