PRJ, Vol. 8 (January 1996); P. 61–66, 4 FIGS, 1 TABLE.

Models for the Hydrogen-bonded Water Molecules to the Chemisorbed Oxyhydroxyl Layer on the Chromium Surface

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نماذج إرتباط جزئيات الماء على طبقة الأوكسي هيدروكسيل الممتزة كيميائياً على سطح الكروميوم

علي سلمان الطائي

لقد إستعمل المطياف الضوئي الألكتروني الحديث لدراسة حزم الإنبعاث الألكتروني بواسطة الأشعة السينية وفوق البنفسجية في الفراغ الخارق المنبعث من تعرض سطح الكروميوم النظيف إلى بخار الماء أولاً ، وسطح الكروميوم المعرض إلى الأوكسجين مسبقاً ثم إلى بخار الماء ثانياً في درجات حرارة تتراوح بين 80 K إلى 623 K

في المراحل الأولى للإمتزاز وجد أن جزئيات بخار الماء تتفكك حال إمتزازها على الطبقة الأولى لذرات السطح مكونة طبقة من الأوكسي هيدروكسيل وجزيئات الماء المتأصرة تناسقياً من خلال ذرات الأوكسجين على المراكز غير المشبعة للسطح .

أما جزئيات بخار الماء فانها تمتز فيزيائياً عند تعرض السطح لأكثر من طبقة من خلال تكون أواصر هيدروجينية مع طبقة الأوكسي هيدروكسيل الممتزة كيميائياً .

فسرت نتائج هذه الدراسة باقتراح ميكانيكية ونماذج لجزئيات الماء الممتزة بواسطة أواصر هيدروجينية على طبقة الأوكسي هيدروكسيل بين درجات حرارة تتراوح بين 80 K و 298 K .

Abstract *XPS and UPS Photoelectron Spectroscopy techniques (Anoble ESCA-5 Spectrometer which permit pressure from* $1\text{–}10^{-11}$ Torr*) have been used to investigate water vapour interaction with clean and pre-oxygen exposed chromium surface in the temperature range* 80–623 k.

Initially at low exposure ($\sigma <$ *monolayer), the interaction of water vapour with clean chromium surface is dissociative at active site of chromium atoms through the formation of an adsorbed oxyhydroxyl layer together with molecular water which is coordinately bonded to the unsaturated site, via the oxygen which strongly held.*

The second layer which represents the physically adsorbed layer occurs at higher than one monolayer coverage through water molecules hydrogen bonded to the chemisorbed oxyhydroxyl layer. Models and the mechanism of the dehydroxylation of this layer when the exposed surface warmed to room temperature, have been suggested by the monitoring of the XPS and UPS spectra.

INTRODUCTION

The interaction of water vapour with clean metal surfaces has been studied and characterized by XPS and UPS in the past decade and the behaviour of the interaction can be summarized in general by three categories.

Firstly, molecular adsorption at low temperature takes place with no evidence for any interaction at room temperature.(1–5) Secondly, dissociative adsorption at room temperature gives chemisorbed oxygen and molecularly adsorbed water. In the third category dissociation of the water, molecule is only partial and surface hydroxyl species dominates.(6–11)

In each case of these studies, the oxygen species

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with $O_{(1s)}$ binding energy between that of chemisorbed oxygen and adsorbed water molecules was assigned to the hydroxyl groups.

In this work, the Photoelectron spectroscopy (XPS) was used to determine surface concentrations of oxygen, hydroxyl and water molecules through monitoring the $O_{(1s)}$ spectral regions, while the (UPS) provided information about the nature of the bonding of the adspecies to the substrate.

Experimental

Spectra from polycrystalline chromium surface were obtained by using a Vacuum Generators model ESCA-5 Spectrometer, fitted with a VGQ7 mass spectrometer for use in monitoring the gas phase(12) during evacuation and thermal treatment. Details of the spectrometer, sample preparation mounting base pressures and operating conditions together with data quantification can be found in previous publications.(13-15)

Fig. 1 shows a series of $He_{(1)}$ spectra for various exposure of H_2O-vapour to clean surface at 80 K, then subsequent heating of the substrate to 623 K, together with the gas phase,(12) while Fig. 2 shows some of the difference spectra corresponding to Fig. 1.

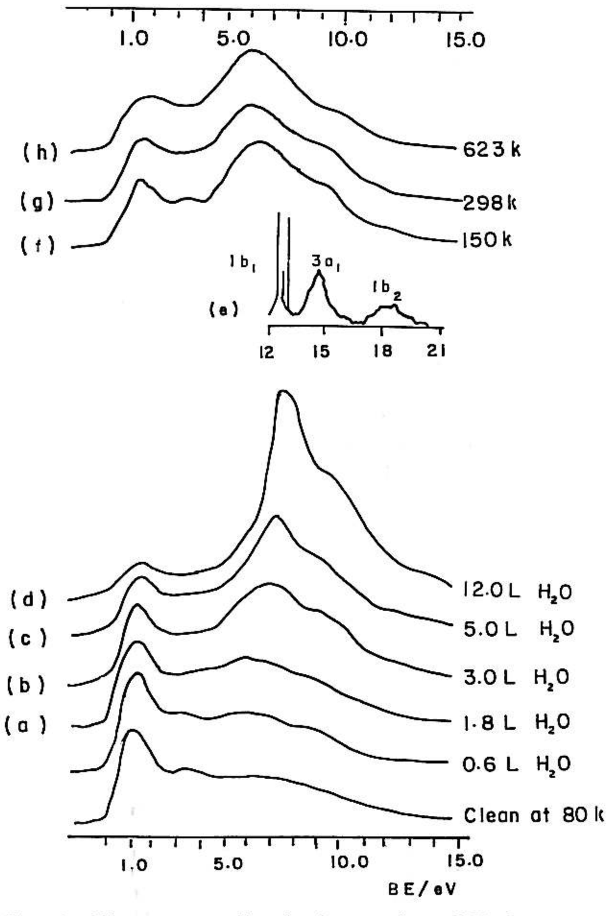


Fig. 1. $He_{(1)}$ spectra for the interaction of H_2O–vapour with a clean chromium surface at 80 k together with the gas phase spectrum of H_2O, and subsequent heating the adlayer to 623 k.

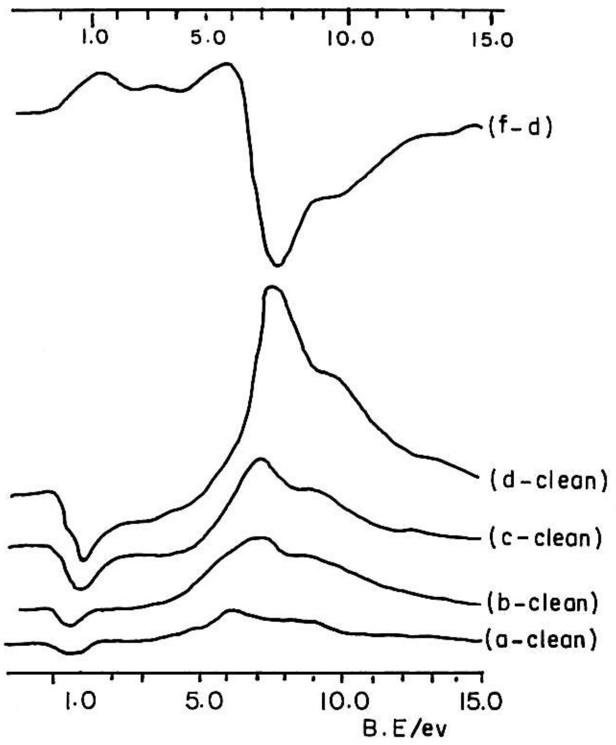


Fig. 2. Shows some of the difference spectra corresponding to figure 1.

The three valence orbitals of the H_2O molecules are $1b_1$, $3a_1$ and $1b_2$, the $1b_2$ provides the bonds between the hydrogen and oxygen holding the molecule together while the $3a_1$ bond between the two hydrogens gives the water about 109° bend,(12) and the $1b_1$ is the non-bonding oxygen orbital of pure 2p character.

The clean surface exhibits an intense band at about 1.0 ev with a second weak feature at 2.5 ev below the fermi level from the 3d level.

Slight changes in the $He_{(1)}$ spectra due to initial interaction of water vapour with clean surface are first observed, which resulted in the development of bands at 5.5 and 9.0 ev figure 1 and clearly in the corresponding difference spectrum (a-clean) Fig. 2.

On increasing the exposure, a more intense band at about 7.0 ev developed with increase of intensity and width of the band at 9.0 ev, at the same time the band at 5.5 ev is still seen from the profile of the 7.0 ev to lower binding energy. With more addition of water vapour, the band at 7.0 ev becomes narrower and is shifted to 7.3 ev and at the same time a weak third band emerged at 13.0 ev with the attenuation of the d-band.

From the difference spectra and by comparison with the gas phase spectrum, there are three regions, 4.5 to 5.5, 6 to 9.0 and 9 to 13.0 ev. The 4.5 to 5.5 ev region is assigned to emission from the $0_{(2p)}$ orbital of the chemisorbed oxygen from observations of the interaction of clean chromium with oxygen.(15) The second region 6.0 to 9.0 ev is composite, being made up to emission from the $O_{(2p)}$ surface hydroxyl and the lb$_1$ orbital of molecularly adsorbed water at about 7.3 ev,(16–18) and the third region which is also composite, is made up of emission from the hydroxyl (at 9.5 ev) and emission from the 3a$_1$ orbital of molecularly adsorbed water at 13.0 ev.

DISCUSSION

Initially, at low exposure ($\sigma <$ monolayer), the interaction of H_2O-vapour with clean surface is dissociative at the active site of chromium atoms through the formation of an adsorbed oxyhydroxyl layer, together with molecular water which is coordinately bonded to the unsaturated sites via the oxygen atom which is strongly held.

The curve-fitting $O_{(1s)}$ spectral region shows three components peaks at 530.1 (due to chemisorbed oxygen), 531.7 (due to chemisorbed hydroxyl species), and 533.5 ev (due to molecular water) respectively.

The $He_{(1)}$ spectra corresponding to this range of coverage shows a band mainly in regions one and two as shown in Fig. 1(a,b), and the difference spectra (a-clean) (b-clean) in Fig. 2, which mainly shows the band due to chemisorbed oxygen atoms (O_{2p}) and chemisorbed hydroxyl species,(16–18) whereas the lb$_2$ orbital from the molecularly adsorbed water in the third region is very weak indicating that water molecule does not have its integrity on the surface with this range of exposure.

The second layer which represents the physically adsorbed layer occurs at higher than one monolayer coverage through water molecules hydrogen bonded to the chemisorbed oxyhydroxyl layer which cannot be distinguished from the OH species of the chemisorbed layer by XPS or UPS techniques (strong hydrogen bonding interaction O^{δ}...... H–OH). This occurs at low temperature between molecularly adsorbed water and surface oxygen.(1,19)

The second type of physical adsorption is represented by H_2O – molecules which are hydrogen bonded to the chemisorbed layer through hydrogen atoms and weakly bonded to the surface through oxygen atom. These two types of physical adsorption may be illustrated by models (1) and (2) respectively.

On increasing the coverage ($\sigma = 2.6$) the main changes are the increase in the intensity of $O_{(1s)}$ at 533.5 ev with a shift in the B.E. to 534.0 ev, the $He_{(1)}$ spectrum, Fig. 1 and 2 shows the bands of the condensed molecular water at about 7.3, 9.5 and 13.0 ev respectively.

As the adlayer is warmed to 150 k, most of the $O_{(1s)}$ intensity at 534.0 ev disappears with a shift to 533.5 ev and a little increase in the intensity of $O_{(1s)}$ at 530.1 and 531.7 ev, with a total concentration of oxygen adlayer left on the surface 2.1×10^{15} atom. cm^{-2} ($\sigma = 1.3$).

The corresponding $He_{(1)}$ spectrum showed disappearance of the molecular orbitals from regions two and three with a shift in the bands of lb$_1$ and 3a$_1$ at 7.3 and 9.5 ev to lower binding energy and much wider than before, with gained intensity at 5.5 ev. The layer which is desorbed at 150 k represents the condensed water.(20)

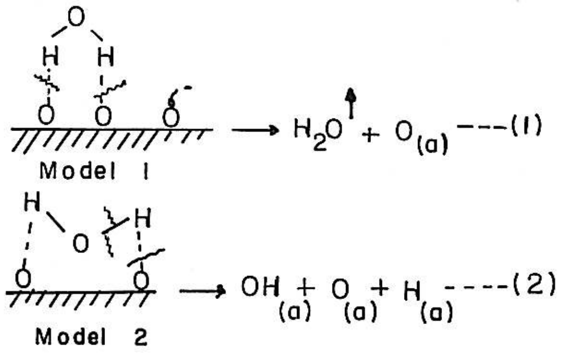
On further warming the substrate to R.T. 298.0 K the intensity of the $O_{(1s)}$ at 530.1 ev increased by half what is lost from the intensity at 531.7 and 533.5 ev respectively (Table 1).

Table 1. Surface concentrations of chemisorbed oxygen, hydroxide and water from the curve-fitted data of XPS–spectra

Treatment	*$\sigma \times 10^{-15}$ of $O_{(1s)}$ chemisorbed hydroxide*	*$\sigma \times 10^{-15}$ of chemisorbed hydroxide*	*$\sigma \times 10^{-15}$ of water*
1.8 L H_2O at 80 k	0.070	0.120	0.123
3 L H_2O at 80 k	0.080	0.480	0.590
6 L H_2O at 80 k	0.20	0.650	1.270
12 L H_2O at 80 k	0.160	1.050	2.982
Warmed to 150 k	0.360	1.360	0.441
Warmed to 210 k	0.540	0.970	0.237
Warmed to 298 k	0.880	0.640	0.120
Warmed to 623 k	1.410	0.170	0.075
30 L H_2O on clean at 298 k	0.500	0.20	—
400 L H_2O at 298 k	1.110	0.50	0.219
Heated to 623 k	1.390	0.27	0.154
Addition of 750 L H_2O over at 298 k	1.390	0.627	0.430
12 L O_2 clean at 298 k	1.50	—	—
12 L H_2O at 298 k	1.120	0.834	0.149
3672 L H_2O at 298 k	1.150	1.05	0.285
Heated to 623 k	1.870	0.282	0.112

The suggested explanation of this observation may be by dehydroxylation through the breaking of hydrogen bonding to desorb water molecules and addition of chemisorbed oxygen atoms to the surface (model 1), through the breaking of oxygen hydrogen bond and hydrogen bond toward the chemisorbed oxygen to form chemisorbed hydroxyls on the surface, chemisorbed oxygen atoms and hydrogen atoms (model 2).

During the heating of the substrate from 298 to 623 k, the decrease in the concentrations of hydroxide and H_2O species at 531.7 and 533.5 ev is paralleled by an increase in the chemisorbed oxygen component at 530.1 ev, which clearly indicated that the decomposition proceeds through the dehydroxylation of chemisorbed hydroxide and dehydrogenation of the coordinative water molecule, the suggested mechanism is:



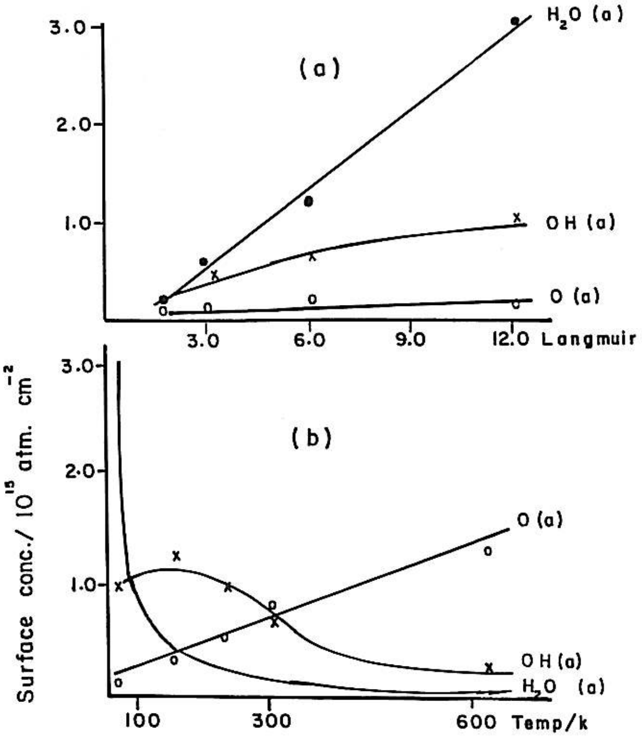


Fig. 3. Shows the variation of (α) oxygen species, $O_{(a)}$ and $H_2O_{(a)}$ concentrations with the exposure at 80 k, (b) $O_{(a)}$ $OH_{(a)}$ and $H_2O_{(a)}$ with temperature of the substrate.

$$OH_{(a)} \rightarrow O_{(b)} + \tfrac{1}{2}H_{2(g)}, \qquad (3)$$

$$H_2O_{(a)} \rightarrow O_{(b)} + H_{2(g)}. \qquad (4)$$

We assigned $O_{(b)}$ on the basis of the core level investigation, which shows that the bulk oxidation started at *R*. Temperature and no bulk oxidation below that temperature.

The hydrogen adatoms may be subsequently recombining and desorbing as molecular hydrogen,$^{(18)}$ where the dehydroxylation takes place above room temperature through desorption of hydrogen gas.$^{(4)}$

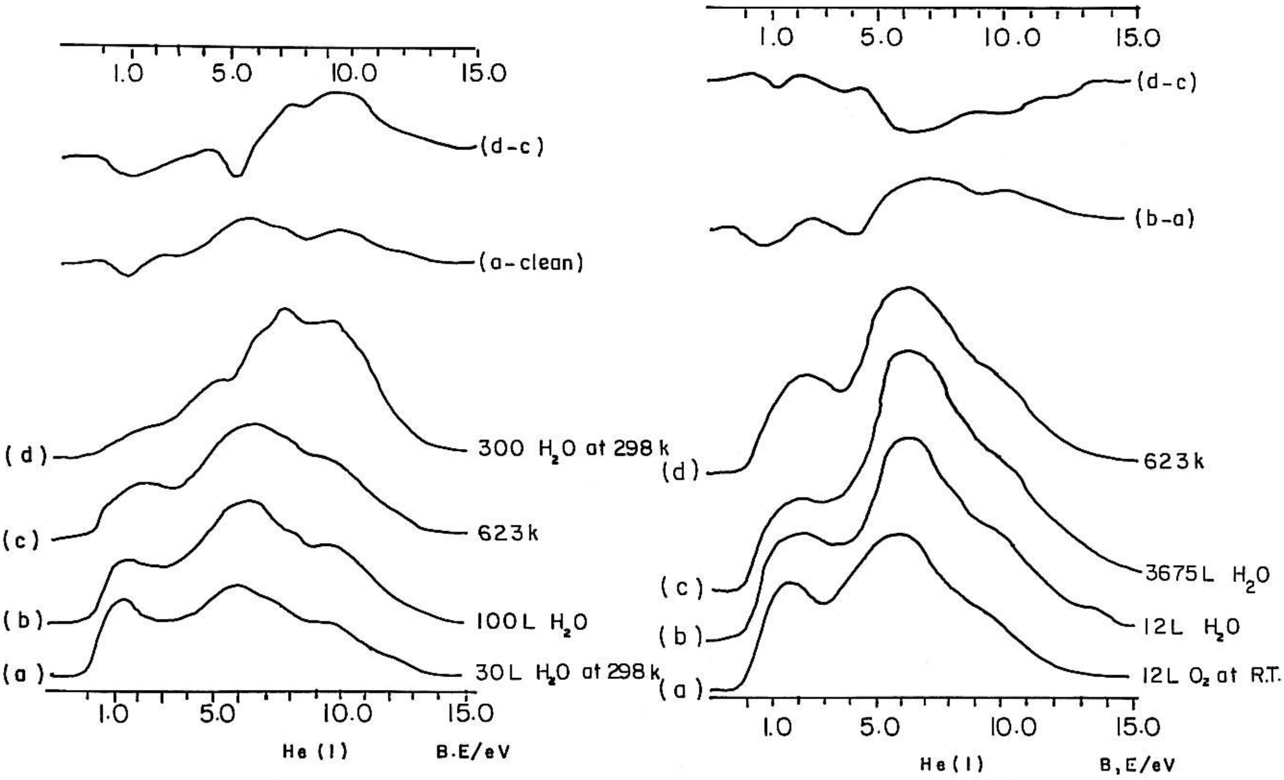
When the clean surface is exposed to H_2O-vapour at room temperature, the $O_{(1s)}$ spectral region after about half monolayer exposure, shows two wide components (from curve-Fit) with about 0.5 ev shift to higher binding energy, and the corresponding $He_{(1)}$ spectrum shows a development of three bands, when the up-take increase in one monolayer coverage the $O_{(1s)}$ component at 534.5 ev increases with a comparable increase in the intensity of the other components at 530.5 and 532.3 ev, respectively.

From these observations, the interaction of H_2O vapour with a clean surface at 298 k occurs by initial dissociation of water to chemisorbed oxygen atoms, followed by hydroxide and the water to form a layer of chemisorbed species, with higher concentration of chemisorbed oxygen atom on the surface than that at 80 k interaction.

On heating the substrate to 623 k, the mechanism of the activation is through the dehydroxylation and dehydrogenation of the hydroxyls and coordinative water molecules as mentioned before.

When this surface is cooled to 298 k, the addition of water vapour resulted in dissociation to hydroxyl and coordinative water adsorption without any change in the concentration of the $O_{(b)}$ at 530.1 ev. This confirmed that during the heating of the adlayer regeneration of the active metallic surface sites by incorporation of the chemisorbed oxygen atoms in to the bulk occurs and the adsorption of water vapour at 298 k leads to dissociation to hydroxyls and coordinative bonding water on the metallic site.

When the clean surface is pre-oxygen exposed at 298 k (σ = one monolayer), and then followed by H_2O-vapour, surface hydroxylation takes place and the concentration of the hydroxyls which is formed equal to twice the loss in the concentration of chemisorbed oxygen at low temperature and when the exposure of H_2O-vapour increased to 367 L, there was no change in the concentration of the chemisorbed oxygen and the only change is the increase in the concentration of the hydroxyls and water species. During the heating of the adlayer to 623 k, dehydroxylation occurs through desorption oxygen atoms to the surface (Fig. 4 which shows the desorption features from the hydroxyl and water bands).



(a) (b)

Fig. 4. (a) $He_{(1)}$ spectra for clean chromium surface exposed to H_2O–vapour, then heating the surface to 300L H_2O at 298 k. (b) $He_{(1)}$ for the partial oxidised surface with H_2O – vapour and heated to 623 k.

The suggested mechanism is that the Cr–O surface has active oxygen adatoms that have not developed the ionicity associated with the $Cr{-}O^{2-}$ bond on the surface (may be chemisorbed oxygen species on the surface) hydroxylated through hydrogen bonding to water molecules which are already coordinated to unsaturated metallic site, or may be decomposition of water molecule into a mixed adlayer of hydrogen atoms and surface hydroxyls on the active site, and then subsequently the hydrogen adatoms bonded to the chemisorbed oxygen adatoms from hydroxyl species; this mechanism can be illustrated by the following equations:

$$O_{(a)} + H_2O \xrightarrow{298\text{ k}} O\ldots\ldots H{-}OH, \qquad (5)$$

$$H_2O \xrightarrow{\text{active site}} OH_{(a)} + H_{(a)}, \qquad (6)$$

$$O_{(a)} + H_{(a)} \rightarrow OH_{(a)}, \qquad (7)$$

The dehydroxylation process is:

$$O\ldots\ldots H{-}OH_{(a)} \xrightarrow{623\text{ k}} 2O_{(b)} + H_{2(g)}, \qquad (8)$$

or

$$2OH_{(a)} \xrightarrow{623\text{ k}} 2O_{(b)} + H_{2(g)}. \qquad (9)$$

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