

The Oxidation of Methanol over Chromium Containing Spinel ($\text{MgAl}_{2-x}\text{Cr}_x\text{O}_4$) and Corundum ($\alpha\text{-Al}_{2-x}\text{Cr}_x\text{O}_3$) Solid Solutions

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The oxidation of methanol has been studied over chromium-containing corundum and spinel phase solid solutions. The corundum phase catalysts ($\alpha\text{-Al}_{2-x}\text{Cr}_x\text{O}_3$) were less active but very much more selective to formaldehyde than the spinel catalysts ($\text{MgAl}_{2-x}\text{Cr}_x\text{O}_4$). At chromium contents below about 10% there were dramatic fluctuations in activity and selectivity as a function of the chromium content for both catalyst systems. Above 10% chromium the activity behavior became relatively constant as [Cr] increased. The reaction selectivity over corundum catalysts settled at 0.7 at 670 K whereas it was zero over spinel catalysts at 470 K. The activity behavior at low Cr contents is discussed in terms of the localized sites which are formed and how these affect the basic activity of the host matrix in generating active oxygen, and in adsorbing methanol. At higher Cr contents electron delocalization between the active sites is thought to be the reason for the stabilization of behavior, though at a very different level for the two catalyst systems.

INTRODUCTION

For many years oxide solutions containing transition metal ions have been successfully used to gain an understanding of the catalyst parameters important in determining activity. The majority of studies have examined simple reactions such as N_2O decomposition (1-3), $\text{H}_2\text{-D}_2$ exchange (4-6), and H_2 oxidation (7).

Concurrent with these studies there has been a very considerable interest in other laboratories in the catalyst parameters important in determining the behavior of partial oxidation catalysts. The Mars-van Krevelen mechanism (8) has underlain much of the work on selective oxidation catalysts. This suggests that the oxidant is lattice oxygen rather than adsorbed oxygen. The selectivity of the reaction is then determined by the relative strengths of the surface oxygen bond, the reactant surface bond, and the product surface bond. A large number of studies have been carried out into the way in which the surface oxygen bond strength controls activity and selectivity (9, 10). The strength of the bond

certainly seems to control oxidation activity, and Sachtler *et al.* appear to have shown that the rate at which that bond strength increases with reduction largely influences selectivity (11). It is clear that a number of factors will influence these parameters. Among them will be the valency of the active ion, the structure of the oxide, the collective electronic state of the catalyst, and the local surface coordination of the active site. These variables can be controlled particularly sensitively utilizing oxide solid solutions and it is therefore appropriate to investigate selective oxidation over such model catalysts.

The chromium oxide catalysts have never been especially notable as partial oxidation catalysts. In solid solutions with MgO , $\alpha\text{-Al}_2\text{O}_3$, and MgAl_2O_4 they have been extensively studied as catalysts for simple reactions (2-6). These data will provide useful background information for the oxidation reactions. Since detailed data exist on alcohol decomposition over these catalysts (14, 15) it was appropriate to investigate the activity of $\alpha\text{-Al}_{2-x}\text{Cr}_x\text{O}_3$ and $\text{MgAl}_{2-x}\text{Cr}_x\text{O}_4$ solid solutions as catalysts

for the oxidation of a simple alcohol. In this paper the oxidation of methanol is discussed.

EXPERIMENTAL METHODS

Materials. Two series of catalysts were studied (Table 1): (1) $\alpha\text{-Al}_{2-x}\text{Cr}_x\text{O}_3$, designated AC N, and (2) $\text{MgAl}_{2-x}\text{Cr}_x\text{O}_4$, designated SMAC N, where in both cases N denotes the number of Cr atoms per 100 Al atoms. Their preparation and solid-state properties have been described elsewhere (12-13). These solid solutions have been

used as catalysts for other reactions, viz., N_2O decomposition (2, 3), $\text{H}_2\text{-D}_2$ exchange (5, 6), and isopropanol decomposition (14, 15).

The surface areas of the catalysts were determined by the BET method using spec-pure krypton at 77 K.

The methanol used was of Analar grade supplied by B.D.H. Chemicals Ltd. Oxygen and helium were high purity grades supplied by British Oxygen Company and were further purified by passage through molecular sieve traps.

TABLE 1

x	$\alpha\text{-Al}_{2-x}\text{Cr}_x\text{O}_3$				$\text{MgAl}_{2-x}\text{Cr}_x\text{O}_4$			
	Catalyst	E_a kJ mol ⁻¹	Orders		Catalyst	E_a kJ mol ⁻¹	Orders	
			CH ₃ OH	O ₂			CH ₃ OH	O ₂
CO ₂ Formation								
0.00	$\alpha\text{-Al}_2\text{O}_3$	120	0	0.9	MgAl_2O_4	85	0.4	0
0.001	AC 0.05	80	0	0.5	SMAC 0.05	64	0.8	0
0.002	AC 0.1	109	0.5	0.4	SMAC 0.1	87	0.4	0.4
0.01	—	—	—	—	SMAC 0.5	85	0.4	0.4
0.02	AC 1	76	0	0.5	SMAC 1	91	0.2	0.8
0.05	AC 3	137	0	0.9	—	—	—	—
0.07	AC 5	128	0	0.9	SMAC 5	104	0	0.6
0.1	AC 7	93	0.5	0.5	SMAC 10	74	0.2	0.3
0.18	AC 10	116	0	0.5	—	—	—	—
0.4	AC 25	104	0	0.5	SMAC 25	116	0	0.2
0.7	—	—	—	—	SMAC 50	104	0	0.5
1.2	AC 150	118	0.4	0.5	—	—	—	—
1.5	AC 400	103	0.7	0.8	SMAC 300	97	0	1
1.8	—	—	—	—	SMAC 10	79	0.2	0.2
2.0	Cr_2O_3	138	0.5	0.8	MgCr_2O_4	86	0.5	0.8
HCHO Formation								
0.00	$\alpha\text{-Al}_2\text{O}_3$	33	1	0.3	MgAl_2O_4	55	0.6	0
0.001	AC 0.05	52	0.9	0.6	SMAC 0.05	37	0.2	0
0.002	AC 0.1	96	0.5	0	SMAC 0.1	45	0.4	0
0.01	—	—	—	—	SMAC 0.05	40	0.4	0
0.02	AC 1	44	0.9	0.5	SMAC 1	44	0.4	0.5
0.05	AC 3	79	0.8	0.3	—	—	—	—
0.07	AC 5	91	0.7	0	—	—	—	—
0.1	AC 7	53	0.5	0.5	SMAC 5	49	0.5	0.2
0.18	AC 10	75	1	0.4	SMAC 10	33	0.5	0.4
0.4	AC 25	80	0.5	0.5	SMAC 25	55	0.5	0.2
0.7	—	—	—	—	SMAC 50	60	0.5	0.1
1.2	AC 150	73	0.3	0.5	—	—	—	—
1.5	AC 400	73	0.9	0.4	SMAC 300	55	0.6	0.6
1.8	—	—	—	—	SMAC 10	70	0	0.6
2.0	Cr_2O_3	87	0.7	0.5	MgCr_2O_4	59	0.5	0.6

Apparatus and procedures. A simple continuous flow reactor was used to study the reaction; helium was the carrier gas. A known partial pressure of methanol was fed into the reactor via a mixing chamber by passing a flow of helium through a methanol saturator. A continuous flow of oxygen was mixed with the methanol in the mixing chamber such that there was always an excess of O_2 for complete combustion and the total flow of gases over the catalyst was about $60 \text{ cm}^3 \text{ min}^{-1}$.

Usually 0.5 g of catalyst was used which gave a bed depth of about 3–5 mm. The catalyst was pretreated by heating in pure helium for 1 hr at 770 K. Reaction was monitored using a gas sampling valve and a Pye Unicam gas chromatograph which first sampled the reactant stream before the reactor and then the product stream. (The constancy and purity of the reaction mixture could thus be continuously monitored.) The products CO_2 , HCHO, and H_2O and reactants oxygen and methanol were separated on a Porapak T column.

After initial pretreatment the catalyst activity was tested at a number of temperatures in the region 450 to 750 K. At each temperature the average of three measurements of steady-state activity was computed where the individual values did not differ by more than 15%. The reaction temperatures were taken in a random order rather than in a rising or falling sequence. Certain catalysts were rechecked for reproducibility. The reaction is very exothermic so temperature control was of great importance. A sensitive temperature controller was utilized which regulated a low thermal capacity furnace whose response to temperature fluctuations was rapid. A thermocouple projecting into the catalyst bed monitored the temperature. If the percentage conversion was kept below 5%, temperature fluctuations were within 5 K. In some cases it was necessary to reduce the amount of catalyst used to ensure that conversion was kept low in the temperature region of interest.

Plots of the log of conversion to HCHO and CO_2 were obtained as a function of $1/T$ for conversions of less than 5% to yield activation energies for these reactions.

Orders of reaction with respect to oxygen and methanol were also obtained in the low conversion region. The procedure used was to monitor activity keeping the flow of one reactant constant and varying the flow of the other, the total flow being kept constant by appropriate adjustment of the helium flow.

RESULTS

The overall activities of the two catalyst systems were rather different. The spinel solutions were much more active than the corundum solutions, whereas the corundum solutions were far more selective to formaldehyde than were the spinels. Figure 1 is a plot of log (percentage conversion m^{-2}) against the chromium content of the catalyst at 470 K for the spinels and 670 K for the corundum catalyst. The fact that the data for the corundum catalysts refer to 670 K emphasizes the considerably higher activity of the spinels. It is of interest to note the rise and fall behavior of activity with Cr content which seems to be characteristic of these solid solution catalyst systems (1, 2, 5, 15, 16).

Direct comparison of the activities of the catalysts at 470 K for the production of CO_2 and HCHO is obtained from Figs. 2 and 3. The strong fluctuations of behavior in the

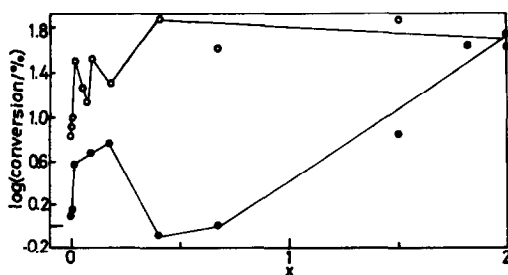


FIG. 1. The percentage conversion of methanol as a function of the chromium content of the catalysts at 470 K for the spinel catalysts, ●, and at 670 K for the corundum catalysts, ○.

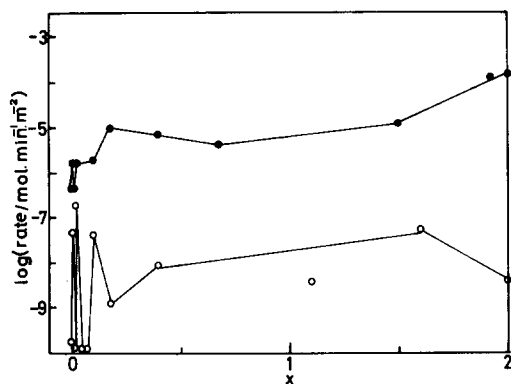


FIG. 2. The variation in the rate of formation of CO_2 at 470 K as a function of the chromium content of the spinel, ●, and corundum, ○, catalysts.

low Cr region are striking. The temperature of presentation will affect the precise form of these plots since the activation energies vary markedly through the series (Table 1). Nevertheless, the form of the graph represents the balance of the reaction activities at this temperature. The lines joining the points merely direct the eye, and they are not meant to suggest a continuous change of activity with Cr. The precise numerical values of the activities are not very important but the relative behavior and the form of these plots suggests that *in general* both catalyst systems have about the same activity to HCHO. It is in CO_2 production that the spinel catalysts tend to be very much more active. As temperature is increased the relative importance of the CO_2 reaction rises particularly rapidly for the spinel catalysts so that selectivity to HCHO is never above 20% in the low Cr region and zero above SMAC 25. On the other hand even at ~ 700 K, except for AC 0.1 which has a selectivity to HCHO of 10%, the corundum catalysts are all above 50% selective. For both sets of catalysts the activation energy to CO_2 is greater than to HCHO, but in general the activation energies over the corundum catalysts are greater than over the spinels (Table 1).

The orders of reaction with respect to oxygen and methanol are also reported in Table 1. It can be seen that again there are

some quite distinct differences between the two systems, especially in the reaction to CO_2 .

DISCUSSION

The very marked differences in activity and selectivity between the two catalyst systems, even though both contain Cr^{3+} in nominally similar site symmetries, emphasises and highlights the importance of the host matrix in determining the surface reactivity.

Before we consider these effects in detail it is important to recognize the similarities in the general behavior of the two sets of catalysts. In both spinel and corundum solutions there are two regions of activity as a function of chromium content (Figs. 1–3). The activity of catalysts dilute in chromium fluctuates dramatically as chromium content increases from 0 to about 10%. Earlier publications have pointed out that below this concentration the Cr sites, be they isolated ions or pairs of ions, are electronically isolated from one another. It is perhaps not surprising therefore that the surface activity of the catalyst is very sensitive to small changes in the localized conformation which result as the chromium content changes in this region. The effect of these local changes, which may be exemplified by the transition from mainly isolated Cr ions, which may be active them-

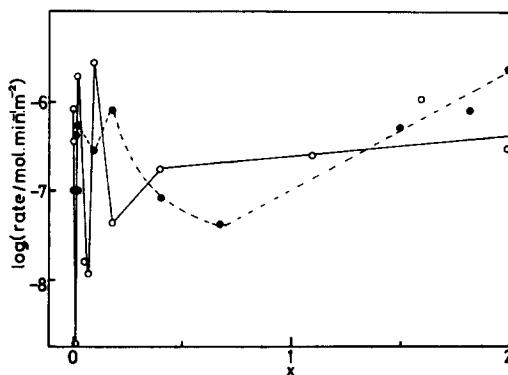


FIG. 3. The variation in the rate of formation of formaldehyde at 470 K as a function of the chromium content of the spinel, ●, and corundum catalysts, ○.

selves or may activate other cations, to Cr pairs (12) cannot easily be transmitted through the structure by polaron hopping or electron superexchange. Thus there is no "averaging" over the whole structure of the effect of increasing chromium content. Instead of gradual changes of behavior there are discontinuous transitions. The evidence is that surface behavior in this insulator region is very sensitive to the precise local grouping of surface atoms. The whole tenor of data on the catalytic behavior of solid solution catalysts dilute in transition metal ions (t.m.i.) demonstrates that very small concentrations of t.m.i. exercise a profound effect on the adsorption and activity behavior of the host matrix (1, 16). A small change in Cr content can strongly influence the form and balance of adsorption strengths between oxygen, hydrogen, and alcohol to change the direction of the reaction.

Beyond about 10% Cr the catalytic behavior stabilizes. In an earlier paper (17) this has been termed the LNL (localized-nonlocalized) point beyond which charge transfer, or polaron hopping, becomes much easier. Thus local changes in the electronic structure of surface sites can now be "averaged" out by charge transfer through the catalyst structure. The extent to which this is effective will be different in the two systems since the conduction of the corundum catalysts is some 2 to 3 orders higher than the spinel catalysts.

Turning to the clear differences in behavior between the spinel and corundum solutions, it is obvious that to discuss the activity of these catalysts solely in terms of the activity of the Cr ions would be naive in the extreme. Indeed, the work on solid solution catalysts has increasingly emphasized the role of the matrix. The data in this paper highlight the importance of the matrix in a particularly dramatic fashion. The solid-state and catalytic data on these catalysts reported in previous papers (2, 12, 14) enable us to gain some understanding of the reasons for the contrasting behavior re-

ported here. It is instructive to review briefly the salient points.

Structurally, corundum and spinel are quite different. The cations in corundum are grouped in well-separated pairs along the *c* axis of a hexagonally close packed oxygen lattice (facing each other across an anion octahedral face) such that each cation has 13 neighbors linked by one, two, or three oxygen anions (12). There are two major consequences of this arrangement for the physical properties of the chromium-containing solid solutions. First, when the solids are dilute in Cr (i.e., <10% Cr) strong direct Cr-Cr bonds can be formed between the *c* axis pairs. Slightly weaker direct Cr-Cr bonds can also occur between basal plane cation pairs of which there are three per cation perpendicular to the *c* axis. Such bonding is localized within the pair. The second major consequence occurs when the Cr content rises beyond 10%. Superexchange becomes possible when Cr-O-Cr-O pathways are established through the structure. Conductivity rises rapidly and at low temperatures antiferromagnetic ordering occurs. Localized bonding within Cr-Cr pairs is lost as collective order is established.

These structural and electronic effects have an important influence at the surface. Study of the most likely planes exposed in polycrystalline materials (6) demonstrates that the cation pairs will be the main feature evident at the surface. It is likely that surface formation will result in substantial differences in the local coulomb charge around the individual cations in a pair. One cation will have an overall positive charge (i.e., cation and anion ligand charges) while the other may have an overall negative charge. At low chromium content if only one member of the pair is Cr this charge will be localized on that atom. If both atoms of a pair are Cr ions there is the possibility of delocalizing the charge imbalance via the *d* orbitals of the two ions.

At high Cr contents, although the unique pair-wise geometry is present, local surface

charge imbalances at the surfaces will be smeared out by charge transfer through the bulk of the solid. The kinetics of this process will be dependent on the bulk conductivity (17).

The structure and properties of Cr-containing spinel solutions (13) are rather different. Spinel is based on a cubic close-packed oxygen matrix. There are six B-site (accommodating Al^{3+} or Cr^{3+}) cation neighbors for each B-site cation. Their geometry is similar to that of the basal plane pairs in corundum (i.e., they share a pair of oxygen anions) but their separation is a little greater and only very weak Cr–Cr bonds are possible. The cation–oxygen distance is also rather greater in spinel ($\sim 2.0 \text{ \AA}$) than in corundum ($\sim 1.8 \text{ \AA}$). The lower number of cation–oxygen–cation interactions means that at high chromium contents the possibilities of superexchange or polaron hopping are much less (17). Conductivity is lower. The surface geometry of spinel is characterized by either relatively isolated B cations or rows of B-cations depending on the surface plane considered (5). As in corundum, formation of the surface can result in local positive or negative charges around the cations depending on the precise surface geometry. Again when Cr ions are isolated that charge will be localized. Cr pairs will be formed as Cr content rises but their bonding will be rather ineffective as compared to corundum. Beyond 10–25% Cr, charge delocalization is possible but it is much less efficient than in corundum.

A careful consideration of published work (2, 3, 5, 6, 14, 15) reveals the marked variations in the surface behavior of these catalysts for the adsorption of hydrogen (5, 6), oxygen (2, 3), and alcohol (14, 15) as the Cr content varies. The present reaction involves a delicate balance of processes involving the adsorption and desorption of each of these species. Thus mild oxidation to HCHO presumably requires an adsorption complex allowing the abstraction of the H atoms. Adsorption to the surface via the H atoms would be favor-

able. Relatively nonlabile fairly strongly adsorbed oxygen will reduce the possibility of the HCHO being further oxidized before desorption. Deep oxidation, however, presupposes labile active surface oxygen and fairly strong adsorption of the alcohol molecule, probably via the oxygen atom. In general the reaction orders with respect to CH_3OH and oxygen support these ideas. Thus low or zero orders are found in the main for CH_3OH in deep oxidation whereas for HCHO production the orders lie between 0.5 and 1. Similarly for deep oxidation the oxygen orders are greater than 0.5 except for some of the spinel catalysts. For mild oxidation they lie below 0.6.

The $\alpha\text{-Al}_{2-x}\text{Cr}_x\text{O}_3$ Catalysts

We turn now to a detailed consideration of the behavior of the corundum catalysts.

Hydrogen adsorption has previously only been studied on well outgassed catalysts (6). There it was found that although Cr in low concentrations raised the capacity for hydrogen, it was Cr–Cr pair sites which were especially favorable as adsorption centers. However, the behavior in the presence of oxygen will undoubtedly be different.

Only some of the corundum catalysts in this concentration region have been studied in detail for alcohol adsorption, but the work of Pepe and Stone (14) suggests that well-outgassed $\alpha\text{-Al}_2\text{O}_3$ is roughly equally dehydrating and dehydrogenating whereas AC 0.1 and AC 1 are dehydrating catalysts. Cr-activated Al^{3+} Lewis acid sites were thought to be responsible. Less well outgassed $\alpha\text{-Al}_2\text{O}_3$ was mainly a dehydrogenating catalyst whilst AC 0.1 and AC 1 yielded about 70% dehydrogenation. AC 10 was much less affected by pretreatment conditions and was almost entirely a dehydrogenation catalyst in which Cr–Cr pair sites were said to be especially active.

Under the conditions of the present reaction there is always an excess of oxygen present. The work of Egerton *et al.* (2) demonstrates that the activity of the cata-

lysts in adsorbing oxygen is also rather sensitive to composition. AC 0.1 tends to be less active than α - Al_2O_3 in adsorbing oxygen whereas AC 1, AC 3, and AC 5 adsorb oxygen in considerable quantities (Fig. 4) although on AC 1 it is more strongly held than on AC 5. This high activity is thought to be due to the Al-Cr pair site again. This center is believed to act as a dissociation point, the oxygen atoms diffusing thereafter to other sites. Cr-Cr pair sites were considered to be less active in oxygen adsorption and hence on AC 7 and AC 10 capacity was reduced.

Applying these data to the present results is not straightforward since from the above it is clear that a given site may be active both in adsorbing CH_3OH and in adsorbing oxygen. There will be competitive adsorption, and there will be mutual influence of one adsorption process on the other.

Catalysts $x = 0 \rightarrow 0.2$. α - Al_2O_3 is very selective to HCHO. In an oxygen atmosphere there are unlikely to be many bare Al^{3+} sites giving rise to strong CH_3OH adsorption and deep oxidation. In the main weaker adsorption via H atoms to Brønsted sites would explain the activity behavior.

AC 0.05 is very much more active to produce CO_2 than α - Al_2O_3 . This may be seen to be a consequence of the increase in the number of strong Lewis sites resulting from Al-Cr pairs. Moving on to AC 0.1, activity falls markedly and activation energies rise. The Al-Cr sites would still be expected to be active; however, the alcohol

and oxygen adsorption data above suggest that competition may occur, strong CH_3OH adsorption will not be great and oxygen coverage may be less than on α - Al_2O_3 . The observed activity is not surprising. AC 1 along with AC 7 are the most active corundum catalysts in this composition zone. They are about 100 times more active to CO_2 at 470 K than α - Al_2O_3 and 2-5 times more active to HCHO. They also have the lowest activation energies. AC 1 is a stronger dehydration catalyst than α - Al_2O_3 (14). Strong adsorption of CH_3OH is also expected (2). This latter may have two effects, (a) to accelerated the deep oxidation of strongly held CH_3OH and (b) to provide weaker Brønsted sites for mild oxidation. The Al-Cr sites are again thought to be important.

AC 3 and AC 5 have the lowest activity and the highest activation energies. CO_2 production is about the same as on α - Al_2O_3 , but HCHO is two orders less. Adsorbed oxygen coverage is very high, probably ~40%. Such coverages were thought to be possible via the formation of O_2^{2-} species. It is likely that such species will reduce the concentration of Brønsted type sites, and hence the fall in mild oxidation. This high surface concentration of oxygen may also reduce the occurrence of strong Lewis sites. There is evidence, though, that O_2^{2-} is not so active as an oxidizing species as O^- . This may also contribute to lower reactivity.

The high activity on AC 7 is probably a consequence of a reduced surface coverage of oxygen resulting from an increase in the Cr-Cr sites which are much less active as oxygen adsorption sites. Activity in N_2O decomposition is similar on AC 1 and AC 7 and it is interesting that their activity here is so similar. AC 10 represents a transition point between catalysts having localized sites and those whose sites are electronically linked. On AC 10 there are many strongly bonded Cr-Cr pair sites which reduce oxygen adsorption, although the strength of adsorption is increased. AC 10

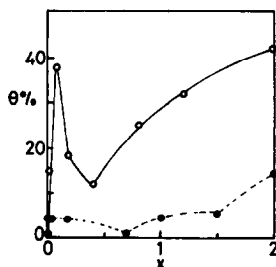


FIG. 4. Oxygen retained at the catalyst surface during N_2O decomposition at 773 K over corundum, O, and spinel, ●, catalysts.

is predominantly a dehydrogenation catalyst and this is reflected in the considerably higher activity to HCHO formation than to CO_2 .

Catalysts Containing More Than 10% Chromium

In this region long-range electron movement becomes possible. The active sites are no longer isolated, and consequently the behavior of the catalysts changes *gradually* with composition. Changes are averaged over the whole active surface. In the corundum catalysts oxygen is more strongly held and high coverages of oxygen result (2). The selectivity to HCHO settles out at about 70% at 670 K. Overall activity tends to rise from AC 25 to AC 400. Thus active sites are increasing in number rather than changing in behavior. These sites may well be Cr–Cr pairs which due to the long-range electron exchange are no longer strongly bonded (12). It has been suggested elsewhere that such sites will be favorable both for hydrogen and oxygen adsorption. Activity is less than on $\alpha\text{-Cr}_2\text{O}_3$, but the much stronger heat of adsorption of oxygen may explain this fall.

The $\text{MgAl}_{2-x}\text{Cr}_x\text{O}_4$ Catalysts

It is possible to discuss the spinel data in the same way, but the deep oxidation data vary comparatively little through the series. This will be a consequence of a rather low concentration of comparatively weak and labile adsorbed oxygen on all the spinel catalysts (Fig. 4). The behavior of the spinel catalysts in alcohol adsorption does vary considerably. SMAC 1 is a strong dehydration catalyst whereas SMAC 5, 10, 25, and 300 are dehydrogenation catalysts. MgAl_2O_4 and MgCr_2O_4 are equally active in both reactions. However this variation in activity seems to have little to do with the overall selectivity since the activity to CO_2 is consistently about 50 times greater than the HCHO. The variation of activity to HCHO seems to follow fairly closely the variation in oxygen coverage data in Fig. 4.

Where oxygen coverage is highest, activity to HCHO is highest. The lowest coverage of oxygen was on SMAC 50 and this is where the activity to HCHO was a minimum.

Fluctuations of activity to CO_2 and HCHO do occur in the low Cr content region, but they are very much less marked than for the corundum catalysts. One reason for this will be the much smaller fluctuations in oxygen coverage with Cr content. The fact that strongly bonded Cr–Cr pairs are not formed in spinel (13) will also be a relevant factor. As for corundum catalysts there is a transition from localized sites to exchange-coupled sites beyond SMAC 25. Again, thereafter catalyst activity changes smoothly with composition. In this case, however, although the capacity for oxygen adsorption increases it is not so great nor is it so strongly held as on corundum. This is probably the reason for selectivity falling close to zero. It leaves the interesting question, however, as to how significant the conductivity factor is in determining the oxygen adsorption energetics and hence the selectivity. The band gap for the spinel catalysts is larger and the conductivity lower than in the case of the corundum catalysts, but it is not clear whether this is the sole factor or whether the surface conformations are also important as they are in the low Cr content region. This point is receiving further attention.

CONCLUSIONS

(1) The overall activity of the two catalyst systems, low activity and high selectivity to HCHO for $\alpha\text{-Al}_{2-x}\text{Cr}_x\text{O}_3$ and high activity and low selectivity to HCHO for $\text{MgAl}_{2-x}\text{Cr}_x\text{O}_4$, is largely governed by the structure of the host matrix. The difference in the extent and strength of oxygen adsorption appears to be particularly important.

(2) The marked difference in reactivity found elsewhere between the low Cr content "insulator" catalysts and the higher Cr

content "semiconductor" catalysts is found for methanol oxidation over these catalysts.

(3) At low Cr contents the active sites are isolated. Their reactivity is a function of the precise conformation of surface atoms. The adsorption behavior of the reactants and products has earlier been found to be very sensitive to these changes, and thus the reactivity behavior fluctuates markedly as the catalyst composition changes.

(4) At high Cr contents the active sites are no longer isolated, electron exchange occurs between them and activity changes gradually with composition. The effect is in the opposite direction for the two systems. Fairly high selectivity to HCHO results for the corundum catalysts whereas selectivity is zero for the spinels.

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