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Acid-base reactions on model MgO surfaces

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Three MgO surfaces of different structures have been employed as models for study of the acid-base properties of MgO. Surface spectroscopies including XPS, UPS, and ISS were used to determine the nature and the absolute coverage of surface intermediates, and the nature of bonding sites upon adsorption of Brønsted acid molecules on these surfaces. Different behavior patterns of the Brønsted acid molecules with varying strengths on the three model surfaces provide insights into the site requirements for dissociation of Brønsted acids on MgO. The base-catalyzed Cannizzaro reaction of formaldehyde was observed on these model surfaces under UHV conditions.

Keywords: Acid-base reactions; MgO; carboxylic acids; alcohols; formaldehyde

1. Introduction

Adsorption experiments using Brønsted acid molecules have traditionally been used to characterize the acid-base properties of MgO surfaces. Among the problems of interest in these studies are the nature of surface intermediates and bonding sites, the strength of Brønsted acids with respect to the MgO surface, and the site requirements for the dissociation of molecules with different acidities. Surface science techniques have certain advantages for understanding these problems in that the experiment can be conducted on well-defined surfaces, with a number of electron spectroscopies available for characterization. For example, an XPS and UPS study by Onishi and coworkers has shown that the well-ordered MgO(100) and the defect-rich MgO(111) planes exhibit different activities for dissociation of Brønsted acid molecules [1]. Similar investigations using three model MgO surfaces have been conducted in this laboratory, and the current paper summarizes the results from these studies. An attempt is made to demonstrate the application of surface science techniques for studying the acid-base properties of materials and the information that can be obtained by this approach.

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2. Experimental

Experiments reported here were all conducted in ultra-high vacuum (UHV) chambers equipped with facilities for X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS), ion scattering spectroscopy (ISS), low energy electron diffraction (LEED), ion bombardment and gas introduction. The clean MgO(100) and Mg(0001) surfaces were prepared by polishing with diamond paste, and sputter-cleaning in vacuum followed by annealing. Thin oxide films were formed on the metal surface by exposure to ca. 100 L O_2 at room temperature. The samples could be heated and cooled in the UHV chambers. The details about the UHV systems and sample preparation and mounting have been described previously [2,3].

3. Results and discussion

3.1. THREE DIFFERENT MODEL MgO SURFACES

Three different model MgO surfaces have been used in this study. They are: 1) the annealed MgO(100) surface, 2) an ion-bombarded MgO(100) single crystal plane, and 3) a MgO thin film surface. The annealed MgO(100) surface was prepared by annealing the clean MgO(100) single crystal at 900 K for 2 hours under UHV conditions. The surface exhibited a sharp LEED pattern with square symmetry, indicative of a well-ordered structure. This surface is expected to contain mostly MgO pairs with 5-fold coordination.

Bombardment of the MgO(100) plane with argon ions produces a surface with more defects than the annealed MgO(100) plane. It has been proposed [4] that the bombardment does not alter the MgO stoichiometry significantly. The primary effect of ion bombardment is an increase in the number of exposed ions and a decrease in the average coordination number of surface Mg-O pairs.

The third model surface is the MgO thin film formed on the Mg(0001) single crystal plane by thermal oxidation in vacuum. Angle-resolved XPS experiments demonstrated that the film was continuous, with a one-to-one stoichiometry, and thickness around 20 Å [2]. Most importantly, this surface has a crystallographic structure different from the MgO(100) plane. It has been proposed on the basis of LEED observations that the MgO thin film formed on the Mg(0001) surface possesses a MgO(100)-like structure, i.e., MgO(100) domains with three orientations 120° relative to each other [5]. However, angle resolved ISS experiments demonstrated that the angular dependence of the ratio of oxygen to magnesium ISS peak area could not be accounted for by the structures of either the MgO(100) surface or MgO(100) domains [6]. Instead, this surface is most likely covered by oxygen, as in the polar MgO(111) structure [6]. Although the exact crystallographic structure of the thin film surface is uncertain, it provides an

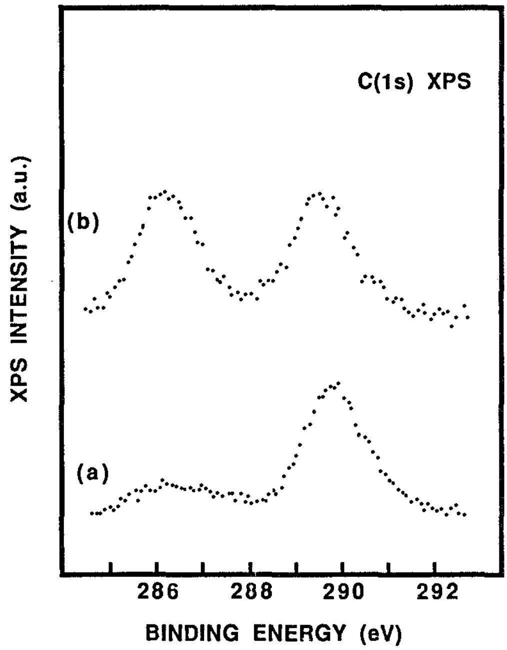


Fig. 1. C(1s) spectra of the (a) formic acid and (b) acetic acid dosed MgO thin film surfaces.

additional model to the annealed and bombarded MgO(100) surfaces. Moreover, charged particle spectroscopies can be carried out on it without electrostatic charging. This leads to high quality XPS data and permits collection of ISS and UPS data without the use of neutralization devices normally required for insulating samples such as bulk MgO.

3.2. SURFACE INTERMEDIATES, RELATIVE ACIDITY AND BONDING SITES

Intermediates derived from Brønsted acid molecules on MgO surfaces can be identified readily by electron spectroscopies. Figs. 1 and 2 display the XPS and UPS spectra from the carboxylic acid-dosed MgO thin film surfaces. The C(1s) XPS peaks at 290.1 eV in fig. 1 and the number and locations of the four peaks in the UPS difference spectrum of fig. 2 are quite consistent with the formation of carboxylate species on the surface via the heterolytic dissociation of the corresponding carboxylic acids [3]. Similar adsorption experiments showed that all the Brønsted acid molecules used in this study, including HCOOH, CH_3COOH, CH_3OH, C_2H_5OH, H_2O and C_2H_2, underwent heterolytic dissociation on all the model surfaces to form the corresponding conjugate base anions [3,7], except that the dissociation of weaker acids on the MgO(100) surface required low temperature adsorption or surface modification by bombardment, as shown below.

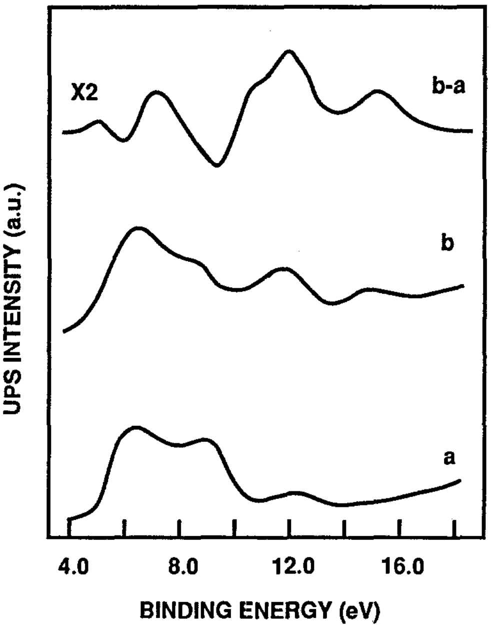


Fig. 2. UPS spectra of the formic acid-dosed MgO thin film surface at different temperatures. (a) Clean MgO thin film surface. (b) HCOOH-dosed surface.

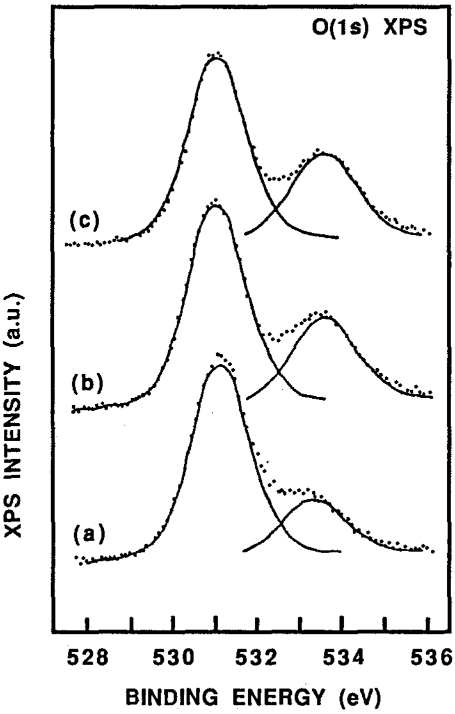


Fig. 3. Displacement of surface hydroxyls by formic acid on the MgO thin film surfaces. (a) Surface dosed with H_2O at 300 K for 100 Langmuirs. (b) Surface in (a) dosed with HCOOH at 300 K, saturated. (c) Clean MgO thin film surface dosed with HCOOH at 300 K, saturated.

Fig. 3 demonstrates how the relative acidities of different molecules can be determined by displacement experiments. It can be seen that the water-dosed MgO thin film surface exhibited an O(1s) XPS peak at 533.1 eV (fig. 3a), corresponding to surface hydroxyl groups [2]. This peak, however, was replaced by an O(1s) peak at 533.4 eV from surface formates upon exposure of the water-dosed surface to formic acid (fig. 3b), indicating that the surface hydroxyl groups are displaced completely by formic acid. In other words, water is a weaker acid than formic acid on MgO. Similar information can also be obtained from blocking experiments and coverage measurements, and the order of the relative acidities of the molecules studied on the MgO model surfaces has been determined as follows [7]:

$$HCOOH, CH_3COOH > H_2O, CH_3OH, C_2H_5OH > C_2H_2.$$

This order is in good agreement with that determined on MgO powders from IR, UV-visible and ESR experiments [8,9], indicating that the surfaces under study are good models of polycrystalline MgO as far as the acid-base properties are concerned.

In the literature the assumption of heterolytic dissociation of Brønsted acids on MgO surfaces and the assignment of adsorption sites have been based on the observation of conjugate base anions by UV-visible and IR, and of the proton

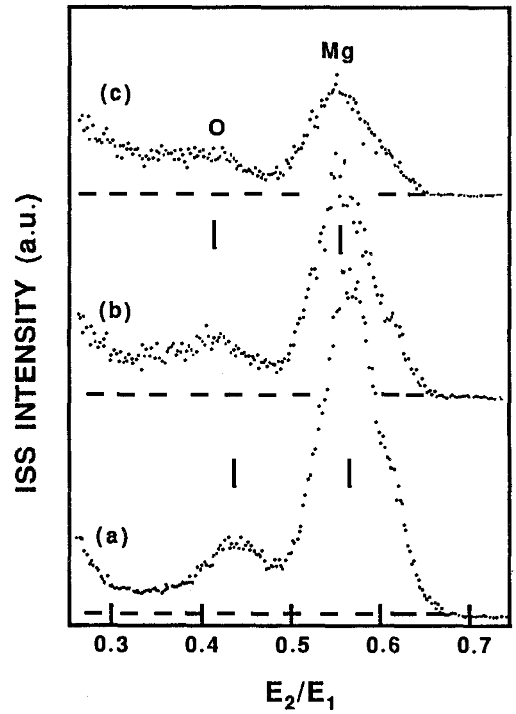


Fig. 4. ISS spectra from (a) the clean MgO thin film surface and thin film surfaces dosed with (b) H_2O, and (c) CD_3COOD to saturation at 300 K.

adsorbed on lattice oxygen by IR spectroscopy [9]. The following experiment with ISS provides direct evidence of the binding of conjugate base anions to surface Mg^{2+} sites [7]. Fig. 4 shows ISS spectra from the clean MgO thin film surface and thin film surfaces dosed with H_2O and CD_3COOD. It can be seen that the clean surface exhibits both oxygen and magnesium peaks. Upon adsorption of acids on the surface, the magnesium peak was attenuated considerably, while much smaller changes in the *absolute* intensity in the vicinity of the oxygen peak occurred. The O/Mg peak height ratio decreased from ca. 0.25 to 0.35 to 0.6 in curves a to c of fig. 4. The preferential attenuation of the Mg^{2+} signal can be ascribed to the blockage of Mg^{2+} sites by the conjugate base anions, i.e., OH^- and CD_3COO^-, since ISS is only sensitive to the topmost layer of solids and is dependent upon the physical collision between probing ions and surface atoms [10]. Alternatively, these adsorbed anions may attenuate the signal from the cations to which they are bound by neutralization of the incident or scattered ions [6]. In any case, the magnesium signal is attenuated more than oxygen signal due to the larger sizes and greater electron densities of the conjugate base anions than of the proton. The greater attenuation of the magnesium signal by carboxylic acids than by water may reflect the larger size of the carboxylates and/or their higher coverage.

3.3. SITE REQUIREMENTS FOR THE DISSOCIATION OF MOLECULES OF DIFFERENT ACIDITIES

Coverages of conjugate base anions from several Brønsted acid molecules on MgO model surfaces at room temperature are listed in table 1. The coverage in monolayers is estimated from the area of the corresponding C(1s) or O(1s) XPS peaks [7]. Three classes of Brønsted acids can be discerned from the results in table 1 in order of decreasing acid strength: 1) carboxylic acids, 2) alcohols and water, and 3) acetylene. For instance, their coverages on the thin film surface run from one to one half and one sixth monolayer, respectively. The results in

Table 1

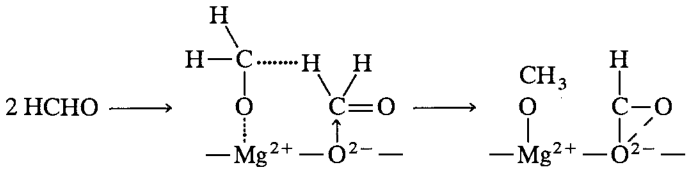
Coverages of dissociated species on model MgO surfaces at 300 K (in monolayers)

	Thin film	Sputtered MgO(100)		Annealed MgO(100)	
Adsorption temperature	150 K	170 K	300 K	170 K	300 K
HCOOH	1.00	–	0.71	0.68	0.67
CH_3COOH	0.93		0.68	–	0.60
CH_3OH	0.56	0.48	0.34	0.37	0
C_2H_5OH	0.44	–	–	–	–
H_2O	0.66	0.80	0.50	0.50	0
C_2H_2	0.16	0.15	0	0	0

table 1 demonstrate that the three model surfaces have different reactivities toward the dissociation of Brønsted acid molecules. MgO thin film and sputtered MgO(100) surfaces exhibit stronger interaction with these molecules than the annealed MgO(100) surface. The coverages on the first two surfaces were consistently larger than that on the annealed MgO(100) surface under the same conditions. The results that distinguish the annealed MgO(100) from other two surfaces most are the absence of adsorption of water and methanol at room temperature, and of acetylene even at low temperature. The lower reactivity of the annealed MgO(100) surface may result from its higher population of five-fold-coordinated Mg-O pairs. In other words, while strong acids such as carboxylic acids can dissociate on all Mg-O pair sites, Mg-O pairs with coordination numbers less than five are necessary for the dissociation of weaker Brønsted acids.

3.4. CANNIZZARO REACTION OF FORMALDEHYDE ON MgO

Different from the general scheme of formaldehyde oxidation into formate species on metal oxide and oxygen-dosed transition metal surfaces, both hydrogenation and oxidation of formaldehyde, i.e., a Cannizzaro-type disproportionation reaction, were observed on formaldehyde-dosed MgO model surfaces [11]. As shown in fig. 5, two C(1s) peaks at 287.4 and 290.3 eV from the formaldehyde-dosed MgO thin film surface at elevated temperatures are indicative of the formation of surface methoxides and formates. Similar results were also obtained from the formaldehyde-dosed MgO(100) surface. The following mechanism is proposed to explain the observed reaction.



Analogous to the solution-phase Cannizzaro reaction, the key step in this reaction is postulated to be a concerted hydride transfer from one formaldehyde molecule to another on the surface. This transfer would be facilitated by the electron donation from the surface lattice oxygen to the carbonyl carbon in the formaldehyde molecule adsorbed on an O^{2-} site, weakening the H-C bond in the molecule. Thus it is likely that the O^{2-} site on MgO surfaces plays essentially the same role in initiating the reaction as the hydroxyl anion in basic aqueous solutions.

4. Conclusions

Brønsted acid molecules, including HCOOH, CH_3COOH, H_2O, CH_2OH, C_2H_5OH, and C_2H_2 undergo heterolytic dissociation on MgO thin film and

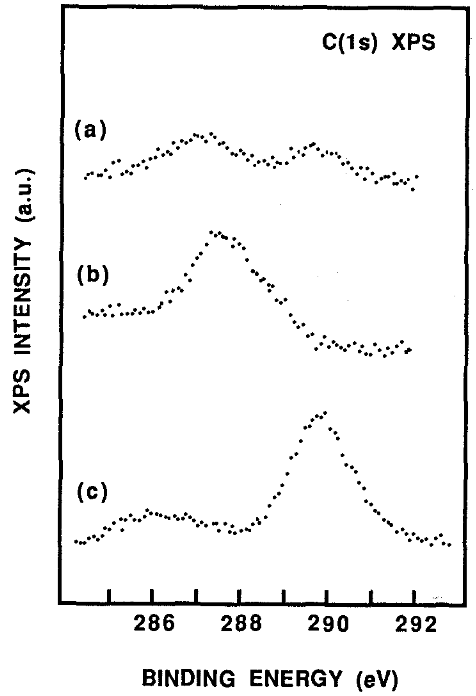


Fig. 5. Comparison of the C(1s) spectrum of (a) the formaldehyde-dosed MgO thin film surface at 350 K and those for (b) CH_3O (ad) and (c) HCOO (ad) species derived from methanol and formic acid, respectively.

sputtered MgO(100) surfaces. There is little C_2H_2 adsorption on the annealed MgO(100) surface, and the dissociation of H_2O and CH_3OH on this surface requires low temperature adsorption. The lesser reactivity of the annealed MgO(100) surface suggests that the Mg-O pairs with coordination number less than five are necessary for the dissociation of weaker acids. The bonding of conjugate anions to surface Mg^{2+} sites is evidenced by ISS experiments. The Cannizzaro reaction of formaldehyde on MgO model surfaces reveals the basic character of surface O^{2-} sites.

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