DEHYDRATION OF CARBOXYLIC ACIDS ON THE MgO(100) SURFACE

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The interaction of formic and acetic acids with the MgO(100) surface has been studied under UHV conditions using XPS and TPD. Both acids dissociated heterolytically on the MgO surface, forming surface formate and acetate species respectively. The carboxylates decomposed at 520 K into dehydration products $H_2O + CO$ from HCOO, and $H_2O + CH_2CO$ from CH_3COOH.

1. Introduction

The decomposition of formic acid over metal oxides generally follows two channels, dehydrogenation and dehydration [1]. The selectivity between these two channels has been reported to correlate well with the acid-base properties of metal oxides. For instance, under continuous flow reaction conditions, dehydrogenation is favored on basic oxides such as MgO (50 to 100% dehydrogenation products, depending on aspects of the sample history such as pretreatment temperature), while dehydration prevails on acidic oxides such as Al_2O_3 (30 to 100% dehydration products) [1]. A spectrum of oxides with intermediate acidity, ZnO, Fe_2O_3, Cr_2O_3, TiO_2 and SiO_2, fall between these two extremes [1]. Parallel behavior has been observed for decomposition of alcohols over metal oxides as well [2], and the selectivity of decomposition of isopropanol to propylene vs. acetone has often been used to monitor the acid-base properties of metal oxides [3–6]. In contrast, a temperature programmed desorption study under ultra high vacuum conditions by Parrott and coworkers [7] has demonstrated that dehydration is the major channel for ethanol and acetic acid decomposition on MgO powders. We have also noted large discrepancies in reported alcohol dehydra-

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tion/dehydrogenation selectivities on ZnO between steady state and TPD studies [8,9]. The work reported here shows that formic and acetic acids decompose on the MgO(100) surface in TPD experiments to form exclusive dehydration products UHV conditions.

2. Experimental

The decomposition of carboxylic acids on the MgO(100) surface was monitored by temperature programmed desorption under UHV conditions, and the surface intermediates were characterized by X-ray photoelectron spectroscopy. Two UHV systems were used in this study. The TPD experiments were conducted in a Physical Electronics UHV system equipped with an UTI 100C quadrupole mass spectrometer. A glass envelope with an 8 mm diameter aperture was placed over the mass spectrometer section to reduce the background contribution to TPD spectra. A VG ESCALAB system was used to conduct XPS measurements. Detailed descriptions of these two systems have been given previously [10,11]. The MgO single crystal (Atomergic), 8×8 mm square with a thickness of 1.5 mm, was polished with 1 micron diamond paste. The clean MgO(100) surface was produced by argon ion bombardment and annealing at 750 K. Heating and cooling were supplied through a tantalum wire fixed around the sample edges. Since the insulating MgO sample was subject to electrostatic charging, all XPS binding energies reported are referenced to the Mg(2p) peak at 50.8 eV. This binding energy was determined from the corresponding peak on a MgO thin film sample as described previously [11].

3. Results

The C(1s) spectra of surface species derived from HCOOH and CH_3COOH on the MgO(100) surface as a function of temperature are illustrated in fig. 1. The MgO sample was exposed to the acids at room temperature to saturation coverage. As shown in fig. 1a, the HCOOH-dosed surface exhibited a C(1s) peak at 290.4 eV. This peak became smaller with increasing temperature and finally disappeared by 550 K. The peak position, however, did not change with temperature. This peak can be assigned to surface formate species as its binding energy is the same as that of a surface formate derived from HCOOH on a MgO thin film surface, which has been identified previously [11]. Similar results were observed on the CH_3COOH-dosed surface as shown in fig. 1b; two C(1s) peaks at 286.6 and 290.0 eV with equal intensity were observed over the entire temperature range before they disappeared above 450 K. These two peaks are at the same position as those of surface acetates on the MgO thin film surface reported previously [11], and can be assigned to the methyl and carboxyl carbons of

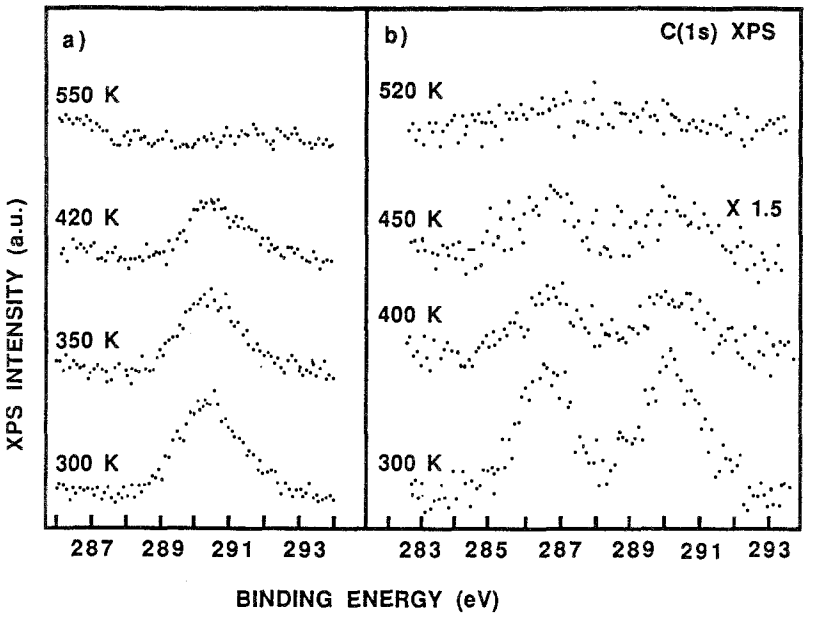

Fig. 1. C(1s) spectra from (a) HCOOH- and 9b) CH_3COOH-dosed MgO(100) surfaces as a function of temperature.

surface acetates, respectively. The 3.4 eV separation of the methyl and carboxyl peaks is in the range characteristic of acetates on oxide surfaces [12]; the corresponding separation for molecular acetic acid is 4.0 eV [13]. Adsorption experiments at lower temperature exhibited essentially the same trends as those shown in fig. 1; little change was observed from 170 K to room temperature. Likewise, little dependence of the carboxylate XPS behavior was found on the annealing treatment of the ion-bombarded Mg(100) surface prior to adsorption.

TPD experiments were performed to investigate the reactions of these surface carboxylates at high temperatures. Fig. 2 displays the results from MgO(100) surfaces dosed with DCOOD and CH_3COOH at room temperature. The CDOOD-dosed surface exhibited coincident D_2O and CO desorption peaks at 520 K, suggesting that surface formate species decomposed into net dehydration products at elevated temperatures. A weak but broad DCOOD peak in fig. 2a, attributed to the recombination of surface formate and hydrogen species, may account for the gradual decrease of the formate C(1s) peak between 300 and 420 K shown in fig. 1a. The CH_3COOH-dosed surface also produced dehydration products exclusively; coincident CH_2CO (ketene) and H_2O peaks were observed at 520 K (fig. 2b). Among the species which were monitored but not detected were hydrogen, methane, methanol and formaldehyde (from formic acid), and hydrogen, acetaldehyde, methane and acetone (from acetic acid). These TPD results indicate that little dehydrogenation or decarboxylation occurred on the formic and acetic acid-dosed MgO(100) surfaces. The formate and acetate species

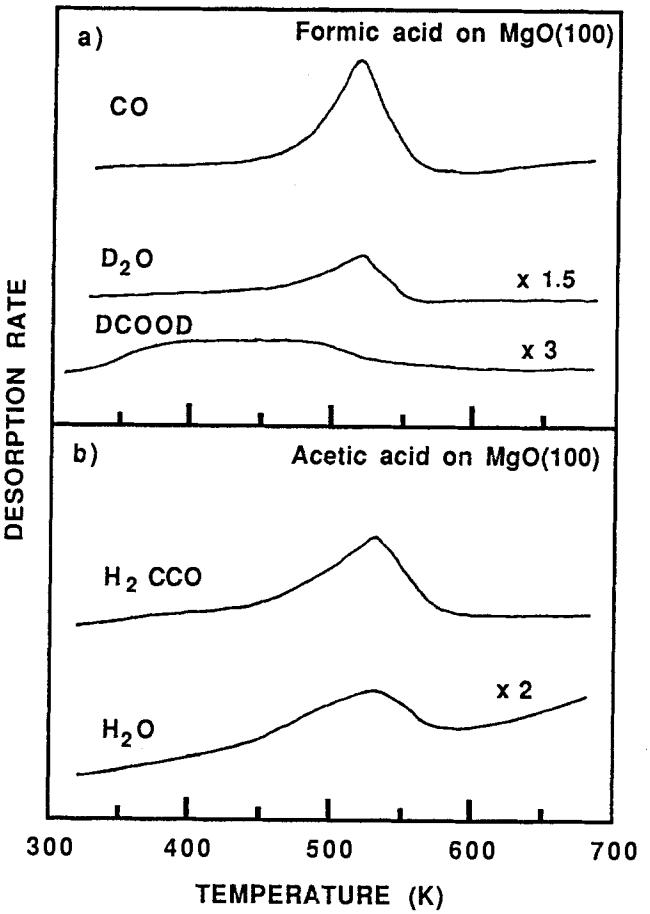

Fig. 2. TPD spectra from the MgO(100) surfaces dosed with (a) HCOOH and (b) CH_3COOH at 300 K. Heating rate = 0.8 K/sec.

exhibited comparable thermal stabilities, as dehydration occurred at the same temperature for both species. This observation is somewhat unusual; acetate species are generally more stable than formates on both oxide [12,14,15] and metal [16,17] surfaces.

4. Discussion

The TPD and XPS results can be summarized by the following reaction sequences. From HCOOH

$$HCOOH(g) \xrightarrow[300\ K]{MgO} HCOO(ad) + H(ad) \quad (1)$$

$$HCOO(ad) + H(ad) \xrightarrow[520\ K]{} CO(g) + H_2O(g) \quad (2)$$

and from CH_3COOH

$$CH_3COOH(g) \xrightarrow[300\ K]{MgO} CH_3COO(ad) + H(ad) \quad (3)$$

$$CH_3COO(ad) + H(ad) \xrightarrow[520\ K]{} CH_2CO(g) + H_2O(g) \quad (4)$$

The hydrogen atoms produced by heterolytic adsorption of Brønsted acids would be bound to surface oxygen anions, and are often represented as hydroxyls. We wish to emphasize however, that there is no evidence in this or our previous studies on MgO surfaces [11,18] for the lability of the surface oxygen atoms. Dehydration of carboxylic acids is a stoichiometric reaction and does not require the net consumption of lattice oxygen. However, on reducible oxides water is produced by reaction of the acid hydrogen with lattice oxygen atoms at temperatures much lower than those of carboxylate deposition; the surface stoichiometry is restored by the carboxylate decomposition reaction [12,15,19]. The coincidence of the water and carbon monoxide or ketene peaks from carboxylic acid dehydration on MgO suggests that, on this oxide, net dehydration does not involve reduction and reoxidation of the surface, i.e., lattice oxygen atoms are not removed.

As we have noted previously [8,9,15,20,21], dehydration/dehydrogenation selectivities of alcohols and carboxylic acids are dubious measures of catalyst acid-base properties. Dehydration/dehydrogenation selectivities are clearly influenced by other factors, including the structure of the reactant, the extent of reduction of the oxide and the redox properties of the oxide. However, based on our work and that of others on both powder and single crystal samples of pure oxides, two generalizations may be made. The first is that temperature programmed desorption experiments generally produce higher dehydration selectivities than observed for catalytic reactions at steady state. The second is that for TPD of any given reactant, dehydrogenation is favored on oxides which are more easily reduced. The second generalization can be explained by the fact that net dehydration of alcohols or carboxylic acids does not require reduction of the oxide but oxidative dehydrogenation does. The first generalization above suggests that the presence of reactants and products in the gas phase (as in a steady state experiment) can influence the reaction selectivity of adsorbed intermediates. We consider below the relevance of these generalizations to the present results.

Alkoxide and carboxylate intermediates on metal oxide surfaces can follow a number of reaction pathways in addition to dehydrogenation and dehydration; these include oxidation, esterification, and etherfication (for alkoxides), and reduction, ketonization, and decarboxylation (for carboxylates). Some of these (e.g., reduction of carboxylates to aldehydes) are favored by partial reduction of the surface, others (e.g., ether formation by alkoxide coupling, ketone formation by carboxylate coupling) by the presence of cations with multiple coordination vacancies on a fully oxidized surface [19,22]. Both of these can be eliminated in the present case. The ideal MgO(100) surface contains five-fold coordinated

Mg^{2+} and O^{2-} ions; these have sufficient basicity to dissociate a variety of molecules including carboxylic acids and alcohols [23]. This surface is representative, however, of the majority of the surface of MgO powders [24], and the acetic acid decomposition selectivity on the MgO(100) surface in the present study was indistinguishable from that reported by Parrott et al. [7] for acetic acid TPD on MgO powders. Thus the absence of activity for formic acid dehydrogenation or acetic acid decarboxylation on Mg(100) cannot be attributed to the absence of specific sites required for these reactions. It is quite consistent, however, with the suggestion that dehydration selectivities on basic oxides are higher on less reducible oxides; MgO is unreduced in these experiments and is highly selective for dehydration.

The question then becomes how this selectivity can be moderated by the presence of species such as alcohols or water in the gas phase. Both Parrott et al. [7] and Shido et al. [25] have addressed this issue. The former workers suggested that dehydrogenation of adsorbed ethoxides to form acetaldehyde occurs by hydride transfer to alcohol molecules; in the absence of molecular species such as in a TPD experiment, no dehydrogenation is observed. Shido et al. [25] examined the formation of formates on MgO powders by reaction of CO with adsorbed hydroxyls, and the rate and selectivity of decomposition of the formates produced in this fashion. They observed dehydration of formates to $CO + H_2O$ exclusively in the absence of gas phase water; in the presence of water formate dehydrogenation selectivities as high as 70% were observed. These results are quite consistent with the results of this study for formic acid-derived formates, and with those of Mars et al. [1] which showed higher formic acid dehydrogenation selectivities on MgO under flow reactor conditions than under vacuum. Shido et al. [25] attribute the effect of water on the formate decomposition selectivity to coadsorption of water on the same MgO sites to which the formate is bound, with the electron density influenced both by electron donation from the oxygen atom of H_2O to the Mg cation, and electron withdrawal by the water hydrogen from surface oxygen anions. Both the donor and the acceptor properties of water (and likewise methanol) were invoked, since stronger donors such as pyridine and tetrahydrofuran did not lead to measurable formate dehydrogenation.

A simpler explanation than either of the above may also be advanced. Iwasawa [26] has suggested that as many as six different types of hydroxyl groups may be distinguished on MgO. Even on well-defined MgO surfaces, two types of hydroxyls are formed by heterolytic dissociation of water: those formed by transfer of protons to lattice oxygen and those which represent the remaining hydroxyl moieties bound atop surface magnesium cations. These two species can be distinguished by XPS: the atop OH groups exhibit O(1s) binding energies 2.1 eV greater than that of lattice oxygen [27]; however, protonation of lattice oxygen does not produce a measurable shift from the position of the lattice O(1s) peak [11]. Coadsorption of Brønsted acids with water on MgO surfaces could open a reaction channel involving these atop hydroxyl groups, presumably leading to

enhanced dehydrogenation selectivities. This channel would not be available in alcohol or carboxylic acid TPD experiments on dehydroxylated surfaces, since no atop hydroxyls would be present. Unfortunately this hypothesis is difficult to test on the MgO(100) surface. We have previously demonstrated that a negligible amount of H_2O dissociation occurs at 300 K on a well annealed MgO(100) surface; the population of five-fold coordinated Mg^{2+} cations with hydroxyl groups appears to require dissociation of water at lower coordination sites and migration of hydroxyls from these sites [27]. Further, in the absence of gas phase water, adsorbed water and its dissociation products are readily displaced by stronger Brønsted acids [20]. Given these limitations, it is not surprising that TPD experiments on MgO powders and single crystals have indicated high dehydration selectivities for alcohols and carboxylic acids.

5. Conclusions

Formic and acetic acids adsorb heterolytically on the five-fold coordinated Mg-O site pairs of the MgO(100) surface to form the corresponding carboxylates. Under UHV conditions dehydration is the only reaction observed in thermal decomposition of these stable carboxylates. The observation of high dehydration selectivities on this basic oxide is consistent with the nonreducible character of MgO and with the absence of coadsorbed water or hydroxyl species under the conditions of these experiments.

Acknowledgements

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