WATER-INDUCED EFFECTS OF HYDROGEN ADSORPTION ON RU (001)

Ho-In Lee* and J.M. White**

Department of Chemical Technology, College of Engineering, Seoul National University,

Seoul 151, Korea

** Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

Abstract—Adsorption and desorption of hydrogen and coadsorption of H_2 with H_2O and CO over Ru(001) surface have been studied under UHV conditions using the technique of TDS. Surface hydrogen interacts with adsorbed water resulting in an additional desorption state at 510 K which is not easily displaced by CO, but the total number of adsorption sites for hydrogen adsorption is independent of the amount of H_2O predosed at room temperature. Hydrogen adsorption is blocked easily by CO dose (more than 0.5 L) or a small amount of O(a) formed from dissociative adsorption of water, and adsorbed hydrogen formed in the absence of significant water is easily displaced by CO dose at even room temperature.

INTRODUCTION

Since Grant and Haas reported a study of small molecules such as CO, CO_2, and O_2 on a well-defined surface of Ru (001) using techniques of LEED and AES in 1970 [1], a fair number of studies of small molecule chemistry on single crystal ruthenium (001) surfaces [2,11], (100) surfaces [12], (101) surfaces [13], (110) surfaces [14], and polycrystalline surfaces [15] have been reported.

In a practical vein, ruthenium is a catalytic material of great interest, particularly for its ability to reduce nitric oxide to nitrogen [16] in the presence of hydrogen and carbon monoxide without the production of nitrous oxide and ammonia and for its methanation activity [15].

In comparison to other transition noble metals like platinum, palladium, rhodium, and iridium, ruthenium has very little activity for the oxidation of carbon monoxide [3,9]. Thus, supported and/or promoted ruthenium has been primarily a methanation and pollution control catalyst.

Madey and Yates [5] have studied the low temperature behavior of water and ammonia using ESDIAD to get the local conformations and flash desorption spectra to characterize the adsorption states. Danielson et al. have examined ammonia, hydrogen, and nitrogen with particular emphasis on the decomposition of ammonia [7].

In spite of this significant number of studies, many questions remain, particularly those related to coadsorption of various species and to thermal effects during exposure and annealing. For example, is it possible to displace one chemisorbed species upon exposure to a second? Can different chemisorbed structures be formed depending upon an annealing cycle? What structures are formed when two species are coadsorbed? Is migration of surface species into the bulk an important process to the surface reaction?

These and other questions provide the motivation for continued study of small molecules on the basal plane of ruthenium and we fully anticipate the answers to be elusive and complex.

Beyond a few papers [5], little is known about the details of water chemisorption and its interaction with other chemisorbed species on Ru (001). Therefore, as part of a continuing series of surface study on Ru (001) [8,11], we report here a study of the adsorption and desorption of hydrogen and its water-induced effects by coadsorption.

EXPERIMENTAL

(1) UHV System

Two different stainless steel UHV chambers were used for the experiments. The one was ion-pumped, equipped with QMS, and designed specifically for TDS, and is shown schematically elsewhere [17]. The volume was about 1.5 l and the pumping was conductance-limited (S/V = 4 s^{-1} for CO). The operational

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* To whom correspondence should be directed.

background pressure was about 2 x 10⁻⁹ Torr. The other was a large chamber having a volume of about 24 1 which was pumped by a 450 1/s - turbomolecular pump and equipped with AES and LEED optics as well as QMS. The operational background pressure was about 4 x 10⁻¹⁰ Torr. The larger system is shown schematically elsewhere [17].

(2) Gas handling system

As seen in Fig. 1, the gas handling system was connected to the UHV system and was constructed of 1/4″ diameter copper tubing with shutoff valves and variable leak valves, and of stainless steel manifold and gas tanks. The manifold was connected to lecture bottles for gaseous reagents, a glass container for water, a TC gauge for the pressure in the manifold, a rotary pump for rough pumping of the manifold, and two gas tanks for storage of two different reagents which are admitted into the UHV chamber via variable leak valves.

(3) Reagents

Hydrogen was purchased from Linde Division of Union Carbide Corporation, and the quoted purity was 99,99%. No more purification, except liquid nitrogen trapping, was given. Water was degassed at liquid nitrogen temperature ten times (allowing the water to warm to room temperature in each cycle).

(4) Substrate

Both samples were cut by spark erosion from a rod of single crystal ruthenium with a diameter of 7 mm and 99.99% purity, which was produced at Materials Research Corporation. The desired orientation of the sample surface was indicated by Laue X-ray backscattering patterns, and deviated within 1° from the (001) face. The detailed sample preparation, mounting, and cleaning methods were discussed elsewhere [17]. For temperatures of the sample, a W-W/26%Re thermocouple was spotwelded to the center of each crystal. The sample could be heated to 1650 K using an ac power

supply, and the temperature was uniform to ± 10 K as checked by an optical pyrometer. Sample heating rate for TDS was changed slightly from one set of experiments to another but was typically 20-35 K/s. Schematic diagram of the Ru-target holder is shown in Fig. 2.

RESULTS AND DISCUSSION

Using flash desorption spectra, the amounts of adsorption of hydrogen as a function of exposure were obtained at 320 K. At 320 K 1 L H_2 exposure gave more than 90% of its saturation coverage. Only a single desorption peak was observed at all the exposures and it shifted from about 410 K to about 380 K with increased exposure from 0.1 L to 10 L. This indicates either first-order desorption kinetics with coverage-dependent desorption energy or a second-order desorption. The results agree fairly well with those reported by Danielson et al. [18]. They say that hydrogen adsorbs rapidly with a sticking coefficient of 0.4 on Ru (001) at 100 K and desorbs with second-order kinetics in the temperature range of 350 K-450 K. It should be noted that at 320 K a saturation coverage of H_2 is much smaller (approximately 10%) than that of CO suggesting that the amount of H_2 adsorption is strongly dependent on the adsorption temperature. In addition, rather a different desorption profile of H_2 is reported on Ru (110) [19] so there is a significant crystal face effect.

Figure 3 shows the displacement of the saturated hydrogen overlayer by a constant leak of 2 x 10⁻⁷ Torr CO. Curve (a) is a TDS spectrum of saturated hydrogen at 320 K, curve (b) is a displacement spectrum of hydrogen as a function of CO exposure, and curve (c) is a TDS spectrum of hydrogen after curve (b) was taken. The area under curve (b) is more than 97% of the area under curve (a) suggesting that predosed hydrogen can be easily and completely displaced by dosing CO at room temperature. Curve (c) has an area less than 5% of

to UHV system

A gas tank
B manifold
C molecular sieve trap
D rotary pump
E lecture bottle
F thermocouple gauge
G glass container
H liquid nitrogen trap
I bellows valve
J vent valve
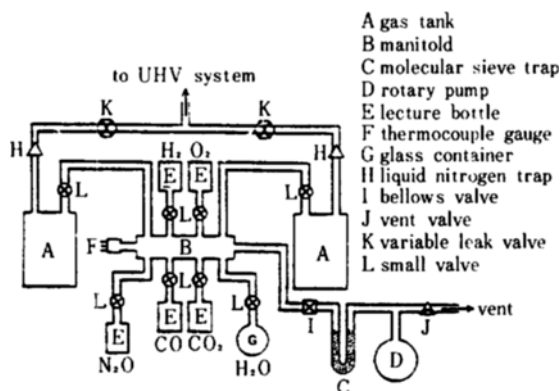K variable leak valve
L small valve

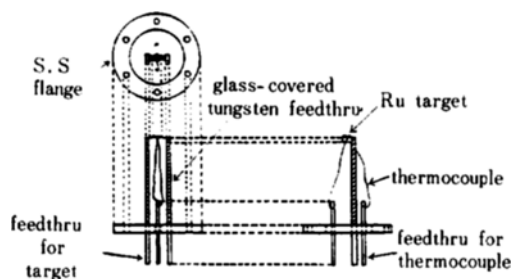Fig. 1. Schematic diagram of the gas handling system.

Fig. 2. Schematic diagram of the Ru-target holder.

curve (a) and might be due to a system response which is the result of outgassing from the inside walls of reaction chamber and ion-pump by a sudden increase of the system pressure during flashing CO. The system response will be discussed later. hydrogen displacement is also noted elsewhere [3,4].

Danielson et al. postulated in their paper [18] that H_2 and NH_3 occupy different sites on the ruthenium surface. It seems rather different for H_2, O_2, and CO according to the present work. That is, H_2 and O_2 appear to occupy the same sites because of the complete blocking of H_2 adsorption by a predose of more than 0.8 L O_2. In order to eliminate the idea that O (a) lowers the sticking of H_2, two different exposures (1 L and 20 L H_2) were flashed from the surfaces predosed 1 L O_2, and the same H_2 TDS area were obtained. H_2 and CO are also supposed to occupy the same adsorption sites because of the complete displacement of hydrogen by CO does as shown in Fig. 3.

Other evidence of hydrogen displacement by CO is worth noting. When CO desorption spectra of 15 L exposure are compared, identical results are obtained for surfaces with and without presaturation with H_2. Hydrogen displacement by CO also occurs in background which is usually less than 2 x 10^{-9} Torr con-

sisted mainly of CO and H_2. Experiments as a function of waiting time in background from few minutes to four days suggest that only a few hours is required to displace the adsorbed hydrogen. There is also some induced interaction with other species in the background, presumably H_2O as evidenced by a very slow accumulation of hydrogen on the surface which can not be displaced by CO. Figure 4 shows a series of H_2 TDS spectra derived from hydrogen background adsorption (about 5 x 10^{-10} Torr H_2) over 5 min as a function of exposure of CO predosed. In this figure we see a sudden drop of the amount of H_2 desorbed between 0.5 L and 1.0 L CO predosed while at lower CO exposures the H_2 desorbed is almost constant. Curve (a) is about 20% of hydrogen saturation at 320 K. Figure 4 suggests that up to a certain amount of predosed CO (between 0.5 L and 1 L CO) hydrogen and carbon monoxide do not compete for adsorption sites. However, adsorbed CO does give a strong repulsive interaction resulting in a shift of the H_2 peak position from 410 K to 375 K over the first 0.5 L CO predosed. Curves (d) and (e) are supposed to be due to system response because of the same shape and position of peaks as those of CO TDS spectra.
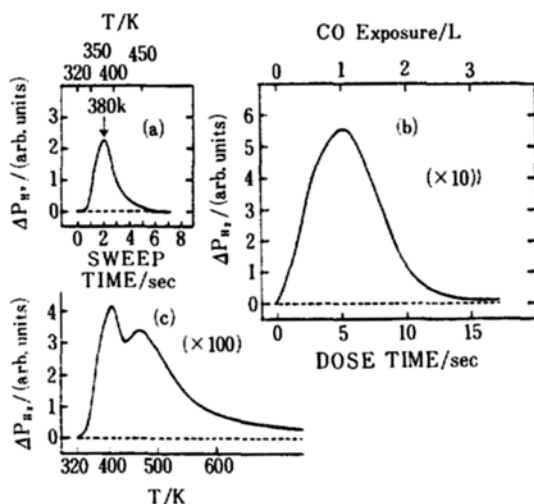

Fig. 3. Displacement spectrum of a saturated hydrogen overlayer by a constant leak of 2×10^{-7} Torr of CO. Curve(a) is a TDS spectrum of the saturated hydrogen at 320K, curve(b) a displacement spectrum of hydrogen as a function of CO exposure, and curve(c) a TDS spectrum of hydrogen after curve(b) was taken. The area under curve(b) is more than 97% of that under curve(a)
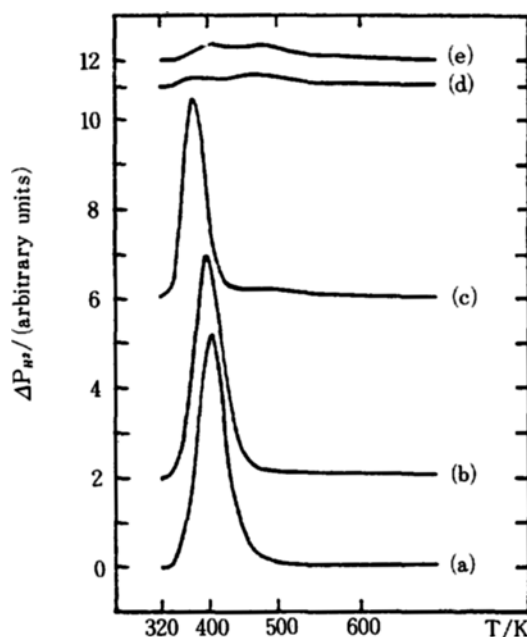

Fig. 4. H_2 TDS spectra derived from hydrogen background adsorption of about 5×10^{-10} Torr of H_2 over 5 min as a function of predosed CO. Curve(a) is about 20% of hydrogen saturation coverage at 320 K. Curves(a), (b),(c),(d), and (e) were obtained from the surfaces predosed with CO of (a) 0 L, (b) 0. 1L,(c) 0. 5L,(d) 1 L, and (e) 20 L.
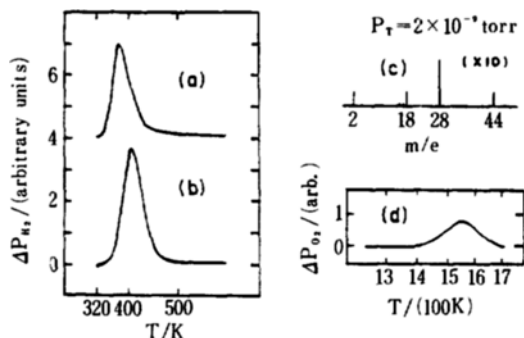
Fig. 5. H₂ TDS spectra arising from background hydrogen adsorption showing the effects of heat-cool cyclings between 320 K and 650 K in the background. Curve(a) is an H₂ TDS spectrum after 15 consecutive heat-cool cyclings, and curve(b) is a background H₂ TDS spectrum without heat-cool cycling after waiting for the same period required for leading up to curve(a). Curve(c) is a background distribution, and curve(d) is a O₂ TDS spectrum after curve(a).

Fig. 6. H₂ TDS spectra which were taken by repeatedly flashing the target after being predosed with 5 L H₂O at 320 K followed by H₂ adsorption from the background for 10 min. Only the first and the last spectra are shown as dotted lines among 8 consecutive H₂ TDS spectra. The positions of the two peaks of the other six spectra between them are shown by filled circles and squares for lower and higher temperature peaks, respectively. Curves(a) and (b) are simply the connections of each group of points for observing easily the changing mode.

Figure 5 shows two hydrogen TDS spectra arising from background H₂ adsorption. The background gas phase distribution is shown in curve (c). Curve (a) is the H₂ TDS spectrum after 15 consecutive heat-cool cyclings between 320 K and 650 K in the background, while curve (b) is a background H₂ TDS spectrum without heat-cool cycling after waiting for the same period required to all the desorptions leading up to curve (a). Curve (d) is an O₂ TDS spectrum after curve (a). There is a decrease in the peak height by about 20% and a shift of the peak position from 410 K to 375 K resulting from the 15 consecutive heat-cool cyclings. The comparison of the two spectra in Fig. 5 suggests that surface oxygen dissociated from background H₂O during 15 consecutive heat-cool cyclings causes H₂ TDS to shift to lower temperature due to the repulsive interaction between O(a) and H(a) and to a decrease of the amount of H₂ adsorption as a result of site blockage.

Figure 6 shows 8 consecutive H₂ TDS spectra which were taken by repeatedly flashing the target after being predosed with 5 L H₂O at 320 K followed by H₂ adsorption from the background for 10 min for each spectrum. The order taken data is from left to right. All these spectra have an extra peak at higher temperature when compared with the H₂ spectrum of Fig. 5 which has only one peak at about 410 K. It is clear that the lower temperature peak decreases monotonously (curve (a)) and the higher temperature peak increases slowly and then keeps almost constant (curve (b)) with number of flashings. But the second peak area grows monotonous-
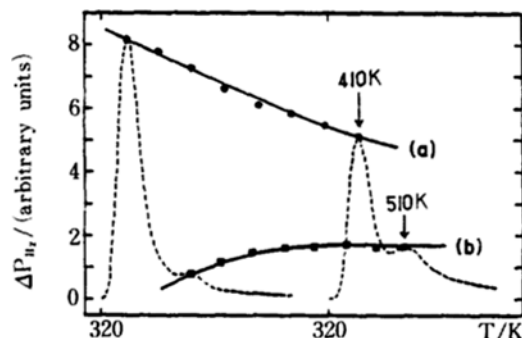
ly due to a long tail. The combined area of the two peaks remains constant (about 0.03 ML). During these experiments the background pressure rose from 1 x 10⁻⁹ to 5 x 10⁻⁹ Torr showing the biggest fractional increase in water. The higher temperature desorption state is not displaced by CO exposed at 320 K unlike in Fig. 3. The results suggest that the total number of sites available for the H₂ adsorption regardless of predosed water remains constant, and that some of them are modified due to the interaction between H(a) and H₂O(a). A detailed mechanism is not yet established although a possible alternate source of the second peak is the desorption of hydrogen dissociated from water.

The inside walls of the vacuum system, including the ion pump wall, slowly adsorb all the gases existing in the background, especially H₂, H₂O, CO, O₂, Ar, and CO₂ which are the major components in our TDS system. The system, therefore, upon a sudden change of system pressure is expected to respond by desorbing certain gases. Figure 7 shows this kind of response, so-called "system response". The figure gives six spectra for the above six major species in the background when the surface is flashed after dosing 15 L CO. When the target is flashed, a sudden change of the system pressure occurs due to the desorption of 15 L CO adsorbed. From the data we find no significant response except H₂ whose spectrum gives the same shape as that of the CO TDS spectrum.
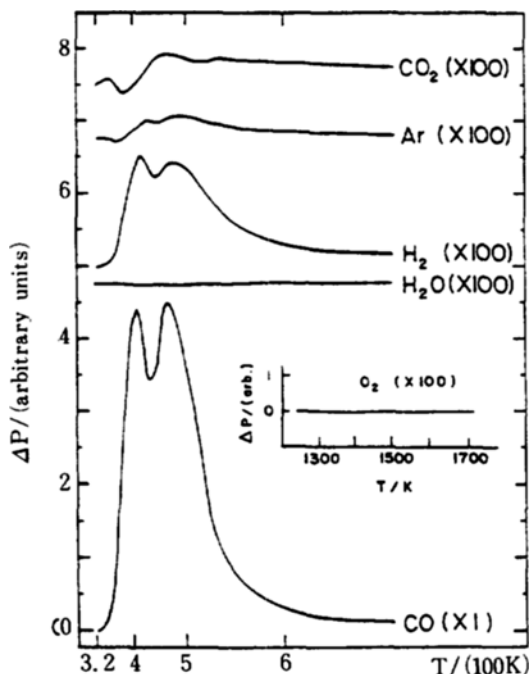
Fig. 7. System responses of major components in the background by flashing the surfaces exposed to 15 L CO.

CONCLUSION

1. Adsorbed water interacts with surface hydrogen to give an additional desorption state at 510 K to hydrogen. This surface hydrogen is not easily displaced by CO.
2. The total number of adsorption sites available for hydrogen adsorption is independent of the amount of H_2O predosed, but some of them are modified by the interaction between $H(a)$ and $H_2O(a)$.).
3. Adsorbed hydrogen formed in the absence of significant water is easily displaced by CO dose at even room temperature.
4. Hydrogen adsorption is easily blocked by a small amount of $O(a)$ suggesting that $H(a)$ and $O(a)$ occupy the same adsorption sites.

Acknowledgement

NOMENCLATURE

ac: alternating current
AES: Auger electron spectroscopy
ESDIAD: electron stimulated desorption ion angular distribution

H(a), $H_2O(a)$, O(a): adsorbed species considered
K: kelvin(s) as a unit of absolute temperature
L: langmuir(s) as a unit of exposure
l: liter(s) as a unit of volume
LEED: low-energy electron diffraction
min: minute(s) as a unit of time
ML: monolayer(s)
QMS: quadrupole mass spectroscopy
Ru(001), (100), (101), (110): Miller index for the considered surface of ruthenium single crystal
S: system pumping speed
s: second(s) as a unit of time
TC: thermocouple
TDS: thermal desorption spectroscopy
UHV: ultra-high vacuum
V: system volume

REFERENCES

1. Grant, J.T. and Haas, T.W.: Surface Sci., **21,** 76 (1970).
2. Madey, T.E. and Menzel, D.: Japan. J. Appl. Phys. Suppl., **2,** Pt.2, 229 (1974).
3. Madey, T.E., Engelhardt, H.A. and Menzel, D.: Surface Sci., **48,** 304 (1975).
4. Fuggle, J.C., Steinkilberg, M. and Menzel, D.: Chem. Phys., **11,** 307 (1975).
5. Madey, T.E. and Yates, J.T., Jr.: Chem. Phys. Lett., **51,** 77 (1977).
6. Feulner, P., Engelhardt, H.A. and Menzel, D.: Appl. Phys., **15,** 355 (1978).
7. Danielson, L.R., Dresser, M.J., Donaldson, E.E. and Sandstrom, D.R.: Surface Sci., **71,** 615 (1978).
8. Lee, H. -I., Praline, G. and White, J.M.: Surface Sci., **91,** 581 (1980).
9. Lee, H. -I. and White, J.M.: J. Catal., **63,** 261 (1980).
10. Praline, G., Koel, B.E., Lee, H. -I. and White, J.M.: Appl. Surface Sci., **5,** 296 (1980).
11. Lee, H. -I., Koel, B.E., Daniel, W.M. and White, J.M.: J. Catal., **74,** 192 (1982).
12. Klein, R. and Shih, A.: Surface Sci., **69,** 403 (1977).
13. Leed, P.D., Comrie, C.M. and Lambert, R.M.: Surface Sci., **72,** 423 (1978).
14. Goodman, D.W., Yates, J.T., Jr. and Madey, T.E.: Chem. Phys. Lett., **53,** 479 (1978).
15. Rabo, J.A., Risch, A.P. and Poutsma, M.L.: J. Catal., **53,** 295 (1978).
16. Schlatter, J.C. and Taylor, K.C.: J. Catal., **49,** 42 (1977).
17. Lee, H. -I. and Lee, M. -D.: J. KIChE, **20,** 355 (1982).
18. Danielson, L.R., Dresser, M.J., Donaldson, E.E. and Dickinson, J.T.: Surface Sci., **71,** 599 (1978).
19. Goodman, D.W., Madey, T.E., Ono, M. and Yates, J.T., Jr.: J. Catal., **50,** 279 (1977).