Formate synthesis on Cu(100)

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Abstract. We show that copper–formate surface species can be synthesized from $CO_2(g)$ + $H_2(g)$ on a well defined single Cu(100) crystal. The presence of the surface formate is confirmed and studied by XPS, HREELS, and TPD. With the use of a high-pressure cell incorporated into the UHV system, the formate formation was studied over a pressure range of 0.5–5.0 bar and a temperature range of 313–363 K. The rate of formate formation was found to have a strong dependence on gas composition (CO_2:H_2) and a weak dependence on total pressure. At 363 K, the initial rate of formate formation on the Cu(100) surface in a 70:30 (CO_2:H_2) gas mixture at 2.3 bar was found to be approximately 3.3×10^{-4} formate molecules per copper atom per second. The activation energy for the formate formation was found to be 53 kJ mol^{-1}. A gas–solid equilibrium model for the formation of surface formate suggests that the rate-limiting step in the synthesis is the reaction of surface atomic hydrogen with CO_2 forming the surface formate.

1. Introduction

The industrial synthesis of methanol is primarily accomplished by passing synthesis gas ($CO/CO_2/H_2$) over a $Cu/ZnO/Al_2O_3$ catalyst followed by distillation of the downstream products [1]. Often, a surface formate species is invoked as an intermediate in the catalytic synthesis of methanol. The formate species has been postulated to exist from both infrared [2] and temperature programmed desorption (TPD) [3] spectra of a supported copper-catalyst exposed to synthesis gas. Formate is also a postulated intermediate in one of the thermal decomposition channels of methoxy on oxidized copper surfaces (Cu(110) [4], Cu(111) [5]). Therefore, data exist which seems to indicate that the surface formate may play an important role in both the synthesis and decomposition of methanol on copper surfaces.

By isotopically labelling the carbon in either CO and CO_2, it has been shown conclusively that the source of the carbon atom in methanol synthesized from a $CO/CO_2/H_2$ gas mixture originates from CO_2 [6–8]. Bowker et al [3] also postulated, from TPD studies, that a copper surface formate can be synthesized from a CO_2/H_2 gas mixture on both a $Cu/ZnO/Al_2O_3$ catalyst or a polycrystalline copper surface [3].

In the present study, we give conclusive evidence that the copper–formate species can be synthesized from a CO_2/H_2 gas mixture over a well defined Cu(100) single crystal. Furthermore, we have characterized the formate synthesis under a variety of synthesis conditions. From these synthesis studies, we have been able to extract the energy of formate formation, to determine the efficiency of synthesis at different gas compositions and total pressures, and to successfully model the formate synthesis

process. An extensive report of our findings of the formate synthesis will be presented elsewhere [9].

2. Experimental procedure

The experiments were carried out in a stainless steel ultrahigh vacuum (UHV) system with a base pressure of 1×10^{-10} mbar. The UHV system is described in detail elsewhere [10]. Briefly, the system is equipped with a x-ray photoelectron spectrometer (XPS), a high-resolution electron energy loss spectrometer (HREELS), a quadrupole mass spectrometer (QMS), a plasma ion gun, and a low-energy electron diffraction (LEED) apparatus. The Cu(100) single crystal was prepared as described in [10], and the quality of the crystal surface was confirmed by XPS and LEED.

The formate synthesis was carried out in the high-pressure cell (HPC) [9]. Once the HPC is isolated from the UHV chamber, the gas mixture can be introduced or pumped away by means of two holes in the bottom of the HPC. The pressure in the HPC is measured with a capacitance Baratron attached to the gas line. Since both CO_2 [11, 12] and H_2 [13] have low sticking coefficients on copper, both the CO_2 (99.998%) and the H_2 (99.9997%) were further purified and confirmed to be free of impurities [9].

To calibrate the formate surface coverage, the ratio of the integrated XPS intensities of the O(1s)/Cu(3p) were compared with the ratio obtained for the oxygen saturated Cu(100) surface. The copper surface is known to saturate at 0.5 mono-layers of oxygen [14]. To saturate the surface with oxygen, the Cu(100) crystal was repeatedly exposed to 1000 L ($1 L = 1 \times 10^{-6}$ Torr s) of O_2 at 500 K until no further oxygen adsorption was observed. The oxygen calibration was performed both before and after the experiments reported here.

3. Results and discussion

3.1. Identification of the synthesized surface formate

XPS, TPD, and HREELS were used to characterize the surface formate. XPS scans of the Cu(3p), C(1s), and the O(1s) lines were taken after each high-pressure exposure to the CO_2:H_2 gas mixture. As indicated above, the formate coverage was calculated by comparing the O(1s)/Cu(3p) ratio with the saturated O/Cu(100) surface and accounting for the two oxygen atoms in the formate molecule. After taking in consideration the appropriate elemental sensitivities, the formate O(1s) to C(1s) ratio was approximately 2:1, as would be expected for the formate molecule.

After the XPS, a TPD experiment was preformed by placing the face of the crystal face 1 mm away from the shield of a differentially-pumped QMS and then heating at a rate of 2 K s^{-1}. The only desorption products from the synthesized surface formate was the simultaneous desorption of CO_2 and H_2 with $T_p = 430$ K (for a saturated formate layer). The desorption temperatures and yields of CO_2 and H_2 from the synthesized formate layer were the same as those obtained from a similar formate coverage obtained from the adsorption of formic acid on Cu(100) [9] and Cu(110) [15].

A HREELS spectra of a synthesized formate layer is shown in figure 1. The spectrum in figure 1 is similar to HREELS spectra reported for surface formate species
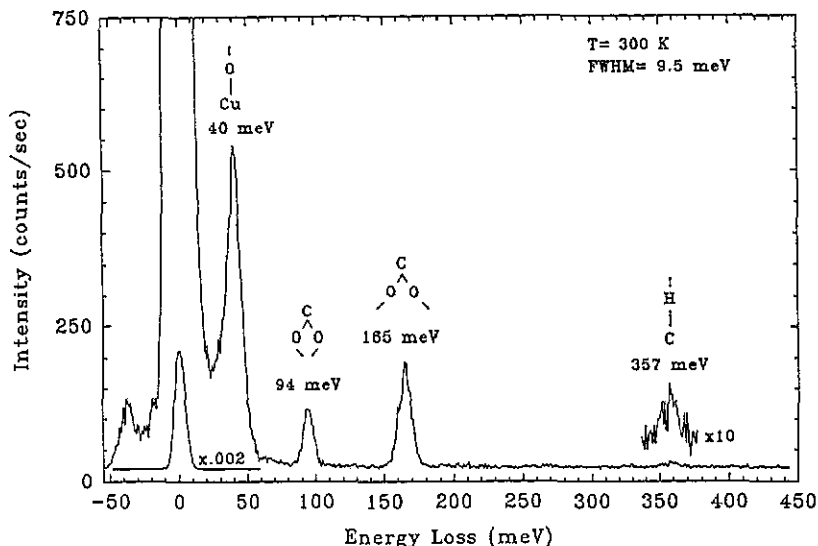
Figure 1. The specular HREELS spectra from a 0.2 monolayers formate coverage on Cu(100) synthesized from a 70:30 CO_2:H_2 gas mixture with a total pressure of 2.3 bar and a crystal temperature of 343 K.

on Cu(100) surface obtained from the adsorption of formic acid on Cu(100) and heating to room temperature [16, 17]. The strong loss feature at 40 meV (322 cm^{-1}) is assigned as the copper–oxygen stretching vibration of the formate–surface complex. The two losses at 94 meV (758 cm^{-1}) and at 165 meV (1331 cm^{-1}) are respectively assigned to the in-plane deformation and the symmetric stretch of the formate's O–C–O bonds. Finally, the loss feature at 357 meV (2879 cm^{-1}) is identified as the formate's carbon–hydrogen stretching mode, clearly indicating the successful synthesis of the surface formate.

3.2. Kinetics of formate synthesis

The rate of formate synthesis on the Cu(100) surface was studied with a 70:30 CO_2:H_2 gas mixture at a total pressure of 2.3 bar and over a temperature range of 313–363 K. The surface formate coverage at each exposure to the gas mixture was measured by XPS (see experimental section). In the present studies, the formate layer was found to saturate at approximately 0.4 monolayers of formate, where 0.5 monolayers is the theoretically expected saturation coverage. An Arrhenius plot of the initial rates of formate formation is shown in figure 2 for three separate sets of experiments. From the slope in figure 2, we calculate the activation energy of the formate formation to be 53 kJ mol^{-1}.

In addition to studying the energy barrier to the formate formation, we have also examined the dependence of the initial rate of formate formation on total gas pressure and gas composition. Details of the characterization of the dependence of the formate synthesis on total pressure and gas composition are given in [9]. Briefly, we found that the synthesis has a weak dependence on total gas pressure and a strong dependence on gas composition. For a Cu(100) crystal at 343 K in a 70:30 CO_2:H_2 gas mixture with a total pressure of 2.3 bar (close to the observed optimum synthesis conditions), we found that the initial rate of formate formation was 3.3×10^{-4} formate
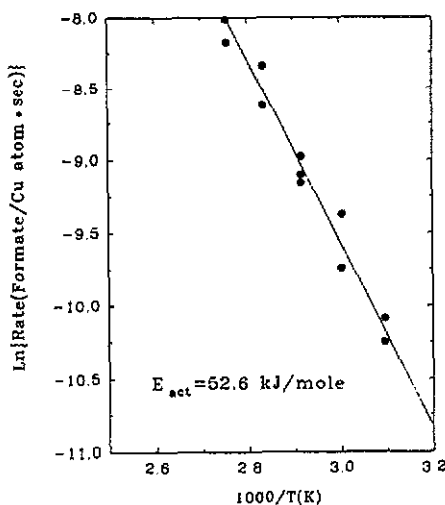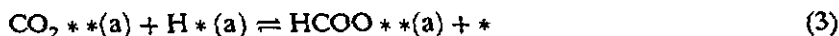
Figure 2. Arrhenius plot for the formation of surface formate. The data set represents three separate sets of synthesis experiments (two crystals) with a 70:30 $CO_2:H_2$ gas mixture at a total pressure of 2.3 bar.

molecules per copper atom per second.

The formate synthesis was modelled by the following gas–solid equilibrium reactions:

$$H_2(g) + 2* \rightleftharpoons 2H * (a) \tag{1}$$

$$CO_2(g) + 2* \rightleftharpoons CO_2 * *(a) \tag{2}$$

$$CO_2 * *(a) + H * (a) \rightleftharpoons HCOO * *(a) + * \tag{3}$$

where $*$ is an adsorption site. Reaction (1) is simply the dissociative adsorption and desorption of hydrogen on Cu(100). The adsorption and desorption of CO_2 on Cu(100) (reaction (2)) has been recently investigated in our laboratories [11]. We have been able to calculate equilibrium constants for reactions (1)–(3) under formate synthesis conditions [9]. The results of the modeling indicate that both the adsorption of hydrogen and carbon dioxide (reactions (1) and (2)) are fast processes compared with the synthesis reaction (3), which is the rate determining step of the overall synthesis process.

4. Summary

We have been able to show conclusively that formate can be synthesized on Cu(100) from a high-pressure gas mixture of $CO_2:H_2$. Furthermore, we have found the activation energy for the formate formation to be 53 kJ mol^{-1}.

Acknowledgments

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