JOURNAL OF CATALYSIS 44, 404–415 (1976)

Hydrogen–Deuterium Exchange Catalyzed by Spinel Solid Solutions, $MgAl_{2-x}Cr_xO_4$

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Received May 30, 1975

H_2–D_2 exchange has been studied over the spinel solid solutions $MgAl_{2-x}Cr_xO_4$, where $x = 0 \rightarrow 2$. The catalysts $x = 0.02 \rightarrow 2$ displayed two zones of activity as a function of temperature, viz. 120 K to ~ 300 K and > 470 K, while catalysts $x = 0 \rightarrow 0.023$ were only active above 470 K. Activity in both temperature zones varied nonlinearly with the chromium content of the catalyst, activity generally falling to a minimum at $x \sim 0.4$ and then rising again to $x = 2$. The results are compared with those obtained on the corundum solid solutions α-$Al_{2-x}Cr_xO_3$. The effectiveness of the isolated sites on catalysts below $x = 0.2$ is discussed. Above $x = 0.4$, the new activity seems to be associated with the increasing ease of electron movement.

It is generally accepted, almost as received truth, that both the structural and electronic character of a catalyst are important in determining its activity. In order to obtain a deep understanding of the mechanisms of catalysis the relative importance of these two parameters needs to be understood for a range of different types of reactions. The use of oxide solid solutions containing catalytically active ions enables a high degree of control to be exercised over the electronic and structural parameters so that their relative importance can be assessed (*1–4*). In earlier work the activity of chromium ions in α-Al_2O_3 for the catalysis of the H_2–D_2 exchange reaction has been studied (*5*). Two zones of activity were observed as a function of temperature, one below about 320 K and the other above 480 K. In both cases, but particularly in the low temperature case, activity varied markedly with chromium content, there being a maximum in activity between AC 7 and AC 10, a minimum at AC 25, and further maximum at α-Cr_2O_3 ("AC *N*" signifies corundum-phase solid solutions, α-$Al_{2-x}Cr_xO_3$, with *N* Cr atoms per 100 Al atoms). It was concluded that the first activity region was due to electronically isolated sites, whose geometry was the especially favorable *c*-axis cation pair sites where the cations face each other across an anion octahedral face and can enter into direct cation–cation bonding. The onset of electron delocalization generated a new activity region whose sites were more dependent on electron mobility.

The spinel structure does not possess the type of cation–cation interaction described above. B-site cations face each other across an octahedral anion edge (*6*). This is far less favorable for direct cation bonding. Thus the study of H_2–D_2 exchange over catalysts formed by the incorporation of Cr into the B-sites of spinel should clarify and extend the conclusions drawn earlier

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on the influence of the electronic and structural factors in this reaction. This paper describes that work. A later paper will deal with H_2–D_2 exchange over Cr in the perovskite $LaAlO_3$ where the only type of cation interaction is via one oxygen atom (i.e., an anion octahedral corner).

EXPERIMENTAL

Materials. $MgAl_2O_4$, $MgCr_2O_4$, and $MgAl_{2-x}Cr_xO_4$ solid solutions used for adsorption and catalysis were prepared in air at 1620 K as previously described (*6*). The chromium content of the catalysts is designated by the nomenclature SMAC *N*, where *N* denotes the nominal number of chromium atoms per 100 atoms of aluminium, or SMCA *N* for chromium-rich solid solutions, where *N* denotes the nominal number of Al atoms per 100 atoms of Cr. The surface areas of the solids were determined by the BET method using Specpure Kr at 77 K (Table 1).

H_2 and D_2 gases were obtained by electrolysis of pure H_2O and D_2O. They were purified by passage through a trap at 77 K and an electrically heated Pd thimble.

Procedures. Adsorption measurements were made using a low volume (20 cm^3) system employing a thermistor as the pressure measuring device. Adsorbed amounts refer to volumes adsorbed after 30 min.

H_2–D_2 exchange was studied in a circulating system of volume 650 cm^3 at a pressure of 660 N m^{-2} in the temperature range 110 to 770 K. Approximately 0.5 g of catalyst was contained in a silica vessel through which a 1:1 mixture of H_2 and D_2 was circulated by means of a reciprocally acting Toepler pump. The catalyst was protected from mercury contamination by a trap cooled in liquid nitrogen. The extent of reaction was followed by continuous sampling of the reacting gases to an A. E. I. MS 10 mass spectrometer previously calibrated for sensitivity to H_2, D_2, and HD. Initial catalyst pretreatment for both catalysis and adsorption consisted of outgassing the oxide for 18 h at 1120 K and 10^{-3} N m^{-2}. Between each reaction or adsorption an outgassing at 1120 K for 30 min was found to give reproducible results.

TABLE 1

Catalysts	Wt% Cr	Surface area (m^2 g^{-1})
$MgAl_2O_4$	0	0.64
SMAC 0.1	0.1	0.82
SMAC 1	0.72	0.68
SMAC 5	3.30	0.70
SMAC 10	6.46	0.73
SMAC 25	13.1	6.7
SMAC 100	31.1	10.1
SMCA 33	43.4	1.4
$MgCr_2O_4$	54.3	1.6

TABLE 2

Hydrogen Adsorption on Spinel Catalysts

Catalyst	Volume adsorbed (in cm^3 m^{-2}) $\times 10^4$			
	At 77 K	At 273 K	At 673 K	At 873 K
$MgAl_2O_4$	22	1.9	1.3	31
SMAC 1	5	1.2	1.2	14.0
SMAC 10	142	0.9	~ 0	~ 0
$MgCr_2O_4$	400	23.8	117	72

For studies of the influence of preadsorbed hydrogen, the catalyst was outgassed as usual and cooled to about 720 K; H_2 gas was then admitted to a pressure of 2.6 kN m^{-2} and the temperature was allowed to fall to 77 K in 20 min; hydrogen was then removed and the reaction was studied at the temperature of interest.

RESULTS

Hydrogen Adsorption

Hydrogen adsorption was studied on four catalysts $MgAl_2O_4$, SMAC 1, SMAC 10, and $MgCr_2O_4$ at a pressure of 13 N m^{-2} and 77, 273, 673, and 873 K. The results are given in Table 2. It can be seen that as the

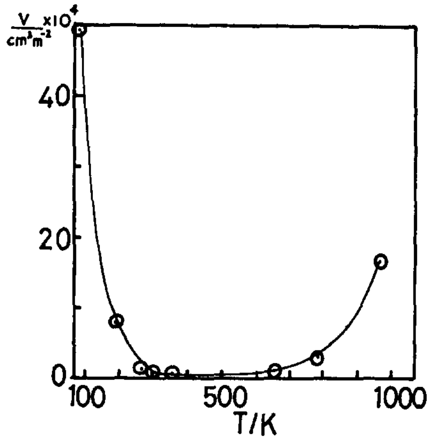


FIG. 1. Adsorption isobar of hydrogen on SMAC 1 at an equilibrium pressure of 13 N m^{-2}.

chromium content increases, the quantity of hydrogen adsorbed increases at 77 K. At 273, 673, and 873 K, however, there is a decrease from $MgAl_2O_4$ to SMAC 10 and then a large increase on $MgCr_2O_4$.

Although the decreasing adsorption from $MgAl_2O_4$ to SMAC 10 at high temperatures contrasts with the behavior of the corundum catalysts (*5*), the isobars are very similar (Fig. 1); indeed, the isobar for $MgCr_2O_4$ shows a maximum at ~650 K similar to that shown by α-Cr_2O_3.

Catalysis

Exploratory work indicated that in the pressure range studied the reaction was approximately first order; accordingly, first-order rate constants have been evaluated using the usual expression (*5*),

$$k = \frac{1}{At}\log\left\{\frac{[HD]_\infty}{[HD]_\infty - [HD]_t}\right\}$$

where A (in m^2) is the surface area of catalyst used, and $[HD]_\infty$ and $[HD]_t$ are the HD concentrations at equilibrium at time t, respectively.

Arrhenius plots showed a single zone of activity for $MgAl_2O_4$ and SMAC 0.1, while three zones of activity were observed for catalysts SMAC 1 to $MgCr_2O_4$ (Fig. 2).

Catalysis in High Temperature Zone (Zone A)

The high temperature zone (500–700 K), designated Zone A, will be described first. The activation energies are collected in Table 3. The variation of activity as a function of the chromium content of the catalyst is conveniently described in Fig. 3 by a plot of log k vs [Cr] at 625 K. Similarly the variation of activity *per chromium* ion is shown in Fig. 4, again at 625 K. From these plots it can be seen that although activity rises from $MgAl_2O_4$ to SMAC 5, the activity per chromium ion decreases continuously from SMAC 0.1 to SMAC 5, with a further sharper drop to SMAC 25. Between SMAC 25 and $MgCr_2O_4$ activity rises, though there is a peak at SMCA 33. Thus, as a function of the chromium content of the catalyst, there are three regions of activity.

Region I. $MgAl_2O_4$–SMAC 5. The addition of ~1% Cr increases the activity by a factor of 10 and the activation energies rise

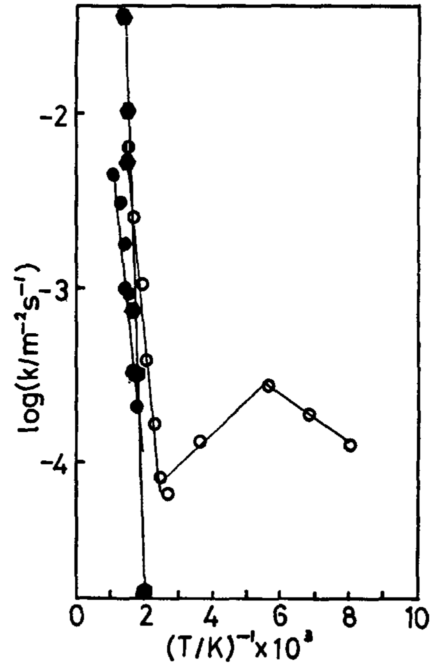


FIG. 2. Arrhenius plots for $MgAl_2O_4$ (●), SMAC 0.1 (●), and SMAC 10 (○).

TABLE 3

Activation Energies (kJ mol^{-1}) for H_2-D_2 Exchange

Catalyst	With vacuum pretreatment		With H_2 pretreatment	
	Zone A	Zone B	Zone A	Zone B
$MgAl_2O_4$	30.1	—	74.7	—
SMAC 0.1	40.6	—	Very high activity, not measurable	—
SMAC 1	44.8	7.5	38.5	—
SMAC 5	34.7	5.0	48.1	—
SMAC 10	34.7	2.5		—
SMAC 25	57.7	15.5	Not studied	
SMAC 100	53.6	8.9	27.6	8.8
SMCA 33	23.4	10.0	27.2	28.5
$MgCr_2O_4$	30.1	6.7	26.4	4.2

from about 29 kJ mole^{-1} on $MgAl_2O_3$ to 42 kJ mole^{-1} on SMAC 1. These activation energies are in striking contrast to those obtained at this Cr content in the corundum catalysts (*5*) where $E_A \sim 80$ kJ mole^{-1}. Furthermore the activity of $MgAl_2O_4$ itself was some 10 times greater than α-Al_2O_3.

Region II. SMAC 10–SMAC 25. In this region absolute activity decreases sharply (Fig. 3). There is also evidence of self-poisoning during the reaction, initial activities being sharply reduced after the first minutes of the reaction. The hydrogen adsorption measurements show that there is a distinct decrease in the amount adsorbed from SMAC 1 to SMAC 10 at 673 and 873 K. The behavior in this region is very similar to that observed in region III of the corundum catalyst.

Region III. SMAC 100–$MgCr_2O_4$. This region is characterized by a definite rise in activity. Nevertheless, there is still evidence of self-poisoning on SMAC 100 and SMCA 33. It is interesting that even though $MgCr_2O_4$ shows little or no inhibition due to self-poisoning, SMCA 33 is more active. Compared to the other catalysts there is a large rise in the amounts of hydrogen adsorbed on $MgCr_2O_4$ at 673 and 873 K and this is clearly correlated with the high activity on this catalyst. A contrast between $MgCr_2O_4$ and the other catalysts is that there is no clearly defined decrease in activity between the high temperature zone and the low temperature

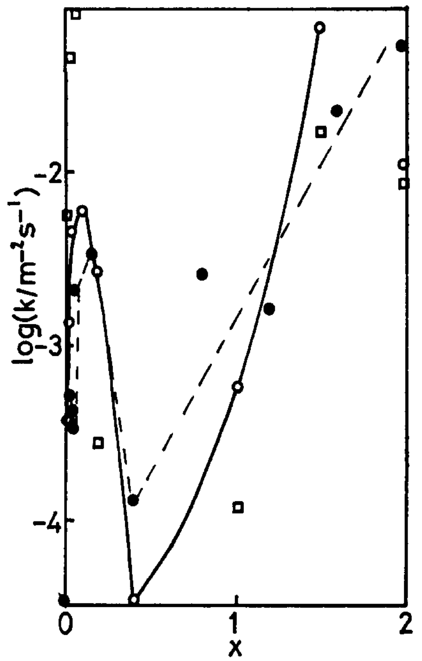


FIG. 3. Variation of activity at 625 K as a function of the chromium content of the catalyst on spinel catalysts (○) and corundum catalysts (*5*) (●). Variation of activity at 625 K after hydrogen preadsorption as a function of the chromium content of the catalysts (□).

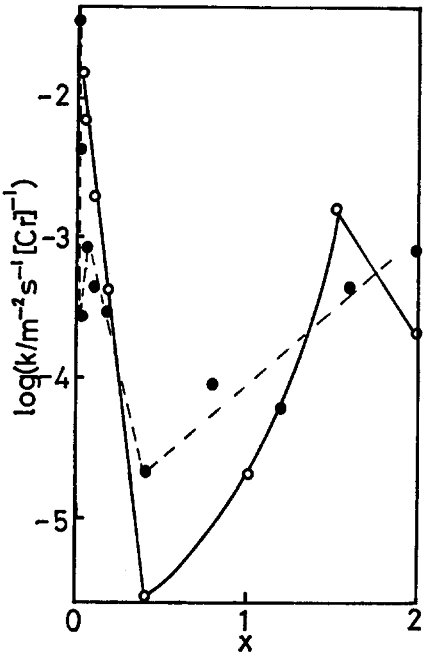


FIG. 4. Variation of activity *per chromium ion* at 625 K as a function of the chromium content of the catalysts.

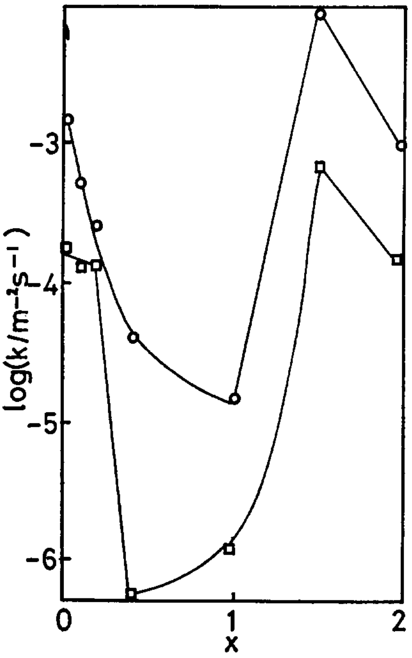


FIG. 5. Variation of activity at 173 K (○) and 123 K (□) as a function of the chromium content of the catalysts.

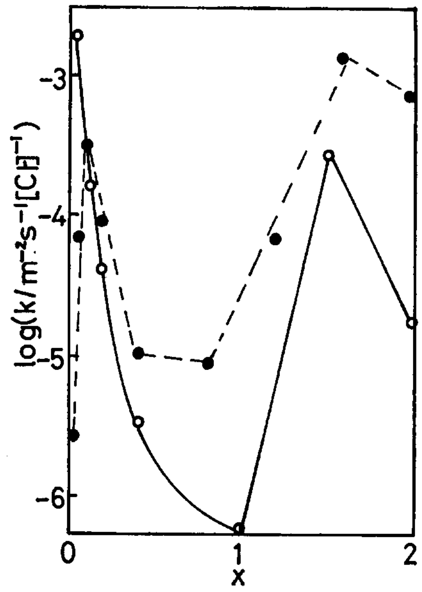


FIG. 6. Variation of activity *per chromium ion* at 173 K and as a function of the chromium content of the spinel catalysts (○), and corundum catalysts (*5*) (●).

zone though there are three distinct zones of activity.

The effect of preadsorbed hydrogen. Figure 3 shows the effect of hydrogen preadsorption on H_2–D_2 activity at 625 K. The activation energies for H_2-pretreated catalysts are presented in Table 3.

In region I, hydrogen preadsorption increased activity by a factor of 10; activation energies were raised slightly. In region II, however, activity was reduced by a factor of 10 and there was a reduction of activation energies. Reduced activity was also found in region III on all catalysts except on $MgCr_2O_4$ where hydrogen pretreatment had no apparent effect.

Catalysis in Low Temperature Zone (Zone B)

We now describe the results for the low temperature zone (100–250 K), designated Zone B. Figure 5 shows the variation of activity as a function of chromium content at 173 and 123 K. In Fig. 6, the activity *per chromium ion* is plotted as a function

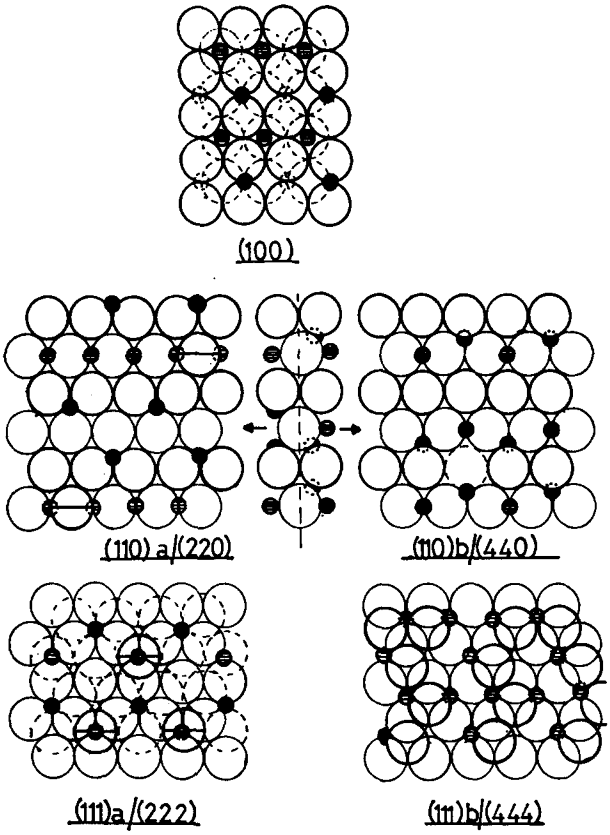


FIG. 7. Surface planes of spinel after dehydration under the pretreatment conditions. ○, Layer 1 anions; ⊖, Suprasurface anions; ○, layer 2 anions; ◌, layer 3 anions on (100) and (110) planes, and layer 4 anions on (111); ⊜, site B surface cations; ●, site A surface cations; ◌, subsurface site A cations on (100).

of [Cr] at 173 K. The analogous curve for the corundum catalyst presents a considerable contrast. It is clear from Fig. 6 that there are again three regions of activity.

Region I. $MgAl_2O_4$ and SMAC 0.1. There is no activity on $MgAl_2O_4$ or SMAC 0.1. Isolated chromium ions are evidently not active of themselves and in spinel they do not appear to promote the activity of Mg^{2+} and Al^{3+}. Furthermore, unlike the situation on α-Al_2O_3, activity on $MgAl_2O_4$ cannot be produced by hydrogen pretreatment at high temperature.

Region II. SMAC 1–SMAC 10. Activity in this region is high at low temperatures; however, the activity falls off quite rapidly with temperature (Fig. 2 and Table 3). It should be noted that while activity falls from SMAC 1 to SMAC 10 at 173 K, there is a slight rise at 123 K. Hydrogen pretreatment at high temperature, however, destroys all activity at these temperatures. The low activation energies compared with the corundum catalysts must result from the lower thermal stability of the active complex. This lower stability will have two consequences: (a) the high temperature end of the log k vs $10^3/T$ plot will be depressed because activity will fall due to the loss of active complexes; (b) the active complex on the spinel may be more reactive at lower temperatures than on corundum catalysts.

Region III. SMAC 25–$MgCr_2O_4$. Activity rises rapidly in this region, peaking at SMCA 33. It is interesting that the

TABLE 4

Coordination and Anion Charge at Surface Cation Sites after Dehydration of Surface

Surface plane	Coordination and anion charge at surface site A (Mg^{2+} ions)	Coordination and anion charge at surface site B (Al^{3+} and Cr^{3+})
(100)	Rows of isolated ions alternating in layer 2 and layer 0 (layer 1 is surface) $\frac{1}{2}$ ions (layer 2), 4-coord, charge $-2\frac{1}{3}$ $\frac{1}{4}$ ions (layer 0), 3-coord, charge -3 $\frac{1}{4}$ ions (layer 0), 2-coord, charge -1	Rows of edge sharing ions in layer 1 All ions, 5-coord, charge $-2\frac{5}{6}$
$(110)_a$	Rows of isolated ions in layer 1 All ions 3-coord, charge $-1\frac{5}{6}$	Rows of edge sharing ions in layer 1 $\frac{3}{4}$ ions 4-coord, charge $-2\frac{1}{3}$ $\frac{1}{4}$ ions 5-coord, charge $-3\frac{1}{3}$ Layer 2 ions 6-coord, charge $-3\frac{1}{3}$
$(110)_b$	None on surface, isolated ions at layer 2 $\frac{3}{4}$ ions 4-coord, charge $-2\frac{1}{2}$ $\frac{1}{4}$ ions 3-coord, charge $-1\frac{1}{2}$	Isolated ions at layer 1 $\frac{3}{4}$ ions 4-coord, charge $-2\frac{2}{3}$ $\frac{1}{4}$ ions 3-coord, charge $-1\frac{2}{3}$
$(111)_a$	Isolated ions at layer 1 All 3-coord, charge $-1\frac{1}{2}$	Isolated ions at layer 1 $\frac{3}{4}$ ions 4-coord, charge $-3\frac{1}{2}$ $\frac{1}{4}$ ions 3-coord, charge $-1\frac{1}{2}$ Layer 3 ions 6-coord, charge $-3\frac{1}{6}$
$(111)_b$	None	Rows of ions criss-crossing the surface at layer 1 $\frac{1}{2}$ ions 4-coord, charge $-2\frac{1}{2}$ $\frac{1}{2}$ ions 5-coord, charge $-3\frac{1}{2}$

activation energies for the reaction are almost the same as for the corundum samples, though except for SMCA 33 the activity is rather lower. The activity over α-Cr_2O_3 and $MgCr_2O_4$ is rather similar. This similarity is further reflected in the fact that hydrogen pretreatment reduces but does not destroy activity in this region.

DISCUSSION

The results presented above demonstrate yet again (*1–5, 7*) the important influence of metal ion concentration on the activity of solid-solution catalysts. In particular the occurrence, as a function of metal ion content, of two regions of rising activity separated by a minimum, increasingly appears to be a general feature of such catalysts (*2–5, 7*). In the present case, although the variation of solid state properties with Cr content (*6*) is less marked than in the corundum solid solutions (*8*), the variation of catalytic activity can be correlated with the changing degree of electronic interaction between the Cr ions in the spinel.

The activity of surface metal ions will be dependent on the valence state of these ions, which in turn is influenced by the electron availability at the surface. The other important parameter, the surface coordination of the active metal ions, also has an influence on the valence state of the surface ions. Figure 7 depicts the three most commonly occurring surface planes as they may appear after dehydration under the pretreatment conditions. Table 4 summarizes the major features of cation coordination and charge at the surface. It is immediately obvious that although each plane is electrically neutral overall, surface B-sites (which accommodate Al and Cr ions) and A-sites (which accommodate Mg ions) may not all be neutral but may have local positive and negative charges, and lowered coordinations. If the cation occupying such a site has an easily varied valency, and this is only true of Cr, reduction or oxidation may occur.

A general feature on all the planes (100), $(110)_a$ and $(111)_b$ is that site B cations form rows across the surface. On the $(111)_b$ plane 4-coordinate cations (oxygen anion charge = −2.5) alternate with 5-coordinate cations (charge = −3.5), while on $(110)_a$ $\frac{3}{4}$ of the cations are 4-coordinate (charge = − 2.33) and $\frac{1}{4}$ are 5 coordinate (charge = − 3.33). The B-site cations on the (100) plane are all 5-coordinate (charge = − 2.83). In contrast, on the $(110)_b$ and $(111)_a$ planes the B-site cations are isolated in the surface with very low coordinations; $\frac{1}{4}$ are 3-coordinate and $\frac{3}{4}$ are 4-coordinate.

It is useful at this stage to summarize the information available from the solid state studies (*6*). It will be recalled that the only possible type of direct cation–cation interaction between B-site cations possessing *d*-electrons in spinel is via the anion octahedral edge. There are six such nearest neighbor interactions per cation. These interactions are weaker than in the *c*-axis pairs and basal plane pairs of corundum. Thus, although there are only four nearest neighbors per cation in corundum, there is a marked effect of the cation pairing on the magnetic properties of AC 1–AC 10. There is little such effect in the spinel solid solutions, though weak pairing of cations presumably via superexchange is evident in the ESR measurements at SMAC 1, increasing to SMAC 25. The large linewidth of the ϕ resonance indicates that these interacting ions are rather isolated from each other electronically. Only isolated Cr is evident below SMAC 1. Above SMAC 25 there is a large increase in exchange interaction evidenced by the decreased linewidth of the ϕ ESR signal between SMAC 10 and $MgCr_2O_4$.

Let us turn again to consider the surface sites; the sites having an excess positive charge (i.e., a low anion charge) 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. Such electron movement will tend to reduce the surface site. Due to the considerable energy required to remove electrons from the inner shells of Mg^{2+} and Al^{3+}, these ions are unlikely to be a significant source of electrons. Thus, electrical stabilization of specimens where the Cr^{3+} ions are isolated will be rather difficult by bulk electron movement. However, as Cr content increases, the number of Cr pairs becomes significant and some sort of electron transfer becomes feasible. It might be expected that some limited reduction of surface sites would occur under our pretreatment conditions. However, due to the localized nature of this electron movement, and because of the likelihood that in this Cr content region (SMAC 1 → SMAC 10) there is some direct overlap of the cation orbitals, complete electron transfer to a Cr ion and reduction of the site is unlikely.

As Cr content increases beyond SMAC 10 the Cr ion "chains" (or rows) increase in length; that is, the number of Cr nearest neighbors increases. Electron transfer or delocalization is thus easier but may be rather localized and inefficient. The surface Cr will be rather more remote from the original donor ion, and thus surface reduction would be more likely and perhaps rather persistent.

Finally, as further Cr is added to the system to form $MgCr_2O_4$, a complete Cr cation system is established and electron transfer through the solid is more facile; thus reduction may occur at the surface rather easily by electron movement, but it may just as easily be destroyed by electron movement, unless crystal field stabilization energy stabilizes the valency state.

This scheme is similar to that suggested for the corundum catalysts (*5*). However, the rather better-developed electron delocalization in α-Cr_2O_3 might lead to easier charge transfer and a lesser tendency to reduction on α-Cr_2O_3 than on $MgCr_2O_4$.

It can be seen that the different regions of catalytic activity are mirrored by these regions of differing intercation interaction and hence differing potential surface reducibility.

Activity in Zone B is peculiar to samples containing chromium and thus these results will be discussed first. In earlier work on corundum it was concluded that low temperature activity took place via hydrogen adsorbed on the cations only. The tenor of the data in this case suggests a similar conclusion.

Zone B

Region I. $MgAl_2O_4 \rightarrow$ SMAC 0.1. It is very significant that activity was not generated in this region. Clearly the suggestion that isolated Cr itself is active in exchange must be abandoned. The activity or otherwise of the isolated Cr ion seems to depend on the identity of the host matrix. Clearly the α-Al_2O_3 lattice is an active catalyst once hydrogen is adsorbed. Spinel, on the other hand, exhibits no activity even after hydrogen pretreatment. Adsorption studies show that hydrogen is adsorbed on $MgAl_2O_4$. in fact in larger quantities than on α-Al_2O_3 (*5*), but the species must be too strongly adsorbed to react at low temperatures. The formation of strongly bound OH is perhaps more likely on the more ionic spinel.

Region II. SMAC 1–SMAC 25. The absence of activity in region I suggests that the high activity generated on SMAC 1, albeit at very low temperatures, is due to the appearance of a new site involving more than one Cr ion, a site similar to the Cr pair site postulated in the corundum catalyst. The high activity at low temperatures and the low activation energies suggests that the active complex may have a lower thermal stability than that present on the corundum catalyst. Although for a given Cr content there are rather more Cr pairs in spinel than in corundum, the electron pairing between the Cr ions is much weaker and this may result in a site whose activity falls off at rather low temperatures as the pairing is destroyed. Nevertheless, the weaker adsorption could account for the high activity at very low temperatures. Even so, at 123 K (Figs. 5, 6) there is only a small rise in activity between SMAC 1 and SMAC 10 (cf. the *rise in $k/[Cr]$* between AC 1 and AC 10 (*5*)) suggesting that some effect is opposing the activity rise which might be expected with increasing numbers of sites. If the ion pairs are weakly coupled, any increase in their distance apart, which would occur as Cr content increases, would further weaken their efficiency as active sites resulting in the observed activity pattern.

Thus the activation energies in this zone are probably not significant as such, and only reflect the results of these opposing effects.

High temperature H_2 pretreatment destroys the activity of the sites in this region. It has been shown that there is probably a tendency for the surface Cr ions to reduce. Under vacuum conditions this reduction is unlikely to go to Cr^{2+}, but in the presence of H_2 the formation of a fairly strongly bound negative H species is likely at the Cr ion site. Such a species will block the Cr sites to reacting molecules in the low temperature reaction. It may be recalled that H_2 preadsorption merely reduced activity in zone B on the corundum catalysts (*5*). It is probable that the weakness of the "covalent" bond between the Cr ions in spinel makes it more susceptible to hydrogen reduction and thus destruction of the low temperature active site. If the postulated site is correct, comparison between AC and SMAC suggests that while the pair site is important for low temperature activity, the strength of the electron pairing between the Cr ions may also play a crucial role.

Region III. SMAC 25 → $MgCr_2O_4$. In this region, activity at 123 K rises from the low level reached on SMAC 25 to high activity on SMCA 33 with a small drop to $MgCr_2O_4$ (Figs. 5 and 6). It is interesting that although activity on the spinels, with the exception of SMCA 33, is somewhat less than on the corundum catalysts, the activation energies are of the same order. Furthermore, in contrast to region II, H_2 pretreatment merely reduces the activity on SMAC 100 → $MgCr_2O_4$. The similarity of the behavior on the SMAC and AC catalysts suggests a similar mechanism of reaction.

In the discussion of the surface planes after vacuum pretreatment it was suggested that in the SMAC 25–SMAC 100 region, some reduction of the surface Cr sites was rather likely. Reduced sites on the surface would weaken any cation–cation coupling, and certainly discourage hydrogen adsorption. However, as Cr content is built up and electron exchange becomes easier, persistent reduction at the surface is increasingly less likely. The resistance of the sites to complete poisoning by high temperature H_2 adsorption reflects two interrelated effects: (a) the increased electron mobility which counteracts a strong form of reductive adsorption; and (b) a short range ordering of spins via the "covalent bonding" of overlapping *d*-orbitals between a group of Cr ions, which will also resist reductive adsorption of H_2 at surface Cr ions belonging to such a group.

It is significant that the highest activity is observed on SMCA 33 where ~10% of the Cr^{3+} of $MgCr_2O_4$ is replaced by Al^{3+}, and where short-range magnetic order has been observed in an especially strong form (*6*). Activity on AC 400 was also higher than on α-Cr_2O_3 (*5*). Clearly a small quantity of Al^{3+} will disrupt the ordered coupling of electron spins and may thus enable more facile transfer of electrons. Such an effect would be beneficial in increasing activity. It could be argued that there is a further effect.

Thus far, much emphasis has been placed on the efficacy of exchange coupled Cr pairs as sites of low temperature activity. It can be objected, with some justification, that surface Cr ions are unlikely to interact with each other in the same manner as bulk Cr ions. This is true, but nevertheless surface Cr interactions must mirror to some approximation those of the bulk, especially when Cr ions near the surface interact electronically with those on the surface, thus imposing electronic constraints on them to behave in a manner similar to bulk Cr.

Now if we examine the surface planes of spinels, we see that three of the five possible ideal planes have rows of adjacent Cr ions. Ideally the *d*-electrons on each Cr^{3+} ion are antiparallel to those of its neighbor, so the following can be envisaged:

$$\begin{array}{cccccc}
H\downarrow & H\uparrow & D\downarrow & D\uparrow & D\downarrow & D\uparrow \\
\mathrm{Cr} & \mathrm{Cr} & \mathrm{Cr} & \mathrm{Cr} & \mathrm{Cr} & \mathrm{Cr} \\
\uparrow & \downarrow & \uparrow & \downarrow & \uparrow & \downarrow
\end{array}$$

Desorption to form H_2, D_2, or HD are equally likely. If, however, Al^{3+} ions are inserted in the Cr ion chain either on the surface or in the bulk, a discontinuity results. Imagining a surface Al^{3+} on the (100), $(110)_a$, and $(111)_b$ planes, the scheme is modified to:

$$\begin{array}{ccccccccc}
D\uparrow & D\downarrow & H\uparrow & H\downarrow & & D\uparrow & D\downarrow & H\uparrow & H\downarrow \\
\mathrm{Cr} & \mathrm{Cr} & \mathrm{Cr} & \mathrm{Cr} & \mathrm{Al} & \mathrm{Cr} & \mathrm{Cr} & \mathrm{Cr} & \mathrm{Cr} \\
\downarrow & \uparrow & \downarrow & \uparrow & & \downarrow & \uparrow & \downarrow & \uparrow
\end{array}$$

It may be suggested that Cr–H bonds adjacent to the Al ions are slightly stronger; thus a constraint is imposed, causing a directed switch movement and increasing the production of HD. Other explanations are possible but a discontinuity in the Cr lattice is clearly useful in promoting activity.

Zone A

When compared with Zone B, activity in this zone divides into three slightly different regions in terms of catalyst content, the main difference being that there appears to be a continuous region from $MgAl_2O_4$ to SMAC 10.

Region I. $MgAl_2O_4$ to SMAC 10. It is clear from the data presented on this region (Figs. 3 and 4) that the sites active on SMAC 0.1 are those active on SMAC 10. Activity per chromium ion drops continuously to SMAC 10. Since isolated Cr ions are clearly active, if not of themselves, certainly in activating the lattice, and since increasing the Cr content decreases the activity per ion (in contrast to the reduction on AC) the site for H_2 adsorption must involve anions. Thus, a heterogeneous adsorption mechanism is postulated. H_2 pretreatment activates the surface, so adsorption cannot be strongly reductive. However, as Cr content increases, activity per ion falls and the activating influence of H_2 pretreatment decreases until poisoning takes place on SMAC 10. This probably reflects the onset of electron movement (or charge exchange) at this Cr concentration and the increasing tendency towards a reducible surface which was postulated earlier.

Activity on the spinels is higher than on the corundum catalysts. This and the lower activation energies clearly indicates that spinel is a more favorable lattice for high temperature H_2–D_2 exchange. This is demonstrated in the contrast between α-Al_2O_3 and $MgAl_2O_4$ activity. The rather greater tendency of spinel to generate OH groups which probably reflects a greater ionicity in the cation–anion bond perhaps explains the higher exchange activity over spinel.

The increased activity per ion found between AC 1 and AC 10 (*5*) is not found in SMAC. Clearly the site which produces this activating effect is absent or not effective on spinel; this is believed to be due to weakness of the coupling between the Cr ion pairs present which is effectively destroyed at these temperatures.

Finally, it is significant that there is a fall in the quantity of H_2 adsorbed at 400°C from $MgAl_2O_4 \rightarrow$ SMAC 10, whereas there was a rise from α-Al_2O_3 to AC 10 (*5*). It is believed that this demonstrates again the efficacy of strong Cr pairs in promoting adsorption by inhibiting reduction of the Cr ions.

Region II. SMAC 10 → SMAC 25. The features distinguishing this region from region I are concerned with (a) the poisoning which takes place after the first minutes of reaction, and (b) the deactivating effect of H_2 pretreatment. This reflects the state of the surface discussed earlier. There is sufficient electron movement to reduce the surface by the formation of H^- or Cr^{2+} or both under the vacuum conditions and then as a result of high temperature H_2 adsorption. Thus, sites

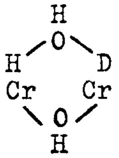
$$Cr^{2+}\text{–}O \quad \text{or} \quad \begin{array}{l} H^- \\ Cr^{2+}\text{–}O \end{array}$$

may be formed which inhibit exchange activity.

The situation in this region is thus broadly similar to region III on the corundum catalysts.

Region III. SMAC 25 → $MgCr_2O_4$. Absolute activity rises even though poisoning effects are still observable up to $MgCr_2O_4$. However, H_2 poisoning decreases through the series and is quite small on SMCA 33 and $MgCr_2O_4$. Again SMCA 33 is more active than $MgCr_2O_4$. It is striking, however, that activity is broadly the same as that found in region IV of the corundum series.

Again the increasing Cr content will increase electron mobility and a persistent reduced surface will be less likely. Thus the sites active on spinel will be very similar to those on corundum. At this temperature there is not too much difference in the electron interaction of the Cr ions on the two structures. It is in the geometry of the Cr sites on the surface that a contrast appears. Rows of Cr ions and O ions are prevalent on spinel, whereas on corundum the surface is mainly dotted with Cr pairs. If the sites are ideally visualized as



there is not too much real difference between them. Furthermore, it is known that short-range order persists to this temperature zone, so some form of antiparallel electron ordering between the Cr ions may well encourage the formation of an active complex favorable for exchange. It was just this type of site which was suggested for activity in regions II and IV of the corundum series.

ACKNOWLEDGMENTS

The assistance of Dr. T. A. Egerton in obtaining the adsorption isotherms is acknowledged. The author thanks Professor F. S. Stone for helpful discussions of this work.

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