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Kinetics of Ethane Hydrogenolysis over Silica-Supported Ruthenium–Group IB Metal Catalysts

MARK W. SMALE AND TERRY S. KING

Department of Chemical Engineering, Iowa State University, 231 Sweeney Hall, Ames, Iowa 50011

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We have studied the ethane hydrogenolysis reaction to determine the effect of adding copper and silver to a silica-supported ruthenium catalyst. Specific activities were measured at a number of temperatures as a function of the fraction of Group IB metal. In addition, the effect of changing the ratio of hydrogen to ethane in the feed gas was used to measure apparent orders of reaction as a function of temperature and Group IB metal added. At the lower temperatures studied we found that the effect of adding copper or silver to the catalyst was virtually the same, the differences being attributed to the greater affinity of copper for defect-like sites on the ruthenium crystallites. At higher temperatures, copper and silver acted differently; copper seemed to be active for the removal of site-blocking hydrogen from the active ruthenium surface, while silver merely blocked the ruthenium sites most active for the removal of hydrogen from the surface. We postulate that the defect-like sites of supported ruthenium crystallites are most active for the desorption of weakly adsorbed hydrogen while the actual carbon–carbon bond cleavage takes place on the basal planes. The increase in specific activity observed as the dispersion of the catalyst decreased was attributed to the increase in relative number of carbon–carbon bond-breaking sites. The order of reaction with respect to hydrogen partial pressure suggests that the adsorbed hydrocarbon intermediate has a stoichiometry of C_2H_3. © 1990 Academic Press, Inc.

INTRODUCTION

The cleavage of a carbon–carbon bond in saturated hydrocarbons represents one class of reactions that is important in the petroleum and petrochemical industries. An example of this class of reactions is the catalytic hydrogenolysis of ethane over transition metal catalysts, which has been studied for over 50 years (*1*) and remains an active area of research. Ethane hydrogenolysis is commonly used as a model reaction when carbon–carbon bond cleavage is studied, since the analysis is not complicated by simultaneous reactions forming products other than methane. For example, Pruski *et al.* (*2*) have used nuclear magnetic resonance to study ^{13}C-enriched ethane adsorbed on a silica-supported ruthenium catalyst. Only ethane and methane were observed on the surface, suggesting that no products other than methane were formed. In contrast, when ethylene was adsorbed on this catalyst a multitude of hydrocarbon species, including surface species containing more than two carbon atoms, were seen.

Kinetic parameters for the ethane hydrogenolysis reaction over a large number of silica-supported metal catalysts were reported by Sinfelt (*3*). The apparent order of reaction with respect to ethane is between 0.6 and 1.0 for a wide range of metals. For many systems, the apparent order of reaction with respect to hydrogen is strongly negative, as low as −2.5, although there is a wide variation among the different metal catalysts. Iron and rhenium are notable exceptions, with the activity of the catalyst increasing as hydrogen pressure is increased.

The mechanism for this reaction is generally accepted to involve adsorption of ethane, dehydrogenation of the adsorbed dicarbon species, cleavage of the carbon–carbon bond, and, finally, hydrogenation of the adsorbed fragments to produce methane,

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which then desorbs (*3–5*). For example, the hydrogenolysis and deuterium exchange of ethane over the Pt(111) surface has been studied by Zaera and Somorjai (*4*). They found that deuterium exchange occurred three orders of magnitude more rapidly than hydrogenolysis, producing a product distribution with maxima corresponding to exchange of one and six hydrogens. A mechanism was postulated that involved the adsorption of ethane onto the surface while a single C–H bond was broken. This species may then associatively desorb together with a hydrogen (or deuterium) atom from the surface. Alternatively, further dehydrogenation occurs to form an ethylidyne species. Breaking of the C–C bond of the adsorbed ethylidyne to form two adsorbed CH_x fragments is then postulated to be the rate-limiting step for hydrogenolysis. Subsequent addition of hydrogen (or deuterium) then occurs rapidly to form the product methane.

Engstrom *et al.* (*5*) studied the mechanism of ethane hydrogenolysis over the Ir(111) and the reconstructed (110)–(1X2) surfaces. The (110)–(1X2) surface contains a large number of low-coordination sites, analogous to the edge and corner sites of a supported metal crystallite. They found that the intermediate dicarbon species (prior to carbon–carbon bond cleavage) was a function of the orientation of the metal surface; for the (111) surface the dicarbon intermediate was proposed to be C_2H_4, whereas on the (110)–(1X2) surface the more highly dehydrogenated C_2H_2 species was suggested to be the intermediate. One difference between this work and that of Zaera and Somorjai (*4*) is that competitive adsorption of hydrogen and ethane was considered in the analysis. Engstrom *et al.* (*5*) point out that neglecting to include this factor would lead to the overestimation of the extent of dehydrogenation of the intermediate dicarbon species by one hydrogen atom.

The hydrogenolysis reaction has often been suggested to be structure sensitive; the activity of the catalyst depends on its morphology (*5–16*). One of the most commonly studied features of structure sensitivity is the variation in catalytic activity with metal dispersion. For example, Carter *et al.* (*6*) studied the effect of crystallite size on the activity for the ethane hydrogenolysis reaction for nickel supported on silica–alumina. The dispersion of a 10 wt% nickel catalyst was varied from 4 to 10% by sintering in a hydrogen atmosphere. These catalysts exhibited a systematic decrease in specific activity as the dispersion decreased, although it appeared that for the least dispersed catalysts the specific activity of the catalysts was almost constant.

The effect of particle size on the ethane hydrogenolysis reaction has also been investigated for both unsupported and silica-supported rhodium catalysts by Yates and Sinfelt (*7*). In this study the dispersion of the supported catalyst was varied by changing the metal loading between 0.1 and 10 wt%. One of the supported catalysts was also calcined at various temperatures to obtain large supported crystallites. For all the catalysts studied the apparent order with respect to ethane was around 0.8. For the uncalcined supported catalysts the apparent order of reaction with respect to hydrogen was -2.1, in contrast to values of -1.4 for the supported catalyst calcined at 1073 K and -1.6 for the unsupported catalyst. The authors did not offer any explanation for these differences. However, the uncalcined supported catalysts will have significantly more edge, corner, and similar low-metal-coordination sites than the other catalysts, so it seems reasonable to attribute the difference in apparent orders of reaction with respect to hydrogen to the presence of these defect-like sites. The authors noted an optimum dispersion to obtain the maximum specific activity for ethane hydrogenolysis. The supported catalysts with metal loadings in the 1 to 10 wt% range were most active. The least active catalysts were the supported catalysts with a metal loading below 1 wt%, the unsupported catalyst, and the catalysts that had been calcined at high temperatures.

Brunelle *et al.* (*8*) have studied the hydrogenolysis and isomerization of *n*-pentane over silica-supported platinum catalysts prepared by ion-exchange and impregnation. The dispersion of the catalysts was varied by calcining at different temperatures. They found that the rate of hydrogenolysis decreased as particle size increased, whereas the rate of isomerization was not a function of dispersion.

Guczi and Gudkov (*9*) reported that the turnover frequency for ethane hydrogenolysis increased as the dispersion increased for the silica-supported platinum catalyst they studied. This catalyst was prepared by an ion exchange method to attain dispersions between 2 and 40%. Schay and Guczi have also obtained values of the apparent orders of reaction with respect to ethane and hydrogen for ethane hydrogenolysis over silica-supported platinum catalysts (*10*). They reported values of 1 with respect to ethane and −2.1 with respect to hydrogen in the 3- to 30-Pa pressure range. Hydrogen-to-ethane ratios in this work were varied between 3 : 1 and 30 : 1.

In contrast to the observations of Guczi and Gudkov, Barbier *et al.* (*11*) observed that the specific activity of alumina-supported platinum catalysts for ethane hydrogenolysis decreased as the dispersion increased for a series of catalysts where the dispersion was varied by the metal loading. This was also true when the dispersion of a constant metal-loading supported catalyst was changed by calcination at different temperatures. However, when the dispersion was varied by sintering constant metal-loading catalysts in a hydrogen atmosphere, an opposite trend was observed. In all cases, the apparent orders of reaction were around 1.1 with respect to ethane and between −1.9 and −2.5 with respect to hydrogen. All the catalysts used were prepared from chloroplatinic acid, and residual chlorine was observed in at least some of the catalysts, which may have affected the results. Barbier *et al.* (*12*) used these same catalysts to study the hydrogenolysis of cyclopentane. The catalyst series in which the dispersion was varied by changing the metal loading exhibited a maximum specific activity corresponding to a crystallite size of about 60 Å. However, as was the case with the ethane hydrogenolysis reaction, changing the dispersion by sintering under hydrogen at different temperatures led to no appreciable change in specific activity. The authors observed that crystallite size was not the only important parameter determining the activity of these catalysts; the relative activity also depended on the method chosen to change the dispersion, although the authors did not postulate why this was so.

Barbier and Marecot (*13*) have investigated the effect of dispersion on the ethane hydrogenolysis reaction for alumina-supported iridium catalysts. They found that decreasing dispersion, either by increasing metal loading or by calcining the catalyst, increased the specific activity for catalysts with dispersions between 8 and 67%. Apparent orders of reaction were around 1 with respect to ethane and −1.8 with respect to hydrogen for all the catalysts studied. These catalysts were prepared by impregnating the support with solutions of chloroiridic acid, so again residual chlorine may be playing a role.

Godbey *et al.* (*14*) have studied the hydrogenolysis of ethane over rhenium on Pt(111) single-crystal surfaces and platinum on Re(0001) single-crystal surfaces. For both single crystals, roughening the surface by argon sputtering increased the specific activity of the catalyst. Rhenium was significantly more active for this reaction than was platinum, but the most active catalysts were those with a surface composition Re_2Pt, while a Pt(111) surface covered with two monolayers of rhenium displayed virtually the same activity as the clean Re(0001) surface. The authors postulated an electronic effect extending only to first nearest neighbors to explain their data. It is interesting to note that the apparent order of reaction with respect to hydrogen for the Pt(111) surface covered by two monolayers of rhenium (which had the same activity as the Re(0001) surface) was −0.7, compared to a value of +0.3 reported for the silica-supported catalyst (*3*).

Doi *et al.* (*15*) have studied ruthenium catalysts prepared from solutions of $Na[Ru_3H(CO)_{11}]$ in methanol using a number of different supports. The catalysts they studied had dispersions ranging from 23 to 55%. They found little relationship between particle size and catalytic activity for these systems. However, it may be that any contribution of dispersion is masked by the effect of using different metal oxide supports. This was also true of the investigation of ethane and propane hydrogenolysis over ruthenium reported by Galvagno *et al.* (*16*), who saw no evidence to suggest that dispersion affects the activity of the catalyst. The apparent order of reaction with respect to hydrogen for ethane hydrogenolysis was measured to be between −2.21 and −1.92 for the silica-supported ruthenium catalyst. This was somewhat more negative than the value of −1.3 previously reported by Sinfelt (*3*). The difference might be associated with the use of different silica supports in these two studies.

The ruthenium–copper bimetallic catalyst is particularly interesting and has received a great deal of attention, since the two metals are virtually immiscible in the bulk (*17*). However, Sinfelt and coworkers have shown that the two metals interact in the supported catalyst, forming bimetallic clusters (*18, 19*).

Sinfelt has studied ethane hydrogenolysis over silica-supported ruthenium–copper bimetallic catalysts (*18, 20*). He found that the activity per hydrogen chemisorption site decreased significantly as the copper content of the system increased. This led to the suggestion that the active site over ruthenium might consist of a number of adjacent ruthenium atoms (a geometric or ensemble effect).

Rouco *et al.* (*21*) have compared the silica-supported ruthenium–copper and ruthenium–silver systems. The catalysts were prepared from aqueous solutions of nitrate salts and supported on high-surface-area (600 m^2/g) silica. Like previous studies (*18, 20*) Rouco *et al.* found that the rate per hydrogen chemisorption site for ethane hydrogenolysis over ruthenium–copper catalysts decreased rapidly as copper was added, although the decrease was not as pronounced as that reported by Sinfelt. The difference might have been related to the different combinations of metal salts and supports used. The ruthenium–silver catalysts showed a modest decrease in specific activity for ethane hydrogenolysis as the silver content was increased, but no significant change in apparent activation energy was observed. It was postulated that the silver was present predominantly as islands on the surface of the ruthenium.

Peden and Goodman (*22, 23*) have investigated the effect of adding copper to a Ru(0001) single-crystal surface for the ethane hydrogenolysis reaction, among others. No geometric effects were observed; instead they found that the effect of adding copper was simply to block active sites on a one-to-one basis. For the pure ruthenium surface the apparent order of reaction with respect to ethane was found to be 0.85, in good agreement with values found for the silica-supported catalysts (*3*). The apparent order with respect to hydrogen was found to be a function of hydrogen partial pressure, changing from positive to negative as the hydrogen pressure rose above 25 Torr.

A supported catalyst crystallite will contain a significant number of edge and corner sites, which will have no analog on a defect-free low-index plane single-crystal surface. Apparently these sites are important for many different catalyst systems. Strohl and King (*24*) have modeled ruthenium–silver catalysts and other segregating systems similar to ruthenium–copper. They found that the segregating element tended to preferentially populate low-coordination, defect-like edge and corner sites of the supported metal crystallites. Once nearly all the edge and corner sites have been filled, two-dimensional islands were seen to form on the low

Miller index surfaces of the particles. Kim *et al.* (*25*) have used photoemission studies of physisorbed xenon to show that copper does indeed tend to segregate to defect sites on ruthenium surfaces. Other experimental work (*26, 27*) has shown that copper does form two-dimensional islands on Ru(0001) surfaces after annealing at 300 K. Wu *et al.* (*28*) have used nuclear magnetic resonance of chemisorbed hydrogen to show that silver does not interact with ruthenium as strongly as copper. They found that in order to cover a given fraction of a supported ruthenium crystallite, much more silver than copper was required.

The Ru–Cu and Ru–Ag also have different behaviors with respect to hydrogen chemisorption. It is well established that hydrogen can dissociatively chemisorb on ruthenium surfaces and migrate to copper (the spill-over effect) both in the case of single-crystal surfaces (*29*) and for the supported catalysts (*30–32*). However, for ruthenium–silver catalysts, this does not occur (*28*).

It is clear that the morphology of a catalyst can affect its activity for ethane hydrogenolysis. Since hydrogen plays an integral part in hydrogenolysis reactions, it seems likely that the interaction of a catalyst surface with hydrogen will also affect the ethane hydrogenolysis reaction. We have investigated the silica-supported ruthenium–copper and ruthenium–silver systems, emphasizing morphology and hydrogen effects in an attempt to elucidate their joint contributions toward the specific activity of these catalysts for ethane hydrogenolysis.

METHODS

The catalysts used were all supported on Cab-O-Sil HS-5 amorphous fumed silica with a surface area of 300 m^2/g as measured by the BET method, and all the bimetallic catalysts contained 4% ruthenium (by weight). We used the incipient wetness technique to co-impregnate the support with an aqueous solution of the metal salts. The metal salt precursors for the catalysts were $Ru(NO)(NO_3)_3$, $Cu(NO_3)_2$, and $AgNO_3$. Using these salts allowed us to avoid contaminating the catalysts with chlorine.

A series of monometallic catalysts with metal loadings of 1 to 12% ruthenium (by weight) was prepared using the same method to allow us to investigate the effect of dispersion. In addition, an unsupported ruthenium powder was prepared by reduction of RuO_2 to give us a catalyst of very low dispersion.

Characterization of the catalysts was done using hydrogen chemisorption and nuclear magnetic resonance of adsorbed hydrogen, as described elsewhere (*28, 32, 33*). We carried out reaction studies using a continuous tubular reactor system, details of which have been previously reported (*34*). Crystalline silica was mixed with 10 to 300 mg of catalyst to provide a bed volume of 3 cm^3 and the catalyst was reduced *in situ* at 450°C for 2 h while flowing hydrogen at a rate of 500 sccm through the reactor. After the reduction step the catalyst bed temperature was lowered at a controlled rate, generally around 40 K h^{-1}, to the desired reaction temperature, during which time we continued to flow hydrogen through the reactor. Once the initial reaction temperature had been achieved, the feed was switched to the reactant mixture and samples of the product were taken and analyzed as previously reported (*34*). Specific activities were calculated in terms of rate of disappearance of ethane per surface ruthenium atom per second.

The activities of the Ru–Ag/silica catalysts were measured as a function of silver content using a 10 : 2 : 1 molar ratio of hydrogen, ethane, and argon. The argon was used as an internal standard for the gas chromatographic analysis. Typically, two measurements of activity at different temperatures were obtained from each catalyst load, each separated by 10 K. Some of the activity data for the hydrogenolysis of ethane of the Ru–Cu/silica catalysts reported here consisted of the data we have previously reported (*34*). Additional experiments with the Ru–Cu/silica catalysts were conducted to determine the kinetic variations with the hydrogen-to-ethane ratio as explained later.

In addition to measuring activity for the ethane hydrogenolysis reaction as a function of Group IB metal loading, we have determined apparent orders of reaction with respect to hydrogen and ethane as a function of temperature for Ru/silica, Ru–Cu/silica, and Ru–Ag/silica catalysts. These values were obtained by changing the hydrogen-to-ethane ratio of the feed gas. If we assume a kinetic expression of the form

$$\text{rate} = k[\mathrm{H_2}]^m[\mathrm{C_2H_6}]^n,$$

it can be shown that this can be transformed into the form

$$\text{rate} = k'R^m(1 + R)^{-(m+n)},$$

where R is the molar ratio of hydrogen to ethane and k' is a function of temperature, total pressure, and the partial pressures of any diluent species (i.e., argon). This equation can be linearized, resulting in a linear expression in two variables (which are not independent). We fit the linearized expression to our data using a least-squares regression to obtain values for the apparent orders of reaction with respect to hydrogen and ethane. This form of kinetic expression can be used to draw implications about the mechanism (*3, 7, 10, 11, 13, 14*). The independence of the results from any mechanistic assumptions is useful in comparing data from different groups.

RESULTS

Ruthenium dispersions of the catalysts used in this study are given in Table 1. Figure 1 shows the turnover frequency (molecules of ethane reacted per second per surface ruthenium atom) for ethane hydrogenolysis as a function of copper loading at a number of different temperatures. We see that the behavior of the system as copper was added depended strongly on the temperature. At the lower temperatures studied, addition of small amounts of copper lowered the turnover frequency dramatically. At copper atomic fractions above 10 to 15%, however, the addition of copper appeared to have little effect. At intermediate temperatures, addition of copper did not change the specific activity of the catalyst, while at the highest temperature studied, addition of small amounts of copper appeared to increase the turnover frequency until a plateau was reached at about 10 to 15% copper. Note that the rate per hydrogen adsorption site plotted versus copper content (*34*) agrees very well with the results of Sinfelt (*18, 20*). Sinfelt's results are given as the rate per strong hydrogen adsorption site at 518 K (see Fig. 6 of Ref. (*18*)). If this data were plotted on Fig. 3 of Ref. (*34*) Sinfelt's results fall where expected, between our results at 508 and 528

TABLE 1

Ruthenium Dispersion of Catalysts

Cu atom fraction	Ruthenium dispersion[a]
0.000	0.290
0.025	0.258
0.061	0.233
0.121	0.161
0.179	0.070
0.235	0.039
0.346	0.024
0.452	0.018
0.553	0.009
0.650	0.003
Ag atom fraction	**Ruthenium dispersion[b]**
0.000	0.290
0.136	0.232
0.200	0.205
0.300	0.172
0.400	0.114
0.500	0.072
Wt% ruthenium	**Ruthenium dispersion[b]**
100	0.016
12	0.190
8	0.230
4	0.260
1	0.300

[a] From NMR of chemisorbed hydrogen.

[b] From strong hydrogen chemisorption.

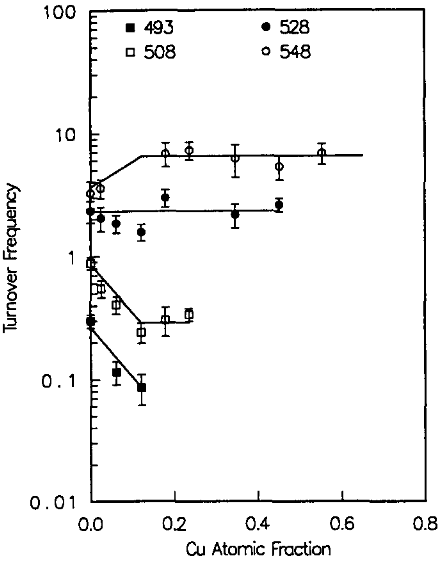

FIG. 1. Rate of ethane hydrogenolysis (±1 standard deviation) per surface ruthenium as measured by proton NMR (P = 1 atm, $H_2:C_2H_6:Ar$ = 10:2:1).

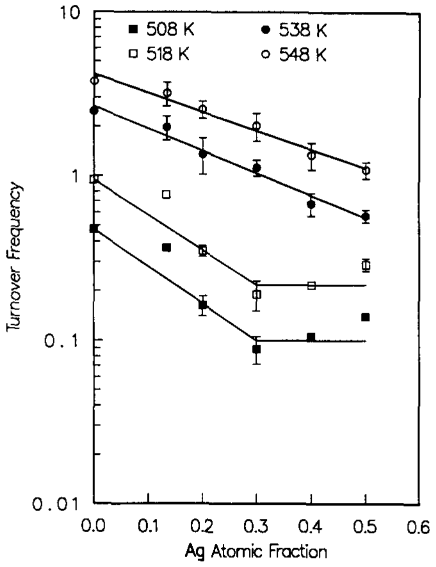

FIG. 2. Rate of ethane hydrogenolysis per surface ruthenium as measured by strong hydrogen chemisorption (P = 1 atm, $H_2:C_2H_6:Ar$ = 10:2:1).

K. Since strong hydrogen chemisorption, however, does not titrate only the ruthenium atoms at the surface but also the copper atoms, the rate expressed per hydrogen adsorption site should not be interpreted as a turnover frequency (*34*).

In contrast to the Ru–Cu catalysts, the Ru–Ag/silica catalysts showed an initial decrease in specific activity as silver was added at all temperatures studied (Fig. 2). The turnover frequency did not level off dramatically at the higher temperatures studied, although some leveling of the turnover frequency versus silver loading curves at the lowest temperatures shown did appear.

The Arrhenius plots for the Ru/silica and Ru–18% Cu/silica catalysts (Fig. 3) show an interesting trend. At a temperature of 515 K the two curves intersected. Below 515 K the two curves suddenly diverged, with the pure ruthenium catalyst activity being substantially above that of the Ru–Cu catalyst. Above 515 K the Ru–Cu catalyst had the same activity or was more active than the pure ruthenium.The Arrhenius plots for the Ru–Ag/silica catalysts (Fig. 4) did not exhibit this behavior. Instead, all the curves were nearly parallel throughout the temperature range we have studied. The Ru–Ag catalyst was less active than the pure ruthenium at all temperatures studied.

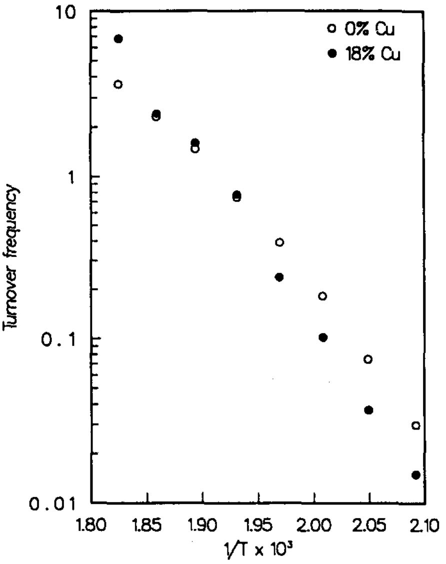

FIG. 3. Arrhenius plots for Ru/SiO_2 and $Ru-Cu/SiO_2$ catalysts (P = 1 atm, $H_2:C_2H_6:Ar$ = 10:2:1).

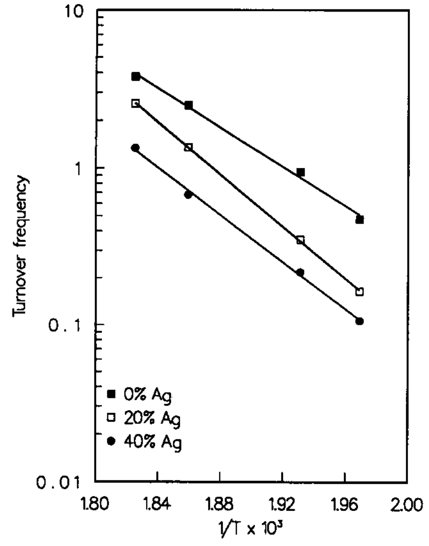

FIG. 4. Arrhenius plots for Ru/SiO$_2$ and Ru–Ag/SiO$_2$ catalysts (P = 1 atm, H_2 : C_2H_6 : Ar = 10 : 2 : 1).

An example of the curve fit used to obtain the apparent order of reaction data is given in Fig. 5. As can be seen, the expression fit the data well over the entire range of hydrogen-to-ethane ratios at both temperatures studied. The values obtained for the apparent orders of reaction for ethane hydrogenolysis over Ru/silica, Ru–18% Cu/silica, and Ru–40% Ag/silica are given in Table 2 and are graphically presented in Figs. 6a–6b. These Group IB metal fractions were chosen because Monte Carlo simulations suggested that nearly all edge and corner sites of the supported crystallites would be occupied by the Group IB metal (*35*). We see that the apparent order with respect to hydrogen for both the pure ruthenium and the ruthenium–silver bimetallic catalysts did not change significantly from 508 to 548 K. For the pure ruthenium catalyst the order with respect to hydrogen remained at about −1.4 and in the case of the ruthenium–silver bimetallic the value was around −2.4. In contrast, the ruthenium–copper bimetallic showed a significant change in the apparent order of reaction with respect to hydrogen between the two temperatures studied. At 508 K, the measured value of −2.28 was almost identical to that for the ruthenium–silver bimetallic while at 548 K the apparent order of reaction with respect to hydrogen was −1.29, close to the value of −1.5 found for the pure ruthenium catalyst. We also noted that the apparent order of reaction with respect to ethane for all the catalyst and temperature combinations studied was around 0.8.

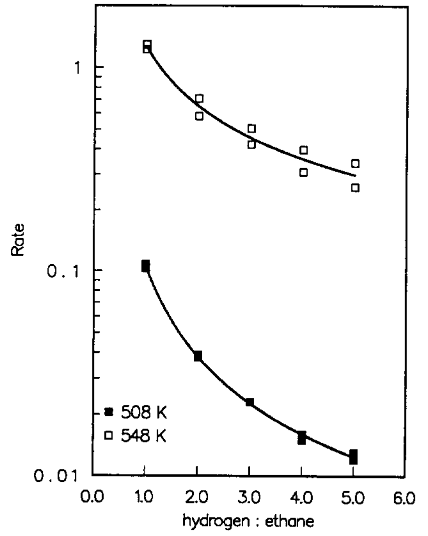

FIG. 5. Rate of ethane hydrogenolysis as a function of H_2 : C_2H_6 ratio for Ru–18% Cu/SiO$_2$ catalyst fitted by expression used to calculate apparent orders of reaction.

TABLE 2

Apparent Order of Reactions for Ethane Hydrogenolysis with Respect to Ethane and Hydrogen

Catalyst	Temp (K)	Order wrt	
		Ethane	Hydrogen
100% Ru	508	0.91	−1.37
	548	0.81	−1.50
18% Cu	508	0.89	−2.28
	548	0.71	−1.29
40% Ag	508	0.72	−2.29
	548	0.83	−2.46

The activity at 508 K of the series of pure

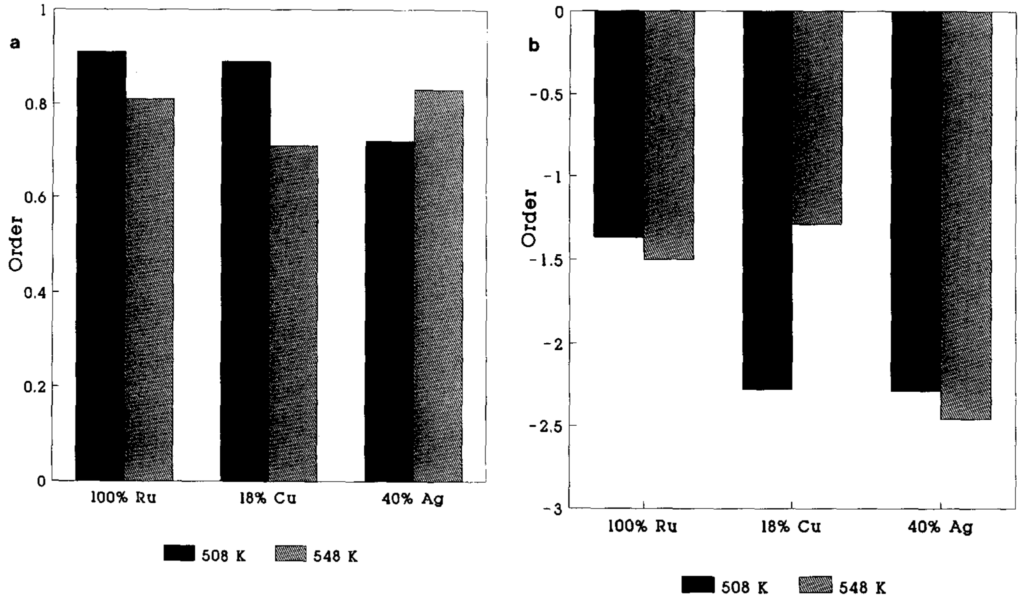

FIG. 6. Apparent order of reaction with respect to (a) ethane and (b) hydrogen for Ru/SiO_2, Ru–18% Cu/SiO_2, and Ru–40% Ag/SiO_2 catalysts at 508 and 548 K.

ruthenium catalysts with different metal loadings is shown as a function of the dispersion of the catalysts in Fig. 7. The ruthenium powder was reduced at 573 K to ensure that it was not sintered. The supported catalysts were all reduced at 723 K. We also made runs for the highest and lowest metal-loading supported catalysts where the reduction temperature was 573 K. The activity of the supported catalysts was not a function of reduction temperature. As can be seen, generally the specific activity decreased as the dispersion increased, although at the lowest dispersions the effect of changing dispersion was minimal.

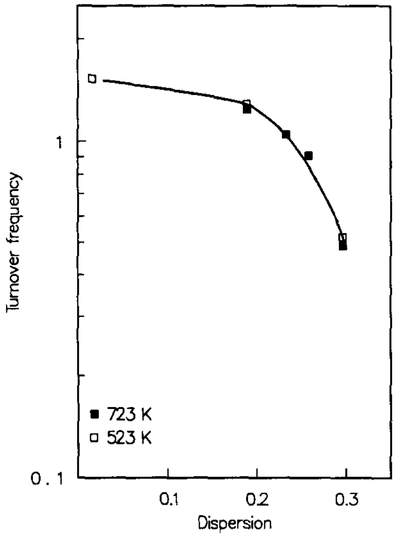

FIG. 7. Specific activity of monometallic Ru catalysts at 508 K as a function of dispersion.

DISCUSSION

We find it useful while attempting to explain our reaction data to have a model of the bimetallic crystallites on the catalyst support. The use of a Monte Carlo simulation technique to model ruthenium–Group IB metal catalysts has been previously described (*24*, *34*, *35*). As with all simulation procedures, we should be aware of the limitations of the technique. The output from the simulation is an equilibrium solution and as such does not take the kinetics of the formation of the bimetallic crystallites into account. Given a sufficiently long reduction step for our catalysts, this should not be

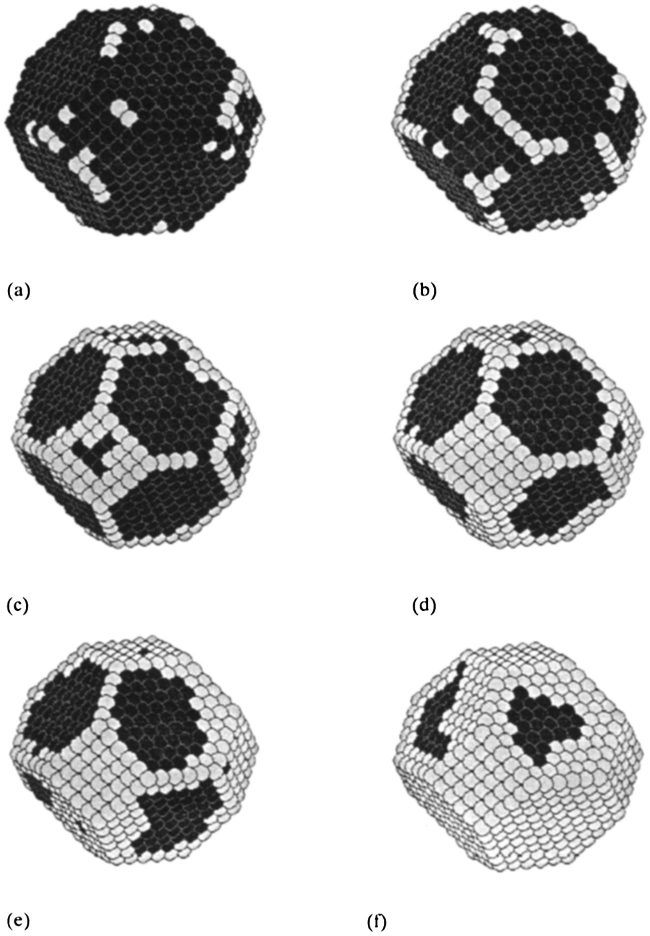

FIG. 8. Monte Carlo simulation results for Ru–Cu/SiO_2 catalysts with a total metal dispersion of 30%: (a) 2% Cu, (b) 5% Cu, (c) 10% Cu, (d) 15% Cu, (e) 20% Cu, (f) 30% Cu.

a restriction to our use of the model. In addition, the simulations do not, in general, allow for modification of the catalyst surface due to adsorbed species. However, simulations have been reported that allow for an adsorbed species such as hydrogen or carbon monoxide (*24*). It was found that the presence of an adsorbate did not significantly change the calculated crystallite morphology in cases where the metal–metal bond is much stronger than the metal–adsorbate bond. A final limitation of the simulations is that they are done with a rigid lattice. The crystal structure used in the simulation is a face-centered cubic lattice while ruthenium has a hexagonal close-packed structure. Since ruthenium does not mix with either silver or copper, but merely provides a surface for the second metal to form aggregates, the general results are not significantly influenced by this limitation. Given these restrictions, we believe that the simulations can give useful qualitative results for an average particle size that can be used to assist our understanding of the systems we have studied.

The Monte Carlo simulation results suggested that when a small amount of copper was added to a ruthenium catalyst, it preferentially populated the edge and corner sites

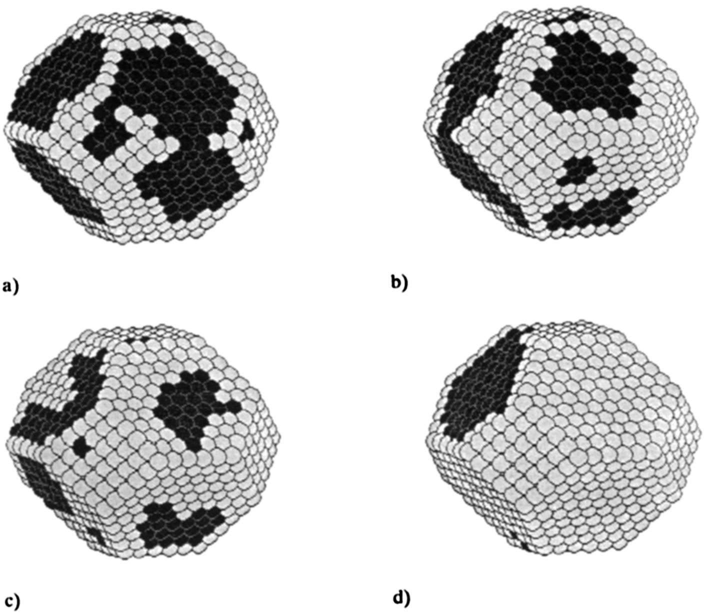

FIG. 9. Monte Carlo simulation results for Ru–Ag/SiO_2 catalysts with a total metal dispersion of 30%: (a) 13% Ag, (b) 20% Ag, (c) 30% Ag, (d) 40% Ag.

of the bimetallic crystallites (Figs. 8a–8c). Only when these sites were filled with copper were the low index planes covered with copper (Figs. 8d–8f). We note that the simulation suggested that the copper tends to form two-dimensional rafts on the low-index ruthenium planes, as has been observed experimentally (*26, 27*). Copper was occupying all the edge and corner sites of the crystallite at Cu : Ru ratios as low as 1 : 9.

Modeling of the ruthenium–silver catalysts gave results similar to those observed for the ruthenium–copper case (Figs. 9a–9d). This system, however, required significantly more of the Group IB metal before there was no longer any ruthenium at the edge and corner sites of the catalyst crystallite. In fact, for a particle with a total metal dispersion of 30%, it was not until over 30 to 40% of the particle was made up of silver that all the edge and corner sites were occupied by the silver. Experimental results have confirmed that silver is less inclined to cover the surface of ruthenium crystallites than copper (*28*).

Figure 1 shows that at the lower temperatures studied, the addition of a small amount of copper to the ruthenium catalyst caused a dramatic decrease in specific activity. For copper to ruthenium atomic ratios above 1 : 9, however, there appeared to be no change in specific activity as copper was added to the system. This breakpoint coincided with the point at which the Monte Carlo simulation predicts that all the edge and corner sites of the bimetallic particles were occupied by copper, suggesting that these sites play a special role in the reaction. At the intermediate temperature studied, no change occurred in specific activity as the copper content of the catalyst was increased. At the highest temperature studied, we observed a reversal in behavior, as the addition of a small amount of copper to the system appeared to increase the turnover frequency for ethane hydrogenolysis. Again, a breakpoint was observed at a copper-to-ruthenium ratio of 1 : 9, above which the addition of copper did not change the specific activity of the catalyst. This change in trend at higher temperatures suggested that the relative importance of the defect sites and low index planes might be changing.

In contrast to the results for ruthenium–copper, we can see in Fig. 2 that the specific activity of the ruthenium catalyst decreased as silver was added to the system at all temperatures studied. The Monte Carlo simulations predicted that copper was much more efficient at covering defect-like sites than silver. If the ethane hydrogenolysis reaction is structure sensitive it would therefore be expected that the effect of adding silver would be less pronounced than adding copper. Moreover, if the Group IB metals played no part in the reaction, we might expect that the effect of covering a given fraction of edge and corner sites with silver or copper would be the same. The fact that copper and silver appeared to affect the catalyst in different ways suggests that either or both of the Group IB metals may be actively participating in the reaction, at least at one of the extremes of the temperature range we have studied. Since hydrogen, which of course takes part in the reaction, is known to migrate from ruthenium to copper, both on single-crystal catalysts (*29*) and silica-supported catalysts (*30–32*) we suspected that the copper might be playing a role in the reaction. In addition, hydrogen does not spill over from ruthenium to silver in the Ru–Ag/silica catalysts (*28*) and, therefore, silver merely occupies surface sites. We ruled out the possibility of an electronic effect since the Arrhenius plots for pure ruthenium and ruthenium–silver catalysts are nearly parallel.

The Arrhenius plots for a pure ruthenium catalyst and one in which 18% of the metal atoms are copper showed interesting differences. At tmperatures above 515 K the two curves were coincident except at the very highest temperature studied. Below 515 K the curve for the pure ruthenium catalyst was higher than that for the 18% copper catalyst. However, at these lower temperatures, the two curves were still running parallel to each other, suggesting that the apparent activation energy at the extremes of the temperature range studied was identical for the two catalysts. This suggested to us that the cleavage of the carbon–carbon bond of a dehydrogenated dicarbon species probably remained the rate-limiting step (*4, 5*) as copper was added to the catalyst. Since copper tends to populate the edge and corner sites of a supported ruthenium crystallite preferentially, the implication was that either the mechanism for ethane hydrogenolysis on these defect-like sites was no different than that on the low-index planes or that the role of the edge and corner sites was not in the facilitation of the carbon–carbon bond cleavage.

In our attempts to explain the disparate behaviors of the silica-supported Ru, Ru–Cu, and Ru–Ag catalysts, it became obvious that investigation of the apparent orders of reaction for these catalysts at the two extremes of temperatures studied could give enlightening results. The values we measured are given in Table 2. Our choice of copper and silver atomic fractions of 0.18 and 0.40, respectively, was dictated by the results of Monte Carlo simulations, which suggested these fractions of the Group IB metals would nearly cover all the edge and corner sites of the ruthenium crystallites. We saw that the apparent order of reaction with respect to ethane was essentially constant at around +0.8 for all six catalyst and temperature combinations we used. This is in good agreement with published results for both supported and single-crystal ruthenium catalysts (*3, 22*).

The behavior of the apparent order with respect to hydrogen, however, was much more interesting. For the pure ruthenium catalyst, the apparent order of reaction with respect to hydrogen did not change appreciably between the two temperatures studied, with the mean value, −1.44, in good agreement with that of Sinfelt, who reported a value of −1.3 for a silica-supported ruthenium catalyst at 461 K.

For the case of the Ru–Ag catalyst we also saw no significant difference in the apparent order of reaction with respect to hydrogen at the two temperatures studied. However, for this bimetallic catalyst the value obtained, about −2.4, was considerably more negative than that found for the pure ruthenium catalyst. Such a large negative value is not unprecedented. Apparent orders of reaction with respect to hydrogen for the ethane hydrogenolysis reaction of around −2.4 have been reported for systems such as silica- or alumina-supported platinum (*3, 11*). In comparison with ruthenium, silver had negligible activity for the hydrogenolysis of ethane, and hydrogen spillover from ruthenium to silver did not occur (*28*). It therefore seemed likely that silver was acting as an inert site blocker. The composition of the Ru–Ag catalyst was chosen such that we expected all the defect-like sites to be occupied by silver, so that any difference observed between the pure ruthenium and the Ru–Ag catalysts was due to the presence of these edge and corner sites in the pure ruthenium catalysts. The decrease in specific activity of these catalysts as the proportion of silver increased, together with the more negative order of reaction with respect to hydrogen of the silver-containing catalyst led us to the hypothesis that the low-coordination ruthenium sites were important in removing hydrogen from the surface.

The hydrogen was generated in part from the dissociative chemisorption of hydrogen in the feed gas. However, although the ethane hydrogenolysis reaction is a net consumer of hydrogen, the intermediate species were highly dehydrogenated (*3–5*). It is probable that the hydrogen removed from the ethane to form the dehydrogenated fragments on the surface was itself adsorbed onto the metal catalyst, further adding to the pool of adsorbed hydrogen. Absence of the sites most active for the removal of hydrogen therefore led to the blocking of active sites on low-index ruthenium surfaces by hydrogen. Therefore, the low-coordination and high-coordination sites each played a different role in the reaction. High-coordination sites (i.e., basal planes) were predominantly active for the carbon–carbon bond cleavage. Hydrogen may adsorb on these sites directly or first dissociate on the edge and corner sites and move onto the high-coordination sites, blocking adsorption and subsequent reaction of ethane. Hydrogen may migrate from high- to low-metal-coordination sites, which were more active for the associative desorption of hydrogen than the highly coordinated ruthenium surface atoms.

The concept that the interaction of hydrogen with a metal surface depends on the coordination of the metal atoms is not unprecedented. A number of groups have studied hydrogen adsorbed on platinum single-crystal surfaces. Christmann *et al.* (*36*) investigated hydrogen on the Pt(111) surface. For a well-annealed surface they observed two adsorption states. When there were defects in the surface a third, more strongly adsorbed, state was noted. Hydrogen–deuterium exchange reaction studies suggested that hydrogen was adsorbed dissociatively on the platinum surface.

Bernasek and Somorjai (*37*) found that at low pressures the stepped Pt(997) and Pt(553) surfaces were significantly more active for hydrogen–deuterium exchange than the Pt(111) surface. They attributed this to an enhanced activity for dissociating hydrogen (or deuterium) at the step sites. Associative desorption on the surface was the predominant mechanism at lower temperatures; at temperatures above 600 K, exchange between a gas-phase molecule and an adsorbed atom was observed. Poelsema *et al.* (*38*) have also studied hydrogen adsorbed on the Pt(997) surface. They observed that desorption of hydrogen occurred via second-order kinetics, as might be expected. Two distinct sites for the adsorption of hydrogen were seen, with heats of adsorption of 22 and 19 kcal/mol being attributed to step edge sites and terrace sites, respectively. The authors noted that the surface hydrogen atoms were mobile, adsorbing on terraces and migrating to step edges.

Salmeron *et al.* (*39, 40*) have studied the hydrogen–deuterium exchange reaction as a function of the approach angle of the reactant over the Pt(322) and Pt(553) single-crystal surfaces. They found that reaction probability was greatest when the reactants approached the open side of the step directly. Measurements using a Pt(111) single-crystal surface indicated that there was a small activation energy barrier (>0.4 kcal/mol) for adsorption of hydrogen, whereas adsorption onto the Pt(332) surface was not activated. The authors found that surfaces of differing routhness, which were indistinguishable from their LEED patterns, had significantly different activities for hydrogen–deuterium exchange. Analysis of the data led to the conclusion that recombination of adsorbed atoms was the rate-limiting step.

Smith *et al.* (*41, 42*) have proposed that edge sites of supported platinum and palladium catalysts are significantly more active for dissociative hydrogen chemisorption than the low-index planes. Moreover, the addition of hydrogen to unsaturated surface species occurred at sites on the low-index planes by hydrogen that migrated from the defect-like sites.

The surface science studies cited above (*36–40*) have shown that hydrogen is more strongly bound to low-coordination sites than to highly coordinated surface metal atoms at low hydrogen overpressures. However, Wu *et al.* (*28, 32, 33*) have shown, using nuclear magnetic resonance of adsorbed hydrogen, that increasing the number of edge and corner sites in supported metal crystallites also leads to an increase in the number of weakly adsorbed hydrogen atoms (defined as the hydrogen desorbed at room temperature by evacuation) per surface ruthenium atom at high hydrogen overpressures (*33*). For example, the amount of weakly adsorbed hydrogen per surface ruthenium atom increased from 0.28 to 0.58 when the dispersion increased from 0.19 to 0.29. Even though the strongly adsorbed hydrogen forms a stronger bond to defect-like edge and corner atoms, there is relatively more weakly adsorbed hydrogen at these sites compared to the basal planes. Since both silver and copper tend to populate defect-like sites, the amount of weakly adsorbed hydrogen can be altered by the addition of the second metal. Indeed, the addition of silver to a supported ruthenium catalyst does significantly reduce the amount per surface ruthenium atom of this highly mobile, weakly adsorbed hydrogen (*28*). The implication is that, at high hydrogen overpressures, ruthenium at edge and corner sites can accommodate multiple hydrogen atoms, both strongly and weakly adsorbed. Desorption of the hydrogen occurs through the weakly adsorbed state.

The suggestion that the edge and corner sites act differently than the basal planes of the supported metal crystallites leads to a complicated reaction mechanism including nonequivalent sites and, possibly, competing reaction steps. However, it is interesting to look at a simplified reaction scheme to consider whether it would be possible for a change in the rate constant for desorption of hydrogen to lead to the change in apparent order of reaction we observe. We therefore start with the reaction scheme:

$$\mathrm{H_2} + 2\,{*} \underset{}{\overset{K_\mathrm{H}}{\rightleftharpoons}} 2\,\mathrm{H}{*}$$

$$\mathrm{C_2H_6} + (n+1)\,{*} \overset{K_\mathrm{E}}{\rightleftharpoons} \mathrm{C_2H_{6-\mathit{n}}}{*} + n\,\mathrm{H}{*}$$

$$\mathrm{C_2H_{6-\mathit{n}}}{*} + {*} \xrightarrow{k} \text{products.}$$

The first two reactions are intended to imply a steady state rather than a true adsorption/desorption equilibrium. Assuming that the surface species are at steady-state coverages and that the coverage of the hydrocarbon species is small compared to that of hydrogen, this scheme leads to a rate expression of the form

$$\text{rate} = \frac{kK_\mathrm{E}P_\mathrm{E}}{(K_\mathrm{H}P_\mathrm{H})^{n/2}\{1 + (K_\mathrm{H}P_\mathrm{H})^{0.5}\}^2}\,.$$

The second step requires that the released hydrogen be accommodated on a surface that is nearly saturated in hydrogen. These released hydrogen atoms may participate in one of three subsequent processes. The first possibility is that the hydrogen could recombine with the adsorbed C_2 species and desorb as ethane. The second possibility is that the hydrogen atoms migrate to a vacant site and strongly adsorb. And the third likely process is that the hydrogen atoms could combine and desorb from the surface. This third possibility leads to hydrogenolysis without blocking additional sites. The defect-like edge and corner atoms provide sites for weakly adsorbed hydrogen to recombine and desorb at an intrinsic rate higher than the basal planes. Hence, for the simplified mechanism given above the term K_H can be modified by variation in the number of sites that allow the highly mobile, weakly adsorbed hydrogen to desorb. Blocking the edge and corner sites with, for example, silver should lead to a lower rate of hydrogen desorption and, hence, a larger effective value of K_H. Note that Foger and Anderson (*43*) report that the effective hydrogen coverage and hydrogen-binding energy on iridium catalysts are modified by the addition of gold and these effects influence hydrocarbon conversion reactions.

Taking the limits of this expression (corresponding to a large or small rate constant for desorption of hydrogen) gives apparent orders of reaction with respect to hydrogen of $-(n + 2)/2$ and $-n/2$. The difference between the apparent orders at these two limits is 1, close to the difference in orders observed for the pure ruthenium and Group IB metal containing catalysts (-1.4 and -2.4, respectively). Our hypothesis that the primary role of ruthenium at the edges and corners of supported crystallites is to increase the rate of removal of hydrogen from the basal planes therefore does not seem unreasonable. It is interesting to note that the data from the ruthenium–silver catalyst, where the low-coordination sites are presumably covered by silver and where K_H would be large, leads to the assignment of about $n = 3$, which is in the range of the surface intermediates suggested for this reaction (*5*). For this value of n the stoichiometry of the adsorbed intermediate is C_2H_3 consistent with an ethylidyne structure. Ethylidyne has been observed on ruthenium surfaces (*44–46*) and has been postulated to be an intermediate in hydrogenolysis reactions (*5*).

Given the hypothesis that the defect-like sites are most active for the dissociation and association of hydrogen while the low-index planes are most active for carbon–carbon bond cleavage, the ruthenium–copper system becomes even more interesting. This is a system where the Group IB metal segregated to the low coordination sites of the supported crystallites even more strongly than does silver. At the same time, we have the well-documented phenomenon of hydrogen spillover for this system (*29–32*). Thus, even though copper is essentially inactive for the hydrogenolysis reaction, it could be active as a source or sink for hydrogen. Therefore, since it appears that hydrogen acts to inhibit the hydrogenolysis reaction, the role of copper in the catalyst may be more than that of simply blocking active sites.

At the lower temperature studied, the apparent order of reaction with respect to hydrogen for the ethane hydrogenolysis reaction was essentially the same as that for the Ru–Ag catalyst. It would appear that at low temperatures, therefore, copper, like silver, simply acted to block hydrogen desorption sites. At the higher temperature studied, however, a dramatic change took place. For this case, the apparent orders of reaction with respect to hydrogen of the pure ruthenium and Ru–Cu bimetallics were almost the same, considerably less negative than the value obtained for the Ru–Ag bimetallic. It would appear that at this higher temperature the copper at the low-coordination sites was effective in removing hydrogen from the surface of ruthenium.

At the lowest copper loadings, the copper was populating edge and corner sites exclusively. These sites were much less active for carbon–carbon bond cleavage than were the low-index planes. Hydrogen chemisorption onto copper is known to be an activated process, with an activation energy around 5 kcal mol^{-1} (*47*), so we would expect that the desorption process on copper is also activated. At the highest temperatures studied, therefore, we suggest that hydrogen can be removed from the surface by copper at defect-like sites. Thus, at high temperatures, addition of copper changed neither the absolute rate of carbon–carbon bond cleavage nor the absolute rate of hydrogen desorption compared to the monometallic ruthenium catalyst. However, the proportion of the surface occupied by ruthenium decreased, while the overall activity was not changed, leading to an apparent increase in the rate per surface ruthenium atom. That is, the edge and corner atoms were not sites for the carbon–carbon bond cleavage step.

The activity of the ruthenium–copper system did not continue to increase as copper was added beyond the point at which it occupied all the high-index sites. This indicated that the dominant effect beyond this point was to block the ruthenium sites that were active for the carbon–carbon bond cleavage. This could be done without decreasing the number of sites available for desorption of the site-blocking hydrogen. It is also possible that the copper on the ruthenium surface may be mobile at the highest temperatures studied. For a number of reasons we do not believe that this is happening. Silver has a lower melting point than copper but the Ru–Ag catalyst shows no evidence for silver mobility. Since we were operating at only about 28% of the mean melting point of ruthenium and copper, it seemed unlikely that the copper mobility was significantly affecting our catalysts.

The behavior of the monometallic ruthenium catalyst as a function of dispersion was opposite to that observed for platinum catalysts (*8*, *9*), although in some cases optimum dispersions have been observed (*7*). In fact, the specific activity of iridium catalysts was seen to decrease as dispersion was increased (*13*), the same trend that we observed for our ruthenium catalysts. Note that the apparent orders of reaction with respect to hydrogen for silica-supported iridium and ruthenium catalysts were quite similar, at -1.6 and -1.3, respectively (*3*), while that for platinum catalysts was -2.5 (*3*). These apparently contradictory results may be reconciled by considering the competing effects of increasing the proportion of edge and corner sites and increasing the proportion of highly coordinated surface atoms. Increasing the proportion of highly coordinated surface atoms would increase the relative number of sites active for the breaking of carbon–carbon bonds. At the same time, however, the relative number of sites for associative desorption of hydrogen atoms would decrease, thereby increasing the effect of hydrogen poisoning. It would therefore be expected that for systems where the apparent order of reaction with respect to hydrogen was highly negative, decreasing the proportion of defect-like sites would be more detrimental than for systems where the order was less negative. Indeed, eventually the activity-enhancing effect of increasing the proportion of sites active for carbon–carbon bond cleavage would overcome the detrimental effect of decreasing the proportion of sites most active for the removal of hydrogen from the surface. This suggested that there should be an optimum crystallite size, which would be a function of the system and of the ethane-to-hydrogen ratio used. We extrapolated the single-crystal data of Peden and Goodman (*22*) from the 20 : 1 $H_2 : C_2H_6$ ratio they used to the 5 : 1 ratio used in this work and found a specific activity of 0.4, lower than the activity of the lowest dispersion catalyst we used. This suggested that there may indeed be an optimum ratio of defect-like to low-index plane sites, although for the case of ruthenium this optimum ratio would be very low. It must be noted, however, that the single-crystal work was done at substantially lower total reactant pressures than those of our studies, so the extrapolation may not be valid.

It would appear, therefore, that the dominant effect of adding a Group IB metal to a silica-supported ruthenium catalyst was to change the rate of hydrogen desorption from the surface. Desorption occurred fastest on the low coordination sites that were preferentially populated by the Group IB metals. Copper and silver were not as active for hydrogen desorption at low temperatures as was ruthenium. At higher temperatures, however, copper appeared to have a significant ability to remove hydrogen from the metal particles.

CONCLUSION

At the lower temperatures studied, adding copper or silver to our silica-supported ruthenium catalysts had virtually the same effect in kind, although the effect in degree of adding copper was much more pronounced. We think that this is because both Group IB metals tended to block the low-coordination sites of the supported ruthenium crystallites preferentially; however, copper is much more effective at doing so. We postulate that this structure-sensitive behavior is due to the ability of defect-like edge and corner sites to desorb hydrogen from the surface. The carbon–carbon bond cleavage takes place only on the basal planes of the ruthenium particles but the edge and corner sites facilitate the desorption of hydrogen, which would otherwise tend to inhibit the ethane hydrogenolysis reaction. At the higher temperatures studied, the silver continues to act in the same way. However, at these higher temperatures we propose that copper is active in the removal of hydrogen from the surface. Fitting the order-of-reaction data to a simple mechanistic model suggests that the adsorbed hydrocarbon intermediate has a stoichiometry of C_2H_3.

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REFERENCES

1. Morikawa, K., Benedict, W. S., and Taylor, H. S., *J. Amer. Chem. Soc.* **58,** 1795 (1936).
2. Pruski, M., Kelzenberg, J. C., Gerstein, B. C., and King, T. S., *J. Amer. Chem. Soc.*, **112,** 4232 (1990).
3. Sinfelt, J. H., *Catal. Rev.* **3,** 175 (1970).
4. Zaera, F., and Somorjai, G. A., *J. Phys. Chem.* **89,** 3211 (1985).
5. Engstrom, J. R., Goodman, D. W., and Weinberg, W. H., *J. Amer. Chem. Soc.* **110,** 8305 (1988).
6. Carter, J. L., Cusumano, J. A., and Sinfelt, J. H., *J. Phys. Chem.* **70,** 2257 (1966).
7. Yates, D. J. C., and Sinfelt, J. H., *J. Catal.* **8,** 348 (1967).
8. Brunelle, J. P., Sugier, A., and Le Page, J. F., *J. Catal.* **43,** 273 (1976).
9. Guczi, L., and Gudkov, B. S., *React. Kinet. Catal. Lett.* **9**(3), 343 (1978).
10. Schay, Z., and Guczi, L., *J. Chem. Res. Synop.*, 66 (1980).
11. Barbier, J., Morales, A., and Maurel, R., *Bull. Soc. Chim. Fr. I* **1–2,** 32 (1978).
12. Barbier, J., Marecot, P., Morales, A., and Maurel, R., *Bull. Soc. Chim. Fr. I* **7–8,** 309 (1978).
13. Barbier, J., and Marecot, P., *Nouv. J. Chim.* **5**(7), 393 (1981).
14. Godbey, D. J., Garin, F., and Somorjai, G. A., *J. Catal.* **117,** 144 (1989).
15. Doi, Y., Miyake, H., and Soga, K., *J. Mol. Catal.* **48,** 123 (1988).
16. Galvagno, S., Schwank, J., Gubitosa, G., and Tauszik, G. R., *J. Chem. Soc., Faraday Trans. 1* **78,** 2509 (1982).
17. Hansen, M., and Anderko, K., "Constitution of Binary Alloys," 2nd ed. McGraw-Hill, New York, 1958.
18. Sinfelt, J. H., *J. Catal.* **29,** 308 (1973).
19. Helms, C. R., and Sinfelt, J. H., *Surf. Sci.* **72,** 229 (1978).
20. Sinfelt, J. H., "Bimetallic Catalysts." Wiley, New York, 1983.
21. Rouco, A. J., Haller, G. L., Oliver, J. A., and Kemball, C., *J. Catal.* **84,** 297 (1983).
22. Peden, C. H. F., and Goodman, D. W., *ACS Symp. Ser.* **288,** 185 (1985).
23. Peden, C. H. F., and Goodman, D. W., *Ind. Eng. Chem. Fundam.* **25,** 58 (1986).
24. Strohl, J. K., and King, T. S., *J. Catal.* **116,** 540 (1989).
25. Kim, K. S., Sinfelt, J. H., Eder, S., Markert, K., and Wandelt, K., *J. Phys. Chem.* **91,** 2337 (1987).
26. Goodman, D. W., and Peden, C. H. F., *J. Chem. Soc., Faraday Trans. 1* **83,** 1967 (1987).
27. Houston, J. E., Peden, C. H. F., Feibelman, P. J., and Hamann, D. R., *Phys. Rev. Lett.* **56,** 375 (1986).
28. Wu, X., Gerstein, B. C., and King, T. S., *J. Catal.*, **123,** 43 (1990).
29. Goodman, D. W., and Peden, C. H. F., *J. Catal.* **95,** 321 (1985).
30. Hong, A. J., Rouco, A. J., Resasco, D. E., and Haller, G. L., *J. Phys. Chem.* **91,** 2665 (1987).

31. King, T. S., Wu, X., and Gerstein, B. C., *J. Amer. Chem. Soc.* **108,** 6056 (1986).

32. Wu, X., Gerstein, B. C., and King, T. S., *J. Catal.*, **121,** 271 (1990).

33. Wu, X., Gerstein, B. C., and King, T. S. *J. Catal.* **118,** 238 (1989).

34. Smale, M. W., and King, T. S., *J. Catal.* **119,** 441 (1989).

35. Kelzenberg, J. C., and King, T. S., *J. Catal.*, submitted for publication.

36. Christmann, K., Ertl, G., and Pignet, T., *Surf. Sci.* **54,** 365 (1976).

37. Bernasek, S. L., and Somorjai, G. A., *J. Chem. Phys.* **62**(8), 3149 (1975).

38. Poelsema, B., Mechtersheimer, G., and Comsa, G., *Surf. Sci.* **111,** 519 (1981).

39. Salmeron, M., Gale, R. J., and Somorjai, G. A., *J. Chem. Phys.* **67**(11), 5324 (1977).

40. Salmeron, M., Gale, R. J., and Somorjai, G. A., *J. Chem. Phys.* **70**(6), 2807 (1979).

41. Smith, G. V., Notheisz, F., Zsigmond, A. G., Ostgard, D., Nishizawa, T., and Bartòk, M., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.). p. 1066. Chem. Institute of Canada, Ottawa, 1988.

42. Smith, G. V., Bartòk, M., Notheisz, F., Zsigmond, A. G., and Pàlinkò, I., *J. Catal.* **110,** 203 (1988).

43. Foger, K., and Anderson, J. R., *J. Catal.* **64,** 448 (1980).

44. Hills, M. M., Parameter, J. E., Mullins, C. B., and Weinberg, W. H., *J. Amer. Chem. Soc.* **108,** 3554 (1986).

45. Greenlief, C. M., Radloff, P. L., Zhou, X. L., and White, J. M., *Surf. Sci.* **191,** 93 (1987).

46. Barteau, M. A., Broughton, J. Q., and Menzel, D., *Appl. Surf. Sci.* **19,** 92 (1984).

47. Balooch, M., Cardillo, M. J., Miller, D. R., and Stickney, R. E., *Surf. Sci.* **46,** 358 (1974).