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Spectroscopic Identification of Adsorbed Species Derived from Adsorption and Decomposition of Formic Acid, Methanol, and Formaldehyde on Cerium Oxide

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The surface species formed from adsorption and decomposition of HCOOH, CH_3OH, and HCHO over dehydroxylated cerium oxide have been identified using *in situ* Fourier transform infrared spectroscopy at temperatures from 300 to 673 K. Bidentate and unidendate formate species were formed upon adsorption of HCOOH at 300 K. It is suggested that the two types of formate species originated from dehydroxylation and deprotonation of the formic acid on the surface. The formate species decompose above 473 K *in vacuo* and subsequently leave a residue of carbonate and isolated OH groups on the surface. At least two kinds of surface methoxy species with characteristic IR bands in the regions 2950–2780 and 1100–1030 cm^{-1} were detected when cerium oxide was exposed to CH_3OH at 300 K. These methoxy species were partly oxidized to form formate species by oxygenation of cerium oxide at 473 K. Dioxymethylene species together with formate species were produced from adsorption of HCHO on cerium oxide at 300 K. Upon warming the samples to 373 K, IR bands due to the dioxymethylene species nearly disappeared while bands of the methoxy species emerged. Band intensities of both dioxymethylene and methoxy species increased markedly when cerium oxide was partially reduced prior to the adsorption. It is concluded that the methoxy and formate species are produced mainly via Cannizzaro reaction, particularly on partially reduced cerium oxide.

I. INTRODUCTION

Characterization of adsorbed species formed during heterogeneous reaction is of prime importance for understanding reaction mechanisms. In order to identify surface species produced in the course of a reaction, the species are usually confirmed by adsorption of the possible compounds by which the adsorbed species may be generated (*1*). Formic acid, methanol, and formaldehyde are three of the simplest molecules produced from the CO + H_2 reaction (*2*). The adsorbed precursors of these simple molecules on the catalyst surface are most likely elementary intermediates (*3–7*) for products from CO hydrogenation. Therefore study of the adsorption of these molecules has currently received much attention. The present study was motivated by our recent results obtained from CO adsorption and hydrogenation on cerium oxide (*8, 9*) and by the fact that cerium oxide has been found to be a very effective promoter or support in supported metal catalysts for both hydrogenation and oxidation processes. However, the role played by ceria in the catalysts is not clearly understood.

CO adsorption on partially reduced cerium oxide produced a considerable amount of formate species even at room temperature, along with species giving rise to additional weak bands in the region 1200–800 cm^{-1}. These bands, which became more prominent during the CO + H_2 reaction at

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mild temperatures, seem to be due to dioxymethylene and methoxy species. The major object of the present work is to identify the adsorbed species evolved from adsorption of formic acid, methanol, and formaldehyde, and to investigate surface reactions during decomposition of these species at elevated temperatures as a reference to elucidate the surface species derived from CO + H_2 reaction on cerium oxide and ceria-supported or promoted metal catalysts. An *in situ* study of the CO + H_2 reaction over cerium oxide by FT-IR will be addressed in a following publication. The adsorption of these molecules has often been used to examine the surface properties of transition metal oxides (*10–13*), but similar adsorption work on cerium oxide has not yet been reported.

II. EXPERIMENTAL

Materials. Cerium oxide employed in this study was prepared by thermal decomposition of cerium hydroxide gel at 773 K for 3 h. The hydroxide gel was obtained through precipitation from an aqueous solution of cerium(III) nitrate with NH_4OH at pH 8–9. After repeated filtering and washing with distilled water, the precipitate was dried in air at 390 K overnight and then calcined at 773 K. The specific surface area of cerium oxide was 20 m^2/g (BET).

H_2 was purified via a Deoxo and then a liquid-nitrogen trap. Liquid formic acid and methanol were transferred to a trap by vacuum distillation and then purified using freeze–pump–thaw cycles. Formaldehyde was obtained by decomposing paraformaldehyde, which was dehydrated and degassed at around 373 K. The vapor (5 Torr) of formaldehyde was stored in a trap and then further purified by a freeze–pump–thaw cycle prior to admission to an IR cell.

Apparatus. IR spectra were recorded on a JEOL JIR-100 FT-IR spectrometer with 256 scans at 4 cm^{-1} resolution using a liquid-nitrogen-cooled HgCdTe detector. All the spectra were recorded in absorbance mode, and the background spectra were recorded before admitting the adsorbate vapors under corresponding conditions of temperature. The cerium oxide was pressed into a self-supporting disk, weight ca. 150 mg, with a diameter of 20 mm. An IR cell with NaCl windows and a furnace for heating the disk *in situ* to 1100 K was connected to a vacuum system which could be kept below 10^{-4} Torr (1 Torr = 133.3 N m^{-2}) by an oil-diffusion pump and a mechanical pump.

Procedure. The sample disk was repeatedly oxidized in O_2 at 873 K and outgassed at 1000 K until surface contaminants were completely removed as indicated by infrared spectroscopy. The sample, denoted CeO_2 (1000 K), was fully oxidized and dehydroxylated. In order to obtain a partially reduced surface, the CeO_2 (1000 K) was subsequently treated with H_2 at 673 K for 2 h and then outgassed at 1000 K for removing surface OH groups. The partially reduced sample is denoted CeO_2 (673-H). After outgassing, the sample disk, either CeO_2 (1000 K) or CeO_2 (673-H), was cooled to room temperature in stepwise fashion for recording background spectra from 673 K at intervals of 100 K. The adsorbate vapor was introduced into the IR cell at room temperature (300 K) and physically adsorbed molecules were removed by evacuation after an equilibration for 5–10 min at the same temperature. Decomposition of the adsorbed species was investigated *in vacuo* at elevated temperatures in a stepwise fashion from 300 K and *in situ* IR spectra were taken at the desired temperatures.

III. RESULTS

1. HCOOH Adsorbed on CeO_2 (1000 K)

Figure 1a shows the spectrum recorded after admission of HCOOH onto CeO_2 (1000 K) for 5 min at 300 K. Upon warming the sample from 300 to 373 K (from Fig. 1a to 1b) *in vacuo*, bands at 1734 and 1684 cm^{-1} obviously decreased in intensity, and they

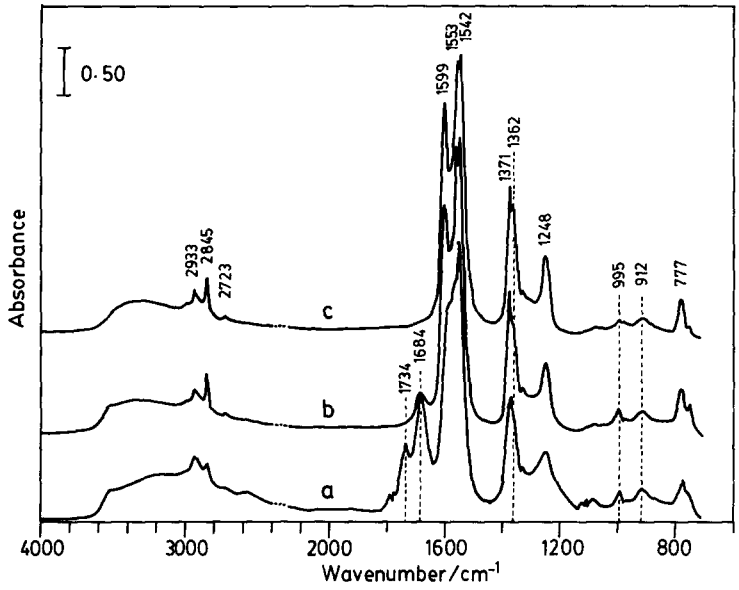
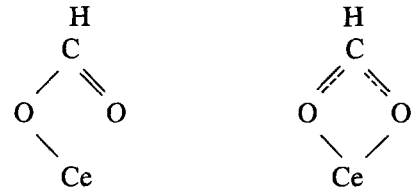


FIG. 1. IR spectra of adsorbed HCOOH on CeO_2 (1000 K) (a) in the presence of HCOOH vapor for 1 h at 300 K; (b) after evacuation for 16 min; (c) at 373 K *in vacuo* for 30 min.

are accordingly ascribed to molecularly adsorbed HCOOH interacting via hydrogen bonding with surface oxygen anions of the cerium oxide. The broad bands ranging from 3600 to 2800 cm^{-1} are clearly due to hydroxyl groups strongly perturbed by hydrogen bonding. Nine distinct bands were observed at room temperature (Fig. 1a) and they became more prominent after evacuation at 373 K (Figs. 1b and 1c). These bands can be clearly assigned to formate species (*9*), i.e., ν (C–H), 2845; ν $(OCO)_{as}$, 1599, 1553, 1542, δ (C–H), 1371; ν $(OCO)_s$, 1362, 1248; and δ (OCO), 777 cm^{-1}.

The band at 2933 cm^{-1} is attributed to a combination band of δ (C–H) and ν $(OCO)_{as}$. A pair of bands at 1599 and 1248 cm^{-1} developed synchronously with an increase in temperture from 300 to 373 K, indicating that the two bands arise from the same species. It has been suggested that the frequency separation between ν $(OCO)_{as}$ and ν $(OCO)_s$ of formate ion should obey the following order (*14, 15*):

(i) Monodentate formate >(ii) free formate ion >(iii) bidentate formate.



Monodentate formate Bidentate formate

In the light of this empirical approach, the bands at 1599 and 1248 cm^{-1} might be attributed to monodentate formate species since the frequency separation, 351 cm^{-1}, is much larger than that of free formate ion (about 250 cm^{-1}). The remaining bands in the region 1600–1300 cm^{-1} are attributed to bidentate formate species because the frequency separation is smaller than 250 cm^{-1}. The two ν $(OCO)_{as}$ vibrations at 1553 and 1542 cm^{-1} indicate that two kinds of bidentate formate species were formed.

The formate species were stable upon heating the sample to 473 K (Figs. 1c and 2d). At 573 K the two bands at 1599 and 1248 cm^{-1} due to monodentate formate species disappeared and the other bands due to bidentate formate species were both reduced

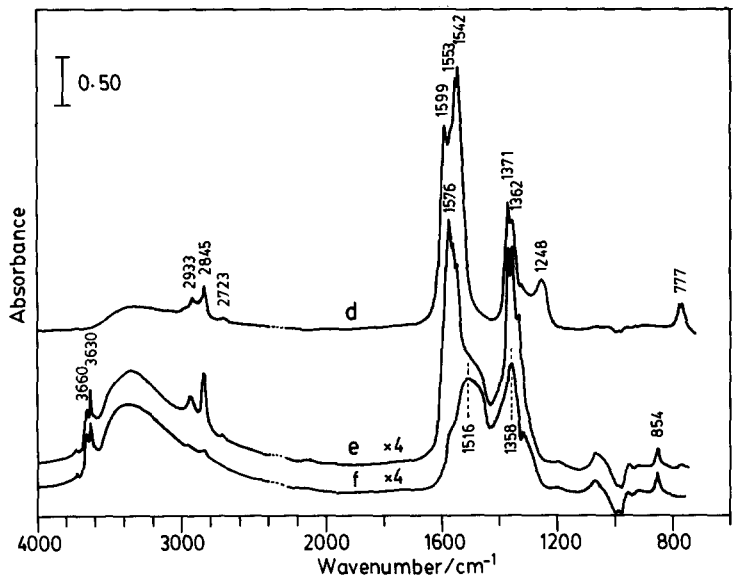


FIG. 2. Continued from Fig. 1. (d) At 473 K for 30 min; (e) at 573 K for 2 min and (f) for 30 min.

markedly in intensity from Figs. 2d to 2e. Meanwhile, sharp bands at 3660 and 3630 cm^{-1} due to isolated OH groups emerged at 573 K. With prolonged evacuation at 573 K as shown in Figs. 2e and 2f, the bands of the formate species gradually vanished while new bands, which are ascribed to carbonate species (*16, 17*), were produced at 1516, 1358, and 854 cm^{-1}.

2. CH_3OH Adsorbed on CeO_2 (1000 K)

In Figs. 3, 4, and 5, the CeO_2 (1000 K) sample was exposed to vapor of CH_3OH at 300 K for 10 min and then evacuated and warmed. Figure 3a shows the spectrum recorded just after evacuating CH_3OH vapor in the IR cell. Several bands in the frequency region 3000–2800 cm^{-1} and three bands at 1103, 1050, and 1031 cm^{-1} were observed. Studies on adsorption of methanol on metals (*11, 18*) and metal oxides (*12, 19, 20*) have concluded that the characteristic bands in 3000–2800 cm^{-1} and near 1050 cm^{-1} are due to (CH_3) and (C–O) of adsorbed methoxy species, respectively. The three distinct bands at 1103, 1050, and 1031 cm^{-1} may suggest that three kinds of methoxy species were derived on the surface from adsorption of CH_3OH at room temperature. A weak band at 1450 cm^{-1} should be attributed to the deformation mode of methyl groups. The broad band centered at 3400 cm^{-1} shows the formation of surface OH groups from dissociative adsorption of CH_3OH. At 373 K *in vacuo* for 30 min (Fig. 3b), all the bands declined slightly owing to desorption of these species, and, in particular, the band at 1031 cm^{-1} was reduced appreciably.

At 473 K (Fig. 4c), the band at 1031 cm^{-1} disappeared, and the other two bands at 1103 and 1050 cm^{-1} were also weakened and shifted slightly to lower wavenumbers. It is interesting to note that at 473 K weak bands at 1547, 1376, and 1360 cm^{-1} appeared due to bidentate formate species as already described previously. The three bands grew rapidly at 473 K as shown in Fig. 4d while the band at 1093 cm^{-1} exhibited a marked decrease in intensity but the band at 1041 cm^{-1} hardly changes. The formation of formate species could be accounted for by the results of oxidation of methoxy species by surface oxygen of cerium oxide. The methoxy species with the band at 1031 cm^{-1} desorbed while the bands at 1050 (1041) and 1103 (1093) cm^{-1} were oxidized into formate

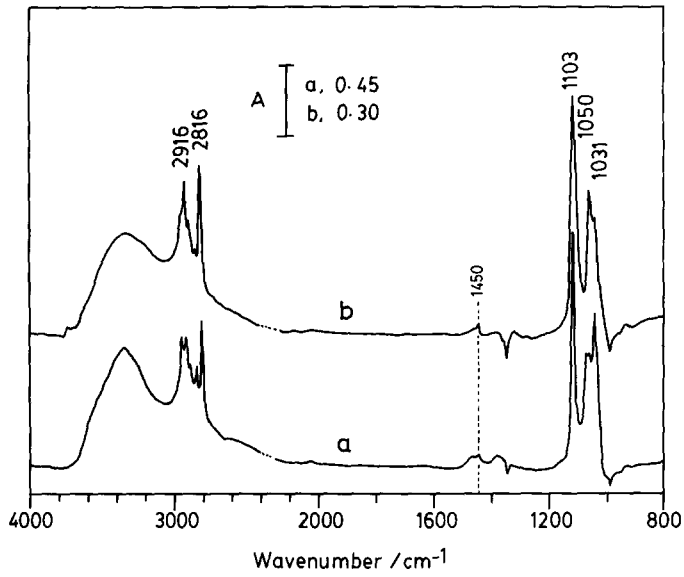


FIG. 3. IR spectra of adsorbed CH_3OH on CeO_2 (1000 K) (a) after a contact with CH_3OH vapor for 3 min, then outgassing for 30 min at 300 K; (b) at 373 K *in vacuo* for 30 min.

species: especially the methoxy giving the band at 1093 cm^{-1} was preferentially transformed into formate species, as the result obtained over MgO (*20*).

At 573 K (from Figs. 4d to 5e) bands at 1093 and 1041 cm^{-1} immediately disappeared and bands due to formate species were apparently reduced. Meanwhile the features near 3630 cm^{-1} from isolated hydroxyls and bands in the range 1600–1300 cm^{-1} from carbonate species resulted from further oxidation of both methoxy and formate species. With a prolonged evacuation at 573 K, formate species were finally ex-

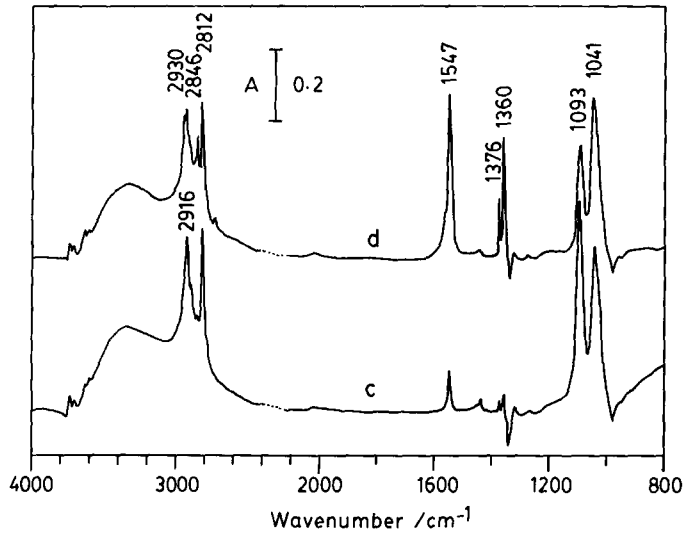


FIG. 4. Continued from Fig. 3. At 473 K *in vacuo* (c) for 2 min, and (f) for 50 min.

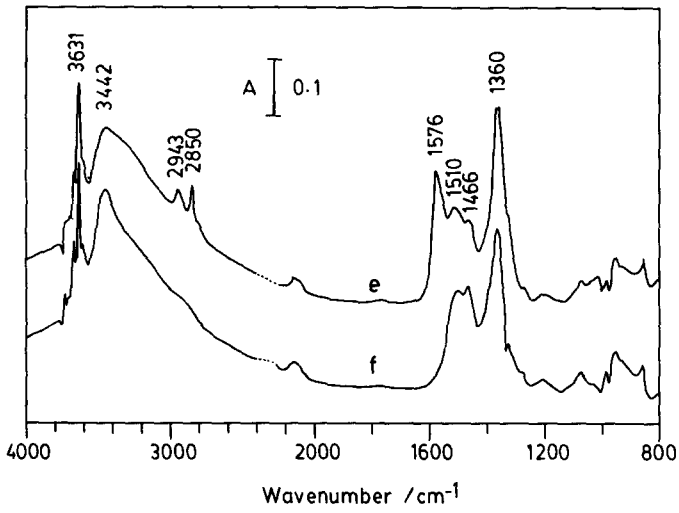


FIG. 5. Continued from Fig. 4. At 573 K *in vacuo* (e) for 1 min, and (d) for 60 min.

hausted in the same way as that presented in Fig. 2.

3. *HCHO Adsorbed on CeO_2 (1000 K)*

Figure 6a illustrates the spectrum of adsorbed HCHO over CeO_2 (1000 K) at 300 K after the evacuation. The distinct bands due to formate species at 2935, 2843, 1595, 1556, 1371, and 1359 cm^{-1} and, in addition, several bands at 1109, 1067, and 916 cm^{-1} were produced. The bands in the region 1200–800 cm^{-1} may be attributed to dioxymethylene or polyoxymethylene species which could be formed during adsorption of HCHO on the surface of the metal and the oxide, particularly at low temperatures (*13, 21*). The assignments of the dioxymethylene or polyoxymethylene species formed on oxides by adsorption of HCHO are often different from those reported in the literature (*10, 21, 22*) since the two species give nearly the same bands below 1200 cm^{-1}. Here three bands produced from the adsorption of HCHO on CeO_2 (1000 K) were tentatively assigned to dioxymethylene adsorbed species.

Heating to 373 K caused a slight weakening of the bands due to dioxymethylene (see Fig. 6b). On standing at 373 K *in vacuo* for half an hour as shown in Fig. 6c, the bands at 1109, 1067, and 916 cm^{-1} were diminished along with a band at 1034 cm^{-1}, probably due to methoxy species as discussed earlier.

It is found that 573 K (Fig. 7) is a critical temperature for decomposition of formate and methoxy species; at this temperature isolated OH groups and carbonate species inevitably resulted.

4. *HCHO Adsorbed on CeO_2 (673-H)*

The adsorption of HCHO was also performed on partially reduced cerium oxide, CeO_2 (673-H) followed by the same procedure as that performed on CeO_2 (1000 K). Figure 8a shows a spectrum of adsorbed species formed from adsorption of HCHO on CeO_2 (673-H) at 300 K, after outgassing. With results roughly analogous to those in Fig. 6a, formate species (bands at 2935, 2832, 1568, 1371, and 1360 cm^{-1}) were also formed. Unlike the results on CeO_2 (1000 K), very intense bands due to dioxymethylene species at 1130, 1076, 964, and 924 cm^{-1} appeared.

Dioxymethylene species were removed upon warming the sample to 373 K, as indicated by the disappearance of their characteristic bands in the region 1200–800 cm^{-1}

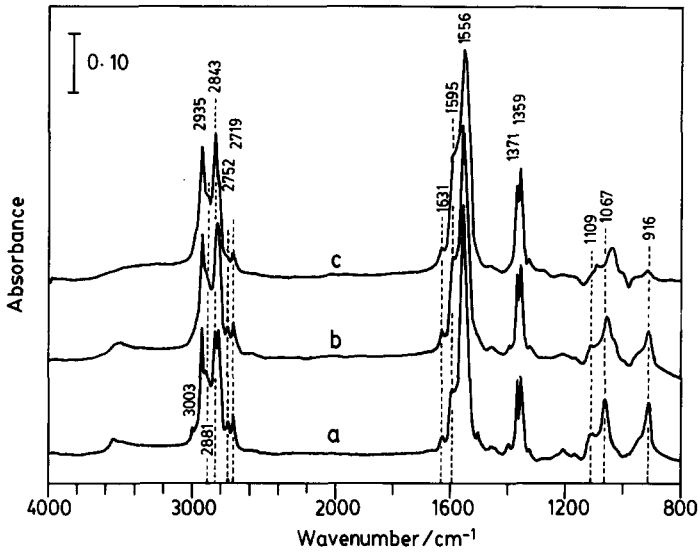


FIG. 6. IR spectra of adsorbed HCHO on CeO_2 (1000 K) (a) after contact with HCHO vapor at 300 K for 5 min, then outgassing for 10 min, at 373 K *in vacuo* (b) for 2 min and (c) for 33 min.

(Fig. 8b). Three new bands at 1620, 1300, and 1028 cm^{-1} appeared. The band at 1028 cm^{-1} is characteristic of adsorbed methoxy species. By comparing the bands at 1620 and 1300 cm^{-1} with the bands at 1599 and 1248 cm^{-1} in Fig. 1a, it can be seen that the two bands from adsorption of HCHO are likely to be due to monodentate formate species.

When the sample was heated to 473 K *in vacuo* the band at 1028 cm^{-1} developed and shifted to a slightly higher frequency, 1034 cm^{-1}, as shown in Fig. 9c. The other bands remained almost unchanged except that the band at 2573 cm^{-1} became much weaker. After treatment for 30 min at 473 K the pair of bands at 1622 and 1296 cm^{-1} was reduced simultaneously (see also Fig. 8b). This again confirmed that the two bands are due to the same species. As shown in Fig. 9c the two bands at 1622 and 1296 cm^{-1} vanish quickly and two weak bands at 2715 and 2573 cm^{-1} disappear at 573 K. Bands due to formate species were also reduced markedly at 573 K while the bands at 2798 and 1034 cm^{-1} were not affected. As shown in Fig. 9f, after a duration of 20 min at 573 K, the band at 1034 cm^{-1} due to methoxy species attenuated. Analogous to their behavior on CeO_2 (1000 K), formate and methoxy species completely decomposed or desorbed at 573 K with the result of generating carbonate and isolated hydroxyls on the surface.

IV. DISCUSSION

1. Two Routes of Dissociative Adsorption of HCOOH

The three different bands at 1599, 1553, and 1542 cm^{-1} due to $(OCO)_{as}$ suggested that at least two kinds of formate species, mono- and bidentate, were generated via adsorption of HCOOH on CeO_2 (1000 K) (see Fig. 1). The following two dissociative routes are proposed to form monodentate and bidentate species,

$$HCOOH + Ce^{4+}O_s^{2-} \rightarrow HCOO_sCe^{4+} + OH^- \quad \text{(dehydroxylation)} \quad (1)$$

$$HCOOH + Ce^{4+}O_s^{2-} \rightarrow HCOO^-Ce^{4+} + O_sH^- \quad \text{(deprotonation)} \quad (2)$$

$$OH^- + O_sH^- \rightarrow H_2O + O_s^{2-}, \quad (3)$$

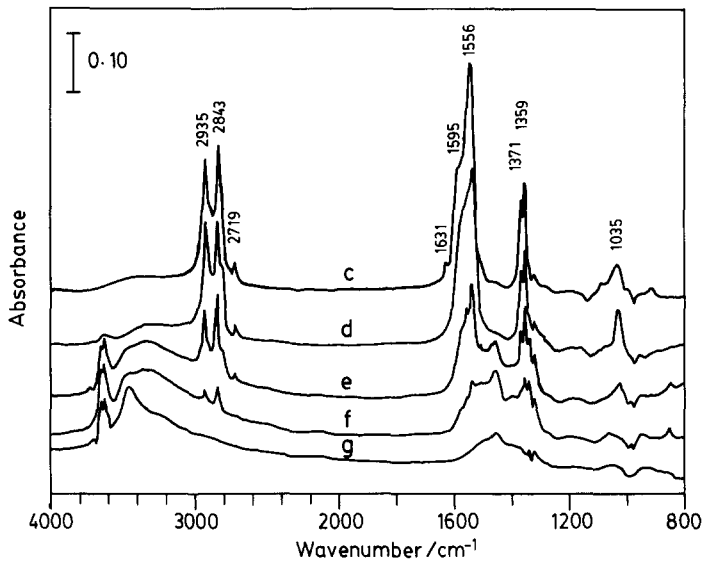


FIG. 7. Continued from Fig. 6. (d) At 473 K *in vacuo* for 10 min; (e) at 573 K *in vacuo* for 2 min and (f) for 15 min; and (g) at 673 K for 2 min.

where O_S indicates oxygen from the surface or the lattice of cerium oxide. As a whole the adsorption of HCOOH on cerium oxide is a dehydroxylation of formic acid. The dehydroxylation produces the formate ion containing a surface oxygen anion. However, the formate species formed by deprotonation of HCOOH most probably coordinate to Ce^{4+} sites in the manner of monodentate, since its proton is simply replaced by a cerium cation.

This explanation is in accordence with our previous results (*9*) where only bidentate formate was derived during the reaction of CO reacted with hydroxyls of cerium oxide, and similar results have been reported for ZrO_2 (*23*), Al_2O_3 (*14*), and MgO (*24*). Obviously, the formate produced from the surface OH and CO is almost the same as that from the dehydroxylation of HCOOH:

$$HCOO_S^-Ce^{4+} \rightarrow CO + HO_S^-Ce^{4+} \quad (4)$$

$$HCOO^-Ce^{4+}O^{2-} \rightarrow \tfrac{1}{2}H_2 + Ce^{4+}\,O_S^{2-}CO_2 \text{ (carbonate)} \quad (5)$$

$$Ce^{4+}O_S^{2-} + \tfrac{1}{2}H_2 \rightarrow Ce^{3+}O_SH^-. \quad (6)$$

2. *Oxidation of Methoxy Species by Surface Oxygen*

Methanol adsorption has been investigated on a number of metals (*19, 20*) and oxides (*12, 25*) with reference to elaborating the mechanism of methanol synthesis of the CO + H_2 reaction. In general, the methoxy species has been substantiated via a deprotonation of methanol,

$$CH_3OH + Ce^{4+}O_S^{2-} \rightarrow CH_3O^-Ce^{4+} + O_SH^- \text{ (deprotonation)}. \quad (7)$$

The three kinds of methoxy species are characterized by different C–O bands (Fig. 3) and may be produced not only by deprotonation but also by dehydroxylation of methanol,

$$CH_3OH + Ce^{4+}O_S^{2-} \rightarrow CH_3O_S^-Ce^{4+} + OH^- \text{ (dehydroxylation)}, \quad (8)$$

because the surface of highly dehydroxylated cerium oxide exhibits many strong Lewis sites where a cleavage of the C–O bond of CH_3OH might be possible.

A separate experiment proved that ce-

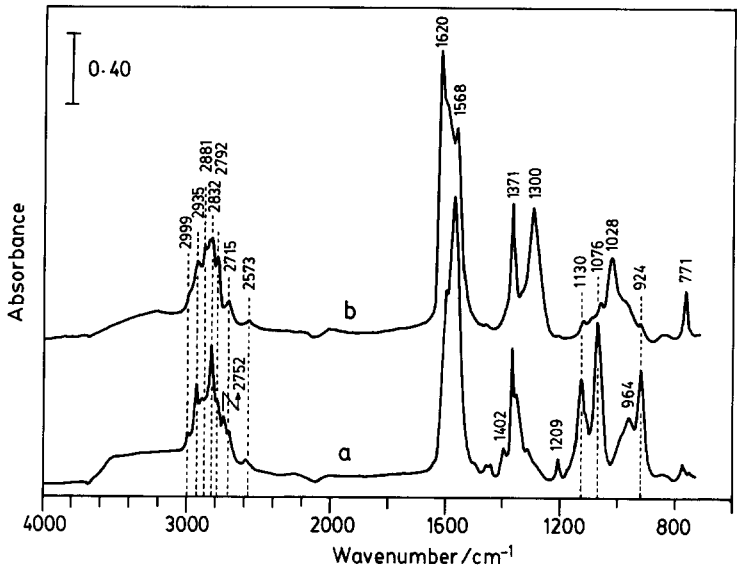


FIG. 8. IR spectra of adsorbed HCHO on CeO_2 (673-H). (a) After contact with HCHO vapor for 15 min at 300 K, then outgassing for 10 min; (b) at 373 K *in vacuo* for 10 min.

rium oxide began to be partially reduced in H_2 at 473 K. The surface oxygen of CeO_2 (1000 K) was active toward oxidation of CO even at room temperature (*16*). The oxidation of methoxy actually causes a partial reduction of the cerium oxide surface. Additional evidence for the participation of surface oxygen could be clarified by the appearance of negative bands near 1340 and 1000 cm^{-1}, which are caused by consumption of surface oxygen. Similar negative bands at 1340 and 1000 cm^{-1} (Fig. 3) were observed when the cerium oxide was reduced by H_2 and these bands would be partly reproduced by oxygen adsorption even at room temperature. Therefore the appearance of these negative bands is indicative of the depeletion of surface Ce–O species. The methoxy species were quickly oxidized into formate (Figs. 4 and 5) at 573 K and the formate species subsequently transferred into carbonate species, similar to that in Fig. 2. Thus, the pathway for oxidation of methanol by surface oxygen is

$$CH_3OH \rightarrow CH_3O \xrightarrow{O_s} HCOO \xrightarrow{O_s} CO_2 \text{ (adsorbed carbonate)}. \quad (9)$$

3. *Surface Cannizzaro Reaction of HCHO*

Figure 6a shows that in addition to minor bands of dioxymethylene species, bands of formate species dominated the spectrum. In contrast to the oxidation of methanol discussed above, we speculate that a part of the formate species is derived from oxidation of HCHO by surface oxygen:

$$HCHO + 2Ce^{4+}O_s^{2-} \rightarrow HCOO_sCe^{3+} + Ce^{3+}O_sH^-. \quad (10)$$

It is interesting that the formate species from oxidation of methoxy did not occur below 473 K, while it was readily formed from oxidation of dioxymethylene even at room temperature. This indicates that on CeO_2 (1000 K) the direct oxidation of dioxymethylene to formate is more facile than the oxidation of methoxy to formate species. If the methoxy is progressively oxidized to formate via a dioxymethylene intermediate, the first step from methoxy to dioxymethylene will be a rate-controlling step. At 373 K, bands due to dioxymethylene species were gradually reduced while weak bands of me-

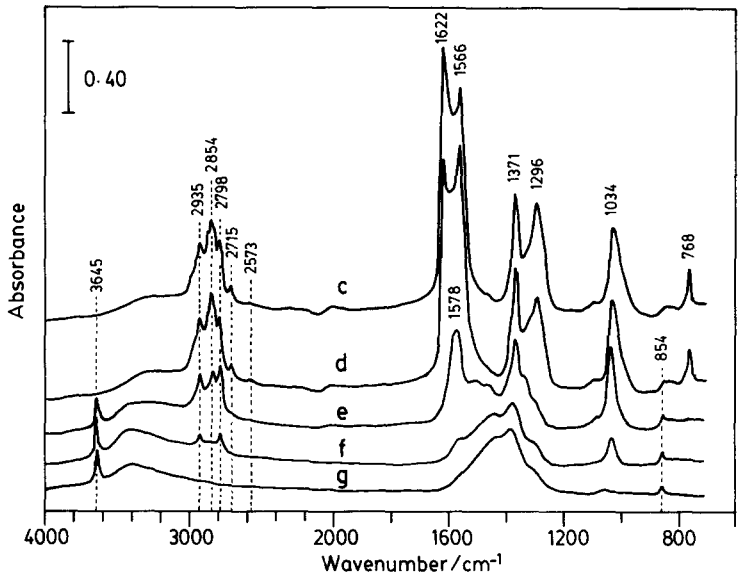


FIG. 9. Continued from Fig. 8. at 473 K *in vacuo* (c) for 2 min and (d) for 15 min; (e) at 573 K *in vacuo* for 2 min and (f) for 20 min; and (g) at 673 K *in vacuo* for 2 min.

thoxy species appeared along with the enlargement of those of formate species (see Figs. 6c and 7d). It seems that formation of methoxy was accompanied by a decrease in dioxymethylene species. This implies that a Cannizzaro reaction occurs (*13*); that is, the methoxy and part of the formate are produced via disproportionation of dioxymethylene:

$$2H_2COO_s^{2-} \rightarrow HCOO^- + CH_3O_s^- + O_s^{2-}. \quad (11)$$

In addition to the oxidation of HCHO by surface oxygen, the contribution of the Cannizzaro reaction to the production of formate species is notable.

Formate species were also produced on CeO_2 (673-H) after exposure to HCHO at room temperature (Fig. 8a).

Meanwhile, much stronger bands of dioxymethylene species were produced on CeO_2 (673-H) than on CeO_2 (1000 K) under the same adsorption conditions. The methoxy species were detected upon warming the sample to 373 K, and it was found that the intensity ratio of the characteristic bands of methoxy/formate is larger over CeO_2 (673-H) than that over CeO_2 (1000 K). Taking into account the fact that the suface active oxygen has been reduced on CeO_2 (673-H), we conclude that the formate species were formed mainly through the Cannizzaro reaction on CeO_2 (673-H) and that the reaction was particularly facilitated at elevated temperatures.

CONCLUSIONS

Based on the above spectroscopic results and discussion, the following conclusions can be made about surface reactions during adsorption and decomposition of HCOOH, CH_3OH, and HCHO on cerium oxide:

(1) Surface species, including formate, methoxy, and dioxymethylene, can be identified by their characteristic IR bands.

(2) Deprotonation and dehydroxylation of HCOOH are proposed to be responsible for the formation of monodentate and bidentate formate species, respectively, and two routes are also possible for the formation of different methoxy species from CH_3OH on cerium oxide.

(3) CH_3OH and HCHO can be oxidized into formate species by surface oxygen of CeO_2 (1000 K) at 473 and 300 K, respectively.

(4) The existence of a Cannizzaro reaction of HCHO was confirmed on cerium oxide and was more favorable on partially reduced cerium oxide.

(5) Formate species, irrespective of their origin, decompose above 573 K as a result of leaving carbonate and isolated OH groups on the surface of cerium oxide.

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