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Coverage-dependent dissociation of H₂O on Pd/MgO(100)/Mo(100)

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Abstract

The adsorption of H₂O on Pd deposited upon MgO(100) thin films prepared on Mo(100) was studied using low-energy electron diffraction, ultraviolet photoelectron spectroscopy and high-resolution electron energy loss spectroscopy. A non-metallic feature of Pd has been observed at the coverage of Pd less than 1.5 monolayer equivalents (MLE) on the MgO(100) films. Partially dissociated H₂O was detected on Pd/MgO(100)/Mo(100), and H₂O dissociates most readily at ~0.5 MLE Pd coverage. This coverage-dependent dissociation has arisen from a combination of the size effect of Pd particles and a vacancy-induced modification of surface reactivity.

1. Introduction

Many fundamental studies have been carried out on the adsorption of H₂O on solid surfaces, principally on metal single crystals and ordered metal oxides, because of their potential application [1, 2]. It is found that, for example, H₂O adsorbs molecularly on clean Pd(100), Pd(110) and Pd(111) surfaces at low temperature [3–5], and dissociates partially on a MgO(100) thin film [6]. However, there is still a lack of knowledge about the adsorption of H₂O on metal/metal-oxide surfaces [7] despite their wide technological applications, such as heterogeneous catalysis, gas sensors, electrochemistry, corrosion and medical implants, due to their complex surface morphology, which renders interpretation difficult [8, 9].

It is well known that metal clusters deposited on metal oxides may have intriguing properties due to finite size effects, surface effects, or support effects [10, 11]. Some distinctive characters of supported Pd clusters have been reported in earlier literature. For

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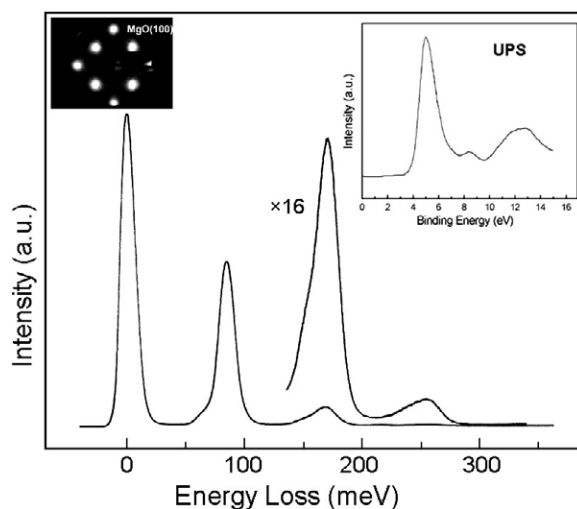


Figure 1. HREEL spectrum of a clean MgO(100) film on Mo(100). The LEED pattern and UP spectrum are given as insets.

instance, the Pd/MgO(100) system has been extensively investigated as a model metal/metal-oxide system [12–16]. Small Pd clusters supported on either thin MgO(100) films or single crystal MgO(100) reveal size effects for CO oxidation [17, 18]. According to a temperature programmed reaction and infrared spectroscopy study, Pd atoms on F-centres (oxygen vacancies) of an MgO(100) film surface and Pd single crystal surfaces reveal different mechanisms in the chemical activity for acetylene cyclotrimerization and CO oxidation [12]. All these distinctive characteristics of Pd clusters/particles on metal oxides stimulated us to explore what will happen when water adsorbs.

In this paper we present a study of H₂O adsorption on Pd/MgO(100)/Mo(100) by low-energy electron diffraction (LEED), ultraviolet photoelectron spectroscopy (UPS) and high-resolution electron energy loss spectroscopy (HREELS). A coverage-dependent dissociation of H₂O is observed. The effects of Pd particle size and substrate surface defects on the activity of H₂O dissociation are discussed based on our experimental results.

2. Experiments

The experiments were performed in a UHV (ultrahigh vacuum) chamber (base pressure 1×10^{-10} mbar) equipped with UP and HREEL spectrometers and a LEED facility, which has been described in detail elsewhere [6].

The substrate Mo(100) was cleaned by flashing to ~ 2000 K until a well-ordered (1×1) LEED pattern was obtained. The thin MgO(100) film was grown *in situ* by deposition of Mg in a 10^{-7} mbar O₂ ambience at 700 K. Then the MgO film was kept under the same O₂ pressure and temperature for 3 min, followed by annealing to 1000 K without O₂ for 5 min. The thickness of MgO(100) film is 3–4 nm. Broad spots in the LEED pattern indicate a defective MgO(100) surface (see the inset in figure 1). The homemade Pd doser was a resistively heated ‘U’-shaped tungsten filament tightly wrapped with Pd wire. After the source was thoroughly degassed, Pd was deposited on the MgO(100) film. The Pd coverage, given by monolayer equivalents (MLE), was estimated by comparing the Pd 4d feature near the Fermi energy (E_F) in the UP spectra with previous experiments, in which the coverage had been monitored by a quartz-

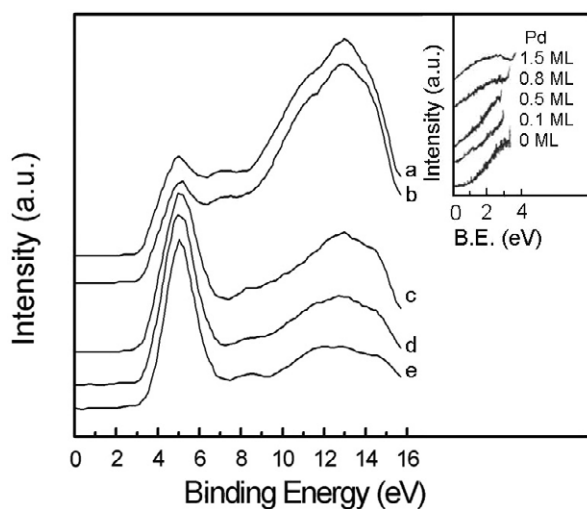


Figure 2. UP spectra of 0.1 MLE Pd/MgO(100) after dosing with 1.5 L H₂O at 120 K (a), and annealing to (b) 150 K, (c) 200 K, (d) 250 K, (e) 300 K. The inset shows the change of Pd 4d features as a function of Pd coverage at RT.

crystal oscillator followed by valence band structure measurements [19]. The rapid changes of the valence band structure as a function of the initial increase of Pd coverage on Al₂O₃ film [7] and silica [10] surfaces were also observed. However, the coverage determined in this study is not accurate, and the maximum error of estimate is ± 0.2 MLE. For HREELS experiments, the energy of the primary electron beam was 8 eV with a resolution of 14 meV (the full width at half maximum of the elastic peak from a clean MgO(100)/Mo(100) surface). In order to reduce the influence of multiple phonon losses from the MgO film, the analyser was set in an off-specular direction of about 5°. A W-5% Re/W-26% Re thermocouple was spot welded to the edge of the Mo substrate for temperature monitoring. Deionized H₂O (18 M Ω) was further purified by several freeze-pump-thaw cycles, after which the samples were exposed to H₂O at 120 K. The exposure of the water given by Langmuir (L, 1L = 1.33×10^{-4} Pa s) is nominal, as taken from an uncorrected ion gauge reading.

In this work, all the spectra were obtained at 120 K, except for those otherwise specified. Each annealing step at the corresponding temperature lasted for 20 s before cooling back to 120 K for spectra collection.

3. Results

The Pd was deposited on MgO(100)/Mo(100) with coverages of 0.1, 0.5, 0.8 and 1.5 MLE, respectively. Note that the coverage of Pd given as MLE is not necessarily for a layer-by-layer growth model. Figure 1 demonstrates the results of HREELS, UPS and LEED for MgO(100) films grown on the Mo(100) surface. In the HREEL, the fundamental mode is at 83 meV (669 cm⁻¹), and the multiple losses are evident. The two peaks at 5.0 and 8.3 eV in the binding energy (BE) below E_F in the UP spectrum (right inset in figure 1) correspond to the O 2p valence band of the MgO(100) film [6]. The broad LEED spots (left inset in figure 1) indicate that the MgO(100) film as prepared is not a perfect ordered surface.

Figure 2 shows the UP spectra for 1.5 L H₂O adsorbed on 0.1 MLE Pd/MgO(100) at different temperatures. At 120 K, the peak at 7.3 eV in figure 2(a) is attributed to the 1b₁

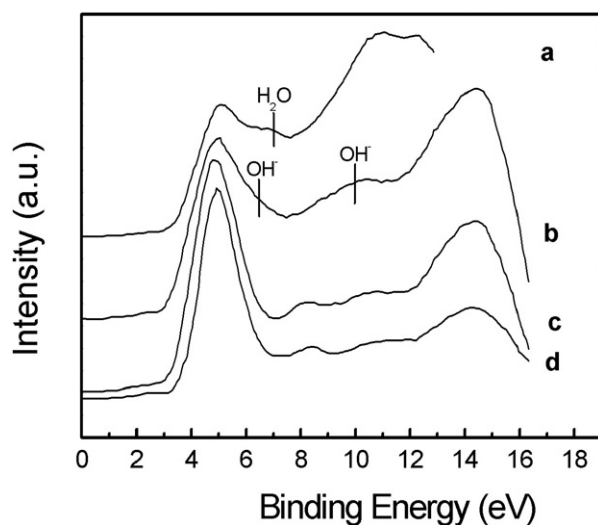


Figure 3. UP spectra of 1.4 L H₂O adsorbed on 0.5 MLE Pd/MgO(100) at 120 K, and annealing to (a) 150 K, (b) 200 K, (c) 250 K, (d) 300 K.

molecular orbital of H₂O [20]. This feature was unchanged after the sample was annealed to 150 K (see figure 2(b)). After annealing to 200 K, the peak for the 1b₁ molecular orbital of H₂O disappears, which means molecular H₂O has desorbed from the surface (figure 2(c)). A very weak peak at ~10.0 eV appears in figure 2(c) compared with figure 2(e), caused by hydroxyl groups, indicating a trace amount of dissociated H₂O on the surface. After annealing at 250 and 300 K (see figures 2(d) and (e)), the signals for dissociated H₂O decrease, which reveals desorption of the hydroxyl. The two peaks at 5.0 and 8.3 eV in figures 2(c)–(e) originate from the O 2p valence band of the MgO(100) film [6]. The change of the Pd 4d features, in the range of 0–4 eV in BE, as a function of Pd coverage was monitored by UPS (inset in figure 2) at room temperature (RT). The size of the Pd clusters can be estimated from the valence band structure compared with the bulk Pd [21]. The Pd feature present around E_F for coverage of Pd up to 1.5 MLE indicates that the small particles deposited on the MgO(100) film are characteristic of non-metallic Pd. However, for 1.5 MLE Pd coverage, an appreciable density of states at E_F can be detected, suggesting a delocalized motion of the valence electrons among large quasi-metallic Pd particles.

Figure 3 gives the UP spectra of 0.5 MLE Pd/MgO(100) with a 1.4 L H₂O exposure. At 150 K, the BE at 7.0 eV (figure 3(a)) indicates molecular adsorption of H₂O. After annealing to 200 K (figure 3(b)), clear peaks at ~6.5 and 10.0 eV appear, typical for the 1 π and 3 σ orbital of OH [1]. Much stronger intensity of OH is visible here, as compared to figure 2, implying that H₂O dissociates more readily upon a 0.5 MLE Pd covered MgO(100) surface. Further annealing treatment at 250 and 300 K causes desorption of dissociated H₂O, as shown in figures 3(c) and (d). One can see that in figure 3, the intensities of peaks at ~6.5 and 10.0 eV decrease, whereas the features for Pd/MgO become clear due to desorption of the hydroxyl group.

Figure 4 presents the UP spectra with 5 L H₂O on 0.8 MLE Pd/MgO(100). In figures 4(a) and (b), the prominent peak at 7.2 eV is related to multilayer molecular H₂O. After annealing to 200 K, the feature of OH at 10.0 eV appears, but it is weaker in intensity compared with that of 0.5 MLE Pd coverage as shown in figure 3(b). This suggests that the dissociation

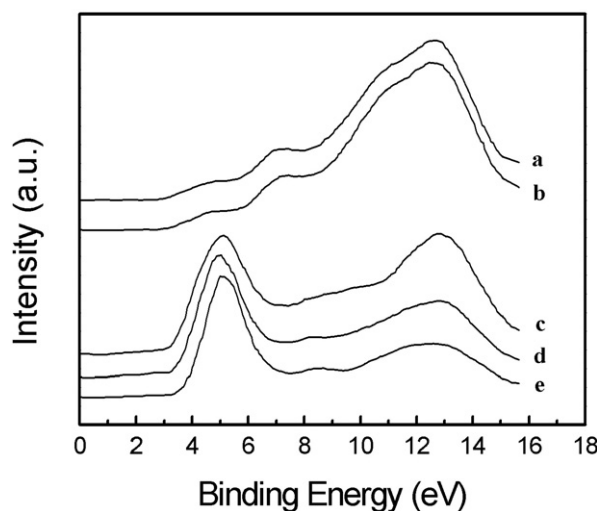


Figure 4. UP spectra of 5 L H₂O on 0.8 MLE Pd/MgO(100) at 120 K (a), and annealing to (b) 150 K, (c) 200 K, (d) 250 K, (e) 300 K.

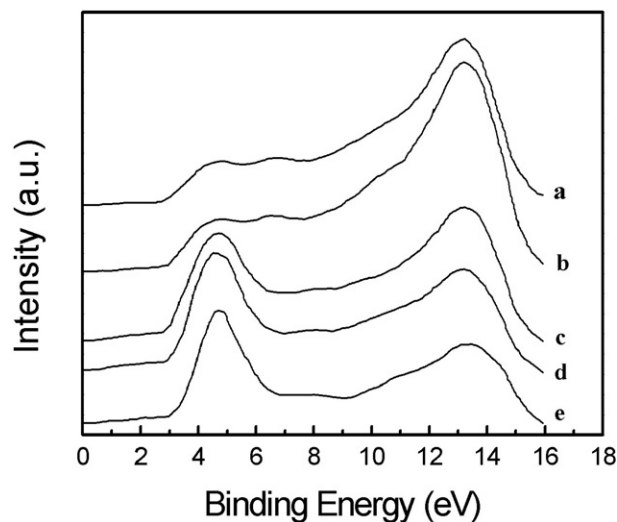


Figure 5. UP spectra of 1.7 L H₂O on 1.5 MLE Pd/MgO(100) at 120 K (a), and annealing to (b) 150 K, (c) 200 K, (d) 250 K, (e) 300 K.

of water upon the 0.8 MLE Pd/MgO(100) surface is less pronounced than that on 0.5 MLE Pd/MgO(100). Heating to 250 and 300 K causes considerable desorption of hydroxyl (see figures 4(d) and (e)).

Figure 5 gives the UP spectra of 1.7 L H₂O adsorbed on a 1.5 MLE Pd/MgO(100)/Mo(100) surface. As discussed above, the features at 6.8 eV in figures 5(a) and (b) are related to the 1b₁ orbital of molecularly adsorbed H₂O. After annealing to 200–300 K, the feature from molecular H₂O disappears, and the peaks at 4.7 and 8.0 eV from the MgO film appear clearly (see figures 5(c)–(e)). We have noticed that those peaks shifted to lower BE compared with a clean MgO film (see the inset in figure 1), indicating the influence of higher coverage of Pd on

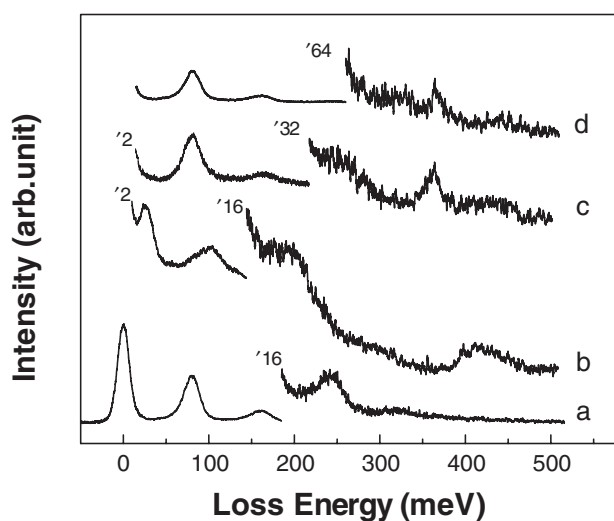


Figure 6. HREEL spectra of 1.5 MLE Pd/MgO(100) at RT (a), and with 1.7 L water at 120 K (b), then annealing to (c) 200 K, (d) 300 K.

MgO. The signals from the hydroxyl group at about 10 eV in figure 5 are weaker than those in figures 3 and 4, however.

Figure 6(a) shows the HREEL spectrum of 1.5 MLE Pd/MgO(100) at RT. The primary phonon loss at 81 meV (653 cm^{-1}) and multiple energy losses at 161 meV (1298 cm^{-1}), 242 meV (1951 cm^{-1}) and 322 meV (2597 cm^{-1}) can be clearly seen. Compared with clean MgO(100)/Mo(100) in figure 1 and the previous result [6], the deposited Pd causes an apparent reduction of the intensity of multiple energy loss. After dosing with 1.7 L H₂O at 120 K, the energy loss spectrum (figure 6(b)) presents four peaks at 25 meV (202 cm^{-1}), 101 meV (815 cm^{-1}), 192 meV (1548 cm^{-1}) and 418 meV (3371 cm^{-1}), which are assigned to H₂O in a hindered translational mode (H₂O–H₂O stretching mode), the libration mode of ice, the internal bending mode of H₂O molecules, and the internal stretching mode of H₂O molecules, respectively [6]. These results are consistent with the vibrational frequencies of H₂O adsorption upon low-index surfaces of Pd [22] within the range of resolution, which strongly suggests adsorption of multiple layers of molecular water on Pd/MgO(100) at 120 K. After annealing to 200 K, molecular H₂O has been desorbed, based on the disappearance of the H₂O features at 25 meV (202 cm^{-1}), 101 meV (815 cm^{-1}) and 192 meV (1548 cm^{-1}), as evidenced in figure 6(c). Therefore, the OH stretching mode at 430 meV (3468 cm^{-1}) in figure 6(c) corresponds to hydroxyl from H₂O dissociation. This feature turns weak as the annealing temperature rises to 300 K, as shown in figure 6(d). The peak at 363 meV (2928 cm^{-1}) most likely has arisen from CH, the possible contaminant from vacuum. Figure 7 is the HREEL spectra of 5.0 L H₂O on 0.4 MLE Pd/MgO(100) at 100 K and after annealing to different temperatures. The multiple layers of water (figure 7(a)) is not desorbed at 170 K as shown in figure 7(b). After 200 K annealing (figure 7(c)), however, the molecular water is desorbed and the OH stretching mode at 430 meV (3468 cm^{-1}) indicates a hydroxyl group on the surface. The weak peak at $\sim 340\text{ meV}$ (2742 cm^{-1}) is from the fourth multiple energy loss of the MgO(100) film. Both the UPS and HREELS spectra reveal that part of the adsorbed H₂O is dissociated on the Pd/MgO(100) surface after annealing to 200 K, and the OH group desorbs as the annealing temperature rises. One interesting result is that, combining the UPS and HREELS results, the Pd coverage seems to play a specific role in H₂O dissociation.

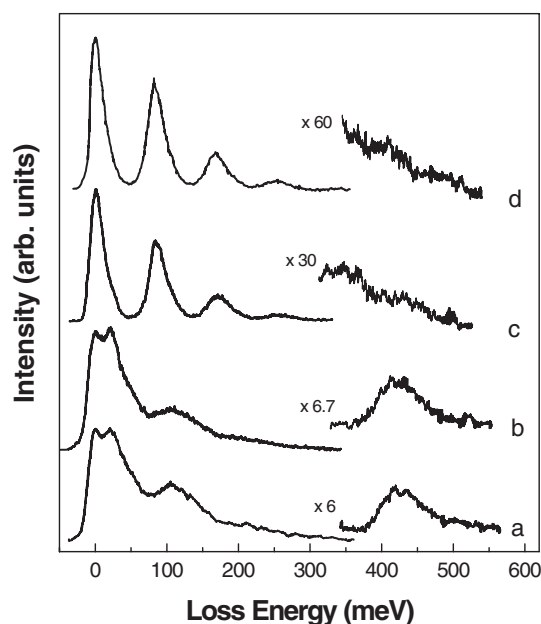


Figure 7. HREEL spectra of H₂O on 0.4 MLE Pd/MgO(100) at 100 K (a), and after annealing to different temperatures, (b) 170 K, (c) 200 K, and (d) 300 K.

4. Discussion

It is noteworthy that the strongest signals for dissociated H₂O correspond to a Pd coverage of ~ 0.5 MLE, which indicates clearly that the H₂O dissociation on Pd/MgO(100)/Mo(100) is Pd coverage dependent. A recent study has shown that water adsorption on Pd/MgO(100) film is enhanced significantly owing to the presence of Pd particles, and the maximum intensity of molecular H₂O adsorbed on the Pd/MgO(100) film sample corresponds to ~ 0.5 MLE coverage [19]. As we have mentioned in the introduction, H₂O is not dissociated on the (100), (110) or (111) surfaces of bulk Pd [3–5]. Pd particles grown on MgO(100)/Mo(100) at RT experience a non-metal to metal transition with increase of Pd coverage. The previous studies also found that the Pd on MgO(100) is always in the form of three-dimensional particles, and the size is strongly coverage dependent [10, 13]. Pseudomorphic particles have been observed for the first Pd layer on the MgO(100) surface [23]. It was demonstrated that Pd clusters larger than 5 nm are a feature of bulk Pd while smaller Pd clusters show different adsorption–desorption behaviours [24]. Moreover, the metal to non-metal transition of Pd particles on MgO(100) was observed at a particle size of ~ 300 atoms by scanning tunnelling microscopy [25]. The size effect of Pd clusters for the chemisorption of CO has been reported for MgO(100) and mica single crystal substrates, as well as for alumina, silica and titania in real catalysis applications [24, 26]. Actually, size effects in metal clusters/particles have been widely studied and discussed in recent years. For instance, the observation of the size dependence of electronic properties in Ag clusters demonstrates the importance of quantum effects [27]. In our experiments, the UP spectra (inset of figure 2) have shown distinct electronic structures for lower coverage of Pd differing from that of bulk Pd.

It is widely accepted that vacancies are very common on real metal oxide surfaces. The vacancy-induced modification of the catalytic activity of Pd clusters promoted by O vacancies on the surface of the metal oxide substrate has been investigated extensively. Thus, the defect-

controlled surface adhesion and nucleation of Pd on MgO(100) has been investigated by atomic-force microscopy [28, 29] and calculations [30]. Further first-principles calculations have shown that on flat MgO(100) terraces, steps, F and F⁺ centres (F and F⁺ centre refer to an oxygen vacancy trapping two and one electrons, respectively), and divacancies (vacancies by losing MgO pairs), where nucleation of Pd may occur, divacancies and F⁺ centres exhibit a much stronger tendency to nucleate Pd dimers [31]. In fact, the substrate MgO(100) film not only can affect the growth of Pd, but it also can even modify the adsorption properties of small Pd particles [32–34]. The defects exist on the as-prepared MgO(100) film, based on the LEED observation. The polarization remains very well localized on the Pd atoms at the vacancies, and these vacancies preferably occupy the regions at the edges and corners of the clusters [35]. The effect of the vacancy would probably be screened by the three-dimensional deposition. Therefore, the initial Pd deposition creates the appropriate catalytically active Pd particles at the vacancies, while higher coverage of Pd can cause a screening effect, which reduces the catalytic reactivity. The defect-enhanced catalytic activity on the Pd/MgO(100) system has been found for other reactions such as CO oxidation [18] and acetylene polymerization [36]. Moreover, the importance of surface F-centres in the activation of Au in Au/MgO catalysis has also been observed [37].

However, the interaction between Pd particles and the surface of the MgO(100) film cannot be excluded, and it may also play an important role in activity. Many studies have demonstrated that the metal particles have an influence on the surface. For instance, the electronic properties of small Ag clusters deposited on MgO(100) film can be significantly altered in the presence of point defects [38]. Moreover, the interaction of CO and H₂ with supported Rh has been shown to change with different oxide supports [39]. One more example is that in the system Au/TiO₂, TiO₂ is not only a support to provide a means of spreading out Au particles over a large surface area, but also a promoter for CO oxidation [40]. Based on the discussion above, however, more detailed studies aimed at understanding the real mechanism for the water dissociation reaction on the Pd/MgO are required.

5. Conclusion

We have studied the adsorption of H₂O on Pd/MgO(100)/Mo(100) and found that H₂O is partly dissociated. At initial coverage, the Pd particles show the properties of non-metal observed by valence band structure. The dissociation of H₂O is Pd coverage dependent, and the maximal activity for the dissociation of water corresponds to about 0.5 MLE Pd. The coverage-dependent activity can be caused by a combination of a size effect of Pd clusters and the vacancy-induced surface modification.

Acknowledgments

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