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# Weakly Bound Hydrogen on Oxygen Modified Ru(001) Surface

The nature of weakly bound hydrogen on metal surfaces is not fully understood and the experimental data are interpreted as being due to (i) physisorbed hydrogen, (ii) chemisorbed molecular hydrogen, (iii) dissociatively chemisorbed hydrogen, or (iv) hydrogen chemisorbed at surface and subsurface pair sites (*1*, *2*). In this note I report briefly on the formation of new adsorption states of weakly bound hydrogen which are observed on an oxygen modified Ru(001) surface. The low-temperature sites are populated by dissociatively chemisorbed hydrogen: weakly bound hydrogen is the majority species and its desorption spectra resemble those of Pd(110) surfaces (*3*).

The experimental system and preparation of sample were described in detail elsewhere (*4*). The ruthenium surface was cleaned by a combination of $Ar^+$ sputtering and thermal cycling with adsorbed oxygen. The results of hydrogen adsorption on a clean Ru surface were in good agreement with published data (*5*, *6*).

While the literature on $H_2$/Ru(001) and $O_2$/Ru(001) adsorption systems is rather extensive (*5*–*16*), that on $H_2 + O_2$ coadsorption is sparse (*17*). From a saturated Ru(001) surface two overlapping hydrogen desorption peaks evolve with activation energies of desorption of 30 and 21 kcal/mol (*5*). Both $\beta$ states originate from recombination of adsorbed atomic species as shown by the exchange experiment using a $H_2 + D_2$ gas mixture (*6*). The states have been correlated with the hcp and fcc types of threefold hollow sites (*5*); spectroscopic and exchange experiments, however, support the idea of surface–subsurface sites (*6*). Oxygen adsorbs dissociatively on a Ru(001) surface at threefold hollow sites in a single adsorption state with a coverage-dependent activation energy of desorption 95 kcal/mol at low coverage limit (*16*). Ordered islands of adsorbed oxygen are formed at coverages well below saturation of the p (2 × 2) structure which occurs at $\theta_0 = 0.25$.

I am aware of only one study (*17*) which explicitly deals with hydrogen and oxygen interactions on Ru(001). White *et al.* have shown that the titration of adsorbed oxygen by hydrogen at low pressures and elevated temperatures proceeds in three regimes and is approximately first order in hydrogen pressure. There are, however, no data available on coadsorption of $H_2$ and $O_2$ on a Ru(001) surface.

Considerable changes in $H_2$ adsorption kinetics are observed when a Ru(001) surface is precovered with low coverage of oxygen $\theta_0 = 0.15$. At this particular coverage a part of metal surface is covered by oxygen islands with the p (2 × 2) structure, as concluded from the observed (2 × 2) LEED pattern, while the remaining part of the metal surface does not contain any chemisorbed oxygen. The saturation coverage of hydrogen decreases to 3/4 of the clean surface value and, due to a higher sticking coefficient, the saturation is achieved after exposure to only 3 Langmuirs (L) $H_2$. In contrast, on a clean Ru(001) surface, exposure to 85 L $H_2$ is needed to saturate the surface (*5*).

Thermal desorption spectra of hydrogen from a clean and modified Ru(001) surface are compared in Fig. 1. For exposure to 1 L $H_2$, which corresponds to 0.4 $\theta^{\mathrm{sat}}_{H_2}$, hydrogen desorbs at 370 K (curve a) with an estimated activation energy of desorption 25 kcal/mol. On oxygen-modified surfaces ($\theta_0 = 0.15$) after exposure to 1 L ($H_2 + D_2$) mixture three desorption maxima ($\beta$,

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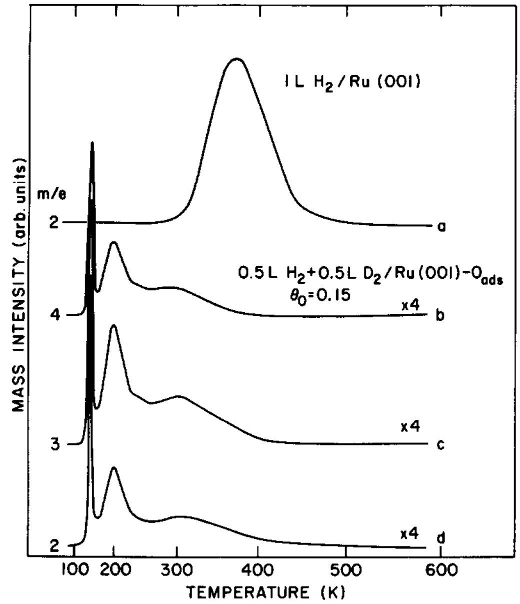

FIG. 1. Thermal desorption spectra of hydrogen from clean (curve a) and from oxygen modified (curves b, c, d) Ru(001) surface.

$\alpha_2$, $\alpha_1$) are found at lower temperatures, namely at 300, 195, and 150 K. Exchange experiments show that the origin of all three states is the recombination of atomic hydrogen and deuterium. In Fig. 1 (curves b, c, d) the desorption products are monitored at *m/e* 4, 3, and 2 after adsorption of 0.5 L $H_2$ and 0.5 L $D_2$ and the resulting rate curves are almost identical. Results of exchange experiments are independent of the order of adsorption of $H_2$ and $D_2$; thermal desorption spectra are strongly dependent on the oxygen coverage and oxygen ordering (*18*). Water as a reaction product was never observed among desorption products from a coadsorbed hydrogen and oxygen layer. Additionally, oxygen coverage does not decrease after hydrogen desorption as deduced from XPS and AES spectra. One can speculate that the oxygen adsorption bond is too strong and has therefore limited reactivity toward coadsorbed hydrogen.

The 150 K maximum ($\alpha_1$ state) has few unusual characteristics that rule out a simple second-order desorption maximum: (i) half width of the peak is 6 K, (ii) its shape is highly asymmetric, (iii) its position shifts by 5 K to higher temperature as $\theta_H$ increases. Similar characteristics were observed for autocatalytic peaks (*19*, *20*) but our isothermal desorption experiments failed to confirm the explosive nature of this state. Estimates of activation energy of desorption from Redhead's (*21*) and Edward's (*22*) equations give physically unreasonable values for an $\alpha_1$ state. Estimates according to Schmidt (*23*) resulted in a value of 8 kcal/mol assuming $\nu = 10^{-2}$ cm$^2$ s$^{-1}$. A zero order process cannot be ruled out since the leading edge of the $\alpha_1$ state obeys the logarithmic law. Estimate of an activation energy for desorption based on the leading edge yields 5 kcal/mol, in reasonable agreement with published data (*3*). Activation energies of desorption of 16 and 21 kcal/mol were estimated for $\alpha_2$ and $\beta$ states using Redhead's plot for second-order desorption.

Integrated areas under desorption peaks show that at $\theta_0 = 0.15$ only one-third of the hydrogen evolves at 300 K, while the remaining two-thirds of it are desorbed at 150 and 195 K. This ratio changes as $\theta_0$ increases up to 0.25. In fact, at saturation of a p ($2 \times 2$) oxygen layer only the $\alpha$ states are observed in desorption spectra. We conclude that the 300 K hydrogen desorption originates from the patches of bare metal while the $\alpha$ states are due to hydrogen recombination and desorption within the oxygen islands (*18*).

Hydrogen and oxygen coadsorbed on Ru(001) exhibit a unique behavior. The fact that weak hydrogen adsorption states are formed within the ordered oxygen islands indicates the electronic effect of coadsorbed oxygen. On bare metal patches outside of oxygen islands the effect of coadsorbed oxygen is less prominent, as seen from a small decrease of desorption of the $\beta$ state. It is worth noting that hydrogen adsorption on an oxygen modified Ru(001) resembles that on a clean Pd(110) surface, at least in terms of desorption kinetics. The results on Pd(110) were interpreted using a model of subsurface hydrogen species (*3*) on crystallographically open Pd(110), and it may be possible that oxygen makes the close-packed hexagonal face of the Ru(001) surface more heterogeneous.

Hydrogen chemisorption measurements are often used to determine adsorption properties like metal surface area, dispersion, and average particle size for supported metal catalysis (*24–26*). The presence of tightly bound oxygen on the surface of ruthenium affects the outcome of these measurements to a great extent (*25*). Data presented in this note show that even low concentrations of oxygen impurity bring about significant changes in hydrogen chemisorption and therefore special care must be taken to remove oxygen completely in order to obtain reliable adsorption characteristics of a ruthenium catalyst.

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