Water-Induced Effects on CO Adsorption on Ru(001)[1]

In this paper we report briefly on CO desorption spectra from perturbed Ru(001) which closely resemble spectra from supported Ru catalysts (1). In particular, we find a high-temperature desorption state, induced by the preadsorption of water and thought to derive from a dissociated form of chemisorbed CO. We speculate that small amounts of water may play a role in methanation (2, 3) by assisting CO bond cleavage.

The procedures and systems used in the experiments have been described in more detail elsewhere (4, 5). Briefly, two different UHV chambers and two different Ru(001) crystals were used with consistent results. Chamber I, equipped with a cylindrical mirror analyzer and quadrupole mass spectrometer, was used for AES, UPS, and TDS measurements and had a base pressure of 1×10^{-10} Torr. Chamber II, equipped with a quadrupole mass spectrometer, was designed for steady-state and transient kinetic measurements. During these experiments its base pressure was 8×10^{-10} Torr and mainly H_2, H_2O, and CO. Crystals were cleaned by high-temperature exposure to oxygen or Ar^+ bombardment. After annealing, independent experiments (6) showed a sharp 1×1 LEED pattern. The surfaces were judged to be clean by AES and/or the CO desorption peak shape and amplitude. Water exposures were done either by backfilling or through a doser (5). Carbon monoxide was dosed by backfilling.

While the literature involving CO/Ru(001) is extensive (4, 6–18), that for H_2O/Ru(001) is sparse (19–22). ESDIAD

(19, 20), LEED (21), TDS (19), EELS (21), and ir (22) measurements all indicate that water adsorbs molecularly at $T \simeq 100$ K, that ordering phenomena occur, and that water clustering (i.e., hydrogen bonding) becomes important even at very low coverages. More important for the work reported here, the TDS work (19) indicates that some dissociation occurs as the substrate is heated to room temperature leaving chemisorbed oxygen and releasing hydrogen. Our own studies show that dissociative adsorption of water occurs upon exposure at $T \simeq 320$ K. In this process H_2 is released and chemisorbed oxygen atoms are retained (24).

Interesting changes in CO desorption spectra were observed when a Ru(001) surface was exposed to water at 500 K and then to CO at either 100 or 320 K. Figure 1 shows three spectra taken in chamber I. Spectrum (A) is the desorption after a saturation dose of CO (10 L) on a clean, 320 K Ru(001) surface. The shape and amplitude are fully consistent with earlier work (7, 18). Spectrum (B) is desorption of a 10-L CO dose at 320 K from a surface predosed with 5 L of H_2O at 500 K. Spectrum (C) is TDS of a 10-L CO dose at 320 K just after (B). The leading edge of (B) follows that of (A) but the CO desorption peak at 465 K shifts down by 30 K. Both major peaks have significantly lower amplitudes. Of more importance, a new low-intensity CO desorption peak appears at 560 K. In both (A) and (B) the crystal was flashed to 850 K during CO desorption and when (B) was followed by cooling to 320 K, readsorption of CO, and reflashing, curve (C), the 560 K peak, was absent, but the structure at lower temperatures was almost the same as in (B). Similar results were obtained when CO was dosed at 100 K.
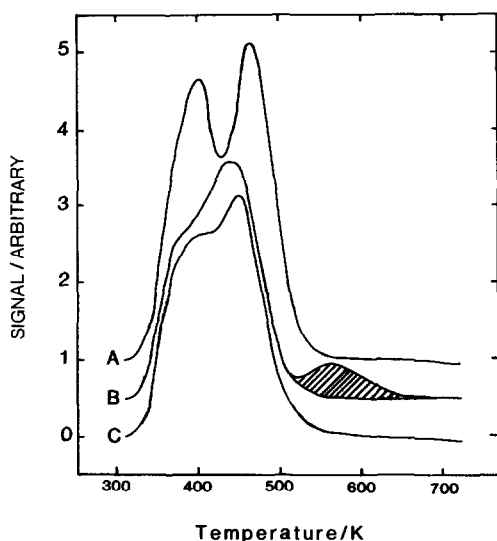
FIG. 1. CO desorption from Ru(001). Heating rate = 13 K s⁻¹. (A) Following 10-L CO exposure at 320 K on clean Ru(001); (B) following 10-L CO exposure at 320 K on Ru(001) predosed with 5 L H_2O at 500 K; (C) 10 L CO following (B).

The water exposure temperature is important. Dosing both H_2O and CO at 320 K gave a CO desorption spectrum with peaks at 405 and 460 K (5 to 10 K shift from (A) of Fig. 1) and some intensity, suggesting the beginning of a new feature, in the region around 600 K but no resolvable peak as in (B) of Fig. 1.

During the TDS experiments of Fig. 1, no detectable amounts of H_2, H_2O, and CO_2 were evolved from the substrate. AES measurements following H_2O adsorption at 500 K (i.e., at the start of (B) in Fig. 1) show that 0.13 ML (monolayer) of oxygen was present. Coverages are based on the number of Ru atoms exposed and are calibrated assuming the 2 × 2 LEED structure observed for our oxygen-saturated surface (6) is 0.5 ML. After flashing, this amount was reduced to about 0.1 ML (start of (C) in Fig. 1). Since neither H_2O nor CO_2 was evolved during flashing, the loss of surface oxygen is attributed to penetration beneath the surface (12). This data suggest that some form of chemisorbed oxygen induces the formation of the high-temperature state of CO.

LEED data show a full set of weak half-order beams after a 5-L exposure to H_2O at 500 K. No half-order beams were observed upon exposure to H_2O at 320 K. These results suggest that disordered oxygen overlayers with some (2 × 2) character are formed at these temperatures.

In separate experiments spanning a much broader range of oxygen coverages, O_2 was used as a source of surface oxygen atoms. Over the oxygen coverage range 0 to 0.5 ML, no high-temperature state was ever observed in subsequent CO desorption. However, the two CO desorption peaks (415 and 465 K) were altered in the same way as spectra (B) and (C) of Fig. 1. These results have been discussed earlier (4). Figure 2 shows, for TDS in chamber II, two CO desorption spectra: (A) is for a clean surface and (B) is for a surface covered with about 0.1 ML of oxygen. There is no hint of a high-temperature CO state in (B). Similar results were obtained for various O_2

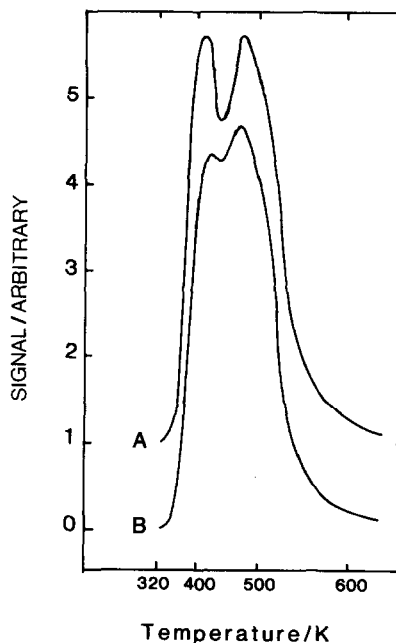FIG. 2. CO desorption from Ru(001). Heating rate = 28 K s⁻¹. (A) Following 15-L CO exposure at 320 K on clean Ru(001); (B) following 15-L CO exposure at 320 K on a Ru(001) surface predosed in O_2 (0.1 ML).

exposure temperatures between 320 and 500 K.

Attempts to detect the high-temperature CO state using HeII UPS were unsuccessful because of the small amount of this species present and our inability to fully depopulate the 435 K state of Fig. 1. After exposure to 5 L H_2O at 500 K, 10 L CO at 320 K, and warming to $\simeq$480 K to remove most of the CO, the UPS spectra were interpretable as a superposition of chemisorbed oxygen atoms (23) and molecular CO (23).

The high-temperature CO desorption was also produced in a steady background of H_2O. Figure 3 shows TDS data taken in chamber II with a background of 1×10^{-8} Torr of H_2O. If the substrate is heated to 1600 K to desorb oxygen, cooled to 320 K (water constantly present), and exposed to 15 L of CO, the flash (A) to 650 K shows the high-temperature state. Immediate cooling and reexposure to 15 L of CO gives no high-temperature state, curve (B), even though 1×10^{-8} Torr of water is present (exposure to $H_2O \simeq 3$ L, but mainly at low T).

Exposure to 5 L H_2O at 500 K in chamber I followed by flashing, without CO exposure, gives no detectable high-temperature CO desorption peak and confirms that the 560 K CO state is not derived from bulk carbon segregating to the surface during high-temperature water exposure. Moreover, we find no evidence for surface impurities such as S or C in any of our experiments, but we cannot rule out small amounts of surface carbon (9) which might reduce the CO bond strength in coadsorption (27). In any case surface carbon does not appear to be a prerequisite to the formation of the high-temperature state. However, the 560 K state is observed when a clean Ru(001) surface is left overnight at room temperature in an ambient of 5×10^{-10} Torr (mainly CO and H_2 with a small amount of H_2O). We speculate that this is the result of a slow reaction between adsorbed CO and background H_2O.
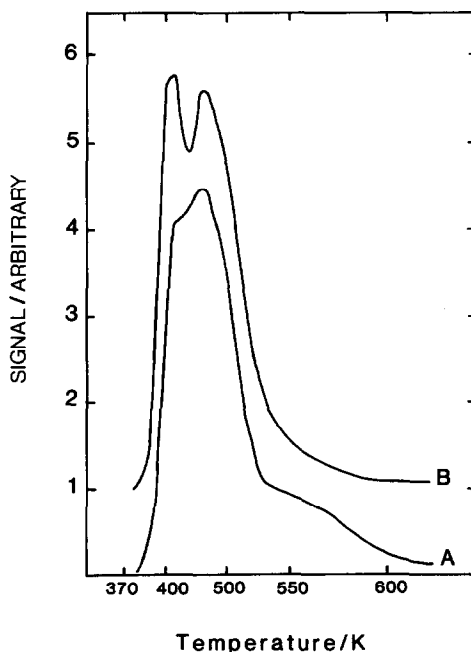
A very similar CO desorption peak

FIG. 3. CO desorption from Ru(001) in a background of 10^{-8} Torr of water. (A) was obtained by flashing to 1600 K to remove adsorbed oxygen, cooling to 320 K in 10^{-8} Torr of H_2O, exposing to 15 L of CO, and flashing to 650 K. (B) was obtained immediately after (A) by cooling to 320 K, reexposing to 15 L of CO, and flashing.

(560 K) has been reported by Fuggle et al. (23) after electron beam damage of a CO-covered Ru(001) surface. These authors give a thorough discussion of this state and a similar state observed on tungsten (25, 26). It is thought that dissociated CO or at least a CO species with both strong metal–carbon and strong metal–oxygen interactions is involved. Electron beam-damaged CO/Ru(001) shows XPS and UPS features characteristic of chemisorbed oxygen just as observed here. We suggest then that chemisorbed oxygen formed by the electron beam interaction may interact with coadsorbed CO to give the high-temperature states.

In a very interesting study on alumina-supported Ru, Low and Bell (1) find evidence for a high-temperature (~600 K) CO desorption state. Our results indicate that the formation of this state does not require

either high-pressure CO exposure or supported Ru. Rather, it depends on the presence of a certain undetermined surface structure. An important quantitative distinction between the high-temperature states observed on single crystal and supported Ru is the much higher relative intensity in the latter case; Low and Bell (*1*) find more than half the CO desorbs in this state while we find only a few percent.

We can only speculate about the differences between the preadsorption of O_2 and H_2O in influencing the formation of the high-temperature CO desorption state. Subsurface oxygen is known to form at 500 K on Ru(001) (*12*) and perhaps different structures are formed from H_2O and O_2. Local surface order may also differ since O_2 delivers pairs of oxygen atoms. Small amounts of hydrogen dissolved in the subsurface region might also play a role. In any event, we note that the catalytic methanation of CO typically involves a gas stream containing small amounts of H_2O which could provide a small coverage of oxygen (in addition to that provided by the disproportionation of CO) and assist in the dissociation of adsorbed CO.

REFERENCES

1. Low, G. G., and Bell, A. T., *J. Catal.* **57**, 397 (1979).
2. For recent work see Proceedings of a Symposium on Advances in Fischer-Tropsch Chemistry, American Chemical Society, Anaheim Meeting, 1978.
3. Vannice, M. A., *Catal. Rev.* **14**, 153 (1976).
4. Lee, H.-I., Praline, G., and White, J. M., *Surf. Sci.* **91**, 581 (1980).
5. Rogers, J. W., Jr., Hance, R. L., and White, J. M., *Surf. Sci.* **100**, 388 (1980).
6. Shi, S.-K., Schreifels, J. A., and White, J. M., *Surf. Sci.* **105**, 1 (1981).
7. Goodman, D. W., Kelley, R. D., Madey, T. E., and White, J. M., *J. Vac. Sci. Technol.* **17**, 143 (1980).
8. Madey, T. E., Engelhardt, H. A., and Menzel, D., *Surf. Sci.* **48**, 304 (1975).
9. Thomas, G. E., and Weinberg, W. H., *J. Chem. Phys.* **70**, 1437 (1979).
10. Goodman, D. W., and White, J. M., *Surf. Sci.* **90**, 201 (1979).
11. Parrott, S. L., Praline, G., Koel, B. E., White, J.

M., and Taylor, T. N., *J. Chem. Phys.* **71**, 3352 (1979).
12. Lee, H.-I., and White, J. M., *J. Catal.* **63**, 261 (1980).
13. Praline, G., Koel, B. E., Lee, H.-I., and White, J. M., *Appl. Surf. Sci.* **5**, 296 (1980).
14. Shi, S.-K., Lee, H.-I., and White, J. M., *Surf. Sci.* **102**, 56 (1980).
15. Shi, S.-K., and White, J. M., *J. Chem. Phys.* **73**, 5889 (1980).
16. Schreifels, J. A., Shi, S.-K., and White, J. M., *Appl. Surf. Sci.* **7**, 312 (1981).
17. Peebles, D. E., and White, J. M., submitted for publication.
18. Madey, T. E., and Menzel, D., in "Proceedings, 2nd Intern. Conf. on Solid Surfaces, 1974, Japan." *J. Appl. Phys. Suppl.* **2**, Pt. 2, 229 (1974).
19. Madey, T. E., and Yates, J. T., Jr., *Chem. Phys. Lett.* **51**, 77 (1977).
20. Madey, T. E., and Yates, J. T., Jr., in "Proceedings, 7th Intern. Vac. Congr. and 3rd Intern. Conf. Solid Surfaces, Vienna, 1977."
21. Thiel, P. A., Hoffmann, F. M., and Weinberg, W. H., in "Proceedings, 4th Intern. Conf. on Solid Surfaces, Cannes, 1980."
22. Kretzschmar, K., Sass, J. K., Hofmann, P., Ortega, A., Bradshaw, A. M., and Holloway, S., *Chem. Phys. Lett.* **78**, 410 (1981).
23. Fuggle, J. C., Umbach, E., Feulner, P., and Menzel, D., *Surf. Sci.* **64**, 69 (1977).
24. Fisher, G. B., and Sexton, B. A., *Phys. Rev. Lett.* **44**, 683 (1980).
25. Umbach, E., Fuggle, J. C., and Menzel, D., *J. Electron Spectrosc.* **10**, 15 (1977).
26. Yates, J. T., Jr., Erickson, N. E., Worley, S. D., and Madey, T. E., in "The Physical Basis for Heterogeneous Catalysis" (E. Brauglis and R. I. Jaffee, Eds.), pp. 75–105. Plenum, New York, 1975.
27. Dalla Betta, R. A., and Sheleb, M., *J. Catal.* **43**, 363 (1976).

H.-I. LEE[2]
B. E. KOEL[3]
W. M. DANIEL
J. M. WHITE

Department of Chemistry
University of Texas
Austin, Texas 78712

[2] Present address: Department of Chemical Technology, College of Engineering, Seoul National University, Seoul, Korea.
[3] Proctor and Gamble Fellow of the Colloid and Surface Science Division of the American Chemical Society.