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Infrared Studies of Oxidaton of 2-Butanol and 2-Methyl-2-propanol Adsorbed on ZnO

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The oxidation of 2-butanol and 2-methyl-2-propanol has been studied on ZnO by infrared spectroscopy. It has been shown that 2-butanol is oxidized to carboxylate species via two types of enolate complex of 2-butanone, and that 2-methyl-2-propanol is predominantly dehydrated to form 2-methylpropene, formation of the carboxylate species being minor. From these results it has been concluded that formation of carboxylate species via olefin plays no important role in the oxidation of secondary alcohol.

INTRODUCTION

Formation of alkoxide as well as carboxylate species from alcohols on alumina has already been reported by various workers (*1–4*). In recent infrared studies (*5–8*), we have found that on metal oxides, such as ZnO, MgO, and NiO, propene, butenes, 2-propanol, and acetone are oxidized to CO_2 and H_2O via formation of carboxylate species. It has been concluded that 2-propanol is dehydrogenated to form acetone, which is oxidized to carboxylate via enolate complex. There seems to be some possibility that secondary alcohol is dehydrated to form olefin, which is oxidized to carboxylates. In fact, it has been proposed that secondary alcohol is oxidized to CO_2 and H_2O via olefin formation on TiO_2 under uv irradiation (*9–11*). In connection with these problems, infrared studies of the oxidation of 2-butanol and 2-methyl-2-propanol adsorbed on ZnO have been carried out in the present work.

EXPERIMENTAL

The apparatus consisted of a conventional closed circulation system, equipped with two infrared cells and a gas-dosing volume in the circulation loop. Details of the apparatus and procedures were reported previously (*6, 7*). After a certain amount of alcohol, ketone, or 2-methylpropene had been introduced into the ir cell, the weakly adsorbed reactants were removed by immersing the trap in liquid nitrogen. The remaining amount adsorbed of each reactant was about 0.3 cm^3/g. Oxygen of about 2 kPa was then circulated over ZnO, the temperature of which was raised in stages. Infrared spectra were recorded at ambient temperature after each treatment of the sample.

The zinc oxide, Kadox 25 (New Jersey Zinc Co.), was the same as that used in the previous work (*6, 7*). 2-Butanol, 2-methyl-2-propanol, and 2-butanone (Tokyo Chemical Industry Co., spectro grade) were dried under vacuum over a degassed molecular sieve and stored over the molecular sieve. 2-Methylpropene was also obtained from Tokyo Chemical Industry Co.

RESULTS

Adsorption of Alcohols and Ketone

Figure 1 shows the infrared spectrum of 2-butanol adsorbed. A number of bands are observed in the CH stretching and bending region together with a broad band due to surface hydroxyl groups, which hardly change on evacuation at 353 K. The observed bands are in good agreement with those of metal butoxide (*12, 13*). It is well

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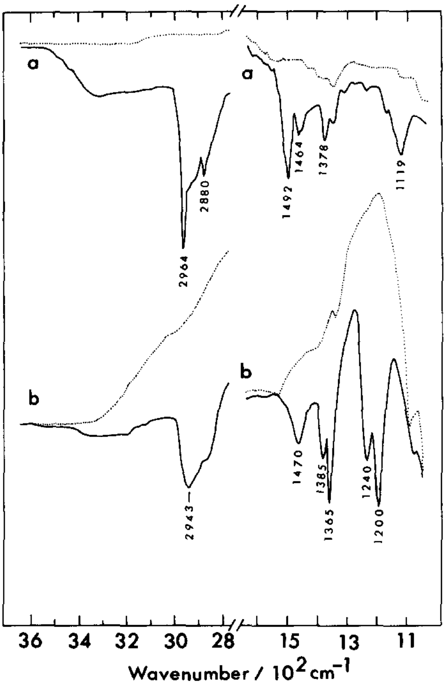


FIG. 1. Infrared spectra of alcohols adsorbed on ZnO. After 1 h of adsorption of alcohols at 293 K followed by 1 h evacuation at 353 K. (a) 2-Butanol (0.30 cm^3/g); (b) 2-methyl-2-propanol (0.31 cm^3/g); a reference disk was not used. In Figs. 1, 2, 3, and 5 the dotted lines show background spectra.

known that 2-propanol is adsorbed dissociatively to form isopropoxide and hydroxyl groups on a metal oxide surface (*1–5, 14*). Thus, formation of butoxide species has been established. Formation of similar butoxide species has been reported on Al_2O_3 (*4*) and on hydroxyapatite (calcium phosphate) (*15*). Similar experiments were carried out with 2-methyl-2-propanol. The characteristic bands for alkoxyl group have again been observed in the region 1100–1200 cm^{-1}.

The infrared spectrum of 2-butanone adsorbed exhibits no bands characteristic of ν(C=O) of 2-butanone at 1746 cm^{-1}. In addition, a new band appeared at 1488 cm^{-1} together with a broad band at 3344 cm^{-1} due to the OH group and a weak band at 3050 cm^{-1} due to the CH_2= group (Fig. 2a). A close similarity of these bands to those obtained with acetone on metal oxides (*5, 8, 14, 16, 17*) suggests that 2-butanone is adsorbed dissociatively on ZnO to form enolate species.

Reaction of Oxygen with 2-Butanol Adsorbed

Oxygen of 2.5 kPa was admitted to the ZnO containing 2-butanol, the temperature of the catalyst being raised in stages under circulation of oxygen (Fig. 3). With the increase in temperature the intensity of the alkoxyl bands decreased and disappeared at 423 K, while the bands due to the enolate complex intensified. In addition, new bands at 1560 and 1426 cm^{-1} appeared at 353 K, and grew with increasing temperature. The band at 1560 cm^{-1} became two peaks above 393 K. The change in the intensity of these bands with increasing temperature is shown in Fig. 4.

In a separate experiment, the reaction of

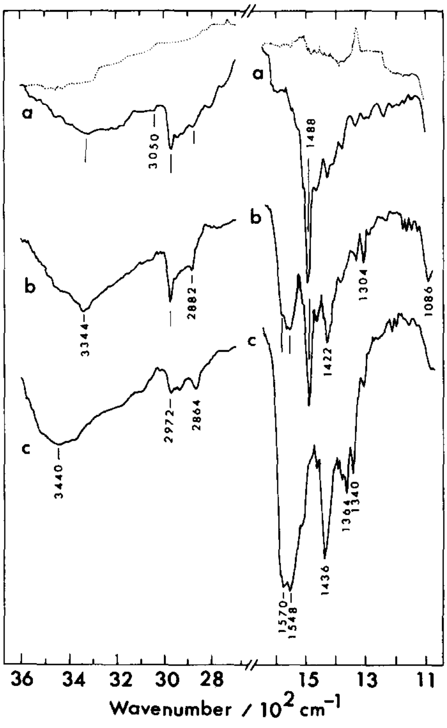


FIG. 2. Interaction of oxygen with 2-butanone adsorbed. (a) After 1 h of adsorption of 2-butanone at 293 K (0.31 cm^3/g); (b) followed by 1 h at 353 K in oxygen (2.7 kPa); (c) 1 h at 423 K in oxygen.

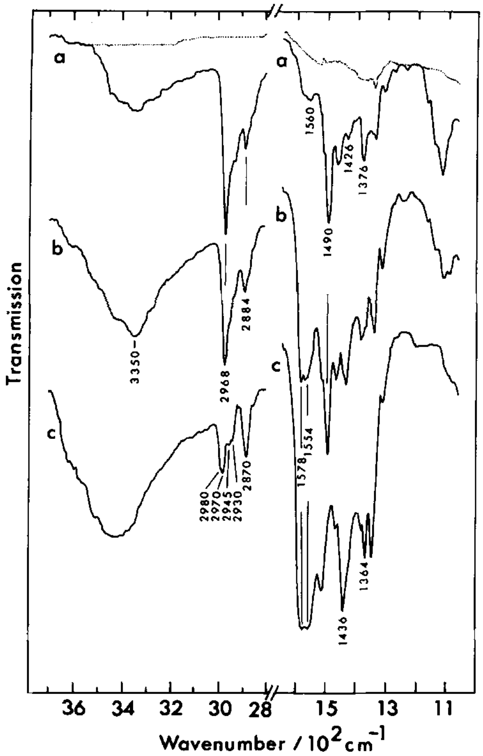


FIG. 3. Interaction of oxygen with 2-butanol adsorbed. (a) After (a) in Fig. 1, followed by 1 h at 353 K in oxygen (2.5 kPa); (b) followed by 1 h at 393 K in oxygen; (c) 1 h at 423 K in oxygen.

oxygen with 2-butanol adsorbed was investigated by analysis of the reaction products in a manner similar to that described previously (*5*, *6*). In the temperature range 393–423 K, 25% of the initially adsorbed 2-butanol was dehydrogenated to form 2-butanone, 4% of that being dehydrated to butenes. Formation of carbon dioxide was observed above 523 K. Below 523 K an appreciable amount of oxygen was taken up or consumed by the catalyst. A very small amount of acetone was also formed in the temperature range from 323 to 393 K.

Similar experiments were carried out with 2-butanone. The results are shown in Fig. 2. Essentially the same spectral behavior was observed except for the alkoxyl bands. Oxygen was taken up by the catalyst at temperatures lower than those for 2-butanol. Only carbon dioxide was formed above 423 K.

Reaction of Oxygen with 2-Methyl-2-propanol Adsorbed

A similar set of experiments was performed using 2-methyl-2-propanol. On heating of the catalyst containing 2-methyl-2-propanol in oxygen, the alkoxyl bands decreased with increasing temperature and disappeared at 523 K, while new bands appeared at 2860, 1574, 1540, 1418, and 1338 cm^{-1} at 393 K (Fig. 5a). These new bands intensified at 423 K and disappeared at 523 K. At 423 K the intensity of the bands in the range 1500–1600 cm^{-1} as well as in the CH stretching region was much weaker than that of 2-butanol and 2-butanone. Below 423 K no appreciable amount of oxygen was taken up by the catalyst. Below 523 K, 60% of the initially adsorbed 2-methyl-2-propanol was converted to 2-methylpropene, carbon dioxide being formed above 523 K.

The results with 2-methylpropene are also shown in Fig. 5. The infrared spectrum of 2-methylpropene adsorbed exhibited bands at 3590, 3048, 2962, 2920, 1620, 1530, 1440, 1364, and 1294 cm^{-1}. It was confirmed that 2-methylpropene was adsorbed dissociatively to form π-allyl species (*18*).

On raising the temperature of the disk in

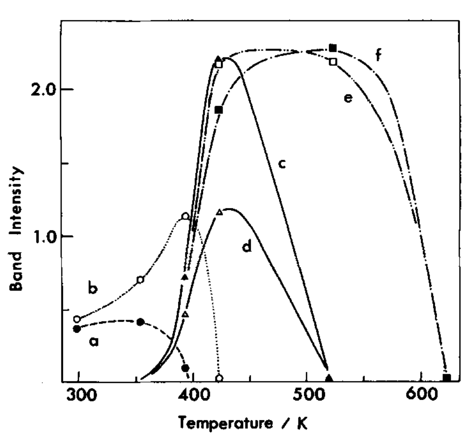


FIG. 4. Change in the band intensities with increasing temperature of ZnO. (a) 1119, (b) 1492, (c) 1578, (d) 1364, (e) 1554, (f) 1426 cm^{-1}.

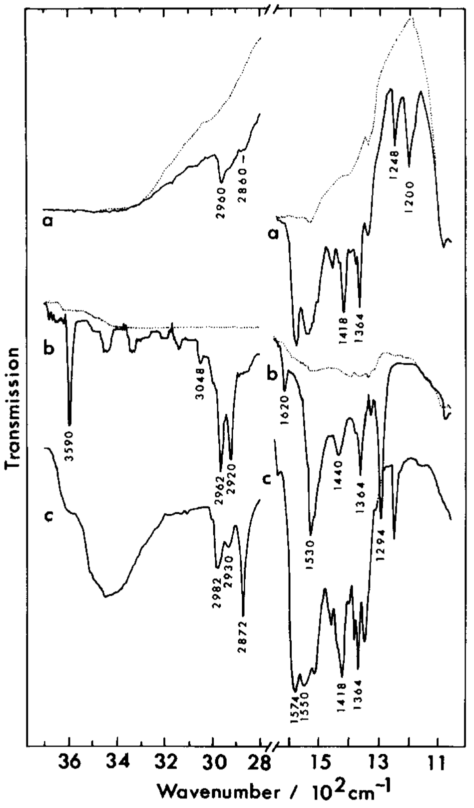


FIG. 5. Interaction of oxygen with 2-methyl-2-propanol and 2-methylpropene adsorbed. (a) After (b) in Fig. 1, followed by 1 h at 393 K in oxygen (2.5 kPa); (b) after 1 h of adsorption of 2-methylpropene (0.4 cm^3/g) at 293 K; (c) followed by 1 h at 423 K in oxygen (2.7 kPa).

oxygen the bands characteristic for π-allyl species (3590, 3048, 2962, 1530, and 1294 cm^{-1}) of 2-methylpropene reduced in intensity and disappeared at 353 K. Simultaneously, new bands appeared in the OH stretching and the CH stretching and bending regions, increasing with the rise in temperature (Fig. 5c). The band intensity of 2982, 2872, 1574, 1550, 1418, and 1364 cm^{-1} passed through maxima at 423–473 K and decreased with increasing temperature.

A large amount of oxygen was taken up at 353 K by the catalyst containing 2-methylpropene. A small amount of acetone was formed below 393 K, carbon dioxide being formed above 473 K.

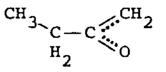
DISCUSSION

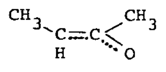
Oxidation of 2-Butanol

The change in the band intensities with increasing temperature is similar to that observed with oxidation of olefins (*6*), 2-methyloxirane (*7*), and 2-propanol (*8*). The bands at 1578 and 1364 cm^{-1} together with that at 2870 cm^{-1} (not shown in Fig. 4) appear at 393 K and disappear at 523 K. The ratio of the intensities of these bands is almost constant in this temperature range. The position of these bands is in agreement with that for the formate species. Thus, the same assignment is applicable; the bands at 2870, 1578, and 1364 cm^{-1} are due to ν(CH), ν_{as}(COO), and ν_s(COO), respectively, of surface formate species.

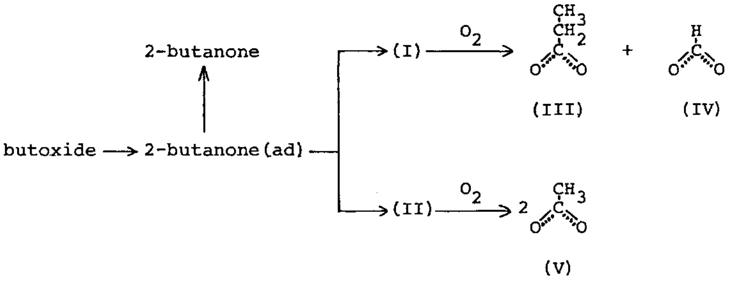
The surface concentration of formate species has been determined from comparison with the intensity of the bands of formate species produced by the adsorption of formic acid. With 2-butanol 20% of the original amount was converted to formate species, while with propene and 2-propanol more than 90% of that was converted.

The appearance of the bands due to formate species suggests that C–C bond cleavage takes place, other carboxylate species being formed. As shown in Figs. 2 and 3, similar spectra have been obtained with the oxidation of 2-butanol and of 2-butanone. This suggests that the same kind of carboxylate ion is formed on both oxidations and that on oxidation 2-butanol is dehydrogenated to form 2-butanone, which is oxidized to the carboxylate ions via the enolate species. 2-Butanone adsorbed is expected to be converted to two types of enolate species as follows:


(I)


(II)

The first is formed by loss of hydrogen from the CH_3 group and the latter, by loss hydrogen from the CH_2 group. The sole band characteristic for the enolate complex is observed at 1488 cm^{-1}. Such a behavior can be explained, since the bands due to the enolate species appear at 1490 cm^{-1} for acetone and 1488 cm^{-1} for 2-butanone, essentially no difference being observed. The enolate species (I) and (II) undergo the scission of C_1–C_2 and C_2–C_3 bonds, respectively. Thus, the oxidation proceeds presumably as follows:



Accordingly, the low intensity of the bands due to formate species seems to be explicable. Such formation of (III) in the reaction of 2-butanol has been also reported in Ref. (*4*). In the CH_3 asymmetric stretching region two bands appear at 2980 and 2970 cm^{-1} which may be due to the complex (III) and (V), respectively. With regard to the COO stretching region, only one pair of bands appears at 1554 and 1434 cm^{-1} owing to the overlapping of the two bands due to the complex (III) and (V) (*19*). The results are summarized in Table 1.

Oxidation of 2-Methly-2-propanol

As described above, about 60% of the 2-methyl-2-propanol initially adsorbed is dehydrated to form 2-methylpropene. As ex-

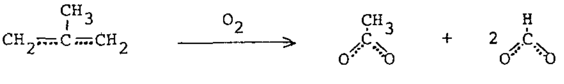
TABLE 1

Wavenumber, $\nu/(cm^{-1})$, of the Bands for the Carboxylate Species Formed from O_2 with 2-Butanol or 2-Methylpropene on ZnO

This work		Propionate[a] on ZnO	Acetate[b] on ZnO	Formate[c] on ZnO	Vibrational mode[d]
2-BuOH	2-Methylpropene				
2980	2982		2983		$\nu_{as}(CH_3)$ (A)
2970		2976			$\nu_{as}(CH_3)$ (P)
2945		2942			$\nu_{as}(CH_2)$ (P)
2930	2930		2925		$\nu_s(CH_3)$ (A)
2870	2872			2870	$\nu(CH)$ (F)
1578	1574			1572	$\nu_{as}(COO)$ (F)
1552	1550	1546	1556		$\nu_{as}(COO)$ (A) and $\nu_{as}(COO)$ (P)
1434	1418	1430	1420		$\nu_s(COO)$ (A) and $\nu_s(COO)$ (P)
1364	1364			1369	$\nu_s(COO)$ (F)

[a] Reference (*7*).
[b] Reference (*6*).
[c] Reference (*20*).
[d] ν_{as}, Antisymmetric stretch; ν_s, symmetric stretch; A, acetate, F, formate; P, propionate.

pected from such behavior, the intensities of the bands due to formate species are much lower as compared to the case for 2-butanol and olefins (*6*). With regard to oxidation of 2-methylpropene the intensities of the bands at 2872, 1574, and 1364 cm^{-1} due to formate species are much higher than that for 2-butanol and 2-propanol (*8*). The bands at 2982, 1550, and 1418 cm^{-1} are in good agreement with those of acetate ions in both position and intensity (*6*). Such behavior appears to be explicable on the basis of the following reaction scheme:



It is to be noted that olefin formed as an intermediate (dehydration reaction) is not adsorbed on the catalyst, while, when olefin is used as the sole reactant, it is strongly adsorbed, easily interacting with oxygen at temperatures below 353 K to form the carboxylate species (*6*). Such a difference in behavior might depend on the presence or absence of the alcohol species, although the true nature is unclear.

Since 2-methyl-2-propanol undergoes only dehydration to form 2-methylpropene, it is concluded that the percentage of 2-methyl-2-propanol being converted to 2-methylpropene is equal to the fraction which can be desorbed without undergoing oxidation over the whole amount of 2-methylpropene formed. A similar situation would be expected for 2-butanol. If butenes were formed during the oxidation of 2-butanol, about 60% of the butenes formed would be desorbed. As described above, little or no formation of butene is observed with the oxidation of 2-butanol, suggesting that oxidation via olefin formation is not the major reaction pathway, in agreement with the conclusion obtained from results of ir studies (Figs. 2 and 3). In connection with this conclusion, the following results are mentioned: If olefin formation played a significant role in the oxidation of 2-butanol, the intensity of the bands due to formate species would be very high, much higher than what was observed.

The discussion described above is based upon the results of the reactions of irreversibly adsorbed species. As far as the reactions of alcohols are concerned, the situation in catalytic reactions is not so much different from that in reactions of adsorbed species, since the adsorption of alcohols is strong on zinc oxide. Further study seems necessary in order to determine to what extent the same conclusion is applicable to both reaction systems.

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