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Ethane Hydrogenolysis over Well-Defined Ru–Cu/SiO$_2$ Catalysts

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This work was undertaken to investigate the behavior of the ethane hydrogenolysis reaction over well-characterized, chlorine-free, silica-supported ruthenium–copper catalysts. The total dispersion of all catalysts was about 29%. The reaction studies were carried out in a laboratory-scale reactor, and catalyst activity was correlated with ruthenium surface composition, as measured previously by using nuclear magnetic resonance spectroscopy of chemisorbed hydrogen. Monte Carlo simulations of the catalyst were used to assist in the interpretation of the results. The reaction studies indicate that catalysts with a Cu : Ru atom ratio greater than 1 : 9 have a constant specific activity (rate per surface ruthenium atom), analogous to the behavior of single crystal surfaces. Below this Cu : Ru ratio, the specific activity drops rapidly as copper is added to the system at the lower temperatures studied. At a Cu : Ru ratio of 1 : 9 the modeling suggests that all edge and corner sites of the catalyst crystallite are occupied by copper. We conclude that the ethane hydrogenolysis reaction over silica-supported ruthenium–copper catalysts is sensitive to the crystallite structure but no geometric effects are observed.

INTRODUCTION

Supported bimetallic catalysts have received much attention from both industrial and academic sectors. The ruthenium–copper catalyst is of particular interest as a model system in that the two metals are virtually immiscible in the bulk (*1*). However, for the supported catalyst, the relatively inactive copper has a large influence on the activity of ruthenium, indicating that the metals are together on the oxide support (*2*).

The use of model reactions can greatly enhance the understanding of these catalysts. One commonly studied reaction is the hydrogenolysis of ethane. This is a relatively simple, clean reaction and as such is a good candidate for use as a diagnostic tool. Ethane hydrogenolysis has been studied over a number of metal catalysts other than ruthenium. Goodman (*3*) has studied the reaction over the nickel (100) and (111) single crystal surfaces and found that the apparent activation energy is lower for the more open (100) surface. His findings indicate that the reaction is structure sensitive over this metal. Ethane hydrogenolysis has also been studied over silica-supported platinum catalysts by Guczi and Gudkov (*4*). They found that the edge and corner atoms of the supported metal crystallites had an enhanced activity as compared to the basal planes. Kane and Clarke (*5*) studied ethane hydrogenolysis over platinum–gold polycrystalline foils and found that the apparent activation energy for the reaction increased with the addition of gold. They indicated that this result was due to the segregation of gold to the defect sites that were most active for the reaction, and they speculated that ethane hydrogenolysis over platinum films is structure sensitive.

Sinfelt *et al.* (*2, 6, 7*) studied the ethane hydrogenolysis reaction over silica-supported ruthenium–copper catalysts. In order to calculate the specific activity of the catalyst (rate per surface ruthenium atom), they had to measure the proportion of the ruthenium in the catalyst that was at a crystallite surface. These measurements were made by titrating the catalyst surface with hydrogen; it was inferred that the hydrogen would only chemisorb on ruthenium. This assumption would appear to be valid because it is known that hydrogen will not

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appreciably chemisorb on a pure copper surface at room temperature. The activity of the ruthenium catalyst per hydrogen chemisorption site thus calculated was seen to decrease as the copper content was increased. This result led to the suggestion that the ethane hydrogenolysis reaction over supported ruthenium–copper catalysts exhibits *geometric effects;* that is, the active site for the reaction consists of a number of adjacent surface ruthenium atoms. Thus the placement of a single copper atom onto a predominantly ruthenium surface would deactivate an ensemble of ruthenium atoms.

Hong *et al.* (*8*) have studied ethane hydrogenolysis over silica-supported Ru–Cu catalysts and reported a dramatic decrease in the rate per total ruthenium atom as the copper content increased. The catalysts in their work used two different ruthenium salts as a catalyst precursor: $RuCl_3$ and $Ru(NO)(NO_3)_3$. Because chlorine is a known contaminant, when the chloride salt was used they were able to compare contaminated and chlorine-free catalysts. Hong *et al.* (*8*) also have suggested ensemble effects to explain this decrease in activity.

In order to report the specific activities of these catalysts, one must measure the proportion of ruthenium atoms in the catalyst that are at a surface. Selective hydrogen chemisorption is often used for this type of measurement. Since hydrogen chemisorbs very little on a supported copper catalyst, the amount of hydrogen chemisorbed on a supported ruthenium–copper catalyst is assumed to be a measure of the ruthenium dispersion. More recently, studies of single crystal ruthenium–copper catalysts by Goodman and Peden (*9*) have shown that hydrogen will adsorb dissociatively on ruthenium surfaces and then migrate to the copper. This result has been confirmed for the case of the silica-supported catalyst (*10*). Spillover of hydrogen from ruthenium to copper indicates that the use of hydrogen chemisorption to measure the dispersion of the supported ruthenium–copper catalysts will lead to overestimation of the number of surface ruthenium atoms. Hong *et al.* (*8*) have also postulated hydrogen spillover for silica-supported ruthenium–copper catalysts.

Peden and Goodman (*11–14*) have investigated the effect of adding copper to single crystal ruthenium catalysts, making allowance for the hydrogen spillover effect. In contrast to the earlier work by Sinfelt *et al.* (*2, 6, 7*), the authors observed no geometric effects for the ethane hydrogenolysis reaction. Instead, the specific activity of the catalyst was unchanged as copper was added.

However, the morphology of a supported metal crystallite is very different from that of a single crystal surface. While the supported particles might be expected to contain surfaces which are analogous to a single crystal, a significant number of the metal atoms in highly dispersed catalysts will be in defect-like sites. Consideration of the thermodynamics of supported bimetallic catalysts allowed Strohl and King (*15*) to model catalysts similar to the ruthenium–copper system. They suggest that the segregating element will preferentially populate the edge and corner sites of the supported crystallites. Addition of the segregating element, copper, to ruthenium particles after these low coordination sites have been filled leads to the formation of two-dimensional islands on the basal planes of the particle. These islands are characteristic of systems that do not mix well. Experimental evidence of the preferential population of ruthenium defect sites by copper has been recently presented by Kim *et al.* (*16*). Also, work with submonolayer amounts of copper deposited on ruthenium single crystals reveals that copper layers grow in a highly dispersed mode at 100 K, but subsequent annealing to 300 K produces two-dimensional islands pseudomorphic to the Ru (001) substrate (*9, 11, 17–20*). In this paper, we shall discuss the activity of supported ruthenium–copper catalysts adjusted to reflect the effect of the hydrogen spillover phenomenon.

METHODS

The details of the catalyst preparation and characterization are reported elsewhere (*21*). 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 contained 4% ruthenium (by weight). We used the incipient wetness co-impregnation technique to prepare the bimetallic catalysts from an aqueous solution of $Ru(NO)(NO_3)_3$ and $Cu(NO_3)_2$. The catalysts were characterized by a number of methods including hydrogen chemisorption and nuclear magnetic resonance (NMR) of chemisorbed hydrogen. The total metal dispersion of the pure ruthenium catalyst was determined by strong chemisorption to be 29% for all copper containing catalysts. The total hydrogen chemisorption was about equal to that of the pure ruthenium catalyst, suggesting that the total metal dispersion for all catalysts was about the same.

After the catalysts were prepared, we carried out reaction studies using a continuous tubular reactor system. The hydrogen was first stripped of oxygen, after which we used molecular sieve traps to dry the feed gases. Flow rates of the purified gases were controlled with Brooks mass flow controllers. To preheat the feed gas, we used temperature-controlled heating tapes. The final preheating was achieved by flowing the feed gas mixture up through the furnace used to heat the reactor tube. The feed then flowed down through the catalyst bed, which was contained in a $\frac{1}{4}$-in. schedule 40 Type 316 stainless steel pipe. A programmable temperature controller was used to control the temperature for the catalyst bed, and the temperature for the controller was measured by means of a type K thermocouple contained in a $\frac{1}{16}$-in. tube positioned axially in the reactor. In order to ensure a rapid response from the temperature controller, we placed the thermocouple so that the temperature measurement was made in the middle of the catalyst bed. The sample was diluted with 100–200 mesh crystalline silica to a volume of 3.0 cm^3. The catalyst was supported in the reactor so that it remained in the 2-in. region of the furnace that was isothermal (± 1 K).

We used automatic sampling valves to introduce the reaction products into a 6-ft-long, $\frac{1}{8}$-in.-o.d. stainless steel gas chromatograph column packed with 80/100 mesh Haysep Q, and the separated products were fed to the thermal conductivity detector (TCD) of a Varian 3700 gas chromatograph. After the column oven was held at 308 K for 10 min, the temperature was ramped at 4 K/min. A commercial data acquisition package on an IBM personal computer digitized and manipulated the signal from the TCD, and the times at which samples of reaction products were taken were controlled by a custom-built microprocessor-based timer.

The catalyst in the reactor was heated to the reduction temperature in 1 h, while it was exposed to a 500 cm^3/min (STP) flow of hydrogen. After the catalyst was reduced for 2 h, normally at 723 K, the temperature was lowered to the desired reaction temperature over a period of 7 h. The flow rate of the hydrogen was unchanged throughout this period. The gas feed was then switched to the reactant mixture, which consisted of a 10 : 2 : 1 molar ratio mixture of hydrogen, ethane, and argon (the argon was used as an internal standard for the gas chromatographic analysis). All the reaction studies were carried out at atmospheric pressure. The volumetric space velocity (STP) inside the reactor was around 20,000 hr^{-1} for all runs. We analyzed samples of the product after 20 min, 1.5, 3.5, and 7.5 h on line.

RESULTS

All activity data are presented in terms of the rate of ethane consumed. Figure 1a shows the activity of the catalyst as a function of time on line for a 1 : 9 Cu : Ru atomic ratio catalyst at a number of different tem-

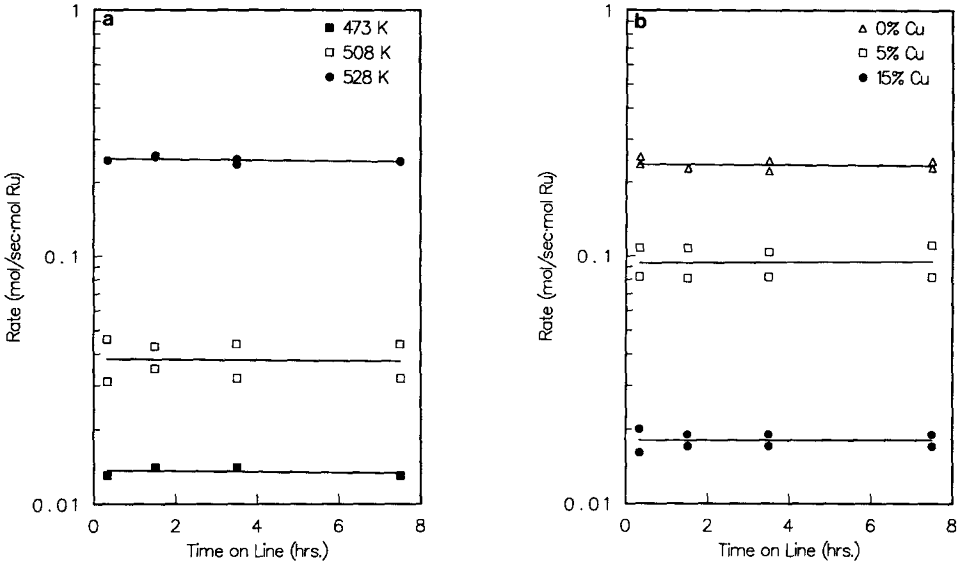

FIG. 1(a). Ethane hydrogenolysis activity of the 1 : 9 (Cu : Ru) atomic ratio catalyst as a function of time-on-stream at various temperatures. (b). Ethane hydrogenolysis activity of silica-supported Ru–Cu catalysts as a function of time-on-stream at 508 K.

peratures, and Fig. 1b shows the activity of several catalysts as a function of time on line at a reaction temperature of 508 K. Note that no significant change in activity occurs between 20 min and 7.5 h. This indicates that any deactivation (or activation) has occurred before the catalyst has been on line for 20 min. The copper neither increased nor decreased the rate of deactivation of the ruthenium catalysts for the ethane hydrogenolysis reaction.

Figure 2 shows the activity (rate per total ruthenium) of the catalysts as a function of the copper atom fraction at a number of different temperatures. The sensitivity of our analytical procedure coupled with the limitations imposed on the reactor to ensure comparable conditions for all runs limited the range of catalyst compositions that could be studied at a given temperature. At the lowest temperatures the high copper content catalysts were too inactive to allow accurate rate determination. As can be seen, the addition of copper leads to a significant decrease in the activity of the catalyst, confirming that the copper and ruthenium are indeed together on the silica support.

Wu *et al.* (*21*) have previously used hydrogen chemisorption and NMR to charac-

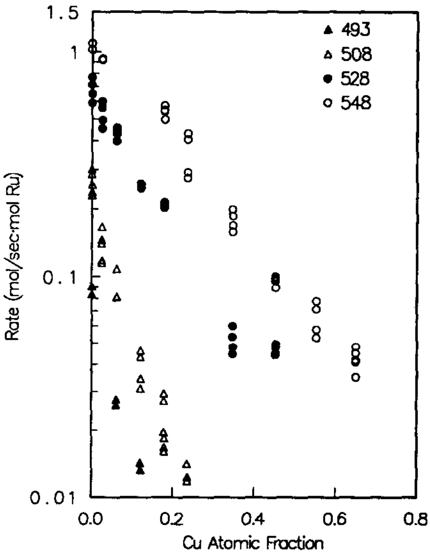

FIG. 2. Rate of ethane hydrogenolysis per total ruthenium atom for silica-supported Ru–Cu catalysts.

TABLE 1

Ruthenium Dispersion of Ru–Cu/SiO_2 Catalysts Measured by Strong Hydrogen Chemisorption and NMR of Protons

Cu atom fraction	Ruthenium dispersion (*21*)	
	Chemisorption[a]	NMR
0.000	0.290	0.290
0.025	0.293	0.258
0.061	0.296	0.233
0.121	0.297	0.161
0.179	0.296	0.070
0.235	0.290	0.039
0.346	0.300	0.024
0.452	0.300	0.018
0.553	0.303	0.009
0.650	0.323	0.003

[a] Assumes hydrogen strongly adsorbs only on ruthenium.

terize the same silica-supported ruthenium–copper catalysts used in these reaction studies. The catalysts were placed in an NMR tube attached to the adsorption apparatus and were reduced at 723 K in flowing hydrogen for 2 h. Then chemisorption measurements were carried out to measure the apparent dispersion of each catalyst. Subsequently, the samples were sealed and proton NMR of the adsorbed hydrogen atoms was used to elucidate the proportion of ruthenium atoms in the sample that were exposed at a surface. As can be seen in Table 1, the two methods for measuring the ruthenium dispersion of the catalyst apparently give strikingly different results. The reason is that the hydrogen chemisorbs not only surface ruthenium atoms but also on surface copper. Hydrogen chemisorption measures both because of the hydrogen spillover effect, where the hydrogen can dissociatively adsorb on the ruthenium surface and then migrate to the copper atoms. On the other hand, the proton NMR results give the true number of surface ruthenium atoms.

The result of using strong hydrogen chemisorption data to calculate the specific activity of the catalysts is shown in Fig. 3. Note that the activity of the catalysts appears to decrease continually as the copper content is increased. It is this phenomenon that has led to the postulation of geometric effects being important in these catalysts. However, this approach over-counts the surface ruthenium atoms because of hydrogen spillover (*8*, *9*).

When the dispersion of ruthenium is measured with NMR spectroscopy of adsorbed protons (*21*), the calculation of turnover frequency gives dramatically different results. As can be seen from Fig. 4, the specific activity or turnover frequency of the catalysts decreased rapidly at low temperatures as small amounts of copper were added to the system. However, after the Cu:Ru ratio exceeded about 1:9, there was no further decrease in rate per surface ruthenium atom. At higher temperatures the turnover frequency either remained constant over the range of compositions studied or increased at low copper content and then remained constant.

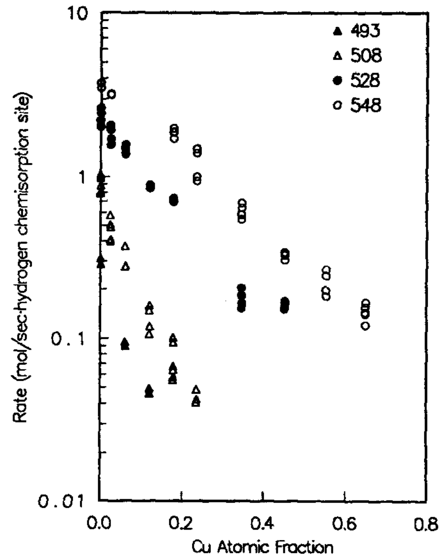

FIG. 3. Rate of ethane hydrogenolysis per surface ruthenium as measured by strong hydrogen chemisorption.

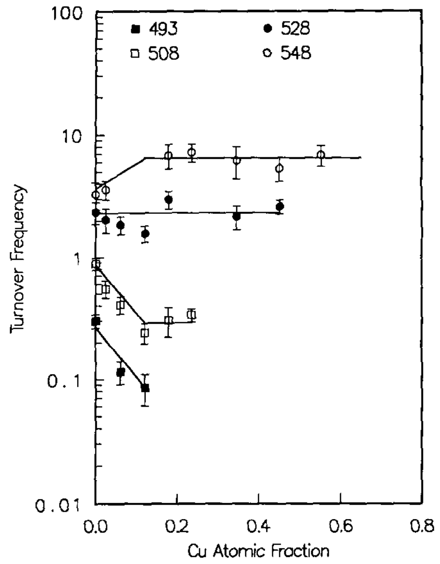

FIG. 4. Rate of ethane hydrogenolysis (±1 standard deviation) per surface ruthenium as measured by proton NMR.

The difference in behavior of the catalysts at different temperatures suggests that investigating the apparent activation energy as a function of copper content of the catalyst should assist our interpretation of the system. Figure 5 shows the results of plotting turnover frequency versus inverse temperature over the 478–548 K region for the pure ruthenium and 18% copper catalysts. We see that the two curves intersect in the 515–540 K temperature range.

DISCUSSION

In order to visualize what the reaction data mean in terms of the catalyst morphology, we find it useful to have a model of the bimetallic crystallites in the catalyst. The Monte Carlo simulation procedure developed previously (*15, 22*) was used to model ruthenium–copper catalysts. While the model used is not strictly accurate because it was written for a face-centered cubic crystal and ruthenium has a hexagonal close-packed structure, it will serve to give a good approximation of the equilibrium state of the metal crystallites.

The Monte Carlo simulation results indicate that when a small amount of copper is added to a ruthenium catalyst, it tends to preferentially populate the defect-like edge and corner sites of the metal crystallite (Figs. 6a–c). As indicated in Figs. 6d–f, further addition of copper leads to two-dimensional clustering on the low index plane surfaces of the particle. The model suggests that the copper does not disperse over the basal planes breaking up ruthenium ensembles. This result is consistent with various observations (*9, 11, 17–20*) showing that copper forms large two-dimensional islands on ruthenium single crystal surfaces. On the other hand, all the edge and corner positions are occupied by copper by the time the Cu : Ru ratio has reached about 1 : 9.

The simulation procedure used a truncated octahedron as the initial configuration, although this is free to change throughout the simulation. It should be noted, however, that other studies starting with different configurations give essentially the same results (*15, 22*). Octahedral structures have indeed been observed experimentally for supported catalysts (*23,*

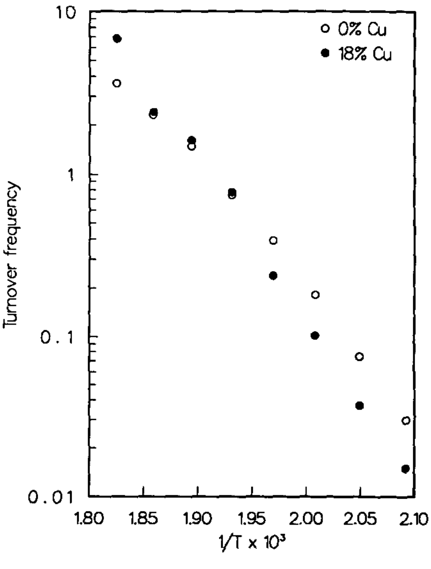

FIG. 5. Arrhenius plots for Ru/SiO$_2$ and Ru–Cu/SiO$_2$ catalysts.

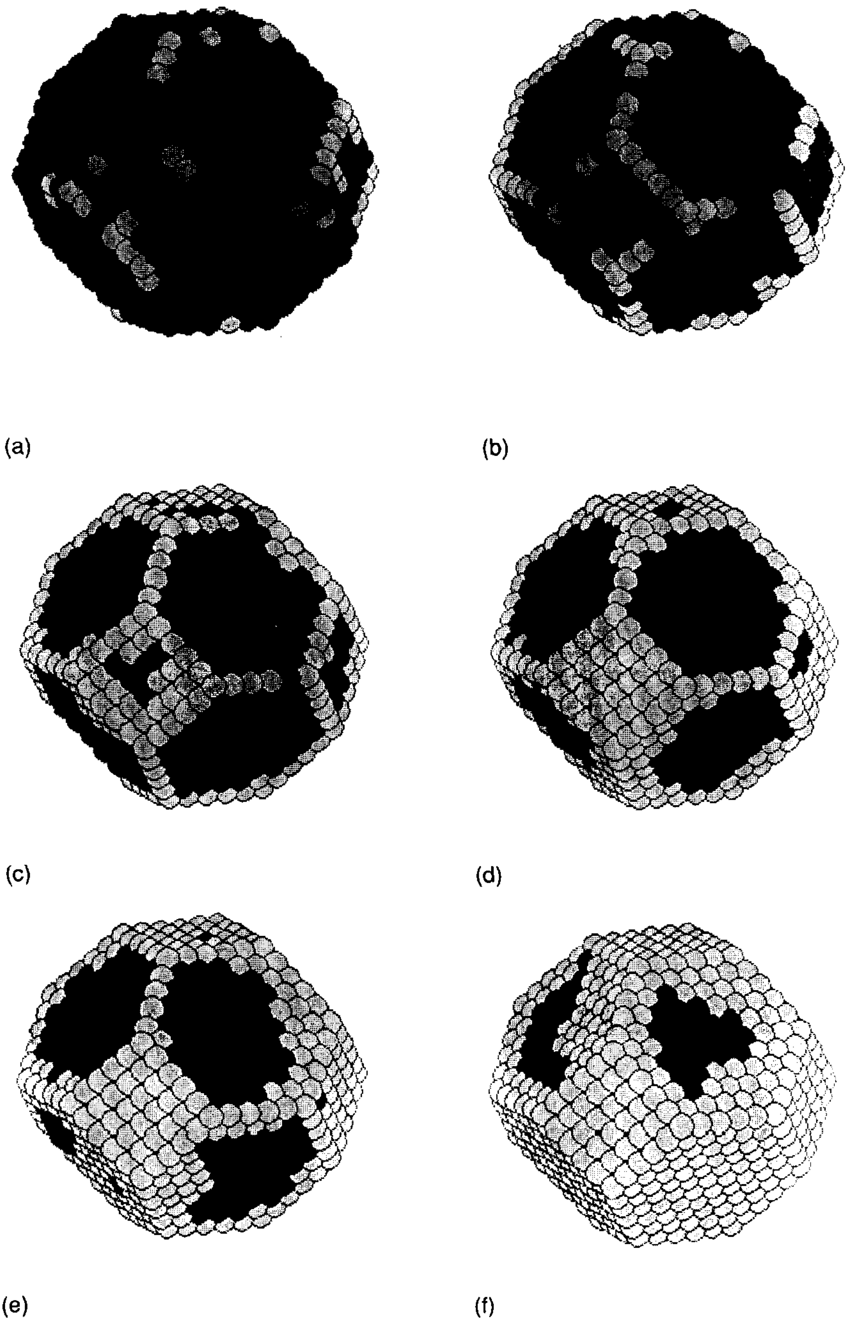

FIG. 6. Monte Carlo simulation results for Ru–Cu/SiO_2 catalysts with a total metal dispersion of 30%; (a) 2% Cu, (b) 5% Cu, (c) 10% Cu, (d) 15% Cu, (e) 20% Cu, (f) 30% Cu.

24), leading us to believe that the simulations are at least qualitatively reasonable.

The Monte Carlo simulations suggest that these catalysts will never show geometric effects because the copper does not intermix with ruthenium on the low-index-plane facets of the crystallites. Therefore, even if the active site for the ethane hydrogenolysis reaction were to consist of an ensemble of ruthenium atoms, we would not expect to observe geometric effects with the ruthenium–copper catalyst series.

If we consider the reaction results for the high copper-loading catalysts, it is apparent that we are, indeed, observing no evidence for geometric effects. Instead, the rate-per-surface ruthenium atom remains constant, which is in agreement with the results of Peden and Goodman (*11–13*) on single crystal catalysts. This observation is not surprising because the results of the Monte Carlo simulations show that at higher copper loadings, the catalyst is essentially composed of single crystal-like facets with copper and ruthenium remaining unmixed.

At the low Cu : Ru ratios, however, a different effect seems to be important. For these catalysts, the activity per surface ruthenium atom, at least at the lower temperatures studied, decreases rapidly. The decrease in activity coincides with the loss of ruthenium from defect-like edge and corner lattice positions predicted by the simulations. After the low coordination sites are filled with copper, additional copper masks the basal planes by formation of two-dimensional islands that grow from the edges of the crystallites. Thus, it seems that the edge and corner atoms of the catalyst crystallite are responsible for a different activity than the basal planes. This supposition is supported by the observation that the specific activity of the catalyst no longer decreases with copper addition after the copper content reaches the point where the model indicates that all edge and corner positions are occupied by copper.

It is interesting to note that our value for the specific rate of the supported catalyst is within a factor of four of that extrapolated from the results of Peden and Goodman (*14*) for a ruthenium (001) single crystal surface using the pressure dependencies they reported.

Comparison of the Arrhenius curves for the pure ruthenium and 18% copper catalysts indicates a sharp divergence around 510 K. It is conceivable that this change in intrinsic rate may be due to edge and corner sites exhibiting a different intrinsic rate than found on the single crystal surfaces. Indeed, previous studies of the ethane hydrogenolysis reaction over different catalyst systems (*3, 5*) have reported a lower activation energy for more open sites. In addition, Enstrom, Goodman, and Weinberg (*26*) have suggested that the ethane hydrogenolysis reaction may proceed through different intermediates on different iridium single crystal surfaces. They also show Arrhenius plots that curve in a very similar manner to our results for the silica supported pure ruthenium catalyst.

An alternative hypothesis is that at the lower temperatures studied, there are some adsorbed species that are blocking sites on the Ru–Cu catalyst more effectively than on the pure ruthenium catalyst. At the higher temperatures studied, this blocking species would desorb, leaving both catalysts with roughly the same specific activity. This would account for the sharp transition over a small temperature range. A possible candidate for the blocking species is hydrogen, which was present in great excess during our experiments. It has previously been reported that the apparent order of reaction with respect to hydrogen for ethane hydrogenolysis is negative for a large number of catalysts (*25*), the value given for a silica-supported ruthenium catalyst being −1.3. Engstrom *et al.* (*26*) attribute the curve in the Arrhenius plots they observed for hydrogenolysis over single crystal iridium to desorption, as the temperature was increased, of surface hydrogen, which tends to block sites at lower temperatures. It seems possible that for our supported Ru–Cu catalysts the copper at the edge and corner sites is inhibiting desorption of hydrogen from the bimetallic crystallites at the lower temperatures studied, leading to an increased blocking of the active sites (Ru) for hydrogenolysis. At the higher temperatures, copper is no longer inhibiting hydrogen desorption, so the copper is not affecting the specific activity of the catalyst. This interpretation suggests that the edge and corner sites are not sites for the hydrogenolysis step but instead serve as a location where hydrogen can recombine and desorb more effectively than from the basal planes. Bernasetz and Somorjai (*27*) have shown that platinum high-index planes are considerably more active than low-index planes for hydrogen–deuterium exchange, and they postulate that H–D formation occurs at step sites.

One can take the data of Feulner and Menzel (*28*) for the activation energy, the pre-exponential, and the sticking probability for desorption of hydrogen on a Ru(001) surface as a function of coverage and use them to determine the temperature at which the surface hydrogen desorbs at the pressure of the results shown in this work. The temperature at which significant desorption occurs at equilibrium ($\theta < 0.5$) is around 505 K to 540 K.

CONCLUSION

Investigation of the ruthenium–copper system must make allowance for the well-documented hydrogen spillover phenomenon. When hydrogen spillover is considered, the interpretation of the behavior of these catalysts for the ethane hydrogenolysis reaction is very different from the interpretation when hydrogen spillover is not considered.

At the lower temperatures studied we have observed a decrease in the specific activity of the ruthenium catalysts as copper is added until a Cu:Ru ratio of 1:9 is reached. Adding more copper to the system does not change the specific activity of the catalyst. At the higher temperature the specific activity either remains constant over the entire composition range or increases somewhat over the low copper content region until a constant activity is attained. The Arrhenius plots for a pure ruthenium catalyst and 18% copper catalyst are almost coincident in the 510 K to 540 K range. Below this temperature the curves diverge sharply. These results lead us to the conclusion that the presence of defect-like sites in silica-supported ruthenium catalysts can greatly affect the activity of the catalyst. This may be due to an inherent difference in activity of defect sites as compared to single crystal surfaces or to the two types of sites having a different ability to allow hydrogen desorption. It is evident, however, that the morphology of the catalyst crystallite plays an important role.

Modeling of silica-supported ruthenium–copper catalysts suggests that the copper does not break up surface ruthenium ensembles. In this case, we would not expect to be able to observe geometric effects with this system; indeed, no geometric effects were observed.

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