The Influence of the Physical Characteristics of Chromia-Alumina on Its Catalytic Activity

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The dehydration and dehydrogenation of isopropanol has been studied on sintered, powdered, and pelleted chromia-alumina catalysts. With the powdered and pelleted catalysts the extent of dehydrogenation passes through a maximum as the temperature is raised from 380°C keeping the contact time constant, while with the sintered catalyst there is a normal increase in extent of dehydrogenation with increase in temperature. The type of semiconductivity and the pore distribution of these catalysts have been investigated. The observed results for the dehydrogenation are discussed and explained on the basis of the semiconductor characteristics and texture of the catalysts.

INTRODUCTION

As adsorption is an essential step in heterogeneous catalytic reactions, a knowledge of the nature of the surface and its interactions with the adsorbate can help in understanding the mechanism of heterogeneous catalytic action. The influence of the structure of the reacting molecule and its chemisorption in determining the selectivity of a chromia catalyst for the dehydration and dehydrogenation of alcohols has been studied by Kuriacose and co-workers (1–4) and they have shown that the selectivity is dependent on the structure of the reactant molecule. It was considered of interest to investigate the extent to which the physical characteristics of the catalyst influence the reaction.

Previous work (5) on the reaction of isopropanol on chromia-alumina pellets showed that the measured rate of dehydrogenation passes through a maximum with increase in temperature and at temperatures above 400°C with increase in contact time. The present investigation is an attempt to study the relationship between the physical characteristics of the catalyst and this peculiar behavior.

METHODS

The reaction studies were carried out at atmospheric pressure in a flow-type reactor. The chromia-alumina catalyst was kindly supplied by the Houdry Process Corporation of New Jersey. Analysis of the catalyst indicated a Cr_2O_3 to Al_2O_3 ratio of 3:7. It was heated at 850°C for 12 hr to prepare the sintered catalyst. The catalyst was activated by treatment with carbon dioxide-free dry air for 4 hr followed by dry hydrogen for 6 hr at 500°C. After each run the catalyst was regenerated by flushing the reactor with nitrogen and then heating the catalyst to 500°C in carbon dioxide-free dry air for 4 hr followed by dry hydrogen for 6 hr. If the catalyst was cooled in the reactant atmosphere and then brought up again to the reaction temperature for carrying out the runs, reproducible results could not be obtained. Even if the catalyst was cooled in the reaction atmosphere, the regeneration procedure outlined above completely restored the activity of the catalyst.

Reactions were carried out at various temperatures on sintered and powdered chromia-alumina catalysts, keeping the
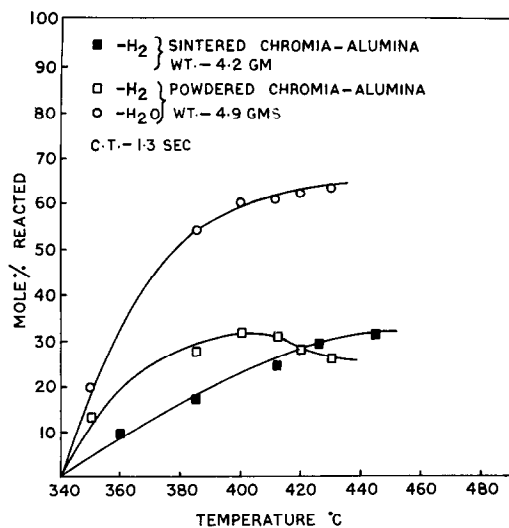
FIG. 1. Effect of temperature on the decomposition of isopropyl alcohol.

contact time constant. The effect of contact time was studied at 385° and 412°C. The liquid products were analyzed by vapor-phase chromatography using a Carbowax column at 75°C and the gases using an Orsat apparatus. Electrical conductivity measurements were made in various atmospheres using a vacuum tube volt-meter. The thermoelectric potential method (6) was employed to investigate the cur-

FIG. 3. Effect of contact time on the decomposition of isopropyl alcohol over pelleted chromia-alumina catalyst.

rent carriers using a nanoamperometer to measure the currents.

Adsorption measurements were made at liquid nitrogen temperature to determine the surface area and pore-size distribution of the various catalysts. The pore-size distribution was computed according to the procedure described by Viswanathan and Sastri (7).
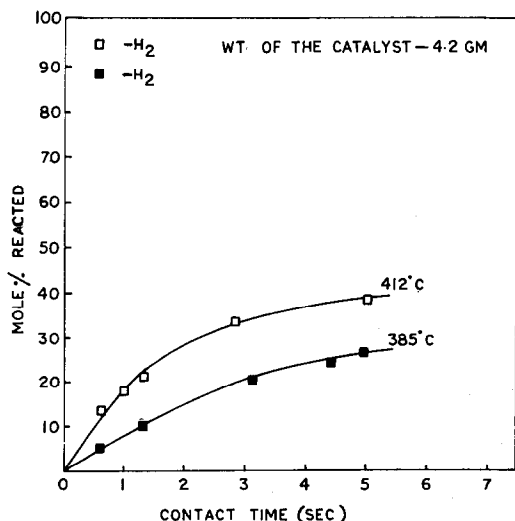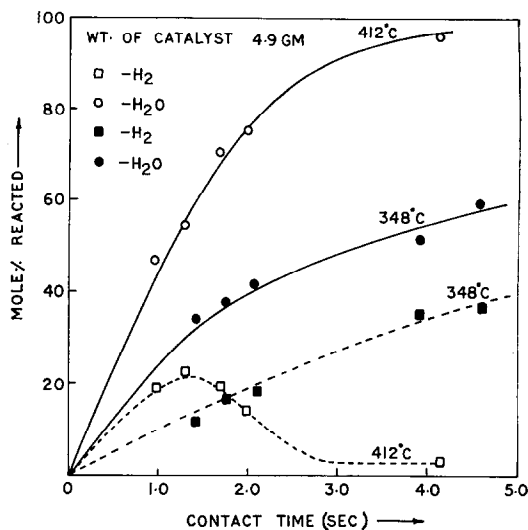

FIG. 2. Effect of contact time on the dehydrogenation of isopropyl alcohol on sintered chromia-alumina at 385° and 412°C.
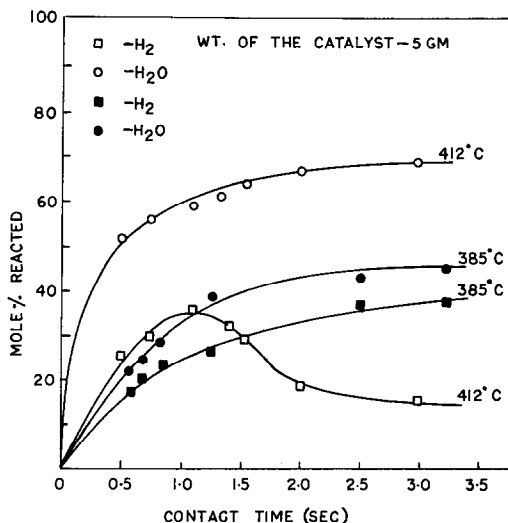

FIG. 4. Effect of contact time on the decomposition of isopropyl alcohol over powdered chromia-alumina.
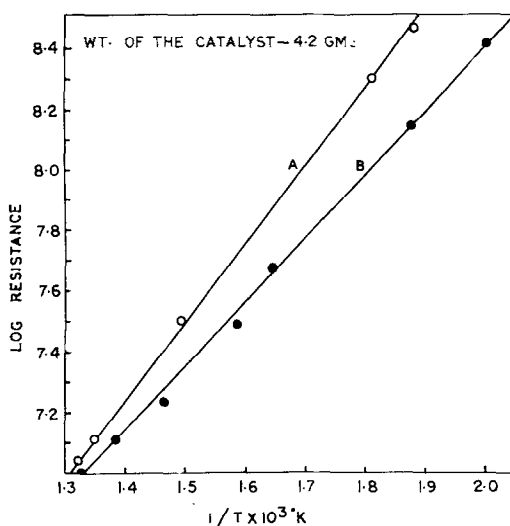
FIG. 5. Arrhenius plot for the variation of resistance with temperature on sintered chromia-alumina catalyst in (A) hydrogen and (B) oxygen atmospheres.

RESULTS

Figure 1 shows that on a sintered catalyst at a constant contact time, the extent of dehydrogenation steadily increased with increase in temperature. The dehydration activity was completely lost. In the case of the powdered catalyst, however, there was both dehydration and dehydrogenation activity and the extent of dehydrogenation passed through a maximum as the temperature was increased at constant contact time. Figure 2 shows that both at 385° and 412°C, with increase in contact time, the extent of dehydrogenation on a sintered catalyst steadily increased, whereas on an ordinary pelleted catalyst (Fig. 3), at temperatures above 410°C, the extent of dehydrogenation passed through a maximum. As can be seen from Fig. 4, on a powdered chromia-alumina catalyst also the results are similar to those obtained on a pelleted catalyst. There was no significant amount of carbon deposition during the reactions, as could be seen from the absence of carbon dioxide in the gas when the catalyst was regenerated.

The thermoelectric potential measurements on the sintered catalyst indicated that the current carriers are the same as in zinc oxide and they do not change with temperature. The logarithm of the electrical
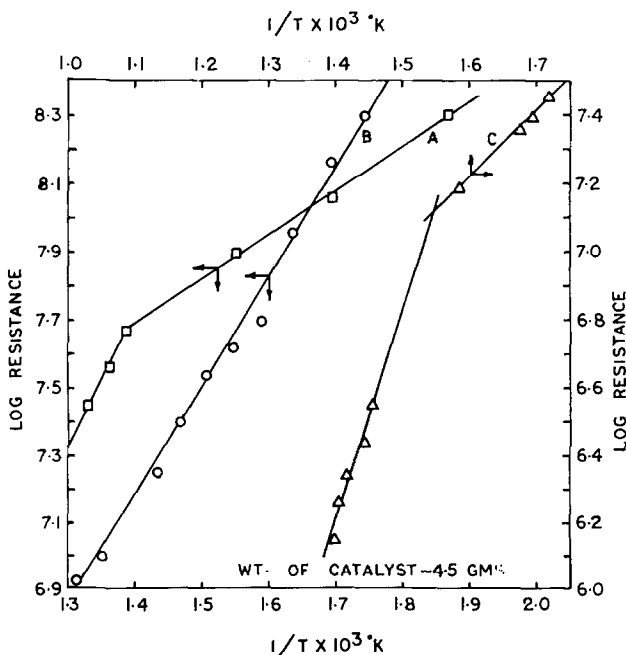

FIG. 6. Arrhenius plot for the variation of resistance with temperature in (A) hydrogen, (B) oxygen, and (C) isopropyl alcohol atmospheres over chromia-alumina pellets.
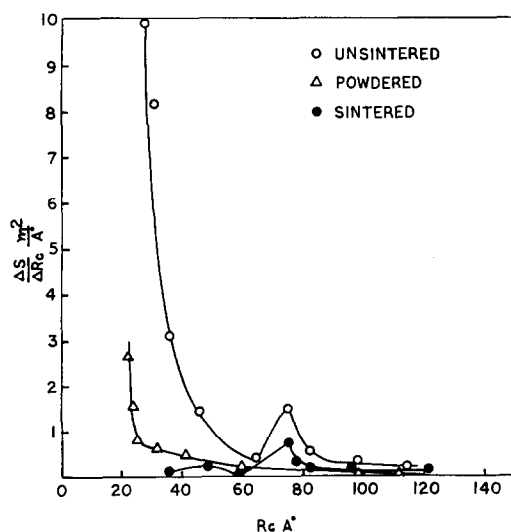
FIG. 7. Pore-size distributions of various chromia-alumina catalysts.

resistance when plotted against the reciprocal of the absolute temperature (Fig. 5) gave a single straight line. In the case of the ordinary pelleted catalyst, the thermoelectric potential measurements indicated that the current carriers are the same as in zinc oxide at temperatures above 400°C, but different at lower temperatures. Further, as can be seen from Fig. 6, the plot of the logarithm of the electrical resistance versus the reciprocal of the absolute temperature gave two straight lines which met in the region of 400°C. In a hydrogen atmosphere the break in the Arrhenius' plot occurs at about 440°C and in isopropanol at about 360°C. An isopropanol atmosphere aids the transition from p-type to n-type semiconductivity better than a hydrogen atmosphere. On the pelleted catalyst at the temperatures at which reaction takes place acetone decreases the resistance of the catalyst and hence aids the p to n transition even better than isopropanol. This could be said only qualitatively, since it was found difficult to make measurements in the presence of an acetone atmosphere due to undesirable reactions taking place on the catalyst.

On sintering, the surface area of the pelleted catalyst decreased from 68 to 24 m^2/g. The powdered catalyst had a surface area of 112 m^2/g. Figure 7 shows the pore-size distribution of the catalysts. In the figure $\Delta S/\Delta R_c$ represents the relative change in surface area for particular regions of pore radii, while R_c represents the pore radius in A° [please see ref. (7)]. There is a considerable loss of micropores both on powdering and on sintering.

DISCUSSION

On sintering the chromia-alumina catalyst, the dehydration activity is completely destroyed. If one assumes that a two-point adsorption of alcohol (8, 9) is necessary for the dehydration activity and that this can take place most readily in the pores (9) one may arrive at the conclusion that on a sintered catalyst there are few pores and the two-point adsorption is not feasible. The considerable decrease in the surface area of the catalyst supports the view that, on sintering, the catalyst has attained almost a flat surface. Results from the pore-size distribution studies show a considerable decrease in micropores, confirming that the pores are destroyed on sintering. One may conclude therefore that the dehydration activity is closely related to the pore structure of the catalyst. Schwab (9) has shown that catalysts with smooth surfaces are more favorable for dehydrogenation.

As observed by many workers (10, 11) one may also attribute the loss of dehydration activity to the loss of water molecules from the surface, due to sintering. Efforts to restore the dehydration activity by introducing water molecules into the catalyst failed to give positive results. One may surmise from this that in the absence of pores the surface hydroxyl groups are incapable of bringing about the dehydration reaction or it may be that the loss of the hydroxyl groups through the removal of water caused by sintering is not reversible.

The dehydrogenation activity of the sintered catalyst can be explained on the basis of the electronic changes of the catalyst. The steady increase in the dehydrogenation activity with temperature shows that, unlike the case of the un-

sintered pellets (5), the reaction mechanism does not change with increase in temperature. This would agree with the fact that the catalyst exists in a single electronic state throughout the temperature ranges studied. The inherent p to n transition of chromia as observed in unsintered chromia-alumina is not exhibited by a sintered catalyst. Sintering has therefore brought about a permanent electronic change in the catalyst, making it impossible for the catalyst to change its semiconductor character with change in temperature. The results for the plot of electrical resistance against the reciprocal of absolute temperature give a single straight line, confirming that there is no transition from p- to n-type semiconductivity with change in temperature. Since the behavior of the sintered catalyst as far as the thermoelectric potential is concerned is similar to that of zinc oxide, it may be assumed that the sintered catalyst is an electron excess or n-type semiconductor catalyst. If according to Schwab (9) the dehydrogenation is facilitated by flat surfaces, the overall decrease in activity observed on sintering may be due to the decrease in the surface area of the catalyst (8, 12). Several workers (13, 14) have found that heat-treatment changes the nature of the solids. One may also attribute the cause for the changes in the activity of the chromia-alumina catalyst on sintering to the change in the structure of the catalyst.

On a sintered catalyst, the results of the effect of contact time on the extent of dehydrogenation at 385° and 412°C indicate no maximum. Since the pores are absent and since there is no dehydration activity on a sintered catalyst, one may suggest that the observed maximum in the dehydrogenation activity on an ordinary pelleted catalyst is due to the dehydrogenation reaction taking place inside the pores of the catalyst or the influence of the products of dehydration. Since the sintered catalyst does not undergo any p to n transition, this may also be considered to be a cause for the absence of the maximum.

It may be expected that powdering the catalyst will remove the pores without altering the electronic character of the catalyst. The procedure would eliminate or minimize the effects of diffusion (15). On the powdered catalyst the results are similar to those observed on the pellets.

The extent of dehydrogenation passing through a maximum as the temperature is increased may therefore be due to a change in the mechanism of the reaction caused by the p to n transition as already explained, and not due to the porous nature of the catalyst. Pore-size distribution studies show that there are not many micropores in the powdered catalyst. The observation of a maximum for the extent of dehydrogenation with increase in contact time on both a pelleted as well as a powdered catalyst around 410°C suggests that the maximum cannot be due to the effect of the pores in the catalyst. The high activity of the powdered catalyst could be due to the increase in the surface area of the catalyst.

With increase in contact time, the partial pressure of acetone increases, causing an increase in the surface concentration of acetone. Electrical conductivity studies on chromia-alumina in the presence of acetone indicate that acetone donates electrons to the catalyst during adsorption. Thus as the contact time increases, the catalyst becomes more n-type. It has been suggested that a p-type semiconductor is a better dehydrogenation catalyst than an n-type semiconductor (8). Thus, as the contact time increases, one could expect the dehydrogenation rate to fall, not only due to the normal inhibition by acetone occupying a part of the surface, but also by its making the catalyst more n-type. These circumstances could lead to the reverse reaction on the surface, viz., the combination of acetone and hydrogen to form isopropanol becoming more important with increase in contact time. The observed maximum in the extent of dehydrogenation with increase in contact time has been attributed to the greater contribution of the reverse reaction as the contact time increases (16). The ability of the catalyst to change its conductivity from p- to n-type depending on the temperature is neces-

sary for the exhibition of this phenomenon, as can be deduced from the fact that on the sintered catalyst which does not show any change in type of current carriers with change in temperature this maximum is not observed. Independent experiments with benzyl alcohol, which does not undergo any dehydration, clearly show that the products of dehydration play no part in this peculiar behavior of the dehydrogenation reaction.

The dehydration activity is preserved in the powdered catalyst, as can be seen from Fig. 2, in spite of a considerable reduction in the micropores. It could therefore be considered that the loss of dehydration activity on sintering is due to the removal of the surface hydroxyl groups.

CONCLUSION

The maximum observed in the extent of dehydrogenation on an unsintered chromia-alumina catalyst as the temperature is raised from 350°C results from the ability of the catalyst to change the type of current carriers with change in temperature. This property also gives rise to a gradual increase in the extent of dehydrogenation at low contact times followed by a decrease as the contact time is increased at temperatures where the catalyst exhibits n-type semiconductivity. The loss of dehydration activity on sintering is due to the irreversible loss of water from the catalyst.

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