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Kinetics of Cyclohexane Dehydrogenation and Hydrogenolysis over Ru(0001) and Cu/Ru(0001)[1]

CHARLES H. F. PEDEN AND D. WAYNE GOODMAN

Sandia National Laboratories, Albuquerque, New Mexico 87185

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The kinetics of cyclohexane dehydrogenation and hydrogenolysis have been measured on initially clean Ru(0001) and Ru(0001) precovered with submonolayer quantities of Cu. The agreement between the results obtained on the model systems with those previously measured on supported catalysts attests to the appropriateness of the model. Postreaction surface analysis of Ru(0001) revealed the presence of a carbonaceous deposit, the amount of which correlated with the reaction rates. Further, this carbon deposit was observed to increase in amount during the initial stages of reaction (induction period), ceasing to grow at a time coinciding with the onset of steady-state reaction. Hydrogenolysis and dehydrogenation rates were greater and smaller during the induction period, respectively, than at steady state. These results suggest that steady-state reaction is occurring on carbon-modified Ru. Addition of Cu results in an enhanced activity for the dehydrogenation of cyclohexane to benzene, occurring with little or no induction time. The mechanism by which Cu alters the catalytic activity of Ru may involve an electronic modification of either or both of the catalyst metals, and/or a synergism between the activities of the two metal components.

INTRODUCTION

The catalytic dehydrogenation of cyclohexane to benzene is an important reforming reaction, being a major contributor to antiknock improvements in petroleum fuels (*1*). The process, along with other hydrogenation and dehydrogenation reactions, occurs on the metal component of the supported catalysts employed. The acidic support material (commonly, alumina) is believed to be active for other reforming reactions such as isomerizations and hydrocracking in addition to its role as the support for the dispersion of the metal component of the catalyst. Catalytic reforming is accomplished predominantly over supported bimetallic (or multimetallic) systems due to their demonstrated improved stability under process conditions over single-component metal catalysts (*2*). Further, improvements in activity and selectivity are often observed when a second metal is added to the catalyst. For example, Sinfelt had observed that addition of a Group IB metal to a Group VIII metal results in improved selectivity for dehydrogenation relative to hydrogenolysis reactions (*3*).

A long-standing question regarding such bimetallic 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. These enhanced properties (improved stability, selectivity, and/or activity) can be accounted for by one or more of several possibilities. First, the addition of one metal to a second may lead to an electronic modification of either or both of the metal constituents. This electronic perturbation can result from direct bonding (charge transfer) or from a structural modification induced by one metal upon the other. Second, a metal additive can promote a particular step in the reaction sequence and, thus, act synergistically with

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the host metal. Third, the additive metal can serve to block the availability of certain active sites, or ensembles, prerequisite for a particular reaction step. If this "poisoned" reaction step involves an undesirable reaction product, then the net effect is an enhanced overall selectivity. Further, the attenuation by this mechanism of a reaction step leading to undesirable surface contamination will promote catalyst activity and durability.

The present studies are part of a continuing effort (*4–9*) to identify those properties of a bimetallic system which can be related to its superior catalytic properties. Our previous studies have addressed the adsorption of CO (*4*) and H_2 (*5*) on very thin (submonolayer to multilayer) deposits of Cu on a Ru(0001) single crystal, as well as the measurement of the high-pressure kinetics of the methanation and ethane hydrogenolysis reactions (*6*) on this model bimetallic catalyst. The specific model system of Cu and Ru was chosen, in part, for the pivotal role played by this metal pair in historical bimetallic studies (*3*). Previous studies on supported Cu/Ru catalysts have addressed the characterization of the catalyst (*10*), in addition to kinetic measurements of the methanation (*11–13*), ethane hydrogenolysis (*3, 14, 15*), and cyclohexane dehydrogenation and hydrogenolysis (*3, 14*) reactions. Cu and Ru are also immiscible in the bulk which facilitates coverage determination by temperature-programmed desorption (TPD) (*5a*) and circumvents the many complications associated with the assay of alloy surface composition.

Our previous studies have shown that a submonolayer Cu film on Ru has significantly altered geometric (*4*) and electronic (*7*) properties from those expected for bulk Cu. These altered properties may be responsible, in part, for the altered adsorption properties of the model Cu/Ru(0001) system (*7b*). For example, we found that CO adsorbed on top of the first monolayer of Cu on Ru is strongly stabilized with respect to CO adsorption on bulk Cu (*4*). However, the properties leading to the increase in binding strength of CO to monolayer Cu films apparently do not affect changes in the Ru specific activity for the methanation and ethane hydrogenolysis reactions (*6*). The overall surface activity for these reactions was 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. In both cases, the Ru 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 (*3, 11–15*) obtained on supported Cu/Ru catalysts. For the supported catalysts, the specific activity of Ru for the methanation and ethane hydrogenolysis reactions is found to be markedly reduced upon addition of Cu. The difference could possibly be due to different 2-D dispersion of the Cu on Ru/SiO_2 and Ru(0001), being atomically dispersed in the former case and in 2-D islands (*4, 6*) in the latter. However, 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 (*8, 16*) have shown that hydrogen movement from ruthenium to copper during ambient chemisorption can invalidate the assumption that adsorbed hydrogen relates directly to the number of exposed Ru atoms. 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, the specific rates obtained for the supported catalysts, corrected for the overestimation of surface Ru by H_2 chemisorption, may compare favorably with the kinetic data reported for Cu/Ru(0001) (*6*). 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 (*3*, *14*).) An activity enhancement for cyclohexane dehydrogenation in the mixed Cu/Ru system relative to pure Ru is most surprising given that Cu is much less active for this reaction than Ru. In this paper, we report just such an activity enhancement for the addition of Cu to a model Ru(0001) catalyst.

Along with the above studies, we report here the results of kinetic measurements of cyclohexane dehydrogenation and hydrogenolysis over clean Ru(0001). The latter experiments have provided a useful frame of reference from which to discuss the kinetic measurements on the model bimetallic Cu/Ru(0001) system. Further, in the studies on initially clean Ru, we have obtained new information regarding the nature of the catalyst surface under steady-state reaction conditions and insight into some of the elementary processes occurring during catalytic reaction.

EXPERIMENTAL

The studies to be described were carried out utilizing the specialized apparatus discussed in detail in Ref. (*17*). This device consists of two distinct regions, a surface analysis chamber and a microcatalytic reactor. The custom-built reactor, contiguous to the surface analysis chamber, employs a retraction bellows that supports the metal single crystal and allows translation of the catalyst *in vacuo* from the reactor to the surface analysis region. Both regions are of ultrahigh-vacuum construction, bakeable, and capable of ultimate pressures of less than 2×10^{-10} Torr. We employ Auger electron spectroscopy (AES) to characterize the sample before and after reaction. The (approximate) 1-cm-diameter × 1-mm-thick ruthenium single crystal, aligned within $\frac{1}{2}°$ of the (0001) orientation, was obtained from Metal Crystals and Oxides of Cambridge, England. The crystal was mechanically polished and the orientation double-checked by Laue X-ray backscattering before being spotwelded to two 0.020-in W heating leads. A W/5% Re–W/26% Re thermocouple was spotwelded to the edge of the crystal for temperature measurement.

After initially cleaning the Ru crystal with previously published procedures (*5a*), the Auger spectrum was free of O, S, and C contamination. In the studies on the model bimetallic catalyst, Cu was evaporated onto the front face of the Ru(0001) crystal surface at room temperature from high-purity Cu wire wrapped around a resistively heated tungsten wire. The Cu source was thoroughly outgassed prior to Cu evaporation and subsequent TPD and Auger analyses showed no measurable contamination of the Ru surface during evaporation.

Reactions on the clean or Cu-covered Ru surfaces were then run in the microcatalytic reactor isolated from the main chamber at crystal temperatures from 575 to 650 K with total reactant gas pressures from 26 to 104 Torr. The kinetic data presented throughout this paper (except where noted) were obtained under steady-state reaction conditions and at low conversions (<5%). Benzene and paraffin hydrocarbon production were measured by a gas chromatograph (GC) equipped with a flame ionization detector (FID). No other products were observed; notably, no cyclohexene was ever detected. The GC column used in this study (6-ft 10% Carbowax 400 on Chromosorb W-HP obtained from Alltech) did not allow for separation of C_1–C_6 paraffins and, thus, only qualitative measurements of hydrogenolysis versus dehydrogenation reaction rates could be made. Relative rates of hydrogenolysis reported here are obtained by ratioing the areas of the GC peaks and normalizing other factors such as time of reaction or total pressure, where appropriate. Rates of benzene production are expressed as turnover frequencies (tof), defined as the

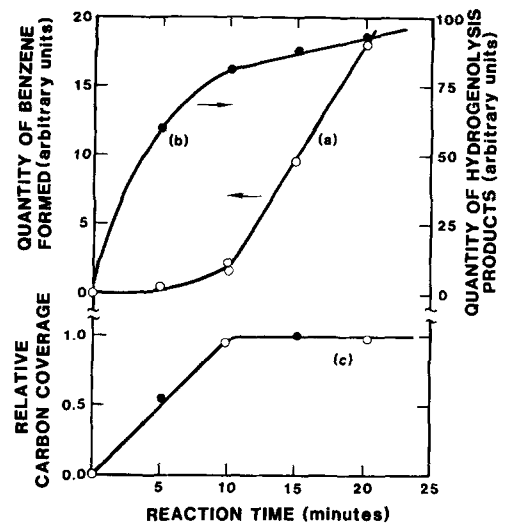

FIG. 1. Amount of (a) benzene formed from the dehydrogenation of cyclohexane and (b) lower carbon number alkanes from cyclohexane hydrogenolysis on Ru(0001) as a function of time. (c) Relative quantities of carbonaceous material present on the surface following reaction at T = 650 K, H_2/C_6H_{12} = 100, P_T = 101 Torr.

number of benzene molecules formed per surface metal atom per second. It should be noted that the rates reported here even for the bimetallic studies 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 (*4*), no appreciable increase in total surface atomic density occurs upon addition of Cu. In the apparatus used in these studies, Cu could be evaporated onto only one side of the crystal surface. Thus, it was necessary to subtract the amount of product formed on the backside of the crystal (edge effects were not accounted for in the subtraction). The amount of product to be subtracted was determined from the experiments on the clean crystal which will be described first.

Following rapid (≈1 min) pumpout of the reactant and product gases, the sample was translated back into the surface analysis region for postreaction characterization. Carbon levels reported here are difficult to quantify since the C_{270} and Ru_{273} Auger signals overlap. Relative amounts of carbon on the surface were determined by ratioing the height of the positive to negative signal near 273 eV obtained in $dN(E)/dE$ mode and normalizing it to the ratio obtained on clean Ru (*18*). Finally in the bimetallic studies, copper coverages were determined subsequent to Auger analysis with TPD as described in Ref. (*5a*).

H_2 gas (99.9995%) was obtained from Matheson Gas Products. Cyclohexane (spectrophotometric grade) was obtained from Mallinckrodt and further purified by multiple distillations at 195 K under vacuum. Postreaction surface analysis as described above indicated the presence of only adsorbed carbon (and copper during the bimetallic studies).

RESULTS

Kinetics on Initially Clean Ru(0001)

At a given temperature, the rate of benzene production from the dehydrogenation of cyclohexane over initially clean Ru(0001) was quite low but rose with time to reach a constant (steady-state) value. This behavior is demonstrated in Fig. 1a for a crystal temperature of 650 K where it can be seen that an induction time of approximately 10 min was required for the onset of steady-state reaction. (It should be noted that, as discussed below, such an induction period was not observed when copper was added to the Ru surface before reaction. Thus, this behavior cannot be attributed to mass transfer or mixing effects in the microreactor.) During the induction time, the formation of lower carbon number alkanes from the hydrogenolysis of cyclohexane was much higher than the rates obtained at steady state (Fig. 1b). Further, we observed a relationship between the carbon coverage present following reaction as measured by AES and the time of reaction as seen in Fig.

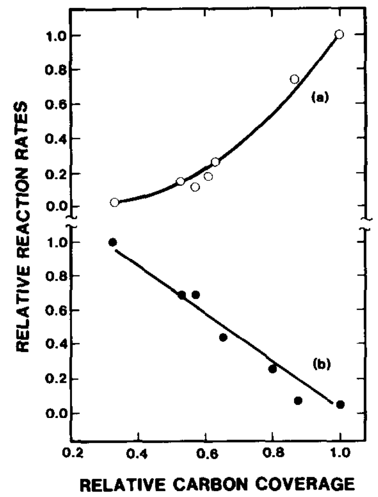

FIG. 2. Relative rates of (a) cyclohexane dehydrogenation and (b) hydrogenolysis as a function of relative carbon coverage present on the surface following reaction (conditions given in Fig. 1).

1c. Note particularly that the onset of steady-state reaction coincides with the time at which deposition of carbon onto the surface ceases (saturation carbon coverage). As noted in the experimental section, it is difficult to quantify this "saturation" carbon coverage with Auger due to the overlap of the Ru and C Auger signals. However, we note a previous study of these reactions over Pt(111) (and Au–Pt(111) alloys) (*19*) which estimated the coverage of "strongly bound, partially dehydrogenated carbonaceous species" to be a monolayer.

The correlation between the rate of reaction and the carbon level remaining after reaction is shown more clearly in Fig. 2. Here it can be seen that the dehydrogenation rates increase exponentially with carbon coverage while the corresponding rates of hydrogenolysis are monotonically reduced.

The discussion to follow will be mainly concerned with the kinetic measurements obtained under steady-state reaction conditions on a Ru surface with a saturation carbon coverage. However, it is instructive to note an additional feature of the induction period, namely, that we observed much longer induction times at higher H_2/C_6H_{12} ratios. In other words, the rates of dehydrogenation (hydrogenolysis) remained low (high) for longer reaction times. Correspondingly, the rate at which carbon was deposited onto the surface was lower under these conditions although the onset of steady-state reaction still coincided with the saturation of the surface with respect to carbon; that is, the relationship between the rates of reaction and the carbon coverage shown in Fig. 2 still applied under these conditions.

The specific rates, expressed as turnover frequencies, of cyclohexane dehydrogenation obtained under steady-state reaction conditions are plotted in Arrhenius form in Fig. 3. The activation energy measured, ≈18 kcal/mol, is very similar to values of 15–21 kcal/mol obtained on other transition metal surfaces in both single crystal and supported catalyst studies (*20*). The response of this reaction to changes in the partial pressures of the reactants is shown in Fig. 4. In these latter measurements, the

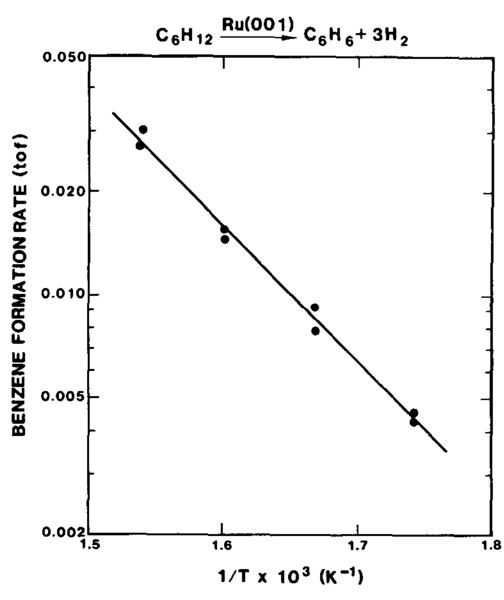

FIG. 3. Arrhenius plot of the rate of cyclohexane dehydrogenation to benzene under steady-state reaction conditions. $H_2/C_6H_{12} = 100$, $P_T = 101$ Torr.

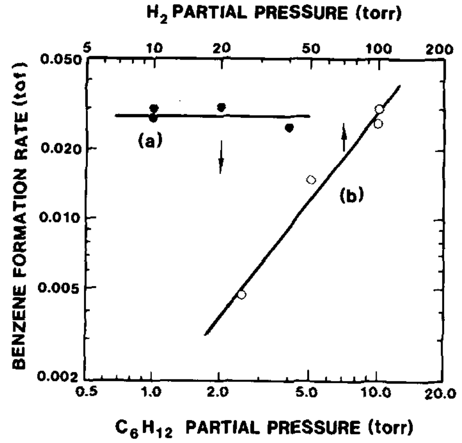

FIG. 4. Cyclohexane dehydrogenation rates as a function of reactant partial pressure. The partial pressure of one reactant is held constant and the other varied. $T = 650$ K, (a) $P(H_2) = 100$ Torr, (b) $P(C_6H_{12}) = 1$ Torr.

pressure of one reactant is held constant while the other is varied. From this figure, it can be seen that the rate of benzene formation is zero order in cyclohexane pressure and approximately first order in hydrogen, again in good agreement with results obtained on supported catalysts (*20*). In order to compare our measured absolute rates with those previously published (*3*), these pressure dependences must be taken into account. (Such a comparison is possible in this case due to the reported structure insensitivity of this reaction (*21*).) If we assume that the pressure dependence is unchanged as a function of total pressure, we extrapolate a turnover frequency of ≈0.05 for hydrogen and cyclohexane pressures of 0.83 and 0.17 atm, respectively, and a temperature of 316°C (589 K), conditions used by Sinfelt (*3*) on supported Ru in obtaining a value of ≈0.08. The good agreement between the single crystal and supported catalyst studies in the activation energy, pressure dependences and absolute TOFs measured attests to the relevance of the model system chosen and further suggests that the postreaction surface characterization carried out in the model studies will, in many respects, reflect the surface condition of the analogous supported-metal particles.

In Figure 5 we have plotted the area of the GC peak for C_1–C_6 hydrocarbons as a function of reactant partial pressures, again keeping the pressure of one reactant fixed and varying the other. From the figure it appears that hydrogenolysis, leading to light alkane products, is negative order in cyclohexane and positive order in hydrogen partial pressures. It should be emphasized that this analysis may be complicated by a change in selectivity for the various alkane components making up the GC peak as a function of the changing reactant partial pressures. This complication may be responsible for the seemingly low activation energy of ≈10 kcal/mol obtained from using the area of the GC peak to measure cyclohexane hydrogenolysis activity. However, we note that there are very few published measurements of cyclohexane hydrogenolysis kinetics (*20*). In addition, it may be significant that this reaction has been reported to be structure sensitive on supported Ru catalysts of varying dispersion (*21*).

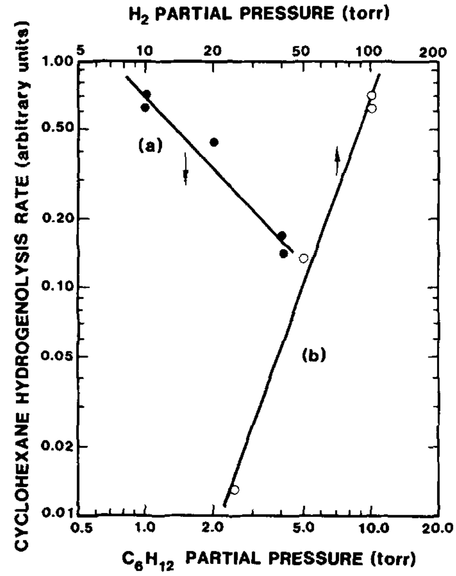

FIG. 5. Cyclohexane hydrogenolysis rates as a function of reactant partial pressure. $T = 650$ K, (a) $P(H_2) = 100$ Torr, (b) $P(C_6H_{12}) = 1$ Torr. See caveat in text.

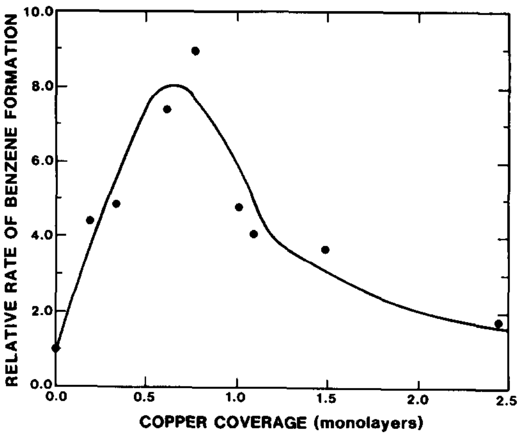

FIG. 6. Relative rate of cyclohexane dehydrogenation as a function of surface Cu coverage on Ru(0001) at T = 650 K, H_2/C_6H_{12} = 25, P_T = 104 Torr.

Kinetics on Cu/Ru(0001)

We begin our discussion of the effect of Cu addition on the kinetics of cyclohexane dehydrogenation and hydrogenolysis with measurements obtained after attainment of steady-state reaction. This will be followed by a discussion of the changes in activity during the induction period upon addition of Cu. As pointed out in the experimental section, we could only dose Cu onto the front face of the Ru(0001) crystal. The back face (and edges) of the single crystal maintained the activity of unpromoted Ru(0001), an activity which was subtracted from the overall rates as described earlier.

In Fig. 6 we have plotted the relative rate of benzene formation as a function of Cu coverage (expressed as fractions of a monolayer (*5a*)). The overall rate of this reaction (on the front face of the crystal only) is seen to increase by approximately an order of magnitude at a Cu coverage of three-quarters of a monolayer (ML). This translates to a *Ru* specific rate enhancement of ≈40, there being only a one-quarter monolayer of Ru sites at this coverage. Above this coverage the rate falls to an activity approximately equal to that of Cu-free Ru. The observed nonzero rates at the higher Cu coverages may be caused by three-dimensional clustering of the Cu overlayers at coverages $>\frac{3}{4}$ ML (*6b*), although other explanations are possible (*19*). Similar data have been obtained for this reaction on epitaxial and alloyed Au–Pt(111) surfaces (*19*).

Differences in the response of the cyclohexane dehydrogenation reaction to changing reactant partial pressures was also evident upon addition of Cu as shown in Fig. 7. The reaction order in hydrogen was approximately the same as on the Cu-free surface. However, the order changed from zero to approximately first order in cyclohexane partial pressure upon Cu addition. The activation energy also varied somewhat when Cu was added to the Ru surface, having values of approximately 15 and 20 kcal/mol at Cu coverages of about 0.6 and 1, respectively. We note, however, that these values are nearly within our estimated experimental error of ±2 kcal/mol. The pressure dependence of the cyclohexane hydrogenolysis reactions (determined with the inherent uncertainties described earlier) remained essentially unchanged upon addition of Cu. Further mechanistic information concerning the role of Cu in al-

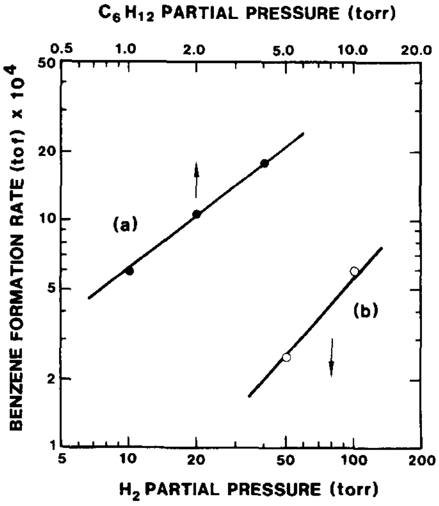

FIG. 7. Cyclohexane dehydrogenation rates as a function of reactant partial pressure on partially Cu covered Ru(0001). θ_{Cu} = 0.76 ML, T = 650 K, (a) $P(H_2)$= 100 Torr, (b) $P(C_6H_{12})$= 1 Torr.

tering the activity of Ru may be contained in our observation that Cu reduced the relative carbon buildup on the surface during reaction although it was not possible to quantify this due to uncharacterized Auger line-shape changes induced by the presence of Cu.

Finally, we note the differences between a Ru(0001) catalyst with or without added Cu with respect to attaining steady-state reaction rates. The enhanced rates of benzene formation observed upon addition of Cu occurred with little or no induction time. Correspondingly, the initial rates of cyclohexane hydrogenolysis, relative to the Cu-free surface, were suppressed. Thus, if we were to compare the dehydrogenation rate enhancement on the Cu/Ru(0001) samples compared to the Cu-free surface at early times (during the induction period) as opposed to comparing steady-state measurements, the effect demonstrated in Fig. 6 would be even more dramatic.

DISCUSSION

In numerous studies to date, it has been demonstrated that unsupported metal single crystals can be used effectively to model the behavior of real working catalysts (*17, 22–25*). Of initial concern in these studies is to determine the relevance of the model system by comparing the kinetic measurements obtained with results from supported catalysts. As expected for structure-insensitive reactions, we found good agreement between our measurements of the specific activity, activation energy, and pressure dependence of cyclohexane dehydrogenation with those reported on supported transition-metal catalysts (*3, 20*). This agreement gives us confidence that the postreaction characterization carried out on the model catalyst in this study is indicative of the surface condition of the analogous supported-metal particles.

Under all the experimental conditions used in the present study, we found significant quantities of an adsorbed, carbon-containing species present following high-pressure reaction. The amount of this deposit, likely containing both carbon and hydrogen (not detectable by AES), was difficult to quantify but was found to increase significantly during initial stages of the reaction. Subsequently, the carbon level reached a constant value, believed to be approximately one monolayer, at a time coinciding with the onset of steady-state reaction. During this induction time, rates of cyclohexane dehydrogenation (hydrogenolysis) were much smaller (larger) than they were at steady state. This behavior was demonstrated in Fig. 1. It should be noted that in numerous previous studies of various catalytic reactions on model single crystal surfaces (*22–25*), we have never observed such an induction time for the attainment of steady-state reaction.

Recently, it has been suggested that some catalytic hydrocarbon reactions (hydrogenations, isomerizations, dehydrocyclizations, and hydrogenolyses) occur on top of strongly bound carbonaceous overlayers which are adsorbed on the metal (*26*). In the present study, we have shown a direct correspondence between the activity of the model catalyst and the quantity of this adsorbed overlayer (Fig. 2), dehydrogenation rates increasing and hydrogenolysis rates decreasing with carbon coverage. These results may be taken as evidence for a mechanism involving reaction on a carbon-modified Ru surface rather than clean Ru. This modified surface likely stabilizes cyclohexane (and possibly other intermediates leading to the product benzene) with respect to carbon–carbon bond scission. The pressure dependence of the dehydrogenation reaction (zero order in cyclohexane and first order in hydrogen) may be taken as further evidence for the operation of such a mechanism. Assuming that the metal surface is covered with approximately a monolayer of carbon (*19*), the reaction rate may then be limited by the production of atomic hydrogen, a process whose reaction probability is most certainly lowered by the presence of carbon. Further, the positive order dependence of the rate on hydrogen partial pressure can be rationalized by a mechanism involving the rehydrogenation of an intermediate C_6H_x species, where $x \leq 5$.

The decrease in hydrogenolysis rates with carbon coverage indicates, at the very least, that carbon–carbon bond scission, generally recognized as the rate-determining step in hydrogenolysis reactions (*27*), is slower in the presence of carbon than on the clean metal surface. In previous studies of the ethane hydrogenolysis reaction over Ru(0001) (*28*), Ni(111), and Ni(100) (*23*), only small, submonolayer carbon coverages were found on the surface after steady-state reaction, again indicating that these types of reactions occur most readily on the clean metal. The inverse relationship between the hydrogenolysis rates and the carbon coverage further suggests that the rehydrogenation of carbon fragments (leading to hydrogenolysis products) competes with the deposition of carbon (formed by some combination of dehydrogenation and/or carbon–carbon bond scission on the metal surface). In further support of this conclusion, at higher H_2 partial pressures, where one might expect greater hydrogenation rates, the induction period before the onset of steady-state reaction (in which hydrogenolysis and dehydrogenation rates are greater and lesser, respectively) was longer.

The order of the hydrogenolysis products with respect to the reactants (approximately negative first order in cyclohexane and approximately second order in hydrogen) is believed to reflect the response of the surface carbon level to changes in cyclohexane and hydrogen pressures (positive w.r.t. cyclohexane and sharply negative w.r.t. hydrogen). Higher or lower surface carbon levels translate to lesser or greater hydrogenolysis products, respectively, as discussed above. It should be noted that for simple hydrogenolysis reactions (e.g., ethane (*6b*)), reaction rates are generally found to be negative order in hydrogen pressure (*20*). However, as was just discussed, these reactions occur on surfaces covered with only small coverages of carbon (*23, 28*) in contrast to the situation reported here for cyclohexane hydrogenolysis. In addition, to our knowledge there has been only one previously published study of the effect of hydrogen pressure on the rate of cyclohexane hydrogenolysis. In this study on Pt single crystals (*29*) Herz *et al.* found the reaction to be approximately zero order in hydrogen pressure.

To begin the discussion of the effect of Cu addition on the activity of Ru(0001) for catalytic cyclohexane reactions, we will again be initially concerned with a comparison of the results on the model system with those obtained on the more realistic supported catalysts. Previously, we have found that submonolayer coverages of Cu on Ru(0001) suppress the overall surface activity for CO hydrogenation and ethane hydrogenolysis monotonically on approximately a one-to-one basis (*6*). That is, the *Ru* specific activity (the rate normalized to the number of Ru surface atoms) is unchanged upon addition of Cu in both of these cases. This is demonstrated for the ethane hydrogenolysis reaction in Fig. 8a which also shows the results of Sinfelt (*3*) obtained on supported Cu/Ru catalysts. As noted earlier, the discrepancy between our results and those reported for supported bimetallic Cu/Ru (*3, 11–15*) can be reconciled if one accounts for a possible error in counting active Ru surface atoms in the supported systems by selective hydrogen chemisorption techniques (*8, 16*). Correcting, in a similar way, the specific rates obtained for the cyclohexane dehydrogenation reaction on supported Cu/Ru (*3*) (uncorrected rates shown in Fig. 8b) would result in an activity enhancement for this reaction upon addition of Cu. As seen in Fig. 8b, we, in fact, observe such an increase in the rate of benzene formation when Cu is added to Ru(0001). Thus, we believe that the results obtained on the model system accurately represent the fac-

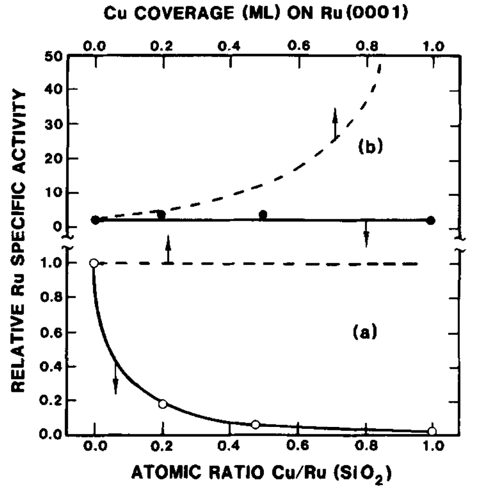

FIG. 8. Relative Ru specific activity as a function of Cu coverage on Ru(0001) (dashed lines), and Cu atomic ratio on silica-supported Cu/Ru catalysts [3] (points and solid curves) for the (a) ethane hydrogenolysis and (b) cyclohexane dehydrogenation reactions. Note that the atomic ratio reported for the supported system likely underestimates the surface coverage of Cu since Cu resides predominantly on the Ru surface in these catalysts (*10*).

tors resulting in the selectivity changes observed in supported bimetallic systems. That is, although hydrogenolysis rates are only affected by a reduction in Ru surface area, selectivity for dehydrogenation may result from enhanced activity for this latter reaction upon addition of Cu to the catalyst.

In the simplest of models, the two reactions (dehydrogenation and hydrogenolysis) are coupled by a common intermediate. Enhanced dehydrogenation rates then result from the reduced activity for the intermediate to undergo further reactions leading to hydrogenolysis products. In this way, Cu may be acting much like C in that the intermediate is stabilized toward C–C bond scission relative to the clean Ru surface. It is important to emphasize, however, that the morphology of the Cu overlayer is likely quite different from that of carbon on Ru; namely, 2-D islands in the former case (*4–6*) and dispersed in the latter. Further, were Cu merely a "C-substitute," it is decidedly better in this respect than C since the rates of dehydrogenation for $\frac{3}{4}$ ML of Cu on Ru, even when normalized to the total metal surface area, represent an enhancement of an order of magnitude over the *steady-state* values for the C-covered Ru surface (Fig. 6). Finally, we note again that bulk Cu is relatively inactive for this reaction (*3*).

As discussed in the introduction, several mechanisms can be proposed which may account for all or part of the altered properties of the Ru catalyst upon addition of Cu. As reported previously (*4*, *5*, *7*), submonolayer Cu films on Ru(0001) have significantly altered geometric, electronic, and adsorption properties from those exhibited by bulk Cu. That the chemistry on Cu can be altered in these systems certainly suggests that the enhanced rates of cyclohexane dehydrogenation may result from an intrinsic activity of this "new" material, strained-layer Cu on Ru. For this reaction, enhanced rates of C–H bond scission, for example, on strained Cu relative to bulk Cu (and carbon-covered Ru) can be envisioned. Such effects were not evident in the other reactions studied (*6*), methanation and ethane hydrogenolysis, possibly due to the difficulty of accomplishing C–O and C–C bond ruptures. For example, although we observe significant stabilization of adsorbed CO on monolayer Cu on Ru(0001) relative to bulk Cu (*4*), the desorption temperature is still well below that of CO on transition metals active in the methanation reaction (*30*).

We have also obtained evidence (*4*) that Ru atoms located at the edges of Cu islands on the surface may also be chemically modified. Notably, we found a CO desorption peak at a temperature intermediate between pure Ru and monolayer Cu on Ru which we assigned to desorption of CO from Cu and/or Ru at the edges of Cu islands on the surface (*4*). Thus, Cu may serve to weaken the chemisorption bond of benzene and then limit self-poisoning by adsorbed product. This latter possibility has been proposed by Sachtler and Somorjai (*19*) to explain the role of Au in Au–Pt(111) catalysts for this reaction. This mechanism satisfactorily accounts for our observation that the reaction changes from zero order in cyclohexane on Ru(0001) to approximately first order upon addition of Cu in that desorption of benzene would no longer be a kinetic limitation in this model.

Alternatively, a mechanism whereby the two metals cooperatively catalyze different steps of the reaction may account for the activity promotion. For example, in the combined Cu/Ru system, Ru may function as an atomic hydrogen source/sink via spillover to/from neighboring Cu. The role of Cu may then be to accomplish the dehydrogenation and rehydrogenation steps of the reaction and/or to stabilize cyclohexane and any subsequent intermediates, leading to the product benzene. In support of this, we found that Cu addition leads to an enhanced rate of benzene production with little or no induction time. Further, Cu reduces the relative carbon buildup on the surface during reaction. This is likely related to the loss of Ru surface area available for carbon deposition in that a carbonaceous layer may not readily form on Cu due to a low probability for C–C bond scission on this metal surface. Thus, Cu may be quite active for many of the reaction steps in cyclohexane dehydrogenation but simply lacks a source of atomic hydrogen to accomplish the complete process, leading to the production of benzene. Such a synergistic reaction involving the *kinetically controlled* spillover of atomic hydrogen from Ru to Cu also satisfactorily accounts for the maximum in the rate curve at $\approx\frac{3}{4}$ of a monolayer (Fig. 6), which is then related to some optimum size and quantity of Cu islands on the Ru surface.

Of course, some combination of the above mechanisms may be operating in that enhanced rates of reaction could be obtained by a synergistic process on modified materials. The possibility that an ensemble effect is responsible for the observed selectivity changes in bimetallic systems (*31*) has been suggested often. In our model system, which again we believe reproduces the chemistry observed on supported catalysts, it is known that Cu forms 2-D islands on the Ru(0001) surface upon deposition (*4*), leaving large open patches of Ru remaining on the surface. While it cannot be determined definitively whether the structure is stable under reaction conditions, as pointed out earlier, the behavior of the model catalyst for the CO hydrogenation and ethane hydrogenolysis reactions (*6*) suggest just such a stability. Then, unless one hypothesizes unrealistically large ensemble requirements, a mechanism involving the operation of an ensemble effect cannot account for the observed selectivity changes on the model Cu/Ru catalyst.

SUMMARY

(1) The activation energy and specific rates of cyclohexane dehydrogenation obtained on initially clean Ru(0001) are in very good agreement with the values reported for supported Ru catalysts.

(2) Catalytic cyclohexane reactions (hydrogenolysis and dehydrogenation) under steady-state conditions occur on a Ru surface covered to a significant extent with a carbonaceous deposit, possibly as much as a monolayer. This overlayer is deposited during an induction period in which the rates of cyclohexane hydrogenolysis and dehydrogenation are greater and smaller, respectively, than they are at steady state. The onset of steady-state reaction coincides with the completion of the carbon overlayer. These results can be interpreted as indicating that many steps of the dehydrogenation reaction occur on a carbon-modified Ru surface.

(3) The addition of Cu to Ru(0001) results in a dramatic enhancement of the rate of cyclohexane dehydrogenation, despite the fact that Cu is much less active for this reaction than is Ru. The enhanced activity observed on Cu/Ru(0001) occurs with little or no induction time.

(4) The mechanism by which Cu alters the catalytic activity of Ru may involve one or more of several possibilities, including an electronic modification of either or both of the catalyst metals, a synergism between the activities of the two metal components, or possibly an ensemble effect (this latter mechanism seems least likely).

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