JOURNAL OF CATALYSIS 90, 305–313 (1984)

Catalytic Activity of Model $Sn_{(1-x)}V_xO_2$ and $Ti_{(1-x)}V_xO_2$ Catalysts for the Decomposition of N_2O: The Influence of Charge Transfer Effects

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Received December 9, 1983; revised March 16, 1984

The catalytic decomposition of N_2O has been studied as a function of x over $Sn_{(1-x)}V_xO_2$ and $Ti_{(1-x)}V_xO_2$ solid solutions in the range $x = 0$–0.2. The host lattices were active and activity fell as a function of vanadium content up to $x = 0.03$. Thereafter activity rose as the V content increased. The surface activity has been correlated with varying charge transfer effects in the catalyst as the V content increases. Although the host has an influence on activity, the V appears to quickly dominate the surface activity of the material. In the main the variations of activity can be explained by reference to the developing electronic state of a V sublattice. © 1984 Academic Press, Inc.

INTRODUCTION

Studies on model solid solution catalysts aimed at understanding the role of the active ion, the host matrix and charge transfer effects have been very successful in clarifying the influence of each parameter (*1–3*). Usually transition metal ions have been incorporated in diamagnetic, insulating host lattices whose catalytic activity was very small compared to that of the dopent oxide. This approach enabled the contribution of each parameter to be highlighted in a rather unambiguous manner. Thus most of the first-row transition metal ions have been investigated in such host matrices as MgO, Al_2O_3, $MgAl_2O_4$, and CaO.

In such host oxides at low dopent concentration the guest ions are essentially isolated. The only significant charge transfer effects to develop are between the dopent ions as their concentration increases. The catalytic behaviour of these materials in quite a wide range of reactions clearly shows that electronic isolation can result in high activity whereas the onset of electron delocalisation between the ions is correlated with a fall in activity (*4–7*). This fall has been attributed to a reduction in electron density for adsorption at the surface site. In some cases when electron exchange becomes efficient and a band structure can be said to have developed, activity rises again.

The role of the host has also been seen to involve host ion site geometry, oxygen mobility, as well as contributing to the adsorption of reactants and products (*7, 8*). In general the activity of the host has been significantly enhanced by the incorporation of the dopent ion. There are, however, many cases of catalysts where dopents are added to modify the activity of an oxide which is itself active. If oxidation/reduction reactions are being considered such oxides are usually semiconductors. Doping such oxides offers the opportunity to investigate the influence of host conductivity on the activity of the guest ion. This is not an easy task, however, since conductivity changes accompany other physical changes which may be more basic. The doping or alloying procedure can be given localised or collective descriptions. When considering the incorporation of an active ion in an insulator a localised picture seems appropriate. The electron density is located at the ion site and is available for adsorption. Delocalisation only occurs as site density grows. When the host is a semiconductor, guest ions are re-

0021-9517/84 $3.00

TABLE 1

Catalyst Surface Areas and Kinetic Parameters for N_2O Decomposition on $Ti_{1-x}V_xO_2$ and $Sn_{1-x}V_xO_2$

Catalyst x in $Ti_{1-x}V_xO_2$	Surface area ($m^2\ g^{-1}$)	E_{app} (kJ mol^{-1})	log A (cm min^{-1})	Catalyst x in $Sn_{1-x}V_xO_2$	Surface area ($m^2\ g^{-1}$)	E_{app} (kJ mol^{-1})	log A (cm min^{-1})
0.00000	5.5	120.8	5.25	0.0000	9.6	109.6	5.25
0.00001	4.4	97.8	3.95	0.0001	9.6	112.1	5.49
0.00005	3.1	197.3	9.60	0.0003	8.4	74.5	3.06
0.00010	5.5	146.3	6.45	0.0007	9.2	111.3	5.28
0.00050	5.5	190.6	8.80	0.0010	10.1	154.4	7.22
0.00100	6.1	219.0	10.39	0.0030	4.2	183.3	8.38
0.00500	5.7	174.7	7.80	0.0070	5.7	125.1	5.07
0.01000	6.2	63.1	1.63	0.0100	5.7	357.7	18.81
0.03000	5.9	243.1	11.38	0.0300	3.8	254.8	11.80
0.05000	5.4	245.8	11.64	0.0700	3.1	178.2	9.31
0.09000	0.8	165.9	7.71	0.0900	0.8	162.8	8.17
0.17000	1.5	132.1	6.15	—	—	—	—

garded as donor or acceptor levels in the band gap. There is evidence from catalysis and other physical measurements that at low concentrations such atomic entities retain a good deal of their own identity and little electronic interaction occurs with the host atoms, due presumably to a lack of "energetic fit" (*9, 10*). Indeed as concentration increases the guest atoms seem to set up their own "bands." In some respects, therefore, the behaviour of the doped system may be expected to be a summation of that of the host plus that of the guest.

Studies of the $Al_{(1-x)}V_xO_3$ catalyst system demonstrated that for a simple reaction such as N_2O decomposition activity could be represented as a summation of the activity on exchange-coupled vanadium sites (*11*). Recent studies of the oxidation of methanol over Al_2O_3, SnO_2, and TiO_2 containing vanadium showed that where selectivity is important a similar approach may be used (*12*). Selectivity requires an efficient electron-exchange system, yet isolation of this system within a host appears to be beneficial. Such isolation is evident in the case of Al_2O_3 and SnO_2 but electron exchange would appear to be possible between V^{4+} and Ti^{3+}. Thus in the latter case V modified the behaviour of TiO_2 whereas in the other two cases new activity developed as electron exchange built up in the V sublattice. The purpose of the work described here is to investigate the influence of these effects on N_2O decomposition.

EXPERIMENTAL

The catalysts $Sn_{(1-x)}V_xO_2$ and $Ti_{(1-x)}V_xO_2$ were prepared with $x = 0.00001$ to 0.2 in the manner described elsewhere (*12*). The materials were characterised by a range of techniques. Catalyst surface areas were determined by adsorption of N_2 at 77 K via the BET procedure. The results are shown in Table 1. Characterisation by X-ray diffraction, uv reflectance, XPS, SIMS, ESR, and conductivity measurements has been reported earlier (*12*).

The N_2O decomposition reaction was studied over each catalyst using a static reactor. The reaction mixture was continuously monitored via a capillary leak to the head of an MS10 mass spectrometer. The reaction was studied at a pressure of 8 kN m^{-2} in the temperature range 800–950 K. The catalysts were first pretreated by outgassing at 1000 K for 18 hr at 10^{-3} N m^{-2}. Reproducible results were obtained by outgassing at 1000 K for 1 hr between runs.

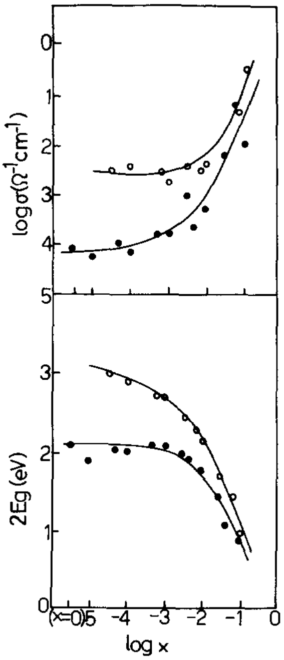

FIG. 1. The activation energy of conduction, E_g/eV (plotted as $2E_g$ = band gap) for $Ti_{1-x}V_xO_2$, (●), and $Sn_{1-x}V_xO_2$, (○), samples as a function of composition.

RESULTS

Since the solid-state parameters are important for the subsequent discussion they will be briefly reviewed here. The X-ray diffraction data showed that solid solution to form a unitary rutile phase occurred in both series up to $x = 0.1$. This was demonstrated by the absence of extraneous diffraction lines above $x = 0.03$ and by the fact that both a_0 and c_0 tended to fall as expected as vanadium replaced Sn and Ti on the lattices. Beyond $x = 0.1$ there was evidence of the development of another phase, especially in the TiO_2 series. The ESR and reflectance data suggest that the valence state of the vanadium is less than five. In the low-concentration samples ESR shows that V^{4+} is present. The XPS data are not able to give reliable information on the valence state of vanadium; however, as the less-electronegative vanadium replaced tin there was an overall increase in the binding energies of all the electrons in the SnO_2 series. The reverse trend was observed in the TiO_2 series. Above $x = 0.1$ in the SnO_2 catalysts the Sn, V, and O peaks were observed to split. This possibly indicates the development of a new phase above this concentration. Thus these solid state data demonstrate that within the range of interest solid solution occurs and V^{4+} ions enter the SnO_2 and TiO_2 lattices.

The conductivity measurements were carried out in a small pressure of N_2O as previously (*3*). Great care was taken to ensure that these dc measurements did reflect the bulk conductivity of the catalyst samples.

Figure 1 shows the variation of the activation of conduction, E_g, and conductivity at 870 K as a function of x for each of the catalyst series. The incorporation of vanadium in the SnO_2 lattice has little effect on the conductivity of the material until $x = 0.01$. Similarly E_g does not fall significantly until that point. On the other hand there is a gradual rise in the conductivity of the TiO_2 samples from $x = 0.0001$. Beyond $x = 0.01$ the conductivities and band gaps of both series change quite rapidly.

The initial rates of reaction were found to be first order in N_2O and consequently absolute velocity constants were calculated using the well known relationship

$$k_{(abs)} = P(N_2)V/[P(N_2O)At], \quad (1)$$

where $P(N_2)$ and $P(N_2O)$ are the pressures of N_2 and N_2O, respectively, V is the volume of the vessel (cm^3), A is the surface area (cm^2), and t is time (min) (*13*).

Activation energies and preexponential factors were obtained and are given in Table 1. It is very interesting to note that all these data for both catalyst systems lie on the same compensation effect plot (Fig. 2). Thus the relationship between activation energy and preexponential is given by

$$E_{(app)}/\text{kJ mol}^{-1} = 17.8 \log (A/\text{cm min}^{-1}) + 30. \quad (2)$$

This may signify a similarity of sites on the two systems.

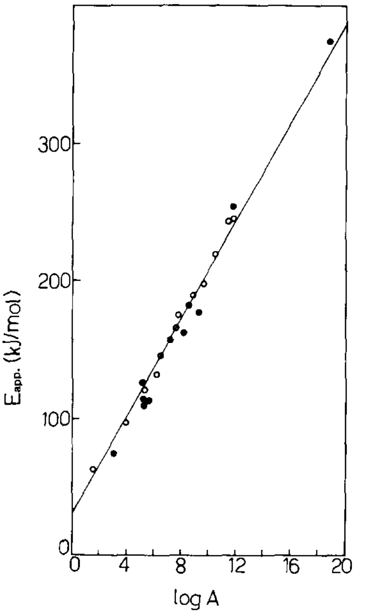

FIG. 2. The compensation effect for N_2O decomposition over $Ti_{1-x}V_xO_2$ (●) and $Sn_{1-x}V_xO_2$ (○) catalysts.

The variation of activity as a function of vanadium content is highlighted for the two catalyst systems in Figs. 3 and 4 where the rate constants at 900 K are plotted against log x. Clearly if a different temperature was chosen the plots would have a somewhat different form. However, the qualitative variation is satisfactorily typical. It can be seen that the initial additions of V do not have a very significant influence on the activity of the host matrix. Indeed, the main effect is to reduce activity and a fall is recorded up to $x = 0.03$ for both catalyst series. A difference between the two is evident in that the activity fall on the SnO_2 catalysts is some two orders of magnitude whereas it is only one order on the TiO_2 series. However, the SnO_2 matrix was about one order more active than TiO_2 at the start. Thus the addition of V to $x = 0.03$ brought the two catalyst series to about the same activity level both in terms of the rate constants and the activation energies and preexponential factors.

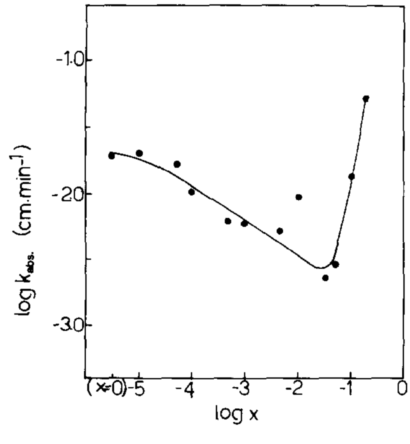

FIG. 3. The variation of activity for N_2O decomposition at 900 K over $Ti_{1-x}V_xO_2$ as a function of catalyst composition.

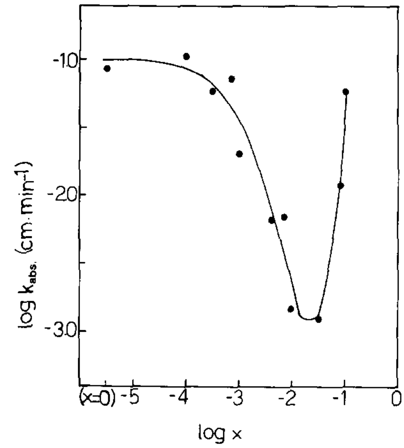

FIG. 4. The variation of activity for N_2O decomposition at 900 K over $Sn_{1-x}V_xO_2$ as a function of catalyst composition.

DISCUSSION

We have seen that the two catalyst systems display rather parallel behaviour. The undoped TiO_2 and SnO_2 exhibit a degree of activity which drops as doping proceeds. This fall is more pronounced in the case of the SnO_2 series. Activity reaches a minimum of about the same level at $x = 0.03$ for both systems. Thereafter activity rises to the maximum dopent level of $x = 0.1$. Earlier studies have dealt with host matrices which were insulators. As indicated in the Introduction, their catalytic behaviour was somewhat different. Normally initial doping led to a significant *increase* in activity which was attributed to the activity of electronically isolated active ions. As dopent ion concentration increased beyond the 5–10 at.% region activity fell sharply, due it is thought to the onset of electron exchange between the active ions, electron density being delocalised through the lattice and thus being less available for surface reactions. Finally a region of increasing activity was reached which was interpreted as being a consequence of the stabilisation of the electron band structure favouring the electronic state of this reaction adsorbate state (*1–3*). In a previous paper it was suggested that the overall rate constant for a series of increasingly doped catalysts could be represented by a summation of rate constants representing the components of the total active system (*11*), thus

$$k_{\text{tot}} = k_{\text{h}} + k_{\text{l}} + k_{\text{c}}, \qquad (3)$$

where k_h represents the activity of the host, k_l is the rate constant for the localised or isolated active ions, and k_c is the rate constant for the exchange-coupled or collective ions. Clearly the contribution of k_h tends to fall whilst k_l rises and passes through a maximum and k_c rises at higher dopent concentrations. Since k_l and k_c are related to the electronic state of isolation of the active ions, which in every study so far have been transition metal ions (tmi) having *d*-electrons, it was thought that their contribution could perhaps be monitored by conductivity measurements. Where the host is an insulator this was relatively easy. It was thus possible to suggest that the activity of isolated active ions would vary as

$$k_\text{l} = \frac{x}{[\exp(-\Delta E/RT) + 1]} A \exp(-E_\text{a}/RT), \qquad (4)$$

where $\Delta E = E_\text{g} - E_\text{e}$ is the difference between the activation energy of conduction, E_g, and the energy required to transfer an electron from the active ion site to the adsorbing molecule, E_e. Obviously to think in terms of a complete transfer is a gross oversimplification; however, it makes the discussion possible. The energy required to remove a d-electron from a vanadium ion is around 1.5 eV. Thus as E_g falls, electron delocalisation begins to occur and surface activity falls.

It has been found helpful to use the polaron concept to describe the transition from isolated tmi centres, where the polarons are small and polaron hopping is a highly activated process due to the many non-tmi ions to be traversed between each tmi, to the electron-exchange situation where polarons are large and can be thought to overlap (*3*).

Turning to the activity shown by tmi linked via an efficient electron-exchange system, here Volkenstein's ideas were found to be helpful (*14*). As the polarons overlap and electron bands are formed, the energy level of the adsorbed N_2O^-, say, may fall below the Fermi level (E_f), causing the probability of the formation of N_2O^- to rise rapidly. For an intrinsic semiconductor when the Fermi level is measured from the bottom of the conduction band $E_\text{f} = E_\text{g}$, thus there will be a critical value of E_g, E_ad, below which the probability of N_2O^- or O^- will rise rapidly and above which it will fall rapidly. Clearly it was very difficult to put a value on E_ad but some have suggested somewhere around 0.8–1 eV (*15, 16*). This certainly fitted in well with earlier observations that it was at this level of E_g that the collective sites seemed to become active. These ideas suggested that

$$k_\text{c} = \frac{x}{\exp[(E_\text{g} - E_\text{ad})/RT] + 1} A \exp(-E_\text{a}/RT). \qquad (5)$$

The application of these ideas to the present set of catalyst materials is complicated by the fact that the hosts are both active as catalysts and semiconductors. On the catalytic side it would not be expected that activity would rise when vanadium was added to the hosts unless the isolated vanadium ion sites were very much more active (*1*). According to the "twin peak" pattern for the activity of isolated tmi derived by Cimino and co-workers, V^{4+}, a d^1 ion, would not be expected to be especially active (*1*). Thus a significant effect on activity would not be expected until the V sites become more numerous. However, it is significant that activity effects do begin to be noticeable around $x = 0.0001$. Clearly V sites must exercise a considerable area of influence and must be the lowest energy sites for surface–adsorbate interactions. This effect of isolated tmi has been noted before (*4, 5*). Thus it appears that even at very low dopent levels the guest V sites begin to exercise a significant influence.

The conductivity data are slightly different for the two systems in that there is very little conductivity variation in the SnO_2 series until above $x = 0.01$ whereas in the TiO_2 series conductivity increases from about $x = 0.0001$. On the other hand the activation energies of conduction vary by only a small amount before $x = 0.003$ and then fall rapidly. It is unlikely that the *d*-electrons of the V^{4+} ions could interact with the electron bands in the host lattices. This would certainly be true for SnO_2 which is a broad *s*-band semiconductor. Ti^{3+} ions are thought to form polarons in TiO_2 and since they too are d^1 ions the possibility of electron exchange with V^{4+} cannot be ruled out. Alternatively a process such as $V^{4+} + Ti^{4+} \rightleftharpoons V^{5+} + Ti^{3+}$ is also possible. The gradual increase in conductivity over a wide range of V concentration may be evidence for either of these mechanisms. However, to a first approximation the V ions can be regarded as independent electronic entities. We can use the polaron concept to describe the situation. At high dilution they will be isolated. We have shown, following the arguments of Mott (*17*), that in this situation conductivity will be given by

$$\sigma = \sigma_0 \exp[-(\Delta\mu + W_H)/kT], \quad (6)$$

where W_H is the polaron hopping energy, which for a small (or isolated) polaron is equal to half the polaron energy, W_p; $\Delta\mu$ is the energy required for the polaron to traverse non-tmi ions. The small polaron energy is given by

$$W_p = \frac{e^2}{8\pi k_p k_o r_p}, \quad (7)$$

where r_p is the polaron radius which is somewhat less than the interatomic distance, k_o is the vacuum permittivity and

$$1/k_p = 1/k_i + 1/k_s, \quad (8)$$

where k_i and k_s are the high frequency and static dielectric constants of the hosts.

As doping increases, the possibility of the polaron charge clouds overlapping will increase giving rise to a change in W_H to

$$W_H = \frac{e^2}{16\pi k_o k_p}[(1/r_p) - (1/R)] \quad (9)$$

where R is the distance between the polaron centres. At this stage $\Delta\mu$ will be close to zero. Clearly the overall conductivity behaviour of the present systems as a function of V content will be a composite of the intrinsic conductivity of the host and the developing conductivity of the vanadium "sublattice." By combining the above Eqs. (6) and (9), it may be possible to rationalise the variations in E_g shown in Fig. 1.

It is extremely difficult to estimate absolute values for W_H because they depend sensitively on the value chosen for k_p; thus using the generally accepted value for $k_o = 8.854 \times 10^{-12}\ J^{-1}\ C^2\ m^{-1}$

$$W_H = 3.6/k_p[(1/r_p) - (1/R)]\ \mathrm{eV}. \quad (10)$$

However, the variation in $W_H/W_{H\infty}$ with x can be readily obtained if an even dispersal of dopent is assumed to obtain a value of R. The effect of $\Delta\mu$ will not be very evident because of the host conductivity; however, it will only be significant up to the concentration of V where each V has one V neighbour, i.e., around $x = 0.05$. Thus $W_H/W_{H\infty}$ will vary with x as shown in Fig. 5. A

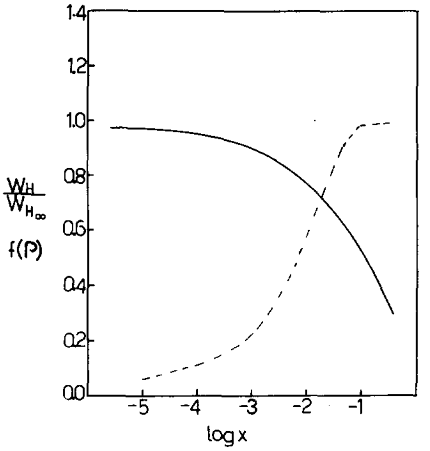

FIG. 5. The variation of the relative polaron hopping energy, $W_H/W_{H\infty}$ ———; and of $f(P) = 1/[\exp([E_g - E_{ad}]/RT + 1)]$ ------- (see text) as a function of solid solution composition x.

sharp fall is noted beyond $x = 0.001$. It is probable that below $x = 0.001$ the observed conductivity is wholly dominated by the host whereas above this vanadium concentration conductivity changes of the form of Fig. 5 will take over. This is in basic agreement with the form of the conductivity changes in Fig. 1. Thus we can see that the conductivity changes are consistent with the model of gradually increasing electron exchange between vanadium ions as its concentration increases.

How then do these conductivity changes impact on the observed activity behaviour of the two systems? The commonly accepted mechanism for this reaction implies that on adsorption N_2O is accompanied by electron transfer to the molecule which then dissociates leaving O^- at the surface. Subsequent oxygen diffusion results in the desorption of an oxygen molecule and the return of two electrons to the catalyst. Thus there is an electron transfer at the site of adsorption. This is likely to be an activated process, and the probability of it occurring will be influenced by the existence of other competing electron transfer processes. The host lattices are as we have seen semiconductors with activation energies of conduction of 1 to 1.5 eV. The energy required to transfer an electron to an adsorbing N_2O molecule is difficult to estimate and will depend on its energy state on the adsorbent. If it is assumed that the source of the electrons will be surface cations or the electron bands, then in the stoichiometric state, since the occupied orbitals are rather deep (i.e., >5 eV), adsorption will depend on the adsorbate energy state being below the Fermi level. However, the presence of reduced cations is very likely and these may well be the source of the host activity since the outer electrons will be energetically much more accessible to the adsorbing molecule. Let us consider the effect of adding vanadium to the host lattices.

Vanadium Doping $x < 0.001$

The addition of V has been shown to have an immediate effect on activity as measured by rate constants and/or activation energies. It can be appreciated that at high dilution the electrons of the isolated V will be more easily transferred to an adsorbing molecule than to the electron bands of the host. Furthermore the *d*-electrons of vanadium are probably more weakly held (ca. 3 eV) than the electrons of the host cations as measured by the Fermi levels of SnO_2 = 4.5–5.0 eV, and TiO_2 = 5.2–5.6 eV (*18*). Thus it is not surprising that the V sites should become sites of preferred adsorption. At 900 K there is little obvious increase in activity and it is difficult to identify a distinctive contribution from a k_1. However, there is a general increase in activation energies and preexponential factors, suggesting an increase in the number of high-energy sites. It is generally recognised that the desorption of oxygen is frequently the rate-determining step; if this is so here the increased activation energy as the V site density increases is reasonable.

Vanadium Doping $0.001 < x < 0.03$

It is in this region that electron hopping between V sites begins to become energetically feasible and competes with the ad-

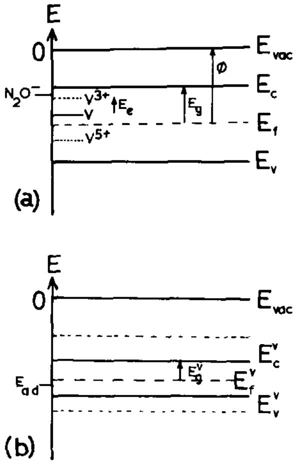

FIG. 6. (a) A schematic illustration of the energy levels of the catalysts with $x < 0.001$, and for $0.001 < x < 0.03$. (b) A schematic illustration of the energy levels for catalysts with $x > 0.03$. The position of the host bands is indicated by narrow-dashed line.

sorption process. The mechanism is probably of the type $V^{4+} + V^{4+} \rightleftharpoons V^{5+} + V^{3+}$. In an earlier paper it was suggested that the energy of transfer to an adsorbed N_2O might be about 1.7 eV (*11*). Thus when the activation energy of conduction between V atoms (Fig. 1) falls below this level activity would be expected to fall. The activation energy for conduction on SnO_2 is 1.5 eV and on TiO_2 is 1.0 eV so it is only when the activation energy for conduction via the vanadium electron hopping system falls below these values that its influence will be observed. In line with these ideas N_2O decomposition activity is observed to fall due to the exchange-coupled V in accordance with the $1/[\exp(-[E_g - E_e]/RT) + 1]$ term in Eq. (4) for k_1.

The argument can be viewed in terms of the relative positions of the Fermi level E_f of the host and the energy level of the isolated vanadium atoms. Fig. 6a schematically shows the band structure of the host lattice. The position of E_f has been idealised to be midway between the valence and conduction bands. The absolute value of E_f below the vacuum level, E_v, is equal to the work function, ϕ, and for both hosts is between 4.5 and 5.5 eV. The energy level of the isolated V ions at low V concentration probably lies between E_f and E_c. If the energy level of adsorbed N_2O lies between the V level and E_c, then adsorption by transfer of electrons from the V level would be favoured as we have argued above. Figure 6a also illustrates the situation when the vanadium concentration reaches a level at which there are sufficient vanadium neighbours to allow electron hopping to occur via oxygen anions without the need to hop over host cations. In other words new atomic levels will be introduced characterised by V^{5+}, V^{4+}, and V^{3+}. We can perhaps assume that the N_2O level will not change since adsorption is still on a catalyst dilute in vanadium. Thus if the energy difference between V^{4+} and V^{3+} or V^{5+} (above E_e) is less than between V^{4+} and adsorbed N_2O electron hopping will be energetically more favourable than electron transfer to accomplish adsorption. If the energy level of adsorbed N_2O level is unchanged it would lie above the bottom of the conduction band for the vanadium system. Thus electron transfer by conduction would be energetically more favourable than electron transfer in adsorption on vanadium sites.

It is interesting to note that both series reach the same minimum point in the two activity plots. Indeed, the kinetic parameters are almost identical, suggesting that the active "lattices" are very similar in both cases.

Vanadium Doping $x > 0.03$

If the only important term in the activity equation was that referring to the loss of activity due to competition between adsorption and electron hopping, the activity plot would have the same form as the E_g plot. However, as electron exchange develops a vanadium band would be expected to form. In Fig. 6b the postulated situation after the development of a vanadium "band structure" is illustrated. It can be seen that the position of the vanadium conduction band is just above the energy of the atomic vanadium orbitals whereas the top of the valence band is significantly below. This is in line with the energy stabilisation consequent on the band formation in VO_2 (*19*). With the development of the vanadium bands the electronic states of the catalysts are now substantially different. The energy state of adsorbed N_2O will be different and if it falls below the Fermi level activity would be expected to rise again. It has been suggested elsewhere that these states have an energy 0.8–1 eV below the conduction band, (*11, 14, 15*). Then, assuming an intrinsic semiconductor, as the activation energy for conduction falls the probability of N_2O^- will rise; hence N_2O decomposition activity will rise according to the term $1/[\exp([E_g - E_{ad}]/RT) + 1]$ in Eq. (5) for k_c and illustrated by the broad-dashed line in Fig. 5, where E_{ad} is the energy of the adsorbate state below the conduction band (Fig. 6b).

An exact description of the rate constant variation according to our model cannot be derived because it is not possible with any confidence to assign values A and E_a for the rate constant associated with each type of site. However, the general form of the activity curves shown in Figs. 3 and 4 are certainly understandable in the light of the discussion above and are qualitatively reproduced by combining the curves in Fig. 5.

There are differences between the SnO_2 and TiO_2 series, although they are not very great. As indicated in the earlier paper on methanol oxidation, the differences may be attributable to the possibility of V^{4+} electrons participating in the TiO_2 electron-exchange system (*12*). Thus there is a smoother activity change in the TiO_2 series and this can be due to V gradually modifying the electronic character of the system compared to the SnO_2 series where more of a step change is observed.

CONCLUSIONS

The results discussed in this paper demonstrate that the ideas developed to understand the activity of tmi in insulating oxides are applicable to semiconducting catalyst hosts. The dopent ions seem to act almost independently and once they are present in sufficient numbers the effect of concentration is very similar to that observed on insulators. Thus it is the onset of electron delocalisation which reduces activity of isolated ions, and subsequently it is the establishment of a facile conduction band system that stabilises the adsorbed intermediate and renews surface activity.

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