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Surface Microcatalysis: The Enhanced Selectivity of Ni(110) (4 × 5)C for Dehydrogenation of Formic Acid

We have studied the catalytic decomposition of formic acid on carbon contaminated Ni ⟨110⟩ in conjunction with our earlier work on the clean Ni ⟨110⟩ surface (*1*). The purpose of this work was to study the effect of surface carbon structures on the catalytic activity and selectivity of nickel in the decomposition of formic acid. This note reports our findings on carburized and graphatized Ni ⟨110⟩.

The apparatus used in this study was described elsewhere (*1*). It consisted basically of an ultrahigh vacuum system with AES, LEED, and flash desorption capabilities.

Our previous work showed that adsorption of formic acid at room temperature on a clean nickel ⟨110⟩ surface produced the flash desorption spectra shown in Fig. 1. CO_2 and H_2 desorbed in sharp peaks with the temperature of maximum desorption rate occurring at 388°K; CO desorbed in a broad peak with its maximum at 438°K; H_2 and CO readily adsorbed on this surface and upon flash heating desorbed with peak maxima at 353 and 438°K, respectively.

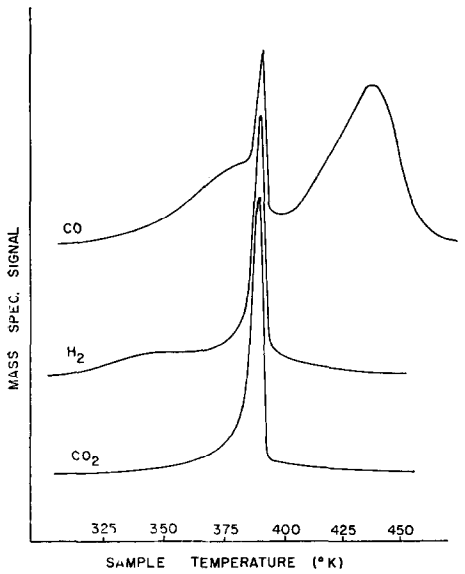

FIG. 1. Flash desorption spectra for 4L exposure of formic acid at 28°C.

Surface carbon was deposited by exposing the hot Ni ⟨110⟩ surface (570–620°K) to ethylene until the Auger spectrum showed no further increase in the size of the carbon (KLL) peak at 271 eV. Typical Auger spectra for the clean surface and the surface with saturation exposure to C_2H_4 are shown in Fig. 2 and curve a of Fig. 3. Hydrogen did not adsorb on the carbon covered surface at 223°K and above. Carbon monoxide adsorbed but desorbed at 348°K instead of 438°K as on the clean surface. In contrast to the clean surface, carbon dioxide adsorption, dissociatively or nondissociatively, was not detected after 10L exposure to the (4 × 5)C surface between room temperature and 223°K; CO_2 adsorbed dissociatively on the clean surface even at 223°K. The initial sticking probability of HCOOH at room temperature on the C_2H_4 exposed surface was unchanged from that of the clean surface; it was near unity. However the H_2/CO_2 desorption peaks from formic acid decomposition were significantly broadened and shifted to 438°K on the carbon covered surface as shown in Fig. 4.

The desorption of CO from the carburized surface due to HCOOH decomposition occurred at about the same temperature as the H_2 and CO_2, but smaller amounts of CO were produced than on the clean surface. The ratio of CO to CO_2 desorbed was not entirely reproducible and varied from 0.10 to 0.20 at saturation HCOOH exposure.

After heating the carburized surface to

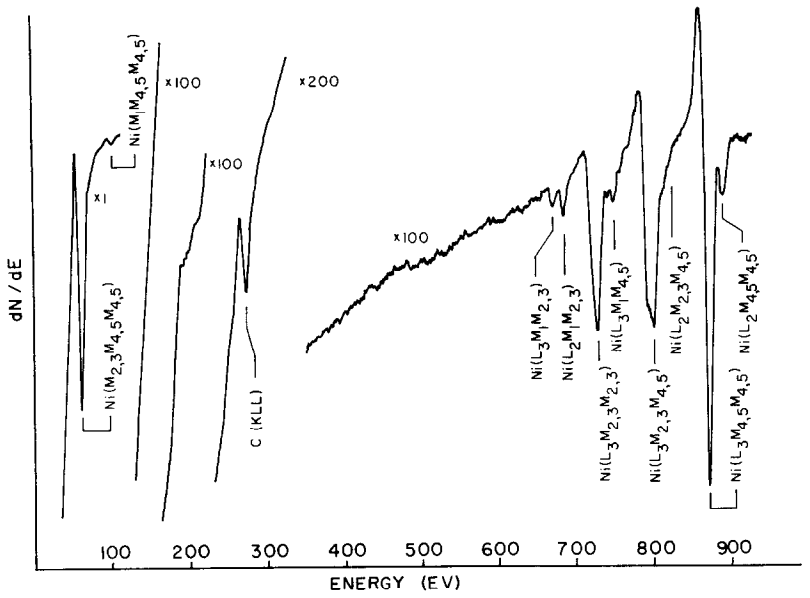

FIG. 2. Typical Auger spectrum of cleaned Ni⟨110⟩ V mod = 3.5 V rms.

775°K, the carbon Auger peak shape changed as shown in curve b on Fig. 3 with only a small decrease in the peak to peak magnitude. H_2 and CO again readily adsorbed on this surface and had flash desorption spectra corresponding to that of the clean surface; the flash decomposition spectrum of HCOOH was restored to that of the clean surface although the flash peaks of CO_2/H_2 occasionally were broader.

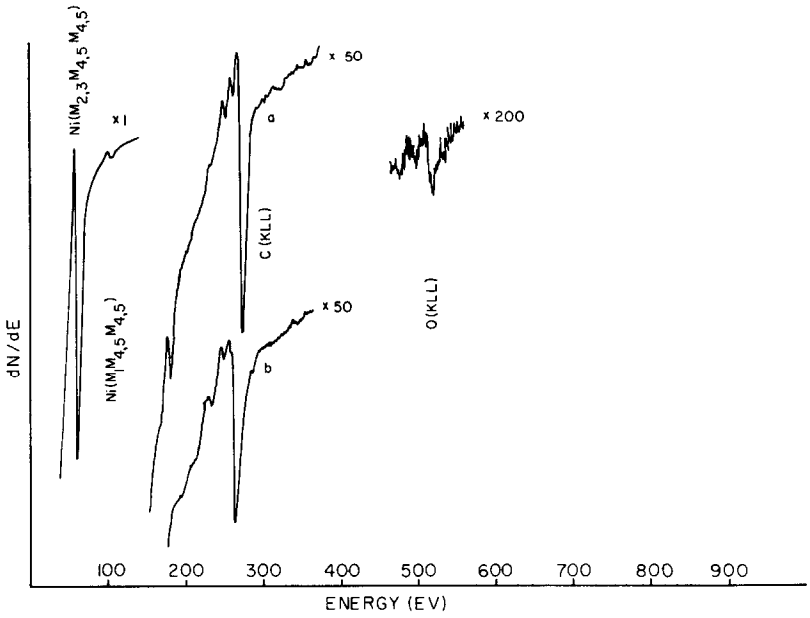

FIG. 3. Auger spectrum of carburized Ni⟨110⟩ with 3.0 V rms modulation voltage: (a) The 4 × 5 carbide Auger spectrum after 20 adsorption-flash decomposition cycles. C_{et} = 1.0. (b) The graphitic Auger spectrum formed after heating surface (a) to 500°C. C_{et} = 0.7.

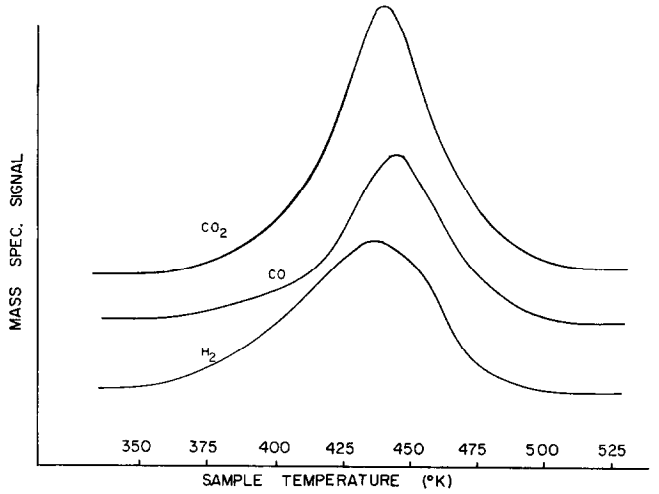

FIG. 4. Flash desorption spectra after exposure to 1.5×10^{14} molecules/cm^2 of HCOOH at 38°C.

Previous studies have shown that under our conditions of ethylene decomposition the Ni⟨110⟩ (4×5)C surface carbide forms (*5, 7*). The Auger line shape for the C (KLL) peak was typical of the carbide structure (*2–4*). Upon heating this structure it is known that surface graphite forms (*5–7*). Our results indicate that surface carbide acts as a catalyst to produce H_2 and CO_2 with greater selectivity than the clean surface, but that the maximum rate occurs at a higher temperature. This selectivity to CO_2 correlates well with the inability of the surface carbide to dissociatively adsorb CO_2. Evidently the decomposition of formic acid and the adsorption of CO_2 to produce CO involve similar binding sites. Heating the carbide surface apparently leads to the formation of graphite islands.

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