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## INFLUENCE OF SUBSTRATE ON THE ACTIVITY OF A CHROMIA CATALYST

By

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### Abstract

The decomposition of acetic acid, cyclohexanol and isopropanol on a chromia catalyst has been studied at 460°C at various partial pressures, employing a flow method using nitrogen as a diluent. Reactions of acetic acid mixed with the alcohols were also studied. The products were analysed by vapour phase chromatography. It was found that the chromia catalyst favoured the dehydration of cyclohexanol and dehydrogenation of isopropanol while being also active for the ketonisation of acetic acid. The dehydration of alcohols is suppressed by the presence of acetic acid at all partial pressures whereas the dehydrogenation is enhanced at high partial pressures of acid and suppressed at low partial pressures. These results have been discussed assuming two kinds of activities for the chromia catalyst, one favouring dehydration and the other dehydrogenation of alcohols.

### Introduction

Chromia is one of a number of dual function catalysts which promote both dehydration and dehydrogenation. From previous work<sup>1-4)</sup> it has been suggested that the type and degree of the activity of a catalyst may be at least partly due to the substrate-catalyst interaction and not entirely determined by the intrinsic properties of the catalyst. The present work is an attempt to investigate whether the type and degree of activity of a chromia catalyst is influenced by the nature of substrates. The basic reaction chosen is the dehydration and dehydrogenation of isopropanol and cyclohexanol. Acetic acid is another kind of molecule which undergoes decomposition on oxide catalysts<sup>5)</sup> to give acetone, water and carbon dioxide. So, the extents of the two types of reactions, dehydrogenation and dehydration have been studied in the presence of acetic acid using a flow type reaction unit as described by PANDAO *et al.*<sup>1)</sup> to determine whether the same properties of the catalyst are responsible for the reactions of the alcohols and the acid.

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*Influence of Substrate on the Activity of a Chromia Catalyst***Experimental Procedure**

The catalyst was prepared by precipitating chromium hydroxide from an approximately normal chromium nitrate solution by the slow addition of normal ammonium hydroxide. The precipitate was washed free of nitrate ions, dried at 110°C in an air oven, ground to a fine powder of less than 240 mesh size and then pressed into pellets using about 2 percent stearic acid as a binding material. The pellets were heated to 500°C at first in a current of carbon dioxide-free air for 6 hours and then in hydrogen for 8 hours. 1.5 g of the catalyst occupying a volume of 2.5 cc was used and after every run the catalyst was regenerated by heating to 500°C, first in carbon dioxide-free air for 4 hours and then in hydrogen for six hours.

BDH analar sample acetic acid was frozen to remove water and further purified by distillation. Cyclohexanol was dried over anhydrous sodium sulphate and fractionally distilled. Isopropanol, BDH sample, was refluxed with sodium and fractionally distilled.

At the beginning of every run, the apparatus was flushed with pure, dry, nitrogen for ten minutes to obtain an inert atmosphere. When the temperature was steady at the desired value, the reactant was fed. Runs were carried out with pure acetic acid, isopropanol and cyclohexanol at atmospheric pressure and at lower pressures by diluting with nitrogen. Acetic acid mixed with cyclohexanol or isopropanol was also used in several runs. The products formed in the first twenty minutes were rejected and after the reaction had attained a steady state, as indicated by the steady evolution of gas, the products were collected for a known interval of time in a trap cooled in ice. At the end of the run, the apparatus was flushed with nitrogen to remove any reactant

TABLE 1. Data for chromatographic analysis of liquid products

| Compound                           | Reaction   | Column employed and temperature |
|------------------------------------|--|---------------------------------|
| Acetone using methanol as standard | Decomposition of acetic acid.                              | Carbowax at 90°C                |
| Cyclohexanone and Cyclohexanol     | Decomposition of cyclohexanol                              | Glycerol at 110°C               |
| Cyclohexanone and Cyclohexanol     | Decomposition of mixtures of acetic acid and cyclohexanol. | XF-1150 at 100°C                |
| Acetone and Isopropanol            | Decomposition of isopropanol.                              | Halcomid at 70°C                |
| Acetone and Isopropanol            | Decomposition of mixtures of acetic acid and isopropanol.  | Halcomid at 70°C                |

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vapour left in the reactor while the temperature was gradually raised to 500°C. The reactivation procedure indicated earlier effectively restores the activity of the catalyst.

The liquid products like acetone and cyclohexanone and the unreacted reactants were analysed using the gas chromatographic technique with suitable columns as indicated in Table 1.

Cyclohexene, the dehydration product of cyclohexanol had a very short retention time on both glycerol and XF-1150 columns. Hence it was estimated by a modification of the bromination method due to KAUFFMANN<sup>6)</sup> employing a bromine-bromide mixture.

In cases where acetic acid was employed as a reactant, it was estimated

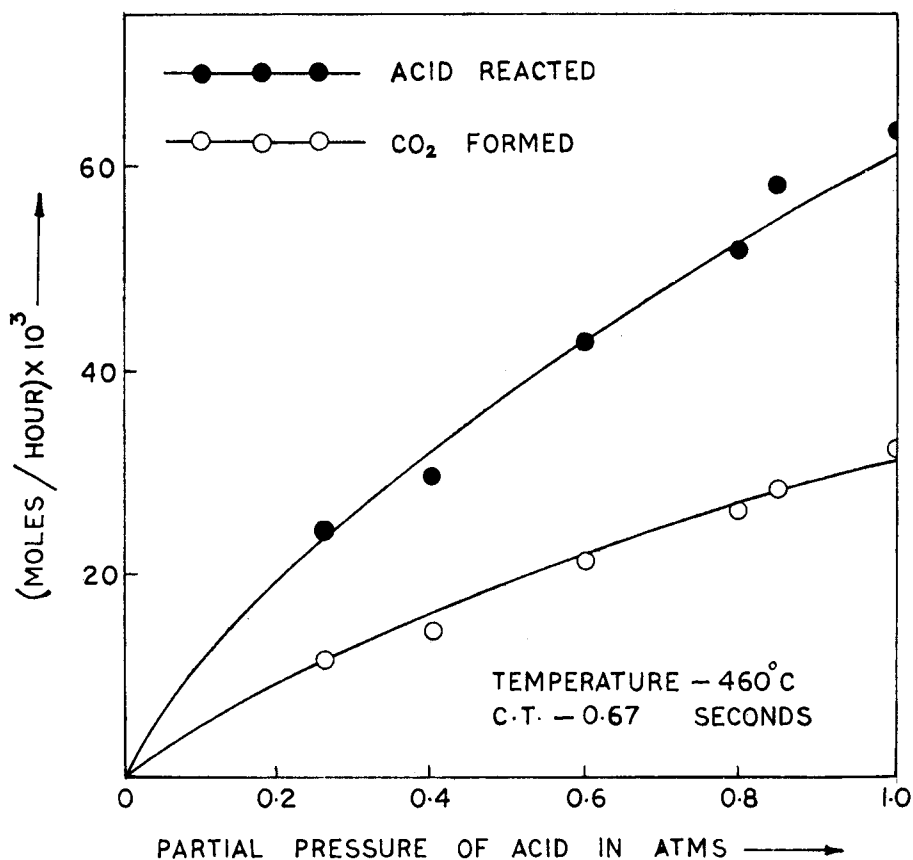


Fig. 1. Effect of partial pressure on the reaction of acetic acid in presence of nitrogen.

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by taking a known weight of the reaction mixture and titrating it with standard alkali. Analysis of the reaction products obtained in the case of mixtures of alcohols and acetic acid revealed the absence of ester formation.

The gaseous products like carbon dioxide and propylene were analysed using an Orsat apparatus.

### Results

The following interesting observations were made when the decomposition of acetic acid, cyclohexanol and isopropanol were studied at different partial pressures of the individual reactants at a constant contact time of 0.7 sec and

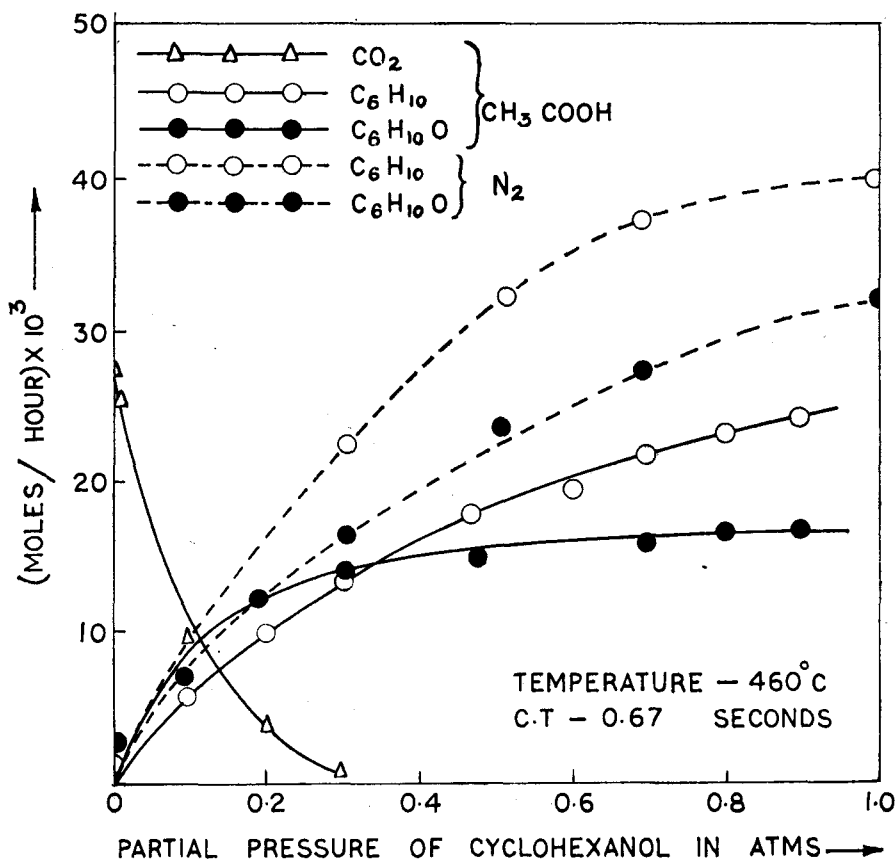


Fig. 2. Effect of partial pressure on the reaction of cyclohexanol in presence of nitrogen and acetic acid.

at a constant temperature of 460°C using nitrogen as a diluent. The low contact time was chosen to ensure low conversion of the reactants. The temperature was chosen arbitrarily to have measureable reaction. There was no pyrolysis under the experimental conditions chosen.

Acetic acid decomposes giving acetone, carbon dioxide and water the conversion increasing with increasing partial pressure of the acid as shown in Fig. 1. Both isopropanol and cyclohexanol underwent dehydration as well as dehydrogenation. In the case of isopropanol, the selectivity of the catalyst, *i.e.*, the ratio of the extent of dehydration to the extent of dehydrogenation, had a value of 0.3 while in the case of cyclohexanol it had a value of 1.3. For both the reactants, the selectivity was independent of the partial pressure

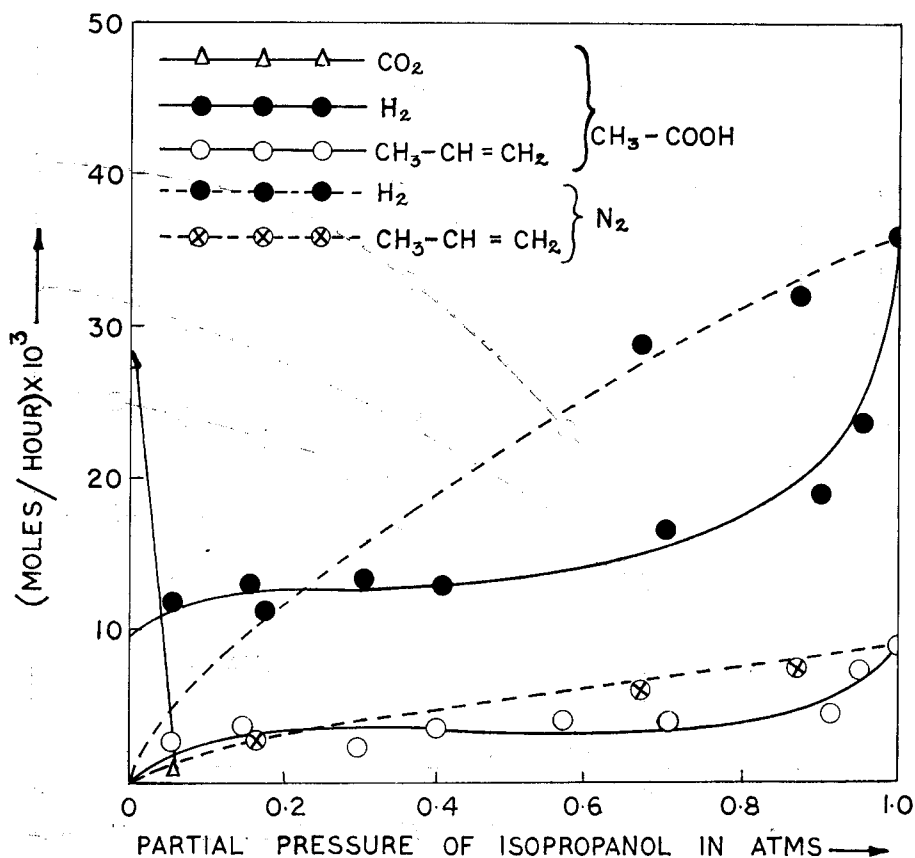


Fig. 3. Effect of partial pressure on the reaction of isopropanol in presence of nitrogen and acetic acid.

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even though the overall conversion was a function of the partial pressure. This taken along with the fact that nitrogen has the same effect as that of helium permits the assumption that nitrogen behaves as an inert diluent.

When mixtures of acetic acid and cyclohexanol were used, the ketonisation of the acid fell rapidly with increasing partial pressures of alcohol as shown in Fig. 2. At the same time, dehydrogenation and dehydration of alcohol increased steadily with increasing partial pressure of alcohol. The dehydrogenation of alcohol dominates over that of dehydration up to a partial pressure of 0.4 atm of alcohol reducing the original selectivity of 1.3 to 0.85. At partial pressure above about 0.4 atm the dehydrogenation reaches a steady value which is less than that in the presence of nitrogen, while dehydration increases with partial pressure though remaining always less than in the presence of nitrogen.

Studies on acetic acid and isopropanol mixtures revealed that the ketonisation of acid fell to a very small value even at a very high partial pressure of the acid. As can be seen from Fig. 3 at 0.95 atm of acid, the ketonisation of the acid was negligibly small. At lower partial pressures of alcohol in the presence of acetic acid, the hydrogen evolved was higher than that in the presence of nitrogen as a diluent but above 0.3 atm it was less. Dehydration increased rapidly with partial pressure of the alcohol and reached a steady value at about 0.1 atm.

### Discussion

The fact that the selectivity is in favour of dehydration for cyclohexanol and dehydrogenation for isopropanol shows that the dehydration and dehydrogenation activities of the chromia catalyst are not functions of the catalyst alone. The interaction between the substrate and the catalyst is at least as important as the intrinsic nature of the catalyst in determining the degree of activity in any individual case. The total adsorption coefficient of an alcohol on chromia can be considered to be made up of two adsorption coefficients, one corresponding to the adsorption of the alcohol in a form favourable for dehydration and the other to the adsorption in the form favourable for dehydrogenation. These two adsorption coefficients are determined by a combination of two factors, the structure of the alcohol and the properties of the catalyst. It is the relative magnitudes of the two adsorption coefficients for an alcohol that determines the selectivity for that particular alcohol. Therefore the same chromia catalyst has different selectivities for different alcohols. These ideas are in general accord with the model proposed by WOLKENSTEIN<sup>7)</sup> for dehydration and dehydrogenation reactions, where the particular kind of activity can be considered to be generated by the interaction between the

substrate and the catalyst. The absence of any change in the selectivity with change in the partial pressure supports this idea.

Using mixtures of acetic acid and isopropanol, it was observed that at all partial pressures of acetic acid the dehydration was less than when nitrogen was used as a diluent. Further, the extent of dehydration increased with partial pressure of isopropanol and reached a steady value at about 0.3 atm. This indicates that acetic acid can interact with the surface of chromia in a manner similar to the adsorption of alcohols leading to dehydration and that even at low partial pressures, acetic acid occupies a part of the area suitable for dehydration in a permanent manner, rendering it inaccessible to alcohol molecules. However, it is found that there is very little ketonisation in these regions of partial pressure of acid as can be seen from Fig. 3. This indicates that the essential condition for ketonisation is that either acetic acid should get adsorbed on both dehydration and dehydrogenation areas or even if adsorption on only one kind of area is enough, the two adsorbed species leading to ketonisation are to be in sufficiently close proximity. If the ketonisation takes place by a Rideal mechanism, *i.e.* a molecule from the vapour phase reacting with an adsorbed molecule, the acetic acid adsorbed on the dehydration area is not the adsorbed species contributing to the reaction. Whichever be the prevalent mechanism, in the region of partial pressure between 0.95 and 0.05 atm the conditions are unfavourable for ketonisation.

Again the fact that acetic acid suppresses the dehydrogenation of isopropanol and brings it down to a level lower than that in the presence of nitrogen as a diluent in the higher partial pressure regions of alcohol, shows that a part of the dehydrogenation area is also permanently poisoned by the acid. Yet the ketonisation is negligible. Hence the Rideal mechanism is unlikely.

All these arguments can be equally well applied to cyclohexanol where similar results have been obtained with this difference that while dehydration is affected to a greater extent in the case of isopropanol it is the dehydrogenation that is considerably affected in the case of cyclohexanol. This could be understood in the light of the fact that the selectivity of the catalyst is in favour of dehydrogenation in the case of isopropanol while in the case of cyclohexanol it is in favour of dehydration.

Apart from the above observations, an interesting feature found both in the case of cyclohexanol and isopropanol is that very high partial pressures of acetic acid increases the dehydrogenation activity of the catalyst to a level higher than with nitrogen as diluent, this, in spite of the fact that at low partial pressures of acid there is a suppression of both dehydrogenation and dehydration. This may be the result of two causes. If it is assumed that acetic acid

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while poisoning a part of the catalyst surface, induces in it an enhanced ability for dehydrogenation, the increase in the dehydrogenation over the normal value at these partial pressures can be accounted for. In the very low regions of partial pressure of alcohol, surface coverage by alcohol molecules is bound to be low whether the diluent is nitrogen or acetic acid although it might be slightly lesser in the case of the latter. Hence the retarding effect due to decreased coverage can be more than compensated for by the additional induced activity. In the higher partial pressure regions of alcohol, coverage due to alcohol molecules becomes important in determining the overall rate, since the surface tends to get saturated. The decrease in the rate caused by the decreased surface coverage consequent on surface poisoning by acetic acid may not, under these conditions, be sufficiently compensated for by the additional induced activity. Because the decreased coverage due to permanent poisoning is not adequately compensated for by the additional induced activity the dehydrogenation activity remains less than in the presence of nitrogen in the higher partial pressure regions of alcohol. The possible second cause is that the presence of a large amount of acid in the vapour phase may facilitate the adsorption of the alcohol in a form conducive to dehydrogenation. This is something quite plausible according to WOLKENSTEIN's suggestion<sup>7)</sup> that the type of reaction a reactant undergoes depends upon the manner of adsorption of the reactant, which in turn depends upon the composition of the gaseous medium the reactant finds itself in. At high partial pressures of alcohol the gaseous medium will be very similar to pure alcohol.

The results discussed above lead to the conclusion that the type and degree of activity of a chromia catalyst is not determined by the intrinsic nature of the catalyst alone but is a response to the demand by the substrate. Presence of substrates other than the reactant under study can alter the response of the catalyst to the reactant.

#### **Acknowledgement**

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