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The Decomposition of Isopropanol over Spinel Solid Solutions $MgAl_{2-x}Cr_xO_4$

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Isopropanol decomposition has been studied over the spinel solid solutions $MgAl_{2-x}Cr_xO_4$ where $x = 0 \rightarrow 2$. There are two zones of activity as a function of chromium content. There is an activity minimum at $x = 0.4$. The active sites on catalysts below $x = 0.4$ are thought to be electronically isolated, whereas above $x = 0.4$ they interact electronically. Dehydration activity is high over catalysts very dilute and very concentrated in chromium. Dehydrogenation activity seems to be favored by chromium pair sites.

INTRODUCTION

Over the past decade a number of investigators have demonstrated the value of oxide solid solutions in unravelling the importance of matrix and electronic effects in oxide catalysis. To reduce the complexity of the problem these studies have focused on simple reactions such as N_2O decomposition (*1*, *2*), H_2–D_2 exchange (*3*), hydrogen oxidation (*4*), etc. Recently work has begun to appear on reaction systems in which selectivity as between two reaction pathways can be investigated as a function of the catalyst parameters (*5*, *6*). This is an important development because the catalyst parameters determining selectivity are also badly understood. In this paper we focus attention on the relative activities of a series of chromium-containing spinel solid solutions in the decomposition of isopropanol. Dehydration and dehydrogenation are the competing reactions. Both water and hydrogen can be strongly held by oxide catalysts. A previous study (*5*) on corundum phase solid solutions containing chromium evidenced dramatic changes in selectivity with chromium content. A study of the same reaction over catalysts having the spinel structure should allow any matrix effects to become evident.

EXPERIMENT

Materials. $MgAl_2O_4$, $MgCr_2O_4$, and $MgCr_xAl_{2-x}O_4$ solid solutions used as catalysts were prepared in air at 1620 K as previously described (*7*). The chromium content of the catalysts is designated by the nomenclature SMAC N where N denotes the nominal number of chromium atoms per 100 aluminum atoms. The surface areas of the solids were determinated by the BET method using Specpure Kr at 77 K (Table 1).

Analar isopropanol vapor was used and was purified by a number of freeze pump cycles.

Procedures. Isopropanol decomposition was studied in a circulating system of volume 440 cm^3 at a pressure of 6.6 kPa in the temperature range 500 to 660 K. Approximately 0.5 g of catalyst was contained in a silica vessel through which isopropanol was circulated by means of a magnetic circulating pump. The extent of reaction was followed by continuous sampling of the reacting gases to an MS 10 mass spectrometer previously calibrated for sensitivity to propene, isopropanol, acetone, and CO_2. Initial catalyst pretreatment consisted of outgassing the oxide for 18 hr at about 970 K and 10^{-3} Pa. Between each reaction an

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TABLE 1

Catalyst	x in $MgAl_{2-x}CrO_4$	Surface area (m^2 g^{-1})	Propene		Acetone	
			E_A (kJ $mole^{-1}$)	log (A/cm min^{-1})	E_A (kJ $mole^{-1}$)	log (A/cm min^{-1})
$MgAl_2O_4$	0	0.64	145	12.1	107	8.6
SMAC 1	0.02	0.68	87	7.1	159	13.2
SMAC 5	0.09	0.70	120	9.8	36	2.5
SMAC 10	0.18	0.73	56	4.0	71	5.8
SMAC 25	0.40	6.7	90	6.8	123	10.3
SMAC 300	1.5	1.4	96	7.4	75	6.4
$MgCr_2O_4$	2.0	1.6	92	7.8	101	8.8

outgassing at 1020 K for 2 hr gave reproducible results.

RESULTS

The reactions were followed for about 30 min. The "absolute" rate constants for dehydration and dehydrogenation were obtained from the initial rates (5 min) assuming a unimolecular reaction in each case. Thus $k_{abs} = (P_{prod}/P_{isoprop})V/At$ cm min^{-1}, where V is the reaction vessel volume, A is the area of the catalyst (cm^2), and t is the reaction time (min) (*1, 2, 8, 10*). Arrhenius plots of k_{abs} were obtained for dehydration and dehydrogenation and from these plots the activation energies and preexponential factors shown in Table 1 were obtained. A marked variation with Cr content is evident.

Figure 1 shows the variation of total decomposition activity at 570 K with Cr content. The activity at this temperature reaches a maximum at SMAC 10, falls to a minimum as SMAC 25, and then rises again to $MgCr_2O_4$. This type of behavior is similar to that found for a number of reactions over model oxide catalysts (*7*).

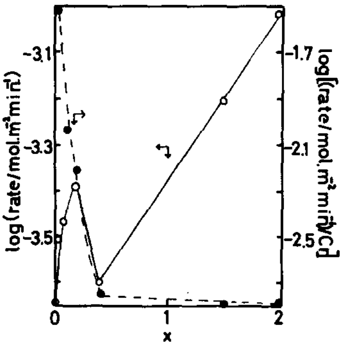


FIG. 1. Variation of overall decomposition activity, ○, and activity per chromium ion, ●, at 570 K as a function of the chromium content of the catalysts.

The activation energies and preexponential factors make it clear that activity and selectivity will be rather dependent on temperature. Within the region of measurable rate this dependence is not too critical. To highlight the role of Cr it is instructive to plot out the variation of selectivity and activity with Cr content.

The selectivity of the catalysts at 570 K varies markedly with chromium content (Fig. 2). Selectivity is defined at a particular temperature as rate (acetone)/[rate(acetone) + rate(propene)]. Reaction selectivity over $MgAl_2O_4$ was about 0.6, whereas SMAC 1 is predominantly a dehydration

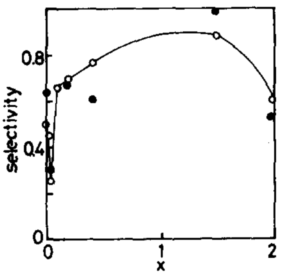


FIG. 2. Variation of selectivity at 570 K (rate to acetone/rate to acetone + ratio to propene) after 5 min, ○, and 30 min, ●, as a function of chromium content.

catalyst with a selectivity of about 0.2. The addition of further chromium generates more strongly dehydrogenating catalysts with selectivities for SMAC 10 to SMAC 300 rising from 0.7 to 1.0. Reaction selectivity over $MgCr_2O_4$ was, however, very similar to $MgAl_2O_4$.

In Fig. 3 the selectivity behavior has been translated into terms of the activity of each catalyst in producing acetone and propene.

The selectivity behavior of the catalysts with respect to temperature and time also showed a marked variation (Fig. 4). $MgAl_2O_4$ and SMAC 25 displayed an increasing selectivity for dehydrogenation with temperature after 5 min, but a decreasing selectivity with temperature after 30 min. In the cases of SMAC 1, 5, and 10 and SMAC 300, however, selectivity increased markedly with temperature after 5 *and* 30 min of reaction. $MgCr_2O_4$ presented a further contrast in that its selectivity was essentially constant with temperature.

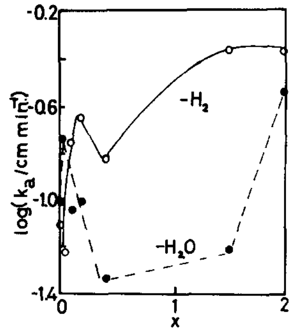


FIG. 3. Variation of activity to dehydrogenation, ○, and dehydration, ●, as a function of the chromium content of the catalysts at 570 K.

DISCUSSION

The decomposition reaction previously studied over the corundum solid solutions (*5*) utilized a flow system. Direct comparison with the present static reactor data is not straightforward, since as reaction proceeds there are increasing partial pressures of products present over the catalyst. Nevertheless the variation of selectivity to dehydrogenation as a function of catalyst composition is broadly similar to that found over the α-$Al_{2-x}Cr_xO_3$ catalysts (*5*). There are, however, some significant differences which together with the similarities highlight the importance of matrix and electronic effects on catalytic behavior in this reaction.

Before considering the catalysts in detail it is instructive to recall that the variation of activity on N_2O decomposition and H_2/D_2 exchange as a function of the Cr content of these catalysts was very similar to that shown in Fig. 1. (*2*, *8*). These activity patterns were understood in terms of the coordination and electronic state of the cations

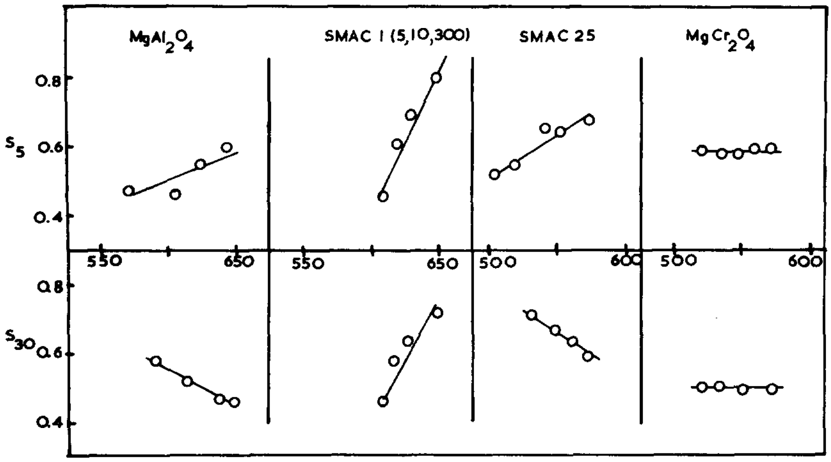
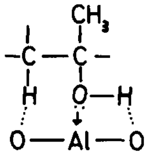


FIG. 4. The variation of selectivity with temperature after 5 and 30 min.

exposed in the surface planes of spinel. An earlier paper (*8*) demonstrated that fully dehydroxylated surface planes would contain coordinatetively unsaturated B-site cations. A general feature on the planes (100), $(110)_a$, and $(111)_b$ is that site B-cations form rows across the surface. Although each plane may be calculated to be electrically neutral overall, surface B-sites (which accommodate Al and Cr ions, both assumed to have +3 charge) and A-sites (which accomodate Mg ions with +2 charge) may not all be neutral but may have local positive and negative charges (i.e., cation charge + anion charge) due to lowered coordination at the surface. On the $(111)_b$ plane 4-coordinate cations (total oxygen anion charge = −2.5) alternate with 5-coordinate cations (anion charge = −3.5), while on $(110)_a$ 3/4 of the cations are 4-coordinate (anion charge = −2.33) and 1/4 are 5 coordinate (anion charge = −3.33). The B-site cations on the (100) plane are all 5-coordinate (anion charge = −2.83). In contrast, on the $(110)_b$ and $(111)_a$ planes B-site cations are isolated in the surface with very low coordinations; 1/4 are 3 coordinate and 3/4 are 4-coordinate. It is clear that sites having an excess positive charge (i.e., low anion charge relative to the cation) will seek to neutralize this by electron movement either by adsorption to form a negatively bound entity or by electron movement from the bulk of the solid. A recent paper from this laboratory (*9*) has demonstrated that electron movement from the bulk of the solid will become significant only when each Cr ion has *at least* one Cr nearest neighbor. Thus before this (localized–nonlocalized, or LNL) point the Cr ion sites, be they single ions or pairs of ions, will be essentially electronically isolated and thus "neutralization" of such sites will not be likely by bulk electron transfer. After the LNL point bulk electron transfer becomes increasingly facile as Cr content rises and this has been observed to have very significant effects on the surface reactivity. It is evident from data presented that this catalytic process is no exception. Let us now consider the catalysts in turn.

$MgAl_2O_4$

This catalyst, the host matrix, has a selectivity of 0.5 but it becomes more dehydrating with time. Coordinately unsaturated Al^{3+} ions with a local net positive charge will form effective Lewis acid sites which would be expected to be the dehydration sites. The low coordination of Mg^{2+} on A sites makes further lowering energetically less favorable, so the activity of Mg^{2+} is not thought to be high. Water molecules will probably be retained at the dehydration sites which would explain the rather high activation energy, desorption being necessary before further alcohol adsorption can occur. Dehydrogenation may occur on basically similar sites whose acidity or positive character is rather less. Thus the site would be a coordinatively unsaturated Al^{3+}. If the Al^{3+} site had a net positive charge a strong bond would be formed between the oxygen and Al^{3+} causing a displacement of charge in the molecule such that H_2O was split off. If the Al^{3+} site was more weakly positive or even negative, the Al^{3+}–O bond would be much weaker and dehydrogenation may result.



SMAC 1

This catalyst showed very strong dehydration activity. Relative to $MgAl_2O_4$, the activation energy for dehydration fell by about 60 kJ mole^{-1} while that for dehydrogenation rose by 50 kJ mole^{-1}. Clearly the incorporation of Cr has had a drastic effect on the surface behavior. A similar effect was observed on the corundum solid solutions (*5*), although there the activation energies for *both* reactions fell. In spite of dehydrogenation activity being low it does rise with temperature, suggesting perhaps that at a low temperature the products of reaction, for example H_2O, block dehydrogenation sites.

This behavior may be interpreted in two ways:

(a) the incorporation of Cr in the surface may introduce especially active sites itself, or

(b) may activate still further the Lewis sites already present in $MgAl_2O_4$.

Pepe and Stone (*5*) suggested that the presence of c.u.s. Cr^{3+} in the surface of corundum solutions may draw oxygen ions away from neighboring Al^{3+} thus generating Lewis sites. Our survey of the surface planes shows that c.u.s. Al^{3+} would be expected, and low coordinate Cr^{3+} may, due to its more covalent character, draw electron density to itself away from neighboring Al^{3+} to neutralize charge imbalance. This electronic effect may also have the effect of generating stronger Lewis sites and hence higher activity. The effect of isolated Cr^{3+} ions in activating the surrounding lattice to retain adsorbed oxygen in N_2O decomposition has also been observed (*10*), and may be evidence of a similar effect.

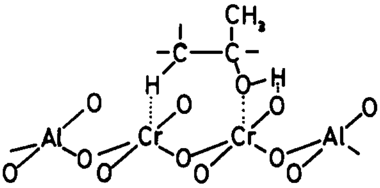
Alternatively the c.u.s. Cr^{3+} sites having a high local positive charge may act as sites of dehydration themselves resulting in partial reduction of the Cr^{3+} as a consequence of the approach of the oxygen lone pair electrons. Dehydration having occurred, desorption of H_2O from a partially reduced Cr^{3+} site could well be easier than from an Al^{3+} site. All charge movement can be conceived of as occurring within the compact center at the surface, the insulator nature of the catalyst being important for the high activity.

SMAC 5

The incorporation of a further few percent of Cr causes a further drastic change in catalytic behavior. Activity to dehydrogenation rises rapidly (the activation energy having fallen by 120 kJ $mole^{-1}$), and at the same time dehydration activity is much lower. This suggests that the activating influence of the Cr ions has been lost if Al^{3+} were the dehydrating sites, and the Cr ions have developed a different activity.

It is in precisely this composition region that the solid state data reveal that weakly coupled isolated Cr pairs are generated. Such sites were beneficial in high temperature H_2/D_2 equilibration (*8*), activity maximizing over this catalyst. the reason for these pair sites having high activity in dehydrogenation rather than in dehydration may well be due to the fact that neighboring Cr atoms could share opposite charge imbalances via their more covalent orbitals thus partly smearing out the strong local positive or negative surface charges.

The "positive" Cr^{3+} would be partially reduced toward Cr^{2+}, and the negative Cr^{3+} of the pair may be oxidized toward Cr^{4+}. These Cr pairs may, therefore, approximate to $d^2(Cr^{4+})$ $d^4(Cr^{2+})$ couples. The "Cr^{4+}" end of the pair could act as a polarizing site for the OH end of the molecule. An adsorption mechanism as follows may be envisaged:



SMAC 10

Activity in both reactions at 570 K was about the same on this catalyst as on SMAC 5. The activation energies, however, were reversed.

The solid state data (*7*) suggest that it is in this catalyst that the first signs of electron delocalization are observed. There was also evidence of some surface reduction during H_2/D_2 exchange (*8*) which is an indication of more facile bulk migration of electrons. Thus although the surface sites may not be different from on SMAC 5, stronger adsorption of hydrogen may be responsible for the higher activation energy in dehydrogenation. The resultant formation of surface OH groups could well supply Brønsted acid sites which if bonding is not too strong could reduce the activation energy for dehydration.

SMAC 25

Although overall activity is very low and although the activation energy for dehydrogenation has risen markedly this catalyst is predominantly active in dehydrogenation. The high activation energy is almost certainly due to persistent surface reduction (*8*). This may occur during pretreatment, or could be a consequence of hydrogen adsorption. Reduction of Cr ions in sites of low coordination in order to neutralize the local positive surface charge will tend to occur as soon as bulk migration of electrons becomes possible. Such sites will tend to trap electrons when the activation energy for charge movement is high and consequently electron mobility will be low and reduction may be persistent. This catalyst is at the LNL point and such behavior would be expected (*9*). This would have two consequences for this reaction; first the strong "positive" sites will be lost resulting in a loss of dehydration activity, and second there will be a possibility of stronger adsorption of hydrogen which may reduce dehydrogenation activity. Both features were observed indicating the important influence charge mobility has on activity.

SMAC 300

This catalyst is very strongly dehydrogenating, selectivity rising to 0.9 at 570 K. The activation energy is considerably reduced. Persistent hydrogen poisoning was rather less evident in the H_2/D_2 exchange studies, which would explain the lower activation energy and higher activity. It is believed that sites involving pairs of Cr ions are still the active centers, but the more rapid electron transfer from the bulk will reduce the likelihood of a strong and *persistent* form of reductive adsorption. The activity rise between SMAC 25 and SMAC 300 can however be mainly attributed to a rise in the number of active sites. It is interesting that this rise is reflected only in the dehydrogenation activity. Activity in dehydration is still very low, presumably for the same reasons as for SMAC 25. Strong acid sides are evidently still absent.

$MgCr_2O_4$

The addition of the last 25% of Cr has little effect on the dehydrogentation behavior but it causes a large increase in dehydration activity, selectivity falling from 0.9 to 0.5. A similar though more dramatic effect was observed on the corundum solid solutions where the selectivity on α-Cr_2O_3 fell to 0.1 (*5*).

It has also been observed that in N_2O decomposition the $MgCr_2O_4$ catalyst was considerably more active than SMAC 300, and its retention of oxygen was much higher (*2*). Perhaps its higher activity in dehydration is correlated with this. High activity in dehydration is often associated with insulator oxides, whereas here and in the corundum solutions the establishment of a fully ordered electron transfer system also generates high activity. Perhaps a mechanism is responsible utilizing the adsorption complex postulated earlier, in this case on Cr sites, in which H_2 or H_2O can be abstracted depending on the strength of the oxygen surface bond, where bulk electron movement may facilitate the acceptance of the oxygen electrons and hence its abstraction as H_2O. A concerted mechanism involving the abstraction of hydrogen followed by oxygen can be envisaged. α-Cr_2O_3 is even more highly dehydrating and it may be no coincidence that its conductivity is considerably higher. It is unfortunate that corundum catalysts having similar solid state properties to SMAC 300 and $MgCr_2O_4$ were not tested, otherwise this relationship between electron availability or charge transfer and increasing dehydration activity might have been clearer.

CONCLUSIONS

Taking the data from this work and that on the α-$Al_{2-x}Cr_xO_3$ catalysts (5) we can draw some general conclusions. The behavior of the spinel catalysts is qualitatively very similar to the corundum series. The presence of Mg^{2+} does not seem to have a strong influence on the activity pattern. The coordination of the A sites will not be easily reduced to generate activity.

Although the reaction is more complex than most of those studied to date over solid solution catalysts the familiar two region activity plot as a function of Cr content is very evident (Fig. 1). The ease with which charge can be transported is clearly important in determining the catalytic behavior.

The role of Cr varies significantly as a function of its concentration and the electronic state of the catalyst. the incorporation of small numbers of Cr ions into the insulator $MgAl_2O_4$ (and α-Al_2O_3) resulted in electronically isolated sites which generated high dehydration activity. Further addition of Cr to about the 5% level resulted in electronically isolated Cr pair sites and important *dehydrogenation* activity. As further Cr is added the LNL point is approached and the activity of these isolated sites falls. In common with many other solid solution catalysts beyond the LNL point where charge transfer is increasingly facile a new regime of activity develops. Dehydrogenation predominates to 75% Cr, still it is believed, on pair sites, though activity per Cr ion is much reduced. An interesting feature is that a new region of high dehydration activity is associated with catalysts having relatively high charge mobility (i.e., $MgCr_2O_4$ and α-Cr_2O_3). Thus is appears that high dehydration activity is associated with catalysts which have the ability to adsorb strongly the oxygen end of the molecule. Such catalysts seem to be either insulators with coordinatively unsaturated cations forming strong Lewis sites or semiconductors with a relatively high charge mobility.

Although the general role of Cr is clear, a precise definition of the identity and behavior of the active sites is difficult. Perhaps a more precise kinetic study together with a surface sensitive spectroscopic technique would be informative.

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