

ACTIVITY AND SELECTIVITY OF ZnO-TiO₂ CATALYSTS

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Mixed oxide catalysts, in most cases, have activity and selectivity superior to those of pure oxides. A systematic study of the nature of interaction between the component oxides, mode of preparation and pre-treatment, surface area, composition etc. of simple binary oxide systems in relation to their catalytic activity could give a clearer picture of the origin of modified activity in them. The present paper deals with such a study on a ZnO-TiO₂ system.

In the ZnO-TiO₂ catalysts studied, X-ray analysis reveals ZnO to exist in the normal active form unlike the inactive sample of ZnO obtained by decomposing the nitrate. The formation of ZnO on TiO₂ stabilises it in the normal active form. TiO₂ (anatase) is a predominantly dehydrating catalyst for the decomposition of isopropanol with little dehydrogenation activity. But the mixed catalysts containing different proportions of ZnO, all exhibit enhanced dehydrogenation activity.

X-ray analysis does not reveal the formation of any compound in these catalysts. Yet there is an enhancement in the dehydrogenation activity. It is concluded that the ZnO-TiO₂ interface is the seat of catalytic activity.

The dehydrogenation activity is found to be a function of the catalyst composition. Catalysts containing even as little as 10 per cent ZnO exhibit no dehydration activity. The loss in dehydration activity is attributed to the reduction in acidity of the mixed oxide.

The effect of the nature of the added oxide and its pretreatment on activity is studied by using a sintered TiO₂ (anatase) sample for impregnation as well as sintering the impregnated mixed oxide (TiO₂ in rutile form). In these preparations also the dehydration activity is suppressed and the seat of dehydrogenation activity is found to be the ZnO-TiO₂ interface.

ZnO shifts the venue of activity to the interface thereby suppressing the dehydration activity of TiO₂ in whatever form the latter is present. The mixed oxide catalysts are thus more selective.

INTRODUCTION

Certain metal oxides, when mixed together, exhibit activity and selectivity superior to those shown by the individual oxides. The enhancement in activity has been attributed to various causes (Bhattacharyya *et al.* 1965; Gutschick *et al.* 1969; Maxted *et al.* 1950; Nicolescu *et al.* 1966; Owen 1947; Selwood & Mooi 1952; Schiavello *et al.* 1971; Schwab 1964; and Slinkin *et al.* 1960; Visser 1950; Yoshida *et al.* 1969). However, in most of the cases the activity has been studied in relation to only one of the properties of the system like the nature of the added oxide, coordination number of the added cation, mode of preparation and pretreatment of the catalyst, surface area, composition, nature of interaction between the component oxides etc. Not many attempts have been made to correlate as many of these aspects

as possible with catalytic activity for a particular system. A mixed oxide preparation of ZnO and TiO₂ exhibits enhanced dehydrogenation activity. The present paper deals with the results of a systematic study of the catalytic activity of this simple binary oxide system for the decomposition of isopropanol.

MATERIALS AND METHODS

ZnO-TiO₂ impregnated catalysts were prepared by soaking TiO₂ powder in Zn(NO₃)₂ solution, allowing it to stand overnight and then decomposing it at 400°C for 6 hours. Catalysts obtained using the commercial sample of TiO₂ are represented as (ZnO-TiO₂)_{imp}. A sintered TiO₂ sample got by heating TiO₂ at 840°C for 12 hours was also used for the catalyst preparation and is denoted as ZnO-(TiO₂)_{sint}. While another sample was obtained by sintering (ZnO-TiO₂)_{imp} and is represented as (ZnO-TiO₂)_{sint}. Experiments were also carried out on mechanical mixtures of ZnO and TiO₂. The percentage of ZnO in each catalyst was estimated by dissolving weighed amounts of catalyst in H₂SO₄ and titrating the ZnSO₄ solution against standardised ferrocyanide. The ZnO content in them (expressed as weight per cent of ZnO) is indicated by a prefix as for (e.g., 10 per cent ZnO-TiO₂). This denotes a catalyst containing 10 per cent by weight of ZnO.

Reactions were carried out in a flow type reactor at atmospheric pressure (cf. Pandao *et al.* 1962). The liquid products were analysed by the vapour phase chromatographic technique using a carbowax column at 70°C. The surface areas of the catalysts were determined from the N₂ adsorption isotherm at liquid N₂ temperatures. The desorption isotherm was also traced for some catalysts to determine the pore-size distribution in them. The solid phases in the catalyst samples were identified by the X-ray diffraction technique. The relative acidities of some catalysts were determined qualitatively using a solution of *p*-ethoxychrysoiodin indicator in benzene which is coloured red in an acid medium.

RESULTS

The conclusions drawn from the X-ray data for some ZnO-TiO₂ catalysts are given in Table I. The variation in surface area of the (ZnO-TiO₂)_{imp} catalysts with

TABLE I
Phases detected by X-ray Analysis in the ZnO-TiO₂ catalysts

Catalyst	ZnO	TiO ₂	Zinc titanate
(10% ZnO-TiO ₂) _{imp}	present (ZnO lines diffuse)	present (anatase)	—
(64% ZnO-TiO ₂) _{imp}	present (sequence of intensities of d lines of ZnO same as that reported in the literature)	—do—	—
(10% ZnO-TiO ₂) _{sint}	—do—	present (rutile)	present
11% ZnO (TiO ₂) _{sint}	—do—	present (anatase)	—

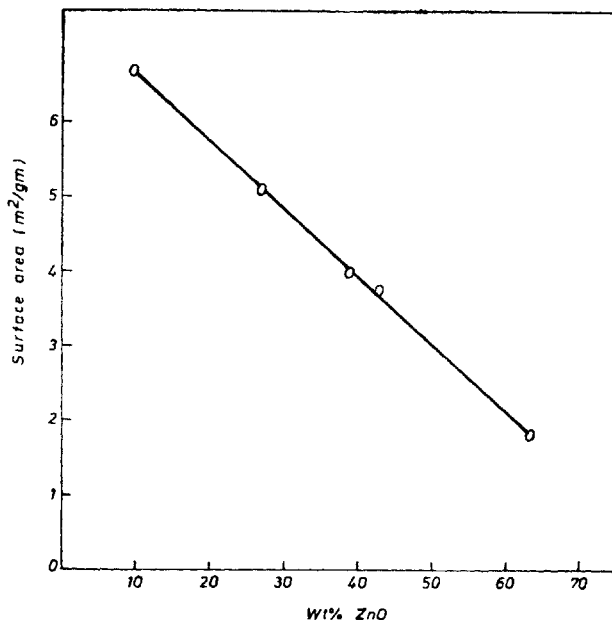


FIG. 1. Surface areas of $(\text{ZnO-TiO}_2)_{\text{imp}}$ catalysts as a function of composition.

composition is given in Fig. 1. The surface area pattern shows a decreasing trend with increasing concentration of ZnO. X-ray analysis does not provide any evidence for compound formation in these catalysts. The regular decrease in surface area observed here can therefore be attributed to the presence of increasing proportions of ZnO whose surface area ($0.15 \text{ m}^2/\text{gm}$) is much smaller than that of pure TiO_2 ($8 \text{ m}^2/\text{gm}$).

TiO_2 is a predominantly dehydrating catalyst with slight dehydrogenation activity. Sintering reduces its surface area and completely suppresses the dehydrogenation activity. While the dehydration activity of the unsintered catalyst is greater than that of the sintered catalyst, the apparent energy of activation for the dehydration reaction on the sintered catalyst (15 Kcal/mole) is less than that on the unsintered catalyst (27 Kcal/mole).

Pure ZnO obtained from the nitrate is inactive for the decomposition of isopropanol. However, $(\text{ZnO-TiO}_2)_{\text{imp}}$ catalysts also obtained by the decomposition of the nitrate show enhanced dehydrogenation activity, there being no dehydration activity at all. Fig. 2 shows the dehydrogenation activity per 4 cc of catalyst and per gram of ZnO of these $(\text{ZnO-TiO}_2)_{\text{imp}}$ catalysts as a function of composition. In both the plots the activity pattern reveals that within the composition range studied a maximum is seen at about 10 per cent ZnO followed by a fall as the ZnO content increases. Decomposition of isopropanol was studied on (10 per cent ZnO-TiO_2)_{sint.} and 11 per cent ZnO-(TiO_2)_{sint.} catalysts also. They too exhibited only dehydrogenation activity. The apparent energy of activation for the dehydrogenation reaction is almost constant ($13\text{--}16 \text{ Kcal/mole}$) for all the ZnO-TiO_2 catalysts except (64 per cent ZnO-TiO_2)_{imp.} for which it is 24 Kcal/mole .

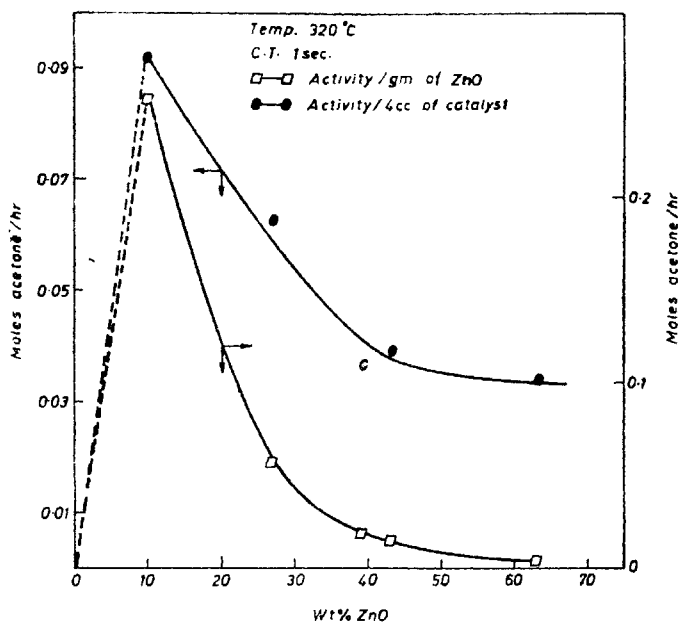


FIG. 2. Dehydrogenation activities of (ZnO-TiO₂)_{imp} catalysts as a function of composition.

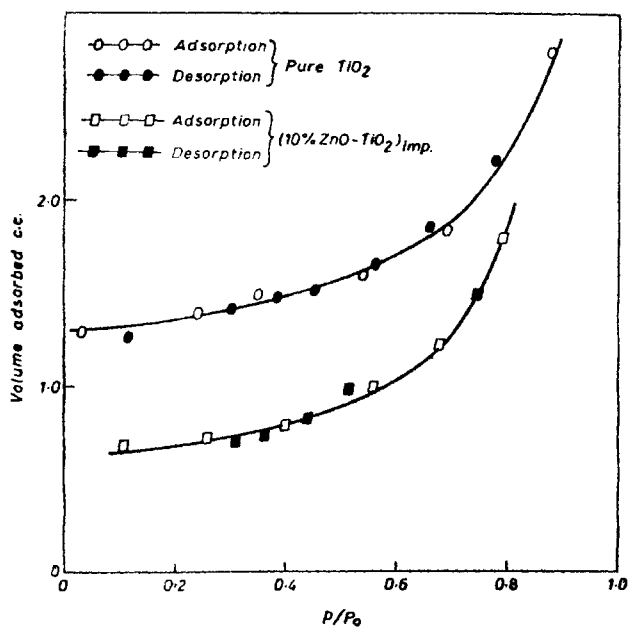


FIG. 3. Nitrogen adsorption-desorption isotherms on TiO₂ and (10% ZnO-TiO₂)_{imp} catalysts.

Fig. 3 shows the N_2 adsorption-desorption isotherms on TiO_2 and (10 per cent $ZnO-TiO_2$)_{imp.} samples. In both the catalysts the adsorption and desorption isotherms coincide. Qualitative acidity measurements showed that unsintered TiO_2 is more acidic than both sintered TiO_2 as well as (10 per cent $ZnO-TiO_2$)_{imp.} catalysts.

DISCUSSION

There is no evidence for the formation of any compound between ZnO and TiO_2 in these mixed oxides. Therefore the cause for the enhancement in the dehydrogenation activity can only be (1) ZnO dispersed on TiO_2 in an active form, (2) formation of an active interface between $ZnO-TiO_2$ and (3) TiO_2 dispersed on ZnO . The apparent energy of activation remains constant upto a composition of 43 per cent ZnO indicating that only one of the above mentioned factors contributes predominantly to the activity upto this composition. It is unlikely that dispersed TiO_2 is the active species in this region because the apparent energy of activation is very much less than that for pure TiO_2 . The maximum observed when the dehydrogenation activity per gram of ZnO is plotted against composition (Fig. 2) shows that the physical state of ZnO , i.e., dispersion, is important in determining activity. If not, the activity would have been a constant for such a plot. It is also significant that the maximum for the activity versus composition and activity per gram of ZnO versus composition plots show good correspondence. Causes (1) and (2) will give rise to the same trend for the dehydrogenation activity. However, a 10 per cent ZnO -kieselguhr catalyst which has ZnO in the normal active and dispersed form does not dehydrogenate isopropanol. So it can be concluded that the interface between active ZnO and TiO_2 is the seat of dehydrogenation activity. Theoretically, we should expect a maximum in the extent of interface at a composition corresponding to 50 mole per cent. Since these are impregnated catalysts, this maximum on the surface can be obtained at a much lower concentration of ZnO .

In the region 36-64 per cent ZnO (Fig. 2) the activity is almost constant indicating that it is becoming less and less dependent on the ZnO content. The apparent energy of activation for the reaction remains constant upto 43 per cent ZnO and then increases to a considerable value in the (64 per cent $ZnO-TiO_2$)_{imp.} catalyst. This suggests that the mechanism of dehydrogenation or the nature of active sites is different in the (64 per cent $ZnO-TiO_2$)_{imp.} catalyst. As the apparent energy of activation for the dehydrogenation reaction on this catalyst and pure TiO_2 are almost the same being 24 and 22 Kcal/mole respectively, dispersed TiO_2 could be the active species on this catalyst. The activity should have decreased further in the region 43-64 per cent ZnO but for the compensation due to the activity of dispersed TiO_2 .

Like the ($ZnO-TiO_2$)_{imp.} catalysts, 10 per cent ($ZnO-TiO_2$)_{sint.} and 11 per cent ($ZnO-TiO_2$)_{sint.} samples have ZnO in the normal active form and exhibit only dehydrogenation activity. The apparent energy of activation for the dehydrogenation reaction on these two catalysts is almost the same as that observed on ($ZnO-TiO_2$)_{imp.} catalysts (14 and 16 Kcal/mole respectively). So in these catalysts also the seat of dehydrogenation activity could be the same namely the interface between ZnO and TiO_2 .

The trend for the dehydrogenation activity per 4 cc. of the different catalysts containing almost the same amount of ZnO is (10 per cent ZnO-TiO₂)_{imp.} (A) > 11 per cent ZnO-(TiO₂)_{sint.}, (B) > (10 per cent ZnO-TiO₂)_{sint.} and (C) > (10 per cent ZnO-TiO₂)_{mixed} (D). The surface area of TiO₂ is reduced on sintering. As B contains TiO₂ in a sintered form, the extent of dispersion of ZnO on it will be less than that in A. Hence its activity is less than that of A. In C, ZnO and TiO₂ are in a sintered condition, and in addition to clustering there is (1) transformation of TiO₂ from the anatase to the rutile form and (2) the formation of the compound zinc titanate. The effective concentration of free ZnO in C is reduced because part of it will be used up for the formation of zinc titanate. Moreover the ZnO-TiO₂ (rutile) interface may not be as active as the ZnO-TiO₂ (anatase) interface though the rutile form of TiO₂ has been reported to be a better dehydrogenating catalyst in comparison to the anatase form (Rubinshtein & Kulikov 1950). So the catalyst C is less active than B. In spite of the fact that there is compound formation between ZnO and TiO₂ in C, its dehydrogenation activity is not much. While sintering might have reduced its catalytic activity by decreasing its surface area, a comparison of the activity of C with A or B which have no detectable compound formation suggests that zinc titanate does not contribute much towards dehydrogenation activity.

In a mechanical mixture like D, the dehydrogenation activity is enhanced a little, while most of the dehydration activity of TiO₂ is retained. In catalyst A where there is a better mixing of the two oxides due to impregnation, dehydrogenation is very much more enhanced while dehydration is completely suppressed. These results show clearly that catalytic activity is a function of the mode of preparation of the catalyst.

Though TiO₂ is a predominantly dehydrating catalyst, impregnated ZnO-TiO₂ catalysts containing even as little as 10 per cent ZnO do not exhibit any dehydration activity. Previous workers have associated dehydration activity with the acidity of the catalyst (Tamele 1950). The suggestion that dehydration takes place in the pores of the catalyst has also been made (Schwab & Schwab Agallidis 1949). The suppression in the dehydration activity caused by the addition of ZnO to TiO₂ may therefore be attributed to the destruction of micropores in which dehydration can occur or due to the destruction of acid sites which could have been originally present in TiO₂. The absence of hysteresis in the adsorption-desorption isotherms for TiO₂ (Fig. 3) shows that it does not contain any micropores. So dehydration in TiO₂ is not likely to be due to the presence of pores. Qualitative acidity measurements using p-ethoxychrysoidin indicator, whose colour is red in an acid medium, showed that the indicator imparted a pink colour to pure TiO₂ while the (10 per cent ZnO-TiO₂)_{imp.} catalyst remained white. This indicates that pure TiO₂ is more acidic than a (10 per cent ZnO-TiO₂)_{imp.} catalyst. So the absence of dehydration on the latter could be due to the decrease in its acidity.

Sintered TiO₂ is found to be a purely dehydrating catalyst with an apparent energy of activation of 15 Kcal/mole which is very much less than that observed on unsintered TiO₂. The dehydration activity is also very much reduced on the sintered catalyst. X-ray analysis shows that the sintered and unsintered TiO₂ exist in the same crystalline modification, i.e., anatase. Acidity measurements revealed

that on sintering TiO_2 , the acidity is reduced. These observations lead to the conclusion that though both the solids maintain the same structure, the mechanism of dehydration and the nature and number of active sites on them are different. The dehydration activities per unit area on both the catalysts remain almost the same. This can happen only if the number of active sites as well as the apparent energy of activation decrease simultaneously. So on sintering, new sites which are more active but fewer in number are created while the sites responsible for dehydrogenation disappear. Apparently, acidity is not the important factor in determining the dehydration activity on this catalyst.

When a (10 per cent ZnO-TiO_2)_{imp.} catalyst is sintered, the TiO_2 is transformed to the rutile modification. But pure TiO_2 sintered under similar conditions retains its anatase form. So the addition of ZnO to TiO_2 helps in the transformation of anatase to rutile while some zinc titanate is also formed. Sintered TiO_2 which is purely dehydrating is unable to exhibit its activity in both catalysts B and C. So, irrespective of whether TiO_2 is present in the anatase or rutile form, ZnO suppresses its dehydration activity.

CONCLUSION

Pure TiO_2 is a predominantly dehydrating catalyst with little dehydrogenation activity. On sintering the dehydration activity of TiO_2 is decreased while its dehydrogenation activity is completely lost even though the crystal structure is retained. Addition of ZnO enables TiO_2 to assume the rutile form on sintering.

The presence of TiO_2 helps in the formation and stabilisation of ZnO in the normal active form. Irrespective of the nature of TiO_2 used and the mode of preparation, the ZnO-TiO_2 interface is the seat of activity in these catalysts as there is no detectable compound formation when the catalysts are not sintered. Even when there is compound formation, as in the case of sintered catalysts, its contribution to dehydrogenation activity seems to be negligible. In catalysts with a high TiO_2 content dispersed TiO_2 is responsible for the dehydrogenation activity. The addition of ZnO to TiO_2 even in small quantities decreases the acidity of the latter and also suppresses its dehydration activity.

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