Catalysis Letters 2 (1989) 35–42

NEW ADSORPTION STATES OF HYDROGEN ON SULFUR MODIFIED Ru(001)

Guo-Qin XU and J.A. HRBEK

Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, U.S.A.

Received 6 July 1988; accepted 22 November 1988

We have carried out studies of hydrogen adsorption on sulfur covered Ru(001) and observed two weak hydrogen adsorption states with desorption temperatures at 135 K and 265 K. The existence of these hydrogen states is attributed to the long-range electronic effects of sulfur adatoms in addition to their site blocking, and also to the repulsive interactions among coadsorbed hydrogen within a p(2×2)-S structure.

1. Introduction

Sulfur adsorbed on single crystal metal surfaces and its effect on coadsorption of simple molecules have been investigated extensively during the past decade as a model of catalyst poisoning. The understanding of the poisoning mechanism is of great technological importance since it can offer ideas for increasing sulfur tolerance in processes where fossil-fuel-based feedstreams are used.

Ruthenium metal is known to be an effective catalyst for Fischer-Tropsch synthesis, whose activity is strongly affected by sulfur adsorption [1,2]. Recent model studies of hydrogen adsorption on sulfur-covered ruthenium single crystal surfaces [3–6] revealed that the principle role of sulfur adatoms was to block the dissociation and recombination sites for hydrogen adsorption and desorption at coverages $\theta_s < 0.25$. No hydrogen adsorption was observed on a fully developed p(2 × 2)-S overlayer ($\theta_s = 0.25$) [4,5]. In the most recent work, the surface diffusion coefficient of hydrogen on S/Ru(001) surfaces, measured by laser induced thermal desorption, dropped rapidly with increasing sulfur coverage [5]. It was proposed that each sulfur adatom must block ten hydrogen adsorption sites (at variance with thermal desorption data, suggesting four blocked sites only) in order to simulate the results of surface diffusion measurements [5].

Our experiments were carried out at low temperature on the Ru(001) surface modified by sulfur with varying coverage and we observed two weakly bound hydrogen states within the p(2 × 2)-S unit cell. Our results demonstrate the first observation of the long-range electronic perturbations by S adatoms of the Ru(001) surface in addition to the steric effect.

2. Experimental

The details of the experimental system and sample preparation were described elsewhere [7]. The techniques used in this experiment were thermal desorption with isotopic exchange, LEED, XPS, and UPS. The sample is cleaned by the combination of Ar^+ sputtering and thermal desorption of adsorbed oxygen.

An electrochemical sulfur doser was built [8] and used for preparation of S/Ru(001) surfaces. The doser was operated at 443 K with an approximate deposition rate of 1×10^{13} S atoms/s.cm^2. After outgassing the doser for several hours, only a small increase in the vacuum chamber base pressure ($< 2 \times 10^{-10}$ torr) during deposition could be observed. After each deposition of sulfur at 100 K the sample was annealed for 2 minutes at 600 K to insure the equilibrium ordering of S adatoms. The coverage of S was measured by XPS and cross-checked by LEED studies. With increasing sulfur coverage, a sequence of LEED patterns was observed, namely, a p(2 × 2), a $(\sqrt{3} \times \sqrt{3})$R30°, a c(4 × 2) and compressed structures for $\theta_s > 0.5$.

In order to eliminate the backside contribution in TDS studies, the backside was saturated with $\theta_s > 0.5$. Since sulfur adatoms at coverages of $\theta_s > 0.33$ block completely the hydrogen adsorption, hydrogen in our TDS studies evolved exclusively from the front of the crystal. A similar masking procedure was used in a quantitative study of hydrogen adsorption on Cu/Ru surfaces [9].

Because in previous studies [4,5] hydrogen sulfide was used as a sulfur source, we used it in several experiments for comparison. The results of hydrogen adsorption and desorption on S/Ru(001) surfaces prepared either by H_2S and the S doser were found to be identical.

3. Results and discussion

In the LEED studies, a p(2 × 2) pattern is observed for coverages $0.1 < \theta_s < 0.25$, suggesting (2 × 2)-S islands formation due to the long-range attractive interaction between the S adatoms. For sulfur coverages < 0.25 the surface consists of p(2 × 2)-S islands and patches of clean Ru. For $0.25 < \theta_s < 0.33$, mixed p(2 × 2) and $(\sqrt{3} \times \sqrt{3})$R30° LEED patterns are observed which clearly shows that the $(\sqrt{3} \times \sqrt{3})$ R30° and p(2 × 2) islands of the sulfur overlayer coexist on the surface.

We have carried out detailed TDS studies of the H_2 interactions with S/Ru(001) for different θ_s and found that H_2 can be adsorbed on surfaces with $\theta_s < 0.33$, but not at $\theta_s \geqslant 0.33$. In fig. 1 we compare the thermal desorption spectra of hydrogen from a clean Ru(001) (fig. 1a) and from S/Ru with $\theta_s = 0.12$ (fig. 1b). A p(2 × 2)S LEED pattern is observed at this particular sulfur coverage. There are three additional features in the TD spectra, labeled α1, α2, and e, in addition to the peaks associated with hydrogen desorption from clean Ru patches. The e maxi-

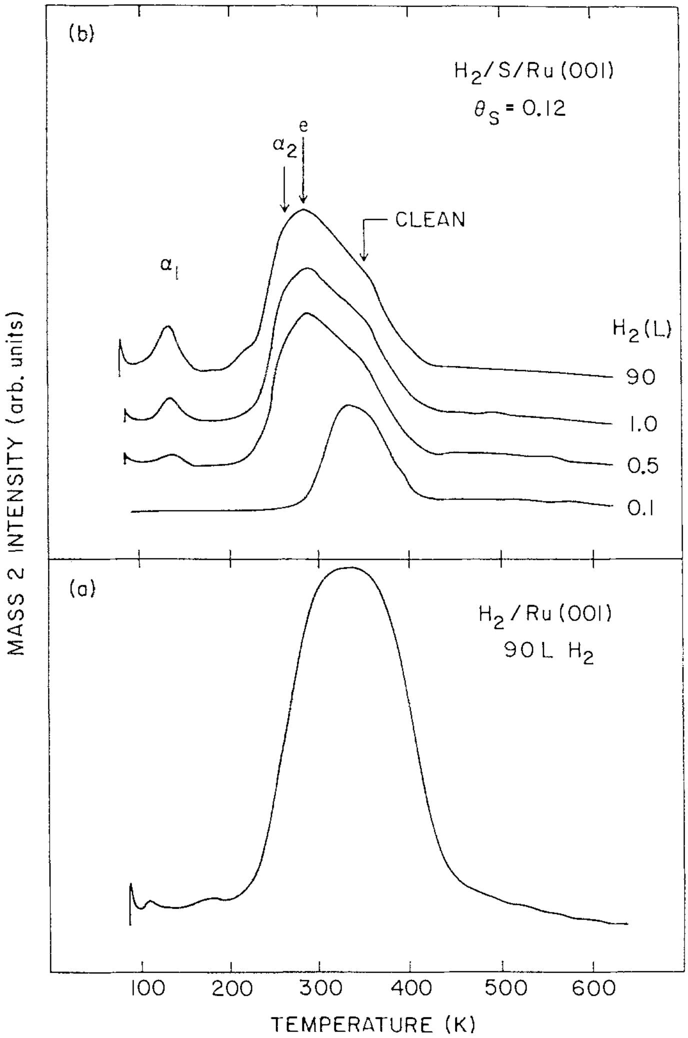

Fig. 1. Thermal desorption spectra of hydrogen adsorbed on a clean (a) and sulfur modified (b) Ru(001) surface.

mum, which appeared as a shoulder at 290 K for $\theta_s < 0.1$, had reached the highest intensity for $\theta_s \sim 0.16$, and then its intensity dropped precipitously. The initial increase of e intensity was accompanied by the concurrent decrease of peaks related to desorption from clean Ru patches. Desorption temperature of e maximum remained constant regardless of sulfur coverage. Once the Ru surface was covered completely with a p(2 × 2)-S overlayer the e maximum disappeared completely from desorption spectra (fig. 2). Such a behavior suggests that the e origin is the desorption of hydrogen from the boundary zone between sulfur islands and clean Ru patches.

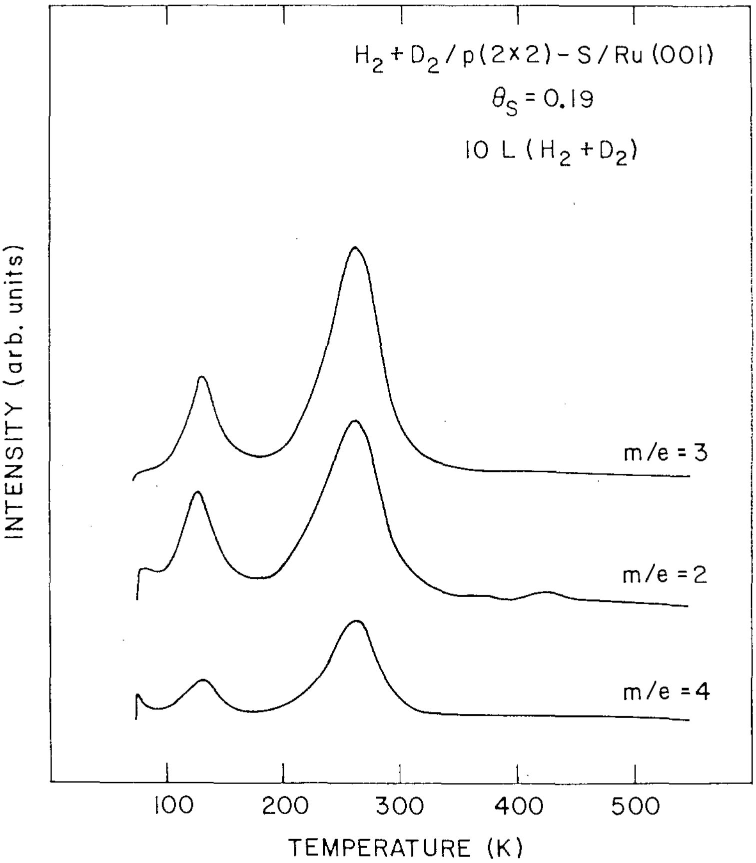

Fig. 2. Thermal desorption spectra of H_2, HD and D_2 from hydrogen-deuterium 1:1 mixture adsorbed on sulfur modified surface.

α1 and α2 are the only desorption peaks of hydrogen observed on Ru(001) covered with a completed p(2 × 2)-S overlayer (fig. 2) and with the mixtures of p(2 × 2)-S and $(\sqrt{3} \times \sqrt{3})R30°$ overlayers. The activation energies of α1 (at 135 K) and α2 (at 265 K) were estimated [10] to be 7.7 and 16.1 kcal/mol, respectively, assuming second-order kinetics and solving the differential equation graphically. The intensities of the α1 and α2 peaks increase with S coverage in the range of $\theta_s < 0.25$ and drop rapidly for $\theta_s > 0.25$. Their ratio is 0.3 and independent of S coverage.

The experimental data clearly suggest that the origin of α1 and α2 is the hydrogen adsorbed within the p(2 × 2)-S unit cell. Once the sulfur coverage reaches $\theta_s = 0.33$ and a $(\sqrt{3} \times \sqrt{3})R30°$ structure is completed, α1 and α2 will disappear and no hydrogen desorption is detected.

The nature of the surface species is very important for understanding the mechanisms of gas-surface reactions. A weakly bound state like α1 would suggest the possibility of adsorbed molecular hydrogen. An isotope exchange experiment

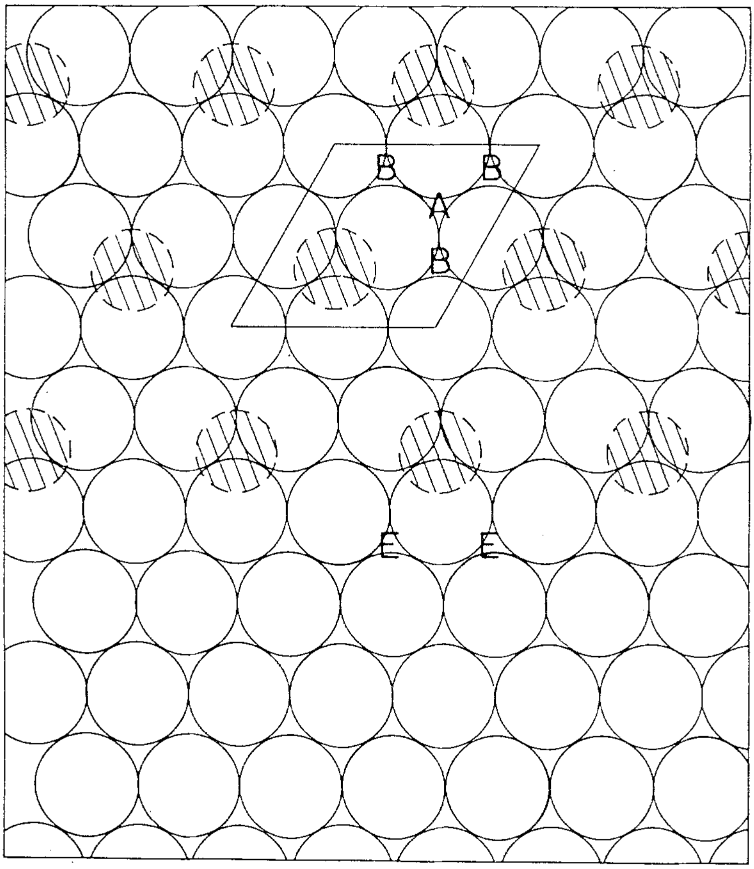

Fig. 3. Real space structure of a p(2×2)-S/Ru(001) surface with three-fold hollow sites within the (2×2) island (A, B) and along the island edge (E).

was therefore carried out, the result of which is shown in fig. 2. The complete scrambling of H and D isotopes demonstrates that the hydrogen in both $\alpha 1$ and $\alpha 2$ peaks is adsorbed dissociatively.

Although extensive work has been done on hydrogen adsorption on Ru(001), it is still not clear whether the saturation coverage of hydrogen on the Ru surface is $\theta_H = 2$ or $\theta_H = 1$ [11,12]. The following discussion is based on the assumption of $\theta_H = 2$. From inspection of fig. 3, which displays a real space model of the Ru surface with a p(2 × 2)-S island, it is obvious that our results rule out the possibility of one S adatom blocking ten Ru sites, as proposed by S. George et al. [5]. This blocking ratio would totally present hydrogen adsorption on the p(2 × 2)-S covered Ru(001). In earlier studies [3,4] the authors had shown that each S adatom blocks four hydrogen adsorption sites (for $\theta_s < 0.25$) by comparing the coverages of hydrogen on S/Ru(001) and clean Ru(001). However, the adsorption of hydrogen on a p(2 × 2)-S covered Ru(001) surface, which would be allowed in case of four blocked sites, was not observed. The relatively high temperature at which the experiments were carried on did not allow hydrogen adsorption in weakly bound states.

In contrast to the previous experiments, our observation of $\alpha 1$ and $\alpha 2$ desorption peaks of hydrogen adsorbed within the $p(2 \times 2)$-S unit cell not only agrees with this one-to-four blocking model, but the low activation energies of the new hydrogen states suggest the long-range electronic modification of the Ru(001) surface by sulfur adatoms.

In reference to fig. 3 we assume that: (i) sulfur and hydrogen adatoms are competing for three-fold hollow sites; (ii) each S atom blocks four three-fold hollow sites; (iii) hydrogen coverage on a clean Ru surface at saturation is $\theta_H = 2$. The two types of unblocked three-fold hollow sites on the S/Ru(001) surface are found within the $p(2 \times 2)$ unit cell and labeled A and B. Notice that the sites are nonequivalent, having different neighbor and next-nearest neighbor sites. The sites located on the edges of the $p(2 \times 2)$-S islands are labeled E.

In an attempt to assign $\alpha 1$ and $\alpha 2$ hydrogen desorption peaks to the corresponding adsorption sites, we consider the interactions between coadsorbates, that is, H to H and S to H. Since the distances of H to H and H to S on the surface are much larger than the regular bond lengths for H_2 and H-S in H_2S, the direct through space interactions between adsorbates can be ruled out. If A and B sites are populated with hydrogen atoms, the hydrogen which sits on the A site may experience the repulsive interactions from the neighboring B hydrogen adatoms and also from the three S atoms. On the other hand, hydrogen occupying the B site will be effected by the proximity of only one A hydrogen adatom and two sulfur atoms. We may therefore expect two desorption states of hydrogen with differing activation energies. The experimental ratio of desorption intensities $\alpha 1 : \alpha 2 = 1/3$, is independent of θ_s, and thus suggests a tentative assignment of A site hydrogen to the $\alpha 1$ desorption state and B site hydrogen to $\alpha 2$. However, additional experiment data (such as vibrational spectra) are needed to confirm the above proposed model.

$\alpha 1$ and $\alpha 2$ hydrogen states are much weaker than the hydrogen states on a clean Ru surface. The decrease in binding energy of ~ 10 kcal/mol must be due to the effect of adsorbed sulfur atoms. The possible mechanism involved here could be the long-range through metal electronic effect of S adatoms. The theoretical calculations of electronic perturbations by S adsorbed on Rh(001) have shown that the effect of sulfur on the surface electron density near the Fermi level, which is important to surface chemical phenomena, does extend beyond the nearest neighbor Rh atoms [13]. Our results suggest that this electronic effect may exist on Ru(001) also, although there is no theoretical work available for direct comparison.

Our results of hydrogen adsorption within the $p(2 \times 2)$-S unit cell are analogous to the case of hydrogen interaction with oxygen modified Ru(001) [14], in which two weakly bound states of hydrogen were also observed and assigned to the hydrogen adsorbed within a $p(2 \times 2)$-O overlayer. The similarity in

H/S/Ru(001) and H/O/Ru(001) behavior is anticipated, considering their position in the periodic table. However, the rather small work function change accompanying sulfur adsorption [3] points to more covalent bonding of sulfur as compared to oxygen, and one would expect differences in the modification of surface properties.

4. Conclusions

Two weakly bound hydrogen adsorption states, $\alpha 1$ and $\alpha 2$, were observed on S covered Ru(001) surfaces, and we propose their origin to be the hydrogen adsorbed on three-fold hollow sites within p(2×2)-S unit cell. If the saturation coverage of hydrogen on a clean Ru(001) is 2, then our results support the idea that each S adatom blocks four hydrogen adsorption sites. The low binding energy of $\alpha 1$ and $\alpha 2$ hydrogen states is caused by the long range electronic effect of S adatoms and possibly by the repulsive interactions among coadsorbates.

Acknowledgements

This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

References

[1] M.A. Vannice, Catal. Rev. 14 (1970) 1.
[2] R.J. Madon and H. Shaw, Catal. Rev. 15 (1977) 69.
[3] S.R. Keleman and T.E. Fischer, Surface Sci. 87 (1979) 53.
[4] J.A. Schwarz, Surface Sci. 87 (1979) 525.
[5] J.L. Brand, A.A. Deckert and S.M. George, Surface Sci. 194 (1988) 457.
[6] G.B. Fisher, Surface Sci. 87 (1979) 215.
[7] J.A. Hrbek, Surface Sci. 164 (1985) 205.
[8] W. Heegeman, K.H. Meister, E. Bechtold and K. Hayek, Surface Sci. 49 (1975) 161.
[9] D.W. Goodman, J.T. Yates Jr. and C.H.F. Peden, Surface Sci. 164 (1985) 417.
[10] P.A. Redhead, Vacuum 12 (1962) 205.
[11] P. Fuelner and D. Menzel, Surface Sci. 154 (1985) 465.
[12] J.T. Yates Jr., C.H.F. Peden, J.G. Houston and D.W. Goodman, Surface Sci. 160 (1985) 37.
[13] P.J. Feibelman and D.R. Hamann, Phys. Rev. Lett. 52 (1984) 61.
[14] J.A. Hrbek, J. Phys. Chem. 90 (1986) 6217.