

# Vibrational Spectroscopy Study of H<sub>2</sub>O on Pd/MgO(100) Films

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A study of water on Pd/MgO(100) films prepared in situ upon Mo(100) single crystals has been performed by using low-energy electron diffraction, high-resolution electron energy-loss spectroscopy, and ultraviolet photoelectron spectroscopy in an ultrahigh vacuum system. The results show that the adsorption of water on MgO(100) film surfaces is enhanced significantly owing to the presence of Pd particles. The formation of a hydroxyl group suggests a dissociation of the water. The size and density of Pd particles on the substrate of MgO(100) films play an important part in the adsorption of water.

## 1. Introduction

Metal clusters supported on metal-oxide surfaces have been widely used as catalysts for various chemical reactions.<sup>1–3</sup> Catalytically active transition metal particles were dispersed on inert oxide substrates in order to maximize the surface exposed to the reactants and to increase the catalytic efficiency. A molecular-scale understanding of the energetics and mechanisms of catalytic reactions could open new avenues to the design of catalysts with specific functions. It is of special interest that nanocatalysts consisting of small size-selected clusters on uniform adsorption sites may act as distinct quantum size effects, for example, in the strong size-dependent chemical reactivity of gas-phase clusters. As a catalyst, MgO is usually used to catalyze the H<sub>2</sub> and D<sub>2</sub> exchange reactions and the dehydrogenation of formic acid or methanol. The studies on the adsorption of H<sub>2</sub>O on freshly cleaved MgO(100) crystals<sup>4</sup> and ordered MgO films have been performed.<sup>5,6</sup> Recently, Pd clusters supported on MgO surfaces have been studied using various experimental methods including high-resolution transmission electron microscopy, helium diffraction, ion scattering spectroscopy, scanning tunneling microscopy, scanning tunneling spectroscopy, surface electron energy-loss fine structure spectroscopy, Auger electron spectroscopy, and electron energy-loss spectroscopy.<sup>7–12</sup> The adsorption of CO on various sites of Pd deposited on a MgO surface has also been discussed using a density functional cluster model approach.<sup>13</sup>

In this work, we report a study on the adsorption of water on the surface of Pd-deposited MgO(100) film, prepared in situ on a Mo(100) substrate in an ultrahigh vacuum system, by low-energy electron diffraction (LEED), high-resolution electron energy-loss spectroscopy (HREELS), and ultraviolet photoelectron spectroscopy (UPS). We will demonstrate that the adsorption of water on MgO(100) thin films is enhanced significantly by the presence of Pd, which depends on the size and distribution of Pd particles on the MgO(100) films. A dissociation of water has been observed.

## 2. Experimental Section

The experiments were carried out in an ultrahigh vacuum system with a base pressure of  $2 \times 10^{-8}$  Pa. The system is equipped with an ELS 22 spectrometer consisting of HREELS and UPS and with Auger electron spectroscopy (AES) and LEED facilities. A molybdenum single crystal (Goodfellow Ltd. 99.999% purity disk, (100) orientation) was used as the substrate. Ultrathin MgO(100) films were grown upon a Mo(100) substrate by evaporating Mg (purity 99.9+%) with  $10^{-4}$  Pa O<sub>2</sub> (Hede Nielsen A/S, purity 99.998%) at 900 K followed by annealing in  $10^{-4}$  Pa O<sub>2</sub> for about 10 min. These MgO thin films were further annealed to 1100 K for about 10 min without O<sub>2</sub>. The thickness of MgO films was 5–6 nm as monitored by a quartz crystal oscillator. Pd atoms were deposited onto the MgO(100) surface at room temperature using an e-beam evaporator. In HREELS measurements, the electron primary energy ( $E_0$ ) was 10 eV and the (elastic peak full width at half-maximum  $\sim 12$  meV) loss spectra were collected at an angle of 8° from the specular direction. The exposure of MgO(100) films to (doubly ion-exchanged, 18.2 M $\Omega$ ) purified H<sub>2</sub>O was carried out using a water doser, and the coverage as taken from uncorrected ion gauge measurements was given, which is assigned by the water exposure; that is, the exposures of water are nominal. A W5%Re/W26%Re thermocouple was spot welded to the edge of the Mo(100) sample for temperature measurements, and the temperatures of the samples were controlled by resistive heating and liquid nitrogen cooling.

## 3. Results and Discussion

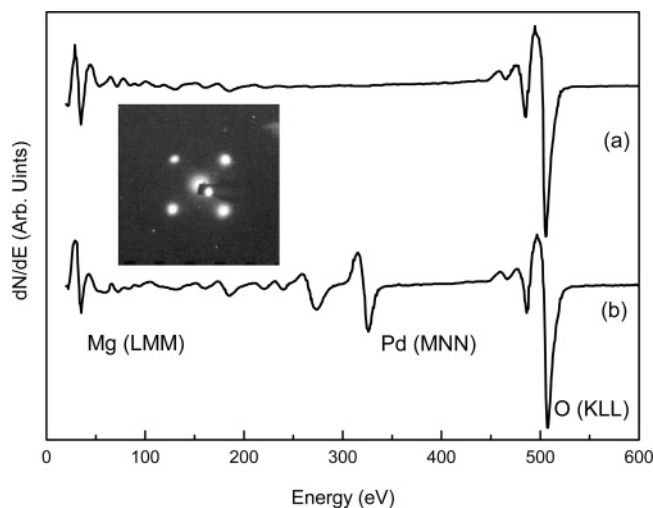
Figure 1 shows Auger spectra of a clean MgO(100) film and 1 ML (monolayer) of Pd deposited on MgO(100) film, respectively. In both cases, AES did not show a metallic Mg (LMM) peak at 44 eV, whereas the Mg peak at 32 eV is distinctly visible and its shape is similar to that of Mg in bulk MgO, indicating that Mg is completely oxidized.<sup>14</sup> It also proves that a 1:1 ratio in atomic densities between Mg and O is established, as calculated by the relative sensitivity factor method. Meanwhile, the LEED pattern of the MgO(100) thin film is shown as an inset in Figure 1. The LEED pattern exhibits a (1  $\times$  1) periodicity with a relatively low background intensity, indicating that the MgO(100) thin film is ordered with a roughly

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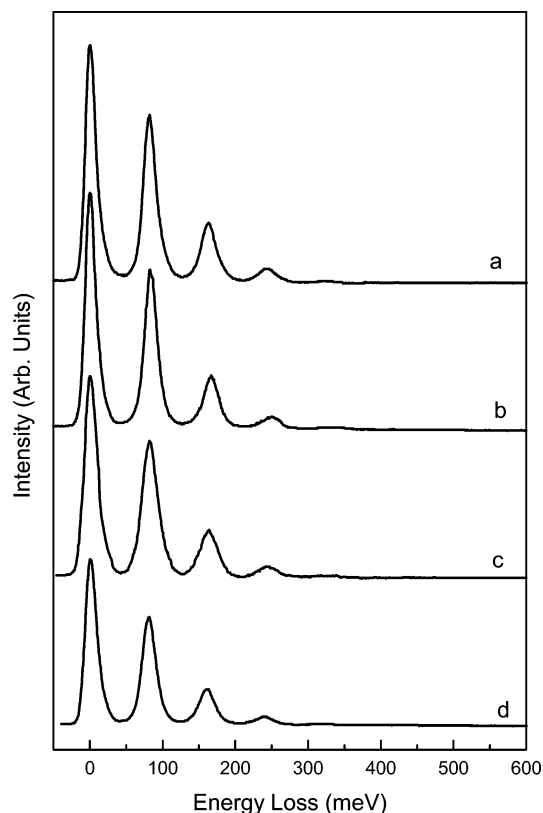
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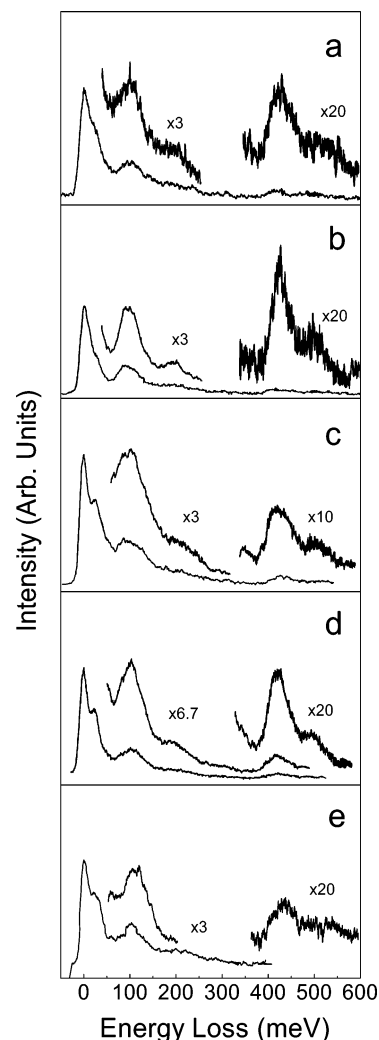
**Figure 1.** Auger spectra of (a) clean MgO(100) film and (b) 1 ML of Pd deposited on MgO(100) film. The inset is a LEED pattern from the MgO(100) film,  $E_p = 65.8$  eV.



**Figure 2.** HREEL spectra of (a) clean MgO(100) thin film, (b) 0.1 ML of Pd/MgO(100), (c) 0.4 ML of Pd/MgO, and (d) 1 ML of Pd/MgO(100). The spectra were collected at a primary electron energy of  $E_0 = 10$  eV and an angle of  $8^\circ$  off the specularly reflected beam direction.

flat surface. The appearance of the Pd (MNN) peak in AES (Figure 1b) indicates that 1 ML of Pd was supported on MgO(100) films.

Figure 2 shows HREEL spectra of a clean MgO(100) film and Pd/MgO(100) films with different coverages of Pd. For clean MgO film, by acquiring the spectra at  $8^\circ$  off-angle scattering geometry with respect to the specular direction, the primary phonon loss at 82 meV yields second, third, fourth, and fifth scattering losses of the phonon events at 164, 246, 328, and 410 meV, respectively (Figure 2a). Deposition of Pd on MgO(100) films results in a reduced intensity of the phonons



**Figure 3.** HREEL spectra of 0.01 L of H<sub>2</sub>O/Pd/MgO(100) films with different coverages of Pd: (a) 0.1 ML; (b) 0.2 ML; (c) 0.4 ML; (d) 0.6 ML; (e) 1.0 ML.

from the MgO surface without a change of the phonon positions (Figure 2b–d).

Figure 3 shows HREEL spectra of H<sub>2</sub>O adsorption with exposure of 0.01 L (1 Langmuir (L) =  $1.33 \times 10^{-4}$  Pa·s) on Pd/MgO(100) films with different coverages of Pd at 100 K. After adsorption of 0.01 L of H<sub>2</sub>O on 0.1 ML of Pd/MgO(100), the phonon losses from Pd/MgO films disappear obviously and the vibrational signals from H<sub>2</sub>O are enhanced significantly (see Figure 3a). The vibrational spectra from H<sub>2</sub>O consist of four bands,<sup>15</sup> which correspond to the frustrated translations, librations, scissoring mode, and O–H stretch of the H<sub>2</sub>O molecules, respectively, as indicated in Table 1. The appearance of the frustrated H<sub>2</sub>O–H<sub>2</sub>O translation loss at about 22 meV indicates that a multilayer of water molecular adsorption is condensed on the surface. The loss due to frustrated rotations (librations) appears at 105 meV. The scissoring mode (intramolecular deformation) occurs at 205 meV. The O–H···O stretch mode causes a broad loss feature centered at 425 meV. This O–H···O stretch feature is considerably broadened due to hydrogen bonding, indicating a multilayer of water on the surface.

With increasing loading of Pd, the intensity of the loss of H<sub>2</sub>O due to frustrated translations increases, suggesting more multilayer water molecules formed on the surface (Figure 3b–d). The loss intensity at 205 meV first increases and then decreases with the increase of the exposures of H<sub>2</sub>O. However,

**TABLE 1: Assignments of the Observed Vibrational Losses of H<sub>2</sub>O/Pd/MgO(100) Film at 100 K and Comparison with H<sub>2</sub>O/Pd(100),<sup>16</sup> H<sub>2</sub>O/MgO(100),<sup>6</sup> H<sub>2</sub>O Ice,<sup>17</sup> and H<sub>2</sub>O Gas<sup>18</sup>**

mode	H <sub>2</sub> O/Pd/MgO(100)	H <sub>2</sub> O/Pd(100)	H <sub>2</sub> O/MgO(100)	H <sub>2</sub> O ice	H <sub>2</sub> O gas
translation	22		26.5	49.6	
librations	105	100.4	105.3	130.2	
scissor	205	205.3	204.6	200.8	197
O—H · · · O stretch	425	419.0	417	399.2	
free O—H stretch			456.8	421.5	453.4
					465.6
$\nu(\text{O—H} \cdot \cdot \cdot \text{O}) + \text{one phonon}$	500				
$\nu(\text{OH}) + \text{one phonon}$			541.1		

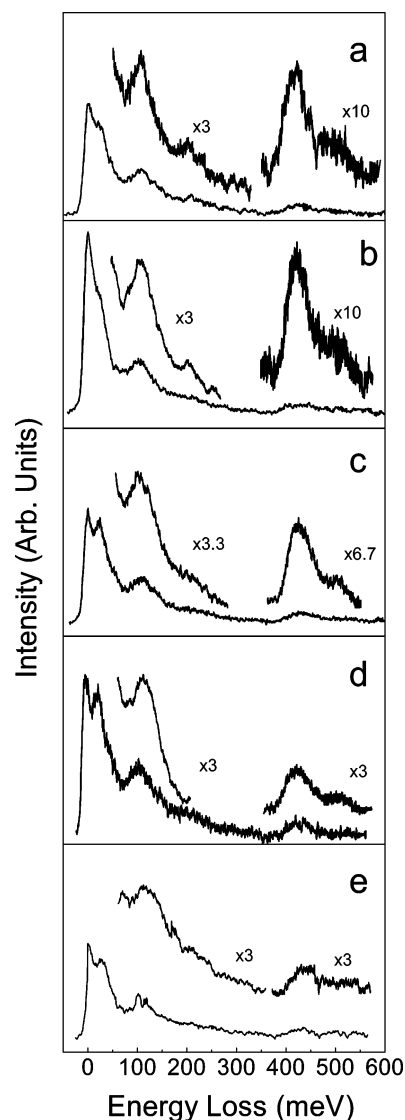
two bands are observed, at 425 and 500 meV, in the O—H stretching region at low exposures of H<sub>2</sub>O. The band at 500 meV, which is higher than that of free OH groups and lower than that of free OH groups plus one phonon, is considered by us to be assigned to O—H · · · O stretch plus one phonon, as compared to that of water vibrations reported by other groups.<sup>6,19–21</sup> This might be caused by either the different geometry structure of the water adsorbed on the surface or the bonding status of the water. It has been found that in our experiments with increasing H<sub>2</sub>O exposures the intensity of the loss at 425 meV first increases and saturates at the exposure of 0.2 L of H<sub>2</sub>O, and the band at 500 meV almost disappears at the exposure of 0.5 L of H<sub>2</sub>O. For a 0.4 ML of Pd onto MgO(100) film, a similar behavior is observed for the adsorption of H<sub>2</sub>O. It is notable that the loss at 22 meV is clearly observed and meanwhile the intensity of the loss at 425 meV reaches a maximum value when increasing the coverage of Pd to 0.4 ML (Figure 3c). In the scissoring region, the loss at 205 meV reaches a maximum value in the intensity at the coverage of 0.4 ML of Pd.

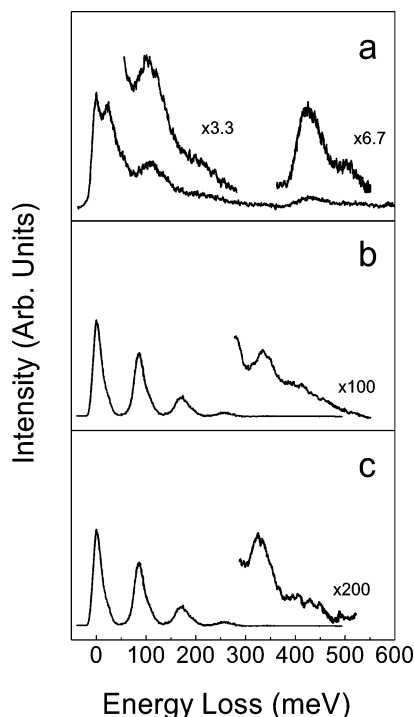
Figure 4 shows HREEL spectra of H<sub>2</sub>O/Pd/MgO(100) films with different coverages of Pd at the exposure of 0.1 L of H<sub>2</sub>O. The Pd dependence of the intensity for every band shows a similar behavior: with increasing Pd coverage, the vibrational intensity from H<sub>2</sub>O first increases and then decreases. However, the maximum intensity of the loss at 22 meV is observed from the 0.4 ML of Pd/MgO(100) film sample, suggesting a multilayer of H<sub>2</sub>O on the surface. Meanwhile, the maximum intensity of the loss at 425 meV is reached. It is noted that the loss at 500 meV disappears at a coverage of 1.0 ML of Pd. It can be seen clearly that the adsorption of water on the surface of MgO(100) is Pd coverage dependent.

The desorption of water on the surface of Pd-deposited MgO(100) film was also investigated. Figure 5 shows HREEL spectra of a H<sub>2</sub>O/0.4 ML of Pd/MgO(100) film with the exposure of 0.1 L of H<sub>2</sub>O at 100 K followed by annealing in the UHV chamber at different temperatures. When the sample is annealed to 150 K, the vibrational loss spectrum from H<sub>2</sub>O remains unchanged (not shown here). Upon annealing to 200 K, the loss at 22 meV decreases rapidly and the multiple scattering loss of the phonon of MgO emerges. Meanwhile, the intensity of the loss at 425 meV decreases rapidly. This is in agreement with the observation through temperature-programmed desorption in previous work by Wu et al.<sup>6</sup> Their results indicated that a desorption behavior appears in the 150–200 K temperature range. When the annealing temperature increases to 273 K, the loss at 22 meV cannot be observed, suggesting a desorption process of the H<sub>2</sub>O multilayers on the surface of the sample. However, the trace of the loss in the O—H stretching region is still visible even at RT. This may imply that a part of decomposed water remains on the surface of the sample, similar to that of MgO(100)/Mo(100) observed in our previous work.<sup>5</sup>

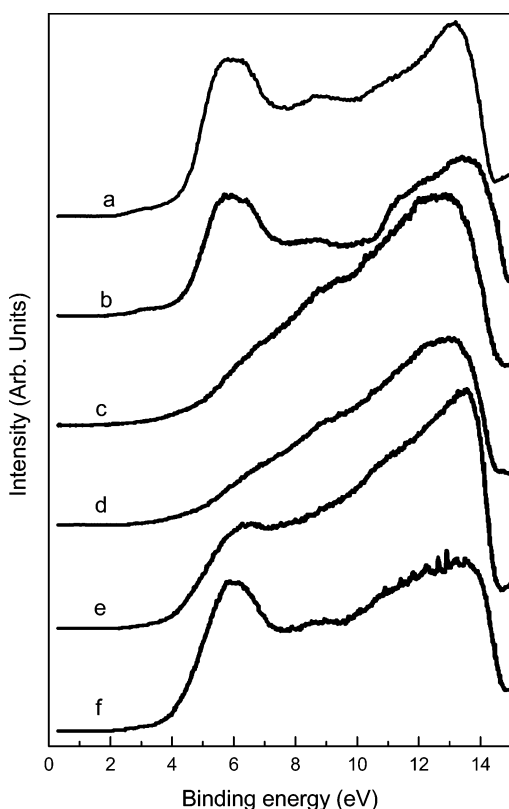
We also observed LEED patterns and measured UP spectra after annealing. Exposing the film to 0.1 L of H<sub>2</sub>O, the ordered

MgO(100) LEED pattern disappears due to the formation of a multilayer of H<sub>2</sub>O on the surface of the film. Upon annealing at temperatures higher than 200 K, the (1 × 1) pattern with broad spots is visible again, indicating the desorption of H<sub>2</sub>O on the surface. This coincides with HREELS measurements. Figure 6 shows UP spectra of H<sub>2</sub>O/0.4 ML of Pd/MgO(100) film with the exposure of 0.1 L of H<sub>2</sub>O at 100 K after annealing at different temperatures. For the clean MgO(100) film, a peak at 5.8 eV can be assigned to the oxygen 2p orbitals of the MgO(100) film (Figure 6a).<sup>22</sup> The band located around 13.2 eV is due to the emission of secondary electrons from the MgO(100) film. In Figure 6b, the shape of the secondary electron band

**Figure 4.** HREEL spectra of 0.1 L of H<sub>2</sub>O/Pd/MgO(100) films with different coverages of Pd: (a) 0.1 ML; (b) 0.2 ML; (c) 0.4 ML; (d) 0.6 ML; (e) 1.0 ML.



**Figure 5.** HREEL spectra of 0.1 L of  $\text{H}_2\text{O}$  on 0.4 ML of Pd/MgO(100) film at 100 K after annealing at different temperatures: (a) 100 K; (b) 200 K; (c) 300 K.



**Figure 6.** UPS spectra of  $\text{H}_2\text{O}/0.4$  ML of Pd/MgO(100) film with the exposure of 0.1 L of  $\text{H}_2\text{O}$  measured at 100 K after annealing at different temperatures: (a) 100 K, clean MgO(100) film; (b) 100 K, no water; (c) 100 K; (d) 150 K; (e) 200 K; (f) 300 K.

changes due to the deposition of Pd. The exposure of 0.1 L of  $\text{H}_2\text{O}$  at 100 K eliminates the 5.8 eV peak, and the new features created by  $\text{H}_2\text{O}$  are not well resolved, as shown in Figure 6c. However, this feature is believed to contain a contribution from water, based on previous UPS studies on  $\text{H}_2\text{O}/\text{MgO}(100)/\text{Mo}$ -

(100).<sup>23</sup> Upon annealing at 150 K, the UP spectrum was not clearly changed as compared to curve c, implying that a multilayer of  $\text{H}_2\text{O}$  still remains on the surface of the sample. Upon annealing at 200 K, the appearance of the peak at 6.2 eV implies that a desorption of a majority of the  $\text{H}_2\text{O}$  adsorbed on the surface of the sample now occurs. It is noted that the spectrum is different from that of the sample before exposure of  $\text{H}_2\text{O}$ . After annealing at 300 K, the peak at 5.8 eV from O 2p in MgO(100) appears again and becomes sharper, similar to that from the sample with no exposure of  $\text{H}_2\text{O}$ . This is consistent with our HREELS and LEED results in which the desorption of adsorbed water on the surface of the sample is almost completed at this temperature.

We observed the enhancement of the adsorption of  $\text{H}_2\text{O}$  on MgO(100) film by the presence of Pd. Previous studies using transmission electron microscopy<sup>8</sup> and helium diffraction<sup>24</sup> confirmed that Pd clusters on MgO(100) were formed due to the nucleation behavior of Pd on MgO by a transient nucleation period followed by a saturation of the density of clusters. It was also reported by Xu et al.<sup>12</sup> that the size of the clusters increased and their density was reduced with increasing coverage of Pd. In recent theoretical studies of CO adsorption on Pd-deposited MgO(100), it has been pointed out by Giordano et al.<sup>13</sup> that a Pd atom deposited on a MgO surface prefers to form a strong bond with one CO molecule sitting on oxide anions at regular or low-coordinated sites; that is, Pd shows a very small tendency to bind more than one CO molecule. Therefore, it is expected that the sizes and distribution of Pd particles should affect the adsorption behavior of water on the surface of MgO(100). However, the present study cannot give more information of the details in the mechanism of the enhancement of the adsorption of  $\text{H}_2\text{O}$  due to the presence of Pd, and a further investigation on the photoemission and the surface morphology is expected.

#### 4. Conclusions

In summary, the adsorption of water on the surface of Pd-deposited MgO(100) films grown on Mo(100) has been studied by HREELS, UPS, and LEED. The results show that the adsorption of water on a MgO(100) film is enhanced significantly by the presence of Pd particles. In addition, the formation of hydroxyl groups on the surface of Pd-deposited MgO(100) films has been observed due to water dissociation.

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