

Adsorption and surface reaction of formic acid on the Cu(977) surface with a (100) microfacet

(¹The Institute for Solid State Physics, University of Tokyo) ○ Wataru Osada,¹ Shunsuke Tanaka,¹ YoungHun Choi,¹ Kozo Mukai,¹ Jun Yoshinobu¹

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Chemical recycling of CO₂ is an attractive approach to mitigate the CO₂ emission originating from human activity. Formic acid (HCOOH) is one of the hydrogenated products of CO₂ and catalytically decompose into H₂ and CO₂. Therefore, it has been expected to be one of the hydrogen carrier/storage materials.¹ In addition, formate species, which are formed on the catalyst surface in the HCOOH decomposition process, is a candidate of the stable intermediate in methanol synthesis on the Cu-based catalyst. Thus, the surface chemistry of HCOOH and formate on the Cu surface is an important issue for chemical CO₂ recycling.

We have investigated the surface chemistry of HCOOH including adsorption, decomposition, and desorption on the Cu(977) surface. Using high-resolution X-ray photoelectron spectroscopy we found that the Cu(977) surface has a higher activity for HCOOH dissociation; the conversion ratio of HCOOH to formate was 29% on Cu(977), while that on Cu(997) is reported to be 17%.² We systematically conducted temperature programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRAS) to reveal the detailed process of HCOOH on Cu(977). Two molecular desorption peaks of HCOOH were observed at ~170 K (α desorption from the terrace) and ~250 K (β desorption from the step). Bidentate formate species were decomposed and desorbed as CO₂ and H₂ at 458 K, which is higher than the decomposition temperature of 450 K on Cu(997).² Thus, on Cu(977), both HCOOH and formate at the step sites were more stably adsorbed than on Cu(997). IRAS spectra show hydrogen-bonding network of HCOOH molecules was developed on Cu(977) unlike Cu(997), which is evidenced by the observation of the out-of-plane bending mode of the O-H bond at ~980 cm⁻¹. In addition, the carbonyl stretching mode of monodentate formate (1650 cm⁻¹) was very broadened at 140-220 K, indicating that the hydrogen-bonded complex was formed between HCOOH and monodentate formate.³ The vibrational peaks related to the complex disappeared at 220-240 K. That temperature region is well consistent with the β desorption, indicating the complex decomposed into HCOOH and formate above 220 K. We conclude the high activity on the Cu(977) surface is due to the stabilization of bidentate formate and the formation of the hydrogen-bonded complex at the step site. A (100) microfacet at the step would produce these factors.

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