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Catalytic Activity of Model Aluminium-Doped TiO_2 Catalysts

II. A Study of Methanol Oxidation

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The oxidation of methanol has been studied over TiO_2 doped with Al in the nominal range $x = 0 \rightarrow 0.1$ for $Ti_{1-x}Al_xO_2$. At a reference temperature of 490 K all the catalysts except TiO_2 were 99% selective in HCHO. Initial additions of Al to $x = 0.001$ resulted in 100-fold increase in activity relative to TiO_2. This has been attributed to the effect of Al in generating new Lewis acid sites, Al^{3+} and Ti^{3+}, and subsequently varying sensitivity with Al concentration. These variations are discussed with reference to the effect of Al^{3+} in promoting the formation of Ti^{3+}, and hence its influence on the electronic interaction between the new active sites.

INTRODUCTION

Earlier studies of the oxidation of methanol over model oxide solid solution catalysts have highlighted the relative importance of, first, the identity of the active site cations, usually transition metal ions (tmi), second, the extent of electron exchange between active sites, and third, the identity of the host lattice (*1*, *2*). These three factors are self-evidently interrelated. Thus Cr dispersed in α-Al_2O_3 generated a highly selective though relatively inactive series of catalysts, whereas Cr in $MgAl_2O_4$ produced catalysts with high activity but little selectivity to formaldehyde. Charge transfer and a strong surface–oxygen bond are important for good selectivity. Both of these features are favoured more by α-Al_2O_3 than by $MgAl_2O_4$.

Highly dispersed active sites can be effective for selective oxidation but their activity has been found to be very sensitive to the precise geometry of the active site and varies sensitively with active ion content (*1*). Once the concentration of tmi active ions has reached a level where electron exchange can occur between them, it appears that not only is it important that this charge exchange should be relatively facile, but it is especially advantageous if the new "sublattice" of exchange-linked active sites is electronically isolated from the host lattice. Thus when vanadium was dispersed in α-Al_2O_3 and SnO_2, highly selective and active catalysts were produced; however, increasing the quantities of vanadium in TiO_2 only modified the catalytic behaviour of TiO_2 to a small extent (*2*).

Despite the earlier controversy over the defect structure of Al-doped TiO_2 (*3–6*), in the previous study we have shown that there is good evidence for the incorporation of Al^{3+} in the TiO_2 lattice up to $x = 0.03$ and that the resulting charge compensating centres include reducible interstitial Ti^{4+} and perhaps lattice Ti^{3+} ions (*7*). Although they have a significant effect on the electronic state of the host lattice and concurrently cause a fall in the metal–oxygen bond strength, it is not until these "charge compensators" are linked by an electron exchange system that they significantly affect activity towards N_2O decomposition. However, for the catalysis of methanol oxidation they provide the possibility for the investigation of a number of interesting parameters. The incorporation of a non-tmi into a semiconductor lattice would be expected to strongly influence activity in the

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first place because the ion is a strong Lewis acid and in the second place because of its strong influence on host conductivity.

From the data reported in the previous paper we can discern a number of regions of Al^{3+} concentration in which activity changes may be expected (*7*). At very low Al^{3+} contents, below $x = 0.003$, the effect of new Lewis acid sites, both Al^{3+} and Ti^{3+}, should be most marked. When impurity band conduction is established above $x = 0.003$ the influence of charge transfer effects may be more evident. Beyond $x = 0.003$ the disruption of charge transfer by increasing numbers of Al^{3+} ions should be reflected in activity changes. Finally, above $x = 0.04$ where there is evidence of phase separation the influence of bulk Al_2O_3 will become important.

It is the purpose of this paper to investigate these effects.

TABLE 1

Activation Energies for the Production of CO_2 and HCHO from the Oxidation of Methanol over $Ti_{1-x}Al_xO_2$ Catalysts

x in $Ti_{1-x}Al_xO_2$	E_{CO_2} (kJ mol^{-1})	E_{HCHO} (kJ mol^{-1})
0.00	157.3	69.2
0.0002	80.0	53.8
0.0003	100.9	79.4
0.001	90.0	74.8
0.002	105.3	72.9
0.003	121.0	84.6
0.004	56.3	52.9
0.008	118.5	115.2
0.031	77.7	61.2
0.044	42.2	63.1
0.067	76.0	77.8
0.083	108.1	93.0
0.1	117.0	104.7

EXPERIMENTAL

The catalysts $Ti_{1-x}Al_xO_2$, $x = 0 \rightarrow 0.1$ used in this study are those whose preparation and solid state properties are described in the previous paper (*7*).

Catalytic activity was studied using a simple continuous-flow reactor at atmospheric pressure. The reactor was a quartz glass tube, 1 cm in diameter. The catalyst was supported on a sintered glass disc. Usually 0.5 g of catalyst was used which gave a bed depth of about 3–5 mm. A glass thermocouple sleeve allowed the temperature of the catalyst bed to be monitored directly. Helium was the carrier gas. A mixture of oxygen, methanol, and helium was passed through a mixer tube filled with glass spheres and then over the catalyst at a total flow rate of about 70 cm^3 min^{-1}. The required partial pressure of methanol was obtained by passing an appropriate flow of helium through a methanol saturator held at 298 K in a water bath. Normally the reaction mixture consisted of a partial pressure of oxygen of 0.3 atm and of methanol of 0.04 atm. The composition of the reaction mixture was monitored before and after the reactor using a Pye Unicam gas chromatograph. The products CO_2, HCHO, and H_2O and reactants oxygen and methanol were separated on a Poropak T column.

The catalyst was pretreated in pure helium for 1 h at 800 K. The reaction was studied at a number of temperatures between 450 and 620 K chosen in a random fashion. Each series was checked for reproducibility by several reaction runs. Precautions were taken to ensure that the exothermicity of the reaction did not interfere with the rate measurements. Conversion was kept below 10% and a sensitive temperature controller controlled a low thermal capacity furnace whose response to temperature fluctuations was rapid.

Activation energies were obtained from plots of log steady-state conversion to HCHO and CO_2, respectively, as a function of $1/T$.

RESULTS

Table 1 lists the activation energies obtained for all the catalysts studied.

The overall activity of the catalysts are compared in Fig. 1 where the temperature required to attain a total conversion of 9%

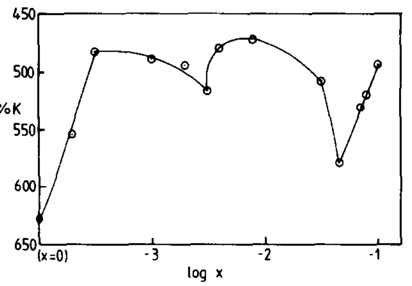

FIG. 1. The variation of the temperature required to attain 9% total conversion as a function of the aluminium content of the catalysts, x.

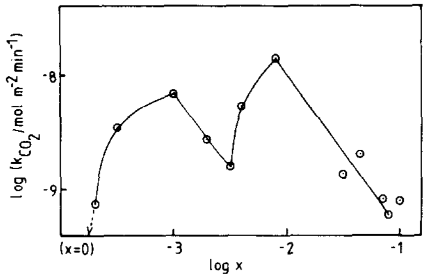

FIG. 3. The variation of activity at 490 K for the production of CO_2 from methanol as a function of the aluminium content, x, of the catalysts.

($T_{9\%}$) is plotted against the aluminium content, x. It can be clearly seen that even the smallest quantities of Al^{3+} give rise to a very significant increase in activity. This is reflected in a fall of $T_{9\%}$ from 630 K for TiO_2 to 480 K when $x = 0.0003$. Activity then falls a little to $x = 0.003$, $T_{9\%} = 510$ K; but between $x = 0.003$ and $x = 0.008$ a further rise is observed to yield $T_{9\%} = 470$ K. From $x = 0.03$ activity decreases to $x = 0.04$ and then rises almost linearly to $x = 0.1$. This behaviour is reproduced almost exactly when the activity in selective oxidation to HCHO is considered. Figure 2 shows the variation in the rate attained at 490 K as a function of the Al^{3+} content of the various catalysts. Because TiO_2 is very much less active than the Al-doped catalysts its activity could not be included in the plot. Furthermore, apart from TiO_2 all the catalysts are 99% selective to HCHO. Within its region of activity TiO_2 is about 60% selective.

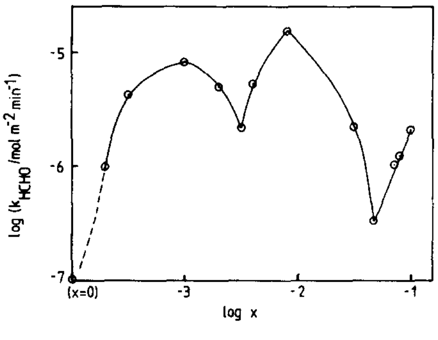

FIG. 2. The variation of activity at 490 K for the production of formaldehyde from methanol as a function of the aluminium content, x, of the catalysts.

The activity of the catalysts for the production of CO_2 is two to three orders of magnitude less than for HCHO. The behaviour at 490 K is shown in Fig. 3. The rise and fall of activity at low Al^{3+} content observed for HCHO is also observed here. However, there is no increase beyond $x = 0.04$.

DISCUSSION

The oxidation of methanol has been studied over TiO_2 by quite a number of workers. In common with the vast majority of oxidation reactions it has been concluded that the reaction proceeds by the Mars–van Krevelen mechanism (*8–12*). Methanol is relatively weakly held at the surface whereas the lattice oxygen is held strongly ($\Delta H_{M\text{–}O} = 430$ kJ mol^{-1}). This leads to a catalyst which is rather selective for HCHO production. It is, however, not very active.

There has been a good deal of discussion as to the manner of the CH_3OH adsorption. Adsorption via the oxygen atom can be envisaged on cation Lewis acid sites (*8, 9*). Coordinatively unsaturated Ti^{4+} ions would perform this role, whilst surface Ti^{3+} would be rather weaker Lewis acid sites. Alternatively, adsorption via methyl and hydroxyl hydrogens to surface oxide ions may be suggested (*11*). In either case, depending on the strength of adsorption of the methanol and the mobility of the surface oxygen, mechanisms can be postulated which lead to either deep oxidation to CO_2 or selective oxidation to HCHO.

The incorporation of small amounts of Al^{3+} into the TiO_2 lattice has been shown to promote the formation of Ti^{3+}, to weaken the Ti—O bond and to increase conductivity and electron exchange through the lattice (*7*). These solid state effects were reflected in surface activity to N_2O decomposition. Although retained oxygen fell sharply as soon as Al was added to the TiO_2 lattice a positive increase in activity was only observed between $x = 0.003$ and $x = 0.03$. This rise was attributed to the establishment of an impurity band between the Ti^{3+} ions. Beyond this concentration activity fell, due, it was suggested, to the disruption of electron exchange owing to increasing numbers of dopent Al ions.

Figures 1–3 show that the oxidation reaction is also profoundly influenced by Al incorporation. Four or five activity regions can be distinguished as a function of Al content.

Aluminium doping $x = 0 \rightarrow x = 0.001$. A sharp rise in activity by a factor of greater than 100 is observed as Al is incorporated. Selectivity also increases from about 60 to 99%. There are probably two contributions to this development of activity. The solid state and N_2O decomposition data have shown that the surface–oxygen bond strength is reduced, although activity in adsorbing oxygen from N_2O is not greatly increased. Thus the surface oxygen will be more labile and this would contribute to higher activity. Second, Al^{3+} are Lewis acid sites and their incorporation in the surface will potentially provide new adsorption centres for methanol. Normally it would be expected that Al^{3+} would be a *strong* acid which would hold the methanol strongly and hence tend to promote deep oxidation. There is some segregation of Al to the surface, so the *isolated* Al^{3+} which would form the strongest Lewis sites may not be exposed at the surface. If isolated Al^{3+} do exist at the surface it is very likely that they will be fully coordinated to oxygen ions because the Al—O bond is extremely strong (ΔH_{M-O} = 1780 kJ mol^{-1}). The much weaker Ti^{3+} acid sites which are generated as a consequence of the Al presence may be the new active sites at the surface.

In this region the dopent concentration is so low that the new active sites must be well dispersed and isolated from each other. If the new sites are Al^{3+} ions they will be electronically isolated from the TiO_2 lattice. If the new sites are Ti^{3+} ions or even anion vacancies they are electronically disengaged from the band structure of TiO_2 forming isolated impurity states in the band gap and thus the electronic isolation of the sites is likely. It is well known that such isolation can further activate the sites in surface reactions (*13, 14*).

Aluminium doping $x = 0.001 \rightarrow x = 0.003$. In this region activity falls by a factor of 6. The oxygen–surface bond strength also falls but this would be expected to increase activity. The source of the decreased activity could be that the Ti^{3+} sites are losing their electronic isolation. The solid state data suggest that conductivity is starting to rise although mobility may not be very high. Thus the ability of the adsorption sites to electronically interact with adsorbing molecules of oxygen and methanol will be reduced by this electron delocalisation within the active site sublattice and activity falls.

Aluminium doping $x = 0.003 \rightarrow x = 0.01$. Here activity rises again by a factor of 10. The solid state and N_2O decomposition data show that there is increased ability to dissociate oxygen and this is associated with the development of an efficient and facile charge exchange system. The oxygen–surface bond is not too strong and reoxidation should be a rapid process. Additionally as Al^{3+} content rises the number of acid sites, Al^{3+} or Ti^{3+}, will increase. These features acting together can explain the further increase in activity at high selectivity.

This is in full accord with our previous conclusions derived from a study of vanadium-containing solid solutions that high and selective activity was favoured by a sublattice of active sites linked by an efficient electron exchange system (*2*). This allows the rapid exchange of electronic charge with the reactants so that adsorption and desorption occur efficiently for the production of the desired products. The description is appropriate in terms of electron band structure. With the establishment of sublattice band structure, the Fermi level is favourable for the adsorption of oxygen to reoxidise the surface, for the weak adsorption of methanol, and for desorption of formaldehyde.

Aluminium doping $x = 0.01 \rightarrow x = 0.1$. This region is first characterised by a fall in activity of approaching two orders of magnitude followed by a rise of about one order. It is a transitional region to a two-phase system. The conduction system which was built up of Ti^{3+} centres and formed a sublattice begins to be broken up by further amounts of Al^{3+}. Charge mobility falls, the band structure is lost and with it facile adsorption of the reactants. This was seen in the previous study of N_2O decomposition (*7*). Normally in the solid solution systems studied to date in which tmi are added to insulator hosts, this type of solid state and surface behaviour is observed between the activity of the *isolated centres* and the *exchange-coupled* active centres. Here *increasing* doping allows us to approach this transition region from the exchange-coupled side, and again it is a region of *decreasing* activity. It must be noted that the activation energy for conduction is still low, about 0.6 eV, but conductivity itself has fallen sharply. It is, we believe, charge transfer within the sublattice of active sites, probably involving Ti^{3+}, which is being disrupted. As we have said before, it seems probable that this sublattice is in some senses distinct from that of the host itself, even though that host is TiO_2.

A further effect of the Al doping is that more and more lattice oxygen will be associated with Al ions. It is likely that this will greatly reduce the amount of such oxygen available for oxidation and thus further reduce activity.

Beyond $x = 0.04$ two or three phases begin to be evident. The SIMS data indicated that the surface concentration of Al was constant and yet the bulk content was increasing. This is consistent with the idea that α-Al_2O_3 islands are separating out and growing in depth (*7*). Although α-Al_2O_3 is moderately active as a catalyst its selectivity is not as high as 60% (*1*). Furthermore, as we have seen, TiO_2 is not very active compared to the doped catalysts. Thus it is possible that the increasing activity is due to a combination of a moderately active doped phase plus increasing quantities of α-Al_2O_3.

CONCLUSIONS

Earlier studies on methanol oxidation over model solid solution oxide catalysts have shown the influence of active site isolation in an insulator matrix (*1*). Sharp fluctuations of activity with precise dopent concentration and hence precise site composition and geometry were observed. As active tmi content increased, activity fell as initial electron delocalisation occurred between tmi, but rose again once a facile electron exchange system had been established. In those studies activity and selectivity were shown to be clearly dependent on electron mobility between the active sites. Oxygen adsorption, surface reoxidation and hydrocarbon adsorption were all influenced by this parameter. In a more recent paper this latter parameter was demonstrated to be important even in a semiconducting host (*2*). The active sites based on the tmi dopents were not significantly influenced by the electronic state of the host. Good activity and selectivity were only generated when electron exchange built up *between* the active sites themselves. Where electronic interaction between dopent and host was likely there was evidence that selectivity and activity changed little with doping.

In the present paper using a non-tmi dopent in a tmi semiconductor oxide it has been possible to promote the formation of host ions of lower oxidation state. These by themselves or together with the dopents generate high and selective oxidation activity when essentially isolated. In agreement with the earlier conclusions this activity increases further when exchange becomes efficient between the sites; however, when this exchange is reduced by larger concentrations of non-tmi dopents, activity falls sharply.

Two general conclusions flow from these results. First it has been demonstrated yet again that isolation of active sites leads to high activity, but the development of a good electron exchange system between the sites themselves leads to high and selective activity. Second, in this case one of the roles of a *promoter* is suggested. It may, as Al^{3+} does here, promote the formation of ions of a new oxidation state. These ions may then disengage electronically from the host lattice and generate new activity.

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