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Copper Site Blocking of Hydrogen Chemisorption on Ruthenium

The effects on hydrogen chemisorption of adding copper to a Ru(0001) surface have been studied. These results show that for two distinctly different preparation procedures, copper attenuates hydrogen chemisorption on ruthenium via a simple site blocking mechanism. The results and conclusions of this study are consistent with the observed effects of Cu on a Ru catalyst for altering hydrogenolysis and methanation activity. © 1985 Academic Press, Inc.

INTRODUCTION

Interest in bimetallic catalysts has risen steadily over the years because of the commercial success of these systems in controlling activity and selectivity by tailoring the elements of the catalysts as well as their composition (*1–12*). Of key interest in these investigations has been the relative roles of "ensemble" and "ligand" effects in defining the catalytic behavior (*13–16*).

The effects upon chemisorption and catalytic activity of diluting an active metal with an inactive one have been extensively studied using the copper–ruthenium system (*7, 17–27*). These studies have included the effect of diluting ruthenium with copper on the hydrogenolysis of ethane (*7, 17, 18, 27*), dimethylpropane (*23*), and *n*-butane (*24*); the hydrogenation of CO (*13, 18, 27*); the dehydrogenation of cyclohexane (*7, 17, 18*); and the chemisorption of hydrogen (*20, 22*), O_2 (*25*), N_2O (*25*), and CO (*21, 22*).

Much of this data has been interpreted in terms of the requirement of certain reactions for a given ensemble size. For example, the work of Sinfelt (*26*) on the Cu/Ru and Cu/Ni systems has suggested that a larger ensemble of nickel or ruthenium atoms is needed for hydrogenolysis than dehydrogenation. Bond and Turnham (*13*) in studying CO hydrogenation over silica-supported Cu/Ru concluded that the active site for the reaction on pure Ru is an ensemble of about four Ru atoms. Shimizu and coworkers (*20*) observed that hydrogen adsorption is markedly reduced by the addition of Cu to Ru(0001) and suggested that a rather large Ru ensemble (~10 atoms) was required for H_2 chemisorption. These results corresponded well with the data of Sinfelt (*7*) who observed that hydrogenolysis activity fell sharply with increasing Cu content in a supported Ru catalyst.

More recently Vickerman and Christmann (*22*) have reexamined hydrogen adsorption on Cu/Ru and concluded that an ensemble of between three and four Ru atoms is required to affect the adsorption of H_2. Cu was assumed to affect H_2 chemisorption both by geometric blocking as well as by an electronic or ligand effect. The discrepancy between this work and the earlier work of Shimizu and co-workers (*20*) was attributed to a recalibration of the copper coverage.

Because of the uncertainty in the literature and as a preliminary to kinetic studies of ethane hydrogenolysis and methanation over Cu/Ru (*27*), we have recently examined the effects of adding Cu to Ru(0001) on hydrogen chemisorption. These results show that for two distinctly different preparation techniques, Cu attenuates hydrogen chemisorption on Ru via a simple site blocking mechanism. These results are consistent with the observed effects of Cu on a model Ru(0001) catalyst for altering hydrogenolysis and methanation activity (*27*).

EXPERIMENTAL

A conventional ultrahigh vacuum system

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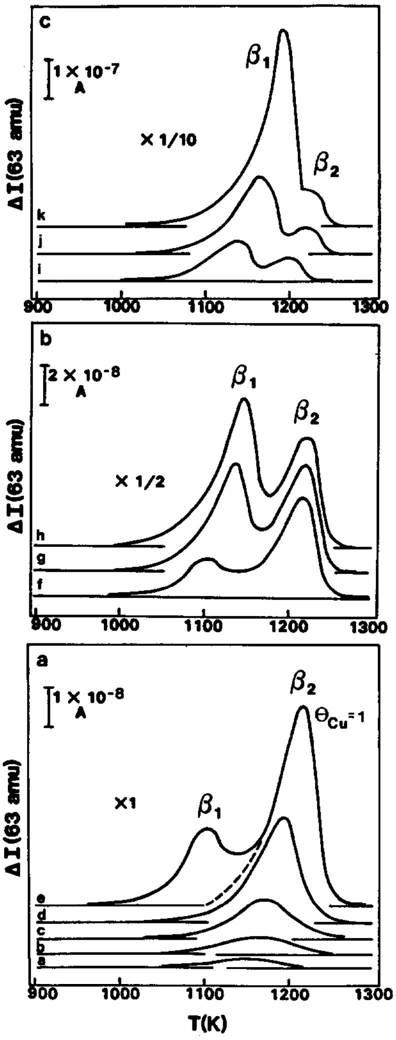

FIG. 1. Copper TPD from a Ru(0001) surface at copper coverages corresponding to (a) low, (b) medium, and (c) high. The TPD temperature ramp was approximately 10 K sec^{-1}.

(base pressure = 1.5×10^{-10} Torr) was used in this work. The apparatus is equipped with two collimated molecular beam dosers which face the front surface of a Ru(0001) single-crystal disk. The crystal can be rotated to either doser for adsorption of gases. Thermal programmed desorption (TPD) can be carried out with the crystal in front of a UTI 100C multiplexing quadrupole mass spectrometer (QMS) using a linear ramp of 10 K sec^{-1}. The mass spectrometer samples four mass peaks every 0.7 sec.

The front face of the Ru(0001) was cleaned using an O_2 beam of flux $\sim 5 \times 10^{14}$ O_2 cm^{-2} sec^{-1} at a crystal temperature of 1450 K for 300 sec. Final cleaning was achieved by heating to 1500 K under vacuum, yielding an Auger spectrum free of O, S, and C contamination.

Copper was evaporated onto the Ru(0001) sample from a resistively heated tungsten wire wrapped with high-purity Cu wire. The Cu source was thoroughly outgassed prior to Cu evaporation and the deposition rate controlled by monitoring the voltage drop across the tungsten filament. The Cu flux from the evaporator was also checked routinely via a microquartz oscillator balance mounted off-axis to the Ru sample. TPD and Auger analysis following Cu dosing showed no measurable contamination of the Ru surface during evaporation.

RESULTS

Figure 1 shows a series of thermal programmed desorption (TPD) spectra of Cu from Ru(0001) corresponding to three regions of Cu coverage—low, medium, and high. The TPD traces were independent of the deposition parameters such as evaporation rate or temperature of the anneal subsequent to evaporation. In the low coverage region (Fig. 1a) the initial buildup of Cu can be seen. The initial stage of Cu growth is indicated by the appearance of an approximately zero-order desorption peak and, following the notation of Christmann and co-workers (*19*), is noted as β_2. This state reflects Cu coverages up to approximately one monolayer (one Cu atom per surface Ru atom). The saturated β_2 state has a desorption maximum at ~1210 K.

Higher Cu exposures (Figs. 1b and c) cause the appearance of a second binding state, β_1, with a desorption maximum at temperatures below that of the β_2 state. The kinetics of the desorption process of the β_1 state are approximately zero order, indicating that the rate of desorption is independent of the Cu concentration on the surface. The general adsorption behavior and

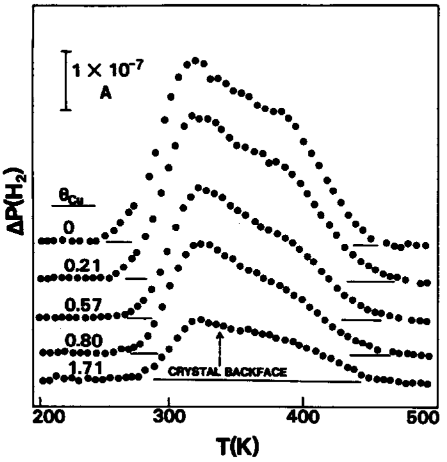

FIG. 2. Hydrogen TPD from a Ru(0001) surface with varying coverages of copper. The copper deposition was carried out at a substrate temperature of 100 K. The hydrogen exposure corresponded to saturation.

peak temperatures in Fig. 1 are completely in agreement with the work of Christmann *et al.* (*19*).

Figure 2 shows a series of thermal desorption curves for a Ru(0001) surface with varying amounts of Cu following an exposure to ~20 Langmuirs (L) of H_2. This exposure was shown to be sufficient to saturate the surface with hydrogen under these conditions. The clean Ru(0001) H_2 TPD spectrum ($\theta_{Cu} = 0$) agrees well with the previously reported spectra of Shimizu *et al.* (*20*). Neither the lineshape nor the desorption maxima is significantly influenced by the Cu. The peak area, however, is proportionately reduced by surface Cu. The TPD spectrum for $\theta_{Cu} = 1.71$ corresponds to the quantity of H_2 which desorbs from the backface of the Ru(0001) crystal, and represents a limiting condition for H_2 desorption above this Cu coverage.

Figure 3 are plots of the saturation coverage of hydrogen at 100 K (determined from the TPD peak areas) versus Cu coverage. In both Figs. 3a and b the Cu was deposited with the Ru(0001) substrate at 100 K. The Cu of Fig. 3b was annealed at 1080 K for 30 sec subsequent to deposition. In either case a ~20-L H_2 exposure following Cu deposition (and annealing for Fig. 3b) constituted a saturation exposure.

DISCUSSION

In order to assess the effect of Cu on the hydrogen adsorption on Ru(0001), the absolute surface coverage of Cu must first be accurately determined. As mentioned above the Cu desorptions of Fig. 1 were independent of the two preparation techniques. That is, deposition of Cu at 100 K with or without a subsequent anneal at 1080 K produced indistinguishable Cu thermal desorption spectra. The evolution of the Cu desorption first entails filling of the β_2 state followed by filling of the β_1 state. As the β_1 state grows, the β_2 state remains essentially unchanged. This is consistent with the assignment of the β_2 state to Cu–Ru interactions and the β_1 state to three-dimensional Cu–Cu interactions (*19*). As discussed by Christmann *et al.* (*19*), the ordering of these TPD features imply Cu–Ru interactions which are several kilocalories per mole more stable than Cu–Cu interactions. The growth mechanism of the Cu overlayer in either case of preparation is suggested by the TPD results which are consistent with a Frank–van der Merwe or layer-by-layer mechanism. Furthermore, the filling of the

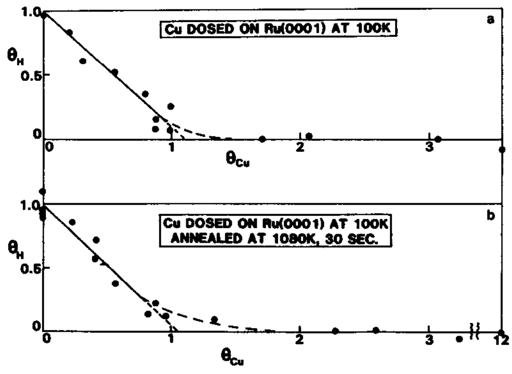

FIG. 3. Hydrogen adsorption site blocking by Cu on Ru(0001) for two preparation procedures. In (a) the Cu was dosed onto Ru(0001) at 100 K with no subsequent anneal. In (b) the Cu was dosed onto Ru(0001) at 100 K and the crystal then heated to 1080 K for 30 sec. The data were determined from the areas of the H_2 TPD following a saturation H_2 exposure.

β_2 TPD peak provides an accurate calibration point for a single monolayer of Cu which, assuming purely epitaxial growth, is 1.59×10^{15} Cu atoms/cm^{-2} (*20*).

The area below a thermal desorption trace is proportional to the initial surface concentration of the desorbing species. Using the filling of the β_2 Cu TPD peak as a quantitative measure of the completion of the first Cu monolayer, the absolute Cu coverage can be defined very accurately from the TPD peak areas. All Cu coverages reported here have been determined in this manner.

The H_2 TPD traces of Fig. 2 are noteworthy for two reasons. First, close inspection shows no significant changes in the TPD lineshapes with increases in the Cu surface concentration. Second, the reduction in the TPD peak areas falls approximately linearly with the Cu coverage taking into account the background contribution of the backface of the sample. These TPD results correspond to Cu evaporation onto a 100 K Ru(0001) with no subsequent anneal. This same Cu deposition procedure followed by a 1080 K anneal for 30 sec produces indistinguishable Cu TPD traces. Obviously TPD results are inadequate to accurately characterize the precise morphology of the Cu overlayer; however, simple considerations suggest two-dimensional island formation. For example, if the Cu in the overlayer were atomically dispersed, significant changes in the H_2 TPD lineshapes would likely occur assuming that Cu atoms in the matrix of chemisorbed H(ads) would mediate H–H repulsive interactions. In addition, modification of the clean surface prefactors for H_2 desorption would also likely occur. These considerations then lead to the conclusion that both preparations described in this work yield submonolayer single-atom-thick Cu overlayers with significant two-dimensional island structures.

The results of Fig. 3 are entirely consistent with the above interpretation of the Cu overlayer structure. The integrated areas of the H_2 TPD peaks following a saturation exposure plotted as a function of Cu coverage indicate a one-to-one blocking of hydrogen adsorption sites by the Cu atoms. As discussed above both preparations produce essentially identical results. If indeed two-dimensional island formation of Cu occurs, these results preclude any comment on the contribution of electronic or ligand effects by Cu in altering the bonding of hydrogen to Ru.

The results and conclusions of this study are decidedly different from the previous studies of Shimizu *et al.* (*20*) and Vickerman and Christmann (*22*) who concluded blocking by a single Cu atom of approximately 10 and 4 hydrogen bonding sites, respectively. In these previous two studies the preparation techniques were somewhat different than those employed here. For example, the Ru(0001) substrate temperature during deposition was either 540 or 1080 K whereas a deposition temperature of 100 K was chosen here. Perhaps these differences or other more subtle parameters such as quench rates during cooling could alter the Cu overlayer morphology. Further studies will be required to define more satisfactorily the important differences between the preparation recipes which lead to the resulting differences in H_2 adsorption behavior.

CONCLUSIONS

(1) Copper overlayers on Ru(0001) prepared at 100 K with or without a subsequent anneal to 1080 K follow a layer-by-layer growth.

(2) Hydrogen chemisorption suggests significant two-dimensional islanding of Cu on Ru(0001) at submonolayer coverages.

(3) Copper at submonolayer coverages blocks the chemisorption of H_2 on Ru(0001) on a one-to-one basis.

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REFERENCES

1. Schwab, G. M., *Discuss. Faraday Soc.* **8,** 166 (1950).
2. Dowden, D. A., *J. Chem. Soc.,* 242 (1950).
3. Hall, W. K., and Emmett, P. H., *J. Phys. Chem.* **63,** 1102 (1959).
4. Sachtler, W. M. H., and Dorgelo, G. J. H., *J. Catal.* **4,** 654 (1965).
5. Ertl, G., and Kuppers, J., *J. Vacuum Sci. Technol.* **9,** 829 (1972).
6. Williams, F. L., and Boudart, M., *J. Catal.* **30,** 438 (1973).
7. Sinfelt, J. H., *J. Catal.* **29,** 308 (1973).
8. Stephan, J. J., Ponec, V., and Sachtler, W. M. H., *Surf. Sci.* **47,** 403 (1975).
9. Helms, C. R., Yu, K. Y., and Spicer, W. E., *Surf. Sci.* **52,** 217 (1975).
10. Burton, J. J., Helms, C. R., and Polizzotti, R. S., *J. Chem. Phys.* **65,** 1089 (1976).
11. Silverman, E. M., and Madix, R. J., *J. Catal.* **56,** 349 (1979).
12. Ponec, V., *Surf. Sci.* **80,** 352 (1979).
13. Bond, G. C., and Turnham, B. D., *J. Catal.* **45,** 128 (1976).
14. Galvagno, S., and Parravano, G., *J. Catal.* **57,** 272 (1979).
15. Betizeau, C., Leclercq, G., Maural, R., Bolivar, C., Charcosset, H., Frety, R., and Tournayan, L., *J. Catal.* **45,** 179 (1976).
16. de Jongste, H. C., Ponec, V., and Gault, F. G., *J. Catal.* **63,** 395 (1980).
17. Sinfelt, J. H., Lam, Y. L., Cusumano, J. A., and Barnett, A. E., *J. Catal.* **42,** 227 (1976).
18. Luyten, L. J. M., Van Eck, M., van Grondelle, J., and van Hooff, J. H. C., *J. Phys. Chem.* **82,** 2000 (1978).
19. Christmann, K., Ertl, G., and Shimizu, H., *J. Catal.* **61,** 397 (1980).
20. Shimizu, H., Christmann, K., and Ertl, G., *J. Catal.* **61,** 412 (1980).
21. Vickerman, J. C., Christmann, K., and Ertl, G., *J. Catal.* **71,** 175 (1981).
22. Vickerman, J. C., and Christmann, K., *Surf. Sci.* **120,** 1 (1982).
23. Rouco, A. J., Haller, G. L., Oliver, J. A., and Kemball, C., *J. Catal.* **84,** 297 (1983).
24. Bond, G. C., and Yide, X., *J. Mol. Catal.* **25,** 141 (1984).
25. Shi, S. K., Lee, H. I., and White, J. M., *Surf. Sci.* **102,** 56 (1981).
26. Sinfelt, J. H., *Acc. Chem. Res.* **10,** 15 (1977); and references therein.
27. Peden, C. H. F., and Goodman, D. W., "Proceedings, Symposium on the Surface Science of Catalysis, Philadelphia, August 1984." ACS Symposium Series.

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