

INTERACTIONS IN IRON OXIDE-ALUMINA CATALYSTS

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In combination with Al_2O_3 , Fe_2O_3 loses its dehydrogenation activity and forms a predominantly dehydrating catalyst. The present studies are aimed at an understanding of the interactions in such a binary system of isomorphous oxides.

In the freshly prepared catalysts, Fe_2O_3 is strongly held to Al_2O_3 , as indicated by its reluctance to dissolution in acid and to reduction during the reaction. Catalysts obtained by different methods of preparation have dehydration activities which appear to be related to the degree of intimacy expected to be caused under the conditions of treatment. Depending on the preparations in which the constituents are present, only one of them, either $\alpha\text{-Fe}_2\text{O}_3$ or $\gamma\text{-Al}_2\text{O}_3$ exist in a crystalline form. On calcination at 800°C , however, the Al_2O_3 in the mixed catalysts is transformed into $\alpha\text{-Al}_2\text{O}_3$ and in the entire range of composition, both Al_2O_3 and Fe_2O_3 remain as well-crystallized phases. Further, the electrical resistance of the fresh catalysts has a single value for the temperature coefficient over a range of temperatures while pure $\alpha\text{-Fe}_2\text{O}_3$ has two values in the same range. Heating of a mechanical mixture of pure oxides results in a material which displays pure dehydration activity but does not have the other properties shown by catalysts obtained by coprecipitation or impregnation.

In the course of repeated usage, the iron oxide part of the catalysts get completely reduced to Fe_3O_4 under the reaction conditions. Simultaneously with such a transformation, a remarkable improvement in the dehydration activity is noticed. The aged catalysts in the regenerated form contain iron oxide as $\gamma\text{-Fe}_2\text{O}_3$ which is completely soluble in acid. The stability of $\gamma\text{-Fe}_2\text{O}_3$ in these catalysts could result from a transformation of the solid solution present in the original catalysts or an unfavourable alteration in the energy of activation for the conversion of $\gamma\text{-Fe}_2\text{O}_3$ to $\alpha\text{-Fe}_2\text{O}_3$ caused by the addition of Al_2O_3 .

The formation of Fe_2O_3 in the presence of Al_2O_3 produces a catalyst in which Fe_2O_3 is tightly bound, either on the surface or in the lattice of Al_2O_3 . The Fe_2O_3 in these catalysts interact with the "bound form" of the two oxides, on ageing, to form a homogeneous material, in which $\gamma\text{-Fe}_2\text{O}_3$ is stabilized.

INTRODUCTION

Mixed oxide catalysts undergo a variety of interactions, the kind and intensity of which is largely determined by the chemical nature of the components and the conditions of preparation and use. In several such cases, the catalytic activity is profoundly affected and the improved efficiency and selectivity of the composite catalysts have been the chief feature responsible for the huge growth of interest in the study of mixed oxide catalysts.

Catalysts of strictly isomorphous oxides like Fe_2O_3 and Al_2O_3 or V_2O_5 and P_2O_5 present difficulties in identification of any new phase formed since only a minor alteration in the lattice parameters of the solids is expected in such cases. Solid solutions may be formed but in these systems it is not a facile process. The conditions used for the preparation of catalysts are usually so mild that the interaction rarely proceeds to any considerable degree of conversion, and hence the products are heterogeneous solids. Such systems demand careful studies before any conclusion regarding the active ingredient of the catalysts is drawn.

Catalysts comprising of reducible oxides, when used to study reactions producing a reducing agent, e.g., dehydrogenation, present special problems, since in these cases the oxides would undergo a change in composition during the reaction and subsequent regeneration. This may make it impossible to form and study a single solid with reasonably reproducible surface properties.

We have reported earlier (Venkatachalam & Kuriakose 1972; and Uma *et al.* 1972) the changes in the catalytic properties and other characteristics of iron oxide-alumina mixed catalysts. The present paper highlights the nature of the chemical interaction between the two solids which is important in determining the activity of the catalysts.

EXPERIMENTAL

Activity measurements and other catalytic studies were carried out in a flow reactor functioning at atmospheric pressure, described earlier (Venkatachalam & Kuriakose 1972). The products were estimated gas-chromatographically using a halcomid column at 70°C . Surface areas of the catalysts were determined by the BET method using Nitrogen as the adsorbate.

In order to ensure that the behaviour of the mixed catalysts is consistent, two different preparations of Fe_2O_3 — Al_2O_3 catalysts were used for studies. The impregnated catalysts used for a few comparative studies were prepared by impregnating γ - Al_2O_3 (E. Merck) with 20 per cent $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Baker Analyzed Reagent) solution and calcining the slurry at 200°C after standing for 24 hours. The 'co-precipitated' catalysts employed in the systematic studies were obtained by dehydrating the hydroxides of aluminium and iron precipitated together at 120°C for 15 hrs (Venkatachalam & Kuriakose 1972). The composition of the catalysts were determined by the dichrometric method for the determination of iron and their structural features analysed by the X-ray diffraction (XRD) method using unfiltered iron radiation. Fe_2O_3 likely to be bound to the Al_2O_3 lattice was determined by treating samples in a manner that would affect the complete dissolution of pure Fe_2O_3 . Approximately 5N HCl prepared in a single stock was used for this purpose. Amounts of catalysts containing 0.10 gm. of Fe_2O_3 were treated with 15 ml. of the acid and the dissolved Fe_2O_3 estimated after 24 hours. The same weight of α - Fe_2O_3 was completely dissolved in less than 6 hours by the same treatment. Sintered catalysts were obtained by heating samples at 800°C for 8 hours. The distinction between Fe_3O_4 and γ - Fe_2O_3 , which have the same structure and unit cell dimensions, was made by the chemical determination of ferrous iron.

Electrical resistance of the catalysts in air was measured at various temperatures by using an Electrometer (Keithley, model 610B). The Ohmic nature of the solid-

electrode contacts was ensured by measuring the current flowing through the solid at different voltages. The resistance value of a given sample of catalyst pellet was not exactly reproducible in these experiments. However, the order of magnitude was found to be the same and the pattern of changes in the value with changing temperature was consistent.

RESULTS

The main reaction of 2-propanol on Fe_2O_3 is dehydrogenation and in the process the catalyst gets reduced to Fe_3O_4 , indicating an initial oxidation followed by pure dehydrogenation (Venkatachalam & Kuriacose 1972). Fe_2O_3 - Al_2O_3 mixed catalysts on the contrary, are predominantly dehydrating. A preliminary study was made on the activity of a few 'impregnated' and 'co-precipitated' catalysts, the results of which are given in Table I. The data correspond to the first run carried out on the fresh catalysts.

TABLE I
Catalytic Activities of a few Fe_2O_3 - Al_2O_3 Catalysts

Catalyst	Activity (mole/hr./gm. of catalyst) $\times 10^3$	
	Water	Acetone
36% Fe_2O_3 - Al_2O_3 impregnated	10.7	16.0
36% Fe_2O_3 - Al_2O_3 impregnated sintered at 800°C for 6 hours	13.7	2.5
53% Fe_2O_3 - Al_2O_3 impregnated	26.0	10.3
41% Fe_2O_3 - Al_2O_3 coprecipitated	57.8	3.2
57% Fe_2O_3 - Al_2O_3 coprecipitated	65.0	4.3

Detailed studies were made with 'co-precipitated' catalysts of five different compositions. The dehydration activity determined at 312°C at a constant 'time of contact', surface area and other data for these catalysts are presented in Table II. Results on the case of dissolution of Fe_2O_3 in the different catalysts expressed as the fraction of total Fe_2O_3 dissolved under specified conditions are also included in Table II.

The fresh catalysts contain all iron oxide as α - Fe_2O_3 . In any of the catalysts, only one of the components, depending on the composition, is revealed as a crystalline phase. Catalysts containing 5 and 19 per cent Fe_2O_3 have only γ - Al_2O_3 . XRD results on typical catalysts shown in Fig. 1 reveal that Al_2O_3 is present in a poorly crystallised form whereas Fe_2O_3 is present as well-crystallised α - Fe_2O_3 . Even an impregnated catalyst with 30 per cent Fe_2O_3 prepared starting from γ - Al_2O_3 shows the presence of only α - Fe_2O_3 . Results obtained for 5 per cent Fe_2O_3 - Al_2O_3 are the same as in Fig. 1 (a) and the pattern for all the other catalysts is the same as for α - Fe_2O_3 . In

TABLE II

<i>Dehydration Activities of different Fe₂O₃-Al₂O₃ Catalysts</i>				
Temperature : 312°C			Contact time : 0.23 sec.	
Catalyst composition (mole % Fe ₂ O ₃)	Free Fe ₂ O ₃ * (wt. %)	Surface Area (metre ² /gm)	Specific Activity (mole/hr. gm. of catalyst) × 10 ³	Activity per unit area (mole/hr./metre ²) × 10 ³
0	—	107	164.7	1.54
5	29.6	70	184.0	2.64
19	32.8	55	79.6	1.45
41	32.1	32	44.7	1.38
57	32.8	39	34.7	0.90
78	73.5	30	17.9	0.59

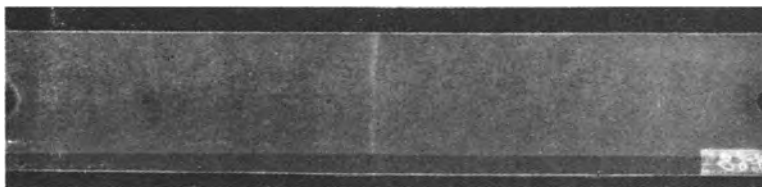
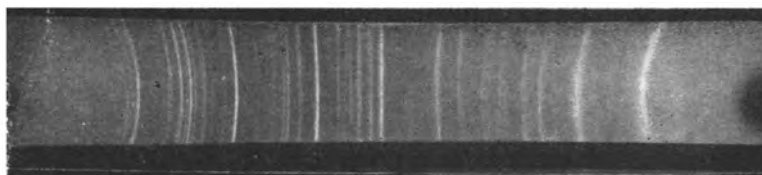
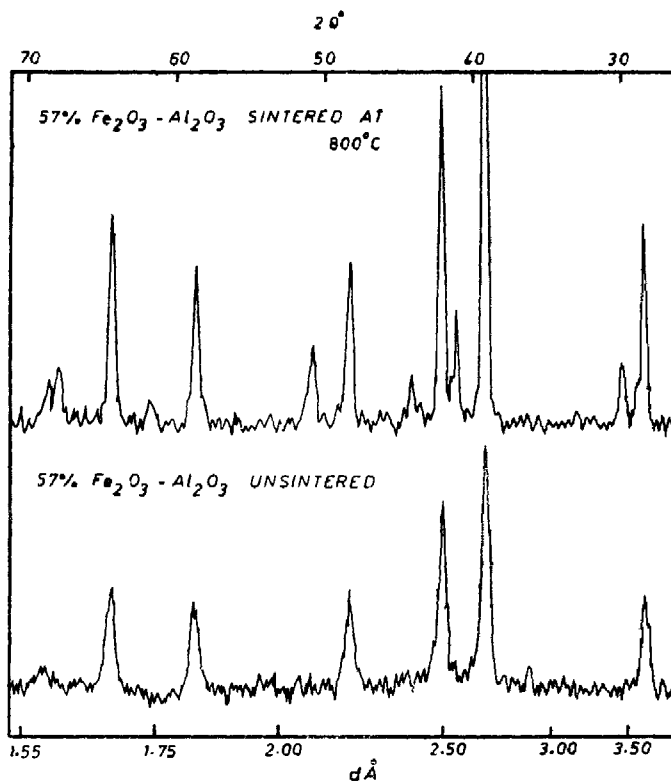
*Fraction of total Fe₂O₃ extractable by treatment with 5N hydrochloric acid for 24 hours.

the case of sintered catalysts, Al₂O₃ has undergone a complete transformation to α-Al₂O₃. Only in the case of 78 per cent Fe₂O₃-Al₂O₃ no diffraction line corresponding to Al₂O₃ can be detected. The 19 per cent Fe₂O₃-Al₂O₃ which when fresh shows the presence only of γ-Al₂O₃ and not Fe₂O₃, gives X-ray patterns of both α-Fe₂O₃ and α-Al₂O₃ after sintering. Pure Al₂O₃ remains unaffected in structure after a similar heat-treatment. The catalyst prepared by impregnating γ-Al₂O₃ and then sintering, gives results similar to the above.

The semiconducting behaviour of the catalysts is represented in Fig. 2 and Fig. 3. While the plots of log resistance vs. 1/T for the catalysts having 5 to 57 per cent Fe₂O₃ give single straight lines down to a temperature of 240°C, the plot for a catalyst with 78 per cent Fe₂O₃ shows two regions of semiconduction characteristic of pure Fe₂O₃ (cf. Gardner *et al.* 1963).

The proportions of total Fe₂O₃ extracted by treatment with acid from the different catalysts is about 30 per cent (Table II) except in the case of 78 per cent Fe₂O₃-Al₂O₃ where it is about 75 per cent.

The mixed catalysts show increased dehydration activity on continued usage. The increase was negligibly small in the case of 5 per cent Fe₂O₃-Al₂O₃ and became more and more significant with increase in the Fe₂O₃ content of the catalysts. Accompanying such a modification in activity were observed structural changes in the iron oxide part of the catalysts. A detailed study was made on catalysts rich in Fe₂O₃ in which iron oxide is present as a crystalline phase. Starting with fresh catalysts containing 57 and 78 per cent Fe₂O₃, the activities were determined for a few runs, till steady activities were reached. These results are given in Table III. The catalyst samples after use for the last run were removed from the reactor after cooling in an atmosphere of oxygen free nitrogen and subjected to XRD analysis. Fresh samples of the same two catalysts were also used for a single run under identical conditions, removed without regeneration and analysed.

FIG. 1 (a). Diffraction pattern of unsintered 19% $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalyst.FIG. 1 (b). Diffraction pattern of sintered 19% $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalysts.FIG. 1 (c). Diffractograms for 57% $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalyst before and after sintering

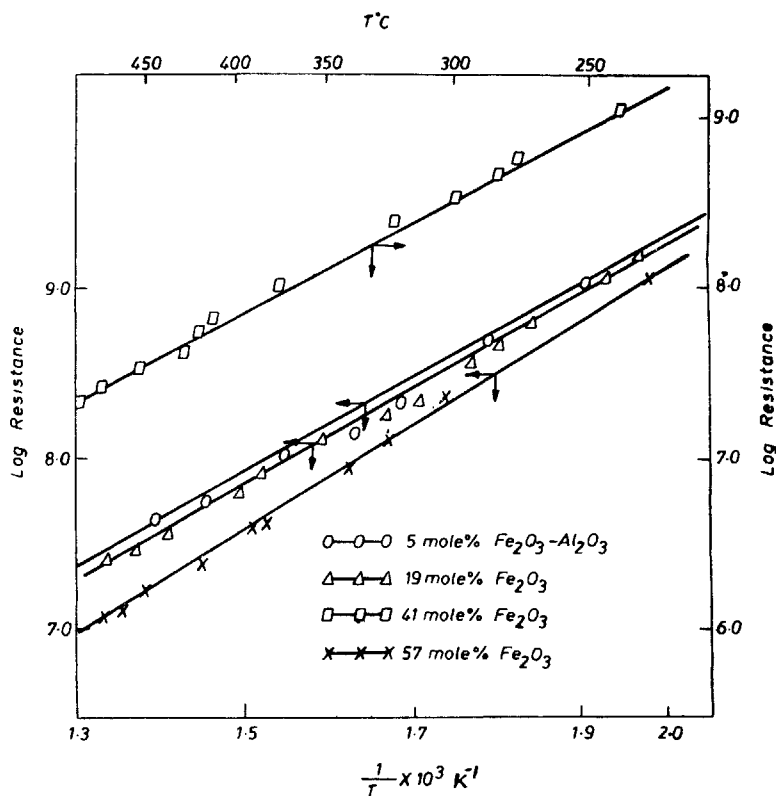


FIG. 2. Semiconducting behaviour of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ (5-57 per cent Fe_2O_3 catalysts).

TABLE III

Increased dehydration activity of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ Catalysts on "Aging"

Temperature : 402°C

Contact time : 0.2 sec.

Run	Catalytic Activity (moles/100 moles of 2-propanol)			
	57% $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$		78% $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$	
	Water	Acetone	Water	Acetone
1	61.0	9.2	13.0	27.3
2	68.0	4.0	34.0	5.3
3	69.0	1.4	45.4	1.6
4	69.5	1.0	62.4	—
5	—	—	62.8	—

The catalysts in which only $\alpha\text{-Fe}_2\text{O}_3$ is present to start with, after the first run with 2-propanol contain both Fe_3O_4 and Fe_2O_3 , however long the particular reaction

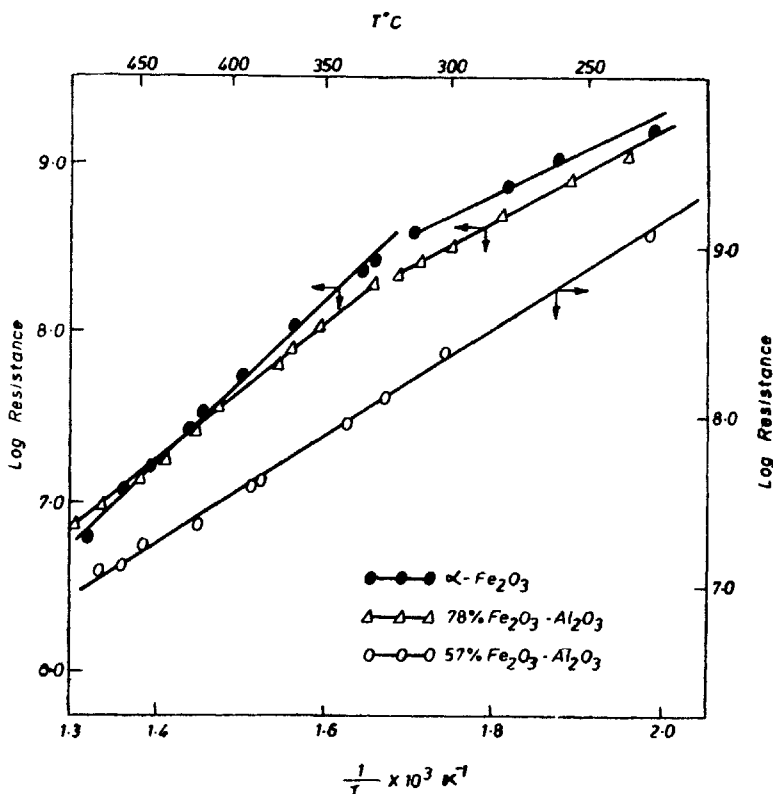


FIG. 3. Comparison of the semiconducting behaviours of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ (57 and 78 per cent Fe_2O_3) and $\alpha\text{-Fe}_2\text{O}_3$ catalysts.

is conducted. After several runs when the catalysts became purely dehydrating they contain only Fe_3O_4 ; the same catalysts when regenerated contain only $\gamma\text{-Fe}_2\text{O}_3$ and no $\alpha\text{-Fe}_2\text{O}_3$. The amount of Fe_2O_3 dissolved by acid from such 'aged' catalysts is almost 100 per cent. In any catalyst the conversion to $\gamma\text{-Fe}_2\text{O}_3$ and improvement in dehydration activity occurred only when it was used at temperatures $> 350^\circ\text{C}$, i.e., the range in which pure Fe_2O_3 reacts with 2-propanol and gets reduced. With sintered catalysts the process of 'aging' is much slower and they have to be used for many more runs before attaining the steady dehydration activity and complete conversion to $\gamma\text{-Fe}_2\text{O}_3$.

DISCUSSION

The results of the present studies may be considered to pertain to two kinds of catalysts; (i) Fresh catalysts in which iron oxide is present as $\alpha\text{-Fe}_2\text{O}_3$ and (ii) Aged catalysts which have improved their dehydration activity in the course of usage and contain all the iron oxide as $\gamma\text{-Fe}_2\text{O}_3$.

(i) *Fresh catalysts* : The 'impregnated' $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalysts are predominantly dehydrating. The 'co-precipitated' catalysts are much better dehydration catalysts

and show a feeble dehydrogenation activity only in the first run. The suppression of dehydrogenation activity which is intrinsic to Fe_2O_3 indicates that the mixed catalyst is an interacted form of the constituent oxides. This is supported by the observation that the dehydration activity is enhanced by conditions which would be expected to promote better intimacy between the solids. Thus it may be seen from Table I that a 36 per cent Fe_2O_3 - Al_2O_3 catalyst on sintering improves its dehydration activity, unlike Al_2O_3 which is known to undergo a reduction in surface area and dehydration activity upon similar treatment. The loss in activity that one would expect in this case due to a reduction in surface area of Al_2O_3 is probably more than compensated by the increased formation of active sites. The higher dehydration activity of 'coprecipitated' catalysts may likewise arise from a better mixing of the oxides.

The strong binding of Fe_2O_3 in the mixed catalysts apparent from its reluctance to dissolve in acid (Table II) probably results from its penetration into the bulk of Al_2O_3 and the new surrounding in which it is consequently placed. A fairly strong interaction is likely to be facilitated because in all the catalysts either of the components is in a finely divided state as suggested by the X-ray data. The reasonably constant proportions of Fe_2O_3 soluble in hydrochloric acid may not be significant since the extractability of Fe_2O_3 may be controlled by factors other than composition. The intensity of interaction as well as the proportion of Fe_2O_3 experiencing it, may vary from catalyst to catalyst. A fortuitous combination of the two factors could lead to the constant fraction of extractable Fe_2O_3 . However it is significant that all the Fe_2O_3 is not extractable.

The mutual influences of Fe_2O_3 and Al_2O_3 are reflected as modifications in their structure and semiconducting behaviour. The failure to detect any-crystalline phase of Al_2O_3 in catalysts containing 41 and 57 per cent Fe_2O_3 is surprising, although in the case of 78 per cent Fe_2O_3 - Al_2O_3 the low concentration of Al_2O_3 may be responsible for its not being detected. It is justified to suppose that Al_2O_3 is present as an amorphous phase in these catalysts for the following reasons :

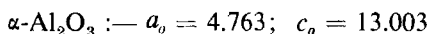
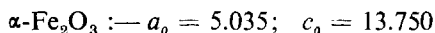
(a) Usual methods of preparation of Al_2O_3 involving the precipitation of aluminium hydroxide are known to form γ - Al_2O_3 when the hydroxide is dehydrated at low temperatures ($\sim 120^\circ\text{C}$) as was done in the course of the preparation of the 'co-precipitated' catalysts. Ferric hydroxide under similar conditions forms the stablest modification of the oxide, α - Fe_2O_3 .

(b) Considering the fact that γ - Al_2O_3 has a structure very different from α - Fe_2O_3 (cf. Wells 1962) and that γ - Al_2O_3 is only a metastable modification, one might expect an inhibitive effect of α - Fe_2O_3 on the crystallization of γ - Al_2O_3 during their simultaneous preparation.

(c) Since the conversion of aluminium hydroxide to α - Al_2O_3 requires heating to temperatures of about 1000°C (Norin 1944), it is not likely that Al_2O_3 gets crystallized in this form under the relatively mild conditions used, by the sole influence of α - Fe_2O_3 .

The overall effect of Fe_2O_3 in inhibiting the crystallization of Al_2O_3 may be less significant in catalysts containing large proportions of Al_2O_3 and so the XRD pattern of γ - Al_2O_3 although diffuse is observed in the case of catalysts with 5 and 19 per cent Fe_2O_3 . The absence of any XRD pattern for Fe_3O_4 in the same catalysts may be

considered to be due to a high degree of dispersion of Fe_2O_3 on Al_2O_3 , which owing to its usually high surface area serves as a support at these compositions. The phase transformations taking place in the catalysts on sintering bear out the above lines of arguments. Comparison of the results of XRD analysis of sintered catalysts containing 5, 19 and 41 per cent Fe_2O_3 reveal that a complete conversion of Al_2O_3 into $\alpha\text{-Al}_2\text{O}_3$ occurs even in catalysts containing as little as 5 per cent Fe_2O_3 . The sharp lines corresponding to $\alpha\text{-Al}_2\text{O}_3$ appearing in all the sintered catalysts (except in 78 per cent $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ where its detection is probably limited by its low percentage) are to be contrasted with their total absence in the case of unsintered catalysts with 41 and 57 per cent Fe_2O_3 and with their poorly defined nature in the catalysts of 5 and 19 per cent Fe_2O_3 . The formation of $\alpha\text{-Al}_2\text{O}_3$ in these catalysts at temperatures much lower than those reported by earlier workers is effected by the presence of $\alpha\text{-Fe}_2\text{O}_3$. The two oxides being strictly isostructural and comparable in cell dimensions (cf. Galasso 1970).



the crystallites of $\alpha\text{-Fe}_2\text{O}_3$ act as nuclei for the crystallization and growth of $\alpha\text{-Al}_2\text{O}_3$. This becomes all the more beneficial since in the original catalysts Al_2O_3 is present either in the metastable $\gamma\text{-Al}_2\text{O}_3$ form or in an amorphous form. In catalysts of 5 and 19 per cent Fe_2O_3 , however, the agglomeration of the dispersed Fe_2O_3 crystallites has to occur first before the crystallization of $\alpha\text{-Al}_2\text{O}_3$ is induced. The influence of Fe_2O_3 is so strong that even when impregnation is done on $\gamma\text{-Al}_2\text{O}_3$ it is transformed completely to $\alpha\text{-Al}_2\text{O}_3$ on sintering at 800°C . The 'coprecipitated' catalysts do not improve in their dehydration activity on sintering unlike 'impregnated' catalysts, probably because the reduction in surface area of these catalysts is more predominant than the increase in extent of interaction of the oxides achieved on heating.

If amorphous Al_2O_3 is taken to be present in the catalysts, and the fraction of total Al_2O_3 present in such a form decreasing with decreasing Fe_2O_3 content of the catalysts, it is possible to explain the properties of the mixed catalysts. The semiconducting property of the catalyst containing even 5 per cent Fe_2O_3 (Fig. 2 would correspond to the case where Fe_2O_3 is dispersed on a semiconducting support. Since an insulator support like $\gamma\text{-Al}_2\text{O}_3$ with Fe_2O_3 crystallites highly dispersed on it would not yield such a result, it is likely that the semiconducting properties of Al_2O_3 are influenced by the presence of Fe_2O_3 . The fact that the amorphous form of Al_2O_3 is semiconducting (Michel to Pouillard 1949) suggests that it exists together with $\gamma\text{-Al}_2\text{O}_3$ in catalysts containing 5 and 19 per cent Fe_2O_3 .

The effect of composition on the dehydration activity of the mixed catalysts may be seen from the data in Table II. High activities are shown by catalysts of low Fe_2O_3 content. The dispersion of iron oxide crystallites combined with the interactive influence of Al_2O_3 probably confers high dehydration activities to these catalysts. An explanation for the progressive fall in the activity as the Fe_2O_3 content increases from 41 to 78 per cent emerges from the above discussion. Considering the presence of Fe_2O_3 in a distinctly crystalline phase it would seem that the agglomeration of the crystallites resulting in a reduction in the active interface of the composite catalyst is responsible for this fall in activity.

Based on similarities in charge and size of Fe^{3+} and Al^{3+} the formation of a solid solution would be the most facile type of interaction between the two oxides. The preparation of this solid solution at and above 600°C by the direct heating of the co-precipitated hydroxides has been described by previous workers (Michel & Pouillard 1949; and Cirilli 1950). Since in the present studies only very mild conditions have been employed, the above type of interaction would not have occurred to a considerable extent. While several of the modified properties show that the two oxides have undergone an interaction, no positive evidence is available to establish the formation of a solid solution, because of the presence of large amounts of unreacted Fe_2O_3 or Al_2O_3 in all the catalysts. It follows then that in these catalysts there is a combination of the two oxides which is most likely to be in the direction of formation of a solid solution. This may include surface deposition as well as substitution which have been demonstrated by Levy and Bauer (1967).

(ii) *Aged Catalysts* : The results concerning the increase in dehydration activity (Table III) and the conversion of $\alpha\text{-Fe}_2\text{O}_3$ to $\gamma\text{-Fe}_2\text{O}_3$ by continued use of the catalysts suggest an intense interaction taking place when the catalysts are reduced during the reaction and subsequently regenerated. The 'aged' catalysts are purely dehydrating and are completely converted to Fe_3O_4 during the reaction, unlike the fresh catalysts. Considering the above result and comparing the complete solubility (in hydrochloric acid) of Fe_2O_3 in the aged samples with its partial solubility in the fresh catalysts, it is clear that the process of 'aging' removes the tight binding between the two oxides found in the fresh catalysts and also brings in a homogenization.

The sequence of phase changes occurring in the mixed catalyst system, viz., $\alpha\text{-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3 \xrightarrow{2\text{-propanol}} \text{Fe}_3\text{O}_4\text{-Al}_2\text{O}_3 \xrightarrow{\text{Air}} \gamma\text{-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ is the same as the one reported by Pouillard (1950) in the case of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solutions. The increase in temperature for the transformation of $\gamma\text{-Fe}_2\text{O}_3$ to $\alpha\text{-Fe}_2\text{O}_3$ observed by Michel and Pouillard (1949) and also by Cirilli (1950) in such solid solutions could explain the extraordinary stability of $\gamma\text{-Fe}_2\text{O}_3$ in these catalysts. It is possible, therefore, that small amounts of the solid solution present in the catalysts act as nuclei controlling these phase transformations. However, the fact that catalysts undergoing only partial reduction initially get converted completely to Fe_3O_4 after a few runs, cannot be explained by the above line of reasoning. Further, the solid solution is expected to be a tightly bound form of the two oxides, contradicting the observation that in the 'aged' catalysts the Fe_2O_3 content is totally soluble in acid. The reducing and oxidizing atmosphere provided to the catalyst alternately is apparently promoting a new kind of mixing, by which Fe_2O_3 in the catalysts is placed in an environment such that the effect due to the presence of Al_2O_3 is fully realized and yet is sufficiently free to show its identity. This leads to the stability of $\gamma\text{-Fe}_2\text{O}_3$, which is in agreement with the observations of De Boer and Selwood (1954) that an increase in the energy of activation for the conversion of $\gamma\text{-Fe}_2\text{O}_3$ to $\alpha\text{-Fe}_2\text{O}_3$ is caused by the simple addition of Al_2O_3 .

The fresh catalysts in the 'co-precipitated' series are obtained by adopting the usual methods employed in the preparation of $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$. During their simultaneous preparation there is a strong mutual influence on the oxides leaving a catalyst with modified structure and activity. The aged catalysts, on the contrary, are formed by usage of the catalysts—a process involving alternate reduction and

oxidation of the iron oxide contained in them. Similar transformation to $\gamma\text{-Fe}_2\text{O}_3$ is not encountered in the case of pure Fe_2O_3 and $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ mechanical mixtures, which means that the presence of the interacted form in the fresh catalysts is a necessary condition for the transformations to take place in the aged catalysts.

CONCLUSION

In the $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalysts there is a mutual influence of the two oxides in modifying the structural characteristics and semiconducting behaviour. The nature of the interaction is very similar to the formation of a solid solution. During the process of usage for reaction and regenerative oxidation, a transformation is effected, which loosens the tight binding of Fe_2O_3 in the mixed catalysts and at the same time stabilizes $\gamma\text{-Fe}_2\text{O}_3$.

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