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Nature of Ruthenium–Copper Catalysts

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The chemisorption and catalytic properties of ruthenium–copper catalysts with a metal dispersion of the order of 1%, in which the dispersion refers to the fraction of metal atoms present in the surface, were investigated and compared with previously published data on supported ruthenium–copper clusters of much higher dispersion. Ruthenium and copper are essentially completely immiscible in the bulk, but there is evidence of definite interaction between the two in ruthenium–copper catalysts. The presence of copper decreases the capacity of ruthenium for hydrogen chemisorption and also suppresses markedly the catalytic activity for hydrogenolysis of ethane to methane. The ethane hydrogenolysis activity of a ruthenium–copper catalyst is strikingly related to its capacity for strong hydrogen chemisorption, the latter being defined as the amount of chemisorbed hydrogen retained by the catalyst after evacuation at room temperature. The interaction between copper and ruthenium occurs at the surface and is likened to that which would exist if copper were chemisorbed on ruthenium. The state of dispersion of a ruthenium–copper catalyst has a major influence on the effect of the copper. The atomic ratio of copper to ruthenium required for a given degree of coverage of the surface by copper increases with increasing dispersion, as is clearly reflected by the results on hydrogen chemisorption and ethane hydrogenolysis.

INTRODUCTION

In a previous publication by one of us (JHS), evidence was presented for an interaction between copper and either ruthenium or osmium when the metals were present in a highly dispersed state on a silica carrier (*1*). The metal dispersion, defined as the fraction of metal atoms present as surface atoms, was of the order of unity in these materials. The degree of coverage of the carrier by the metal was of the order of only 1%. The presence of copper inhibited markedly the catalytic activity of ruthenium and osmium for hydrogenolysis and also decreased the chemisorption of hydrogen and carbon monoxide on these metals. These experiments clearly indicated that copper was not isolated from the ruthenium and osmium in the catalysts. It was proposed that highly dispersed "bimetallic clusters" of copper with ruthenium or osmium existed on the surface of the carrier. Interestingly, ruthenium–copper and osmium–copper are metal combinations which exhibit very low miscibility in the bulk state. Nevertheless, there is interaction between copper and ruthenium or osmium which has important consequences, despite the fact that miscibility in the bulk is very limited. The interaction may be considered analogous to that in chemisorption, manifesting itself as a surface rather than a solution effect. Thus, one might think of copper atoms chemisorbed on

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either ruthenium or osmium. If one then visualizes chemisorption of copper atoms to a high degree of coverage on ruthenium or osmium entities composed entirely of surface atoms, one can see how bimetallic clusters may exist with compositions far outside the range of those possible in bulk solid solutions. While the picture just described may not be a precise model of bimetallic clusters, it serves to illustrate the important features.

For a highly dispersed bimetallic cluster whose components exhibit limited miscibility in the bulk, it is interesting to consider what happens as the degree of dispersion of the system is decreased. In the case of ruthenium–copper, for example, one might expect that increasing the size of a bimetallic cluster would lead to a ruthenium–copper aggregate which may be visualized as a core of ruthenium covered by a layer of copper. This would correspond to the "cherry" model of Sachtler for bimetallic systems with a pronounced miscibility gap (*2*). If this is indeed the case, one would expect for a system containing a small amount of copper relative to ruthenium that large ruthenium–copper aggregates would exhibit a much greater effect of copper on chemisorption and catalysis than would highly dispersed bimetallic clusters of similar composition. This follows because of the segregation of copper to the surface in the large aggregates, resulting in a much higher copper content in the surface for a given low total copper content than would be the case for the highly dispersed ruthenium–copper clusters. With this idea in mind, a study was made of the chemisorption and catalytic properties of large ruthenium–copper aggregates for comparison with the previously reported data on bimetallic clusters. The ruthenium–copper aggregates were not supported on a carrier, and the degree of dispersion was lower than that of the supported bimetallic clusters by almost two orders of magnitude. Data on these catalysts were obtained for the chemisorption of hydrogen, the hydrogenolysis of ethane, and the dehydrogenation and hydrogenolysis of cyclohexane.

EXPERIMENTAL

Apparatus and Procedure

Adsorption measurements were made in a high vacuum apparatus which has been described in detail elsewhere (*3*, *4*). The catalytic studies were conducted in two separate flow reactor systems, one for ethane hydrogenolysis and the other for cyclohexane dehydrogenation, as described previously (*1*, *5*, *6*). The reactor employed for ethane hydrogenolysis is a stainless-steel tube approximately 1 cm in diameter and 8 cm in length, mounted in a vertical position and surrounded by an electrical heater. The catalyst is supported on a fritted stainless-steel disk located about half way down the length of the reactor tube. Quartz wool is packed on top of the catalyst to hold it in place. A 3-mm axial thermocouple well extends upward through the fritted steel disk so that the tip of the enclosed thermocouple is located at the center of the catalyst bed. The reactant gases, with helium diluent, are first passed through a preheat coil and then downflow through the catalyst bed. The flow rates of reactants and helium are measured by simple constriction-type flow meters. The total gas flow rate is maintained at 1 liter/min. Reaction products are analyzed with a silica gel chromatographic column connected to the outlet of the reactor. In the present work, a catalyst charge of approximately 0.2 g., of 45–60-mesh particle size, was used. The reactor for the cyclohexane dehydrogenation studies was similar to that used for the ethane hydrogenolysis runs. Reactor dimensions were approximately 1 cm in diameter and 18 cm in length. The fritted disk was located about 6 cm from the bottom of the reactor tube. A catalyst charge of about 1 g was employed in the cyclohexane dehydrogenation runs. The catalyst was diluted with inert alundum granules to a volume of 5 ml. A layer of these same alundum granules was placed on top of the catalyst bed to serve as a preheat section. A measured flow of cyclohexane was delivered to the reactor with a motor-driven syringe. On entering the preheat section of the reactor, the cyclohexane was vaporized and brought to reaction temperature in admixture with hydrogen prior to passage down through the catalyst bed. The hydrogen flow rate was determined with a rotameter. The syringe was connected to the reactor inlet by a section of Teflon tubing. The reaction products were analyzed by a Perkin–Elmer Model 226 gas chromatograph connected to the reactor outlet.

X-ray diffraction measurements on the catalysts were made with a Phillips diffractometer employing copper $K\alpha$ radiation.

Materials

The ethane used in this work was obtained from the Matheson Company, and hydrogen from the Linde Company. As determined by chromatographic analyses, the ethane contained less than 0.01% of hydrocarbon impurities. Cyclohexane of spectrophotometric grade was obtained from Fisher Scientific Company, Fair Lawn, N. J. The hydrogen was purified by passing it through a Deoxo unit containing palladium catalyst to remove trace amounts of oxygen as water, and then drying with a molecular sieve.

The ruthenium–copper catalysts were prepared in several ways. Some were prepared by coprecipitation from an aqueous solution of ruthenium trichloride and copper nitrate, using an aqueous solution of ammonia and hydrazine as the precipitating agent. Approximately 1 mol of hydrazine was employed per mole of ruthenium and copper ions in solution. Two moles of ammonia were used per mole of copper ions and 3 mol/mol of ruthenium ions. The precipitate formed was separated from the solution by filtration and washed thoroughly with distilled water, after which it was dried overnight at 110°C. In the preparation of pure ruthenium or copper, the procedure was similar except that one of the metal salts was not included in the original solution. Another method employed in preparing ruthenium–copper catalysts involved sequential precipitation, in which the ruthenium trichloride solution was first contacted with the ammoniacal hydrazine solution. The precipitate formed in this step was filtered out of solution and subsequently reslurried in water. A solution of copper nitrate was then added to this slurry. On subsequent addition of ammoniacal hydrazine solution, further precipitation occurred in the presence of the original precipitate. The total precipitate was then dried in the same manner as the coprecipitated preparations.

In either of the methods just described, the dried precipitate was charged to a quartz tube and flushed with helium. Hydrogen was subsequently introduced into the helium to give a stream containing 5 mol% hydrogen, and the temperature was increased to 150°C. After approximately 1 hr at 150°C, the material was heated to 400°C, and the reduction was continued overnight. The system was then cooled to room temperature and the catalyst passivated by gradual admission of air to a stream of helium or nitrogen passing through the tube. The passivated catalyst was then stored in closed bottles until it was needed for experiments. In some cases, portions of the catalyst were heated at 500 or 600°C in hydrogen for an additional 2 hr and then treated in exactly the same manner as the catalyst which was reduced at 400°C. Prior to use in adsorption or catalytic studies, the catalysts were re-reduced *in situ* in flowing hydrogen at 400°C for 2 hr.

In the preparation of the catalysts, the initial precipitation does not accomplish reduction to the final desired metallic form of the catalyst. This is achieved only after the subsequent treatment of the dried precipitate with hydrogen. After treatment with hydrogen, the final material consists of bimetallic aggregates of ruthenium and copper, the nature of which will be discussed in a subsequent section of the paper.

In the case of the coprecipitated catalyst preparations, precipitation of the copper from solution was usually incomplete relative to ruthenium, so that the final catalyst contained a lower ratio of copper to ruthenium than would have been expected on the basis of the amounts of reagents used. This was not observed for the catalysts prepared by sequential precipitation. The catalysts were analyzed for copper content by atomic absorption spectrometry on solutions prepared by digesting the catalysts with a mixture of nitric, sulfuric, and perchloric acids. Complete solution of the copper in the catalysts is obtained by this procedure.

RESULTS

Typical data on surface areas and hydrogen chemisorption for ruthenium and ruthenium–copper catalysts, the latter prepared by the sequential precipitation procedure described in the Experimental section, are given in Table 1. The surface areas were obtained by the Brunauer–Emmett–Teller method (*7*) using argon as the adsorbing gas. An estimate of metal dispersion, defined as the fraction of metal atoms present in the surface, can be made from the surface areas. Adopting values of 6.5 and 7.6 Å^2 as the areas occupied by copper and ruthenium atoms, respectively, in the surface (*3*), we obtain values of 615 and 450 m^2/g for the specific surface areas of copper and ruthenium at 100% dispersion. The catalysts in Table 1 thus have dispersions of the order of 1%. From the surface areas of the catalysts, one can determine the number of copper atoms in the catalyst per unit surface area. For the catalysts in Table 1, this quantity varied from 0 to 5×10^{15}/cm^2. The upper value would correspond to about three to four monolayers of copper, if all the copper were concentrated at the surface. X-ray diffraction patterns on the ruthenium–copper catalysts give lines for ruthenium but not for copper. This suggests a model of the catalyst in which copper is present as a thin layer or as small clusters at the surface of a crystallite composed essentially of pure ruthenium.

TABLE 1

Properties of Ruthenium–Copper Catalysts[a]

Composition (atom% copper)	Hydrogen treatment temperature (°C)[b]	Surface area (m^2/g)	Hydrogen chemisorption[c] (cm^3 (STP)/m^2)	
			Total[d]	Strongly adsorbed[e]
0	400	5.1	0.13	0.077
	500	4.6	0.15	0.093
1.5	400	6.6	0.12	0.071
	500	5.4	0.082	0.039
	600	4.8	0.049	0.014
3	400	7.0	0.10	0.051
	500	7.2	0.070	0.026
5	400	6.5	0.075	0.031
	500	6.2	0.050	0.007

[a] Ruthenium–copper catalysts prepared by sequential precipitation method.

[b] All catalysts reduced initially at 400°C in a 5% hydrogen in helium stream overnight. Temperatures higher than 400°C signify additional heating in the dilute hydrogen stream at the temperature in question.

[c] At room temperature.

[d] At equilibrium pressure of 10 cm Hg.

[e] Amount retained after evacuation for 10 min at room temperature.

The hydrogen chemisorption data were obtained at room temperature, after *in situ* reduction in hydrogen and subsequent evacuation at 400°C, and are expressed as volume adsorbed per unit surface area of catalyst. Data are given in Table 1 on the total adsorption of hydrogen at an equilibrium pressure of 10 cm Hg and on the

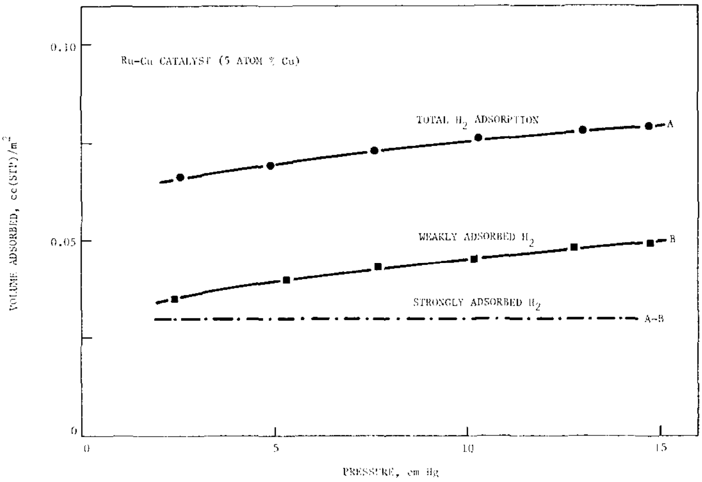

FIG. 1. Typical adsorption isotherms at room temperature for hydrogen on a ruthenium-copper catalyst. Isotherm A represents the total adsorption of hydrogen on the catalyst after reduction and evacuation at 400°C. Isotherm B represents the weakly adsorbed hydrogen, determined by running a second isotherm after evacuation of the sample for 10 min at room temperature following the completion of isotherm A. The difference between the isotherms, A − B, represents the strongly adsorbed hydrogen.

strongly chemisorbed hydrogen. The latter represents that part of the chemisorbed hydrogen which cannot be removed from the catalyst by evacuation at room temperature for 10 min. The total hydrogen chemisorption at room temperature is determined from an isotherm obtained on the catalyst after *in situ* reduction and evacuation of the catalyst at 400°C. After completion of the isotherm, the catalyst sample is evacuated at room temperature for 10 min and a second isotherm obtained to determine the amount of weakly chemisorbed hydrogen. The difference between the two isotherms therefore represents the strongly chemisorbed hydrogen. While the total chemisorption is pressure dependent, the strongly chemisorbed part is not. Typical data on hydrogen chemisorption are shown in Fig. 1 for a ruthenium-copper catalyst containing 5 atom% copper.

In the upper field of Fig. 2 the amount of strongly chemisorbed hydrogen is shown for a series of ruthenium-copper catalysts as a function of the copper content. The catalysts were prepared by the sequential precipitation method and were heated in hydrogen at 500°C for 2 hr prior to use in the adsorption experiments. The incorporation of copper in the catalysts decreases markedly the amount of strongly chemisorbed hydrogen. The copper also strongly suppresses the catalytic activity of ruthenium for the hydrogenolysis of ethane to methane, as shown by the data in the lower field of Fig. 2 for the same series of catalysts. The incorporation of 5 atom% copper decreased the amount of strongly chemisorbed hydrogen by more than 90% and the activity for ethane hydrogenolysis by almost five orders of magnitude.

The rate data on ethane hydrogenolysis were obtained at low conversion levels (0.1–3%) by a method described previously (*8*). The partial pressures of ethane and hydrogen were 0.030 and 0.20 atm, respectively. Arrhenius plots of rate data are given in Fig. 3 for the series of catalysts considered in Fig. 2. The rates are expressed as molecules of ethane converted per second per square centimeter of catalyst surface. The apparent activation energy for the

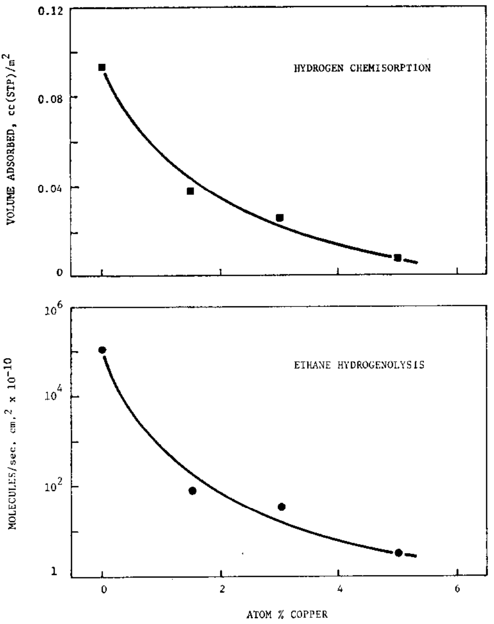

FIG. 2. Hydrogen chemisorption capacity and ethane hydrogenolysis activity of ruthenium–copper catalysts as a function of copper content. The hydrogen chemisorption data were obtained at room temperature and represent the strongly chemisorbed fraction determined as in Fig. 1. The ethane hydrogenolysis activities are reaction rates at 245°C and ethane and hydrogen pressures of 0.030 and 0.20 atm, respectively. The catalysts were prepared by heating in hydrogen at 500°C.

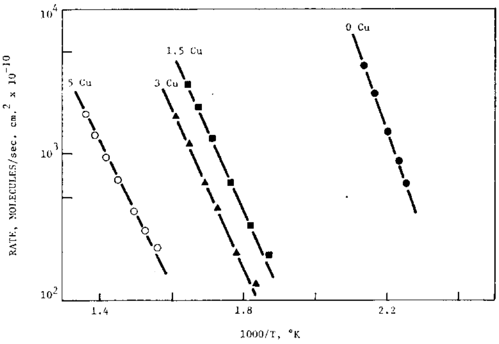

FIG. 3. Arrhenius plots for ethane hydrogenolysis on ruthenium and ruthenium–copper catalysts prepared by heating in hydrogen at 500°C. The numbers associated with the individual lines represent atomic percentages of copper in the catalysts. The reaction rates were determined at ethane and hydrogen pressures of 0.030 and 0.20 atm, respectively.

pure ruthenium catalyst is 32 kcal/mol, in good agreement with previously reported values for supported ruthenium (*1*, *3*). The apparent activation energies for the ruthenium–copper catalysts are somewhat lower, about 25 kcal/mol, despite the fact that the catalysts are much less active. A compensation effect is therefore operative. The rates of ethane hydrogenolysis shown in Fig. 2 were obtained from the Arrhenius plots in Fig. 3. A temperature of 245°C was chosen for comparing ethane hydrogenolysis activities of various catalysts in this paper, since it was an intermediate temperature in the range of temperatures covered on the various catalysts and served to minimize the extent of data extrapolation via the Arrhenius plots. Also, this temperature had previously been used in comparisons of the ethane hydrogenolysis activities of supported ruthenium–copper catalysts (*1*).

Increasing the temperature of treatment of the ruthenium–copper catalysts in hydrogen (5% hydrogen in helium) over the range of 400 to 600°C was found to decrease markedly the amount of strong hydrogen chemisorption and the ethane hydrogenolysis activity, as shown in Fig. 4. In striking

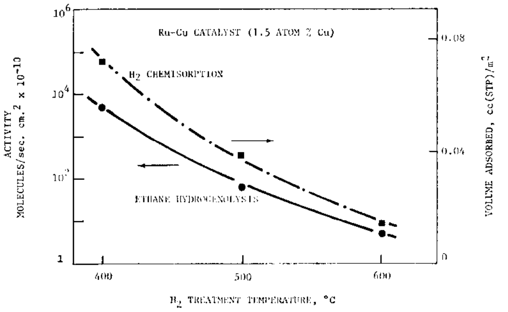

FIG. 4. The effect of hydrogen treatment temperature on the hydrogen chemisorption capacity and ethane hydrogenolysis activity of a ruthenium–copper catalyst. The hydrogen chemisorption refers to the strongly adsorbed fraction determined at room temperature. The ethane hydrogenolysis activities are rates at 245°C and ethane and hydrogen pressures of 0.030 and 0.20 atm, respectively.

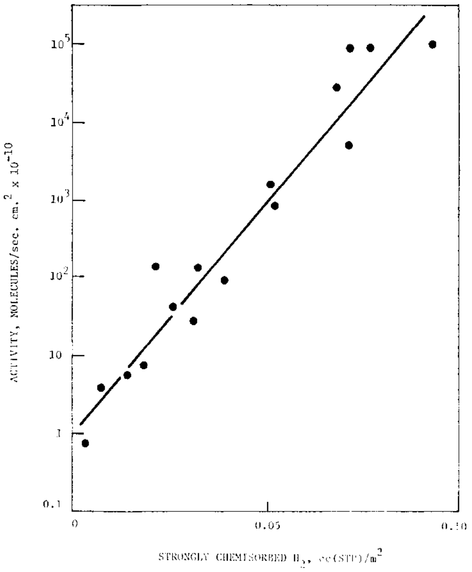

FIG. 5. Correlation of ethane hydrogenolysis activity and amount of strongly chemisorbed hydrogen for ruthenium-copper catalysts. The ethane hydrogenolysis activities are rates at 245°C and ethane and hydrogen pressures of 0.030 and 0.20 atm, respectively. The amount of strongly chemisorbed hydrogen at room temperature is determined as in Fig. 1.

contrast, pure ruthenium did not show such an effect. In the case of pure ruthenium, the amount of strong hydrogen chemisorption per unit area actually increased slightly with increasing hydrogen treatment temperature (see Table 1), and the ethane hydrogenolysis activity remained essentially unchanged. The effect is thus associated with the presence of copper in the catalyst. Interestingly, the BET surface areas of the catalysts are affected only slightly by increasing the hydrogen treatment temperature, as shown by the data of Table 1.

The ethane hydrogenolysis activity of a ruthenium–copper catalyst is strikingly related to its capacity for strong hydrogen chemisorption. Data on the various catalysts listed in Table 1 and a number of others, including catalysts prepared by both the coprecipitation and sequential precipitation methods, are shown in Fig. 5. In addition to the studies of ethane hydrogenolysis, data on conversion of cyclohexane on several ruthenium–copper catalysts were also obtained. On ruthenium, cyclohexane undergoes two reactions, dehydrogenation to benzene and hydrogenolysis to low carbon number alkanes. The product of the latter reaction is predominantly methane, even at very low conversions. Addition of copper to ruthenium was found to decrease hydrogenolysis activity sharply but to have a much smaller effect on dehydrogenation activity. Data are shown in Fig. 6. Reaction rates are given for a temperature of 316°C and cyclohexane and hydrogen partial pressures of 0.17 and 0.83 atm, respectively. Clearly, incorporation of copper improves the selectivity of conversion of cyclohexane to benzene.

DISCUSSION

Ruthenium and copper exhibit very low miscibility in the bulk state. Nevertheless, copper has a marked effect on surface processes occurring on ruthenium. For the ruthenium–copper catalysts of the present work, which consist of aggregates of the order of hundreds of angstroms in size, the

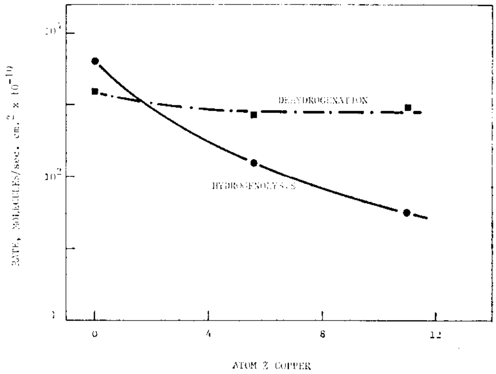

FIG. 6. The rates of dehydrogenation and hydrogenolysis of cyclohexane on ruthenium–copper catalysts as a function of composition. The rates are shown for a temperature of 316°C and for cyclohexane and hydrogen pressures of 0.17 and 0.83 atm, respectively. The catalysts were reduced at 400°C.

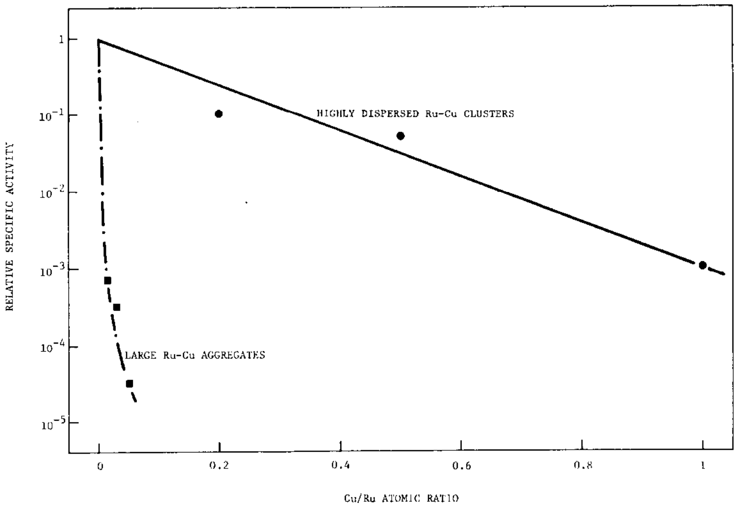

FIG. 7. Influence of the state of dispersion of ruthenium–copper catalysts on the relationship between ethane hydrogenolysis activity and catalyst composition. The large ruthenium–copper aggregates have a metal dispersion of the order of 1%, while the highly dispersed ruthenium–copper clusters have a metal dispersion of the order of 50%. The catalysts were all treated in hydrogen at 500°C prior to use. The data on the highly dispersed ruthenium-copper clusters were taken from Ref. (*1*).

chemisorption and catalytic data indicate that the copper serves to cover the surface of the ruthenium. Specifically, the presence of copper at the surface of ruthenium decreases markedly the extent of strong hydrogen chemisorption and the activity for hydrogenolysis of hydrocarbons. Copper itself exhibits no strong chemisorption of hydrogen, and its activity for hydrogenolysis is negligible by comparison with that of ruthenium (*9*, *10*).

The temperature at which a ruthenium–copper catalyst is heated in hydrogen prior to use has a marked effect on its properties, at least when the amount of copper present corresponds to only a couple of monolayers. The marked decrease in capacity for strong chemisorption of hydrogen and in ethane hydrogenolysis activity when the hydrogen treatment temperature is increased from 400 to 600°C, despite the fact that the surface area decreases only slightly, suggests that the coverage of the ruthenium by the copper increases with increasing temperature in this range. At the lowest temperature, the copper at the surface of the ruthenium is probably present in the form of three-dimensional clusters, leaving many small areas of pure ruthenium exposed at the surface. As the temperature is increased, the copper apparently spreads out over the surface, decreasing the amount of ruthenium exposed. The effect of temperature on the spreading of the copper is presumably associated with increased mobility of copper at the higher temperatures. The absolute temperature corresponding to 600°C is about two-thirds the absolute melting temperature of copper. At such a temperature the mobility of copper would be expected to be high.

A prime objective of the current investigation on unsupported ruthenium–copper catalysts was to compare the results with previously published results on supported ruthenium–copper clusters (*1*) to determine the influence of the state of dispersion of the catalyst. Such a comparison is given in Figs. 7 and 8. The dispersion, defined as the percentage of metal atoms present in the surface, is of the order of 1% for the

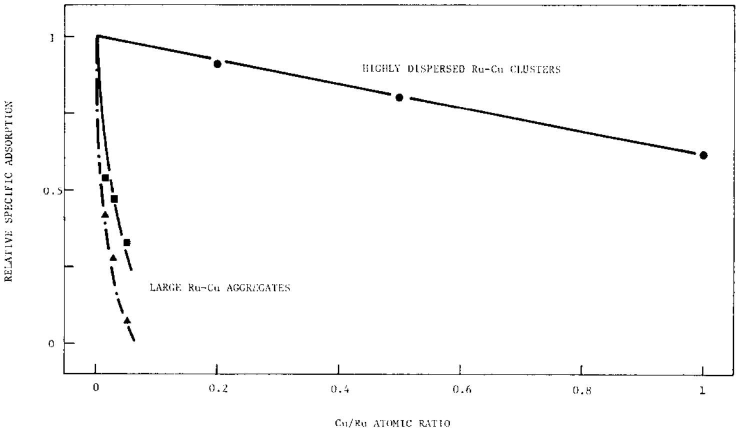

FIG. 8. Influence of the state of dispersion of ruthenium–copper catalysts on the relationship between hydrogen chemisorption capacity and catalyst composition. The catalysts are the same as in Fig. 7, the data on the highly dispersed ruthenium–copper clusters having been taken again from Ref. (*1*). The square and triangular points represent total hydrogen chemisorption and strongly chemisorbed hydrogen, respectively, on the large ruthenium–copper aggregates of the present study.

large ruthenium–copper aggregates of the present study and of the order of 50% for the supported bimetallic clusters. In the case of the highly dispersed ruthenium–copper clusters, the ethane hydrogenolysis activity decreases by a thousandfold when one atom of copper is present per atom of ruthenium in the catalyst, as shown in Fig. 7. For the large ruthenium–copper aggregates, the same inhibiting effect is found when the amount of copper is only 1 to 2% of the amount of ruthenium in the catalyst. A similar conclusion is reached in a comparison of hydrogen chemisorption data, as shown in Fig. 8. The comparisons in Figs. 7 and 8 are for catalysts which have been heated in hydrogen at a temperature of 500°C prior to use. Clearly, the highly dispersed ruthenium–copper clusters require a much higher atomic ratio of copper to ruthenium than the large ruthenium–copper aggregates to achieve a given inhibiting effect. For ruthenium–copper catalysts we adopt the view that copper is bonded chemically to ruthenium at the surface and consider the interaction to be analogous to that which would exist in the chemisorption of copper on ruthenium. As the size of a ruthenium–copper aggregate decreases, the atomic ratio of copper to ruthenium required to achieve coverage of a given fraction of the surface by copper increases. It may be useful to express these considerations in a slightly modified way. Since ruthenium and copper are virtually completely immiscible in the bulk, we may assume for all practical purposes that the copper in a ruthenium–copper aggregate is confined strictly to the surface. If we consider a ruthenium–copper aggregate containing a monolayer of copper, the atomic ratio of copper to ruthenium in the aggregate will increase with decreasing aggregate size. As the degree of metal dispersion approaches unity, the atomic ratio of copper to ruthenium will approach a value of the order of unity. The resulting ruthenium–copper entity may then be taken as one model of a highly dispersed bimetallic cluster of the two elements. Thus, a highly dispersed bimetallic cluster may have compositions far outside the range of those possible in a bulk solid solution of the two metals.

The striking correlation between ethane hydrogenolysis activity of ruthenium–copper catalysts and their capacity for strong hydrogen chemisorption is significant. The requirements of sites for strong hydrogen chemisorption would thus appear to be important in the formation of the chemisorbed intermediate in ethane hydrogenolysis. It has been concluded previously that the intermediate in ethane hydrogenolysis is a dehydrogenated, dicarbon species which is bonded to more than one surface metal atom (*9*, *10*). The rupture of the carbon–carbon bond in such an intermediate is facilitated by strong binding of the intermediate to the surface. Since it is reasonable for strong hydrocarbon chemisorption to correlate with strong hydrogen chemisorption, the relation between hydrogenolysis activity and strong hydrogen chemisorption is understandable. It would seem that the mode of chemisorption of ethane required for ethane hydrogenolysis may be even more demanding than strong hydrogen chemisorption with regard to the nature of the surface site required. Thus, if strong hydrogen chemisorption requires an adjacent pair of unoccupied ruthenium atoms in the surface, the chemisorption of ethane in hydrogenolysis may require a site comprising a larger number of surface metal atoms. This could account for the result that a given amount of copper, particularly at the lowest levels employed, has a much greater effect on ethane hydrogenolysis activity than on the amount of strongly chemisorbed hydrogen. However, there is also the possibility that the extreme sensitivity of the ethane hydrogenolysis activity to copper content reflects a continuous decline in the intrinsic activity of structurally suitable sites as copper covers a progressively larger fraction of the surface. The heat of adsorption of hydrogen should then also decrease with increasing copper coverage, but the amount of strongly chemisorbed hydrogen as determined in this investigation may not reflect this as sensitively as does the hydrogenolysis activity.

The lower apparent activation energy of ethane hydrogenolysis on the ruthenium–copper catalysts as compared to pure ruthenium is not readily explained in the absence of more complete information on the kinetics than was feasible to obtain in the present work. The existence of compensation effects in heterogeneous catalysis is well known in comparisons of catalysts, so that the apparent activation energy itself may not give a true indication of catalytic activity (*11*). In the present case, the much lower activities of the ruthenium–copper catalysts relative to pure ruthenium necessitated the use of substantially higher temperatures for the measurement of reaction rates. It is possible that the rate-determining step may shift from one temperature range to the other. Alternatively, for a given rate-determining step, variations in degree of coverage of the catalytic sites by chemisorbed intermediates in the different temperature ranges may be reflected in the apparent activation energy.

In agreement with previous work from this laboratory (*1*, *5*), the data on cyclohexane reactivity on ruthenium–copper catalysts show a much smaller effect of copper on dehydrogenation activity than on hydrogenolysis activity. The results are also consistent with the results of Sachtler and co-workers (*12*) indicating that reactions of carbon–hydrogen bonds are less influenced than reactions of carbon–carbon bonds when copper is alloyed with an active metal such as nickel. The different effects of copper on dehydrogenation and hydrogenolysis activity in the present work may be rationalized by an argument similar to that presented previously (*5*). It is likely that different chemisorbed intermediates are involved in the dehydrogenation and hydrogenolysis reactions of cyclohexane. The latter reaction appears to be sensitive to surface structure whereas the former reaction appears to be structure insensitive, the terminology corresponding to that of Boudart (*13*). The chemisorbed intermediate in hydrogenolysis is probably a hydrogen-deficient surface residue which forms a number of bonds with surface metal atoms. The probability of finding a suitable array of active metal atoms to accommodate such a chemisorbed intermediate is greatly decreased when inactive copper atoms are interspersed among the active metal atoms in the surface. By contrast, the chemisorbed intermediate in dehydrogenation presumably does not require a site consisting of a number of active metal atoms arranged in a special configuration and is therefore relatively less sensitive to dilution of the surface with inactive copper atoms.

To conclude the discussion, the present results on unsupported ruthenium–copper catalysts, in conjunction with previous results on highly dispersed ruthenium–copper cluster catalysts, lead to a working model of this catalyst system which is applicable over a very wide range of metal dispersion.

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