

Reactant-Promoted Reaction Mechanism for Water–Gas Shift Reaction on ZnO, as the Genesis of Surface Catalysis

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The behavior of reaction intermediates in the catalytic water–gas shift reaction (WGSR) on ZnO surfaces has been studied by means of FT–IR spectroscopy, and a reactant-promoted mechanism including intermediate–reactant interaction is proposed. On-top (terminal) hydroxyl groups on Zn ions which are formed by the first-adsorbed water molecules react with CO to produce bidentate and bridge formates. Seventy percent of them were decomposed to original CO and surface hydroxyls and only 30% of them were converted to H₂ and CO₂ (adsorbed) under vacuum. On the contrary, 100% of the formates were converted to the WGSR products, H₂, and CO₂ in coexistence with second-adsorbed water molecules. The rate of the formate decomposition was promoted by a factor of more than 10 by the presence of a second water molecule. The activation energy of the decomposition of the surface formates decreases in the presence of water; 155 kJ mol⁻¹ under vacuum and 109 kJ mol⁻¹ with ambient water. The rate-determining step of the decomposition is the scission of the C–H bond of the formates according to isotope effects. In the absence of ambient water vapor, adsorbed CO₂ species exist as unidentate carbonate and carboxylate on ZnO surface. At room temperature most of CO₂ (ad) exist as carboxylate, and the population of unidentate carbonate increases with an increase in temperature. When the second water molecule coexists on the surface, carboxylate converts into unidentate carbonate. The surface carbonate and carboxylate were thermally stable even at 680 K by themselves, whereas they begin to desorb at room temperature in the coexistence of the adsorbed water. Steady-state rate of catalytic WGSR agree with the decomposition rates of the bidentate formate and the unidentate carbonate; the two decomposition rates are balancing during the steady-state WGSR on ZnO. Water molecules not only act as a reactant to form the formate, but also activate the bidentate formate(ad) to decompose to H₂ and unidentate carbonate(ad) and promote the desorption of the carbonate as CO₂. © 1991 Academic Press, Inc.

INTRODUCTION

Under catalytic reaction conditions, reaction intermediates coexist with other adsorbates on catalyst surfaces, and the intermediates are thought to be influenced by the coadsorbed species. In several systems, the activation of the intermediate by coadsorbate is suggested (1–3). Nishimura *et al.* showed (1) that ethanol that coordinates on Nb monomer attached on SiO₂ is too stable and does not decompose to acetaldehyde by itself. The coordination of the second ethanol molecule on the Nb site is necessary to proceed the catalytic dehydrogenation (self-assisted reaction mechanism). Yamashita *et al.* observed (3) that

the IR peaks of surface formates on Cr₂O₃ shifted by the presence of methanol and they suggested an associate effect that may be important for catalytic methanol decomposition. Thus, it may be of great interest to clarify the activation of reaction intermediates by coadsorbates in order to understand essential factors for the genesis of solid catalysis. In a previous paper, we reported that the activation of surface formates by coadsorbed water is necessary to catalytically proceed water–gas shift reaction (WGSR; CO + H₂O → CO₂ + H₂) on MgO (4).

The WGSR system has advantages for studying the behavior of reaction intermediates as follows: (1) As the local structures

of the surface OH groups are estimated by the frequency of OH stretching vibrations ($\nu(\text{OH})$), we can estimate the structures of sites on which the formate intermediates exist (2). The structure of the formate can be determined by comparing the value of $\Delta\nu = \nu_{\text{as}}(\text{OCO}) - \nu_{\text{s}}(\text{OCO})$ with those of known metal complexes (5). Thus the surface formates which have been demonstrated to the intermediates of WGSR (6, 7), methanol decomposition (3), and formic acid decomposition (8) can be well characterized, at least in the absence of coadsorbates. In the present study, we have extended the reactant-promoted reaction phenomenon observed with MgO surface to other oxides which are active for WGSR. Zinc oxide is known to catalyze methanol decomposition (3), formic acid decomposition (8), and WGSR (6, 7). As surface hydroxyl groups on ZnO react with CO to form surface formates (9), we can investigate the behavior of the formates in the absence and presence of coadsorbates and the role of the intermediate-coadsorbate interaction in the genesis of the ZnO catalysis for WGSR.

EXPERIMENTAL

Zinc oxide powder used in this work was Kadox-15 from New Jersey Zinc Co. Its surface area was calculated to be $30 \text{ m}^2 \text{ g}^{-1}$ by BET measurements for N_2 adsorption. CO (99.99%), D_2 (99.99%), and D_2O (99%) were further purified by repeated freeze-pump-thaw cycles.

ZnO (ca. 25 mg) was pressed at a pressure of 150 kg cm^{-2} into a self-supporting disk of $20 \text{ mm}\phi$ in diameter and ca. 0.1 mm in thickness. The ZnO disk was placed in an IR cell which was combined with a closed circulation system. The ZnO disk was oxidized with O_2 at 773 K for 3 h and evacuated at the same temperature for 1 h. Then H_2O vapor was introduced into the system at 473 K, followed by evacuation at 673 K for 1 h. To replace surface OH groups by OD groups, D_2O was employed instead of H_2O . In this paper, ZnO(H) represents ZnO whose surface hydroxyl groups are OH, and ZnO(D) stands for ZnO having OD.

IR spectra were recorded on a JEOL JIR-10 Fourier-transform infrared spectrometer with a double beam using a liquid nitrogen-cooled MCT detector. The measurements were performed at room temperature (Figs. 1-4) or at reaction temperatures (Figs. 5 and 7) and in 60 or 256 scans at a 2 cm^{-1} or 4 cm^{-1} resolution.

TPD and kinetic studies were performed in a closed circulating system. Desorption species or reaction products were analyzed by MS spectrometry (ULVAC MSQ-150A) and/or gas chromatography (SIMADZU GC-8A).

RESULTS

1. Surface Species Observed by IR

Figure 1 shows the change of IR spectra by exposing ZnO(H) to $\text{CO}(P_{\text{CO}} = 1.33 \times 10^3 \text{ Pa})$ at various temperatures for 30 min, followed by evacuation for 3 min. IR spectra were measured at 303 K. The background absorption is subtracted in each spectrum. When CO was introduced at 323 K, weak bands appeared at 1610, 1580 ($\nu_{\text{as}}(\text{OCO})$ region) and 1360 cm^{-1} ($\nu_{\text{s}}(\text{OCO})$ region) and these bands grew at 373 K. When CO was introduced at 423 K, the peak at 2876 and 2972 cm^{-1} ($\nu(\text{CH})$ region) appeared and the band at 1610 cm^{-1} disappeared. In $\nu_{\text{as}}(\text{OCO})$ region, the peak at 1575 and 1371 cm^{-1} developed by introduction of CO at 473 K. At 523 K other peaks appeared at 1507 and 1467 cm^{-1} in $\nu_{\text{as}}(\text{OCO})$ region, and 1339 and 1404 cm^{-1} in $\nu_{\text{s}}(\text{OCO})$ region. When CO was introduced to ZnO(D), the peaks at 2180, 2170, 1577, 1568, 1342, and 1336 cm^{-1} were observed instead of the bands at 2972, 2875, 1581, 1572, 1371, and 1363 cm^{-1} , respectively. On the contrary, the bands at 1507, 1467, 1339, and 1404 cm^{-1} did not shift by the change from OH to OD.

Figure 2 shows the change of IR spectra by evacuation at various temperatures after introduction of $1.33 \times 10^3 \text{ Pa}$ of CO to ZnO(H) at 453 K. The bands at 2875, 1572, 1371, and 1383 cm^{-1} which are attributed to $\nu(\text{CH})$, $\nu_{\text{as}}(\text{OCO})$, $\nu_{\text{s}}(\text{OCO})$, and $\delta(\text{CH})$ begin to decrease at 550 K, accompanied by an

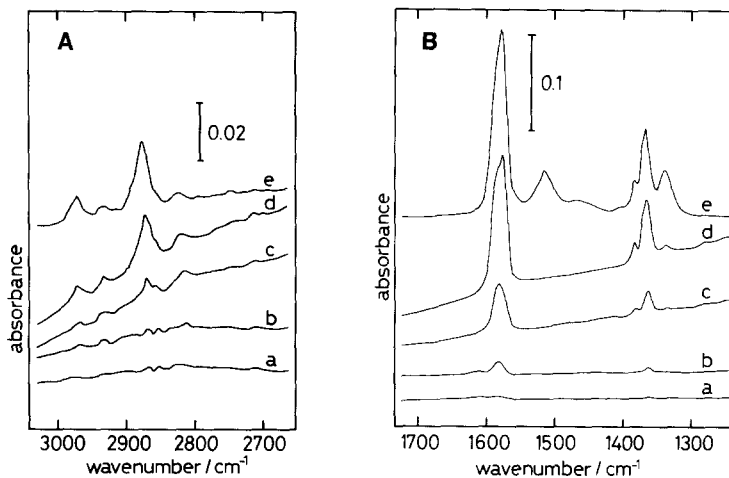


FIG. 1. IR spectra of surface formates and carbonates on ZnO in $\nu(\text{CH})$ (A) and $\nu(\text{OCO})$ (B) region. The sample was evacuated at 673 K, followed by exposure to CO ($P_{\text{CO}} = 1.33 \times 10^3$ Pa) for 30 min at (a) 323 K, (b) 373 K, (c) 423 K, (d) 473 K, and (e) 523 K.

increase of the bands at 1507, 1467, 1404, and 1339 cm^{-1} .

The bands at 2875(2972), 1572(1581), and 1371(1363) cm^{-1} are ascribed to the same surface species because they always behave in a similar way. As hydrogen isotope shifts were observed with these bands, this species must contain hydrogen. Since a relatively low frequency of $\nu(\text{CH})$ like 2825 cm^{-1} suggests that the species possesses a CH moiety (not CH_2 or CH_3), the bands at

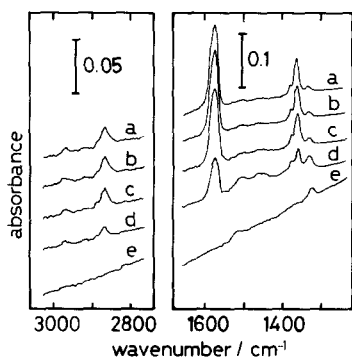


FIG. 2. IR spectra of surface formate and carbonates on ZnO. The sample was evacuated at 673 K, followed by exposure to CO ($P_{\text{CO}} = 1.33 \times 10^3$ Pa) at 473 K for 30 min. After that, the sample was evacuated for 30 min at (a) 453 K, (b) 493 K, (c) 523 K, (d) 553 K, and (e) 593 K.

1572–1581 cm^{-1} and 1371–1363 cm^{-1} may be assigned to $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ for surface formates as discussed hereinafter. As the absorption bands at 1507, 1467, 1404, 1339 cm^{-1} do not shift by hydrogen isotope substitution, these bands are attributed to surface species that contain no hydrogen. The IR peaks at 1507 and 1339 cm^{-1} behaved in a similar way to the bands at 1467 and 1404 cm^{-1} (see also Figs. 6 and Fig. 7). These peaks ($\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$) formed by CO adsorption on ZnO can be attributed to two kinds of adsorbed CO_2 species ($\text{CO}_2(\text{ad})$). The process of CO_2 adsorption is reviewed by Little (10) and IR spectra of CO_2 -containing metal clusters have been reported (11, 12). The frequencies of $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ for unidentate carbonate, bidentate carbonate, and carboxylate are 1480 and 1370 cm^{-1} , 1600 and 1280 cm^{-1} , and 1500–1550 and 1330 cm^{-1} , respectively. Comparing the frequencies for $\text{CO}_2(\text{ad})$ on ZnO with these values, $\text{CO}_2(\text{ad})$ is suggested to exist as a unidentate carbonate and carboxylate: Table 1 lists the IR absorption bands of adsorbed species on ZnO.

Figure 3 shows IR spectra of OD groups. The bands observed at 2715, 2706, 2682, and 2669 cm^{-1} are attributable to terminal OD

TABLE I
Absorption Bands of Adsorbate on ZnO Surface

Adsorbate	$\nu(\text{CH})$ cm^{-1}	$\delta(\text{CH})$ cm^{-1}	$\nu_{\text{as}}(\text{OCO})$ cm^{-1}	$\nu_{\text{s}}(\text{OCO})$ cm^{-1}
Bidentate formate ^{a,b}	2875(2170)	1383	1572(1568)	1371(1342)
Bridge formate ^{a,b}	2972(2180)	1383	1581(1577)	1363(1336)
Unidentate carbonate ^b			1460	1370
Carboxylate ^b			1508	1334

^a Wavenumber for H-formate (D-formate).

^b The assignment is described in Discussion.

groups on three-coordinated zinc ions, terminal OD groups on two-coordinated zinc ions, bridge OD groups involving two-coordinated O ions, and hollow-site OD groups involving three-coordinated O ions, respectively. In a later section we discuss the validity of the assignments. By introducing 1.33×10^3 Pa of CO at 473 K, the peak at 2706 cm^{-1} decreased. When the sample was evacuated at 573 K, the intensity of the bands at 2682 cm^{-1} and 2669 cm^{-1} de-

creased. Further change did not occur upon evacuation at 673 K.

Figure 4 shows IR spectra of formates in the presence of water vapor. The peaks for $\nu(\text{CH})$, $\nu_{\text{as}}(\text{OCO})$, and $\nu_{\text{s}}(\text{OCO})$ shifted from 2875, 1572, 1371 cm^{-1} to 2848, 1605, 1320 cm^{-1} , respectively, by the addition of H_2O vapor (4.0×10^2 Pa). The value of $\Delta\nu$ ($\nu_{\text{as}}(\text{OCO}) - \nu_{\text{s}}(\text{OCO})$) became 280 cm^{-1} which is characterized as a unidentate formate (4, 5). When water was evacuated, IR bands returned to the previous positions. The peak positions of the surface formate in the presence of various adsorbed molecules are shown in Table 2. The conversion of bidentate to unidentate formate was ob-

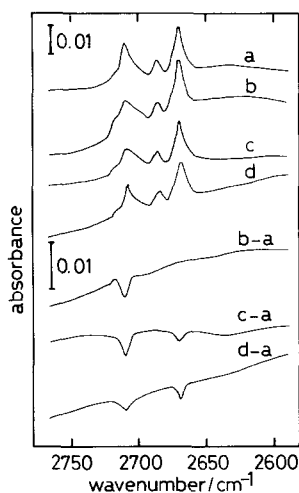


FIG. 3. $\nu(\text{OD})$ stretching bands of OD groups on ZnO(D); (a) after evacuation at 673 K; (b) after exposing sample (a) to CO at 473 K ($P_{\text{CO}} = 1.33 \times 10^3$ Pa); (c) after evacuating sample (b) at 573 K, (d) after evacuating sample (c) at 673 K.

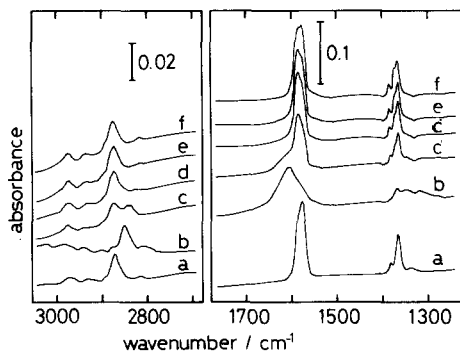


FIG. 4. IR spectra of surface formates on ZnO. (a) CO exposure at 453 K ($P_{\text{CO}} = 1.33 \times 10^3$ Pa); (b) exposure of sample (a) to H_2O at 303 K ($P_{\text{H}_2\text{O}} = 4.0 \times 10^2$ Pa); after (b), the sample was evacuated at (c) 303 K, (d) 373 K, (e) 423 K, and (f) 473 K.

TABLE 2
IR Bands and Decomposition Rate Constants of Bidentate Formate in the Presence of Electron-Donating Molecules^{a,b}

Molecules	$\nu(\text{CD})$ cm^{-1}	$\nu_{\text{as}}(\text{OCO})$ cm^{-1}	$\nu_{\text{s}}(\text{OCO})$ cm^{-1}	$k_{-}/10^{-4} \text{ s}^{-1}$
None	2170	1568	1336	0.34
Water	2156	1591	1336	5.3
Ammonia	2130	1593	1334	28.0
Methanol	2160	1577	1336	7.7
Pyridine	2146	1577	1336	8.1
THF	2154	1579	1336	6.0

^a The decomposition rate constants were measured at 553 K.

^b IR spectra were measured at 303 K.

served when water or ammonia were admitted, but it was not clearly observed in the case of pyridine, tetrahydrofuran (THF), and methanol.

Figure 5 shows the spectral change of surface formate (DCOO) upon exposure to am-

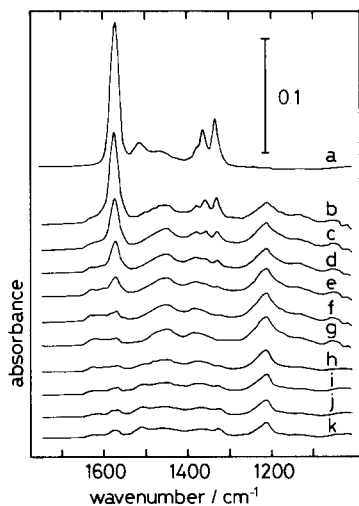


FIG. 5. IR spectra of surface formates (DCOO) on ZnO. (a) CO exposure at 503 K ($P_{\text{CO}} = 1.33 \times 10^3$ Pa), followed by evacuation at the same temperature; after (a), the sample was exposed to NH_3 ($P_{\text{NH}_3} = 4.0 \times 10^2$ Pa) at 503 K for (b) 3 min, (c) 11 min, (d) 20 min, (e) 30 min, (f) 45 min, and (g) 60 min; after (g), the sample was evacuated at 503 K for (h) 3 min, (i) 11 min, (j) 20 min, and (k) 30 min.

monia at 503 K. When ammonia was introduced, the $\nu_{\text{as}}(\text{OCO})$ band attributed to unidentate formate appeared at 1625 cm^{-1} . When ammonia was evacuated, the band of unidentate formate shifted back to 1568 cm^{-1} . While the main bands $\nu_{\text{as}}(\text{OCO})$, $\nu_{\text{s}}(\text{OCO})$ decreased with an increase in exposure time, the bands of unidentate formate maintained their intensity.

Figure 6 shows IR spectra of $\text{CO}_2(\text{ad})$ pro-

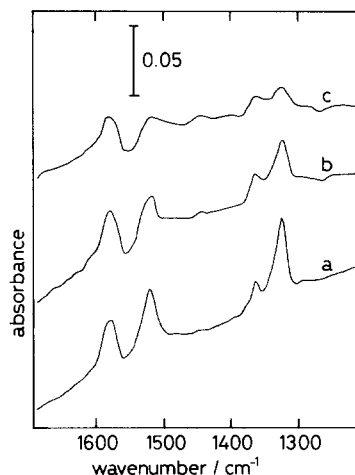


FIG. 6. IR spectra of surface carbonates on ZnO. The sample was exposed to CO at 573 K ($P_{\text{CO}} = 1.33 \times 10^3$ Pa), followed by evacuation. IR spectra were measured at (a) 303 K, (b) 423 K, and (c) 553 K.

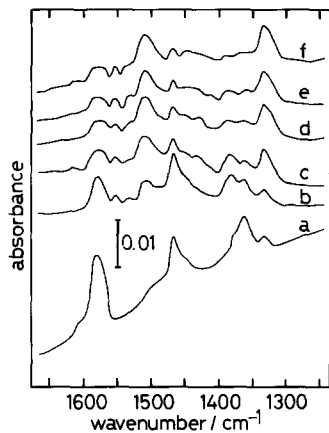


FIG. 7. IR spectra of surface carbonates species on ZnO. The sample was evacuated at 673 K followed by exposure to CO at 573 K ($P_{\text{CO}} = 1.33 \times 10^3$ Pa). After evacuation, the sample was further exposed to H_2O ($P_{\text{H}_2\text{O}} = 4.0 \times 10^2$ Pa) at 553 K for (a) 3 min, and (b) 10 min; after (b) the sample was evacuated at 553 K for (c) 2.5 min, (d) 10 min, (e) 20 min, and (f) 30 min.

duced by the decomposition of surface formate. The spectra were measured at (a) 303 K, (b) 423 K, and (c) 553 K. At 303 K, the peaks at 1510 and 1333 cm^{-1} for carboxylate are strong and bands at 1460 and 1400 cm^{-1} for unidentate carbonate are very weak. At 553 K, the peaks at 1460 and 1400 cm^{-1} developed, while the peaks at 1510 and 1333 cm^{-1} reduced. Thus, at room temperature most of the $\text{CO}_2(\text{ad})$ is in the carboxylate form and the proportion of carbonate increases as the temperature increases.

Figure 7 shows the change of the IR spectra of $\text{CO}_2(\text{ad})$ upon exposure to water vapor. The bands at 1460 and 1370 cm^{-1} are observed in the presence of water. When water was evacuated, the intensity of these bands decreased and the bands at 1510 and 1333 cm^{-1} developed. Hence, $\text{CO}_2(\text{ad})$ exists as unidentate carbonate in the presence of water, whereas carboxylate becomes preferable in the absence of water.

Adsorbed CO_2 yielded spectra similar to those for $\text{CO}_2(\text{ad})$ produced by the decomposition of surface formates: Unidentate carbonate and carboxylate were observed. Carboxylate was more stable than uniden-

tate carbonate and the proportion in unidentate carbonate increased with an increase of temperature. The conversion of carboxylate into unidentate carbonate was also observed when water was introduced.

2. TPD Spectra

TPD spectra of the surface formates formed by the reaction between surface OD of ZnO and CO at 493 K were taken at a heating rate of 3 K min^{-1} in Fig. 8. Desorption peaks for CO and D_2 appeared at 550 K. The ratio of CO to D_2 was about 7 : 3. The desorption of CO_2 gave no definite peak, showing a gradual increase with temperature. The amounts of CO_2 and H_2 were almost the same.

Figure 9 shows TPD spectra of the surface formates coadsorbed with water. Water vapor was introduced at 303 K. Desorption of D_2 and CO was observed at 550 K, and that of CO_2 and water appeared at 660 and 720 K, respectively. In contrast to the case of the absence of water, the amount of desorbed CO was very small, where the equal amount of D_2 and CO_2 were preferentially formed.

TPD spectra of HCOO and $\text{HCOO} + \text{H}_2\text{O}$ were almost the same as those of DCOO and $\text{DCOO} + \text{D}_2\text{O}$, respectively.

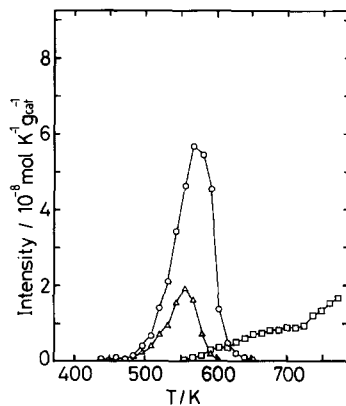


FIG. 8. TPD spectra of surface formates (DCOO) produced by CO and surface OD on ZnO preevacuated at 673 K; (O) CO, (□) CO_2 , (Δ) D_2 .

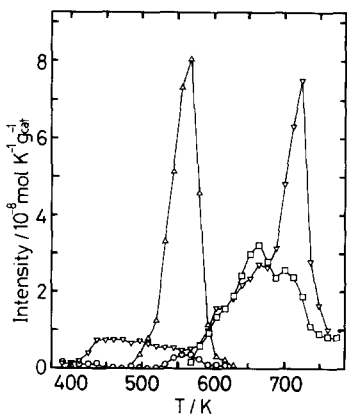


FIG. 9. TPD spectra of surface formate (DCOO) and D_2O coadsorbed on ZnO; (○) CO, (□) CO_2 , (△) D_2 , (▽) D_2O .

3. Kinetic Studies

Figure 10 shows Arrhenius plots for the decomposition of surface formates. The marks ○ and □ were the rates calculated from the decrease of the IR peak intensity for $\nu_{as}(OCO)$ of DCOO, and the plots ●, ■, and ▲ were the rates obtained from the amount of desorbed D_2 and CO.

k_+ represents the rate constant of the forward decomposition of formate ($HCOO \rightarrow H_2 + CO_2(ad)$) and k_- stands for the rate constant of the backward decomposition of formate ($HCOO \rightarrow -OH + CO$). The forward decomposition rate was enhanced by the presence of water. The activation energy for k_+ decreased from 155 to 109 $kJ\ mol^{-1}$. The backward rate was suppressed to almost zero in the presence of water.

The rate constants for forward decomposition (k_+) of DCOO as a function of adsorbed amount of water are plotted in Fig. 11. The value, in Fig. 11, of k_+ linearly increased with an increase of the adsorbed amount of water.

The forward decomposition rates of DCOO in the presence of donor molecules such as water, methanol, ammonia, pyridine, and THF are listed in Table 2. All the donor molecules promoted the forward decomposition irrespectively of whether

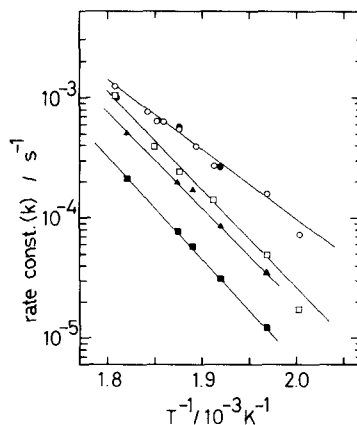


FIG. 10. Arrhenius plots for the decomposition of DCOO. (□) $k_+ + k_-$ under vacuum, (○) $k_+ + k_-$ in the presence of 4.0×10^2 Pa of water, (■) k_+ under vacuum, (▲) k_- under vacuum, (●) k_+ in the presence of 4.0×10^2 Pa of water, k_+ represents the rate constant for the forward decomposition ($DCOO + (D) \rightarrow D_2 + CO_2(ad)$) and k_- represents the rate constant for the backward decomposition ($DCOO \rightarrow CO + OD$). $k_+ + k_-$ were calculated from the decrease of IR peak intensity, and k_+ and k_- were calculated from the formation of D_2 and CO, respectively.

they can convert bidentate formate into unidentate formate or not. It is suggested that the decomposition was more promoted by introduced gases with stronger donating ability.

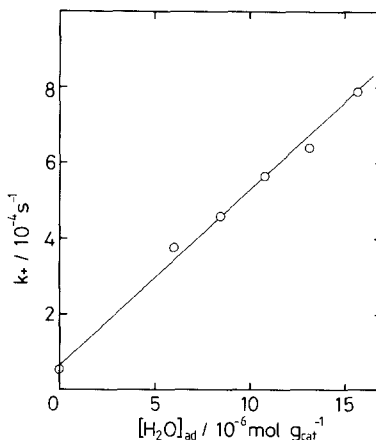


FIG. 11. Rate constants (k_+) for the forward decomposition of formates as a function of the adsorbed amount of water at 533 K.

TABLE 3

Rate Constants for the Formation of Hydrogen or Carbon Dioxide (k_+) in Various Combinations of Labeled Water and Formate^a

Combination	$k_+/10^{-4} \text{ s}^{-1}$
HCOO ⁻ + H ₂ O	7.9
HCOO ⁻ + D ₂ O	7.0
DCOO ⁻ + H ₂ O	5.4
DCOO ⁻ + D ₂ O	5.3
Carbonate + H ₂ O	1.0
Carbonate + D ₂ O	1.0

^a The decomposition rate constants were measured at 530 K in the pressure of water of 400 Pa.

Table 3 shows the rate constants for the forward decomposition of surface formate (k_+) in various combinations of labeled water and formate, and the desorption rate constant for the decomposition of unidentate carbonate in the presence of H₂O or D₂O. The reaction rates for HCOO + H₂O and HCOO + D₂O are $(7.5 \pm 0.5) \times 10^{-4} \text{ s}^{-1}$, while those for DCOO + H₂O and DCOO + D₂O are ca. $5.3 \times 10^{-4} \text{ s}^{-1}$. An isotope effect of (D/H = 0.7) was observed with the hydrogen of formate. No hydrogen effect was observed upon the decomposition of unidentate carbonate.

The steady-state reaction rates for catalytic WGS, the amount (M) and decomposition rate constants (k) of surface formates and unidentate carbonates under various conditions are listed in Table 4. The rate of hydrogen formation in the decomposition of formates is given by the product of the amount and decomposition rate ($M_f \times k_f$), and that of CO₂ formation by the decomposition of carbonates is given by $M_c \times k_c$. It was found that the steady-state reaction rates were almost the same as the rates of two elementary reaction steps.

DISCUSSION

1. Active Hydroxyl Groups for the Formation of Surface Formate

The local structure of surface hydroxyl groups on ZnO has been investigated by

means of IR spectroscopy (13–16). In general, the frequency of $\nu(\text{OD})$ decreases as the coordination number of the oxygen increases, and as for on-top (terminal) OD groups, the frequency of $\nu(\text{OD})$ increases with an increase of the coordination number of the bottom-metal (Zn) ions (17, 18). Hence, taking into account the crystal structure of ZnO, the absorption bands at 2715, 2706, 2682, and 2669 cm^{-1} are attributable to on-top OD groups on three-coordinated Zn ions, on-top OD groups on two-coordinated Zn ions, bridge OD groups and three-fold OD groups, respectively.

In Fig. 3 the peak at 2706 cm^{-1} decreased when CO was introduced at 473 K and at the same time surface formates were produced, suggesting that OD groups on two-coordinated Zn ions react with CO to produce surface formates. When the sample with the formates was evacuated at 573 K at which temperature the formates are decomposed, the bands at 2682 and 2669 cm^{-1} decreased as shown in Fig. 3. This implies that the deuterium atoms of bridge and threefold hollow OD groups desorbed to form deuterium molecules by combining with the D atoms of formate (DCOO) ions as shown in Fig. 8.

2. Surface Formate Produced from Surface OH and CO

The structure of formates on ZnO can be estimated by the value of $\Delta\nu = \nu_{\text{as}}(\text{OCO}) - \nu_{\text{s}}(\text{OCO})$. When $\Delta\nu$ is larger than free formate ion (ca. 230 cm^{-1}), the surface formate is assigned to be unidentate: When $\Delta\nu$ is smaller than the free ion, the surface formate is referred to as bidentate, and when $\Delta\nu$ is as large as that of the free ion, the surface formate is assigned as bridge formate (5). The values of $\Delta\nu$ for the formates on ZnO surface were 204 and 222 cm^{-1} . Thus, the formate whose bands for $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ were observed at 1572 and 1371 cm^{-1} , respectively, is of bidentate type, and the bands at 1581 and 1363 cm^{-1} are attributed to bridge or bidentate formate. We cannot decide the type of latter formate because $\Delta\nu$ of bridge and bidentate formate overlaps at ca. 220 cm^{-1} (4), but the C–H stretching

TABLE 4

 Comparison of the Calculated Reaction Rates for Each Step and the Observed Steady-State Rates for Water Gas Shift Reaction^a

Reactant	<i>T</i> /K	<i>M</i> _f ^b	<i>M</i> _c ^b	<i>k</i> _f ^c	<i>k</i> _c ^c	<i>k</i> _f × <i>M</i> _f ^d (H ₂)	<i>k</i> _c × <i>M</i> _c ^d (CO ₂)	Reaction rate ^d
H ₂ O + CO	543	0.4	2.6	12.9	2.0	5.2	5.2	5.3
H ₂ O + CO	558	0.25	1.8	26.6	3.8	6.7	6.8	6.7
D ₂ O + CO	543	0.5	2.0	7.6	2.0	3.8	4.0	4.0
D ₂ O + CO	558	0.33	1.3	15.3	3.8	5.0	4.9	5.0

^a *P*_{H₂O} or *P*_{D₂O} = 4.0 × 10² Pa, *P*_{CO} = 6.7 × 10² Pa.

^b *M*_f^b and *M*_c^b represent the adsorbed amounts of bidentate formate and unidentate carbonate, respectively, under reaction conditions in 10⁻⁶ mol g_{cat}⁻¹.

^c *k*_f and *k*_c represent the forward decomposition rate constants of bidentate formate and the desorption rate of unidentate carbonate, respectively, under reaction conditions in 10⁻⁴ s⁻¹.

^d In 10⁻¹⁰ mol s⁻¹ g_{cat}⁻¹.

frequency $\nu(\text{CH})$ has a large difference between the two cases as shown in Table 1. The big difference indicates the different type of surface formates. Thus, the formate which shows peaks at 1581 and 1363 cm⁻¹ may be assigned to bridge-type formate. As described above active hydroxyl groups were on top OH on Zn₂C, where 2C represents two coordination, showing a coordinatively unsaturated sphere around Zn₂C. The fact that the bidentate formate is of a majority type is compatible with the structural demand.

When water and ammonia were admitted to surface formates at room temperature, the IR bands for bidentate formate shifted from 2170, 1568, 1336 cm⁻¹ to 2156–2130, 1591–1593, and 1334–1336 cm⁻¹, respectively, as shown in Table 2. The bandwidth of $\nu(\text{CD})$, $\nu_{\text{as}}(\text{OCO})$, $\nu_{\text{s}}(\text{OCO})$ became larger by introducing water and the value of $\Delta\nu$ also increased from 235 cm⁻¹ to 255 cm⁻¹ in Fig. 4. Similar change has been observed with Zn(HCOO)₂ when Zn(HCOO)₂ was exposed to ammonia (19), where Zn(HCOO)₂(NH₃)₂ is formed, and at the same time the structure of the formate changes from bidentate to unidentate. Thus, the present change in $\Delta\nu$ on ZnO is suggested to be due to the structural change of bidentate formate to unidentate formate by the adsorption of H₂O or NH₃. This kind of

conversion does not occur by the adsorption of methanol, THF, and pyridine. Hence, to convert from bidentate into unidentate, two hydrogen bondings may be required. The shift of IR peaks for the bridge formate by water adsorption was much smaller than that for the bidentate formate. When adsorbed water was evacuated, the peaks returned to the previous positions more rapidly as compared with the case of the bidentate formate. Hence, the interaction between bridge formate and adsorbed water may be weaker than that between bidentate formate and adsorbed water.

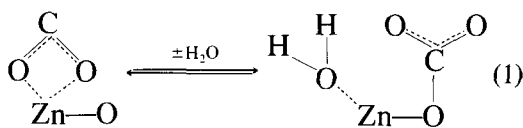
When CO was allowed to interact with ZnO(H) at 323 and 373 K, a weak band at 1610 cm⁻¹ was observed, but this band disappeared at 423 K as shown in Fig. 1. The frequency of this band is the same as $\nu_{\text{as}}(\text{OCO})$ of unidentate formate. Thus, the unidentate formate is formed preferably at lower temperatures. At higher temperatures it is unstable and converted to bidentate or bridge formates. The process of formation of formate on ZnO is quite similar to that on MgO (4).

3. Adsorbed CO₂ Species

As mentioned above, unidentate carbonate and carboxylate are present in equilibrium. At 303 K, the carboxylate is a dominant species and the proportion of

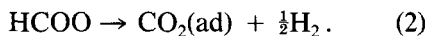
unidentate carbonate increases with temperature. Thus carboxylate is more stable than unidentate carbonate under vacuum. Assuming a canonical distribution the difference of the heat of adsorption between these is calculated to be ca. 3 kJ mol^{-1} from Fig. 6.

The carboxylate was also converted to the unidentate carbonate by addition of water vapor as shown in Fig. 7. This change was also observed when electron donors such as pyridine, THF, and ammonia were introduced to the carboxylate surface. Thus the driving force of the transformation is likely to be an electron donation to the Zn ions on which the carboxylate adsorbs



4. Decomposition of Formate and CO_2 (ad)

Surface formates produced by OH and CO decompose by the following steps; one is backward decomposition to surface OH and CO and the other is forward decomposition to H_2 and carbonate or carboxylate. As the amount of H_2 and CO_2 was the same, the unimolecular-type decomposition shown by Eq. (2) is believed to be unimportant.



Further, the intensities of 2685 and 2668 cm^{-1} , which are attributed to bridge OD and three-fold hollow-site OD, decreased when the formate decomposes, as shown in Fig. 3. These results indicate that H_2 was produced by the reaction of the formate with the hydroxyl groups on the bridge (minor) and hollow (major) sites.

As shown in Fig. 10 the forward rate of the formate decomposition increased more than five times by the presence of ambient H_2O , accompanied with the decrease in the activation energy from 155 kJ mol^{-1} to 109 kJ mol^{-1} . This fact demonstrates that water

activates the surface formate to promote the forward decomposition for the formation of $\text{H}_2 + \text{CO}_2(\text{ad})$. Electron donors also increased the decomposition rate as shown in Table 2. The driving force for the forward decomposition of formates is suggested to be electron donation to the Zn ion on which the bidentate formate adsorbs.

The rate of the forward decomposition to produce $\text{H}_2 + \text{CO}_2(\text{ad})$ was found to be proportional to the amount of adsorbed water on ZnO as shown in Fig. 11. This suggests that the adsorbed water enhanced the formate decomposition to produce H_2 . Again, the peak shift for the bidentate formate by water addition suggests a certain interaction between them.

The idea that the promotion of the forward decomposition rate might be observed as a result of the shifts of equilibrium between reactants and products by the introduction of water, is denied by the following facts: First, not only the ratio of the forward decomposition increased but also the rate itself increased. Furthermore, the activation energy decreased. Second, when other electron donors were employed instead of water, the rate of the forward decomposition increased. If the equilibrium balance is a dominant factor, and unless the surface formate is activated, the decomposition rate would not increase and the activation energy should remain the same.

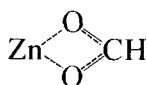
Figure 5 shows IR spectra of the surface formates in the presence of ammonia. The logarithm of the peak intensity for the bidentate formate linearly decreased with reaction time. On the contrary, that for the unidentate formate kept the same intensity. There are two possibilities for explaining this result: one is that the decomposition occurs through the unidentate formate, where the concentration of the unidentate formate can be nearly constant, and the other is that the unidentate formate is stable and does not obey the decomposition. The former possibility is excluded because the unidentate formate showed almost the same intensity even after the bands of the biden-

tate formate vanished. Thus we may conclude that the decomposition of formate proceeds through the bidentate formate.

When water was present instead of ammonia at 503 K, the bands of unidentate formate were not observed, suggesting the preferable formation of the bidentate formate in the presence of adsorbed water. The bidentate formate behaved in a way similar to that in the presence of ammonia. The idea that the surface formates do not decompose through the unidentate formate is also supported by the fact that the degree of promotion of the formate decomposition by electron donors was not correlated with the population of unidentate formate in the presence of the electron donors.

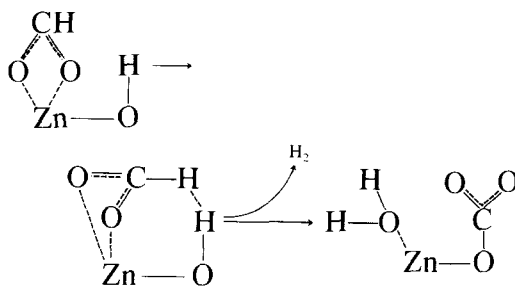
An isotope effect in the decomposition rate was observed with the hydrogen atom of formate as shown in Table 3. Almost no isotope effect was observed with the hydrogen atoms of surface hydroxyls. The decomposition rate of HCOO was 1.4 times larger than that of DCOO (Table 2). Thus the rate-determining step is suggested to be the dissociation of the CH bond of formate.

We cannot decide which unidentate carbonate and carboxylate is a direct product formed by the decomposition of formate, because unidentate carbonate and carboxylate on ZnO are in a fast equilibrium. However, the bidentate formate may decompose to the unidentate carbonate for the following reasons: (1) Electron donors have a direct interaction with the formate



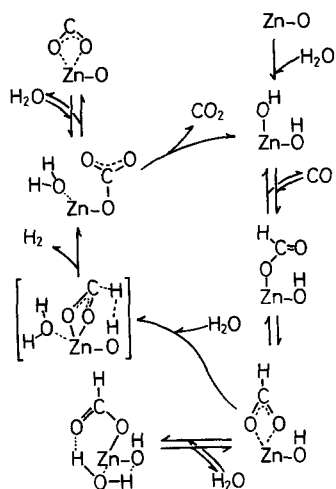
to promote its decomposition to form H_2 and $\text{CO}_2(\text{ad})$, and the same electron donor molecules were observed to convert carboxylate to unidentate carbonate. Hence, in the presence of water or in a steady state, the decomposition of bidentate formate to unidentate carbonate is natural. (2) As already mentioned, H_2 is produced from the H atom of formate and the H atom of the hydroxyl leaving the unsaturated O atom to lead to

the bonding with the C atom of the H-lost formate. Thus the bidentate formate may be decomposed to hydrogen and unidentate carbonate, in the presence of water, as



When undissociative electron donors such as pyridine and THF were admitted to the carboxylate surface, the carboxylate was converted to the unidentate carbonate at room temperature, but no desorption of CO_2 was observed. When a dissociative electron donor such as water was introduced, the carboxylate was converted to the unidentate carbonate and the desorption of CO_2 by the decomposition of the carbonate was enhanced, accompanied by the subsequent dissociation of the adsorbed water to form Zn-OH and O-H hydroxyls. Accordingly, it may be concluded that the pre-desorbed state of CO_2 is the unidentate carbonate.

Finally we compare our results with the TPD study of formic acid adsorbed on ZnO single-crystal surfaces in UHV conditions (20, 21). We showed that 70% of the surface formates decompose to $-\text{OH} + \text{CO}$ and 30% of them are converted to $\text{H}_2 + \text{CO}_2(\text{ad})$, where CO and H_2 desorb at the decomposed temperature and $\text{CO}_2(\text{ad})$ desorbs at the higher temperature. On the contrary, the UHV-TPD results of formic acid show that formic acid is always a major desorbed species in the wide temperature range. Sixty percent of the decomposed products were $\text{CO}_2 + \text{H}_2$ and 40% of them were $\text{CO} + \text{H}_2\text{O}$, where CO_2 and H_2 desorbed at the same temperature. This contradiction may be due to the fact that interadsorbate interaction was not excluded in the UHV-TPD experimental conditions because the major



SCHEME 1. A reaction mechanism for water-gas shift reaction on ZnO.

species of TPD is formic acid. The reason why CO_2 and H_2 desorbed at the same temperature in the TPD measurement can possibly be explained by the contribution of coadsorbed formic acid, as demonstrated in the present study of formic acid.

5. Reaction Mechanism for Catalytic Water-Gas Shift Reaction Based on Intermediate-Reactant Interaction

As shown in Table 4, the rates of the formations of CO_2 and H_2 were obtained from the decomposition rate of unidentate carbonate ($k_c \times M_c$) and the decomposition rate of formate ($k_f \times M_f$), respectively, showing the agreement of both rates. These values also agreed with the steady-state rate for catalytic WGSR. Thus, it is confirmed that WGSR on ZnO catalytically proceeds through bidentate formate and unidentate carbonate, where the rates of the two elementary reaction steps balancing in a steady state.

Scheme 1 shows the reaction mechanism of catalytic WGSR on ZnO surface, drawn in the context of the present experiments. The first water molecule dissociates at mainly $\text{Zn}_{2\text{C}}\text{-O}_{3\text{C}}$ pair to form surface hydroxyl groups. On-top hydroxyl groups on Zn react with CO to produce surface for-

mates through unidentate formates. Seventy percent of the formates reversibly decomposed to the original OH and CO under vacuum and only 30% of them reacted with the hollow-site OH groups to produce H_2 and $\text{CO}_2(\text{ad})$. When the second water molecule adsorbed on the Zn atom, almost all the surface bidentate formates were able to decompose to H_2 and $\text{CO}_2(\text{ad})$ (unidentate carbonate) as illustrated in Scheme 1. The rate was promoted by a factor of more than 10 as compared with that in the absence of the second water molecule. The decomposition of the formates does not occur through the unidentate formate as already discussed. An isotope effect was observed with the hydrogen atom of the formate and not observed with the hydrogen atom of the OH and introduced H_2O , indicating that the rate-determining step in the decomposition of formate or equally in the formation of H_2 is the dissociation of the C-H bond of the formate.

The $\text{CO}_2(\text{ad})$ produced by the decomposition of the bidentate formate in the presence of the second water molecule is the unidentate carbonate as proved by IR. When the adsorbed water is evacuated, the unidentate carbonate is partly converted to the carboxylate. The decomposition of the unidentate carbonate to form CO_2 was also markedly promoted by the second water molecule adsorbed on the Zn atom. The accompanying dissociation of the adsorbed water to Zn-OH and O-H may assist the CO_2 desorption from the carbonate. In the steady-state reaction the rates of the two reaction steps (formate \rightarrow carbonate + H_2 and carbonate \rightarrow CO_2) are balancing in the presence of adsorbed water.

CONCLUSIONS

(1) The intermediates of WGSR on ZnO are bidentate formate and unidentate carbonate. Both of them are affected by the water molecule which coexists as a reactant on ZnO surface.

(2) Bidentate formate is produced by the reaction of terminal OH groups and CO.

(3) Decomposition process of the formate

is markedly influenced by the water molecule. Under vacuum, about 70% of the formate is decomposed to original surface OH groups and CO and only 30% of them are converted into H₂ and CO₂(ad). On the contrary, 100% of the formate are converted into H₂ and CO₂(ad) with water coexistence.

(4) The water molecule not only affected the selectivity of the decomposition but also activated the formate. The rate constant of the forward decomposition of the formate increases by a factor of more than 10 by the presence of water, accompanied by the decrease in activation energy for the forward decomposition from 155 to 109 kJ mol⁻¹.

(5) The activation process was suggested to proceed through electron donation from the oxygen atom of water to the Zn ion on which the formate adsorbs.

(6) The rate-determining step of the forward decomposition is dissociation of CH bond of the formate.

(7) Unidentate carbonate and carboxylate exist as adsorbed CO₂ species which are formed by the formate decomposition. They are present in equilibrium and the carboxylate is more stable than the unidentate carbonate under vacuum 3 kJ mol⁻¹.

(8) Electron donors such as water, pyridine, and THF convert carboxylate into unidentate carbonate, but undissociated electron donors like pyridine and THF did not enhance the desorption of CO₂. The enhancement of the desorption of CO₂ needs a dissociative electron donor such as a water molecule. Dissociation of the water molecule to form Zn-OH (terminal) and O-H (hollow site) was observed to assist unidentate carbonate to desorb as CO₂.

(9) A reactant-promoted mechanism for WGS on ZnO including activation of intermediates and the intermediate-reactant interaction was observed.

(10) In this mechanism the water molecule plays three roles in catalytic WGS: first, the water molecule itself is a reactant; second, the reactant remarkably promotes the forward decomposition of the formate; and

third, the second water molecule assists the desorption of CO₂. The reactant-promoted mechanism may reveal a general aspect of catalysis phenomena.

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