Adsorption of Water on Fe$_3$O$_4$(111) Studied by Photoelectron and Thermal Desorption Spectroscopy

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Abstract

The adsorption of water on Fe$_3$O$_4$(111) films grown epitaxially onto Pt(111) was investigated by ultraviolet photoelectron spectroscopy (UPS) in adsorption-desorption equilibrium and by thermal desorption spectroscopy (TDS). With increasing coverage both methods reveal the existence of three species on the surface: Dissociatively chemisorbed water (γ), physisorbed monomeric water (β) and hydrogen bonded condensed ice (α). The corresponding isosteric heats of adsorption q_{st} and desorption energies E_{des} were determined by UPS and TDS, respectively. For the α- and β-species they compare well, for the γ-species E_{des} is higher indicating an activation barrier for the dissociative adsorption, which is also supported by the observed slow adsorption kinetics. The dissociation is assumed to occur at iron cations with neighboring oxygen anions acting as proton acceptors.

Introduction

The adsorption of water on metal oxide surfaces is of great interest in catalysis reseach and other fields like corrosion and electrochemistry. Molecular and dissociative adsorption has been observed on several oxides, where the latter is mostly related to lower coordinated surface defect sites[1-3]. The dehydrogenation of ethylbenzene to styrene is an important synthesis reaction in chemical industry, which is performed over iron oxide based catalysts at temperatures around 900 K in an ethylbenzene-steam mixture [4-6]. The water removes carbonaceous deposits from the catalyst surface as known from several previous studies[7-9], but it is not assumed to take part in the rate determining step of the reaction. Recent studies over single crystalline iron oxide model catalysts films revealed evidence for an active role of water in the reaction mechanism[10,11]. In this context the adsorption behavior of water on iron oxide surfaces is of particular interest.

Well ordered Fe$_3$O$_4$(111) films which are at least 150 Å thick were grown onto Pt(111) substrates as described in detail in ref.[12]. Fe$_3$O$_4$ crystallizes in the cubic inverse spinel structure. As determined by a dynamic LEED (low energy electron diffraction) intensity analysis, the Fe$_3$O$_4$(111) surface exposes ¼ monolayer (ML) of iron cations in the topmost layer, which are located on top of a densely packed hexagonal oxygen layer[13]. Here we present an investigation of the adsorption of water on the Fe$_3$O$_4$(111) surface. The adsorbed species were identified by UPS and the thermodynamics of the adsorption was investigated with UPS and TDS. From adsorption isobars measured by UPS isosteric heats of adsorption were determined and compared to desorption energies determined from TDS measurements.

Experimental

The UPS measurements were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of 5x10^{-11} mbar which contained a high-resolution LEED system, a double-pass cylindrical mirror analyzer (CMA, Physical

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Electronics), a resonance lamp (He I line 21,2 eV) for UPS and a manipulator which allows sample cooling and heating. The TDS measurements were performed in a separate UHV chamber with a base pressure of 2×10^{-10} mbar, which is equipped with a backview LEED optics and a quadrupole mass spectrometer (QMS). Both chambers contained an Ar$^+$-sputter gun, an iron evaporator and a gas inlet system. The sample holder is described in detail elsewhere[14] .

Deionised, triply destilled water for the adsorption measurements was filled into a small glass tube, connected to the vacuum chambers and degassed by several freeze-thaw cycles. The Pt(111) substrate was cleaned by repeated sputter-annealing and oxidation-annealing cycles until a sharp (1x1) LEED pattern was observed and no more contaminants were detected by Auger electron spectroscopy (AES). The epitaxial Fe$_3$O$_4$(111) film exhibited a sharp LEED pattern and was prepared as described before[15].

The UP valence band spectra were measured in adsorption-desorption-equilibrium at constant water partial pressures and stepwise varying the sample temperature analogous to the procedure described before [10, 15]. This results in temperature-dependent equilibrium water coverages. The establishment of equilibrium needed up to about 6 minutes depending on the pressure and the kind of the adsorbed species. In the TDS experiments, water was adsorbed onto the sample at T=100 K. Exposures are given in Langmuir units with $1L=1.33 \times 10^{-6}$ mbar s. The heating rate was always 5 K/s.

Results and Discussion

Fig. 1a compares UP spectra of the clean and of the water covered Fe$_3$O$_4$(111) surface for three selected temperatures. At these temperatures, the species labeled γ and β are approximately saturated and the α species has formed a thick layer. The accurate peak positions of the water induced features as deduced from difference spectra (spectrum of the adsorbate minus spectrum of the clean surface, not shown here) are marked. The spectrum at 140 K (α-species) shows three water induced bands at -6.5, -9.6 and -12.5 eV below the Fermi energy E_F. The spectrum at 160 K (β-species) also shows three peaks at -6.1, -8.3 and -12.1 eV below E_F. These three features are due to the *1b$_1$*, *3a$_1$* and *1b$_2$* molecular orbitals (MO) of water, respectively. Their relative energy positions and especially that of the *3a$_1$* orbital indicate that the α-species is a condensed ice layer whereas the β-species is monomerically physisorbed water[16]. The spectrum at 235 K (γ-species) shows only two signals at -5.8 and -9.8 eV below E_F. We interpret them as orbitals of chemisorbed water dissociated into hydroxyls and protons which form OH groups on the surface[17] . The identification of the species is described in detail elsewhere[18] .

From the adsorbate induced intensity as well as from the attenuation of the substrate emission, the water coverages Θ were deduced. Temperature dependent equilibrium coverage curves (isobars) for three different water partial pressures are shown in fig. 1b. The saturation cover-

ages Θ$_{sat}$ for the β- and γ-species as known from the valence band emission spectra agree with the discontinuities in these isobars. We arbitrarily define the saturation coverage Θ$_{sat}$ for γ+β as 1 monolayer. The isosteric heats of adsorption q$_{st}$ as a function of coverage Θ (fig. 3) are determined according to the Clausius-Clapeyron equation from these isobars, as described in detail elsewhere [10, 15]. We observe an isosteric heat of adsorption of 37 kJ/mol for the α-species and 48 kJ/mol for the β-species. The isosteric heat of adsorption for the γ-species is ≥ 55kJ/mol and seems to decrease with coverage.
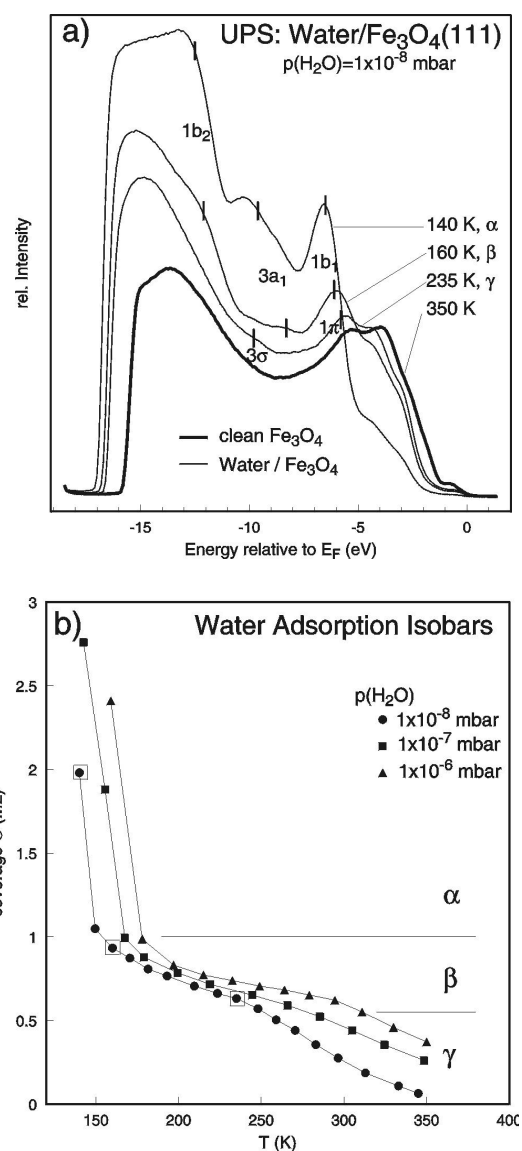

Figure 1: a) He I UP spectra of the clean and water covered Fe$_3$O$_4$(111)surface measured in adsorption-desorption-equilibrium with water at p(H$_2$O) = 1×10^{-8} mbar and the indicated sample temperatures. Three different species adsorb sequentially with increasing coverage. The energy positions of the emission maxima deduced from difference spectra are marked. For the identification of the α-, β- and γ-species see text. b) Adsorption isobars at three different water partial pressures. The data points marked by squares correspond to the spectra shown in (a). The coverage regimes for the different species are indicated.
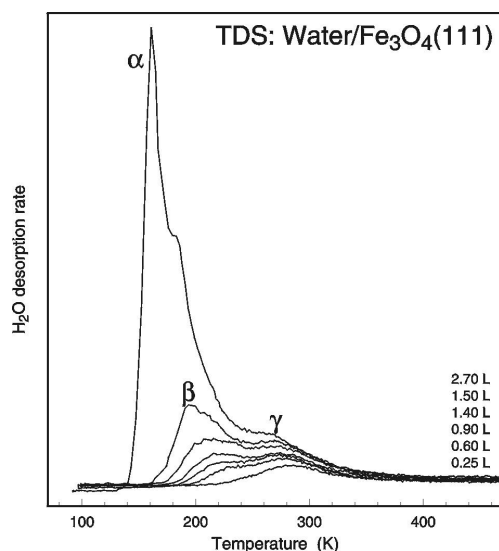
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Figure 2: TD spectra of water on Fe$_3$O$_4$(111) after exposures to the indicated amounts at T=100 K. Insert: LEED pattern of the clean Fe$_3$O$_4$(111) surface at E=60eV.

Fig. 2 shows the TD spectra of water adsorbed onto the Fe$_3$O$_4$(111) surface. There are three desorption maxima. At low exposure, the signal labeled γ appears with a peak maximum at about 270 K. With increasing coverage it shifts towards lower temperatures, which we interpret to be due to repulsive lateral interaction of the adsorbate species. Upon higher exposures an additional species labeled β is observed which starts to desorb at 190 K. Finally, a third peak α appears with a desorption maximum at 165 K. The saturation coverage of the first layer species (γ+β) before the onset of condensation is arbitrarily scaled as 1 ML. Similar desorption peaks are observed by Vurens et al.[19]. They investigated an „iron oxide multilayer" film which probably had the same surface structure as the film prepared here.

For the determination of desorption energies and frequency factors, usually the threshold analysis or leading edge method is applied[20]. However, water adsorption at 100 K does not result in a strictly sequential filling of the different observed states. Always mixtures of adsorbed species are found and in contrast to the equilibrium measurements using UPS the saturation peak area of the γ-species remains always smaller than for the β-species(see fig. 2). For the α species with zero order kinetics, the desorption process is described by a simple exponential relation (Polanyi-Wigner) from which the desorption energy E$_{des}$ = 36 kJ/mol can be determined. For the β and γ species E$_{des}$ was obtained from a simulation based on the Polanyi-Wigner equation. Because of the repulsive lateral interaction, the desorption peaks are broad and can only be simulated by a sum of theoretical desorption curves. Assuming a frequency factor of ν=10^{13} s^{-1}, second order kinetics for the γ- and first order kinetics for the β-species, the mean desorption energies are around 70 kJ/mol for the γ-species and 50 kJ/mol for the β-species (fig. 3).

The temperatures where saturation of the species was observed in the UPS measurements correspond to the onset temperatures of the desorption peaks in TDS. There-

fore we conclude that the species identified by UPS (dissociatively chemisorbed γ, physisorbed β and condensed α) correspond to the three desorption maxima observed in the TDS measurements. The desorption energies E$_{des}$ and the isosteric heats of adsorption q$_{st}$ agree well for the α- and β-species as can be seen in fig. 3. Their order of magnitude is in the same range as the sublimation enthalpy of ice I at 0 K (47.3 kJ/mol)[21]. For the γ-species, E$_{des}$ is larger than q$_{st}$. This appears reasonable, if the adsorption of the dissociated species is activated. An activated adsorption is also supported by the observation that the establishment of the adsorption-desorption-equilibrium in UPS measurements took considerably more time for the γ- than for the β- and α-species.
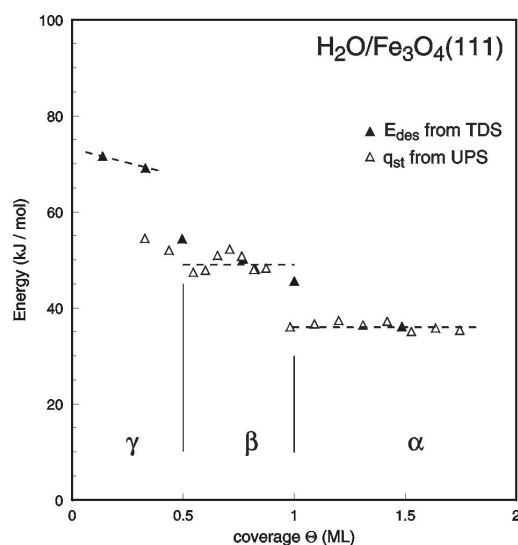

Figure 3: Comparison of the isosteric heats of adsorption q$_{st}$ and desorption energies E$_{des}$ of water adsorbed on Fe$_3$O$_4$(111) as a function of the adsorbate coverage.

In the UPS measurements the saturation coverages of β and γ are equal, whereas in the TDS measurements it is higher for the β-species. Also this is a consequence of the activation barrier for dissociative adsorption of the γ-species which makes the adsorption kinetics slow, so that is it does not get saturated at the low adsorption temperature in TDS and not either during the heating ramp for desorption. The saturation coverages of β+γ however,is the same both in the UPS and TDS measurements. This means that the lower occupation of γ-species is balanced by a higher occupation of the molecular β-species in TDS.

Summary and Conclusions

The adsorption of water on Fe$_3$O$_4$(111) films grown epitaxially on Pt(111) was investigated by UPS in adsorption-desorption equilibrium and by TDS. Both methods reveal the existence of three different adsorbed species on the Fe$_3$O$_4$(111) surface. These are dissociatively chemisorbed water (γ), physisorbed monomeric water (β) and hydrogen bonded condensed ice (α). They were identified by their UP

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valence band spectra and by their desorption peak positions in the TD spectra.

Desorption energies E$_{des}$ and isosteric heats of adsorption q$_{st}$ were determined to be 70 and 55 kJ/mol for the dissociated γ-species (OH), 50 and 48 kJ/mol for physisorbed β-water and 36 and 37 kJ/mol for condensed α-ice, respectively. The difference in the values for the γ-species indicates an activation barrier for dissociative adsorption of water on Fe$_3$O$_4$(111). We suggest the dissociation of water to take place at Lewis-acidic iron cation sites with neighboring oxygen anion sites acting as acceptors for the produced protons. Both are exposed on the relaxed Fe$_3$O$_4$(111) surface as known from a structural LEED analysis. This shows, that in an oxi-dehydrogenation of ethylbenzene to styrene water could provide active oxygen or hydroxyl species to accept the protons from the ethylbenzene molecule.

Acknowledgements

References (9)

[1]   R. L. Kurtz, V. E. Henrich; Phys. Rev. **B26**, 6682 (1982).

[2]   W. J. Lo, Y. W. Chung, G. A. Somorjai; Surface Science **71**, 199 (1978).

[3]   N. B. Brookes, F. M. Quinn, G. Thornton; Vacuum **38**, 405 (1988).

[4]   E.H. Lee; Calal. Rev. **8** (1973) 285.

[5]   T. Hirano; Appl. Catal. **26** (1986) 65.

[6]   T. Hirano; Appl. Catal. **28** (1986) 119.

[7]   M. Muhler, J. Schütze, M. Wesemann, T. Rayment, A. Dent, R. Schlögl, G. Ertl; J. Catal. **126**, 339 (1990).

[8]   M. Muhler, R. Schlögl and G. Ertl; J. Catal. **138** (1992) 413.

[9]   W.P. Addiego, C.A. Estrada, D.W. Goodman, M.P. Rosynek, R.G. Windham; J. Catal. **146** (1994) 407.

[10]   D. Zscherpel, W. Ranke, W. Weiss and R. Schlögl; J. Chem. Phys. **108**, 9506 (1998).

[11]   W. Weiss, D. Zscherpel, R. Schlögl; Catal. Lett. **52** (1998) 215.

[12]   W. Weiss; Surface Science **377**, (1997) 943.

[13]   W. Weiss, A. Barbieri, M.A. VanHove, and G.A. Somorjai; Phys. Rev. Lett. **71**, 1848 (1993).

[14]   W. Weiss, M. Ritter, D. Zscherpel, M. Swoboda and R. Schlögl; J. Vac. Sci. & Technol. **A 16**, 21, (1998).

[14]   W. Weiss, M. Ritter, D. Zscherpel, M. Swoboda and R. Schlögl; J. Vac. Sci. & Technol. **A 16**, 21, (1998).

[15]   W. Ranke, W. Weiss; Surface Science ,in press

[16]   D. Schmeisser, F. J. Himpel, G. Hollinger, B. Reihl, K. Jacobi; Phys. Rev. **B27**, 3279 (1983).

[17]   P.A. Thiel, T. E. Madey; Surf. Sci. Rep. **7**, 211 (1987).

[18]   Y. Joseph, W. Ranke, W. Weiss to be published

[19]   G.H. Vurens, D.R. Strongin, M. Salmeron and G.A. Somorjai; Surface Science **199**, L387 (1988).

[19]   G.H. Vurens, M. Salmeron and G.A. Somorjai; Surface Science **201**, 129 (1988).

[20]   E. Habenschaden, J. Küppers; Surface Science **138**, L147 (1984).

[21]   D. Eisenberg, W. Kauzmann; Structure and Properties of Water (Clarendon, Oxford, 1969), 101.