JOURNAL OF CATALYSIS 95, 321–324 (1985)

Hydrogen Spillover from Ruthenium to Copper in Cu/Ru Catalysts: A Potential Source of Error in Active Metal Titration

Bimetallic catalysts have been extensively studied because of their commercial and fundamental scientific importance (*1–12*). A key to the basic understanding of mixed metal systems is the deciphering of the relative roles of "electronic" and "ensemble" factors in controlling the catalytic behavior of these materials. By varying the composition of bimetallic catalysts deductions have been made regarding the relative importance of these two factors (*13–16*).

Chemisorptive methods have been widely used to obtain information on the surface composition of these alloys (*17, 18*) and employed to define the absolute number of active metal atoms exposed, a number critical to absolute rate determinations. The assumptions of these methods are that only the catalytically active metal will dissociate molecular hydrogen and that the active metal, in turn, will adsorb approximately one hydrogen per surface metal atom. For the often studied systems of Cu/Ni and Cu/Ru these assumptions would appear to be valid given the following two reasons. First, both nickel and ruthenium do indeed dissociate hydrogen with a chemisorption density of ~1 hydrogen atom per surface Ni (*19*) or Ru (*20*) atom. Second, pure copper does not dissociate molecular hydrogen (*21*). In fact, several years ago Balooch *et al.* (*22*) showed, using molecular beam techniques, that hydrogen adsorption on copper is an activated process with an activation energy of ~5 kcal/mol. Of critical importance to the accuracy of chemisorption methods for active metal titration is that no significant spillover of the chemisorbed species occurs from the active to the inactive component.

The Cu/Ru(0001) model system has been studied extensively by Ertl, Christmann, and co-workers (*23–27*). These authors have specifically addressed the adsorption of hydrogen onto a copper-precovered Ru(0001) surface (*24, 25*). H_2 adsorption at 150 K showed no evidence of hydrogen spillover from Ru to Cu. Recent work (*28*) on this same bimetallic system using similar hydrogen adsorption temperatures supports this conclusion. We report here that for hydrogen adsorption at 230 K spillover does occur in a Cu/Ru bimetallic system from the active ruthenium to the inactive copper.

The experiments were carried out with a combined reactor-UHV analysis chamber described previously (*29*). 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 s^{-1}. The mass spectrometer samples 4 mass peaks every 0.7 s.

Prior to cleaning, the backside and edges of the Ru(0001) crystal were masked by a 10-Langmuir exposure of H_2S with the sample at 600 K. This sulfiding procedure was shown to attenuate hydrogen chemisorption to less than 10% of the clean surface. The front face of the Ru(0001) crystal was then cleaned using an O_2 beam of flux 5×10^{14} O_2 cm^{-2} s^{-1} at a crystal temperature of 1450 K for 300 s. Final cleaning was achieved by heating to 1500 K under vacuum, yielding an Auger spectrum free of O,

0021-9517/85 $3.00

S, and C contamination. Hydrogen desorption following a saturation exposure gave a TPD with an area approximately equal to ½ that for the unmasked sample.

Copper was evaporated onto a 100 K 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 quartz microbalance mounted off-axis to the Ru sample. TPD and Auger analysis following Cu dosing showed no measurable contamination of the Ru surface during evaporation.

Figure 1 summarizes the results of two hydrogen chemisorption experiments which are to be discussed. The Ru substrate was first cleaned and then, prior to H_2 adsorption, Cu was evaporated onto the Ru(0001) surface at a coverage of 0.7 monolayers. The procedures of Figs. 1a and b differ only in the substrate temperature at which the H_2 adsorption was carried out. For Fig. 1a, the adsorption temperature was 100 K. For Fig. 1b, this temperature was 230 K. It is evident that more H_2 is accommodated by the Cu/Ru(0001) surface which is held at 230 K during the H_2 adsorption than that maintained at 100 K during an identical exposure. Hydrogen adsorption at 100 K has been shown to quantitatively titrate exposed Ru atoms in a Cu/Ru matrix (*28*). That is, at a 100 K exposure temperature no population of Cu by hydrogen takes place and each exposed Ru atom chemisorbs a single H atom. The results for adsorption of H_2 at 230 K show that the elevated exposure temperature leads to enhanced H_2 adsorption significantly above that for the 100 K adsorption. For a hydrogen exposure such as that used in Fig. 1, adsorption of H_2 onto the clean Ru(0001) surface is invariant with temperature below temperatures of ~300 K. That is, hydrogen adsorption at 100 K produces a TPD indistinguishable from that measured after adsorption at 230 K. Figure 1c is equal to the difference of b-a and thus shows directly the H_2 adsorption enhancement at 230 K on the Cu-covered ruthenium surface. This result is only consistent with significant spillover of H_2 from Ru to Cu at the higher adsorption temperature.

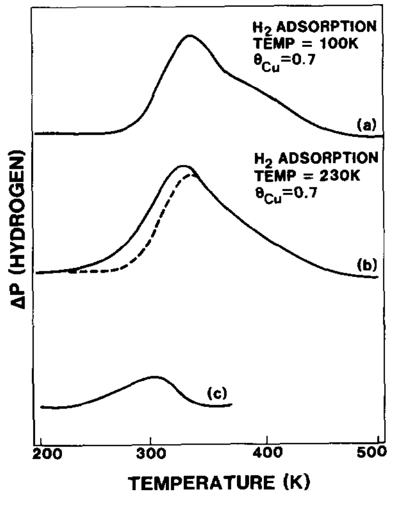

FIG. 1. TPD of hydrogen following a saturation exposure at (a) 100 K and at (b) 230 K on a copper-covered Ru(0001) surface. The copper coverage is 0.7 monolayers. The dashed line in (b) indicates the trace of the superposition of (a) onto (b). (c) is the difference (b) − (a).

Figure 2 shows a comparison of Fig. 1c (solid line) and H_2 desorption from copper reported by Greuter and Plummer (*21*) (dashed line). In this latter case hydrogen adsorption was facilitated by utilizing an atomic hydrogen source. The striking similarity of these two TPD traces supports the conclusion that the origin of the hydrogen TPD of Fig. 1c is indeed hydrogen desorption from copper.

The TPD traces of Fig. 2 have been normalized for comparison. The absolute H_2 quantities in either case are difficult to define; however, a comparison of Fig. 1c with a saturation coverage of H_2 on a copper-free surface suggests that the amount of H_2 spillover is approximately 10% on this 70% copper-covered surface. Longer exposures than that used in Fig. 1b produced little enhancement in the H_2 adsorption. This result

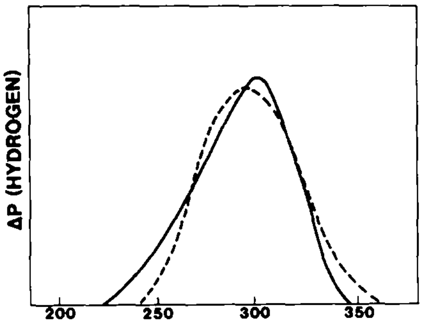

FIG. 2. A comparison of hydrogen TPD from pure copper (dashed line) measured by Greuter and Plummer (*21*) and the difference (b) − (a) of Fig. 1c (solid line). The TPD traces have been normalized for ease of viewing. The exposure temperature used by Greuter and Plummer was 260 K. The exposure temperature used for Fig. 1b was 230 K.

and that the spillover is far from complete are consistent with the spillover process being kinetically controlled. H_2 pressures accessible at elevated pressures but inaccessible in these experiments will likely expedite surface diffusion of hydrogen atoms and thus could lead to a more complete population of surface copper atoms by hydrogen. In support of this conclusion recent studies (*30*) show quantitative spillover of hydrogen from Ru to Cu upon deposition of Cu onto a fully hydrogen-covered Ru substrate. In fact, deposition of Cu to levels greater than 10 monolayers results in hydrogen adsorbed onto a copper surface with no measurable amounts of Ru as determined by Auger spectroscopy. In addition, the desorption kinetics of the hydrogen associated with the copper are shown to be comparable to hydrogen bonded to Ru based upon the H_2 desorption temperatures. These results indicate that differentiation of hydrogen bound to Cu and hydrogen bound to Ru, once spillover has occurred, is virtually impossible using selective chemisorption techniques.

Therefore if exposures well in excess of those used here (e.g., those customarily employed in chemisorptive measurements), can lead to extensive rates of spillover of hydrogen from Ru to Cu, then chemisorption measurements could result in significant over counting of surface Ru atoms. The similarities in desorption kinetics would preclude differentiation of two hydrogen types. This overcounting of Ru could lead to calculated turnover frequencies much smaller than the "true" Ru activities. For example, if one Ru ensemble populates 1000 adjacent Cu sites with hydrogen, then the turnover frequencies as determined by hydrogen chemisorption would be low by 1000. Haller and co-workers (*31, 32*) have recently suggested that just such spillover of hydrogen from ruthenium to copper in supported bimetallics during chemisorption could complicate the determination of specific rates for hydrogenolysis.

Similar conclusions as those presented here have been recently drawn by Crucq *et al.* (*33*), for the Cu/Ni system. From hydrogen adsorption isotherms on pure Ni and CuNi alloys, these authors concluded that hydrogen adsorption takes place on mixed ensembles of Cu and Ni atoms via a spillover mechanism, molecular hydrogen being dissociated on pure Ni ensembles.

In summary, we report here that spillover of hydrogen from Ru to Cu can occur in a mixed Cu/Ru bimetallic catalyst. This spillover may or may not be complete, but, in any case, this phenomenon could lead to error in counting active metal sites in an inactive matrix using hydrogen selective chemisorption. This possibility should be considered in future discussions and measurements of absolute rates or turnover frequencies based on hydrogen chemisorption for bimetallic catalysts composed of "active" and "inactive" components (e.g., Cu/Ru, Cu/Ni, etc.).

ACKNOWLEDGMENTS

We acknowledge with pleasure the partial support of this work by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences. We also acknowledge the skilled technical assistance of Kent Hoffman throughout the course of this work.

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Received November 17, 1984; revised February 12, 1985