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Catalytic Activity of V-Sn Oxides for Oxidation Reactions

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The rate of oxidation of C_3H_6, C_2H_4, C_3H_8, and CO has been investigated over V–Sn oxides of various compositions. The rate shows two maxima at V–Sn(V/Sn=2/1) and (1/8) oxides. Comparison between the rate of reduction of the oxides with C_3H_6 and that of the corresponding catalytic oxidation suggests that the oxygen species responsible for oxidation differs for V–Sn(2/1) and V–Sn(1/8) oxides. The amount of oxygen desorbed in the temperature range 400—530 °C varies with the composition of the V–Sn oxides, showing a maximum at V–Sn(2/1) oxide. With V–Sn(1/8) oxide, little or no oxygen desorption is observed. On the basis of these results together with those of structural studies, it is concluded that the rate maximum with V–Sn(2/1) oxide arises from formation of an amorphous material from which lattice oxygen is easily released, while the rate maximum with V–Sn(1/8) oxide is associated with the presence of V^{4+} ions dissolved in SnO_2.

It has been shown by many workers that catalytic oxidation over V_2O_5 proceeds *via* lattice oxygen,[1] its activity being promoted by addition of the second component such as MoO_3, SnO_2, *etc.* As regards the V_2O_5–SnO_2 system, several explanations have been proposed for the effect of promoters.[2–5] Sachtler *et al.*[2] reported that the promoter action of SnO_2 in V–Sn oxides is due to the lowering of ΔG for oxygen release from the oxide which arises from the dissolution of V ions in the SnO_2 lattice.

In the present work, the rate of C_3H_6, C_2H_4, C_3H_6, and CO oxidation has been measured over V–Sn oxides of various compositions. Oxygen desorption experiments as well as measurements of the rate of reduction of the oxides with C_3H_6 have been carried out. On the basis of these results together with those of structural studies such as X-ray diffraction, IR, and ESR, the nature of the promoter effect has been discussed.

Experimental

Materials. V–Sn oxide catalysts were prepared as follows. The precipitate obtained from solutions of tin(II) chloride and ammonia was added to a solution containing the required quantity of ammonium metavanadate. The resulting precipitate was washed, dried, and heated in the air at 450 °C. The atomic ratio V/Sn of the catalysts and their surface area determined by the BET method are as follows. (V/Sn=1/0), 2.1; (4/1), 12.3; (2/1), 14.7; (1/2), 26.1; (1/8), 43.2; and (0/1), 6.8 m^2/g.

Apparatus and Procedure. Catalytic oxidation and reduction of the oxides were carried out in a closed circulation system (290 cm^3). In order to obtain the initial rates, the conversions were kept below $\approx$5%. The reaction products such as acryladehyde, CO_2, and CO were analyzed by gas chromatography. Carbonaceous deposits formed during the course of reduction were converted into CO_2 by oxidization with oxygen at 450 °C. The amount was then determined.

X-Ray diffraction patterns of the catalysts were obtained on a Rigaku Denki D-3F X-ray diffractometer using Cu $K\alpha$ radiation with a Ni filter. IR spectra were recorded on a Hitachi G2 spectrometer, the samples being prepared by the KBr pellet technique, and ESR spectra on a JES-ME-1X spectrometer. Oxygen desorption from V–Sn oxides was investigated by means of a Töpler pump. It was confirmed by gas chromatography that desorbed gas consists entirely of oxygen.

Results

Catalytic Oxidation of C_3H_6 over V–Sn Oxides and Their Reduction with C_3H_6. The rate of C_3H_6 oxidation on various V–Sn oxides at 320 °C (Fig. 1) shows two maxima at V–Sn(2/1) and (1/8) oxides. Similar maxima are observed in low oxygen pressure experiments. Selectivity toward acrylaldehyde formation was determined for all the V–Sn oxides at similar conversion values, which were obtained by adjusting the catalyst weight as well as the reaction time (Fig. 2). The

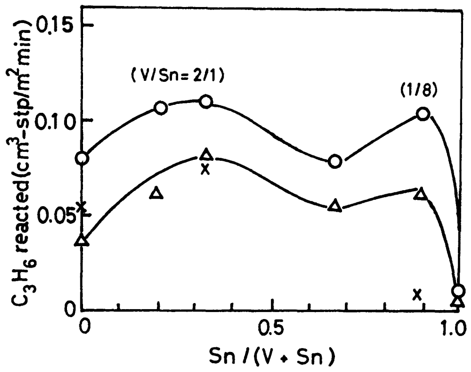

Fig. 1. Rates of C_3H_6 oxidation at 320 °C.
$P_{C_3H_6}$=35 Torr (1 Torr=133.3 Nm^{-2}); P_{O_2}; —△—, 8; —○—, 40 Torr; X, rates of reduction of the oxides with C_3H_6.

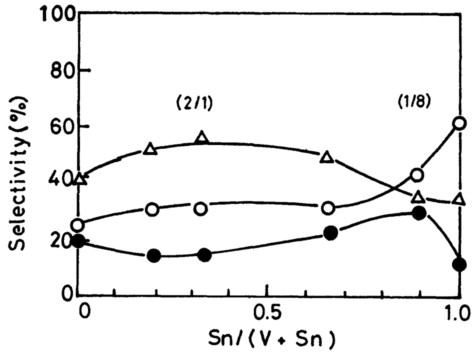

Fig. 2. Selectivities of C_3H_6 oxidation.
Experimental conditions are the same as in Fig. 1.
—●—, Acrylaldehyde; —○—, CO_2; —△—, CO.

selectivity toward acrylaldehyde formation is ≈20% for V_2O_5, ≈15% for V–Sn(2/1) oxide and ≈30% for V–Sn(1/8) oxide. As regards CO and CO_2 formation, with V_2O_5, V–Sn(4/1) and (2/1) oxides the ratio of the amount of CO to that of CO_2 in the products is *ca.* 2, being essentially the same, while with SnO_2 and V–Sn(1/8) oxide, CO_2 formation is larger than CO formation. This indicates that the same mechanism is involved in CO and CO_2 formation for the former group of oxides.

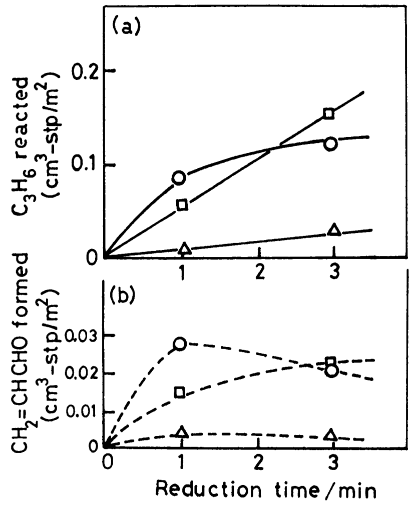

Fig. 3. Reduction of V–Sn oxides with C_3H_6 at 320 °C. $P_{C_3H_6}$=35 Torr; —○—, V–Sn (2/1) oxide; —□—, V_2O_5; —△—, V–Sn (1/8) oxide.

Figure 3a shows the rate of reduction of various oxides with C_3H_6. The initial rates of reduction obtained from the plots are 0.06—0.05 for V_2O_5, 0.08 for V–Sn-(2/1) oxide and 0.01 cm^3/m^2 min for V–Sn(1/8) oxide. The initial rate values are also given in Fig. 1. Carbonaceous deposits were formed during the course of reduction. The amount formed for one minute was found to *ca.* 0.03 for V_2O_5, 0.05 for V–Sn(2/1) oxide and 0.04 cm^3/m^2 for V–Sn(1/8) oxide. No significant difference among the three catalysts suggests that the extent of inhibition by carbonaceous deposits is essentially the same for all the catalysts.

Comparison of catalytic oxidation at two different oxygen pressures (Fig. 1) yields the reaction order 0.3—0.5 in oxygen for all the V–Sn oxides investigated. The difference between the rate of reduction of the oxides with C_3H_6 and that of the corresponding catalytic oxidation is considerably larger for V–Sn(1/8) oxide than for V_2O_5 and V–Sn(2/1) oxides. It seems that the oxygen species responsible for oxidation differs for both groups of oxides.

In the initial stage of the reaction acrylaldehyde formation is larger over V–Sn(2/1) oxide than over V_2O_5 (Fig. 3b). In fact, the initial selectivity toward acrylaldehyde formation obtained with V–Sn(2/1) oxide is 30%, being higher than the selectivity with V_2O_5(≈20%). As regards the selectivity in the later stage, the situation is reversed. V_2O_5 is more selective than V–Sn(2/1) oxide, indicating that further oxidation of acrylaldehyde to CO and CO_2 occurs more efficiently over V–Sn(2/1) oxide.

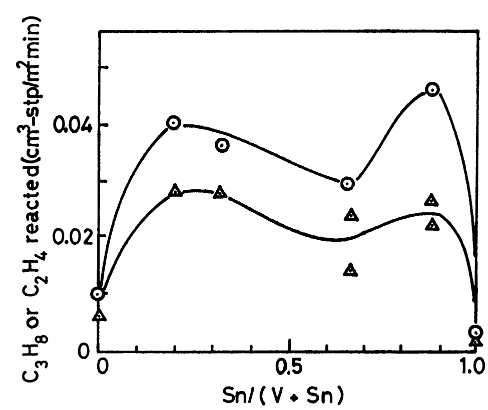

Fig. 4. Rates of oxidation of C_2H_4 and C_3H_8 at 320 °C. $P_{\mathrm{C_2',C_3}}$=40 Torr; P_{O_2}=40 Torr; —⊙—, C_2H_4; —△—, C_3H_8.

Catalytic Oxidation of C_2H_4, C_3H_8, and CO. The rates of oxidation of C_2H_4 and C_3H_8 are shown in Fig. 4. With the V–Sn(2/1) and (1/8) oxides, two maximum rates of oxidation similar to those with C_3H_6 oxidation are observed. No partial oxidation products were formed. Rate enhancement by the addition of SnO_2 is more significant for C_2H_4 and C_3H_8 oxidation than for the C_3H_6 oxidation.

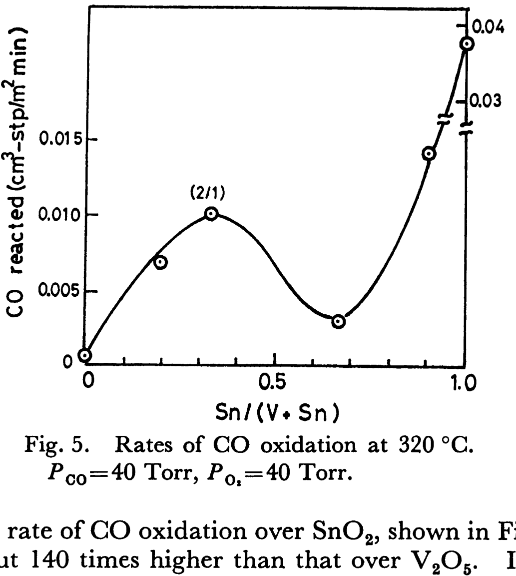

Fig. 5. Rates of CO oxidation at 320 °C. P_{CO}=40 Torr, P_{O_2}=40 Torr.

The rate of CO oxidation over SnO_2, shown in Fig. 5, is about 140 times higher than that over V_2O_5. If the V–Sn oxide is a mixture of V_2O_5 and SnO_2, its catalytic activity would increase monotonously with increasing SnO_2 content, in disagreement with the result shown. The rate of CO oxidation passes through a maximum at V–Sn(2/1) oxide. Another maximum seems to be masked by a high rate of oxidation of CO over SnO_2. Thus, the existence of two different types of maximum rate of oxidation has been established.

Oxygen Desorption from V–Sn Oxides. Oxygen easily desorbs from V–Sn oxides at 350—500 °C.[2] It was found that the dissociation pressure of oxygen over V–Sn oxides depends upon the amount of sample, decreasing with increase in the amount of oxygen removed from the oxides.[2] Accordingly, dissociation pressure measurements appear to be inadequate for comparison of the ability to release oxygen from various oxides.

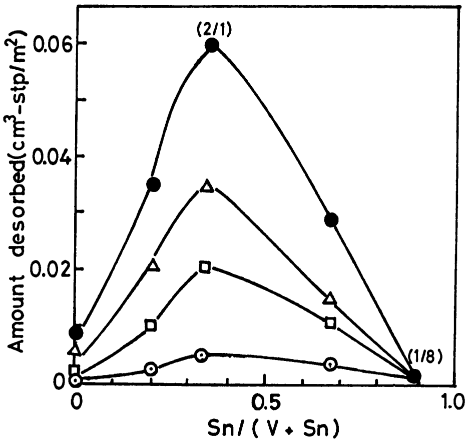

Fig. 6. Oxygen desorption from V–Sn oxides.
—○—, 450 °C; —□—, 500 °C; —△—, 530 °C; —●—, amount desorbed up to 530 °C; desorption time, 1 h at each temperature.

After the catalyst had been treated with oxygen at 400 °C followed by evacuation at 150 °C for 10 h, the temperature of the catalyst was raised stepwise up to 530 °C, the amount of oxygen desorbed being determined. During the course of experiments the pressure over the catalyst was kept below 10^{-2}Torr. As seen in Fig. 6, the amount of oxygen desorbed changes with the composition of V–Sn oxide, showing a maximum at V-Sn(2/1) oxide, in a similar manner to that observed with the rate of oxidation. With V–Sn(1/8) oxide, little or no oxygen desorption is observed. The oxygen desorption begins around 400 °C, being predominant in the temperature range 450—530 °C. This suggests that the oxygen desorbed originates from lattice oxygen and not from adsorbed oxygen. The interaction of vanadium oxide with tin oxide would lead to formation of some active part, from which oxygen release takes place easily.

Structure of V–Sn Oxides. *X-Ray Diffraction*: X-Ray diffraction studies of the V–Sn oxides showed only diffraction lines due to V_2O_5 and SnO_2. No lines indicating formation of a new compound between V_2O_5 and SnO_2 appeared, in agreement with the results of previous workers.[2,6] It appears that the active part described above exhibits no definite diffraction lines. As a result of the interaction of vanadium oxide and tin oxide an amorphous material might be formed. In fact, with V–Sn(4/1), (2/1), and (1/2) oxides, the intensities of the lines due to V_2O_5 were found to be much smaller than what are expected from the composition of V–Sn oxides. V–Sn(4/1) oxide showed lines due to V_2O_5 alone. With V–Sn(1/8) oxide only lines which are attributed to SnO_2 appeared, the observed lattice constants being somewhat smaller than those of the crystalline SnO_2. The sizes of V_2O_5 and SnO_2 crystals in various V–Sn oxides, determined from the broadening of the diffraction lines,[7] were >200 nm and 10—20 nm, respectively.

IR: IR spectra of V–Sn(2/1) oxide (Fig. 7a) show bands at 1020 cm^{-1} (V=O stretching vibration) and 818 cm^{-1} (V–O–V stretching vibration). Similar spectra were obtained with V–Sn(4/1) and (1/2) oxides.

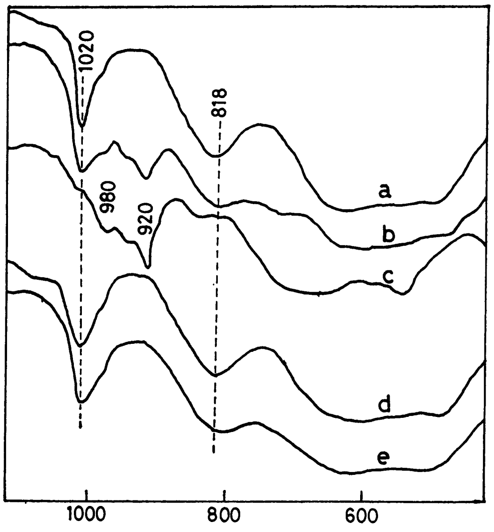

Fig. 7. IR spectra of V–Sn (2/1) oxide before and after the reduction by C_3H_6 and CO.
Before reduction (a), after reduction with C_3H_6 at 320—350 °C; 1.1 atom% (b) or 6.3% (c) of lattice oxygen was removed: After reduction with CO at 450—500 °C; 2.0% (d) or 3.8% (e). 1 wt% of V–Sn oxide in KBr (≈50 mg).

V–Sn(1/8) oxide exhibited no IR absorption due to V_2O_5. IR spectra of SnO_2 showed a broad band at ≈620 cm^{-1}. In order to examine the amorphous part in the V–Sn oxides, the intensity of the band at 1020 cm^{-1} observed with the V–Sn oxides has been determined as a function of the concentration of vanadium ions in the KBr pellets. Similar experiments have been carried out for V_2O_5 with the result that Lambert-Beer's law is applicable (Fig. 8). The intensity of the band at 1020 cm^{-1} with the V–Sn oxides is about 30% of the intensity observed with V_2O_5, suggesting that a considerable fraction of vanadium oxide in V–Sn oxides exhibits no IR absorption. Figure 7a shows that

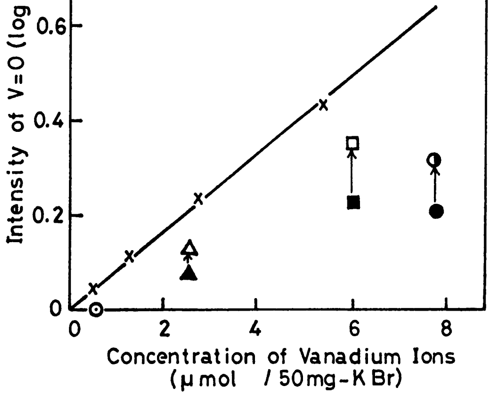

Fig. 8. Estimation of V_2O_5 concentration in V–Sn oxides.
×, V_2O_5; ○, V–Sn (1/8) oxide; ▲, (1/2); ■, (2/1); ●, (4/1); △, □, ◑, After calcination at 600 °C; 2 wt% of V–Sn oxide in KBr.

no alternative new bands appear. So far no explanation can be offered. The new bands might be masked by the bands due to V_2O_5 or SnO_2. It appears that the part which exists in the amorphous state corresponds to the part which exhibits no IR absorption.

It seems necessary to consider the effect of crystal size of the sample upon the intensity of the IR band. Since only V=O groups in the surface layer are responsible for IR absorption, the intensity of the band at 1020 cm^{-1} would increase with increase in the surface area of V_2O_5 crystals, *i.e.*, with decrease in particle size. From the extent of broadening of diffraction lines, it was concluded that the size of V_2O_5 crystals in V–Sn oxides is somewhat smaller than that in V_2O_5 specimen. The fraction of the amorphous state to the total amount of V_2O_5 in the V–Sn oxides seems to be larger than that shown in Fig. 8.

When the V–Sn oxides are calcined at 600 °C, the intensity of the band at 1020 cm^{-1} increase from $\approx$30% to $\approx$60% of those expected from the composition of the V–Sn oxides. This suggests that the amorphous part in the V–Sn oxides is decomposed to form V_2O_5 and SnO_2.

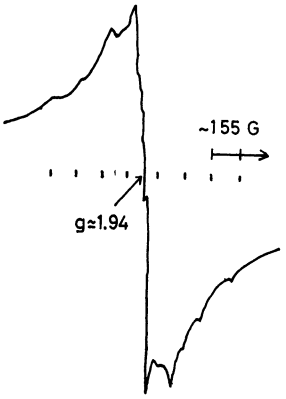

Fig. 9. ESR spectrum of V–Sn (1/8) oxide at 77 K after reduction with C_3H_6.

ESR: ESR measurements have been carried out with V–Sn(2/1) and (1/8) oxides, which exhibited the maximum oxidation activities. With V–Sn(2/1) oxide, only a broad signal appeared at $g=1.96$. After reduction with C_3H_6 there was no hyperfine structure at 77 K. On the other hand, after reduction with C_3H_6 V–Sn(1/8) oxide showed a signal having a hyperfine structure (Fig. 9) with $g=1.94$ and $A\approx155$ G at 77 K, in agreement with the results of Kasai,[8)] who reported a signal with $g_z=1.942$ and $A_z=155$ G for V^{4+} ions dissolved in the SnO_2 crystalline. On the basis of these results together with a slight contraction of SnO_2 lattice in V–Sn(1/8) oxide described above, it is concluded that with V–Sn(1/8) oxide some fraction of vanadium ions are dissolved in the SnO_2 lattice as V^{4+} ions.

Discussion

Two maxima are observed at V–Sn(2/1) and (1/8) oxides for the rate of oxidation of various reactants such as C_3H_6, C_2H_4, C_3H_8, and CO, although in the case of CO one maximum is masked by a high activity of pure SnO_2. Considering the marked difference between the rate of reduction of the oxides with C_3H_6 and that of the corresponding catalytic oxidation observed with V–Sn(1/8) oxide, it is concluded that the oxygen species responsible for oxidation differs for V–Sn(2/1) and (1/8) oxides.

The rate of catalytic oxidation as well as of oxygen desorption shows a maximum at the same composition of V–Sn oxide (V/Sn=2/1). From the results together with those of structural studies such as X-ray diffraction and IR absorption, it is concluded that the maximum rate of oxidation observed with V–Sn(2/1) oxide can be attributed to formation of amorphous material from which lattice oxygen is easily released. The fraction of vanadium ions in the amorphous state is roughly constant with V–Sn(4/1), (2/1), and (1/2) oxides, being somewhat in contradiction with the maximum activity observed with V–Sn oxide (Fig. 8). When tin oxide is added to vanadium oxide, both enhancement of the activity due to formation of the amorphous part and decrease in the number of vanadium ions present in unit mass occurs simultaneously. Such a decrease in the number of vanadium ions would cause decrease in the activity of V–Sn oxides resulting from the presence of vanadium ions. Thus, the maximum activity with V=Sn(2/1) oxide is explicable.

The following results suggest that the reactivity of the amorphous material differs from that of the crystalline V_2O_5 and SnO_2. With the reduction of V–Sn(2/1) oxide by CO (Fig. 7), the intensity of the band due to V=O scarcely changes (Figs. 7d, e), while it decreases markedly in the case of the reduction by C_3H_6(b, c). New bands appear in the region 920—980 cm^{-1}. Similar spectra have been reported by Vadelievre *et al.*[9)] and Inomata *et al.*[10)] There is no marked difference between the amount of oxygen removed by the reduction in both cases. This suggests that the reduction by C_3H_6 proceeds on V_2O_5 crystals as well as on the part which exhibits no IR absorption, *i.e.*, the amorphous part, while the reduction by CO is limited to such an amorphous part alone, thus cofirming the above conclusion.

Another maximum, *i.e.*, the maximum rate observed with V–Sn(1/8) oxide is not associated with the oxygen release. From the results of ESR and X-ray diffraction studies, it appears that the maximum rate observed with V–Sn(1/8) is associated with the presence of V^{4+} ions in SnO_2 lattice. According to the work of Kon *et al.*,[11)] Yoshida *et al.*,[12)] and Takita *et al.*,[13)] the presence of V^{4+} ions appear to facilitate the formation of adsorbed oxygen species which play a significant role in the oxidation reaction. A similar situation would be expected for V–Sn oxides. A marked enhancement in the rate of oxidation of C_3H_6 by the presence of gaseous oxygen observed with V–Sn(1/8) oxide might support this conclusion. However, the reactivity of adsorbed oxygen appears to be similar to that of lattice oxygen, since there is little or no difference between the product distributions for the C_3H_6 oxidation over V–Sn(2/1) and (1/8) oxides. It seems very diffcult to distinguish adsorbed oxygen from surface lattice oxygen, *i.e.*, adsorbed oxygen can be regarded as a special type of surface lattice oxygen.

Considering the fact that two maximum activities are observed with the V–Sn oxides, it seems unlikely that the lowering of ΔG for oxygen release from the oxide is closely associated with dissolution of V ions in the SnO_2 lattice as suggested by Sachler *et al.*[2] The maximum activity observed with V–Sn oxides containing a small amount of V ions as described above has not been found by Sachtler *et al.*[2] and other workers.[3,4] They used silica or pumice supported V–Sn oxides, in contrast to the present work which deals with unsupported V–Sn oxides. Lack of the maximum rate of oxidation of CO over V–Sn oxides reported by Tarama *et al.*[5] appears to be attributed to the preparation of their catalyst by fusion of mixture of V_2O_5 and SnO_2, where formation of the amorphous material is unexpected.

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