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TWO-DIMENSIONAL PHASE SEPARATION: CO-ADSORPTION OF HYDROGEN AND CARBON MONOXIDE ON THE (111) SURFACE OF RHODIUM*

Ellen D. Williams**, Patricia A. Thiel**,
W. Henry Weinberg† and John T. Yates, Jr.‡
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, CA 91125

ABSTRACT

The co-adsorption of CO and H_2 on Rh(111) at low temperature ($\sim$ 100 K) has been studied using thermal desorption mass spectrometry (TDS) and Low-Energy Electron Diffraction (LEED). The probability of adsorption of CO on rhodium pretreated with hydrogen has been found to decrease slowly with increasing amounts of hydrogen on the surface. In addition, the effect of surface hydrogen on the CO LEED patterns indicates segregation of hydrogen and CO. These results can be explained in terms of a strong repulsive CO-H interaction and a mobile precursor model of CO adsorption.

INTRODUCTION

Studies of the co-adsorption of hydrogen and CO on transition metals are of practical importance due to their relevance to the formation of hydrocarbons from the products of coal gasification. The two commonly posited intermediates in hydrocarbon formation are the following: (1) An active surface carbon species formed by dissociation of CO, and (2) A hydrogen-CO complex formed by interaction of chemisorbed hydrogen and CO.[1,2] Recent experimental work on both pure and supported transition metals has shown that CO dissociation is the more important step of the two in methane formation.[3-9] At the same time, there is increasing evidence to suggest that surface complexes of CO and hydrogen do exist[10-12] and that direct hydrogenation of molecular CO is an alternative route to hydrocarbon formation.[3]

In this study, the co-adsorption of hydrogen and CO on the atomically smooth (111) surface of rhodium has been investigated. The adsorption experiments were performed under ultra-high vacuum and at a surface temperature of approximately 100 K. No evidence for reaction of hydrogen and CO under these conditions was observed.

The individual chemisorption of hydrogen and CO has been studied previously and is well characterized.[13-15]

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**National Science Foundation Predoctoral Fellow.

†Camille and Henry Dreyfus Foundation Teacher-Scholar.

‡Sherman Fairchild Distinguished Scholar, 1977-78. Permanent Address: National Bureau of Standards, Washington, D.C. 20234.

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RESULTS

Thermal desorption mass spectrometry (TDS) was used to determine activation energies for desorption,coverage-exposure relationships and adsorption kinetics for both hydrogen and CO in the co-adsorbed system. For brevity, these results are only summarized here.

The activation energy for desorption of hydrogen decreases markedly upon co-adsorption with CO. This decrease can be from 1.5 to 3 kcal/mole depending upon the coverage. The desorption energy for CO does not change when it is co-adsorbed with hydrogen. This is not surprising since all the hydrogen has been desorbed from the surface by the temperature at which desorption of CO begins.

At low coverages of CO, hydrogen adsorption occurs readily, reaching a lower saturation value than on the clean surface. At mid- to high-coverages of CO, hydrogen adsorption is efficiently blocked. The adsorption of CO onto a hydrogen covered surface demonstrates some interesting behavior as shown in Fig. 1. The open and filled circles represent CO adsorption onto two different clean surfaces, and the stars represent CO adsorption onto a surface precovered with 0.58 monolayer of hydrogen. The experimental data have been compared with coverage-exposure behavior predicted using first-order Langmuir adsorption kinetics and adsorption via a mobile precursor.[16,17] The parameters used in the calculations were chosen to give good agreement with the clean surface data. The values used were, for the

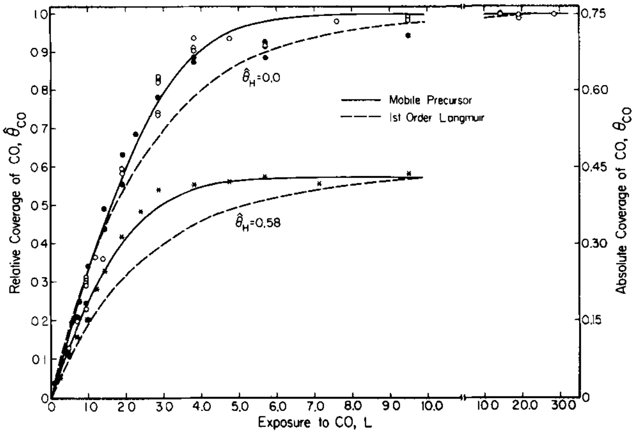

Figure 1. Comparison of coverage-exposure data with curves predicted by first-order Langmuir and mobile precursor adsorption kinetics.

Langmuir model,

$$\frac{d\hat{\theta}}{d\varepsilon} = 0.4(\hat{\theta}_s - \hat{\theta}), \qquad (1)$$

and for the mobile precursor

$$\frac{d\hat{\theta}}{d\varepsilon} = 0.525 \frac{\hat{\theta}_s - \hat{\theta}}{0.5 + \hat{\theta}_s - \hat{\theta}} \qquad (2)$$

where $\hat{\theta}$ is the coverage of CO normalized to unity at saturation on the clean surface, $\hat{\theta}_s$ is the measured relative saturation coverage of CO for the given initial coverage of hydrogen, and ε is the exposure in Langmuirs.

It is clear from Fig. 1 that the mobile precursor model fits the experimental data quite well, whereas the Langmuir model fails badly. The same level of agreement was found for other initial coverages of hydrogen. A major factor in the poor agreement of the Langmuir model is that it predicts too rapid a decrease in the initial slope of the coverage-exposure curve with increasing hydrogen coverage. The reason for this is that sites occupied by hydrogen atoms are considered to be blocked completely for CO adsorption. The mobile precursor model, on the other hand, allows physical adsorption of a CO molecule above a hydrogen atom, as well as above another CO molecule or an empty site prior to chemisorption. For this reason the mobile precursor model predicts a less rapid decrease in initial slope with increasing hydrogen coverage.

Low-Energy Electron Diffraction (LEED) was used to study the geometrical structure of the co-adsorbed system. The LEED patterns due to individual adsorption of hydrogen and CO have been investigated previously.[13-15] No ordered structures observable by LEED form during adsorption of hydrogen. Upon adsorption at 100 K, CO forms three ordered structures, at different coverages. At low coverage, CO forms a weak p(2x2) structure which increases in intensity steadily from zero coverage, suggesting island formation. At a coverage slightly less than one-quarter monolayer, local formation of a $(\sqrt{3} \times \sqrt{3})R30°$ structure ($\sqrt{3}$ structure) begins. This structure increases rapidly in intensity, reaching a maximum at the optimum coverage of one-third monolayer. Further exposure to CO causes compression of the overlayer until a (2x2) structure with three molecules per unit cell is reached at saturation.

No new LEED patterns were observed for co-adsorbed hydrogen and CO. However, the clean surface CO structures do form, under some circumstances, with modified intensity during co-adsorption. The effect of exposing the different CO superstructures to hydrogen and the formation of the CO superstructures on hydrogen covered surfaces have been investigated by monitoring the intensity of the LEED beams as a function of exposure to either hydrogen or CO.

Addition of hydrogen to the fully ordered (θ_{CO} = 0.23) p(2x2) structure causes a rapid decrease in intensity of the p(2x2) pattern.

Similarly, addition of hydrogen to the fully ordered (θ_{CO} = 0.35) $\sqrt{3}$ structure causes a loss in intensity of the $\sqrt{3}$ pattern. Clearly, hydrogen atoms cannot occupy a position within either the p(2x2) or the $\sqrt{3}$ unit cell without perturbing the neighboring CO molecules.

The effect of hydrogen on the $\sqrt{3}$ structure for coverages of CO less than one-third is illustrated in Fig. 2. The dashed line shows the intensity-exposure behavior for CO adsorption on the clean surface. If exposure to CO is terminated before maximum ordering occurs, and followed by exposure to hydrogen, the solid curves result. At θ_{CO} = 0.25 and 0.30, hydrogen increases the amount of the ordered $\sqrt{3}$ structure on the surface. At θ_{CO} = 0.21, where only the p(2x2) CO structure is present, addition of hydrogen causes a transformation from the p(2x2) to the $\sqrt{3}$ structure. The maximum intensities obtained by addition of hydrogen are less than the maximum reached for CO adsorption alone. The asymmetric decrease in intensity with hydrogen exposure beyond the maxima is due to the decreasing probability of adsorption of hydrogen (18).

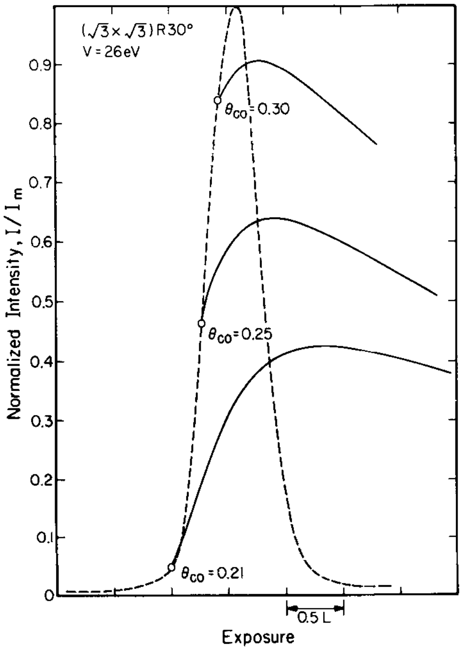

Fig. 2: LEED intensity as a function of exposure for the $\sqrt{3}$ structure. Dashed line shows the result of exposing the clean surface to CO. Solid lines show the result of terminating CO exposure at various coverages and initiating exposure to hydrogen. The surface temperature is approximately 100 K. Intensities are normalized to unity at the maximum intensity of the $\sqrt{3}$ structure on the clean surface.

Addition of hydrogen to the partially ordered (θ_{CO} < 0.23) p(2x2) structure does not increase the order as for the $\sqrt{3}$ structure. Rather, there is a steady loss of intensity which is slower for lower coverages of CO.

Exposure to hydrogen caused no change in intensity of the partially ordered (θ_{CO} = 0.5 and 0.7) (2x2) structure. This may be due to the small probability of adsorption of hydrogen when a high coverage of CO is present.

The adsorption of CO onto a hydrogen precovered surface mimics adsorption onto the clean surface, as shown in Figs. 3 and 4. In both figures, curve (a) represents the intensity-exposure behavior for adsorption onto the clean surface. Curves (b) - (e) are for CO

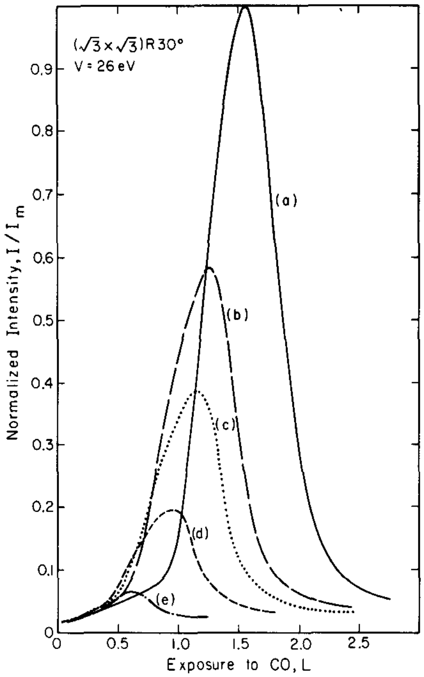

Fig. 3: LEED intensity as a function of exposure to CO for the √3 structure on a surface covered with varying amounts of hydrogen.

(a) $\hat{\theta}_H = 0$ (d) $\hat{\theta}_H = 0.75$

(b) $\hat{\theta}_H = 0.42$ (e) $\theta_H = 0.92$

(c) $\hat{\theta}_H = 0.58$

Intensities are normalized to unity at the maximum intensity of the √3 structure on the clean surface.

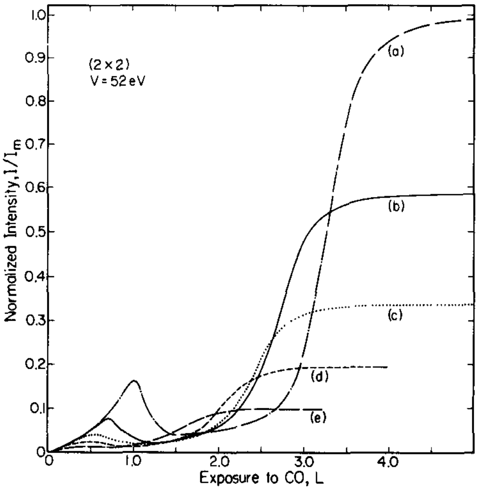

Fig. 4. LEED intensity as a function of exposure to CO for the two (2x2) structures on a surface covered with varying amounts of hydrogen.

(a) $\hat{\theta}_H = 0$ (d) $\hat{\theta}_H = 0.58$

(b) $\hat{\theta}_H = 0.26$ (e) $\hat{\theta}_H = 0.75$

(c) $\hat{\theta}_H = 0.42$

Intensities are normalized to unity at maximum intensity of the high coverage (2x2) structure.

adsorption onto a surface covered with increasing amounts of hydrogen. As on the clean surface, on a hydrogen-covered surface, CO first forms a p(2x2) structure which is transformed quickly to a $\sqrt{3}$ structure. Then the final (2x2) structure is formed by continuous compression of the $\sqrt{3}$ structure. However, on the hydrogen covered surface, the CO structures form at lower coverage and with lower intensity than on the clean surface.

DISCUSSION

The LEED results indicate that the structure of the mixed overlayer is different depending on the order of adsorption of hydrogen and CO. The results of the thermal desorption experiments, together with the intensity-exposure behavior give a consistent picture of the co-adsorbed system. As discussed in more detail elsewhere (18), the effect of adding hydrogen to the fully or partially ordered p(2x2) and $\sqrt{3}$ structures indicates clearly that there is a long range repulsive interaction between hydrogen atoms and CO molecules.

The nature of the CO-hydrogen repulsive interaction is of considerable interest. The disruption of the p(2x2) CO structure by addition of hydrogen shows that this interaction occurs over a hydrogen-CO distance as large as 3.1 Å. The hard core radius of CO, determined from the distance of closest approach in the saturation structure is 1.55 Å. The radius of a chemisorbed hydrogen atom is probably less than 0.75 Å.[19] Thus, the repulsive interaction between hydrogen and CO must be a through-metal effect rather than a result of orbital overlap.[20,21]

A comparison of LEED intensities for the formation of the p(2x2) structure, in the presence and in the absence of hydrogen, shows that little more CO is disordered in the presence of hydrogen than on the clean surface.[18] Since the p(2x2) structure cannot coexist with intermingled hydrogen atoms, the hydrogen and CO must be segregated on the surface. The $\sqrt{3}$ structure and the (2x2) structure follow the same intensity coverage behavior, indicating that the same degree of segregation of hydrogen and CO persists over the entire accessible coverage range.

The segregation of the co-adsorbed species requires some mechanism by which hydrogen and CO "find" others of their own kind. Chemisorbed hydrogen is thought to be relatively mobile even at low temperature. Hydrogen atoms could thus simply migrate away from the region of influence of a CO molecule. On the other hand, it is difficult to imagine migration of CO molecules on the scale necessary to form relatively large islands. Fortunately, the possibility of a physically adsorbed mobile precursor to adsorption for CO provides an elegant alternative to large scale migration. The probability for the precursor to chemisorb near a hydrogen atom would be decreased by the repulsive CO-hydrogen interaction. The precursor would then be likely to move away from sites near hydrogen atoms, and to chemisorb in sites near other CO molecules where the interactions are more favorable. The growth of islands of CO would be a straightforward result of this mechanism.

The mechanism for formation and growth of CO islands on a hydrogen covered surface deduced from these measurements is illustrated schematically in Fig. 5. The nucleation of an island is shown in Fig. 5(a). There, the initial chemisorption of a CO molecule causes

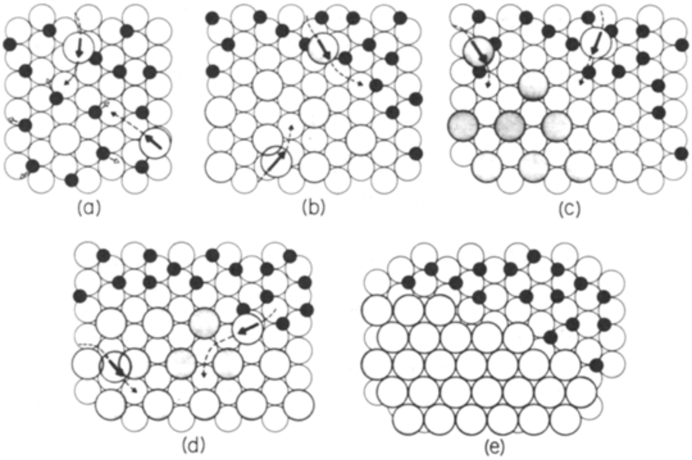

Fig. 5: Schematic illustration of adsorption of CO onto a surface covered with hydrogen. Open circles are Rh atoms with d = 2.7 Å. Shaded circles are CO molecules with d = 3.1 Å. Shaded circles with arrow are physically adsorbed, mobile precursor CO molecules. Solid circles are H atoms with d = 1.5 Å (estimated). Adsorption sites shown have been chosen arbitrarily. Hydrogen and CO trapped in the "wrong" regions are not shown for clarity. See text for discussion.

migration of hydrogen atoms away from its vicinity due to the repulsive hydrogen-CO interaction. Physically adsorbed CO molecules adsorb preferentially near the original CO molecule, minimizing the CO-hydrogen interaction and initiating island formation. As more CO adsorbs, statistically some nucleation sites will fail to develop. Pockets of CO, either lone molecules or small clusters, will then be trapped in regions of high hydrogen density. Similarly, some hydrogen atoms may be trapped in the growing CO islands. These trapped species are not shown in Fig. 5. In Fig. 5(b), the p(2x2) island has reached its maximum size. At this point, addition of a CO molecule at the edge of the island, which would cause either a decreased CO-H distance or a decreased H-H distance becomes energetically less favorable than addition of a CO to the interior of the island causing a decreased CO-CO distance. Transformation of the island to the $\sqrt{3}$ structure begins, and this is shown after completion in Fig. 5(c). A simple calculation using the experimental results indicates that the islands of $\sqrt{3}$ structure occupy three-halves as much surface area at their maximum intensity as the islands of p(2x2) structure at their maximum intensity. Therefore, once transformation of the p(2x2) islands to a $\sqrt{3}$ structure is complete, further growth by addition of CO molecules to the edges of the islands must occur. This process is shown beginning in Fig. 5(c) and at completion in Fig. 5(d). When the islands occupy so much area that addition of CO at the edges causes too great an increase in CO-H and H-H repulsive energy, island growth stops; and further addition of CO occurs within the island, causing compression of the CO overlayer to the high coverage (2x2) structure shown in Fig. 5(e). At this point, no further adsorption of CO occurs and saturation is reached.

CONCLUSIONS

(1) Adsorption of CO on Rh(111) proceeds via a physically adsorbed intermediate, a mobile precursor to adsorption.

(2) There is a repulsive interaction between co-adsorbed CO molecules and hydrogen atoms on rhodium. This results in complete segregation of hydrogen and CO following adsorption of CO onto an adlayer of hydrogen at 100 K. The repulsive interaction is a through-metal effect rather than a result of orbital overlap.

REFERENCES

1. M. A. Vannice, Catal. Rev. 14, 153 (1976).
2. G. C. Bond, Catalysis by Metals, Academic Press, New York, 1962.
3. J. A. Rabo, A. P. Risch and M. L. Pontsma, J. Catal. 53, 295 (1978).
4. M. Araki and V. Ponec, J. Catal. 44, 439 (1976).
5. R. D. Kelley, T. E. Madey and J. T. Yates, Jr., J. Catal. 50, 301 (1977).
6. T. E. Madey, D. W. Goodman and R. D. Kelley, J. Vacuum Sci. Technol. 16, 433 (1978).
7. R. D. Kelley, T. E. Madey, K. Revesz and J. T. Yates, Jr., Appl. Surface Sci. 1, 266 (1978).
8. B. A. Sexton and G. A. Somorjai, J. Catal. 46, 167 (1977).
9. D. J. Dwyer and G. A. Somorjai, J. Catal. 52, 291 (1978).
10. K. Kraemer and D. Menzel, Ber. Buns. Ges. 79, 649 (1975).
11. V. H. Baldwin and J. B. Hudson, J. Vacuum Sci. Technol. 8, 49 (1971).
12. J. C. Bertolini and B. Imelik, Surface Sci. 80, 586 (1979).
13. J. T. Yates, Jr., P. A. Thiel and W. H. Weinberg, Surface Sci. 84, 427 (1979).
14. P. A. Thiel, E. D. Williams, J. T. Yates, Jr. and W. H. Weinberg, Surface Sci. 84, 54 (1979).
15. D. G. Gastner, B. A. Sexton and G. A. Somorjai, Surface Sci. 71, 519 (1978).
16. P. Kisliuk, J. Phys. Chem. Solids 3, 95 (1957).
17. R. Gorte and L. D. Schmidt, Surface Sci. 76, 559 (1978).
18. E. D. Williams, P. A. Thiel, W. H. Weinberg and J. T. Yates, Jr., J. Chem. Phys. 72, 0000 (1980).

19. K. Christmann, R. J. Behm, G. Ertl. M. A. Van Hove and W. H. Weinberg, J. Chem. Phys. 70, 4168 (1979).
20. T. B. Grimley and M. Torrini, J. Phys. C 6, 868 (1973).
21. T. Einstein and J. R. Schrieffer, Phys. Rev. B 7, 3629 (1973).