Identification of New Decomposition Intermediates of Formic Acid on the O/Mo(110) Surface

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In this communication, we identify the reaction intermediates of formic acid decomposition on an oxygen-modified Mo(110) surface. MoO_x is one of the most widely used oxidation catalysts,[1] while the formate species has been proposed to be an important intermediate in oxygenate synthesis.[2,3] Therefore, an understanding of this adsorption system is of interest both fundamentally and practically.

The experiments were carried out in an ultra-high-vacuum (UHV) chamber, which has been described in detail previously.[4] The oxygen precovered surface was prepared by dosing O_2 (99.998% purity) at 100 K and subsequently annealing to 600 K. A saturation oxygen coverage was achieved with an exposure of 100 langmuir, which gives an O(510 eV)/Mo(186 eV) AES ratio of 0.30. At an O/Mo AES ratio of 0.16, a (2 × 2) LEED pattern has been observed and assigned to correspond to an oxygen coverage of 0.25 monolayer.[5,6]

TPD spectra of H_2, H_2O, CO, CO_2, and HCOOH after dosing multilayer formic acid on an oxygen-saturated Mo(110) surface at 100 K are shown in Figure 1. Molecular desorption (masses 29 and 46) on the O/Mo(110) surface shows two desorption peaks at 160 and 255 K, which can be assigned to the desorption from the multilayer and the first chemisorbed layer, respectively. No hydrogen desorption feature was observed; however, extensive water desorption is evident between 100 and 500 K.

The HREELS spectrum in Figure 2, taken after dosing approximately five layers of formic acid at 90 K, is very characteristic of condensed formic acid. The spectrum acquired after annealing to 190 K exhibits peaks at 235, 450, 635, 1045, 1250, 1730, and 2950 cm^{-1}. The features at 450 and 635 cm^{-1} can be assigned to the Mo−O vibrations, while the peak at 1390 cm^{-1} is due to molecularly adsorbed formic acid. The features at 235 cm^{-1} are assigned to the lattice vibration of molecularly adsorbed formic acid and the Mo−O vibration of a formate species; the peak at 1730 cm^{-1} corresponds to the C=O vibrational mode. The features associated with molecularly adsorbed formic acid disappear upon further annealing to 250 K, consistent with the observed desorption of formic acid at 255 K in the TPD experiments. In addition to the Mo−O modes at 450 and 630 cm^{-1}, the spectrum acquired after annealing to 250 K is dominated by features at 235, 1045, 1730, 2950, and 3570 cm^{-1}, which are assigned to the Mo−O, C−O, C=O, C−H, and O−H vibrational modes, respectively.

According to the relevant coordination chemistry,[7,8] a formate species can be bonded to a metal center via a monodentate, a bidentate, or a bridging configuration. The splitting, $\Delta\nu$, between the OCO symmetric and asymmetric stretching vibrations in a formate complex has been shown to indicate its particular bonding configuration. For monodentate-bonded
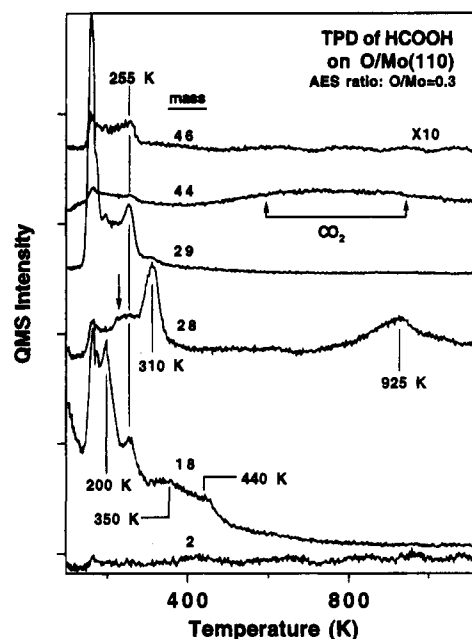

Figure 1. TPD spectra of formic acid from the O/Mo(110) surface following a saturation exposure at 95 K.
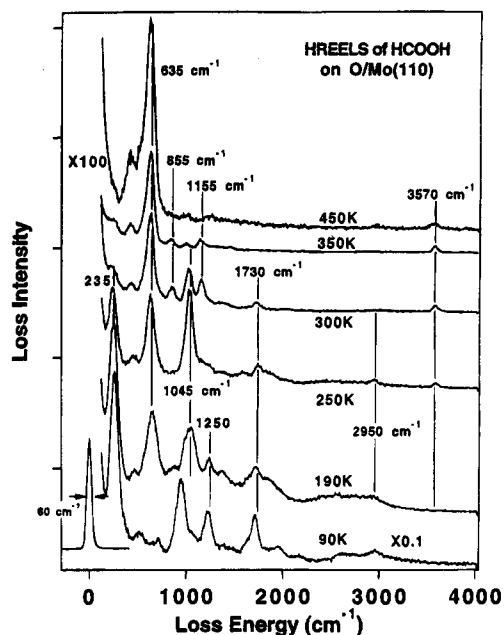

Figure 2. HREELS spectra taken after dosing 5 layers of formic acid to the O/Mo(110) surface with an O/Mo AES ratio of 0.30 and annealing to the indicated temperature.

formate, it is not meaningful to refer to the two OCO stretching vibrations as symmetric and asymmetric. Rather, two well-separated vibrational modes are evident due to two inequivalent single (C−O) and double bonds (C=O). The C−O stretching vibration in a monodentate-bonded formate, by analogy, should be comparable to the C−O vibrational mode in esters (RCO-OR′), which is usually very intense and found between 1000 and 1300 cm^{-1}.[9]

For formic acid adsorption on clean Mo(110), HREELS shows a feature at ~1350 cm^{-1}, rather than the intense feature at 1045 cm^{-1} observed for formic acid on O/Mo(110). This 1350 cm^{-1} feature has been assigned to the OCO symmetric

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vibration of a bridge-bonded formate.[10] On the O/Mo(110) surface, however, the presence of distinct C−O (1045 cm^{-1}) and C=O (1730 cm^{-1}) vibrational modes and the large separation between these two features clearly indicate the formation of a monodentate-bonded formate.

From vibrational spectroscopic studies, the formate species has been proposed as a reaction intermediate on various transition metal surfaces, including Pt(110),[11] Pt(111),[12,13] O/Pt-(111),[13,14] Ni(110),[15] O/Pd(100),[16] Pd(111),[17] O/Pd(111),[17] Rh-(111),[18] O/Rh(111),[18] O/Ag(111),[19] Cu(100),[20] Cu(110),[21] and Ru(001).[22,23] For most transition metals, a bridge-bonded formate has been identified, although a monodentate formate has been proposed for the O/Pt(111)[13] and Ru(0001)[23] surfaces, based on the appearance of an OCO asymmetric vibrational mode. This monodentate formate is stable only at relative low temperatures and is converted to bridge-bonded formate upon heating to 190−200 K. However, as shown by Dubois et al.,[24] the coexistence of molecular formic acid, even in trace quantities, leads to tilting of the formate species due to hydrogen bond formation between the formate species and an adjacent formic acid.

A monodentate formate has been proposed for several oxide surfaces.[25−29] Because the surface selection rule usually invoked for metal surfaces is not valid for oxide surfaces,[30] the identification of a monodentate species on oxide surfaces is largely based on geometrical arguments.[31] It is noteworthy, however, that the magnitude of the splitting between the symmetric and asymmetric OCO modes in these studies[25−31] is more characteristic of bidentate-bonded, rather than monodentate-bonded, formate.

The spectrum acquired after annealing to 300 K shows a decrease in the intensity of the formate-related features. At the expense of the formate features, two new peaks appear at 855 and 1155 cm^{-1}. These new features are assigned to correspond to $CO_2^{\delta-}$ adsorbed in a bent-bond configuration (see Figure 3). A $CO_2^{\delta-}$ species has been identified previously, subsequent to dosing CO_2, on Re(0001),[32] Pd(110),[33] and Ni(110).[34] Table 1 compares the vibrational frequencies of $CO_2^{\delta-}$ on these surfaces.

Further support for the presence of $CO_2^{\delta-}$ is found in the vibrational modes of C−H and O−H. As the characteristic

Table 1. Frequencies and Assignment of $CO_2^{\delta-}$

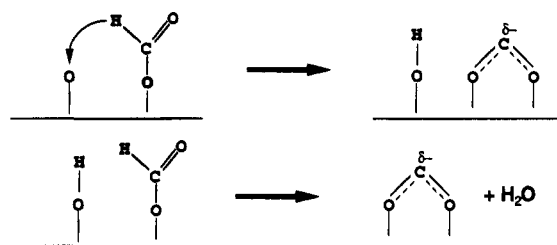|	ν(M−O)	δ(OCO)	ν(OCO)	ref
Re(0001)		650	1230	32
Pd(110)		770	1200	33
Ni(110)	410	750	1130	34
Mo(110)		855	1155	this work

Figure 3. Proposed mechanism for the decomposition of formate to form the $CO_2^{\delta-}$ species.

features of $CO_2^{\delta-}$ appear, the peak intensities of the features characteristic of the formate C−H vibrational modes attenuate, and those characteristic of the hydroxyl group grow in intensity. Furthermore, during the anneal to 300 K, water is the only hydrogen-containing desorption product. The lack of hydrogen evolution upon heating indicates hydrogen transfer from a formate species to an adjacent surface oxygen (or hydroxyl) to form the $CO_2^{\delta-}$ species and a hydroxyl group (or H_2O). This decomposition pathway is shown schematically in Figure 3.

The identification of a $CO_2^{\delta-}$ species as a decomposition intermediate of adsorbed formate is the first such observation, to our knowledge, although CO_2 has been observed frequently as a desorption product. That $CO_2^{\delta-}$ forms on O/Mo(110) can be attributed to the stability of the monodentate-bonded formate on this surface. As indicated in Figure 3, coadsorbed oxygen provides an energetically favorable pathway for hydrogen transfer from the mondentate-bonded formate. Surface oxygen also likely assists in stabilizing the $CO_2^{\delta-}$ species by blocking clean Mo(110) sites that would otherwise facilitate $CO_2^{\delta-}$ decomposition. It should be added that the $CO_2^{\delta-}$ species cannot be formed directly on O/Mo(110) via CO_2 adsorption, because of the relatively weak interaction between CO_2 and Mo and O/Mo.

The decomposition of formate has been extensively studied on late transition metal surfaces. From these studies, three mechanisms for formate decomposition have been proposed:[35] (i) C−H bond cleavage, yielding CO_2 and H_2; (ii) C−O bond cleavage to form CO and H_2O (or H_2); and (iii) the "hot hydrogen" mechanism,[36] where the hydrogen atom produced by C−H bond cleavage inserts into the C−O bond of a neighboring formate, to produce CO and a hydroxyl group. The results of the present study indicate that a new mechanism for formate decomposition is operative on early transition metals that form strong metal−oxygen bonds.

In summary, the adsorption of formic acid on an oxygen-modified Mo(110) surface leads to the formation of a formate species bonded in a monodentate configuration. Upon heating, this formate species decomposes to form a stable $CO_2^{\delta-}$ species.

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