STUDIES ON THE DECOMPOSITION OF ISOPROPYL ALCOHOL ON Mg $Al_{2-x}Fe_xO_4$

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ABSTRACT

Decomposition of isopropyl alcohol was carried out on the solid solution system $MgAl_{2-x}Fe_xO_4$ (x = 0 to 2). The system exhibited both dehydrogenation and dehydration activities. The selectivity for dehydration did not vary monotonically with change in x, but reached a minimum at x = 0.40. Mechanistic studies were made with a view to identifying the rate-determining step. The nature of the active sites was predicted by means of specific poisoning experiments and interesting correlations were obtained between activity for dehydrogenation and certain physicochemical properties of the system. The important conclusion drawn is that dehydrogenation of the alcohol, as well as the electrical and magnetic properties, are basically influenced by a fundamental property of the spinel system, namely, the symmetry of the catalytically acive Fe^{3+} site.

INTRODUCTION

Magnesium ferrite belongs to a class of catalysts which are effective for oxidative dehydrogenation of hydrocarbons with 4 to 6 carbon atoms. The first patent for the commercial process was granted to Bajars, Croce and Gabliks [1]. Following this, superior commercial catalysts, magnesium chromium ferrites and zinc chromium ferrites, were developed and patented by Rennard and Kehl [2,3]. Since then, oxidative dehydrogenation on commercial catalysts was studied in different laboratories [4,5,6]. Other potential uses of these catalysts include ammoxidation of monoolefins to diolefins, aldehydes and nitriles [7] and oxidation of hydrocarbons [8]. The catalytic effectiveness of ferrites for the above mentioned reactions arises because of the ease with which iron can exchange its oxidation state between 2 and 3. Another important attribute of these materials, from the commercial standpoint, is their stability under extremely reducing conditions, which is due to the spinel structure. Thus the reduction of Fe^{3+} to Fe^{2+} takes place without altering the lattice configurations so that upon reoxidation, the original state is retained. In contrast

to the spinel ferrites, the catalyst Fe_2O_3 loses its activity as it is reduced to FeO and metallic iron.

In the present investigation, decomposition of isopropyl alcohol has been undertaken because it is a very useful test reaction [10]. Isopropyl alcohol can undergo dehydration and dehydrogenation, and the selectivity effects give much information on the nature of the catalysts and aid in catalyst selection. The solid-solution system $MgAl_{2-x}Fe_xO_4$, apart from its commercial interest, is particularly suited for a systematic study in view of the interesting variation of its solid state properties, reported in an earlier paper [11]. Firstly, the structure of the spinel changes from inverse to normal as x in the system is decreased from 2 to 0. The magnetic and electrical properties also vary gradually as x in the system is varied.

In this paper, the catalytic properties of the ferrite system for the decomposition of alcohol are evaluated and discussed in terms of their solid-state properties.

EXPERIMENTAL
Preparation of catalysts

The catalysts were prepared by the coprecipitation of the hydroxides at a pH of 9.5 to 10 using a mixture of NH_4OH and NH_4Cl. The starting materials were the nitrates (all British Drug Houses, A.R.). The precipitates were dried at 80°C and then calcined at 950°C for 24 h. The resulting compound was analyzed by X-ray and chemical methods. In the case of $MgFe_2O_4$, the compound was leached with dilute HCl in order to remove excess MgO. Table 1 gives the composition of each compound, together with its BET surface area. The details of the X-ray characterization are given in a previous article [11].

TABLE 1
Composition of catalysts and surface areas

S no.	Catalyst $MgAl_{2-x}Fe_xO_4$	Surface area $/m^2 \, g^{-1}$
1	x = 0.0	49.5
2	x = 0.02	46.5
3	x = 0.25	39.5
4	x = 0.30	38.5
5	x = 0.40	30.1
6	x = 1.3	25.1
7	x = 1.6	22.3
8	x = 1.8	20.5
9	x = 2.0	18.3

Measurement of electrical conductivity

The electrical conductivity of the pelletized samples was measured by applying a suitable voltage across the pellet and measuring the the current using a microammeter (Hewlet-Packard, model 425A).

Adsorption measurements

Adsorption of vapors was made gravimetrically using a sensitive quartz spring (McBain balance).

Determination of surface acidity

Protonic acidity was measured by an ion-exchange method [12], while total acidity was determined by titration with n-butylamine [12].

Catalytic test

Decomposition of isopropyl alcohol was carried out in a fixed-bed flow reactor operated in an integral mode as described earlier [13]. The catalyst sample was held between two glass wool plugs, surrounded by glass beads to facilitate heat exchange. The temperature of the catalyst bed could be measured to within ±0.1°C with a chromel-alumel thermocouple reaching out to the sample through a thermowell. Isopropyl alcohol (British Drug House , A.R.) was distilled before use and checked for purity by GC. The reactant was fed into the reactor through a preheater by means of a motor-driven syringe pump (Sage Instruments Co., White Plains, N.Y., U.S.A., Model 255.2) for accurate control and metering of the feed rate. The liquid products were condensed in a Liebig condenser and collected in a trap immersed in a salt-ice mixture. The gaseous products were collected in a calibrated gas burette by displacement of saturated brine solution. Initially, 15 min was allowed for the attainment of steady state before collecting and analyzing the products. The partial pressure of alcohol was varied by diluting it with gaseous nitrogen. The liquid products were analyzed using a vapor-phase chromatograph (Varian 1800) with a thermal-conductivity cell as the detector. Standard Carbowax 20M (on Chromosorb) column was used with H_2 as the carrier gas. The gaseous products were analyzed using a dimethyl sulpholane column at 30°C.

RESULTS AND DISCUSSION

Decomposition of isopropyl alcohol on the solid-solution system $MgAl_{2-x}Fe_xO_4$ has been investigated in the temperature range 255 - 360°C. The catalysts studied have the composition $x \leq 0.40$ and $x \geq 1.3$. The catalysts in the composition range $0.4 < x < 1.3$ were not studied because of secondary phase formation [11]. Analysis of dehydration and dehydrogenation reaction products revealed that when x has values 0 and 0.02 the system exhibits only dehydration activity, to the complete exclusion of dehydrogenation activity. All the other catalysts exhibit both dehydration and
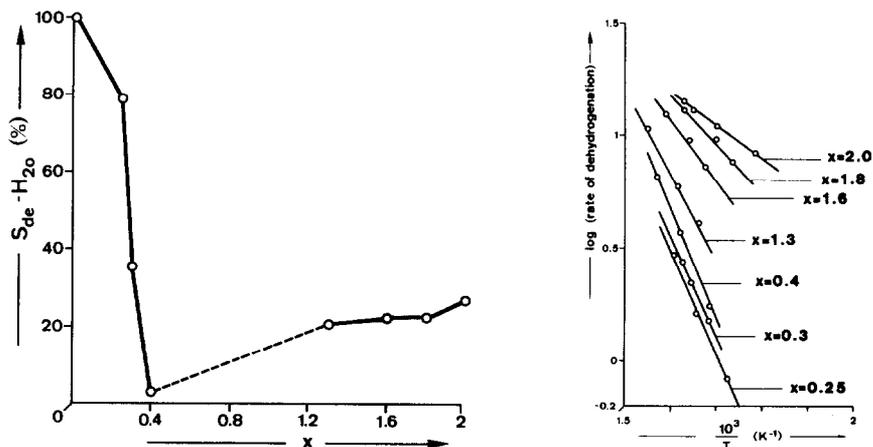
FIGURE 1   Selectivity for dehydration S_{de-H_2O} of isopropyl alcohol vs. x in $MgAl_{2-x}Fe_xO_4$.

FIGURE 2   Arrhenius plots for dehydrogenation of isopropyl alcohol on $MgAl_{2-x}Fe_xO_4$ (x = 0 → 2). Rate is expressed as mol s^{-1} g^{-1}.

dehydrogenation activities, although with varying selectivities. Figure 1 shows the variation of selectivity for dehydration (S_{de-H_2O}) with change in x for the system. The selectivity is evaluated by averaging the values obtained over a range of temperatures. It can be seen from the figure that the selectivity reaches a minimum at x = 0.40, increases to a value of 22 % at x = 1.3 and then remains fairly constant with further increase in x.

From the contact time versus time plots, the initial rates of the reaction were calculated and were utilized for the construction of Arrhenius plots (Figures 2 and 3. From these plots activation energies for dehydration and dehydrogenation were calculated. The kinetic parameters were assembled and are presented in Table 2.

Mechanistic studies   These studies are aimed at identifying the rate-limiting step for dehydration and dehydrogenation reactions. Catalysts with x ≥ 1.3 and x ≤ 0.40 behaved differently with respect to mechanism, and hence they will be treated separately.

Dehydrogenation on catalysts with x ≥ 1.3   Product-inhibition studies revealed that the products acetone or hydrogen have negligible effect on the yields. This is shown in Figure 4 for a typical catalyst with x = 1.6. Hence, desorption of products may not figure in the rate-determining step. To further supplement this result, conductivity measurements in situ have been made in different flowing atmospheres (alcohol, acetone and H_2) at a constant contact time and at different temperatures. Figure 5 shows typical curves for the sample with x = 1.6. In Figure 5 $\Delta log\ \sigma$ refers to changes in log σ at any instant. It can be seen that adsorption
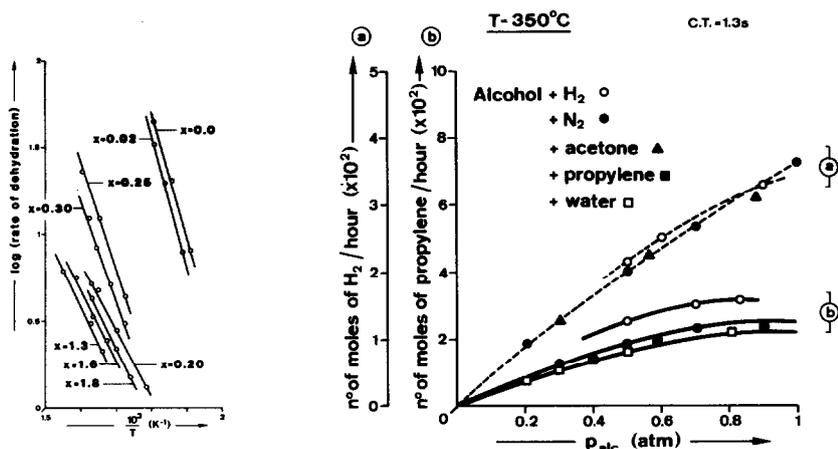
FIGURE 3 Arrhenius plots for dehydration of isopropyl alcohol on $MgAl_{2-x}Fe_xO_4$ (x = 0 → 2). Rate is expressed as mol s^{-1} g^{-1}.

FIGURE 4 Effect of substrates on the decomposition of isopropyl alcohol on $MgAl_{2-x}Fe_xO_4$ (x = 1.6).

of alcohol, acetone and hydrogen takes place by an acceptor mechanism, wherein the electron transfer takes place from the adsorbate to the n-type catalyst. It is further seen from the figure that at any temperature the conductivity changes by more than two orders of magnitude when acetone or hydrogen is fed, while with alcoho as the feed, the conductivity changes by merely one order of magnitude. Moreover, in the case of acetone or hydrogen, the changes in conductivity with time are much sharper than with alcohol as the feed. Of course, the highest change in conductivity is realized when alcohol is fed at 300°C ($\sim 10^3$ ohm^{-1}), because the reaction products also contribute to the conductivity. It is also seen that at 100°C, the conductivity change could be observed only in the case of acetone or hydrogen. Any observable change in conductivity with alcohol as the feed takes place only at 165°C, suggestin that adsorption of alcohol is a highly activated step. Thus adsorption of alcohol could be the rate-determining step on these catalysts.

   Dehydrogenation on catalysts with x ≤ 0.4   Product-inhibition studies reveal that acetone inhibits the reaction. This is shown in Figure 6 for the catalyst with x = 0.30. Also, hydrogen does not affect the rate of reaction on any of these catalysts. Conductivity measurements in situ (Figure 7) show that adsorption of acetone takes place only at 170°C, whereas alcohol and hydrogen are adsorbed, even at 120°C, with measurable changes in conductivity ($\Delta\log \sigma \cong 1$). This points to the fact that acetone adsorption could be relatively more activated than that of alcohol or hydrogen (see Table 3), indicating that the former is more strongly adsorbed. Thus it can be concluded that desorption of acetone is the slowest step on these catalysts.

TABLE 2

Kinetic parameters for the decomposition of isopropyl alcohol on $MgAl_{2-x}Fe_xO_4$
(x = 0 to 2)

Catalyst $MgAl_{2-x}Fe_xO_4$	Activation energy /kcal mol^{-1} Dehydrogenation	Dehydration	Frequency factor /s^{-1} m^{-2} Dehydrogenation	Dehydration
x = 2.0	6.9	17.5	3.8×10	5.5×10^3
x = 1.8	9.9	17.4	4.4×10^2	4.4×10^3
x = 1.6	12.2	17.6	2.1×10^3	3.2×10^3
x = 1.3	16.6	17.8	4.0×10^4	2.7×10^3
x = 0.40	21.0	-	9.8×10^5	-
x = 0.30	20.2	26.8	4.2×10^5	1.6×10^7
x = 0.25	20.0	28.5	2.5×10^5	6.6×10^7
x = 0.02	-	34.1	-	2.0×10^{10}
x = 0.0	-	34.0	-	2.8×10^{11}

TABLE 3

Heats of adsorption of reactants and products

Catalyst $MgAl_{2-x}Fe_xO_4$	ΔH_{alc} /kcal mol^{-1}	$\Delta H_{acetone}$ /kcal mol^{-1}	ΔH_{water} /kcal mol^{-1}
x = 2.0	2.2	2.5	6.0
x = 1.6	3.3	2.9	5.8
x = 0.4	11.5	16.6	-
x = 0.30	14.2	13.2	16.4
x = 0.0	16.2	-	21.2

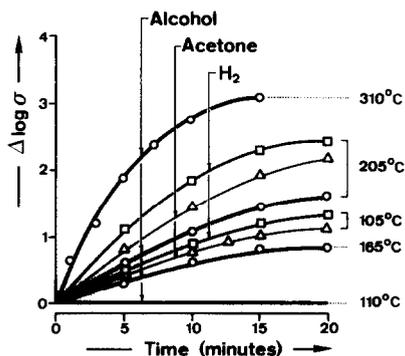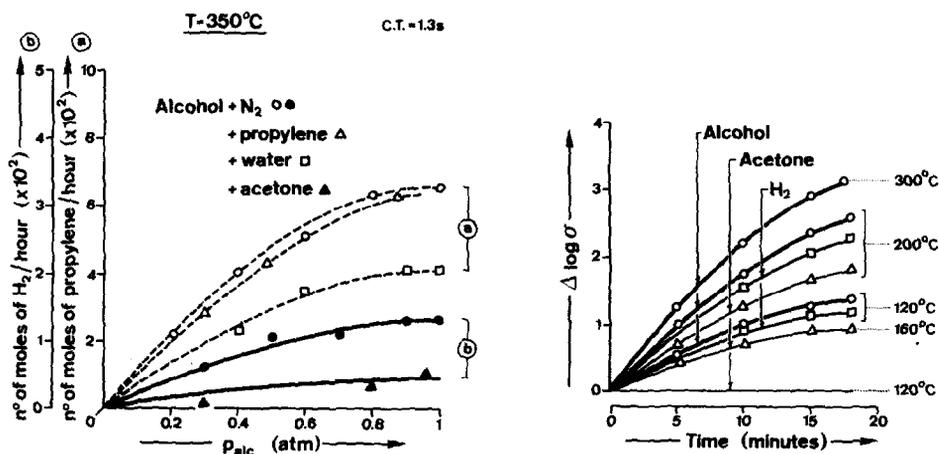FIGURE 5 Conductivity changes of $MgAl_{2-x}Fe_xO_4$ (x = 1.6) in various substrate atmospheres.

FIGURE 6   Effect of substrates on the decomposition of isopropyl alcohol on $MgAl_{2-x}Fe_xO_4$ $(x = 0.3)$.

FIGURE 7   Conductivity changes of $MgAl_{2-x}Fe_xO_4$ $(x = 0.3)$ in various substrate atmospheres.

<u>Dehydration reaction on catalysts with x ≤ 0.40</u>   The results of the product-inhibition studies (Figure 6) show that water has an appreciable inhibiting effect on the dehydration yield. The figure shows this effect in the case of a catalyst with $x = 0.30$. Hydrogen enhances the dehydration activity, presumably because it induces protonic acid sites on the surface. The heat of adsorption of water is rather high (16.4 kcal mol^{-1} for a catalyst with $x = 0.30$) indicating that it is strongly adsorbed. Thus product-inhibition studies, in conjunction with heat of adsorption values, lead to the conclusion that desorption of water is the rate-controlling step.

<u>Dehydration reaction on catalysts with x ≥ 1.3</u>   Neither water nor propylene inhibits the reaction, as is evident from Figure 4. Thus the desorption of products may not figure in the rate-controlling step. From the available data, it is not possible to decide whether surface reaction or adsorption of alcohol is the rate-limiting step.

Nature of the active sites

<u>Dehydrogenation reaction</u>   It has been seen that $MgAl_2O_4$ does not exhibit any dehydrogenation activity and the activity for this reaction commences only when Fe^{3+} is introduced. However, the absence of dehydrogenation activity for the catalyst with $x = 0.02$ may be due to intrinsically low activity of isolated Fe^{3+} ions. Thus Fe^{3+} may be considered as a possible active site for dehydrogenation. This is further confirmed experimentally by studying alcohol adsorption on a catalyst activated
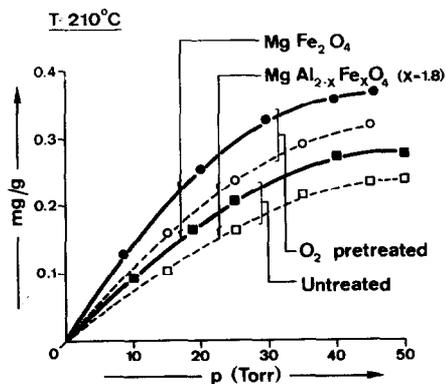
T- 210°C

FIGURE 8 Adsorption isotherms of alcohol on untreated and oxygen pretreated catalysts.

under vacuum (10^{-5} mm Hg) for 4 h at 400°C and on an oxygen-pretreated catalyst. Oxygen pretreatment was carried out by soaking the evacuated catalyst for 3 to 4 h in O_2 and the pumping off the physically adsorbed oxygen for 5 min. From Figure 8 it is seen that alcohol adsorption is enhanced after pretreatment with oxygen. It is reasonable to assume that the oxygen-pretreated catalyst will have more Fe^{3+} than the untreated catalyst. Thus, the increased adsorption on oxygen pretreatment can be explained by assuming that Fe^{3+} is the active center for alcohol adsorption.

Dehydration reaction No correlation was found between the dehydration activity and the electrical conductivity. Thus, the electrical properties of the catalysts do not seem to play any role in the dehydration reaction.

In order to learn about the nature of the active sites, specific poisoning experiments were carried out by saturating the surface with pyridine and ammonia before starting the reaction. Both suppressed dehydration, although to different extents (see Table 4). This shows that the reaction is acid-catalyzed. It is generally known [14] that pyridine interacts specifically with Lewis acid sites, while ammonia interacts indiscriminately with both protonic and Lewis acid sites. From Table 4, it may be seen that on catalysts with $x \leq 0.40$, pyridine suppresses dehydration only to some extent as a small dehydration activity is still retained. As we move to catalysts with $x \geq 1.3$, it is found that pyridine suppresses dehydration activity to a very large extent, with the exception of $MgFe_2O_4$. In the case of ammonia pretreatment, dehydration activity is almost absent on all catalysts (see Table 4).

From the above observations, it is possible to arrive at the following conclusions:

(a) On catalysts with $x \geq 1.3$, only Lewis acid sites are active for dehydration (with the exception of $MgFe_2O_4$).

(b) On catalysts with $x \leq 0.40$, both protonic and Lewis acid sites are responsible

TABLE 4

Effect of poisons on dehydration activity of various catalysts[a]

Catalyst MgAl$_{2-x}$Fe$_x$O$_4$		Conversion without pretreatment /mol%	Conversion after pretreatment with pyridine /mol%	Conversion after pretreatment with ammonia /mol%
x	T/°C			
2.0	340	4.1	2.3	0.5
1.8	340	2.9	0.2	0.5
1.6	350	2.8	0.2	0.4
1.3	335	2.7	0.3	0.4
0.40	330	-	-	-
0.30	330	8.8	2.3	0.3
0.25	315	11.0	2.8	0.7
0.02	270	12.5	5.8	0.8
0.0	275	16.2	6.1	1.0

[a]all conversions are expressed per g of catalyst; contact time = 2.0 s.

for the activity; this is also true for MgFe$_2$O$_4$. In the case of MgFe$_2$O$_4$, a small amount of protonic acid sites seems to be important, probably because the catalyst was leached with dilute HCl (to remove the slight excess of MgO in the spinel), washed with water and dried at 120°C before the catalytic tests.

To supplement the above data, acidity measurements were made and the results are shown in Table 5. Probably n-butylamine titration values predominantly represent Lewis acidity. From Table 5, it may be seen that, while Lewis acidity is present on all the catalysts, protonic acidity is shown only by catalysts with x ≤ 0.40. Protonic acidity is almost immeasurable on catalysts with x ≥ 1.3 (except MgFe$_2$O$_4$).

The variation in selectivity for dehydration (S$_{de-H_2O}$) as a function of x (Figure 1) can be rationalized in the light of the nature of the active sites. Initially, S$_{de-H_2O}$ is 100 % for MgAl$_2$O$_4$ because there are practically no active sites for dehydrogenation. Even when x = 0.02, S$_{de-H_2O}$ remains at 100 %, presumably because of intrinsically low activity of isolated Fe^{3+} ions for dehydrogenation, as pointed out earlier. As x is increased further, the number of active sites for dehydrogenation increases, accompanied by a decrease in the type and strength of acid sites responsible for the dehydration reaction. Thus, there is a steep fall in S$_{de-H_2O}$. However, the minimum at x = 0.40 in Figure 1 is difficult to understand. It was, in fact, found that during the first 2 to 3 min of the reaction (well before the attainment of a steady state), there was a substantial amount of propylene in the products (corresponding to about 20 % selectivity for dehydration). One possible explanation is that water, which is formed initially, effectively blocks the acid sites, thereby deactivating the catalyst by the time a steady state is

TABLE 5

Surface acidity data on various catalysts

Catalyst x value for $MgAl_{2-x}Fe_xO_4$	Protonic acidity /mmol g^{-1}	Total acidity /mmol g^{-1}
2.0	0.013	0.092
1.8	-	0.153
1.6	-	0.130
1.3	-	0.110
0.40	-	0.084
0.30	0.012	0.092
0.25	0.016	0.100
0.02	0.038	0.103
0.0	0.039	0.104

reached. On the catalyst with $x \geq 1.3$, S_{de-H_2O} again rises to about 20 % because these samples have considerable Lewis acidity which is not, apparently, attacked by water. The varying nature of the interaction with water on all these catalysts needs to be further investigated by spectroscopic studies.

Correlation of dehydrogenation activity with physico-chemical properties

Comparison of the activity of catalysts ($x \geq 1.3$) for the dehydrogenation reaction has been made on the basis of the values of activation energy. The activity pattern observed is $MgFe_2O_4 > MgAl_{0.2}Fe_{1.8}O_4 > MgAl_{0.4}Fe_{1.6}O_4 > MgAl_{0.7}Fe_{1.3}O_4$. This is further checked by comparing the yields of acetone or hydrogen for 40 min process time at the same contact time (Table 6). This gives the pattern in terms of the sustained activities of the catalysts. One again arrives at the same activity pattern as obtained earlier.

Several correlations could be drawn between dehydrogenation and physico-chemical

TABLE 6

Dehydrogenation yields obtained after 40 minutes process time. (T = 340°C, contact time = 2.7 s).

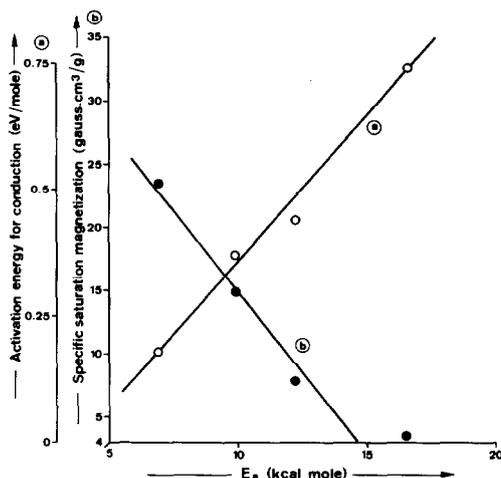| Catalyst x value for $MgAl_{2-x}Fe_xO_4$	Yield /mol m^{-2}
2.0	0.14
1.8	0.10
1.6	0.07
1.3	0.04

FIGURE 9 Correlation between dehydrogenation activity and (a) electrical
conductivity, (b) saturation magnetization on $MgAl_{2-x}Fe_xO_4$ (x = 1.4 → 2.0).

properties:

(a) The activity varies linearly with activation energy for conduction (Figure 9). The
higher the degree of n-type conductivity, the higher the dehydrogenation activity.
This is consistent with the mechanism proposed earlier. Adsorption of alcohol (which
occurs by transfer of electrons from the adsorbate to the catalyst) is the rate-
limiting step on these catalysts. On a catalyst with lower activation energy for
n-type conduction, such a transfer of electrons from adsorbate becomes relatively
more facile in comparison to a catalyst with higher activation energy for conduction.
The conductivity on these samples is due to a $Fe^{2+} \rightarrow Fe^{3+}$ + e type process. When
the alcohol is adsorbed by donation of electrons on a Fe^{3+} site, the charge on that
site diffuses to an adjacent site more easily when the activation energy for the
same is smaller than when it is higher.

(b) The catalytic activity decreases linearly with increase in the ratio $(Fe^{3+})_{tetra}/$
$(Fe^{3+})_{octa}$ (see Figure 10a). The latter quantity is computed from cation distribution
values already reported [11]. It may be noted that the ratio $(Fe^{3+})_{tetra}/(Fe^{3+})_{octa}$
increases as x is decreased from 2 to 1.3. The correlation observed in Figure 10a
may be rationalized on the basis of the fact that the Fe^{3+}-O bond distance is more
when Fe^{3+} is in octahedral symmetry than when it is in tetrahedral symmetry. Hence,
Fe^{3+} will be more readily available for adsorption of alcohol when it is in an
octahedral site than in a tetrahedral site.

(c) The activity for dehydrogenation increases linearly with increase in the lattice
parameter (see Figure 10b). The overall effect of any lattice expansion is to
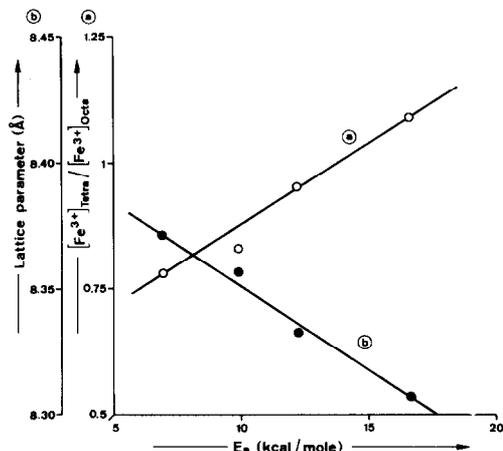increase the Fe^{3+}-O distance, whether Fe^{3+} is in an octahedral site or in a tetra-

FIGURE 10   Correlation between dehydrogenation activity and (a) the ratio
$(Fe^{3+})_{tetra}/(Fe^{3+})_{octa}$, (b) lattice parameter of $MgAl_{2-x}Fe_xO_4$ ($x = 1.3 \rightarrow 2.0$).

hedral site. The increase in the Fe^{3+}-O distance should facilitate the adsorption
of the alcohol.

(d) The saturation magnetization also correlates linearly with the activity for
dehydrogenation (Figure 9). Specific saturation magnetization at room temperature
has been chosen for this purpose. This correlation suggests that the catalytic
activity might be related to the extent of the magnetic ordering in the catalyst.
It appears that the increasing magnetic ordering (resulting from exchange interaction
between the Fe^{3+} ions) facilitates the charge-transfer phenomenon involved in the
adsorption of alcohol.

The correlations derived above, between the catalytic activity on the one hand
and the physico-chemical parameters on the other, are in general agreement with
those discussed by Krylov [10]. However, the present work answers an important
question as to whether the dependence of the catalytic activity on each of these
parameters is direct or indirect. If one considers the internal dependence of the
solid-state properties (discussed in [11]) it is clear that the electrical and
magnetic properties of the system very much depend on, and are sensitive to,
variations in the cation distribution values. As the catalytic activity correlates
with cation distribution values, it is logical to expect a similar correlation
between catalytic activity and electrical and magnetic properties. It then turns
out that the correlation between catalytic dehydrogenation activity and electrical
and magnetic properties is essentially because both depend largely on the cation
distribution. Thus, the important conclusion that emerges from the present work
is that the site symmetry of the catalytically active Fe^{3+} ions could be the crucial
fundamental property influencing both the catalytic and solid state properties of
the present system.

Stability of the catalysts Stability tests were made on the samples which showed strong dehydrogenation activity ($x \geq 1.3$). These ferrites showed good stability under highly reducing reaction conditions. Two checks were made to determine the stability: (i) Conversion levels over a long process time (40 min after reaching a steady state) and (ii) comparison of X-ray diffraction lines of a used catalyst with those of a fresh one.

Conversion levels were steady and did not drop for over 40 min process time, after a steady state was reached. This enabled the evaluation of sustained activities of the catalysts in terms of conversions over 40 min process time, which are presented in Table 6.

X-ray diffraction analysis of the used catalysts showed that all of them gave the reflections due to spinel 220, 440, 311 and 400 planes, although there was a slight decrease in intensities as compared to fresh catalysts. Further, they did not show any lines due to FeO or Fe phases. Thus, there is no bulk reduction of the catalysts and the spinel structure is essentially retained under the reaction conditions. However, surface reduction could take place which is not detectable by X-ray diffraction. This is in contrast to Fe_2O_3 catalysts, which undergo bulk reduction under reducing conditions [9].

Comparison with commercial catalysts The commercial catalysts, closely related to the catalysts under study, are $MgFe_2O_4$ and $MgCr_{2-x}Fe_xO_4$. The reaction studied on these catalysts is oxidative dehydrogenation (OXD) of n-butenes to butadiene [6,15]. Although the reaction studied on our ferrite catalysts is different, it is worthwhile comparing the general conclusions because both types of reactions involve dehydrogenation. Here, the comparison is made only with the iron-rich samples ($x \geq 1.3$) since they are more closely related to the commercial catalysts than the iron-deficient samples ($x \leq 0.40$).

Firstly, it was found that on $MgFe_2O_4$ and $MgCr_{2-x}Fe_xO_4$, no bulk reduction of the catalyst takes place during the OXD reaction, even in the absence of oxygen [6,15]. The surface reduction is limited to the Fe^{2+} state in the temperature range 300 - 400°C. In our case also, only surface reduction seems to take place during use in the reactor, as already pointed out earlier. For the OXD reaction, the easy reducibility of Fe^{3+} to Fe^{2+} and its reoxidation is postulated to be important. In a similar fashion, for the dehydrogenation of alcohol we have suggested Fe^{3+} as the active site for the adsorption of alcohol. While the Fe^{3+} site may be reduced to Fe^{2+} during adsorption and subsequent reaction, it regains the Fe^{3+} state by diffusing the electron to an adjacent Fe^{3+} ion. This is already explained in the text on the basis of the correlation of catalytic activity with n-type semiconductivity. However, it should be added that, under the present scheme, if the activity has to be sustained for as long as 40 min as observed, there should be diffusion of Fe^{3+} from the bulk to the surface.

SUMMARY AND CONCLUSIONS

(a) The mechanisms for dehydrogenation and dehydration of alcohol have been found to change as x in the system $MgAl_{2-x}Fe_xO_4$ is varied.

(b) The variation in selectivity as the iron content in the system is changed is closely related to the changes in the type and strength of active sites.

(c) While the correlations obtained between the catalytic activity and physico-chemical parameters are in general agreement with those discussed by Krylov, the present work leads to the conclusion that the site symmetry of the Fe^{3+} ion is crucial in influencing the solid-state properties, as well as the catalytic properties.

ACKNOWLEDGEMENTS

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