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THE SURFACE INTERMEDIATE H_2COO

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The oxidation of D_2CO was studied on Ag (110) with temperature programmed reaction spectroscopy. D_2CO was oxidized to $D_2COO_{(a)}$ upon adsorption, and this surface intermediate decomposed at approximately 225 K to yield deuterium and $DCOO_{(a)}$. Adsorbed DCOO decomposed to deuterium and CO_2 at elevated temperatures. The present experiment further demonstrated that $D_2COO_{(a)}$ is a reaction intermediate during formaldehyde oxidation by group IB metals, and that this intermediate is not thermally stable since it dissociates to deuterium and adsorbed formate well below room temperature.

In a previous communication it was concluded that the surface intermediate H_2COO was stabilized upon the adsorption of H_2CO on a partially oxidized Cu(110) surface at ≈180 K [1].

$$H_2CO_{(g)} + O_{(a)} \rightarrow H_2COO_{(a)} \,. \tag{1}$$

This reaction intermediate was inferred from the lack of water formation at low temperature during the temperature programmed reaction spectroscopy (TPRS) experiment [2] and the direct interaction of H_2CO with adsorbed atomic oxygen upon adsorption. The adsorbed H_2COO intermediate subsequently decomposed to hydrogen atoms and adsorbed HCOO when the surface was heated.

$$H_2COO_{(a)} \rightarrow H_{(a)} + HCOO_{(a)} \,, \tag{2}$$

$$H_{(a)} + H_{(a)} \rightarrow H_{2(g)} \,. \tag{3}$$

The stability of the H_2COO intermediate could not be directly determined because hydrogen evolution was desorption limited from the Cu(110) surface. The hydrogen atoms recombined and desorbed from the Cu(110) surface at ≈340 K [1]. It was inferred from the temperature programmed data that $H_2COO_{(a)}$ was dehydrogenated to $HCOO_{(a)}$ at ≈260 K on Cu(110) because a trace amount of water desorbed at

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this temperature. The oxidation of H_2CO was studied on Ag (110) to determine whether the $H_2COO_{(a)}$ also forms on other surfaces, and since hydrogen desorbs from the Ag (110) surface at much lower temperatures than from the Cu(110) surface the presence and stability of this intermediate could be *directly* observed with TPRS.

Molecular hydrogen or deuterium do not chemisorb easily on the group IB metals, but their atoms do [3,4]. Thus, the ionizer region of the UTI-100C quadrupole mass spectrometer was employed to generate deuterium atoms which were incident on the surface. An extremely small D_2 signal was observed to desorb from the Ag (110) surface during heating subsequent to D atoms exposure at about 180 K, but D_2 desorbed from the Cu(110) surface [1] in relatively large quantities under the same conditions ($\approx 10^{-6}$ Torr D_2 and 100 s exposure). The observation of D_2 desorption from Cu(110) was a clear indication that D atoms were deposited on the surface from the hot filament. The absence of D_2 desorption from Ag (110) showed that hydrogen atoms recombined and desorbed from the Ag (110) surface for temperatures $\leqslant$180 K. Pritchard [4] similarly concluded that at 195 K hydrogen atoms recombined and completely desorbed from silver films and not from copper films.

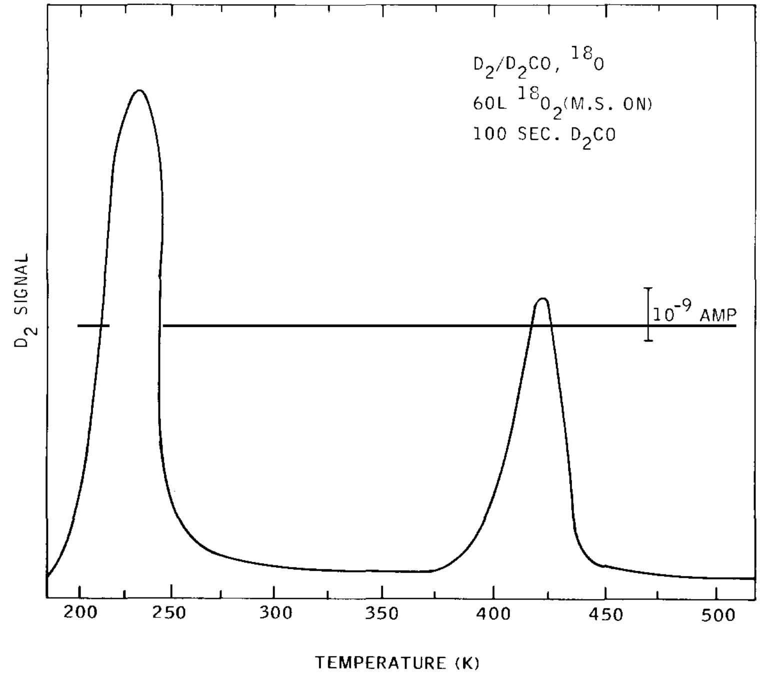
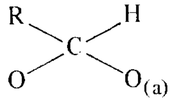


Fig. 1. TPRS of D_2 from oxidation of D_2CO on Ag(110).

Thus, the evolution of hydrogen above 200 K from the Ag (110) surface during a temperature programmed experiment can be taken as a clear indication of a reaction limited step which evolves hydrogen.

The desorption spectrum of D_2 subsequent to the adsorption of D_2CO on a partially oxidized Ag (110) surface was carefully measured and presented in fig. 1. The low temperature D_2 peak suggests that $D_2COO_{(a)}$ decomposed at approximately 225 K on Ag (110) to yield deuterium atoms and adsorbed DCOO since D_2 is not desorption limited on this surface. The high temperature deuterium peak corresponds to the decomposition of surface DCOO to deuterium atoms and CO_2. The present experiment further demonstrated that $H_2COO_{(a)}$ is a reaction intermediate during formaldehyde oxidation by group IB metals, and that this intermediate is not thermally stable since it dissociates to a hydrogen atom and adsorbed formate well below room temperature. Intermediates of the type



may form during heterogeneous oxidation of aldehydes on a variety of other metals and could possibly act as reactive intermediates in these surface reactions.

References

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