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Oxidation of Propylene, Acetone, and Acetaldehyde Adsorbed on Sn–Mo Oxide

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Oxidation of propylene adsorbed on Sn–Mo oxide has been investigated by ir spectroscopy. Strongly adsorbed propylene as well as ethylene on Sn–Mo oxide showed the spectra which were expected from associatively adsorbed species. On raising the temperature of the catalyst with adsorbed propylene in the presence of oxygen or in a vacuum, adsorbed propylene was dehydrogenated by lattice oxygen to form only surface OH groups without formation of carboxylate ions, in contrast with the behavior of the oxide catalysts for complete oxidation such as ZnO and Co_3O_4 described previously. Similar behavior was observed with adsorbed acetone. On the other hand, in the case of acetaldehyde, formation of carboxylate ions was observed.

INTRODUCTION

We have investigated the oxidation of olefins adsorbed on oxides by ir techniques as well as by analysis of reaction products (*1–3*). In the case of ZnO, adsorbed olefin was converted to surface formate and acetate ions as well as OH groups with oxygen uptake and then was oxidized to CO_2 and H_2O (*1, 3*). A similar oxygen uptake was observed with oxides such as Co_3O_4, NiO, Fe_2O_3, and CuO (*2*). It is of interest to investigate how the behavior of oxidation of the propylene adsorbed on oxides such as Co_3O_4 and ZnO varies from that with selective oxidation catalysts such as Bi–Mo and Sn–Mo oxides. The ir studies with Sn–Mo oxide appear to be promising compared to other selective oxides because of its high activity for olefin adsorption. Accordingly, the ir studies of oxidation of propylene adsorbed on Sn–Mo oxide have been undertaken in the present work. Furthermore, in order to decide whether or not the conclusion obtained with adsorbed propylene is generally applicable to other systems, similar measurements have been extended to adsorbed acetone and acetaldehyde.

EXPERIMENTAL

Materials. The 15-wt% Sn–Mo oxide–SiO_2 (Sn/Mo = 9, atomic ratio) catalyst was prepared by impregnating of Aerosil (Degussa) with a solution containing desired amounts of ammonium paramolybdate and tin chloride (II). The slurry was dried at 100°C and heated at 450°C for 15 hr. The Sn–Mo oxide–SiO_2 (100–140 mg) was pressed in a disk of 20-mm diameter. In order to check whether a true mixed oxide was formed, the SnO_2–SiO_2 and MoO_3–SiO_2 catalysts (15 wt%) were prepared in a similar manner. The adsorption of propylene was investigated with the results shown in Table 1. The behavior of adsorption observed with the Sn–Mo oxide–

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SiO_2 is completely different from that with the SnO_2–SiO_2 as well as the MoO_3–SiO_2. Thus, formation of the mixed oxide is confirmed.

Propylene as well as ethylene (Takachiho Co., 99.9 mol%), acetone (Tokyo Kasei Co., 99.5 mol%), acetone-d_6 (Merke Co., 99.5% isotopic purity), and acetaldehyde (Merke Co., 99 mol%) were used without further purification. Oxygen was obtained from a cylinder and purified by passing through silica gel at dry ice temperature.

Apparatus and procedure. A conventional vacuum system was used in conjunction with an ir cell, its details being given previously (*4, 5*). The temperature of the catalyst containing adsorbed propylene was raised in stages in the presence of oxygen or in a vacuum. The spectra were recorded at room temperature before and after each temperature rise by using a Japan spectroscopic IR-G grating infrared spectrometer with a spectral slitwidth of 1.5 cm^{-1} at 1500 cm^{-1}. A matched-path-length cell containing a similar disk was placed in the reference beam of the spectrometer in order to offset the background of the catalyst. The reaction products during such temperature rises were collected in liquid nitrogen traps and analyzed by gas chromatography. Simultaneously, the oxygen uptake was determined manometrically.

TABLE 1

Amount of Propylene Adsorbed

	SnO_2–SiO_2[a]	MoO_3–SiO_2[a]	Sn–Mo oxide–SiO_2[a]
	(cm^3 STP/140 mg of catalyst)		
Remaining amount after desorption at room temperature	0.09	0.02	0.22
After desorption at 120°C	0.01	—	0.22

[a] Surface area: ~170 m^2/g.

Prior to experiments the pretreatment of the catalyst with oxygen at 450°C followed by evacuation at this temperature was repeated several times.

RESULTS AND DISCUSSION

Adsorption of Propylene and Ethylene

Figure 1, curve a shows the spectrum of propylene adsorbed on Sn–Mo oxide in the presence of gaseous propylene. Evacuation of the catalyst at room temperature led to disappearance of the bands at 3650, 3075, and 1645 cm^{-1}. Simultaneously, the amount adsorbed was reduced from 0.44 to 0.22 cm^3 STP. The band at 3650 cm^{-1} coincides in position with that for perturbed surface OH groups reported in the literature,

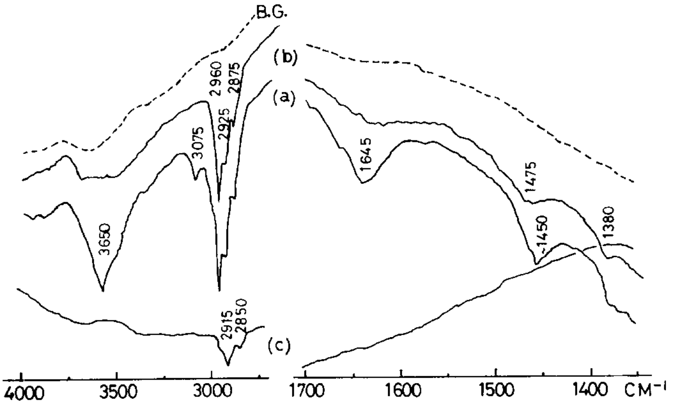


FIG. 1. Adsorption of propylene and ethylene on Sn–Mo oxide–SiO_2 (surface area, 170 m^2/g). (a) After 15 hr of adsorption of C_3H_6 (18 Torr) on Sn–Mo oxide–SiO_2 (140 mg) at 25°C. (b) After 1 hr of evacuation at 25°C. (c) After 20 hr of adsorption of C_2H_4 (12 Torr) on Sn–Mo oxide–SiO_2 (104 mg) followed by 1 hr of evacuation at 25°C.

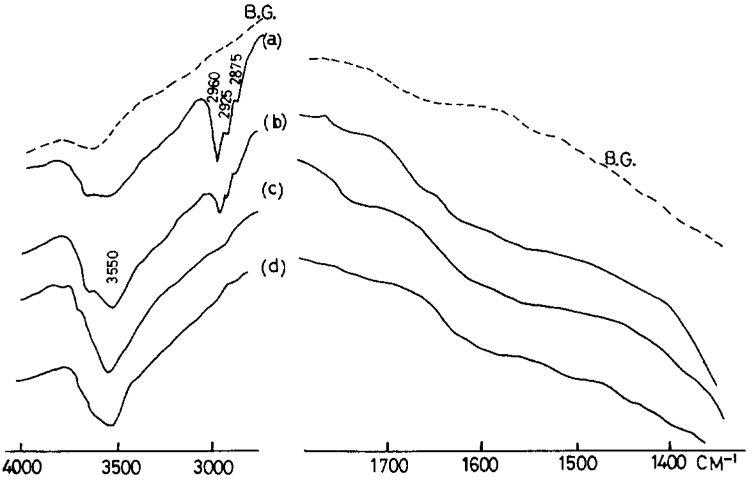
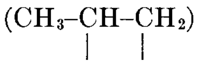


FIG. 2. Oxidation of propylene adsorbed on Sn–Mo oxide–SiO_2 (140 mg). (a) After the procedure for curve b, Fig. 1, followed by 1 hr of exposure to oxygen (1 Torr) at 25°C. (b) After 1 hr at 150°C. (c) After 1 hr at 200°C. (d) After 1 hr at 310°C. Remaining amounts of C_3H_6 adsorbed: (a) 0.22, (b) 0.22, (c) 0.22, and (d) 0.17 cm^3 STP.

permitting its assignment (*6*). The bands at 1645 and 3075 cm^{-1} belong to physically adsorbed propylene, being attributable to C=C stretching and to $=CH_2$ asymmetric stretching vibrations, respectively.

As regards the bands at 2960, 2925, 2875, 1475, and 1380 cm^{-1} which are retained after evacuation, the position of the bands suggests that the adsorbed species has no olefinic character, e.g., the possibility of a π-allyl species being excluded. A saturated adsorbed species should be formed. Thus, the bands at 2960, 2925, 2875, 1475, and 1380 cm^{-1} can be assigned to $\nu_{as}(CH_3)$, $\nu_s(CH_3)$, $\nu_{as}(CH_2)$, $\delta_{as}(CH_3)$, and $\delta_s(CH_3)$, respectively. From these considerations it may be concluded that on Sn–Mo oxide, propylene undergoes fission of the π-bond in C=C, resulting in formation of associatively adsorbed species



$$(CH_3\text{-}\underset{|}{C}H\text{-}\underset{|}{C}H_2)$$

in agreement with the conclusion drawn by Orlov *et al.* (*7*) who have made ir studies on the same system. The possibility that these bands are due to a surface species formed by polymerization of propylene may be excluded because of a lower coverage of adsorbed propylene.

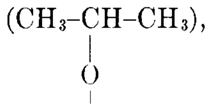
Similar experiments have been carried out with adsorbed ethylene. Little desorption was observed on evacuation of the catalyst containing ethylene at room temperature. The remaining amount adsorbed was 0.10 cm^3 STP (Fig. 1, curve c). The bands at 2915 and 2850 cm^{-1} which remained after desorption may be attributed to $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$, respectively. Thus, in the case of ethylene, the formation of a similar associatively adsorbed species is confirmed.

Oxidation of Adsorbed Propylene

The spectral change on raising the temperature of the catalyst containing adsorbed propylene in the presence of oxygen is shown in Fig. 2. The bands at 2960, 2925, and 2875 cm^{-1} attributable to associatively adsorbed propylene decrease in intensity with increasing temperature. Simultaneously, the intensity of the band at 3550 cm^{-1} which is assigned to surface OH groups increases, passing through a maximum around 200°C. It should be noted that no appreciable absorption is observed in the region of 1800–1350 cm^{-1}, suggesting no formation of carboxylate ions.

Similar experiments have been carried out under evacuation instead of in the presence of oxygen. It was found that the bands at 2960 cm^{-1} etc., due to the CH_3 as well as CH_2 groups of adsorbed propylene, disappeared at a temperature similar to that in the presence of oxygen. In other words, there seems to be no difference between the spectral behavior in the presence and absence of oxygen. This suggests that lattice oxygen participates in the hydrogen atom abstraction from adsorbed propylene to form surface OH groups. In fact, no oxygen uptake occurred during the temperature rise of the catalyst in the presence of oxygen from 0 to 150°C, in contrast with the behavior of oxides such as ZnO and Co_3O_4 described previously (*1*, *2*). At 200°C, only 0.04 cm^3 STP of oxygen was taken up, which may arise from removal of some lattice oxygen as water.

Butein (*12*) and S. Tan *et al.* (*13*) found that propylene is oxidized to form acetone on Sn–Mo oxide in the presence of water vapor. Butein proposed that formation of acetone proceeds via the intermediate



$$(CH_3\text{-}\underset{\substack{|\\ O\\ |}}{CH}\text{-}CH_3),$$

which is formed from the reaction of propylene with surface OH groups. In our experiments neither surface OH groups nor H_2O remained on the surface of the Sn–Mo oxide, since it had been evacuated at 450°C. Accordingly, formation of such an intermediate would be unexpected.

Oxidation of Adsorbed Acetone

Similar experiments have been carried out with adsorbed acetone in order to decide whether or not the conclusion obtained with adsorbed propylene is generally applicable to other adsorbed species. The adsorption of acetone on Sn–Mo oxide led to appearance of the bands at 2990, 2910, 1680, 1580, and 1450–1350 cm^{-1} (Fig. 3). Similar experiments with acetone-d_6 led to disappearance of the bands corresponding to those at 1450, 1425, 1395, and 1380

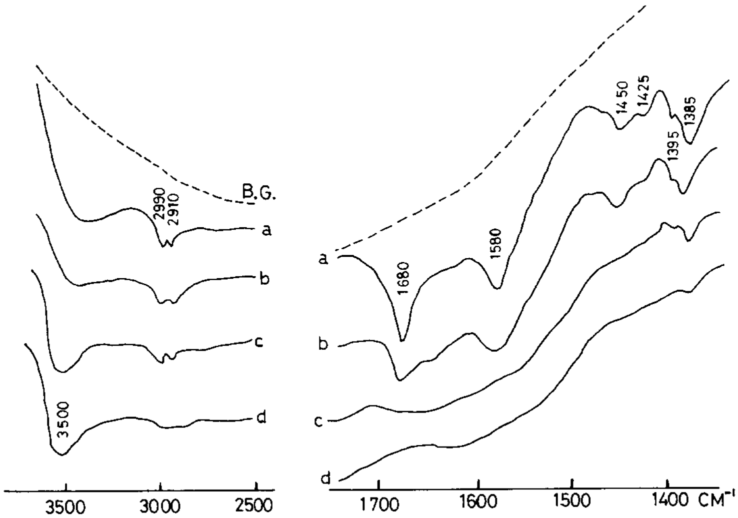


FIG. 3. Oxidation of acetone adsorbed on Sn–Mo oxide–SiO_2 (125 mg). (a) After 15 hr of adsorption of acetone followed by 0.5 hr of evacuation at 25°C, and after exposure to oxygen (2 Torr) at 25°C. (b) After 1 hr at 100°C. (c) After 1 hr at 155°C. (d) After 1 hr at 200°C. Remaining amounts CH_3COCH_3 adsorbed: (a) 0.22, (b) 0.17, (c) 0.16, and (d) 0.14 cm^3 STP.

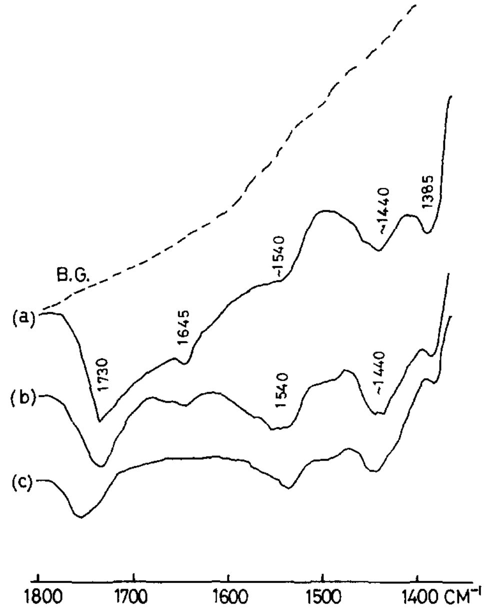
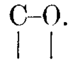


FIG. 4. Oxidation of acetaldehyde adsorbed on Sn–Mo oxide–SiO_2 (125 mg). (a) After 18 hr of adsorption of acetaldehyde followed by 0.5 hr of evacuation and after exposure to oxygen (1 Torr) at 25°C. (b) After 1 hr at 155°C. (c) After 1 hr at 250°C. Remaining amounts of CH_3CHO adsorbed: (a) 0.97, (b) 0.88, and (c) 0.79 cm^3 STP.

cm^{-1}, while the bands corresponding to those at 1680 and 1580 cm^{-1} are shifted to 1667 and 1558 cm^{-1}, respectively. Such behavior is expected since the former group of bands is due to bending vibrations of CH_3 groups and the latter to carbonyl stretching vibrations, respectively.

On increasing the temperature of the catalyst containing undeuterated acetone up to 150°C under evacuation, the bands at 1685, 1425, and 1385 cm^{-1} decreased in intensity, while the bands at 1580, 1452, and 1395 cm^{-1} remained unchanged, suggesting the presence of two types of acetone adsorption. Two such types of adsorption have already been observed with MgO and NiO (*4*). In a manner similar to that described earlier, the former bands are attributable to the coordinately adsorbed acetone, the latter bands to the dissociatively adsorbed acetone ($CH_2 \dots C(CH_3) \dots O$).

The temperature of the catalyst with adsorbed acetone was raised in stages in the presence of oxygen. The spectral change with increasing temperature is shown in Fig. 3. With increasing temperature the bands at ca. 2900 and 1500–1350 cm^{-1} which are attributable to CH_3 groups, decrease in intensity and disappear at 200°C. Simultaneously, the band at 3500 cm^{-1} due to surface OH groups is intensified. No new bands appear in the region of 1600–1350 cm^{-1}. Such a behavior is essentially the same as that with adsorbed propylene, thus confirming applicability of the conclusion that in the oxidation the adsorbed species are dehydrogenated to form surface OH groups without formation of carboxylate ions. The band at 1680 cm^{-1} attributable to C=O groups disappears at 200°C, possibly as the result of fission of the C=O bond to form the associatively adsorbed species



$$\underset{|}{C}-\underset{|}{O}.$$

Strong adsorption of SiO_2 would make it impossible to observe the band due to C–O which is expected to appear at ca. 1000 cm^{-1}.

Formation of Surface Carboxylate Ions in Oxidation

In connection with the conclusion described above, the thermal stability of surface formate and acetate ions on Sn–Mo oxide has been examined. On adsorption of formic acid vapor on Sn–Mo oxide, the bands at 1565 and 1370 cm^{-1} attributable to formate ions appeared. The intensity of these bands was unchanged when the temperature was raised to ~200°C. A similar thermal stability was observed with the case of acetate ions. The lack of formation of formate ions on SiO_2 reported by Hirota *et al.* (*8*) suggests that the formate ions observed with Sn–Mo oxide–SiO_2 catalyst are formed on Sn–Mo oxide.

It is therefore concluded that failure to detect surface carboxylate ions in the oxidation of adsorbed propylene and acetone on Sn–Mo oxide is not attributable to instability of the carboxylate ions but arises from the fact that Sn–Mo oxide lacks the ability to form carboxylate ions. The behavior of the oxidation with Sn–Mo oxide where only surface OH groups and no carboxylate ions are formed is markedly different from that with the oxide catalysts for complete oxidation such as Co_3O_4 and ZnO, where adsorbed olefins are oxidized to form carboxylate ions with oxygen uptake. Such characteristics of the selective oxidation catalysts appear to be attributable to the character of their lattice oxygen, since it has been established by various workers (*9*) that lattice oxygen is responsible for oxidation.

According to the work of Haber *et al.* (*10*) and Sachtler *et al.* (*11*), acrolein on MoO_3 as well as benzaldehyde on V_2O_5 are oxidized by lattice oxygen to form the corresponding carboxylate ions, somewhat in contradiction to the results in the present study. Accordingly, the ir spectra of acetaldehyde on Sn–Mo oxide have been investigated (Fig. 4). The bands at 1730 and 1645 cm^{-1} appear to arise from the coordination of two different carbonyl groups. The nature of two such types of coordinately adsorbed acetaldehyde is unclear. On increasing the temperature of the catalyst in the presence of oxygen, the bands due to carbonyl groups decrease in intensity while the bands at 1540 and ~1445 cm^{-1} are intensified (Fig. 4). A similar spectral change was observed on raising the temperature in a vacuum instead of in the presence of oxygen. This suggests that coordinately adsorbed acetaldehyde is oxidized by lattice oxygen to form acetate ions as has been suggested by Haber *et al.* and Sachtler *et al.* Such a difference in the behavior of formation of carboxylate ions from adsorbed acetone or acetaldehyde may be attributed to the fact that carbonyl groups at the terminal positions of molecules are easily oxidized to carboxylate ions, e.g., as in the case of acetaldehyde.

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