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Hydrogenation of Carbon Dioxide by Water: Alkali-Promoted Synthesis of Formate

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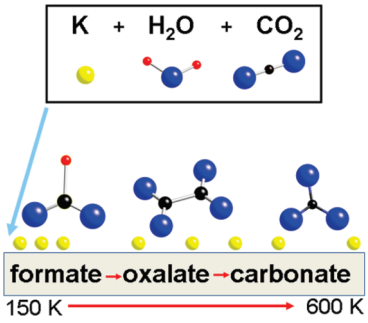
ABSTRACT Conversion of carbon dioxide utilizing protons from water decomposition is likely to provide a sustainable source of fuels and chemicals in the future. We present here a time-evolved infrared reflection absorption spectroscopy (IRAS) and temperature-programmed desorption (TPD) study of the reaction of $CO_2 + H_2O$ in thin potassium layers. Reaction at temperatures below 200 K results in the hydrogenation of carbon dioxide to potassium formate. Thermal stability of the formate, together with its sequential transformation to oxalate and to carbonate, is monitored and discussed. The data of this model study suggest a dual promoter mechanism of the potassium: the activation of CO_2 and the dissociation of water. Reaction at temperatures above 200 K, in contrast, is characterized by the absence of formate and the direct reaction of CO_2 to oxalate, due to a drastic reduction of the sticking coefficient of water at higher temperatures.

SECTION Surfaces, Interfaces, Catalysis



Nature uses carbon dioxide as a building block in photosynthesis, a process that is the basis of life and its continuance on Earth.[1] Carbon dioxide is also believed to be one of the reactants in the synthesis of simple organic molecules in the early universe[2] and prebiotic synthesis.[3] These processes are based on the chemical transformation of carbon dioxide. The current intense interest of the scientific community in these processes is motivated by the idea that the photon-driven CO_2 conversion to fuels and chemicals is a viable route to carbon recycling[4−6] and may one day lead to a sustainable carbon-neutral economy.

As a kinetically and thermodynamically stable molecule, CO_2 has to be activated by strong reducing agents.[4] One possible mechanism of activation is insertion of CO_2 into a metal–hydrogen bond, a reaction studied extensively on many organometallic complexes.[7−9] Other options include: electrochemical CO_2 reduction,[5] photoreduction of CO_2 by H_2O using light as an energy source,[10,11] and use of dispersed metal as a catalyst and reductant.[12]

The activation of CO_2 by alkali metals has received considerable attention in various surface science studies that demonstrated the formation of a CO_2^- intermediate, dissociation of CO_2,[13−18] and formation of oxalate and carbonate alkali compounds.[15,17,19] Previous work has also demonstrated that on potassium-promoted Ru(001), both CO and CO_2 can be hydrogenated at elevated pressures of hydrogen to form formate.[20−22] Because it is known that on K-modified Ru[23] and Pt[24] surfaces, water dissociates readily to H + OH, the question arises as to whether water can be used as a cheap and abundant source for the hydrogenation of carbon dioxide to hydrocarbons. The present study represents the first attempt to investigate the mechanism of alkali promotion of the hydrogenation of CO_2 by reaction with coadsorbed H_2O as the source of hydrogen.

We conducted experiments studying the interaction of $CO_2 + H_2O + K$ by evaporating thin films of potassium on Cu (111) in a controlled atmosphere of carbon dioxide and water. During evaporation, the reaction was followed by time-evolved IRAS. Figure 1 presents time-evolved IR spectra obtained during reactive evaporation of potassium at 150 K in the presence of CO_2 and H_2O at 2×10^{-8} Torr each. The spectra show the growth of several vibrational bands, which are assigned to potassium formate on the basis of previous vibrational studies of potassium formate obtained from the decomposition of formic acid.[25,26] We assign the band at 2785 cm^{-1} to the C–H stretch and a weak band at 1388 cm^{-1} to the CH bending mode. The bands at 1619 and 1367 cm^{-1} are assigned to the asymmetric and symmetric OCO stretch, respectively, and the band at 766 cm^{-1} is assigned to the OCO bending mode. On the basis of previous isotope substitution studies,[25,26] we assign the remaining band at 2696 cm^{-1} to the overtone of the CH bend 2δ(CH), whose intensity is enhanced by a Fermi resonance with the C–H stretch. The good agreement of the present vibrational data with data for bulk crystalline potassium formate[27] suggests a structural model where the formate is in a bridge-bonding configuration.[26] (See Table T1 in the Supporting Information.)

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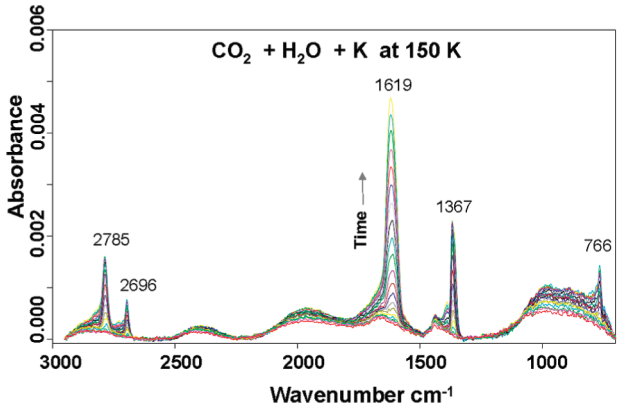

Figure 1. Time-evolved FTIR spectra obtained during the reactive evaporation of potassium in the presence of H_2O and CO_2 on Cu(111) at 150 K. Spectra have been collected at 50s time intervals, but only every second spectrum is shown (K-deposition rate: 0.002 ML/s).

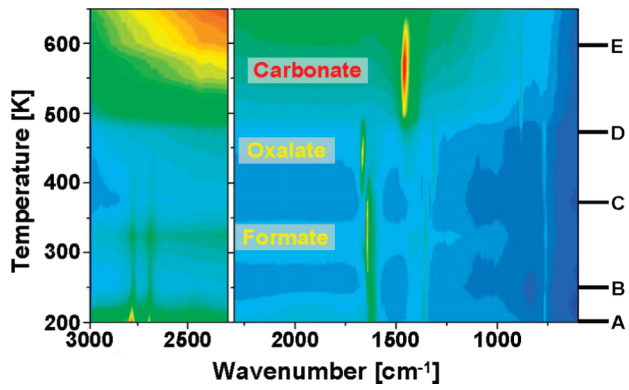

Figure 2. Contour plots of time-evolved vibrational spectra obtained during heating of the surface shows the formation and decomposition of the different alkali compounds. The right panel color palette (blue to red) correspond to the absorbance range 0 to 0.0173; the left panel absorbance range is 0 to 0.0059. The IRAS spectra were collected in 50 s time intervals at a heating rate of 0.5 K/s.

Interestingly, vibrational bands attributable to potassium formate are observed only after the layer thickness reaches about 3 ML, suggesting that the reaction of $CO_2 + H_2O$ to formate requires metallic potassium.

Adsorption temperature plays a decisive role in reaction selectivity. Time-evolved IRAS spectra obtained during reactive evaporation of potassium at 250 K are characterized by the absence of formate. Instead, we observe vibrational modes at 1479 and 887 cm^{-1}, indicating the formation of carbonate. (See Figure S1 in the Supporting Information.)

Time-evolved vibrational spectra obtained during heating of the potassium formate layer in Figure 1 allows us to investigate the thermal stability and decomposition pathways of the formate. Figure 2 presents a contour plot of vibrational frequency versus substrate temperature, with three distinctly different species as the surface is heated from 100 to 750 K. The C−H stretch region shows C−H bands due to formate up to 425 K. At higher temperature, the CH bands disappear altogether with a shift in the C−O stretches, indicating a new species, oxalate. Finally, after heating above 500 K, the asymmetric and symmetric C−O stretches are completely replaced by a single band at 1460 cm^{-1} accompanied by a second mode at 882 cm^{-1}. The latter species, carbonate, is stable up to 675 K.

Figure 3 shows selected individual vibrational spectra from the time-evolved heating sequence shown in the contour plots of Figure 2, characteristic of different molecular states of the adlayer. Heating from 200 (spectrum A) to 250 K (spectrum B) results in small shifts and sharpening of the vibrational bands assigned to formate. At the same time, the very broad features observed in Figure 1 at 1000, 2000, and 2400 cm^{-1} have disappeared. TPD spectra, discussed below, show that the loss of these features is related to the desorption of water, suggesting that the bands are due to excess water ice or water from hydrated alkali species. In fact, the desorption of "excess" water from hydrated alkali species offers a straightforward explanation for the simultaneous frequency shifts observed for the formate. Because the loss of water affects bonding between K and O, it is not surprising that the asymmetric C−O

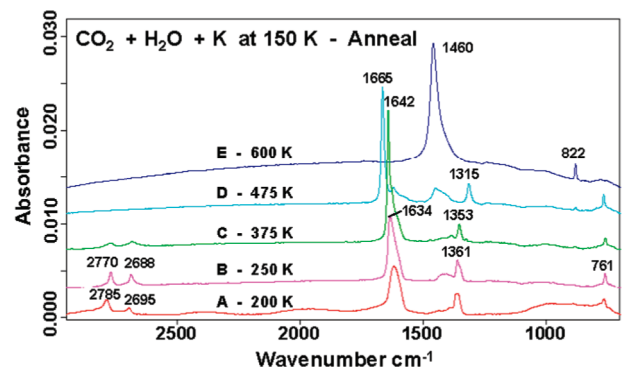

Figure 3. Vibrational spectra of different alkali compounds obtained during annealing of the surface: (A−C) formate at 200, 250, and 375 K; (D) oxalate at 475 K; and (E) carbonate at 600 K.

stretch ν_a (OCO) shows the largest frequency shifts (1619 to 1642 cm^{-1}). The ν_a (OCO) stretch is quite sensitive with respect to the preparation method of potassium formate, a fact noted already by Ito and Bernstein.[28] Further heating from 250 to 375 K results in significant sharpening of ν_a (OCO) at 1642 cm^{-1} and a large decrease in the intensity of the C−H stretch ν_s (CH). The latter mode has A_1 symmetry in C_{2v}, whereas the asymmetric OCO stretch ν_a(OCO) is of B_1 symmetry. In fact, a closer examination of spectra B and C reveals that in addition to the C−H stretch, the other A_1 modes, ν_s (OCO) at 1361 cm^{-1} and δ(OCO) at 761 cm^{-1}, decrease in intensity as well. Because in IRAS only modes with a dipole moment perpendicular to the surface are observed, we conclude that the changes caused by heating result in a change of the orientation of the formate within the multilayer. The fact that we observe both A_1 and B_1 modes indicates that the multilayer contains formate ions with multiple orientations similar to the crystal structure observed for solid bulk potassium formate.[27]

Heating to 475 K results in the complete disappearance of the C−H bands as well as larger shifts in the C−O stretch

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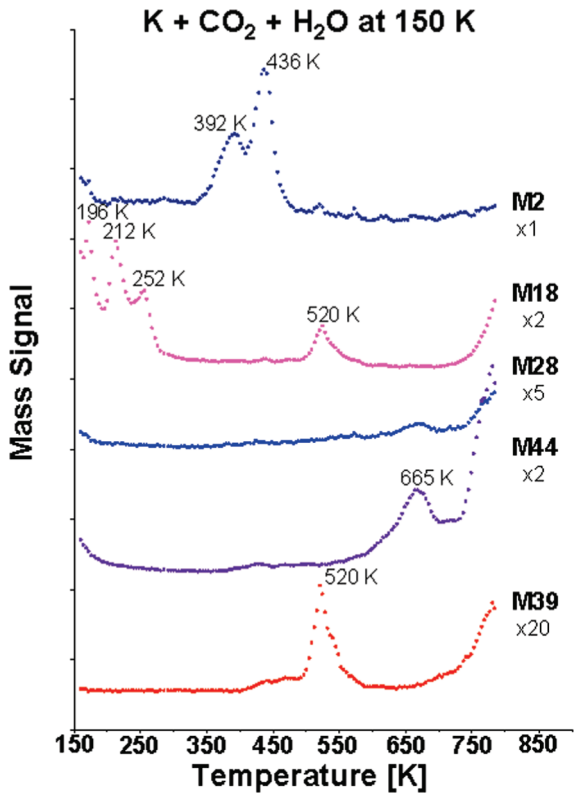

Figure 4. Thermal desorption mass spectra obtained after the reactive evaporation of potassium in the presence of H_2O and CO_2 at 150 K as in Figure 1 (heating rate = 2 K/s).

region (Figure 3). On the basis of previous work,[15,17] we assign the vibrational bands in spectrum D of Figure 3 to potassium oxalate, with the C−O stretches ν_a(OCO) at 1665 cm^{-1} and ν_s (OCO) at 1315 cm^{-1} and the OCO bend δ(OCO) at 767 cm^{-1}. C−H bond breaking leading to an oxalate intermediate has been previously observed for potassium formate produced by the decomposition of formic acid on K/Ru(001)[26] and K/Co(1010).[25] Further heating leads to the loss of the oxalate bands and the appearance of two new bands at 1460 and 882 cm^{-1}, as shown in spectrum E of Figure 3. These bands are characteristic of carbonate, with the mode at 1460 cm^{-1} assigned to the asymmetric OCO stretch ν_a(OCO) and the band at 882 cm^{-1} to the OCO out-of-plane motion π(OCO). The formation of carbonate resulting from the decomposition of multilayer potassium oxalate has been previously observed in several cases, for example, for CO_2/K/Ru(001),[15] CO_2/O_2/K/Co(1010),[19] and after formate decomposition on K−Ru(001)[26] and K/Co(1010).[25] (See Table T2 in the Supporting Information.)

TPD spectra of a potassium formate layer, obtained after the reactive evaporation of potassium in the presence of H_2O and CO_2 at 150 K, are presented in Figure 4. The spectra were obtained during temperature-programmed heating at a rate of 2 K/s, simultaneously monitoring mass 2 (H_2), 18 (H_2O), 28 (CO), 39 (K), and 44 (CO_2). Heating from 150 to 300 K is characterized by desorption of water in multiple peaks (M18 trace). Because we observe changes in IRAS in this temperature range that correspond to changes in the structure and orientation of the formate, we suggest that desorption of water, either from ice or from hydrated potassium species, must be responsible for the structural changes of the formate previously discussed. Heating from 350 to 450 K results in major desorption of hydrogen (M2) with peaks at 392 and 436 K. Because we observe at the same time in IRAS the disappearance of the C−H stretch, we conclude that the decomposition of the formate proceeds via C−H bond breaking. Further heating leads to the simultaneous desorption of H_2O (M18) and K (M39) at 524 K. This desorption is accompanied in IRAS by the loss of a band at 3622 cm^{-1}, which is assigned to the O−H stretch of KOH.[23] (See Figure S2 in the Supporting Information.) This indicates that the H_2O/K desorption at 520 K is related to the decomposition of KOH because at this temperature neither H_2O nor metallic K would be stable on its own on the Cu(111) surface. Finally, heating above 650 K results in the desorption of CO_2 (M44) from the decomposition of carbonate, which is also observed in IRAS in this temperature range.

Reaction Pathways $CO_2 + H_2O + K$. The vibrational data indicate two different pathways for the reaction of $CO_2 + H_2O$ in the presence of potassium. At low temperature, 150 K and below, we observe the formation of potassium formate, whereas at temperatures of 200 K and above, potassium carbonate forms.

Reaction at 150 K. The reaction pathway to potassium formate can be described by the overall reaction

$$CO_2 + H_2O + 2K \rightarrow HCO_2K + KOH \qquad (1)$$

The IR data presented in Figure 1 confirm the formation of bridge-bonded potassium formate. IRAS data also confirm the presence of KOH, with an O−H stretch observed at 3620 cm^{-1}. Because we observe the formation of potassium formate at temperatures as low as 100 K, this facile reaction must be due to the potassium-promoted dissociation of H_2O and activation of CO_2, as observed in previous studies of the reaction of K + CO_2[15,19] and K + H_2O.[23,24] Therefore, it is plausible to suggest that reaction 1 proceeds through intermediate steps involving the activation of CO_2 and the dissociation of water

$$H_2O + 2K \rightarrow KOH + KH \qquad (1a)$$

$$CO_2 \rightarrow CO_2^* \qquad (1b)$$

$$CO_2^* + KH \rightarrow HCO_2K \qquad (1c)$$

Step 1a, the dissociation of H_2O, is confirmed by observation of KOH in IRAS (ν(OH) at 3620 cm^{-1}). Although we do not have direct spectroscopic evidence of the activated CO_2* species in step 1b, previous matrix isolation[29] and surface studies[15] of CO_2 activation by potassium leave little doubt that the adsorption of CO_2 is activated by potassium because of charge transfer resulting in a transition from a linear to a partially charged, bent CO_2 radical anion. Likewise, our data provide little information of the role of H liberated from water dissociation in step 1a. There are three options, the first of which involves atomic H reacting directly with a neighboring activated CO_2* species. The other two alternatives involve K−H bond formation, where K−H would react with a neighboring K-CO_2* species or where an activated CO_2* species is inserted into a K−H bond. The latter has well-known

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analogues in organometallic chemistry.[4,7−9] The electron-deficient carbon in CO_2 has a strong affinity toward nucleophiles and electron-donating species. Mechanistically, hydridic hydrogen of metal-H directly attacks the electrophilic carbon of CO_2; a metal-O bond forms while the M−H bond breaks.[30,31] Therefore, insertion of CO_2 into a K−H bond can lead directly to formate formation.

Reaction above 200 K. Reactions at temperatures above 200 K are characterized by a distinctly different reaction pathway. The vibrational data for reaction at 250 K do not show any evidence of potassium formate. (See Figure S1 of the Supporting Information.) Instead, we observe potassium carbonate as the only reaction product. This suggests that CO_2 reacts either directly to carbonate or indirectly via an oxalate intermediate

$$2CO_2 + 2K \rightarrow [K_2C_2O_4] \rightarrow K_2CO_3 + C + O \qquad (2)$$

Both vibrational and TPD data show no evidence of adsorbed H_2O or OH species at temperatures of 200 K and above. The TPD data presented in Figure 4 show that water ice and most of the molecular water desorb at these temperatures. Therefore, the greatly reduced sticking coefficient for H_2O will shift the competition between H_2O and CO_2 for adsorption sites on the potassium surface in favor of CO_2. In addition, the subsequent rapid carbonate formation may act as a site-blocker, further suppressing the adsorption and dissociation of water. Regarding the oxalate intermediate in reaction 2, we note that although we do not have direct spectroscopic evidence in the present case, earlier studies of CO_2 with bulk potassium show facile formation of oxalate and its subsequent decomposition to carbonate.[15]

Decomposition Pathways. The present IRAS and TPD data indicate that the decomposition of formate proceeds via C−H bond breaking at 350−425 K, resulting in the formation of oxalate. The oxalate starts to decompose at 500 K to carbonate, which is stable up to 675 K. This suggests the following decomposition reaction scheme

$$2HCO_2K \rightarrow K_2C_2O_4 + H_2(g) \qquad (3)$$

$$2KOH \rightarrow K_2O + H_2O(g) \qquad (4)$$

$$K_2C_2O_4 + 2K_2O \rightarrow 2K_2CO_3 + 2K(g) \qquad (5)$$

Evidence of C−H bond breaking in reaction 3 is provided by the loss of the C−H vibration in IRAS and the simultaneous evolution of hydrogen in TPD. At the same time, a pronounced shift in the C−O stretches results in a vibrational spectrum characteristic of potassium oxalate. The decomposition of KOH (reaction 4) is observed between 475 and 500 K with the loss of the O−H stretch in IRAS and the evolution of H_2O and K in TPD. Interestingly, the decomposition of oxalate to carbonate (reaction 5) is observed in the same temperature range. This suggests that reactions 4 and 5 are coupled and that the decomposition of KOH drives the decomposition of the oxalate.

Formate is clearly an intermediate of importance in the catalytic conversion of CO_2.[32] It was identified as such in the proton-coupled two-electron reduction of CO_2.[4,6] Its role in a large scale industrial process of methanol synthesis[33] (CO/CO_2 hydrogenation using $Cu/ZnO/Al_2O_3$ catalyst) is still subject of debate,[34] as is its function in the closely related water−gas shift reaction.[35] Although formate is identified as one of the intermediates in these reactions, discussions about its role in the CO_2 transformation continue in recent publications.[34,36] Continuing scientific interest in the catalytic CO_2 reduction chemistry led to recent identification of the formate in the $CO_2 + H_2O$ reaction at higher pressures on Cu surface[37] and in the hydrothermal reaction of carbon dioxide with water in the presence of iron particles.[12]

In conclusion, we demonstrated that potassium, codeposited with CO_2 and H_2O on a cold Cu(111) surface, facilitates the formation of formate species by reduction of carbon dioxide and by dissociation of water. Water splitting serves as a source of hydrogen for CO_2 hydrogenation. Thermal stability and decomposition pathways studies by TPD and IRAS point to a relatively high stability of formate and its sequential and selective conversion to oxalate and carbonate.

SUPPORTING INFORMATION AVAILABLE Details of the experimental procedure, vibrational spectra of carbonate species, the O−H stretch region, and the assignments tables for formate, oxalate, and carbonate. This material is available free of charge via the Internet at http://pubs.acs.org.

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