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Supported "Bimetallic Cluster" Catalysts

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Silica-supported ruthenium–copper and osmium–copper catalysts have been investigated for the hydrogenolysis of ethane to methane and for the dehydrogenation of cyclohexane to benzene. Cyclohexane also exhibits a hydrogenolysis reaction on these catalysts, yielding methane as the predominant primary product. The ruthenium or osmium concentration in the catalysts was held constant at 1 wt%, while the atomic ratio of copper to ruthenium, or copper to osmium, was varied from 0 to 1. Despite the low metal concentration and attendant high metal dispersion, and the fact that copper is virtually totally immiscible with ruthenium or osmium in the bulk, the incorporation of the copper inhibited markedly the specific activity of ruthenium or osmium for hydrogenolysis. The specific activity for dehydrogenation of cyclohexane to benzene was affected very little. It is proposed that highly dispersed "bimetallic clusters" of ruthenium–copper and osmium–copper exist on the carrier.

INTRODUCTION

Studies on metal alloy catalysts have long been of interest for investigating the relationship between catalytic activity and the electronic structure of metals (*1–10*). For the most part, alloy catalysts have been investigated in such forms as powders, wires, or films. However, catalytic studies on supported bimetallic systems of very low metal concentration, and correspondingly high dispersion, have received much less attention. In considering such systems, one may pose the question: Will the individual components exist as separate entities on the carrier, or will there be mixing of atoms of the individual metals in the form of heteroatomic groupings on the carrier surface? If the first situation applies, there would be no direct interaction between atoms of the different metals, and one would expect to find a simple type of additive catalytic behavior of the individual metallic entities. However, if the second situation applies, one might expect to find a different behavior, especially if the individual metals have very different catalytic activities for the reaction of interest.

In the case of supported metal catalysts containing a single metal component at low concentration (of the order of 1 wt%), the size of the metal crystallites is often less than about 50 Å (*11–13*). This has been shown by chemisorption measurements and by techniques such as high-resolution electron microscopy and low-angle X-ray scattering (*11–13*). The preparation of such highly dispersed metal catalysts is fairly straightforward. The catalysts are often prepared by simple impregnation techniques in which the carrier is contacted with an aqueous solution of an appropriate salt or acid of the metal. This is followed by drying and subsequent reduction of the metal at elevated temperature in hydrogen. A supported bimetallic catalyst may be prepared in precisely the same manner, except that the impregnating solution contains salts or acids of two metals. While it seems possible that heteroatomic crystallites or agglomerates would be formed by such a procedure, it is not a simple matter to show directly that this is the case when the degree of metal dispersion is very high. In this situation, however, a catalytic reaction can serve as a sensitive probe to obtain evidence of interaction between the atoms of the two metallic components. In the case of supported bimetallic combinations of a Group VIII and a Group IB metal, we have observed that the hydrogenolysis of ethane to methane is a very useful reaction for this purpose. The catalytic activities of the Group IB metals for this reaction are many orders of magnitude lower than those of the Group VIII metals (*14*). For a number of supported bimetallic combinations of a Group VIII and a Group IB metal, we have found the hydrogenolysis activity per atom of Group VIII metal to be as much as three orders of magnitude lower than that of a catalyst containing the Group VIII metal alone on the support. This indicates that the two metals do not behave as separate, independent entities on the carrier. Examples of such catalytic effects are not limited to combinations of metals that exhibit high mutual solubility in the bulk state. In a highly dispersed state, systems of interest include a variety of metallic combinations that do not correspond to known bulk alloys. For this reason, we have chosen the term "bimetallic clusters" rather than alloys in referring to highly dispersed supported bimetallic systems where the catalytic behavior indicates significant interaction between the metallic components. The present paper reports studies of ethane hydrogenolysis and cyclohexane conversion on supported ruthenium–copper and osmium–copper systems, in each of which the miscibility of the metals in the bulk state is extremely low (*15*).

EXPERIMENTAL

Apparatus and Procedure

The apparatus for the catalysis studies and for the gas adsorption measurements has been described elsewhere (*8*, *16*, *17*). Briefly, the catalytic studies were made in two separate flow reactor systems, one for ethane hydrogenolysis and the other for cyclohexane dehydrogenation (*8*). The reactors are operated at atmospheric pressure, and reaction products are analyzed by gas chromatography. The ethane hydrogenolysis runs are conducted with helium dilution of ethane and hydrogen, while the cyclohexane runs are made by passing cyclohexane over the catalyst in the presence of hydrogen alone. The adsorption apparatus consists of a conventional high vacuum system capable of being evacuated to a pressure of 10^{-6} Torr, and the amount of adsorption is determined volumetrically.

X-ray diffraction measurements on the catalysts were made with a Phillips diffractometer employing copper Kα radiation. The catalysts were reduced for 3 hr in hydrogen at 500°C prior to the X-ray diffraction scans.

Materials

The supported bimetallic catalysts used in this work were prepared by a simple coimpregnation procedure, using aqueous solutions of salts or acids of the two metals in question. The support was a form of silica known as Cabosil HS5 (300 m^2/g surface area), obtained from the Cabot Corporation, Boston, Massachusetts. Approximately 2.2 ml of impregnating solution, with appropriate concentrations of metal salts or acids, was employed per gram of silica. The metal salts or acids used in the impregnations were copper nitrate, ruthenium trichloride, and chloroosmic acid. After impregnation, the resulting material was dried and pressed into wafers which were subsequently crushed into small granules. The ruthenium-containing catalysts were dried in air at 110°C, while the osmium-containing catalysts were dried in a vacuum oven at 70°C. The catalysts consisting of a single supported metal were prepared in the same manner as the bimetallic catalysts, the only difference being that the impregnation solution contained only one metal salt or acid. In all cases the catalysts were reduced in situ in flowing hydrogen at 500°C for three hours prior to adsorption and catalytic runs.

The ethane used in this work was obtained from the Matheson Company, and hydrogen from the Linde Company. As determined by chromatographic analysis, the ethane contained less than 0.01% hydro-

TABLE 1
SUMMARY OF BIMETALLIC CATALYSTS INVESTIGATED

Catalyst system[a]	Metal content wt%	Atomic ratio of metals	
		Cu/Ru	Cu/Os
Ru-Cu	1 Ru, 0 Cu	0	
	1 Ru, 0.126 Cu	0.20	
	1 Ru, 0.315 Cu	0.50	
	1 Ru, 0.63 Cu	1.00	
Os-Cu	1 Os, 0 Cu		0
	1 Os, 0.082 Cu		0.25
	1 Os, 0.166 Cu		0.50
	1 Os, 0.33 Cu		1.00

[a] All catalysts supported on silica.

carbon impurities. The hydrogen was purified by passage through a Deoxo unit containing palladium catalyst to remove trace amounts of oxygen as water, followed by drying with a molecular sieve. The cyclohexane was spectrophotometric grade obtained from Fisher Scientific Company, Fair Lawn, New Jersey.

RESULTS

The catalysts employed in this work are listed in *Table* 1. None of the reduced ruthenium or osmium catalysts, with or without copper present, gave X-ray diffraction lines of any metallic phase. This indicates high metal dispersion, i.e., crystallite sizes lower than about 50 Å. By contrast, a sample containing only copper on silica, at a concentration of 1 wt%, gave diffraction lines characteristic of metallic copper. The crystallite size as determined from the width of the line at a diffraction angle (2θ) of 43.31° was 200 Å. The absence of lines due to copper in the X-ray diffraction scans on the ruthenium-copper and osmium-copper catalysts indicates that the ruthenium and osmium interact with the copper, with the result that large copper crystallites are not formed.

Data on the chemisorption of hydrogen and carbon monoxide were also obtained on the various catalysts. Adsorption isotherms were obtained at room temperature. Typical isotherms are shown in Fig. 1 for several of the catalysts. The isotherms show the volume of gas adsorbed per gram of ruthenium or osmium in the catalyst. In the case of carbon monoxide, an isotherm represents the difference between an initial isotherm and a second isotherm obtained after 10-min evacuation at room temperature. This procedure corrects for adsorption of carbon monoxide on the support (*18*). The isotherms in Fig. 1 all show a slight dependence of the amount adsorbed

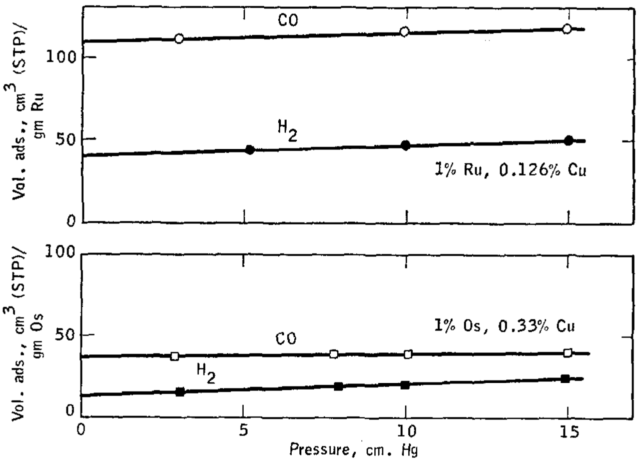

FIG. 1. Typical adsorption isotherms at room temperature for hydrogen and carbon monoxide on silica-supported ruthenium-copper and osmium-copper catalysts. The isotherms show the volume adsorbed per gram of ruthenium or osmium in the catalyst. The carbon monoxide isotherms represent the difference between an initial isotherm and a second isotherm obtained after 10 min evacuation at room temperature.

on pressure. In the analysis of the adsorption data, the procedure was adopted of extrapolating the isotherms to zero pressure to estimate the amounts of strongly adsorbed hydrogen and carbon monoxide. From these extrapolated values the quantities H/Ru, CO/Ru, H/Os, and CO/Os are readily calculated, representing, respectively, the number of hydrogen atoms and carbon monoxide molecules adsorbed per atom of ruthenium or osmium in the catalyst. Figure 2 shows the dependence of these quantities on the atomic ratio of copper to the other metal, ruthenium or osmium, in the catalyst. The quantities decrease with increasing copper content in the catalysts. Strongly adsorbed hydrogen or carbon monoxide on pure copper supported on silica (at 1 wt% concentration) was found to be negligible. Values of CO/Ru and CO/Os are somewhat higher than the corresponding values of H/Ru and H/Os, respectively, for all of the catalysts except pure osmium on silica. In the case of the latter catalyst, the CO/Os ratio is unity, indicating very high dispersion of the osmium, and the H/Os ratio is actually greater than unity, approximately 1.2.

In the catalytic studies, data were obtained on the rate of hydrogenolysis of ethane to methane on all of the catalysts. The rates were determined at low conversion levels (0.1–5%), as described previously (*16–18*). The partial pressures of ethane and hydrogen were 0.030 and 0.20 atm, respectively. Arrhenius plots of the rate data for the ruthenium and ruthenium–copper catalysts are given in Fig. 3. The rates refer to the number of ethane molecules converted per second per atom of ruthenium in the catalyst. The apparent activation energy is 33 ± 2 kcal/mole for all the catalysts in Fig. 3. Arrhenius plots are not given for the osmium–copper catalysts, since attempts to obtain such data were complicated by a decline in activity with time. For these catalysts, reaction rates reported in this paper are limited to initial rates of 245°C, representative of

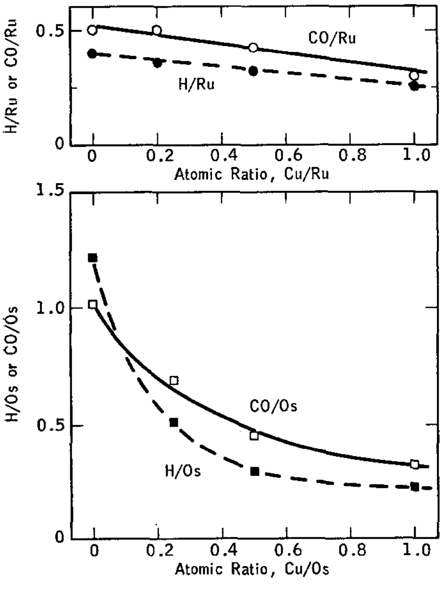

FIG. 2. The chemisorption of hydrogen and carbon monoxide at room temperature on silica-supported ruthenium–copper and osmium–copper catalysts. The catalysts all contain 1 wt% ruthenium or osmium, with varying amounts of copper. The adsorption data are expressed by the quantities H/Ru, CO/Ru, H/Os, and CO/Os, which refer respectively to the number of hydrogen atoms or carbon monoxide molecules chemisorbed per atom of ruthenium or osmium in the catalyst.

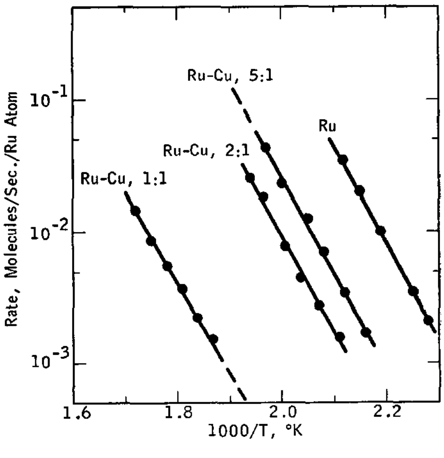

FIG. 3. Arrhenius plots for ethane hydrogenolysis over silica-supported ruthenium and ruthenium–copper catalysts. The catalysts all contain 1 wt% ruthenium with varying amounts of copper. Atomic ratios of ruthenium to copper are shown on the figure to identify the different ruthenium–copper catalysts. The reaction rates, expressed as molecules per second per ruthenium atom in the catalyst, were determined at ethane and hydrogen pressures of 0.030 and 0.20 atm, respectively.

the first 15 min of exposure of catalyst to reactants. In the case of the pure supported osmium, however, activity decline was not a problem. Therefore, the temperature dependence of the rate r was determined. The data for pure supported osmium are represented by the expression

$$r = 4.0 \times 10^{15} \exp(-35000/RT) \quad (1)$$

where the rate is expressed as molecules of ethane converted per second per atom of osmium in the catalyst.

Activities of the ruthenium–copper and osmium–copper catalysts for ethane hydrogenolysis are shown in Fig. 4 as a function, respectively, of the atomic ratios of copper to ruthenium and copper to osmium. The activities, expressed per atom of ruthenium or osmium in the catalysts, are compared at 245°C. In the case of the pure supported osmium, which was much more active than all of the osmium-copper catalysts, the rate was determined by extrapolation of lower-temperature data using Eq. (1). The activities of the ruthenium and ruthenium–copper catalysts were determined directly from the Arrhenius plots in Fig. 3. Of these catalysts, only the ruthenium required a substantial extrapolation to obtain the rate at 245°C. In both the ruthenium–copper and osmium–copper systems, the ethane hydrogenolysis activity decreases markedly with increasing copper concentration. Pure copper supported on silica, at 1 wt% concentration, was inactive for ethane hydrogenolysis at temperatures as high as 450°C.

Figure 5 shows rates of dehydrogenation r_D and hydrogenolysis r_H of cyclohexane at 316°C on the various ruthenium–copper and osmium–copper catalysts as a function of the atomic ratio of copper to ruthenium or copper to osmium, respectively. The rates were determined at cyclohexane and hydrogen partial pressures of 0.17 and 0.83

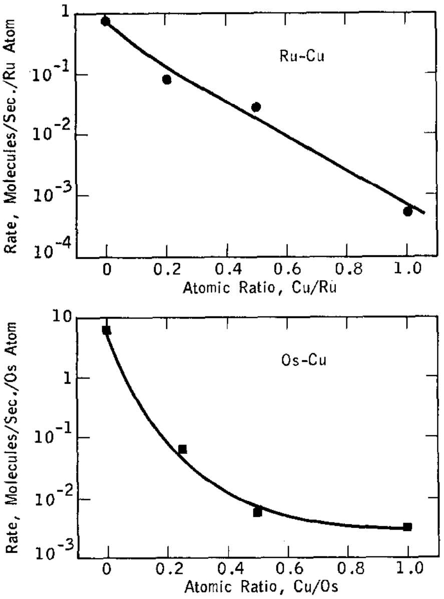

FIG. 4. The effect of copper on the ethane hydrogenolysis activities of ruthenium and osmium. The catalysts all contain 1 wt% ruthenium or 1 wt% osmium supported on silica, with varying amounts of copper. The activities, expressed as rates per atom of ruthenium or osmium in the catalyst at 245°C, were determined at ethane and hydrogen pressures of 0.030 and 0.20 atm, respectively.

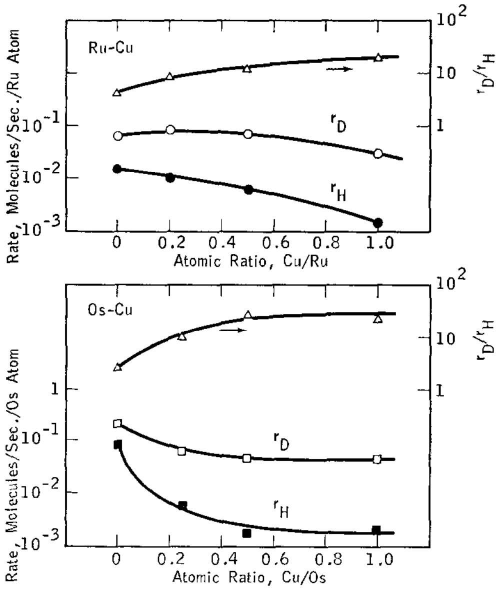

FIG. 5. The rates of dehydrogenation r_D and hydrogenolysis r_H of cyclohexane on silica-supported ruthenium–copper and osmium–copper catalysts as a function of composition. The rates, per atom of ruthenium or osmium in the catalyst, were determined at 316°C at cyclohexane and hydrogen pressures of 0.17 and 0.83 atm, respectively. The selectivity r_D/r_H is also shown as a function of catalyst composition. The catalysts all contain 1 wt% of ruthenium or osmium, with varying amounts of copper.

atm, respectively, at low conversion levels (0.7–7%), as described previously (*8*). Figure 5 also shows the selectivity, r_D/r_H, defined as the ratio of the rate of dehydrogenation to the rate of hydrogenolysis, for the various catalysts. The product of the dehydrogenation reaction is benzene, while the product of the hydrogenolysis reaction is predominantly methane (>80%). For both the ruthenium–copper and osmium–copper systems, the rate of hydrogenolysis decreases substantially with increasing copper content. The effect on the rate of dehydrogenation is much smaller, and in the case of ruthenium–copper the first increments of copper appear to enhance the rate slightly. As a consequence, the selectivity in both catalyst systems increases with increasing copper content. At the conditions employed for obtaining the rate data in Fig. 5, pure copper supported on silica (1 wt% concentration) gave a cyclohexane dehydrogenation rate of 1×10^{-3} molecules per second per copper atom. No hydrogenolysis activity was detected for the pure copper.

The rates shown in Figs. 3–5 are all expressed per atom of ruthenium or osmium in the catalyst. The quantities H/Ru, H/Os, CO/Ru, and CO/Os in Fig. 2 give the number of active adsorption sites per atom of ruthenium or osmium in a given catalyst. By dividing the rates in Figs. 3–5 for each of the catalysts by the corresponding value of H/Ru or H/Os in Fig. 2, for example, we obtain the activity per hydrogen adsorption site. Specific activities determined in this way are shown in Fig. 6 as a function of the atomic ratio of copper to ruthenium or copper to osmium in the catalyst. Specific activities could have been derived equally well using the values of CO/Ru or CO/Os, in which case the specific activities in Fig. 6 would differ from the values shown by a factor of 1.2 to 1.5. For the purpose here, this difference is of no consequence. Figure 6 shows that the specific activity for cyclohexane dehydrogenation is affected very little by catalyst composition over the range investigated, while the specific activities for hydrogenolysis of ethane or cyclohexane decrease markedly with increasing copper content.

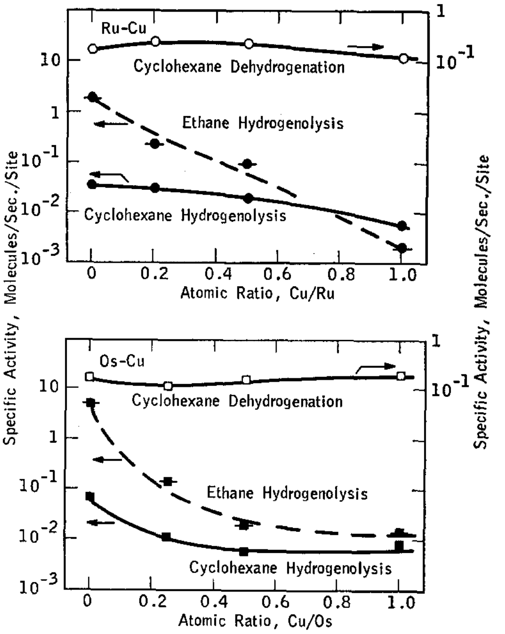

FIG. 6. Specific activities of silica-supported ruthenium–copper and osmium–copper catalysts for the hydrogenolysis of ethane and for the dehydrogenation and hydrogenolysis of cyclohexane. The activities for ethane hydrogenolysis are compared at 245°C and ethane and hydrogen partial pressures of 0.030 and 0.20 atm, respectively. The activities for cyclohexane dehydrogenation and hydrogenolysis are compared at 316°C and cyclohexane and hydrogen partial pressures of 0.17 and 0.83 atm, respectively.

DISCUSSION

The results of the present work on supported ruthenium–copper and osmium–copper catalysts provide evidence of interaction between copper and the Group VIII metal, despite the fact that the metals are present at a concentration of the order of only 1% on a very high surface area carrier. If copper and the Group VIII metal existed as separate entities on the carrier, one would not expect the hydrogenolysis activity of the bimetallic catalyst to be significantly different from that of the supported Group VIII metal alone. The copper itself would contribute negligible hydrogenolysis activity to the catalyst.

However, since incorporation of copper with the Group VIII metal gives a catalyst with markedly lower hydrogenolysis activity, the metal components are clearly not isolated from each other on the carrier. It is particularly intriguing that such an effect is observed with supported ruthenium–copper and osmium–copper, since copper is virtually totally immiscible with ruthenium or osmium in the bulk state (*15*). It may also be noted that the crystal structure of copper is different from that of ruthenium and osmium. Copper has a face-centered cubic structure, while ruthenium and osmium have close-packed hexagonal structures.

In highly dispersed ruthenium–copper and osmium–copper systems, it appears that "bimetallic clusters" are formed on the surface of the carrier. In considering the nature of such bimetallic clusters, it is useful to examine the data on hydrogen and carbon monoxide chemisorption. As copper is incorporated with either ruthenium or osmium on the carrier, the extent of adsorption per atom of Group VIII metal in the catalyst decreases. This indicates a decrease in the number of Group VIII metal atoms present in the surface of the clusters. Assuming that copper atoms in the surface of a cluster do not chemisorb hydrogen, one might tentatively conclude for the ruthenium–copper system that the number of surface ruthenium atoms decreases by a factor slightly lower than two when the Cu/Ru atomic ratio is increased from 0 to 1 at a constant ruthenium content of 1 wt%. On the same basis, the number of surface osmium atoms in the osmium–copper system decreases by a factor of approximately four when the Cu/Os atomic ratio is increased from 0 to 1 at a constant osmium content of 1 wt%. While the number of surface ruthenium or osmium atoms decreases with incorporation of copper in the catalysts, the magnitude of the change is small compared with the enormous decrease in the activities of the catalysts for the hydrogenolysis of ethane. The decrease in activity for this reaction may be considered from two points of view. First, since it has been concluded previously that the intermediate in ethane hydrogenolysis is a highly unsaturated dicarbon surface residue multiply bonded to surface metal atoms (*14*), one might expect the reaction to be sensitive to surface structure and composition. If atoms of ruthenium or osmium in the surface are interspersed extensively with atoms of copper, the concentration of adsorbed intermediate could be very sensitive to restrictions in the number of sites comprising multiplets of ruthenium or osmium atoms. Second, the presence of copper may affect the electronic properties of ruthenium and osmium atoms in the clusters, so that the strength of bonding of these atoms with hydrocarbons is modified. In view of the enormous effect of copper on the activities of ruthenium and osmium for ethane hydrogenolysis, it would appear that an electronic factor is involved in addition to a purely structural factor.

The data on cyclohexane reactivity on ruthenium–copper and osmium–copper catalysts show a much smaller effect of copper on dehydrogenation activity than on hydrogenolysis activity. For the dehydrogenation of cyclohexane to benzene, the specific activity remains almost constant when copper is incorporated with either ruthenium or osmium over the range of compositions investigated, despite the fact that copper is much less active than ruthenium or osmium for the reaction. The behavior is very similar to that which we have reported earlier for unsupported copper–nickel alloys (*8*), and may be rationalized by an argument similar to that presented in the copper-nickel paper. The results of the present work thus provide further evidence of the high degree of specificity of bimetallic systems comprising copper and a Group VIII metal in catalyzing certain types of hydrocarbon transformations. Other work from this laboratory indicates that such specificity is characteristic of Group VIII–Group IB bimetallic systems in general (*19*).

The hydrogenolysis reaction of cyclohexane has the interesting feature that the product is predominantly methane. It would appear that higher carbon-number fragments formed in the initial stages of the surface reaction do not desorb readily from the surface, but instead undergo secondary cracking reactions. This results eventually in the formation of C_1 fragments which are hydrogenated to methane. It is possible that different adsorbed intermediates are involved in the dehydrogenation and hydrogenolysis reactions of cyclohexane. The latter reaction appears to be sensitive to surface structure whereas the former appears to be structure-insensitive, employing the classification suggested by Boudart (*11*). The surface intermediate involved in the hydrogenolysis of cyclohexane, by analogy with conclusions drawn in ethane hydrogenolysis, is probably a dehydrogenated surface residue which is multiply bonded to surface metal atoms.

In concluding the discussion, it is pertinent to examine briefly the implications of the proposal that a highly dispersed bimetallic cluster phase may exist even in a system which exhibits severe miscibility limitations in the bulk. The proposal that bimetallic clusters are present in the ruthenium–copper and osmium–copper catalysts of the present work is based primarily on catalytic data. The existence of bimetallic clusters in either of these systems would imply a strong effect of the degree of metal dispersion on the stability of the bimetallic phase. Thus, the bimetallic phase would exist only for sufficiently small metal crystallites, so that conditions leading to extensive metal crystal growth would result in phase separation. Extensive evidence in support of such a phenomenon has been summarized recently by Ollis (*20*).

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