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Infrared Studies of Interaction of Oxygen with 2-Propanol and Acetone Adsorbed on MgO and NiO

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The interaction of oxygen with 2-propanol and acetone adsorbed on MgO has been studied by infrared spectroscopy as well as analysis of reaction products. It was found that 2-propanol was adsorbed on MgO to form isopropoxide species, which was oxidized to surface formate and acetate complexes around 160°C in the presence of oxygen. In a similar temperature range formation of acetone as well as uptake of oxygen was observed. Similar experiments with acetone adsorbed on MgO showed that its oxidation to the carboxylates took place even at room temperature. It is concluded that the isopropoxide species is dehydrogenated by adsorbed oxygen to form acetone, which is oxidized to the carboxylates. 2-Propanol adsorbed on NiO interacted with oxygen to form surface formate and acetate complexes even at room temperature.

INTRODUCTION

In a previous paper (*1*), we reported the infrared studies of the adsorption of acetone on MgO and NiO, which showed that acetone interacted with these oxides to form coordinately and dissociatively adsorbed species. In connection with the mechanism of heterogeneous oxidation reaction, it seems of interest to extend such studies to the interaction of oxygen with acetone adsorbed on oxides. The interaction of oxygen with olefins adsorbed on oxides has already been investigated by the analysis of reaction products in the gas phase (*2*, *3*). In the present work, therefore, it has been undertaken to investigate the interaction of oxygen with 2-propanol and acetone adsorbed on MgO and NiO by using infrared spectroscopy as well as by the analysis of reaction products.

EXPERIMENTAL METHODS

Materials

The procedures for preparing the sample disks of magnesium oxide and nickel oxide and also their pretreatment were similar to those reported previously (*1*).

Acetone and 2-propanol (Tokyo Chemical Ind. Co., spectro grade) were dried under vacuum over degassed molecular sieve and purified by freeze–pump–thaw cycles. Acetone-d_6 (Merck Co., Uvasol) was used without further purification except for degassing by freeze–pump–thaw cycles. 2-Propanol-d_7 [$CD_3CD(OH)CD_3$]† was prepared by the exchange of 2-propanol-d_8 (Merck Co., Uvasol) with the deuterated PEG 1500 column of gas chromatog-

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† In order to distinguish between the H atom bonded to the tertiary carbon atom and that of OH group, 2-propanol-d_7 was used, although such attempts were unsuccessful.

raphy (*4*). 2-Propanol-d_7 contained 4% of 2-propanol-d_6[$CD_3CH(OH)CD_3$]. Oxygen was obtained from a cylinder and purified by passing through molecular sieve immersed in liquid nitrogen.

Apparatus and Procedures

The ir cell was the same as that used previously (*1*). All spectra were measured at room temperature using a Hitachi EPI-G2 grating infrared spectrophotometer with a spectral slit width 2.8 cm^{-1} at 1000 cm^{-1}. After recording the background spectrum, the reactant vapor (5 Torr) was introduced to the cell. Then, the cell was evacuated at various temperatures. After that, oxygen of 10–30 Torr was admitted to the disk, the temperature of which was raised in stages. Spectra were recorded before and after each treatment of the samples such as heating or admission of oxygen.

For studies of the oxygen uptake and the reaction products, a closed circulation system was used. After adsorption of a known amount of reactant at 0°C, oxygen was circulated over the catalyst at the pressure of 10–30 Torr. The reaction products such as acetone, carbon dioxide, and water were collected in the liquid nitrogen traps attached to the reaction vessel, and were analyzed by gas chromatography using a 2 m PEG 1500 column. The amounts of oxygen uptake or consumed by the reactions were determined manometrically. After the experiment at 0°C, the temperature of the catalyst was raised in stages, similar measurements being carried out.

RESULTS AND DISCUSSION

2-Propanol Adsorbed on MgO

The ir spectrum of 2-propanol adsorbed on MgO at 25°C showed the bands at 1464, 1368, 1172, and 1134 cm^{-1}, which did not change appreciably on raising the evacuation temperature of the MgO disk up to 150°C. These bands were in agreement with those due to the surface isopropoxide formed on metal oxides such as γ-Al_2O_3 (*5*), NaOH doped γ-Al_2O_3 (*6*), and TiO_2 (*7*). Thus, the formation of the stable isopropoxide species was confirmed. A summary of the bands of isopropoxide species and their assignments is shown in Table 1.

Figure 1 shows the spectra of 2-propanol-d_7 adsorbed on MgO. The bands appear at 1179, 1087, and 1061 cm^{-1}, which are attributable to $\nu(CO)$, $\delta_{as}(CD_3)$, and $\delta_s(CD_3)$ of surface isopropoxide species, respectively (*8*) (Table 1). The temperature of the disk was raised up in the presence of oxygen. Below 160°C no spectral change was observed. As shown in Fig. 1, at 160°C new bands appear at 1600, 1578, 1418, and 1358 cm^{-1}, while the band at 1179 cm^{-1} due to alkoxide reduces in intensity. On raising the temperature of the MgO disk up to 205°C, the new bands increase in intensity, while the band at 1179 cm^{-1} disappears. In addition, another new band appears at 1710 cm^{-1}. Evacuation of the disk at room temperature led to the disappearance of the band at 1710 cm^{-1}, while other bands did not change appreciably. Acetone was detected in the desorp-

TABLE 1

OBSERVED FREQUENCIES OF SURFACE ISOPROPOXIDE SPECIES PRODUCED BY REACTION OF 2-PROPANOL ON MgO AND NiO (cm^{-1})

On MgO		On NiO		
2-Propanol	2-Propanol-d_7	2-Propanol	2-Propanol-d_7	Vibrational mode[a]
1464	1087	1460	1085	δ_{as} (CH_3 or CD_3)
1368	1061	1368	1055	δ_s (CH_3 or CD_3)
1172	1179	1157	1165	ν (CO)
1134		1140		

[a] δ_{as}, asymmetric bend; δ_s, symmetric bend; ν, stretch.

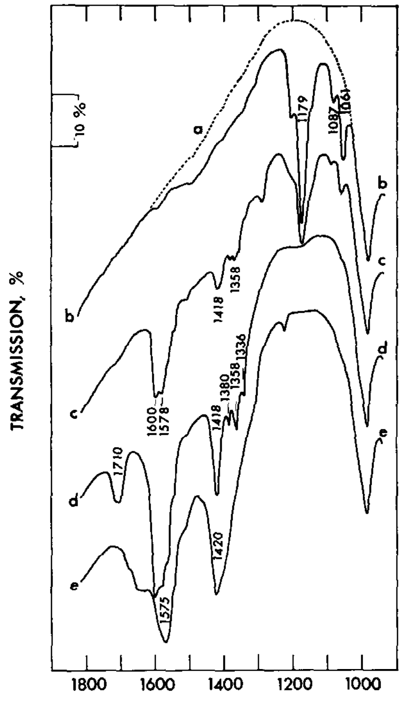


FIG. 1. Spectra of 2-propanol-d_7 adsorbed on MgO. (a) MgO (103 mg) outgassed at 500°C; (b) after 20 hr adsorption of 2-propanol-d_7 at 25°C followed by 1 hr evacuation at 50°C; (c) after admission of 10 Torr of oxygen at 25°C followed by 1 hr contact of oxygen at 160°C; (d) after 1 hr at 205°C; (e) after 1 hr at 315°C. (In Figs. 1, 3, and 4, the ordinates are displaced to avoid overlapping of traces.)

tion products. This suggests that the band at 1710 cm^{-1} is due to physically adsorbed acetone. At 315°C, the bands at 1600, 1380, 1358, and 1336 cm^{-1} disappear, while the bands at 1575 and 1420 cm^{-1} still remain in the spectrum.

As regards the bands at 1575 and 1420 cm^{-1}, the corresponding bands were observed at 1586 and 1422 cm^{-1} with undeuterated 2-propanol. This suggests that these bands are due to the carboxylate groups produced by oxidation of surface isopropoxide. As shown in Table 2, the characteristic bands of the carboxylate groups of magnesium acetate are observed at 1570 and 1422 cm^{-1}. Consequently, the bands at 1586 and 1422 cm^{-1} are attributable to the asymmetrical [$\nu_{as}(CO_2^-)$] and symmetrical stretching vibrations [$\nu_s(CO_2^-)$] of the carboxylate groups of acetate ions (*9*), respectively. The position of the bands is similar to the vibrations of acetate ions on MgO reported by Kagel and Greenler (*10*) and Sokolov, Kadushin, and Krylov (*11*).

As regards the bands at 1600, 1380, 1358, and 1336 cm^{-1} (Fig. 1), the corresponding bands were observed at 1603, 1384, and 1366 cm^{-1} with 2-propanol. As shown in Table 2, these bands are in agreement with those of $HCOO^-$ and $DCOO^-$ reported by Kagel and Greenler (*10*) and also with those of magnesium formate (*12*). This suggests that these bands are due to the carboxylate groups of formate ions. It has been reported (*10*, *13*) that the symmetrical vibrations of formate ions show much smaller intensity than the asymmetrical one. Such a decreased intensity of the bands at 1380, 1358, and 1336 cm^{-1}, therefore, would be expected. According to Kagel and Greenler, above 300°C the formate species on MgO changed to other species such as carbonate or carbon dioxide, while the acetate species on it remained unchanged. As seen in Fig. 1, there are the two carboxylate species at 200°C but only acetate species at 300°C, thus confirming the above assignment. It is concluded, therefore, that the isopropoxide on MgO is oxidized to acetate and formate ions in the presence of oxygen in the temperature range above 160°C.

In a separate experiment the reaction of oxygen with 2-propanol adsorbed on MgO was investigated by analysis of reaction products in the gas phase. Oxygen was admitted to the MgO containing 2-propanol at 0°C and the catalyst temperature was raised up in stages under the circulation of oxygen. The amounts of oxygen uptake as well as those of reaction products at each stage are shown in Fig. 2. It is seen that around room temperature little or no oxygen uptake is observed. Above 100°C, an appreciable amount of oxygen uptake takes place, which is expected from the formation of the carboxylate groups described above. In the temperature range where no

TABLE 2

OBSERVED FREQUENCIES OF CARBOXYLATE BANDS PRODUCED BY REACTION OF 2-PROPANOL AND ACETONE ON MgO (cm^{-1})

This work					Donaldson, Knifton and Ross[a]	Kagel and Greenler[b]		Sokolov, Kadushin and Krylov[c]	
2-Propanol CH_3COO^- $HCOO^-$	2-Propanol-d_7 CD_3COO^- $DCOO^-$	Acetone CH_3COO^- $HCOO^-$	Acetone-d_6 CD_3COO^- $DCOO^-$	Mg $(CH_3COO)_2$	Mg $(HCOO)_2$	CH_3COO^- $HCOO^-$	$DCOO^-$	CH_3COO^-	Vibrational mode[d]
1586	1575	1586	1578	1570		1582		1575	ν_{as} (A)
1422	1420	1408	1406	1422		1445		1445	ν_s (A)
1603	1600	1610	1602		1603	1602	1600		ν_{as} (F)
1384	1380	1380			1385	1370	1345		ν_s (F)
1366	1358	1368	1345		1374	1359	1336		
	1336				1366	1340	1325		

[a] Ref. (*12*).

[b] Ref. (*10*).

[c] Ref. (*11*).

[d] ν_{as}, asymmetric stretch; ν_s, symmetric stretch; A, acetate ion; F, formate ion.

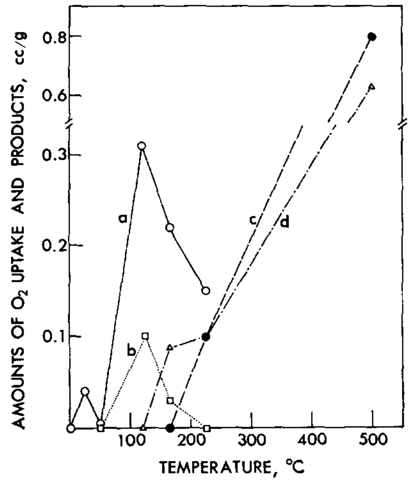


FIG. 2. Reaction of oxygen with 2-propanol adsorbed on MgO. (a) oxygen uptake or consumed by the reactions; (b) acetone formed; (c) CO_2 formed; (d) H_2O formed. Two grams of MgO were used. Amount of 2-propanol adsorbed at 0°C was 0.5 cc/g.

formation of carbon dioxide took place, the ratio of the amount of oxygen uptake to that of the amount of 2-propanol initially adsorbed was 1.6. It is seen that the uptake of oxygen and the formation of acetone occur simultaneously. Such a phenomenon together with the appearance of the band at 1710 cm^{-1} in the ir spectra (Fig. 1) suggest that the isopropoxide on MgO is oxidized to the carboxylate species via acetone. Thus, the following reaction scheme is proposed:

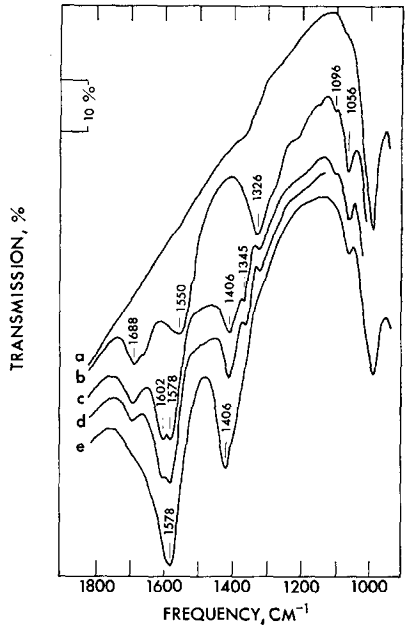
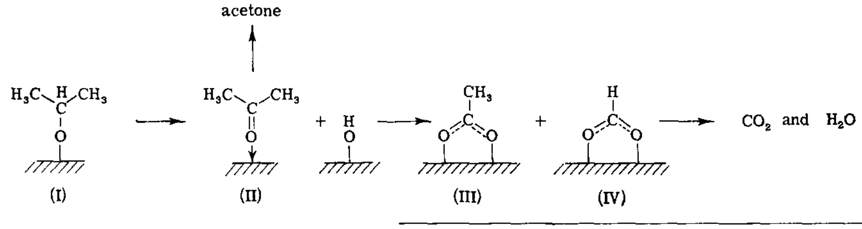


FIG. 3. Spectra of acetone-d_6 adsorbed on MgO. (a) MgO (129 mg) outgassed at 500°C; (b) after 2 hr adsorption of acetone-d_6 followed by 2 min evacuation at 25°C; (c) 20 hr after admission of 22 Torr of oxygen at 25°C; (d) after 2 hr at 80°C; (e) after 2 hr at 190°C.

ature. This suggests that the oxidation of acetone to the carboxylates should be very rapid around 160°C, which is a prerequisite for the reaction scheme described above.

Acetone Adsorbed on MgO

Figure 3 shows the spectra of acetone-d_6



Isopropoxide (I) is dehydrogenated by adsorbed oxygen to form acetone (II), which is oxidized to the carboxylate complexes (III and IV). Minor amounts of acetone (II) are desorbed in the gas phase. As discussed below, in the presence of oxygen acetone adsorbed on MgO is oxidized to the carboxylate species even at room temperature. adsorbed on MgO. As described in the preceding paper (*1*), the band at 1688 cm^{-1} is attributable to coordinately adsorbed species and the bands at 1550 and 1326 cm^{-1} are due to dissociatively adsorbed species ($CH_2{=}C(CH_3){=}O$). On admission of oxygen to the MgO disk at room temperature, new bands appear instantaneously at 1602,

TABLE 3

Observed Frequencies of Carboxylate Bands Produced by Reaction of 2-Propanol on NiO (cm^{-1})

This work				
2-Propanol CH_3COO^- $HCOO^-$	2-Propanol-d_7 CD_3COO^- $DCOO^-$	Ni $(HCOO)_2$	Rufov *et al.*[a] CH_3COO^-	Vibrational mode[b]
1550	1540		1560	ν_{as} (A)
1418	1404		1400	ν_s (A)
1580	1570	1580		ν_{as} (F)
1376	1346	1378		ν_s (F)
1340	1324			

[a] Ref. (*14*).

[b] ν_{as}, asymmetric stretch; ν_s, symmetric stretch; A, acetate ion; F, formate ion.

1578, and 1406 cm^{-1}. On raising the temperature of the disk up to 80°C, the intensity of the new bands increases, while the intensity of the band due to carbonyl groups decreases. At 190°C, only the bands at 1578 and 1406 cm^{-1} remain in the spectrum. The bands at 1578 and 1406 cm^{-1} can be assigned to $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$ of acetate ions, respectively, on a similar basis to that described for 2-propanol on MgO (Table 2). In a similar manner the band at 1602 cm^{-1} may be assigned to $\nu_{as}(CO_2^-)$ of formate ions. Although the band due to the symmetrical stretching vibration of carboxylate groups is unclear, as a tentative assignment a very weak band at 1345 cm^{-1} may be mentioned. Such behavior may result from its low intensity described above. In a separate experiment it was found that on admission of oxygen to the MgO-containing acetone an appreciable amount of oxygen uptake took place at room temperature. This would be expected from the fact that in the case of acetone on MgO the formation of the carboxylate species takes place at room temperature as described above.

2-Propanol Adsorbed on NiO

Similar experiments were carried out with NiO. The results are summarized in Tables 1 and 3.

Figure 4 shows the spectra of 2-propanol-d_7 adsorbed on NiO. The bands at 1165, 1085, and 1055 cm^{-1} can be assigned to $\nu(CO)$, $\delta_{as}(CD_3)$, and $\delta_s(CD_3)$ of surface isopropoxide, respectively, by analogy with 2-propanol on MgO. When oxygen is admitted to the isopropoxide covered surface of NiO at room temperature, the bands appear at 1570–1540 (broad), 1404, 1346,

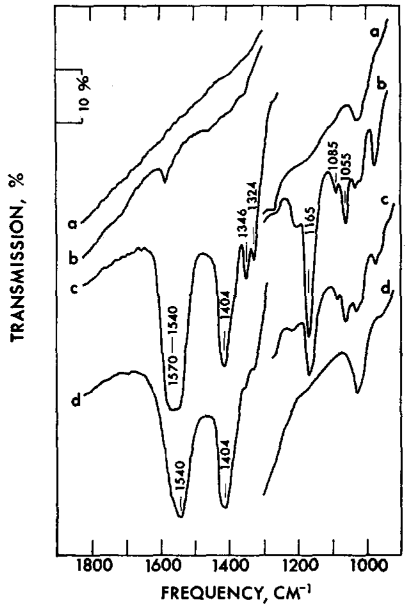


Fig. 4. Spectra of 2-propanol-d_7 adsorbed on NiO. (a) NiO (126 mg) outgassed at 450°C; (b) after 2 hr adsorption of 2-propanol-d_7 at 25°C followed by 1 hr evacuation at 100°C; (c) 2 hr after admission of 27 Torr of oxygen at 25°C; (d) after 30 min at 165°C.

and 1324 cm^{-1}. On raising the temperature of the disk up to 70°C, no spectral change was observed. At 165°C, only the bands at 1540 and 1404 cm^{-1} remain, while the other bands disappear. The bands at 1540 and 1404 cm^{-1} can be assigned to the $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$ of acetate ions, respectively, in a similar manner to that for MgO. Considering that nickel formate shows the absorption at 1580 [$\nu_{as}(CO_2^-)$] and at 1378 cm^{-1} [$\nu_s(CO_2^-)$], it appears that the broad band at 1570–1540 cm^{-1} results from overlapping of the two bands due to the $\nu_{as}(CO_2^-)$ of formate and of acetate ions. The bands at 1346 and 1324 cm^{-1} may be assigned to the $\nu_s(CO_2^-)$ of formate ions. Thus, essentially the same conclusion can be drawn: 2-propanol adsorbed on NiO is oxidized to surface acetate and formate ions. The spectral change on raising the temperature is explicable in the same manner, i.e., on the basis of a difference in the reactivities of formate and of acetate ions.

It should be mentioned that in the case of oxidation of 2-propanol on NiO acetone was not detected in the desorption products. Such behavior may arise from a much more rapid oxidation of the isopropoxide on NiO owing to its higher activity than MgO.

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