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Cyclohexane Dehydrogenation over a Strained-Layer Cu/Ru Catalyst[1]

Addition of a second metal to a single-component catalyst has been a commercially successful method of enhancing catalytic activity and/or selectivity (*1*). A long-standing question regarding such "bimetallic" (*1*) systems is the nature of the properties of the mixed metal system which give rise to its enhanced catalytic performance relative to either of its individual metal components. The present studies are part of a continuing effort (*2–5, 13, 14*) to identify those properties of a bimetallic system which can be related to its special catalytic properties. The specific model system of Cu and Ru was chosen due to the immiscibility of these two metals as well as the pivotal role played by this metal pair in historical bimetallic studies (*1*). The immiscibility of these two metals facilitates coverage determination by temperature-programmed desorption (TPD) (*3*) and circumvents the many complications associated with the assay of alloy surface composition.

Previous studies have addressed the geometric (*2*) and electronic (*5*) structure of Cu overlayers on Ru(0001), the adsorption of CO (*2*) and H_2 (*3*) on submonolayer-to-multilayer deposits of Cu, as well as the measurement of the high-pressure kinetics of the methanation and ethane hydrogenolysis reactions (*4*) on this model bimetallic catalyst. These studies have identified dramatic differences in the electronic and chemical properties of monolayer Cu films relative to bulk Cu.

However, these altered properties do not affect changes in the Ru specific activity for the methanation reaction in a Cu/Ru(0001) catalyst (*4*). The overall surface activity is found to decrease monotonically with decreasing Ru surface area upon Cu addition. That is, Cu serves merely to block active Ru sites on a one-to-one basis. Apparently, CO, although more tightly bound to Cu on Ru than to bulk Cu, is, nevertheless, unable to overcome the activation barrier to dissociation, a critical step to the product, methane (*6*).

Similarly, Cu acts as an inactive diluent for ethane hydrogenolysis, blocking active Ru sites on a one-to-one basis (*4*). In both cases, the specific activity, or the reaction rate normalized to the number of surface ruthenium atoms, is unchanged upon addition of Cu.

These kinetic studies appear to differ significantly from kinetic measurements (*7–12*) obtained on supported Cu/Ru catalysts. For the supported catalysts the specific activity of Ru for methanation and ethane hydrogenolysis is found to be markedly reduced upon the addition of Cu (*7–12*). A key to the assignment of specific rates for Ru in supported Cu/Ru catalysts is the assumption that traditional H_2 chemisorption techniques can accurately count the exposed Ru sites. Recent studies (*13*) have shown that hydrogen movement from ruthenium to copper during ambient chemisorption can invalidate the assumption that adsorbed hydrogen relates directly to the exposed Ru. Therefore, specific rates calculated for Ru, based upon the assumption that one adsorbed hydrogen corresponds to one exposed Ru atom, may yield erroneously low values. If this is indeed the case,

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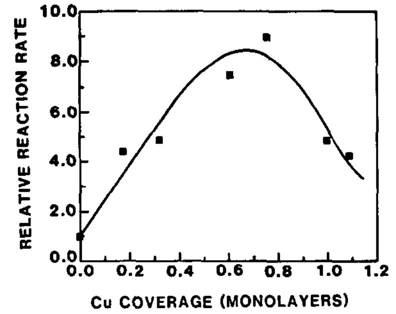

FIG. 1. Relative rate of reaction versus surface Cu coverage on Ru(0001) for cyclohexane dehydrogenation to benzene. P_T = 101 Torr. H_2/cyclohexane = 100. T = 650 K.

the specific rates obtained for supported catalysts, corrected for the overestimation of surface Ru by H_2 chemisorption, may compare favorably with the data reported for Cu/Ru(0001) (*4*).

These arguments suggest that Ru specific rates for methanation and ethane hydrogenolysis on supported Cu/Ru catalysts approximate those values found for pure Ru. As a consequence, the rates for the cyclohexane dehydrogenation reaction on supported Cu/Ru, similarly corrected, must *exceed* those specific rates found for pure Ru. (The uncorrected specific rates for the supported Cu/Ru system remain essentially unchanged upon addition of Cu to Ru (*7*).) An activity enhancement for cyclohexane dehydrogenation in the mixed Cu/Ru system relative to pure Ru is most surprising given that Cu is *less active for this reaction than Ru*. In this note, we report just such an activity enhancement for the addition of Cu to a model Ru(0001) catalyst.

The experiments were carried out in the combined catalytic reactor/UHV surface analysis chamber described previously (*3*, *4*). A detailed description of the experimental procedures and conditions will be published elsewhere (*14*). It should be noted that the rates reported here are normalized to the total number of surface atoms derived from the geometrical surface area and the surface atom density (1.58×10^{15} atoms/cm^2) of the Ru(0001) single crystal. Since Cu in the first monolayer forms 2-D islands pseudomorphic to the Ru(0001) substrate (*2*), no appreciable increase in total surface atomic density occurs upon addition of Cu.

Figure 1 shows the effect of the addition of Cu to Ru on the rate of cyclohexane dehydrogenation to benzene. The overall rate of this reaction is seen to increase by approximately an order of magnitude at a copper coverage of 3/4 of a monolayer. This translates to a Ru specific rate enhancement of ~40. Above this coverage, the rate falls to an activity approximately equal to that of Cu-free Ru. The observed non-zero rates at the higher Cu coverages are believed to be caused by three-dimensional clustering of the Cu overlayers (*2*). Similar data have been obtained for this reaction on epitaxial and alloyed Au/Pt(111) surfaces (*15*).

The rate enhancement observed for submonolayer Cu deposits may relate to an enhanced activity of the strained Cu film for this reaction due to its altered geometric (*2*) and electronic (*2*, *5*) properties. Alternatively, a mechanism whereby the two metals cooperatively catalyze different steps of the reaction may account for the activity promotion. For example, dissociative H_2 adsorption on bulk Cu is unfavorable due to an activation barrier of approximately 5 kcal/mol (*16*). In the combined Cu/Ru system, Ru may function as an atomic hydrogen source/sink via spillover to/from neighboring Cu. A kinetically controlled spillover of H_2 from Ru to Cu, which has been proposed (*13*), is consistent with an observed optimum reaction rate at an intermediate Cu coverage.

Finally, we note the differences between a Ru(0001) catalyst with or without added Cu with respect to attaining steady-state reaction rates. On the Cu-free surface, an induction time of approximately 10 min is required to achieve steady-state activity. During this time, production of benzene is quite low while the hydrogenolysis to lower alkanes, primarily methane, is significantly higher than at steady state. During this induction time the carbon level (as determined by Auger spectroscopy) rises to a saturation value coincidental with the onset of steady-state reaction. This behavior suggests that a carbonaceous layer on the metal surface effectively suppresses carbon–carbon bond scission, or hydrogenolysis, on the Ru surface.

Cu addition leads to an enhanced rate of benzene production with little or no induction time. That is, the initial rate of cyclohexane hydrogenolysis, relative to the Cu-free surface, is suppressed. Further, Cu reduces the relative carbon buildup on the surface during reaction(*14*). Thus, Cu may play a similar role as the carbonaceous layer in suppressing cyclohexane hydrogenolysis while concurrently stabilizing those intermediates leading to the product benzene. In addition, copper may serve to weaken the chemisorption bond of benzene and thus limit self-poisoning by adsorbed product. This latter possibility has been proposed by Sachtler and Somorjai (*15*) to explain the role of Au in Au/Pt(111) catalysts for this reaction. A weakening of benzene chemisorption satisfactorily accounts for our observation that the reaction changes from zero order in cyclohexane on Ru(0001) to approximately first order upon the addition of Cu. A more complete presentation and discussion of the kinetics measured on clean, carbon-covered, and Cu-covered Ru(0001) will be published elsewhere (*14*).

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