JOURNAL OF CATALYSIS 58, 149–153 (1979)

The Decomposition of Formic Acid on W(100) and W(100)—(5×1) C Surfaces

The catalytic properties of metals can be significantly altered by the formation of surface carbides. Previous investigations found that the formation of surface carbides on nickel single-crystals resulted in changes in both the mechanism and kinetics of formic acid decomposition (*1*). For both clean Ni(110) and Ni(100) surfaces formic acid decomposed via the dehydration of formic acid to formic anhydride and the subsequent autocatalytic decomposition of formic anhydride to yield H_2, CO, and CO_2 (*2, 3*). Formation of well-ordered carbide overlayers on both surfaces resulted in the decomposition of formic acid to H_2 and CO_2 via a formate intermediate with the concurrent suppression of the autocatalytic kinetics (*4, 5*).

In a previous study the surface carbides of tungsten were characterized with respect to their structure and their chemisorption properties (*6*). It was shown that surface carbides of tungsten inhibited the dissociative adsorption of CO and H_2. In order to better understand how carbon modifies the catalytic properties of tungsten the decomposition of formic acid has been studied by temperature-programmed reaction spectroscopy (TPRS) on clean and carburized W(100) surfaces.

The experiments were carried out in a stainless-steel UHV chamber previously described (*6*). Briefly the system contained a CMA for Auger electron spectroscopy (AES), a quadrupole mass spectrometer, four-grid LEED optics, and a coolable crystal holder/manipulator. The W(100) sample was heated by radiation from a tungsten filament located in back of the crystal for TPRS experiments. The (100)-oriented tungsten crystal was a polished disk 10 mm in diameter and 0.5 mm thick. It was cleaned by electron bombardment heating to 1500 K in 10^{-6} Torr oxygen for 2 to 3 hr, with subsequent flashing to 2500 K in vacuum. This produced a clean W(100) surface as judged by AES and LEED. A W(100) − (5 × 1)C surface was prepared by cracking ethylene at 1500 K as described previously (*6*). Its structure and composition were verified by AES and LEED.

The preparation of the formic acid sample has been described previously (*2*). The formic acid was admitted to the system through a 22-gauge stainless-steel syringe which provided a collimated beam to the face of the crystal. Product desorption spectra were obtained by facing the crystal directly into the ionizer of the mass spectrometer and heating by radiation from a tungsten filament to 800 K. After heating to 800 K an Auger spectrum was taken to determine carbon and oxygen coverages. LEED and AES results were correlated for a series of surface carbides, oxides, and dissociated CO adsorption to provide calibration standards for carbon and oxygen coverages (*6*). Electron beam effects were negligible as evidenced by AES taken while scanning the surface.

Formic acid was adsorbed on a clean W(100) surface at 300 K. For exposures of less than 0.7 L the only desorption

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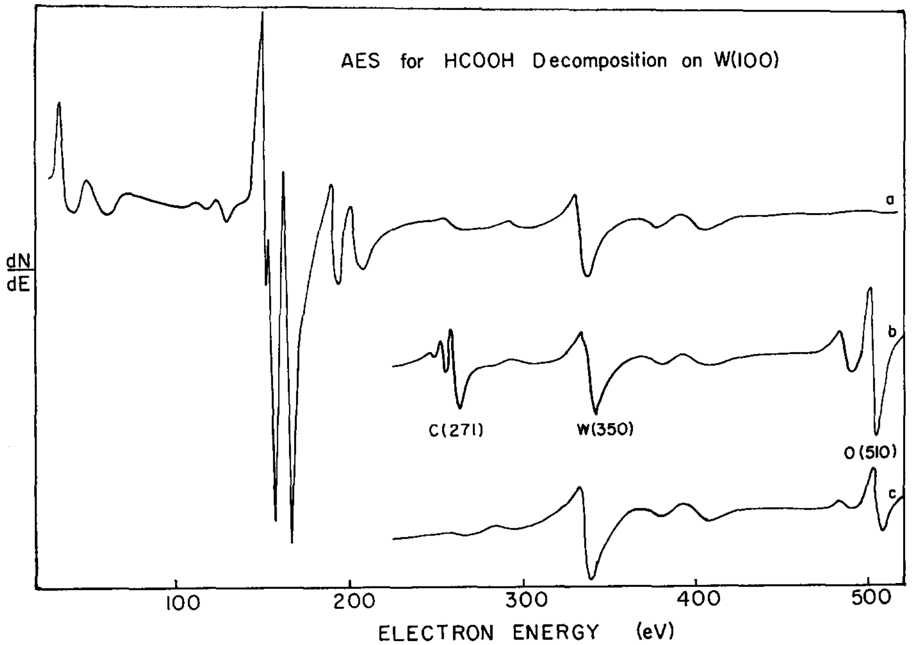

FIG. 1. Auger electron spectra for formic acid decomposition on W(100): (a) clean W(100); (b) after adsorption of HCOOH at 300 K and heating to 800 K; (c) after heating to 1500 K.

product observed below 800 K was H_2. The hydrogen desorption spectra were similar to those for coadsorbed H_2 and CO (*7*). AES revealed that at 800 K the surface was covered with carbon and oxygen in a ratio of 1:2. After heating the surface to 1500 K AES showed that all the carbon had desorbed as CO(β) leaving adsorbed oxygen remaining, as shown in Fig. 1. This oxygen was then removed by flashing to 2500 K in vacuum.

When the exposure of formic acid was increased beyond 0.7 L, CO_2 was observed to desorb at 580 K. For exposures of formic acid from 0.7 to 5 L the CO_2 product peak increased in magnitude but always occurred at the same temperature. H_2 and a small amount of H_2O were also observed to evolve at the same temperature as CO_2. For formic acid exposures of greater than 5 L no further changes were noted in the desorption spectra. After heating a surface presaturated with formic acid to 800 K the surface showed carbon and oxygen remained adsorbed. Further heating to 1500 K removed the carbon as the β-states of CO desorbed, but AES showed that oxygen remained on the surface.

These results indicated that the initial reaction of formic acid on clean W(100) was complete dissociation to adsorbed hydrogen, carbon, and oxygen. After the surface was nearly saturated by adsorbed carbon and oxygen the tungsten was no longer catalytically active for complete dissociation, rather a formate intermediate was stabilized on the surface which subsequently decomposed to H_2, and CO_2. The kinetic parameters for the formate decomposition were determined from the variation of peak temperature with heating rate. Formate decomposition proceeded by a first-order process with an activation energy of 38.0 kcal/mol, and a pre-exponential factor of 1×10^{14} sec^{-1}.

A W(100) − (5 × 1)C surface was prepared as described previously (*6*); it was chosen for further study because of its stability and reproducibility. This surface structure has been ascribed to a surface reconstruction in which a close packed plane of ditungsten carbide is formed in registry with the W(100) substrate below. It has been shown that this surface adsorbed CO only as a molecular species, and did not dissociate CO as a clean W(100) surface did. Formic acid was adsorbed on this surface at 300 K. For 0.1- to 5-L exposure H_2 and CO_2 were observed as the major reaction products. Hydrogen desorbed in two peaks, one at 350 K and a second peak coincident with the CO_2 peak at 540 K. A small CO product peak (corrected for CO_2 cracking) was also observed at 540 K. Additionally at high exposures of formic acid (>1 L) a small amount of water was also found to be evolved at 540 K. An Auger spectrum taken after heating to 800 K showed that adsorbed oxygen was also a reaction product (see Fig. 4).

The results for the carbide surface indicate that the decomposition of formic acid occurred via a formate intermediate. The initial decomposition of formic acid to formate and hydrogen gave rise to the H_2 peak at 350 K. At 540 K the formate decomposed to yield H_2 and CO_2. Some of the CO_2 decomposed to CO and surface oxygen, and some of the surface oxygen was then reduced by hydrogen. The kinetic parameters for the decomposition of the formate on the carbide surface were determined by variation of peak position with heating rate; the activation energy was 36.5 kcal/mol with a pre-exponential factor of 2×10^{14} sec^{-1}.

Comparison of the results for the clean and carbide surfaces indicated that a surface carbide passivated the tungsten surface so that it no longer completely dissociated formic acid. In this respect the carbide surface was similar to a surface that was saturated with carbon and oxygen from dissociated formic acid, on which a formate was also the predominant intermediate. The similarity of the reaction rate for formate decomposition on the two surfaces further supports this analogy. The major difference between the two surfaces was the presence of oxygen on the surface passivated by dissociated formic acid, which inhibited the formation of the formate and resulted in only one-tenth as much formate being formed on the initially clean surface as compared to the carbide surface (note mass spectrometer scales in Figs. 2 and 3).

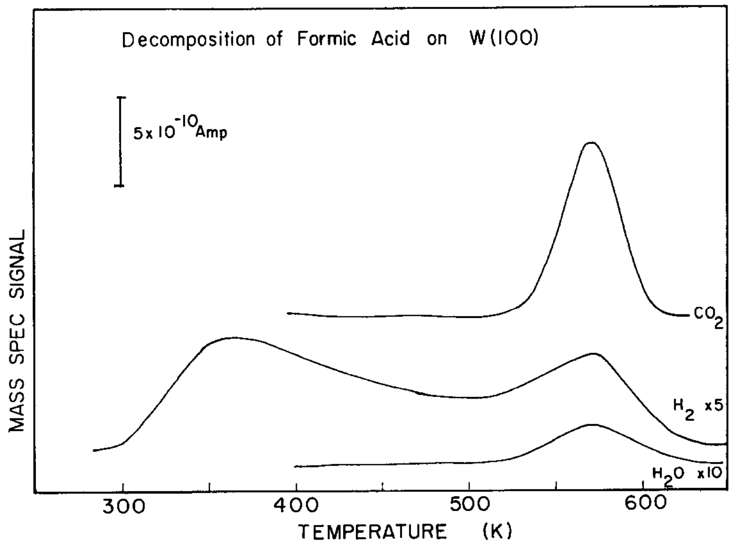

FIG. 2. Product desorption spectra for formic acid decomposition on W(100).

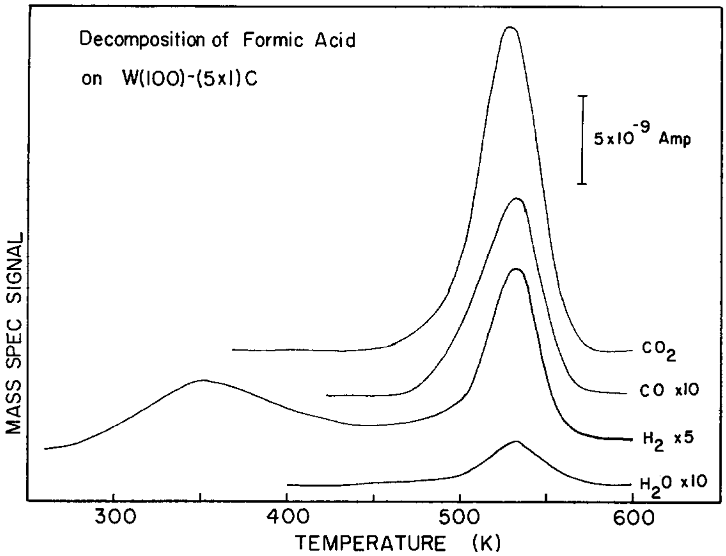

Fig. 3. Product desorption spectra for formic acid decomposition on W(100) − (5 × 1)C.

The evolution of CO was accompanied by oxygen buildup on the carbide surface, indicating that some CO_2 decomposed. Surface hydrogen atoms reduced some of the surface oxygen thus accounting for the water formation. As water was seen to form only after the formate decomposed on the initially clean W(100) surface, and was not seen to be formed where the low-temperature hydrogen peak occurred (see Fig. 2), it appears that the strongly adsorbed oxygen was not reduced, but

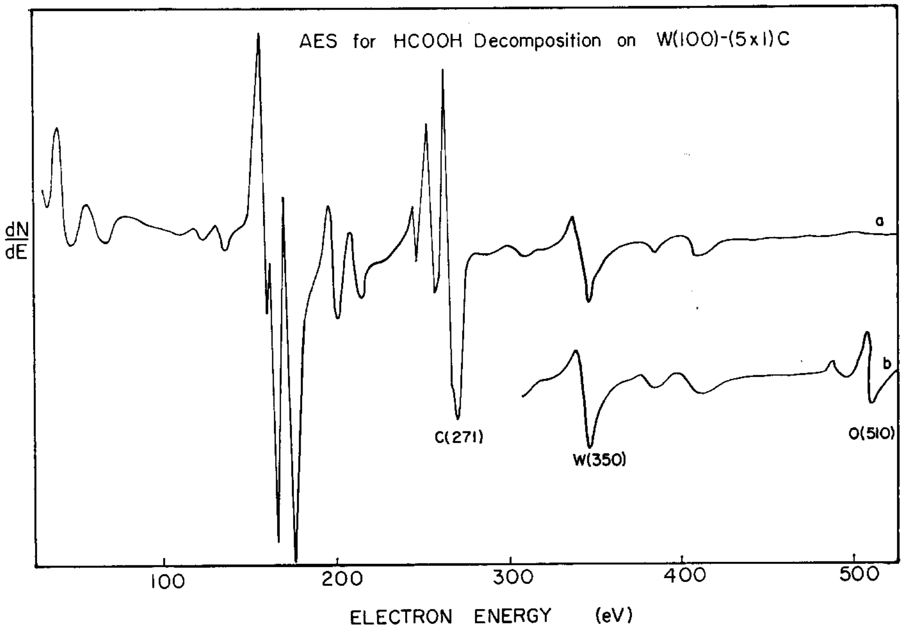

Fig. 4. Auger electron spectra for formic acid decomposition on W(100) − (5 × 1)C: (a) clean W(100) − (5 × 1)C; (b) after adsorption of HCOOH at 300 K and heating to 800 K.

only the more weakly bound oxygen formed during decomposition of the formate on top of the oxycarbide layer.

A surface carbide of tungsten significantly altered the mechanism for formic acid decomposition as was observed for surface carbides of nickel. The carbon passivated the very active clean tungsten surface. The results for formic acid decomposition was similar to those obtained for CO chemisorption; a surface carbide passivated the surface so that molecular intermediates predominated, as opposed to the atomic intermediates found on the clean tungsten surface. Additionally it was observed that a surface passivated by adsorbed carbon and oxygen from the decomposition of formic acid behaved similarly to a surface carbide, which was also found in the case of CO adsorption on a W(100) surface saturated with dissociated CO. However, the presence of oxygen was observed to reduce the activity of the surface much more than carbon. These results show that alloying tungsten with carbon passivates the very active tungsten so that it behaves more like the catalytically interesting group VIII and IB metals, which adsorb CO nondissociatively (*8*), and Fe, Cu, Ag, and Au on which the decomposition of formic acid appears to proceed primarily via a formate intermediate (*9, 10*).

ACKNOWLEDGMENT

The authors gratefully acknowledge the support of the National Science Foundation by the NSF-MRL Program through the Center for Materials Research at Stanford University. We also wish to express our appreciation for the National Science Foundation equipment Grant NSF-ENG-75-14191 without which this work could not have been accomplished.

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Received October 13, 1978