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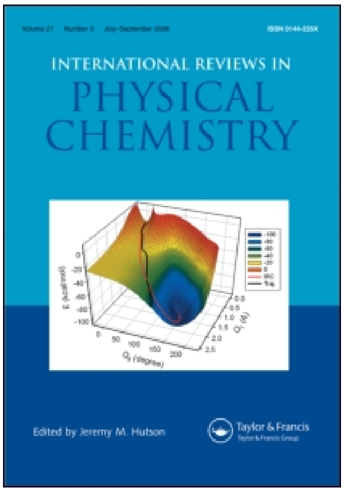

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Ruthenium-copper: a model bimetallic system for studies of surface chemistry and catalysis

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Ruthenium–copper: a model bimetallic system for studies of surface chemistry and catalysis

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The combination of metallic elements ruthenium and copper is an intriguing one for studies of the surface chemistry and catalytic properties of bimetallic systems. Although the two metals are completely immiscible in the bulk, they form bimetallic entities in which copper is present on the surface of ruthenium. The initial conclusions about the nature of these entities were derived solely from measurements of chemisorption isotherms and reaction rates on ruthenium–copper catalysts. Later studies of the catalysts using physical probes such as X-ray photoelectron spectroscopy and extended X-ray absorption fine structure provided valuable confirmation of the early conclusions. Eventually, studies were initiated with specimens prepared by vapour deposition of copper on to the surfaces of ruthenium single crystals. These investigations have employed most of the sophisticated probes of modern surface science. As one can readily see from the literature, the ruthenium–copper system has attracted much attention in surface chemistry and catalysis. It has become an important model system for elucidating fundamental questions related to the performance of bimetallic catalysts. This review brings together the results of published work on typical ruthenium–copper catalysts and their single crystal counterparts.

1. Introduction

Bimetallic systems have long been of interest in catalysis. Much of the early work by scientists in this field utilized metal alloys to investigate the so-called ‘electronic factor’ in catalysis by metals (Couper and Eley 1950, Dowden and Reynolds 1950, Schwab 1950, Best and Russell 1954, Hall and Emmett 1958, 1959). One type of alloy which attracted much attention was a combination of metals from groups VIII and IB of the periodic table.

For many reactions, including hydrogenation, dehydrogenation, and hydrogenolysis reactions of hydrocarbons, the metals of Group VIII are active catalysts (see e.g. Sinfelt 1975). By comparison, the metals of Group IB are relatively inactive. In terms of the energy band theory of electrons in metals, the former possess d-bands with states which are not completely occupied by electrons while the latter have filled d-bands. According to an early view of the electronic structure of an alloy comprising metals from groups VIII and IB (Mott and Jones 1936), there is a single d-band which becomes increasingly filled as the amount of the Group IB metal increases. By investigating the dependence of catalytic activity on alloy composition, catalytic chemists reasoned that the influence of electronic structure could be determined.

Many studies of the effect of alloy composition on catalytic activity were conducted with this objective in mind. However, they were not very fruitful in elucidating the electronic factor in the simple manner originally envisioned. The approach was based on the premise that the catalytic activity of a metal surface is determined by the electronic structure of the metal in the bulk. Today, this premise has been largely supplanted by the view that catalysis is determined by localized properties of the metal atoms in the surface. In this regard, it is important to recognize that the composition of the surface region of an alloy may be very different from the composition in the bulk. If accumulation of one of the components in the surface serves to lower the suface energy of the system, the surface will then be enriched in that particular component. Moreover, the atmosphere in contact with the surface can have a marked effect on the surface composition (Bouwman *et al.* 1972, Williams and Boudart 1973). Hence, conclusions regarding the electronic factor which are based on bulk composition are subject to significant uncertainty.

The matter is complicated further by the possibility that, apart from any electronic effects, purely structural features which depend on the surface composition may have a marked influence on some reactions. Such reactions are said to be structure sensitive, the terminology having been introduced by Boudart (1969). The chemisorbed intermediate for a reaction of this kind on the surface of a catalytically active metal typically requires a site consisting of an array of metal atoms. A single metal atom in the surface is not adequate as a site. If an alloy consists of a catalytically active metal component in combination with an inactive one, and a large array of metal atoms of the active component is required to accommodate the chemisorbed intermediate for a reaction, the random interspersion of inactive atoms among the active metal atoms will greatly decrease the availability of the required arrays and lower catalytic activity markedly (Ponec and Sachtler 1972, Sinfelt *et al.* 1972). Arrays of active metal atoms have sometimes been called 'multiplets' (Balandin 1958) or 'ensembles' (Ponec and Sachtler 1972, Dowden 1973).

Although studies with metal alloys as catalysts have not provided a simple way to probe the electronic factor, they have been very fruitful in other respects (Sinfelt 1983). The work has shown that alloys may exhibit major selectivity effects in catalysis, i.e. their influence on reaction rates can depend markedly on the kind of reaction (Sinfelt *et al.* 1969, 1971, 1972, 1976, Ponec and Sachtler 1972, Beelen *et al.* 1973, Sinfelt 1973 a). Research in the area has also led to the development of highly dispersed bimetallic catalysts, i.e. 'bimetallic clusters' (Sinfelt 1973 a, 1977, 1987), some of which have found widespread application in industrial catalysis, especially in petroleum reforming processes for the production of gasoline of high antiknock quality (Sinfelt 1983, 1985).

Of particular interest was the discovery that bimetallic systems of interest for catalysis need not be limited to combinations of metallic elements that form alloys, i.e. solid solutions, in the bulk. A good example was provided by the ruthenium–copper system, the subject of this article. Although ruthenium and copper are virtually completely immiscible in the bulk (Hansen 1958), bimetallic ruthenium–copper entities can be prepared in which the effect of copper on the catalytic behaviour of ruthenium is similar to its effect on the behaviour of nickel in nickel–copper alloys. The presence of copper leads to a marked suppression of the catalytic activity of either ruthenium (Sinfelt *et al.* 1971, 1976, Sinfelt 1973 a) or nickel (Sinfelt *et al.* 1971, 1972) for the hydrogenolysis of carbon–carbon bonds in alkanes. However, the activity for a dehydrogenation reaction such as the conversion of cyclohexane to benzene is affected much less, and can actually increase. The selectivity of the ruthenium or nickel for the dehydrogenation reaction is thereby increased significantly.

Since the ability to form bulk alloys is not a necessary condition for a bimetallic system to be of interest as a catalyst, it is misleading to use the term alloy in referring to bimetallic catalysts in general. Terms such as bimetallic aggregates or bimetallic clusters (for highly dispersed systems) are therefore preferred when making general references to the bimetallic entities present in catalysts.

In the ruthenium–copper system the two components exhibit significant interaction at an interface, despite the fact that they do not form solid solutions in the bulk. In a typical bimetallic aggregate or cluster, the central core consists of ruthenium. The copper is present at the surface of the ruthenium, much like a chemisorbed layer. This provides the explanation for its marked influence on the catalytic properties of ruthenium (Sinfelt *et al.* 1976).

After the initial studies of the present author and co-workers on ruthenium–copper catalysts were reported, investigations were conducted in the laboratory of Gerhard Ertl with specimens prepared by depositing copper on the surface of a ruthenium single crystal (Christmann *et al.* 1979, 1980, Shimizu *et al.* 1980, Vickerman *et al.* 1981). Subsequently, the ruthenium–copper system has attracted the attention of many scientists who are interested in obtaining a more detailed understanding of bimetallic catalysts from experiments utilizing single crystals. For such investigations the immiscibility of ruthenium and copper has the desirable feature that copper can be deposited on the surface of ruthenium without any complication arising from diffusion of copper into the bulk.

The purpose of this review on the ruthenium–copper system is to bring together the results and conclusions of the published work on catalytic materials and single crystal specimens. The review seemed worthwhile because the ruthenium–copper system has become a model in studies of an intriguing type of bimetallic entity. In the first part of the review, results of investigations on catalytic materials are considered. These include the original catalytic data obtained by the author, with conclusions derived from the data about the structures of the catalysts. Subsequent catalytic data obtained by other investigators are also considered. The review of the catalytic data is followed by a discussion of results of spectroscopic studies of the structures of ruthenium–copper catalysts. The second part of the review is concerned with the results of investigations utilizing single crystals and their relation to the findings on catalytic materials.

2. Investigations on Ru–Cu catalysts

2.1. *Catalytic activity and selectivity*

The initial investigation which stimulated interest in the ruthenium–copper system was conducted with catalysts in which the ruthenium and copper were dispersed on the surface of silica (Sinfelt 1973 a). In such a catalyst the silica is called a carrier or support. The silica used in the ruthenium–copper catalysts had a very high surface area, approximately 300 m^2/g. The catalysts contained 1 wt% ruthenium and amounts of copper chosen to given Cu/Ru atomic ratios ranging from 0·2 to 1·0. They were prepared by wetting the silica carrier with an aqueous solution of ruthenium and copper salts. The resulting materials were dried in air at a temperature of 383 K and subsequently exposed to a stream of hydrogen at 775 K to accomplish reduction of the ruthenium and copper. A copper-free catalyst containing 1 wt% ruthenium was prepared by the same procedure. The average diameter of the metal clusters in these catalysts, as subsequently determined by electron microscopy (Prestridge *et al.* 1977), was approximately 30 Å. For metal clusters of this size, the ratio of surface atoms to total atoms in the clusters is roughly equal to 0·5. This fraction is commonly known as the metal dispersion (Boudart 1969). The extent of coverage of the silica surface by the clusters was of the order of 1%. Measurements of reaction rates on the catalysts provided the first evidence of interaction between ruthenium and copper in catalysts containing the two elements. The results supported the hypothesis that bimetallic clusters of the two elements were present.

Catalyst samples in the form of granules about 0·5 mm in size were used in the investigation of the catalytic properties. An individual granule of catalyst may be viewed as a porous mass of silica with metal clusters distributed throughout the pores. The external area of such a granule is negligible in comparison to the area of the surface inside the granules.

The catalytic studies were conducted in a flow reactor, in which reactants in the gaseous state were passed through a bed of catalyst granules. In such a system, molecules of reactants diffuse from the gas stream into the pores of the granules to be chemisorbed on the metal clusters. A reaction occurs on the metal clusters, and molecules of product are desorbed into the pores. The product molecules must then diffuse out of the granules into the gas stream flowing through the void space between the granules. The composition of the gas stream changes as it is depleted of reactants and enriched in product in its passage through the catalyst bed.

One of the reactions studied was the hydrogenolysis of ethane to methane

$$C_2H_6 + H_2 \rightarrow 2CH_4.$$

This reaction is generally not a desired one in industrial practice. In the use of metal catalysts for a more valuable reaction such as the aromatization of alkanes or cycloalkanes, the usual objective is to suppress reactions involving hydrogenolysis of carbon–carbon bonds. From this point of view, studies of the ethane hydrogenolysis reaction on metals have been valuable in providing ideas for the inhibition of hydrogenlysis activity. Such inhibition can lead to a substantial improvement in the selectivity with which a metal catalyses a desired reaction.

At a given set of conditions, the rate of ethane hydrogenolysis on ruthenium is many orders of magnitude higher than it is on copper (Sinfelt 1973 b). Moreover, the initial investigation of ethane hydrogenolysis on the ruthenium–copper catalysts showed that the reaction rates were markedly lower than the rate on a catalyst containing ruthenium alone (Sinfelt 1973 a). For the catalyst with a Cu/Ru atomic ratio equal to one, the rate was three orders of magnitude lower, as shown in figure 1. Rates expressed in two different ways are shown as a function of the Cu/Ru atomic ratio in the catalyst. In the upper field of figure 1, the rate is expressed as the number of molecules of ethane converted to methane per second per atom of ruthenium in the catalyst. In the lower field, it is the number of molecules converted per second per surface site. An estimate of the number of surface sites associated with the metal clusters in a catalyst was made from a hydrogen chemisorption isotherm obtained at room temperature. In making the estimate, it was assumed that hydrogen molecules dissociate into atoms on chemisorption, and that one hydrogen atom is chemisorbed per surface site. A further discussion of the use of hydrogen chemisorption isotherms for this purpose is deferred to a subsequent paragraph in this section of the paper. The rates in figure 1 are for a temperature of 518 K. They were obtained from Arrhenius plots of data obtained at conversion levels in the range of 0·1 to 5% at ethane and hydrogen partial pressures of 0·030 and 0·20 atm., respectively. The experiments were conducted at low conversions to approach the conditions of a differential reactor as closely as possible.

Either way of expressing reaction rates in figure 1 leads to the same conclusion. There is a dramatic effect of copper in suppressing the catalytic activity of ruthenium for ethane hydrogenolysis. These results were crucial in providing evidence that

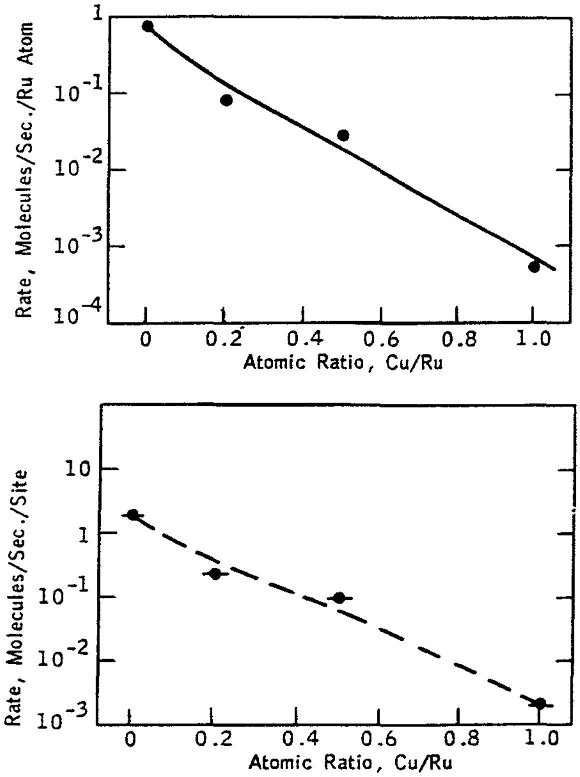

Figure 1. Rates of hydrogenolysis of ethane to methane at 518 K on silica-supported ruthenium–copper catalysts with different Cu/Ru atomic ratios. In the upper field of the figure, the rate is the number of molecules of ethane converted per second per ruthenium atom in the catalyst. In the lower field, it is the number converted per second per surface site (Sinfelt 1973 a).

bimetallic clusters of ruthenium and copper were present on the silica, since they demonstrated clearly that a significant interaction existed between the ruthenium and copper. If these two elements had existed exclusively as separate entities on the silica carrier (i.e. isolated from one another in the form of pure monometallic clusters), the hydrogenolysis activity of the ruthenium would not have been affected significantly by the presence of copper in the catalyst. However, since incorporation of copper with ruthenium gave a catalyst with markedly lower hydrogenolysis activity, the metal components were clearly not isolated from each other on the carrier. Thus, although ruthenium and copper are virtually completely immiscible in the bulk, they exhibit significant interaction with each other in the dispersed metallic clusters which exist in the ruthenium–copper catalysts.

Another reaction studied on the ruthenium–copper catalysts was the dehydrogenation of cyclohexane to benzene

$$C_6H_{12} \rightarrow C_6H_6 + 3H_2.$$

In marked contrast to the ethane hydrogenolysis reaction, this type of reaction is a highly desirable one in industrial practice. The dehydrogenation of cyclohexane homologs to aromatic hydrocarbons plays a key role in processes for the reforming of petroleum fractions to product gasoline components of high antiknock quality. On pure ruthenium clusters, the dehydrogenation reaction is accompanied by substantial hydrogenolysis of the cyclohexane ring, a reaction yielding products containing a very high fraction of lower carbon number alkanes. The predominant hydrogenolysis product is methane, even at very low conversions. The production of methane is represented by the overall reaction

$$C_6H_{12}+6H_2 \rightarrow 6CH_4.$$

An attractive feature of Ru–Cu clusters, as compared to pure Ru clusters, is their lower rate of hydrogenolysis relative to dehydrogenation. Thus, Ru–Cu clusters are more selective for the desired reaction, as will be shown. Rates of dehydrogenation r_D and hydrogenolysis r_H obtained at a temperature of 589 K and at cyclohexane and hydrogen partial pressures of 0·17 and 0·83 atm., respectively, are shown in the upper two fields of figure 2 as a function of the Cu/Ru atomic ratio in the catalyst. Pure copper is much less active than pure ruthenium for either the dehydrogenation or hydrogenolysis of cyclohexane. As for the ethane hydrogenolysis data in figure 1, the rates in figure 2 are expressed in two ways. In the top field, the rates refer to the number of molecules of cyclohexane converted per second per atom of ruthenium in the catalyst for the particular reaction of interest. The rates in the middle field of the figure refer to the number converted per second per surface site. The method of determining the number of surface sites was described in the discussion of figure 1.

The addition of copper to ruthenium decreases the rate of hydrogenolysis of cyclohexane over the whole range of compositions spanning Cu/Ru atomic ratios from 0 to 1. The effect on the rate of dehydrogenation is somewhat less pronounced, and close inspection of the rates (in either method of presentation) actually indicates passage through a maximum as the Cu/Ru ratio is varied in the range shown. A similar maximum has been observed by the author and his associates in a study of dehydrogenation of cyclohexane on nickel–copper alloys (Sinfelt *et al.* 1972). In the discussion of the results for the nickel–copper alloys, it was suggested that the rate-limiting step on pure nickel was desorption of benzene. It was also suggested that benzene was bound less strongly to the surface of a nickel–copper alloy than to pure nickel, leading to a more rapid desorption of the molecule and hence to a higher rate of conversion of cyclohexane to benzene. A suggestion that a similar argument could be made to rationalize the results on the Ru–Cu clusters has also been advanced by the present author (Sinfelt 1973 a).

In the bottom field of figure 2 the selectivity of cyclohexane conversion, defined as the ratio r_D/r_H of the rate of dehydrogenation to the rate of hydrogenolysis, is shown as a function of the Cu/Ru atomic ratio. The selectivity of ruthenium is improved markedly by the interaction with copper in bimetallic clusters of the two elements. On pure ruthenium clusters, conversion of cyclohexane to benzene represents approximately 75% of the total reaction, compared to 95% for ruthenium–copper clusters with a Cu/Ru atomic ratio equal to 1.

Haller and associates at Yale University subsequently extended the investigation of the hydrogenolysis of ethane and the reactions of cyclohexane on ruthenium–copper catalysts to examine the possibility that catalyst preparation variables played a role (Haller *et al.* 1983, Rouco *et al.* 1983, Hong *et al.* 1987). Their results showed the same kinds of catalytic effects as those observed earlier by the present author. However, there were quantitative differences associated with variations in the properties of the silica, with the type of metal salt used in the preparation, and with the procedure used in

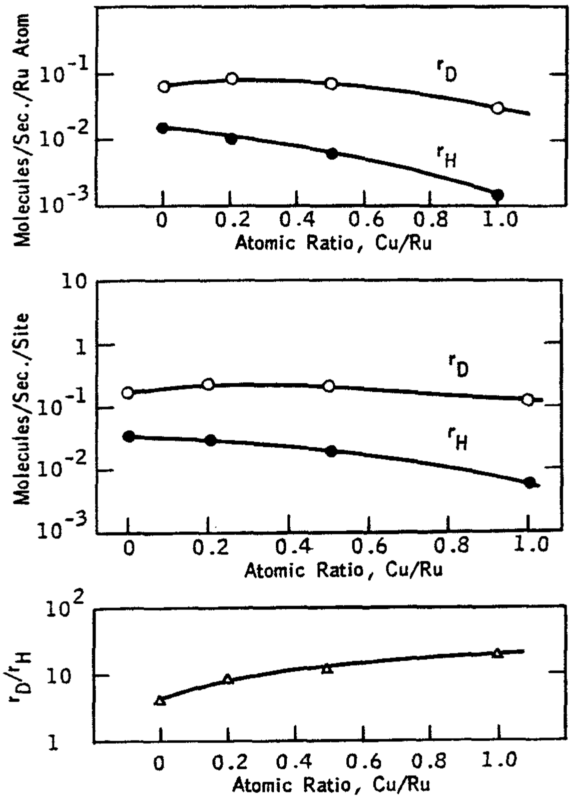

Figure 2. Dehydrogenation and hydrogenolysis of cyclohexane at 589 K on the ruthenium–copper catalysts of figure 1. Rates of dehydrogenation r_D and hydrogenolysis r_H are shown in the upper two fields of the figure, expressed per ruthenium atom in the catalyst in the top field, and per surface site in the middle field. The bottom field of the figure shows the selectivity r_D/r_H (Sinfelt 1973 a).

depositing the metal salts on the silica. A reason for such quantitative differences will be given in a subsequent discussion of the structural features of ruthenium–copper catalysts.

Studies of reaction rates on silica supported Os–Cu catalysts show precisely the same types of effects as those observed with the Ru–Cu catalysts (Sinfelt 1973 a). In common with the Ru–Cu system, the components of the Os–Cu system are also virtually completely immiscible in the bulk. Thus, we have another example in which highly dispersed bimetallic clusters are present in a catalyst despite the bulk immiscibility of the components.

Studies of the effect of copper on the catalytic activity of ruthenium have been extended by Bond and Yide (1984 a, b) to hydrogenolysis reactions of larger alkane molecules, including propane, n-butane, and isobutane. The effects were like those reported for ethane in the 1973 paper of the present author, for silica supported Ru–Cu catalysts prepared and treated in a comparable manner; i.e. rates of hydrogenolysis on the Ru–Cu catalysts were markedly lower than the rate obtained on a catalyst containing ruthenium alone on silica.

A similar influence of copper on the catalytic activity of ruthenium has been observed for the hydrogenation of carbon monoxide to hydrocarbons (Bond and Turnham 1976).

The effect of copper in suppressing the catalytic activity of ruthenium for hydrogenolysis reactions of alkanes is a general feature of bimetallic catalysts consisting of a Group VIII metal in combination with a Group IB metal, whether or not the components are miscible with one another in the bulk (Sinfelt *et al.* 1969, 1971, 1972). The effect of copper on the selectivity of ruthenium for dehydrogenation relative to hydrogenolysis, as illustrated in figure 2 for cyclohexane, is also a characteristic feature of this type of combination of metallic elements (Sinfelt *et al.* 1971, 1972, Sinfelt 1973 a).

2.2. *Structural features*

Our knowledge of the structure of Ru–Cu catalysts has been obtained with a combination of chemical and physical probes. In the early stages of the research on these catalysts, chemical probes such as the catalytic hydrogenolysis of ethane to methane and the chemisorption of hydrogen were especially important, since the physical probes then available were generally unsatisfactory for investigating highly dispersed catalyst systems. At a later stage of the research, physical probes such as X-ray photoelectron spectroscopy, extended X-ray absorption fine structure (EXAFS), and analytical electron microscopy were developed to the point where they could also provide useful information.

2.2.1. *Elucidation of structure with chemical probes*

The simplest explanation of the results in figure 1 is that copper covers the ruthenium surface. A ruthenium–copper cluster is then visualized in which the ruthenium exsts as a central core with copper present only at the surface. As the size of such a ruthenium–copper cluster increases, the ratio of surface atoms to total atoms in the cluster, i.e. the metal dispersion, will decrease. A given degree of coverage of ruthenium by copper can then be attained with a proportionately lower Cu/Ru atomic ratio in the cluster. Correspondingly, one would expect the Cu/Ru atomic ratio required for a given degree of suppression of the rate of ethane hydrogenolysis to decrease in proportion to the decrease in the metal dispersion.

This expectation was tested in a later investigation (Sinfelt *et al.* 1976) of rates of ethane hydrogenolysis on bimetallic aggregates of ruthenium and copper which were much larger than the ruthenium–copper clusters on which the data in figure 1 were obtained. These bimetallic aggregates were not supported on a carrier. They were prepared by precipitation from aqueous solutions of salts of the metals, followed by treatment in hydrogen at a temperature of 773 K. From surface areas determined from gas adsorption measurements, their dispersion was estimated to be about 0·01, which compares with an approximate value of 0·5 for the ruthenium–copper clusters of figure 1. The influence of this difference in metal dispersion on the relationship of the rate of ethane hydrogenolysis to catalyst composition is shown in figure 3. The ordinate of the figure, which is labelled relative activity, is the rate relative to the rate for the ruthenium reference catalyst. For the line representing the highly dispersed Ru–Cu clusters, the reference catalyst consists of silica supported clusters of pure ruthenium. The reference catalyst for the line representing the large Ru–Cu aggregates is pure ruthenium in the form of large aggregates. The atomic ratio of copper to ruthenium corresponding to a given decrease in the hydrogenolysis rate is observed to be much lower for the large ruthenium–copper aggregates than for the more highly dispersed ruthenium–copper clusters. The observed ratios differ by a factor roughly equal to the ratio of metal dispersions. This indicates that the copper in a ruthenium–copper aggregate or cluster is confined to the surface, which is consistent with the extremely low miscibility of the two metals in the bulk.

It was mentioned earlier that the work of Haller and associates has revealed that variables in the preparation of ruthenium–copper catalysts can play a role in determining the degree to which the catalytic activity of ruthenium is altered by the presence of copper. One reason becomes immediately apparent from figure 3. If the metal dispersion is sensitive to the method of preparation, one would expect the effect of a given amount of copper on the hydrogenolysis activity of ruthenium to be smaller for a catalyst in which the metal is more highly dispersed. Indeed, Haller *et al.* (1983) report data in support of this expectation for ruthenium–copper catalysts prepared with different ruthenium and copper salts and with different silica supports.

A preparation variable which can have an important effect is the temperature of treatment of the material in hydrogen prior to its use as a catalyst. Treatment in hydrogen at an elevated temperature is a common step in the preparation of metal catalysts. Its usual purpose is to ensure that the metal is satisfactorily reduced prior to use. The temperature employed in this step can determine how well the metal is reduced or in some cases can have a significant influence on the structure or morphology of the metal entity present in the material. An effect of the latter type is observed with unsupported bimetallic aggregates of ruthenium and copper similar to the large Ru–Cu aggregates used in obtaining one of the sets of data in figure 3. In the following discussion, we consider Ru–Cu aggregates containing 1·5 at.% copper. When the temperature of treatment of the aggregates in hydrogen is increased from 400 to 600°C (673 to 873 K), the aggregates are changed in a manner which leads to a marked decline in their catalytic activity for ethane hydrogenolysis, and also to a large decrease in their capacity for chemisorption of hydrogen (Sinfelt *et al.* 1976). As shown in figure 4, the catalytic activity, defined as the rate of hydrogenolysis at a temperature of 518 K and at

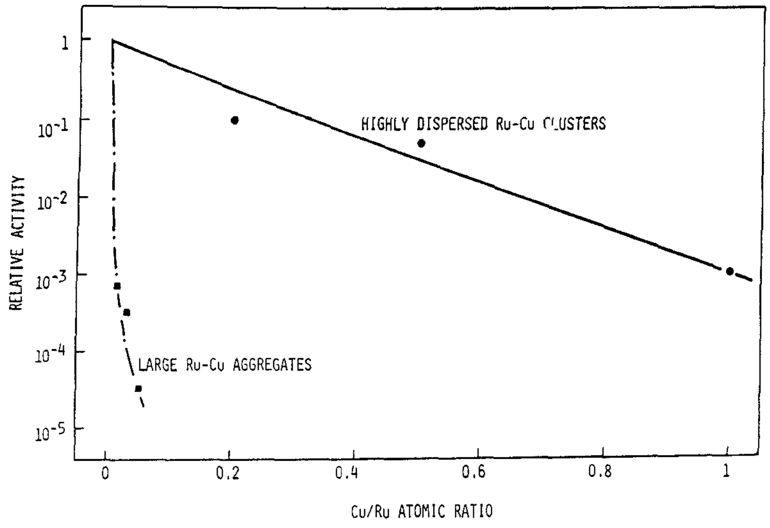

Figure 3. Influence of the state of dispersion of ruthenium–copper catalysts on the relationship between ethane hydrogenolysis activity and catalyst composition (Sinfelt *et al.* 1976).

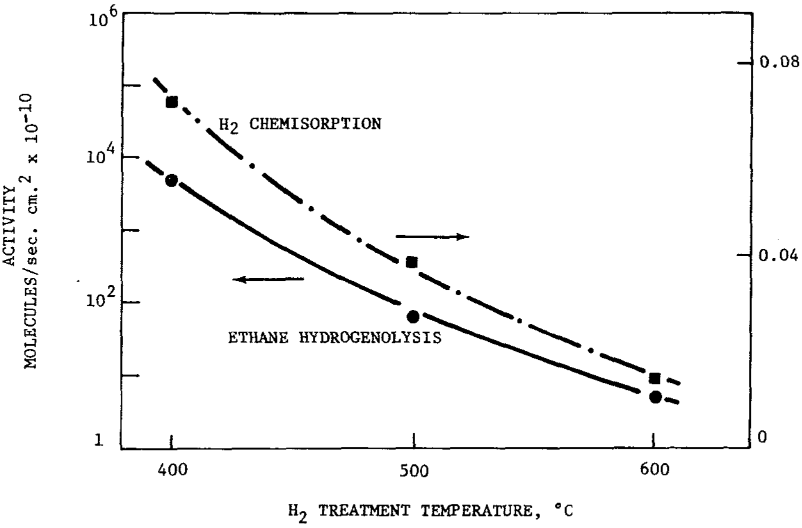

Figure 4. The effect of the temperature of hydrogen pretreatment of Ru–Cu aggregates on their capacity for hydrogen chemisorption and their catalytic activity for ethane hydrogenolysis. The aggregates contained 1·5 at.% copper (Sinfelt *et al.* 1976).

ethane and hydrogen partial pressures of 0·030 and 0·20 atm, respectively, declined by three orders of magnitude. Correspondingly, the capacity for chemisorption of hydrogen at room temperature decreased by a factor of five. The changes in the Ru–Cu aggregates leading to these effects were accompanied by only a modest decrease in surface area (from 6·6 to 4·8 m^2/g). The chemisorption data in figure 4 are for strongly chemisorbed hydrogen, which refers to the amount which is retained by the surface after the completion of an adsorption isotherm and a subsequent evacuation of the adsorption cell at room temperature for a period of 10 min to a pressure of approximately 10^{-6} Torr. The hydrogenolysis activity in figure 4 is the rate per square centimetre of surface, while the chemisorption capacity is the volume adsorbed per square metre. The surface areas used in obtaining these quantities were determined by the low temperature (77 K) physical adsorption of argon, i.e. by the well-known method of Brunauer *et al.* (1938).

The results in figure 4 suggest that coverage of ruthenium by copper increases with increasing temperature of hydrogen treatment, since copper possesses a vanishingly small catalytic activity for the hydrogenolysis of ethane and is not expected to chemisorb hydrogen in a strongly bound form. Correspondingly, the extent of uncovered ruthenium surface must decrease very substantially. A copper content of 1·5 at.% in ruthenium–copper aggregates with the surface areas cited is sufficient for monolayer coverage of the ruthenium by copper if the latter is uniformly distributed on the surface. However, in aggregates treated at the lowest temperature, the copper at the surface is probably present in the form of three-dimensional clusters, leaving many 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 (873 K) is about two-thirds of the absolute melting temperature of copper. At such a temperature the mobility of copper would be expected to be high.

In figure 4 the decline in hydrogenolysis activity is enormous compared to the decline in hydrogen chemisorption capacity. On dividing the hydrogenolysis activity by the chemisorption capacity, we obtain a quantity which is proportional to the activity per hydrogen chemisorption site. This quantity decreases by a factor of 200 when the temperature of treatment of the Ru–Cu aggregates in hydrogen is increased over the range shown. Sites which are effective for the hydrogenolysis of ethane are therefore affected to a much larger extent than are the sites which are suitable for the chemisorption of hydrogen.

In hydrogen chemisorption experiments on ruthenium–copper samples, it has been suggested that spillover of hydrogen from ruthenium to copper may occur (Haller *et al.* 1983, Rouco *et al.* 1983, Goodman and Peden 1985). Although exposure of pure copper to molecular hydrogen does not lead to chemisorption (Culver *et al.* 1959, Greuter and Plummer 1983), the result is different if the copper is exposed to hydrogen atoms (Pritchard and Tompkins 1960). There is a significant activation barrier for the dissociation of hydrogen molecules on copper (Alexander and Pritchard 1972, Balooch *et al.* 1974). In the suggested spillover process, molecular hydrogen would first dissociate on ruthenium, after which chemisorbed hydrogen atoms would presumably be transported from ruthenium to copper. If massive hydrogen spillover occurred, an increase in the degree of coverage of ruthenium by copper would not produce the expected decline in amount of hydrogen chemisorbed per unit surface area. The five-fold decrease actually observed in figure 4 therefore indicates that hydrogen spillover was not massive in these chemisorption experiments, although one cannot totally dismiss the possibility that it may have occurred to a small degree. To the extent that it does occur, it will introduce additional uncertainty in any attempt to use hydrogen chemisorption data to obtain quantitative information on the amount of ruthenium surface not covered by copper.

The structure of Ru–Cu clusters is changed markedly by exposure to air at elevated temperatures. Bond and Yide (1984 a) report that silica supported Ru–Cu clusters treated in air at 623 K are destroyed, yielding separate oxide phases of ruthenium and copper. On subsequent reduction by a hydrogen–hydrocarbon mixture at 413–433 K, separate crystallites of ruthenium and copper are formed. A second reduction at 623 K leads to restoration of Ru–Cu bimetallic clusters. The conclusions of these workers were based on measurements of rates of hydrogenolysis of n-butane. The Ru–Cu clusters generated at the higher reduction temperature were much less active for n-butane hydrogenolysis than the metal clusters which were produced by the lower temperature reduction, a result which is consistent with the data presented in figure 4.

2.2.2. *Physical probes of structure*

The unsupported Ru–Cu aggregates considered in figure 3 had surface areas in the range of 5–7 m^2/g. Monolayer coverage of ruthenium by copper in such aggregates is possible for a copper content in the vicinity of 1·5 at.%, if all of the copper is present at the surface. X-ray diffraction patterns on Ru–Cu aggregates of this type exhibit lines for ruthenium but not for copper. Such observations are consistent with a model of an aggregate in which copper is present as a thin layer or as small clusters at the surface of a crystallite composed essentially of pure ruthenium.

Evidence in support of this model is also provided by studies employing X-ray photoelectron spectroscopy (XPS) (Helms and Sinfelt 1978). This type of spectroscopy is also known as electron spectroscopy for chemical analysis (ESCA). In XPS measurements electrons are emitted from a substance as a result of irradiation by X-rays. In order for an electron to be emitted from an atom by an incident X-ray photon, the energy of the X-ray photon must be at least as high as the binding energy of the electron within the atom. The energy of the X-ray photon in excess of the binding energy is imparted to the emitted electron as kinetic energy. Since an atom possesses electrons with various binding energies corresponding to the different electron energy levels, irradiation by X-ray photons of a particular energy leads to emission of electrons with a definite set of kinetic energies corresponding to lines in an XPS spectrum. The intensity of a spectral line in XPS is a measure of the number of emitted electrons with a particular kinetic energy. From the kinetic energy of the emitted electrons associated with a particular line, and the known energy of the incident X-ray photons, one can determine the binding energy of an electron in a particular level in the emitting atom. Since an electron-binding energy is a characteristic feature of the atoms of a given element, the determination of binding energies by XPS makes it possible to identify the kinds of elements present in a material. Data on intensities of the lines provide information related to the amounts present.

A feature of particular interest in XPS is its surface sensitivity. Electrons emitted by atoms in sub-surface layers of a material are subject to inelastic scattering processes which serve to decrease the probability that the electrons will emerge from the material with the expected kinetic energy. The deeper the atoms are located in the material, the lower this probability becomes. For atoms at a given depth, the probability of an electron escaping from a material with its kinetic energy unchanged depends on the magnitude of the kinetic energy. In other words, the mean free path of the electrons for inelastic scattering is a function of the kinetic energy.

In XPS studies of unsupported ruthenium–copper aggregates, the ratio of the intensity of the Cu $2p_{3/2}$ line (932 eV binding energy) to that of the Ru $3d_{5/2}$ line (280·2 eV binding energy) has been used as a measure of the degree of coverage of ruthenium by copper (Helms and Sinfelt 1978). While one does not obtain precise absolute values of coverage in this manner, variations of the intensity ratio I_{Cu}/I_{Ru} are useful for following changes in coverage as a function of the conditions employed in the preparation of the aggregates.

In figure 5 the intensity ratio for ruthenium–copper aggregates containing 1·5 at.% copper is shown as a function of the temperature of hydrogen treatment in the XPS chamber. The chamber was evacuated prior to the intensity measurements. The ratio increases when the hydrogen treatment temperature is increased from 400 to 600°C. The increase in this range of temperature indicates an increase in the extent of coverage of the ruthenium by the copper and is consistent with our earlier conclusions based on the hydrogen chemisorption and ethane hydrogenolysis data shown in figure 4, i.e. the increased mobility of the copper at the higher temperature permitted it to spread over the surface.

It is of interest to relate XPS data on ruthenium–copper aggregates to data on hydrogen chemisorption on these materials. There is a good basis for considering such a relationship for ruthenium–copper aggregates heated in hydrogen at various temperatures in the range of 400–600°C, since variations in the Cu/Ru intensity ratio accompany changes in the degree of coverage of ruthenium by copper. In figure 6 the amount of hydrogen chemisorbed at room temperature, expressed as molecules of hydrogen adsorbed per square centimetre of surface, is shown as a function of the Cu/Ru intensity ratio obtained in the XPS measurements. As noted already, the intensity data are for the copper $2p_{3/2}$ and ruthenium $3d_{5/2}$ lines. The upper part of the figure shows data on the total chemisorption of hydrogen (at 100 Torr equilibrium

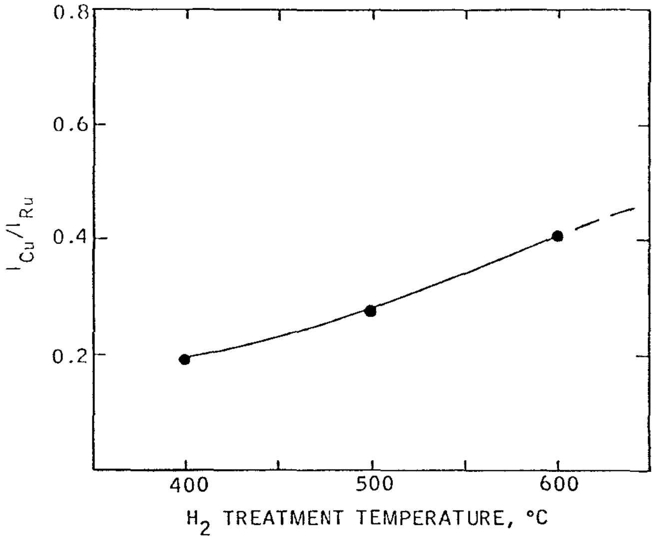

Figure 5. X-ray photoelectron spectroscopy (XPS) data on the Ru–Cu aggregates of figure 4. The data show the effect of the temperature of hydrogen pretreatment on the ratio I_{Cu}/I_{Ru} of the intensity of electron emission from copper atoms ($2p_{3/2}$ level) to that from ruthenium atoms ($3d_{5/2}$ level) (Helms and Sinfelt 1978).

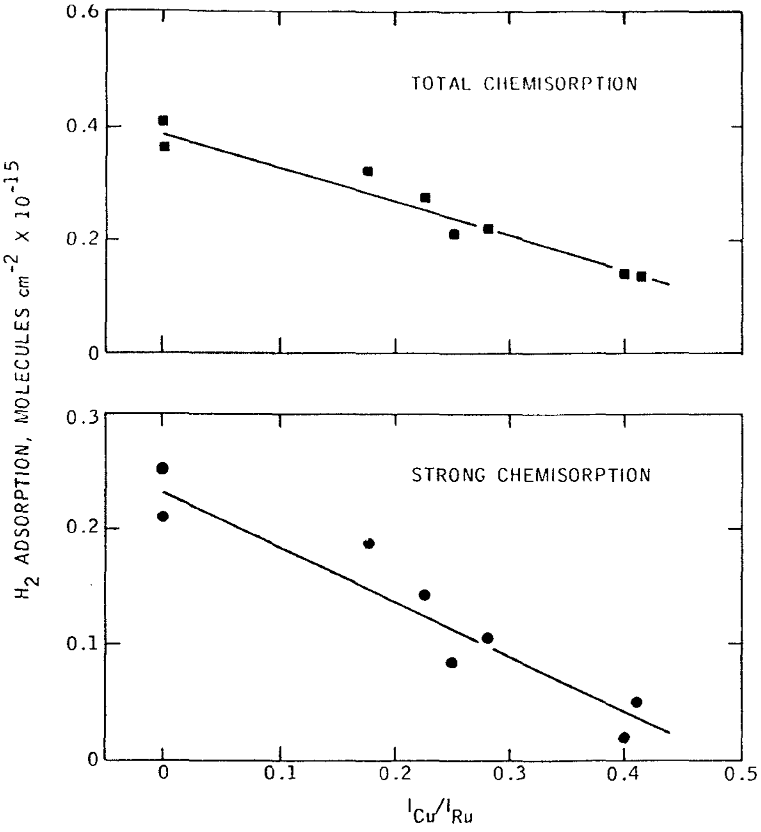

Figure 6. Correlation of hydrogen chemisorption capacity of ruthenium–copper aggregates with the XPS intensity ratio I_{Cu}/I_{Ru} of figure 5 (chemisorption data at room temperature) (Helms and Sinfelt 1978).

pressure). The lower part shows data on the strongly chemisorbed fraction, i.e. the amount which cannot be removed by evacuation to 10^{-6} Torr at room temperature. Both total and strong chemisorption decrease as the Cu/Ru intensity ratio increases, but the percentage decrease is greater for the strong chemisorption. As indicated earlier, pure copper exhibits no strong chemisorption of hydrogen. As the coverage by copper increases, the amount of strongly chemisorbed hydrogen decreases. While the total chemisorption also decreases, the effect is more complex, since the total chemisorption is pressure dependent and since copper itself appears to chemisorb hydrogen weakly. The data in the upper part of figure 6 show a total hydrogen chemisorption of $0{\cdot}4 \times 10^{15}$ molecules cm^{-2} on the pure ruthenium aggregates, which corresponds to $0{\cdot}8 \times 10^{15}$ atoms cm^{-2}. This is somewhat lower than one might expect for monolayer coverage on ruthenium, and indicates either that such a monolayer is not attained at a pressure of 100 Torr or that the ruthenium surface is partially contaminated.

Another physical probe which has proved to be very useful for structural investigations of Ru–Cu catalysts is extended X-ray absorption fine structure (EXAFS). While the phenomenon of EXAFS has been known for a long time (Kronig 1931, 1932 a, b), its capabilities as a method for obtaining structural information were not exploited for a long time afterwards. The exploitation has been aided greatly by advances in methods of data analysis (Sayers *et al.* 1971, Lytle *et al.* 1975) and experimental techniques, the latter having been associated primarily with the application of high-intensity synchrotron radiation as an X-ray source (Kincaid and Eisenberger 1975). The application of EXAFS in catalyst studies is of particular interest, since for a number of very highly dispersed catalysts of technological importance it appears to be the only method capable of yielding detailed structural information.

When X-rays are absorbed by matter other than monatomic gases, a plot of absorption coefficient against X-ray energy exhibits oscillations on the high energy side

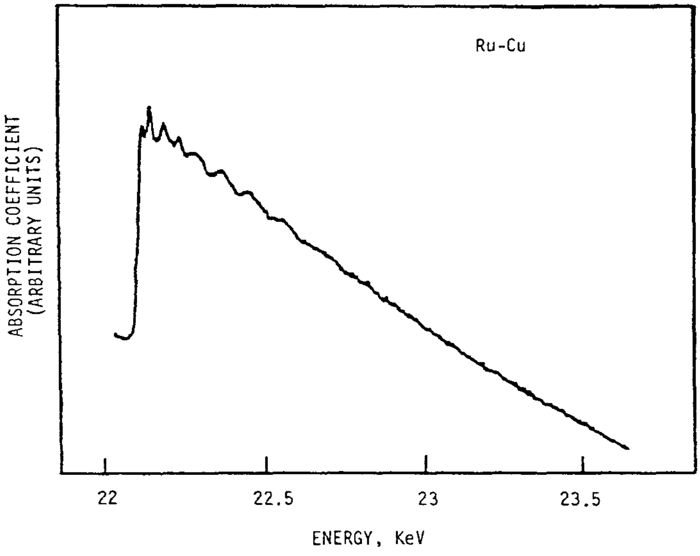

Figure 7. X-ray absorption spectrum for a ruthenium–copper catalyst at 100 K in the region of the *K* absorption edge of ruthenium (Sinfelt *et al.* 1980).

of an absorption edge. The oscillations constitute the extended X-ray absorption fine structure (EXAFS) which is commonly observed in an X-ray absorption spectrum. The region of a spectrum of usual interest for an EXAFS investigation of structure begins at an energy of approximately 30 eV beyond an edge and extends over a range of 1000–1500 eV. An X-ray absorption spectrum at a temperature of 100 K in the region of the K-absorption edge of ruthenium is shown in figure 7 for one of the silica-supported Ru–Cu catalysts for which catalytic data are given in figures 1–3. The catalyst in question is the one with a copper to ruthenium atomic ratio equal to one (Sinfelt *et al.* 1980). The K-absorption edge of ruthenium is observed at an X-ray energy of approximately 22·1 keV. The electrons ejected from the ruthenium atoms are scattered by neighbouring ruthenium and copper atoms. The oscillations in the absorption coefficient are attributed to interference between waves associated with the ejected electrons and waves associated with the electrons after they are scattered by neighbouring atoms. As can be seen from figure 7, oscillations in the absorption coefficient are observed on the high energy side of the edge. The oscillations damp out over an energy range of about 1000 eV.

A photoelectron ejected from an atom as a result of X-ray absorption is characterized by a wave vector K given by the equation

$$K=(2mE)^{1/2}/\hbar \tag{1}$$

where m is the mass of the electron, $\hbar$ is Planck's constant divided by 2π, and E is the kinetic energy of the photoelectron. In the treatment of EXAFS data, the absorption coefficient in the region of the EXAFS is divided into two parts. One part is independent of the environment of the absorber atoms and is identical to the absorption coefficient for the free atom. The other part is the oscillating part which constitutes EXAFS. Division of the latter part by the former normalizes the EXAFS oscillations. The normalized oscillations are represented by the quantity $\chi(K)$, in which K is the photoelectron wave vector. The determination of $\chi(K)$ from experimental EXAFS data has been discussed in detail elsewhere (Lytle *et al.* 1975, 1980, Via *et al.* 1979).

A plot of the function $K\cdot\chi(K)$ against K is shown in the upper left-hand section of figure 8 for the ruthenium EXAFS data presented in figure 7 for the Ru–Cu catalyst. A Fourier transform of $K\cdot\chi(K)$ yields a function $\Phi(R)$, where R is the distance from the absorber atom (Sayers *et al.* 1971). The transform has real and imaginary parts. Only the magnitude of the transform, which is everywhere positive, is considered here. It is shown in the upper right-hand section of figure 8. The prominent peak is associated with scattering of photoelectrons by nearest neighbour metal atoms about ruthenium absorber atoms. It is centered at a value of R which is not a true interatomic distance because of phase shifts (Sayers *et al.* 1971).

In the analysis of EXAFS data, it is useful to invert the Fourier transform over a limited range of R. This procedure determines the contribution to EXAFS arising from shells of atoms within that range of R. In figure 8, for example, the region of the Fourier transform for values of R between 1·7 and 3·1 Å is isolated in the lower right-hand section of the figure. An inverse transform of this region, which brackets the primary peak, yields the function shown in the lower left-hand section of figure 8. This function, $K\cdot\chi_1(K)$, represents the contribution to the ruthenium EXAFS due to backscattering of electrons by nearest neighbour metal atoms (ruthenium and copper). The subscript 1 on χ signifies nearest neighbours.

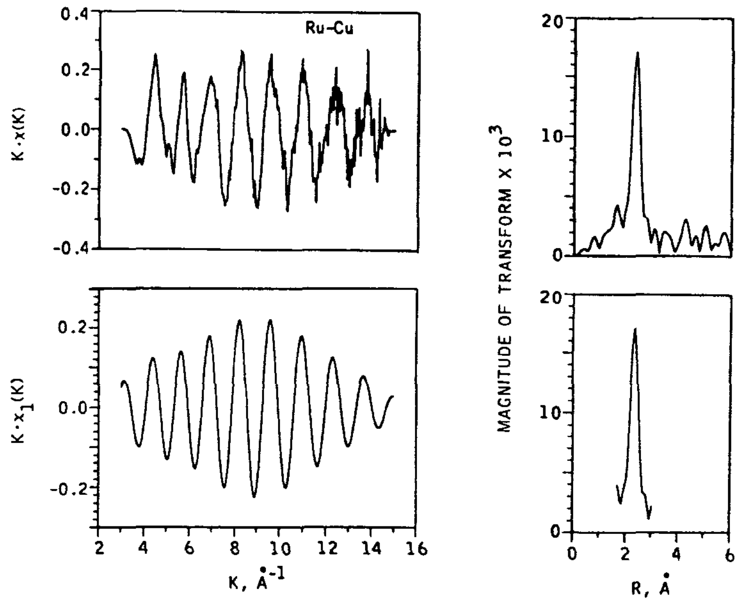

Figure 8. Normalized EXAFS data (ruthenium K absorption edge) for the ruthenium–copper catalyst of figure 7, with associated Fourier transform, filtered transform, and inverse of the filtered transform. The inverse transform isolates the EXAFS due to the nearest neighbour metal atoms (Sinfelt *et al.* 1980, Sinfelt 1987).

In addition to the EXAFS associated with the K-absorption edge of ruthenium in the Ru–Cu catalyst, there is also EXAFS for the K-edge of copper. The copper EXAFS data are treated in the same manner as the data for ruthenium. Utilizing the sequence of steps illustrated in figure 8, one isolates the contribution of nearest neighbour metal atoms to the copper EXAFS. This EXAFS function is shown in the lower half of figure 9. In the upper half of figure 9, the analogous function for a reference material containing pure copper clusters dispersed on silica is shown for comparison. The copper clusters constitute 1 wt% of the total mass of the material. The two EXAFS functions in figure 9 differ considerably in shape and in the average magnitude of the oscillations (note the difference in scale of the ordinates). These data are indicative of substantial differences in the environment of the copper atoms in the two materials, and provide convincing evidence that copper and ruthenium are intimately associated with each other in the Ru–Cu catalyst. They are consistent with the catalytic data in figures 1 and 2, which provided the basis for the conclusion that bimetallic clusters of ruthenium and copper are present in silica supported Ru–Cu catalysts.

From a quantitative analysis of the EXAFS data on the Ru–Cu clusters, information has been obtained on interatomic distances and on the average numbers of ruthenium and copper atoms coordinated to a ruthenium or copper reference atom in the clusters (Sinfelt *et al.* 1980). It was found that the average number of nearest neighbour metal atoms (ruthenium plus copper) about a copper atom was smaller than that about a ruthenium atom. From such a result, we conclude that the copper is present at the surface of the clusters, since a surface atom has fewer neighbouring atoms than an atom in the interior of a cluster. The conclusion is consistent with that derived from the catalytic data of figure 3.

Useful information on the properties of Ru–Cu catalysts has also been obtained from analytical electron microscopy studies, in which transmission electron

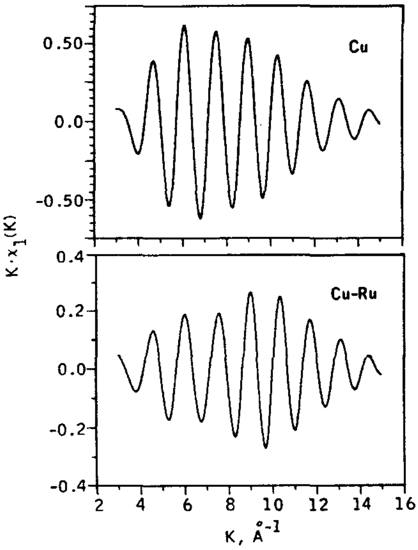

Figure 9. Comparison of the copper EXAFS (*K* absorption edge) of copper and ruthenium–copper clusters at 100 K. The EXAFS shown is the part due to nearest neighbour metal atoms (Sinfelt *et al.* 1980, Sinfelt 1987).

microscopy is coupled with energy dispersive X-ray spectroscopy and electron diffraction to obtain morphological, analytical, and structural data on individual metal clusters or crystallites in the catalysts (Shastri *et al.* 1986). In these studies the energy-dispersive X-ray spectrum obtained for an individual metal cluster in the size range of 15–40 Å exhibited lines characteristic of both ruthenium and copper. Moreover, an electron diffraction pattern for a given cluster also provided evidence for the presence of both elements. Other studies of Ru–Cu catalysts employing secondary ion mass spectrometry, in which secondary $^{102}Ru^+$ and $^{63}Cu^+$ ions are emitted from the catalysts as a result of their bombardment by fast argon atoms, have shown that the intensity of emission of the ruthenium ions decreases with increasing Cu/Ru atomic ratio (Lai and Vickerman 1984). The results of both of these investigations provide strong supporting evidence for the existence of bimetallic clusters of ruthenium and copper in the catalysts, and are consistent with the view that the copper is present at the surface in such a cluster.

3. Studies on single crystal specimens

As noted in the introduction, the initial investigations on ruthenium–copper catalysts stimulated extensive research with single crystal specimens. In work of this type, copper atoms are evaporated from a copper source on to the surface of a ruthenium single crystal. Ruthenium has a hexagonal close packed (hcp) structure. The surface exposed to the copper is typically a basal plane of the ruthenium crystal, i.e. the (0001) plane, which is sometimes also represented as the (001) plane. The research on the single crystal specimens has included studies of the morphology of the copper on the surface, in addition to investigations of the chemisorption and catalytic reactions of some of the same types of molecules used in the initial work on ruthenium–copper catalysts.

3.1. *Morphology of Cu on Ru(0001)*

In work initiated by Ertl and associates on the deposition and growth of copper films on the (0001) plane of a ruthenium single crystal, it has been reported that the morphology of the copper depends on the temperature of the ruthenium during the deposition (Christmann *et al.* 1979, 1980, Christmann and Ertl 1984, Vickerman *et al.* 1983). The investigations utilized a combination of methods, including Auger electron spectroscopy (AES), thermal desorption spectroscopy (TDS), low energy electron diffraction (LEED), and work function measurements.

In experiments in which the ruthenium crystal was maintained at a temperature of 540 K during the copper deposition, it was concluded that the copper initially formed two-dimensional clusters even at the lowest coverages. At some point before completion of a monolayer, it was concluded that three-dimensional aggregates of copper were formed. From thermal desorption spectroscopy data, the activation energy for desorption of the copper was obtained over a range of surface coverages. Data were obtained in two separate investigations (Christmann *et al.* 1980, Vickerman *et al.* 1983). In the later investigation, it was reported that the activation energy was approximately 370 kJ/mol over a range of copper coverages from less than one-tenth of a monolayer to approximately one monolayer.

When the temperature of the ruthenium crystal was held at 1080 K during the copper deposition, it was concluded that the copper was dispersed as atoms on the ruthenium surface at the lowest coverages and that well-ordered two-dimensional islands formed as the coverage increased. Growth of the two-dimensional islands continued until a full monolayer was completed. Correspondingly, the activation energy for desorption of the copper varied markedly with copper coverage, increasing from 200 kJ/mol at the lowest coverages to 370 kJ/mol at coverages in the vicinity of a monolayer. The increase in activation energy was accompanied by an increase of six orders of magnitude in the pre-exponential factor in the Arrhenius equation. The increase in activation energy with coverage was attributed to the lateral binding between copper atoms associated with the formation and growth of the two-dimensional clusters. It was also reasoned that this change in the structure of the copper surface layer would lead to an increase in the entropy of desorption, which in turn would account for the increase in the pre-exponential factor. When the extent of deposition of copper was increased beyond the amount required to give a monolayer, the subsequent growth of the copper film was reported to occur layer-by-layer.

Other experiments by this same group showed an increase in work function of the ruthenium surface when copper was deposited on it. Again, data were obtained in two separate investigations (Christmann *et al.* 1980, Vickerman *et al.* 1983). The results of the later study exhibited a steady increase in work function with increased copper deposition to a plateau value at a coverage in the vicinity of one monolayer. It was concluded that a small amount of electron transfer occurred from ruthenium to copper, corresponding to a surface dipole moment of approximately 0·2 Debye.

Results of other investigators on the nature of copper deposits on Ru(0001) differ in several respects from those of Ertl and associates. In experiments conducted by Houston *et al.* (1986 a), copper was deposited on a ruthenium single crystal maintained at a temperature of 100 K. Measurements similar to those performed by the Ertl group were made after various amounts of copper had been deposited. From AES and LEED measurements, it was concluded that the copper grows as two-dimensional islands. The growth extends to a full monolayer, after which further copper deposition produces additional complete monolayers by the same two-dimensional growth process (layer-by-layer). The authors also concluded that the first copper layer was pseudomorphic with the Ru(0001) surface, and that subsequent layers have the Cu(111) structure. Thus, in contrast to the results of Ertl and associates for copper deposition on Ru(0001) maintained at 540 K, they found no evidence for the formation of three-dimensional aggregates of copper before a single monolayer was completed. Three-dimensional clustering of the copper was observed when the sample was annealed at 900 K after the copper deposition, but only for depositions in excess of the amount required for two monolayers. The growth mechanism for the first two monolayers appeared to be similar to that for the unannealed sample.

The work of Houston *et al.* showed a decrease in the work function of the surface when copper was deposited on the ruthenium. Deposition of one monolayer of copper decreased the work function by about 1·0 eV. When the sample was annealed at 900 K after the copper deposition, the extent of decrease was slightly lower. The change in work function differed in sign from that reported by the Ertl group, and indicated a small amount of electron transfer from copper to ruthenium. A decrease in work function is easier to understand, since the bulk of the available information on the work function of Ru(0001) (Himpsell *et al.* 1979, 1981, 1982, Jablonski *et al.* 1985) indicate a higher value, 5·1–5·5 eV, than the accepted value of 4·94 eV (Michaelson 1977) for Cu(111). The observation of an increase in work function in the earlier investigations of the Ertl group was apparently due to an inadvertent error in the measurement of the sign of the work function change by means of a Kelvin probe (see a paper by Park *et al.* 1987, in which their reference 25 cites a private communication from K. Christmann).

In the investigation by Park *et al.* in 1987, which utilized a sample of Ru(0001) grown epitaxially by vapour deposition of copper on to a Mo (110) surface, the findings were generally consistent with those of Houston *et al.* The only significant difference was the magnitude of the decrease in work function observed when copper was deposited on Ru(0001). The decrease found by Park *et al.* was about 60–70% smaller. This difference, and the general differences between the work of either of these groups and the earlier work of the Ertl group, indicate that subtle differences in the properties of the Ru(0001) surface or in the conditions for copper deposition can have a major effect on the results and conclusions. Factors such as surface cleanliness and roughness would appear to have an important influence on the morphology of copper on ruthenium.

3.1.1. *Xenon photoemission as a probe*

The effect of differences in the roughness of a ruthenium surface on the morphology of copper deposited thereon is clearly evident in our recent ultraviolet photoelectron spectroscopy (UPS) studies of xenon physisorbed on ruthenium–copper surfaces (Kim *et al.* 1987). In these studies the xenon was generally physisorbed at a temperature of 60 K. The sample was exposed to xenon at a pressure in the range of 10^{-8}–10^{-7} Torr for varying times. After a desired exposure, the sample was closed off from the xenon, and the pressure in the system decreased rapidly to about 10^{-10} Torr. A spectrum was then obtained by irradiating the physisorbed xenon with the radiation from a helium resonance lamp (He I, 21·1 eV). At 60 K, a monolayer of xenon is formed after a xenon exposure of 10–15 langmuirs (1 langmuir = 10^{-6} Torr s). In some experiments at high xenon coverages, or in experiments at higher adsorption temperatures of 75–90 K, spectra were taken while the system was open to the xenon at a constant pressure between 10^{-7} and 10^{-6} Torr.

The irradiation of the physisorbed xenon atoms leads to emission of electrons from $5p_{3/2}$ and $5p_{1/2}$ states. For xenon adsorbed on a smooth Ru(0001) surface, the binding energies of electrons in these states (relative to the Fermi level of the ruthenium) are approximately 5·6 and 6·8 eV, respectively, at monolayer coverage (Wandelt *et al.* 1981). With a value of 5·5 eV for the work function of Ru(0001), the binding energies relative to the vacuum level are approximately 11·1 and 12·3 eV, which are about 1·1 eV lower than the corresponding value for gaseous xenon atoms. For xenon adsorbed on surfaces comprising different crystallographic planes of a variety of metals, it has been observed that either 5p binding energy relative to the vacuum level is virtually constant (Wandelt 1984). That is, the sum of the work function of the metal and the electron binding energy relative to the Fermi level for a given 5p state of xenon is independent of the metal and the particular plane chosen as the surface. For a non-uniform surface, the binding energy relative to the Fermi level depends on the kind of site on which the xenon is adsorbed (Küppers *et al.* 1979, Wandelt 1984). Consequently, a xenon photoemission spectrum for a surface with various types of sites is more complex than a spectrum for a uniform surface.

Features due to defect sites are apparent in photoemission spectra for xenon atoms adsorbed on a rough Ru(0001) surface for which the defects constitute about 15% of the total sites (figure 10). The surface was obtained by bombardment of a smooth Ru(0001) surface with 2 keV argon ions. The smooth Ru(0001) surface was originally prepared by annealing a carefully cleaned sample *in situ* at a temperature of 1500 K. The features

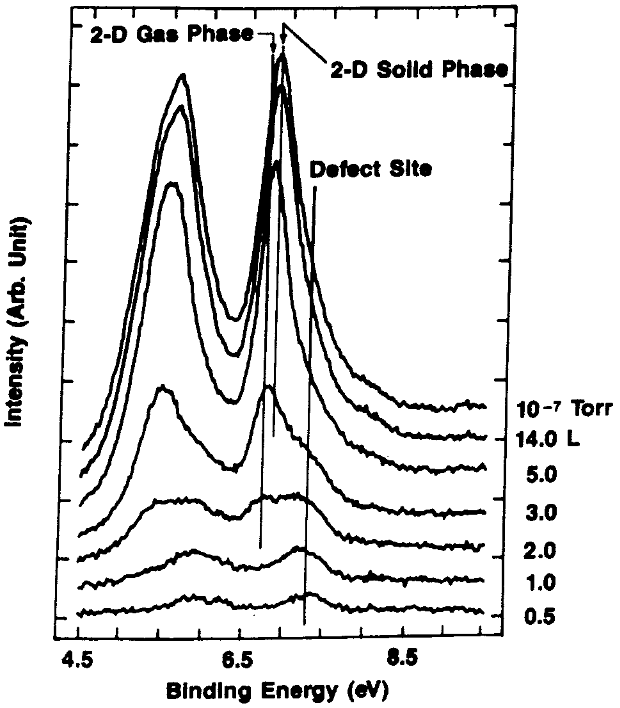

Figure 10. Xe $5p_{3/2,1/2}$ photoemission spectra for Xe atoms adsorbed on a rough Ru(0001) surface prepared by bombardment with argon ions. The spectra were obtained after various Xe exposures (0·5–14 L, where L is an abbreviation for langmuir), except for one spectrum obtained while Xe was present at a pressure of 10^{-7} Torr. The dose of argon ions was equivalent to 0·5 monolayer. An exposure of 14 langmuirs corresponds to complete monolayer coverage (Kim *et al.* 1987).

attributed to xenon atoms on defect sites are the $5p_{3/2}$ and $5p_{1/2}$ lines centered at binding energies of about 5·9 and 7·3 eV in the spectra obtained after low xenon exposures (0·5 and 1 langmuir). According to a line shape analysis, these lines do not grow when the exposure is increased above 2 langmuirs, which indicates that the defect sites are filled. After 2 langmuirs exposure, other lines associated with the remainder of the Ru(0001) surface become evident, and, after 3 langmuirs exposure, they are the major lines. At monolayer coverage they are centred at binding energies of 5·6 and 6·8 eV, as in the case of a smooth Ru(0001) surface. The sequential appearance and growth of the different lines with increasing xenon exposure indicate that xenon atoms adsorbed on the Ru(0001) surface at 60 K are mobile and that they preferentially occupy the defect sites. The intensities of the lines at 5·9 and 7·3 eV observed at the lowest xenon exposures were found to increase with increasing degree of argon ion bombardment and to decrease upon annealing. These findings are consistent with the assignment of the lines to xenon atoms adsorbed on the defect sites.

Our xenon photoemission studies of Ru–Cu surfaces were concerned with the following questions: How is the interaction of copper with a given crystal plane of ruthenium affected by the presence of defects in the plane, and how does information on single-crystal specimens relate to actual catalyst surfaces? To address these questions, we studied Cu/Ru surfaces prepared by deposition of submonolayer amounts of copper on smooth and rough Ru(0001) surfaces and on a ruthenium powder. The ruthenium samples were maintained at a temperature of 100 K during the copper deposition. The smooth and rough Ru(0001) surfaces were prepared in the manner described in the previous paragraph. The ruthenium powder had a surface area of approximately 5 m^2/g and was typical of the material used as a reference catalyst in the investigation on unsupported ruthenium–copper catalysts which provided the data for the broken line in figure 3.

Photoemission spectra for xenon physisorbed on a surface prepared by vapour deposition of 0·4 monolayer of copper on to smooth Ru(0001) are shown in figure 11. We refer to this surface as Cu/smooth Ru(0001). Prior to adsorption of xenon, the surface was annealed at a temperature of 520 K. The spectra were obtained after various xenon exposures (0·5–14 langmuirs), except for one spectrum obtained with xenon present at a pressure of 10^{-7} Torr. The $5p_{3/2}$ and $5p_{1/2}$ lines for xenon on Ru(0001), with maxima at energies of approximately 5·6 and 6·8 eV at monolayer coverage, are clearly evident in the figure. The presence of these lines is reasonable, since 60% of the ruthenium surface was not covered by copper. For xenon exposures of 5 langmuirs and higher, a Xe $5p_{1/2}$ line at approximately 7·7 eV is also observed. This line is associated with Cu(111) islands on the surface, since a line at the same energy is expected for a monolayer of Cu(111) on ruthenium (Kim *et al.* 1987). Spectra on the unannealed surface did not exhibit a line at 7·7 eV, indicating that the islands were formed as a result of the annealing at 520 K. In the spectrum obtained after a xenon exposure of 3 langmuirs, a line at an energy of about 7·3 eV is observed. This line is associated with Ru–Cu mixed sites such as those present at edges of copper islands. It is interesting to note that xenon atoms are adsorbed on Ru and Ru–Cu mixed sites in preference to being adsorbed on copper islands. Thus, xenon atoms adsorbed during exposures up to 3 langmuirs are not present on the copper islands. Only after an exposure of 5 langmuirs is the line for xenon on copper islands observed.

The spectra for xenon exposures $\geqslant 5$ langmuirs can be fitted very well with three sets of $5p_{3/2,1/2}$ lines, as shown in figure 12 for the 11 langmuir spectrum. Since an exposure of 11 langmuirs leads to an almost complete xenon monolayer, the Xe/Ru,

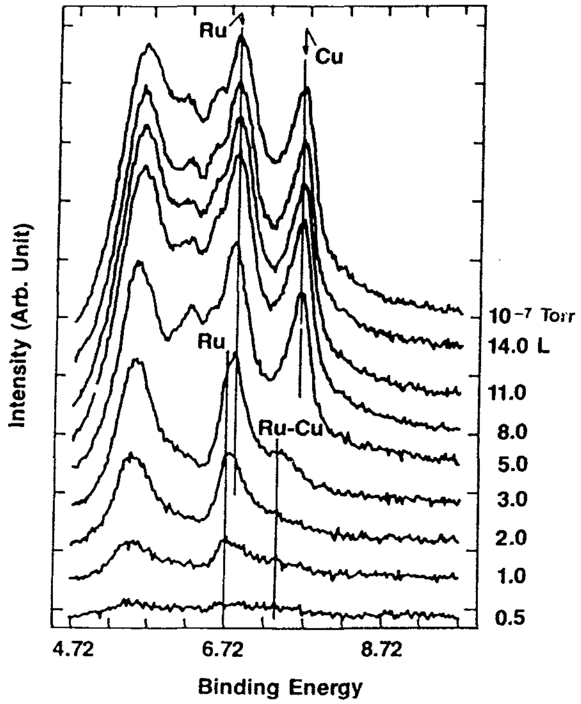

Figure 11. Xe $5p_{3/2,1/2}$ photoemission spectra for Xe atoms adsorbed on a surface prepared by vapor deposition of 0·4 monolayer of copper onto a smooth Ru(0001) surface maintained at 100 K. The surface was annealed at 520 K prior to Xe adsorption. The spectra were obtained after various Xe exposures, except for one spectrum obtained with Xe present at a pressure of 10^{-7} Torr (Kim *et al.* 1987).

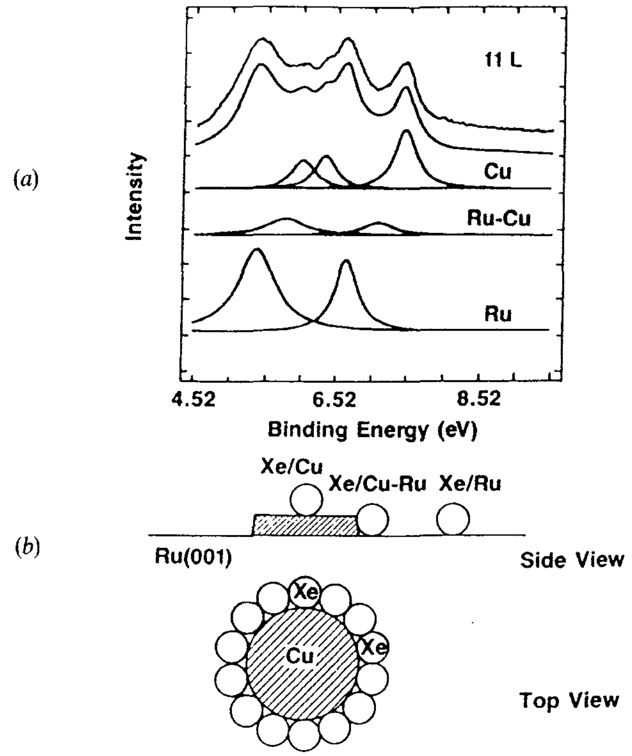

Figure 12. (*a*) Deconvolution of the 11 langmuir spectrum from figure 11. (*b*) Schematic representation of Xe adsorption sites (Kim *et al.* 1987).

Xe/Ru–Cu, and Xe/Cu line intensities provide a measure of the exposed Ru(0001) area, the total perimeter of the copper islands, and the copper-covered area, respectively. If we assume that the copper islands are circular in shape, their size (assuming they are uniform) can be determined from the Xe/Ru–Cu and Xe/Cu line intensities. We estimate that the copper islands consist of about 200 copper atoms. The Xe $5p_{3/2}$ doublet in the spectral lines shown for the copper islands in figure 12 is characteristic of xenon atoms which themselves form islands on a flat copper substrate (Kim *et al.* 1987).

The 7·7 eV line is absent from photoemission spectra for xenon adsorbed on the specimen prepared by deposition of 0·3 monolayer of copper on to rough Ru(0001). We refer to this specimen as Cu/rough Ru(0001). It was annealed at 520 K prior to xenon adsorption at 60 K. The only $5p_{1/2}$ lines observed in the spectra are those at 6·8 and 7·3 eV, as shown in figure 13. Thus, Cu(111) islands are not present. The line at 7·3 eV is observed at xenon exposures as low as 0·5 langmuir. It is too intense to be assigned solely to xenon atoms on ruthenium defect sites (compare figures 10 and 13). In addition, its growth mode is different. That is, its intensity increases continuously for xenon exposures up to 11 langmuirs, unlike that of the line at 7·3 eV for xenon on ruthenium defects in figure 10. Moreover, it differs significantly from the line at 7·3 eV in the spectrum for the Cu/smooth Ru(0001) surface in figure 11. At full surface coverage by xenon, it is more intense. Also, its intensity relative to that of the line at 6·8 eV exhibits a different dependence on xenon exposure, as can be seen readily from a comparison of figures 11 and 13. In figure 13 we note that it is surpassed in intensity by the line at 6·8 eV only after a xenon exposure of 3 langmuirs, whereas in figure 11 the

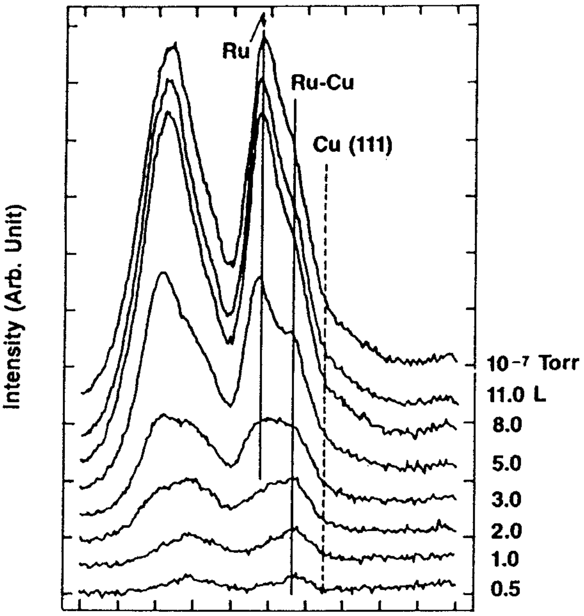

Figure 13. Xe $5p_{3/2,1/2}$ photoemission spectra for Xe atoms adsorbed on a surface prepared by vapour deposition of 0·3 monolayer of copper on to a rough Ru(0001) surface. The surface was annealed at 520 K prior to Xe adsorption. The spectra were obtained after various Xe exposures. One spectrum was also obtained with Xe present at a pressure of 10^{-7} Torr (Kim *et al.* 1987).

line at 7·3 eV is already less intense than the line at 6·8 eV after an exposure of 1 langmuir. These results indicate more extensive interaction of adsorbed Xe atoms with Ru–Cu mixed sites on the Cu/rough Ru(0001) surface than on the Cu/smooth Ru(0001) surface. The simplest explanation for this is a higher concentration of Ru–Cu mixed sites on the rough Ru(0001) surface, as a consequence of the more highly dispersed nature of the copper on this surface. The higher degree of dispersion of the copper is presumably due to the presence of the defects, which interfere with the formation of large copper islands.

Spectra of xenon physisorbed on the surface existing after deposition of copper on the ruthenium powder are shown in figure 14. The powder was kept at a temperature of 100 K during the deposition, and was subsequently annealed at 650 K prior to the low temperature xenon adsorption. The copper coverage was estimated to be 0·5 monolayer. The spectra in figure 14 were obtained with xenon present at various pressures. They bear a much closer resemblance to the spectra in figure 13 for the Cu/rough Ru(0001) surface than to those in figure 11 for the Cu/smooth Ru(0001) surface. The presence or absence of a line at 7·7 eV is the feature of primary interest here. In common with the spectra for the Cu/rough Ru(0001) surface in figure 13, the spectra in figure 14 show no evidence of a line at 7·7 eV. In marked contrast, such a line is clearly evident in the spectra for the Cu/smooth Ru (0001) surface in figure 11, at least after xenon exposures of 5 langmuirs and higher. Since this line is identified with the presence

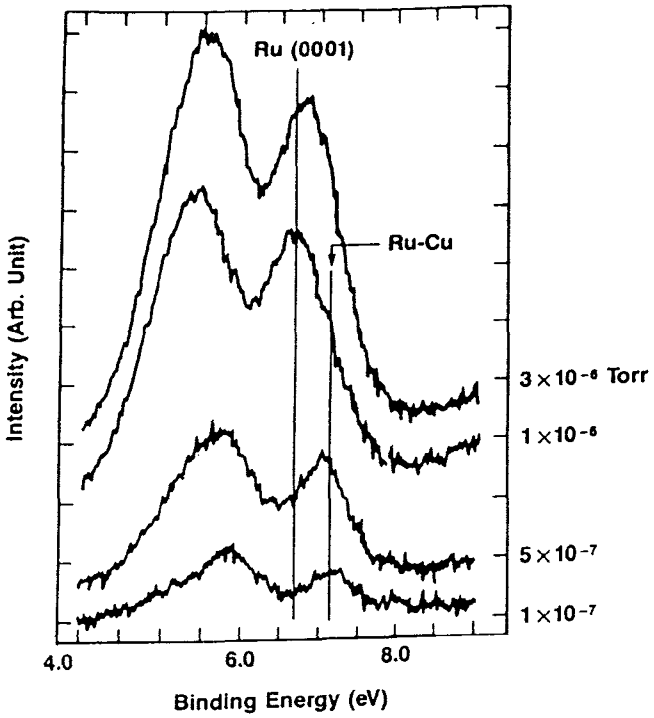

Figure 14. Xe $5p_{3/2,1/2}$ photoemission spectra for Xe atoms adsorbed on a surface prepared by vapour deposition of 0·5 monolayer of copper on to a Ru powder. The Xe atoms were adsorbed at 80 K. The spectra were obtained with Xe present at various pressures. The spectrum taken at a pressure of 10^{-6} Torr corresponds to complete monolayer coverage (Kim *et al.* 1987).

of copper islands on the ruthenium surface, we conclude that the Cu/Ru powder surface, like the Cu/rough Ru(0001) surface, does not exhibit such islands. Only on the smooth Ru(0001) surface are the copper islands observed. Thus, the way in which copper is distributed over the surface of ruthenium is sensitive to the detailed nature of the surface. Moreover, copper deposited on a smooth Ru(0001) surface does not provide a good model of a ruthenium–copper catalyst. A surface corresponding more closely to that of a typical catalyst may be obtained by the introduction of defects into the Ru(0001) surface prior to deposition of the copper.

3.2. *Electronic interaction between copper and ruthenium*

In the first investigations on Ru–Cu catalysts (Sinfelt 1973 a, Sinfelt *et al.* 1976), the conclusion that copper associated with ruthenium in preference to forming separate copper crystallites suggested that a significant chemical or electronic interaction between the two elements existed. However, a study of unsupported Ru–Cu catalysts by X-ray photoelectron spectroscopy (XPS), while providing additional evidence that copper formed an adsorption layer on ruthenium, showed that the interaction between ruthenium and copper is not revealed simply by shifts in core level binding energies (Helms and Sinfelt 1978). The absence of core level shifts for other bimetallic systems of Group VIII and Group IB elements, such as nickel–copper and palladium–silver, had also been noted (see, for example, Watson and Perlman 1975). It has been suggested that the extent of charge transfer from one type of atom to the other is small in such systems (Lang and Ehrenreich 1968). As discussed earlier, work function measurements on Cu/Ru(0001) are consistent with a small transfer of electronic charge from copper to ruthenium (Houston *et al.* 1986 a).

Ultraviolet photoelectron spectroscopy (UPS) has been employed by several groups to probe the electronic properties of Cu/Ru(0001) surfaces (Richter *et al.* 1981, Vickerman *et al.* 1983, Houston *et al.* 1986 b, 1987). This type of spectroscopy provides information on the valence bands of the metals. The conclusions reached by the various groups differed significantly. In the work of Vickerman *et al.* (1983), the Cu/Ru surfaces were prepared by depositing copper on the ruthenium at temperatures near 1000 K. No significant shifts in the energies of either the copper or ruthenium d-states were detected. It was concluded that the copper was present as a two-dimensional layer with an electronic band structure of its own, essentially unperturbed by the underlying ruthenium. On the other hand, Richter *et al.* (1981), who apparently used Cu/Ru surfaces prepared at room temperature, reported that the d-band of copper was shifted to a lower energy and was broadened. They suggested a mixing of the d-states of copper and ruthenium. Such a mixing of d-states was again proposed by Houston *et al.* (1986 b, 1987), who also used Cu/Ru surfaces prepared at room temperature in their angle-resolved UPS experiments. They concluded that the mixing of Cu(3d) and Ru(4d) states produces a Ru–Cu interface state, i.e. a state which exists only when there is an interface between the two metals. The state was identified with a feature appearing in the spectra at an energy about 1·5 eV below the Fermi level. Such a feature was not observed in spectra for either clean Ru(0001) or for the surface of bulk copper. These investigators also made theoretical calculations which provided support for the existence of such a state at an energy within 0·1 eV of the experimental value. The calculations were made with the surface linearized augmented plane wave (SLAPW) method (Andersen 1975, Hamann *et al.* 1981, Mattheiss and Hamann 1986). Another interface state at an energy about 3·6 eV below the Fermi level was also indicated by the calculations. It was concluded that the two interface states were a bonding–antibonding pair of states largely formed from Cu(3d) and Ru(4d) orbitals. The experimentally detected state was the antibonding one. At the energy calculated for the bonding state, there are also pure Cu d-states, and hence this state was not resolved in the spectra.

X-ray absorption spectroscopy has also been utilized to probe electronic interaction between ruthenium and copper (Sham *et al.* 1988). In this work, bimetallic clusters of ruthenium and copper were formed on the (111) face of a copper single crystal by a procedure which involved deposition of $Ru_3(CO)_{12}$ on the copper at 223 K, decomposition of the carbonyl by electron bombardment, and subsequent annealing at high temperature (723 K). Various types of experimental data were used to demonstrate that ruthenium entities produced by the decomposition of the carbonyl were covered by copper transported from the bulk crystal during the annealing step. Conclusions regarding the electronic interaction of ruthenium with copper were derived from data on the intensity and width of the absorption threshold resonance line at the L_{III} absorption edge of ruthenium. The resonance involves electronic transitions from the $2p_{3/2}$ core level to unoccupied d-states of the absorbing atom (Cauchois and Mott 1949). From the intensity of the line one can therefore obtain information on the number of unoccupied d-states. The intensity of the line for the ruthenium–copper clusters was smaller than it was for a thin film of pure ruthenium. The width of the line was also slightly smaller. It was therefore concluded that copper has the effect of decreasing the number of unoccupied d states of the ruthenium and of narrowing the d-band as well.

3.3. *Chemisorption of gases on Cu/Ru(0001)*

3.3.1. *Hydrogen chemisorption*

The chemisorption of hydrogen on surfaces prepared by deposition of copper on Ru(0001) was first investigated by the Ertl group (Shimizu *et al.* 1980). The temperature of the ruthenium was 540 K during the copper deposition. In thermal desorption spectroscopy studies of hydrogen preadsorbed at 200 K, it was observed that the hydrogen chemisorption capacity of the ruthenium surface was suppressed drastically by the presence of the copper. From the slope of a log–log plot of hydrogen adsorption versus the fraction of surface ruthenium atoms not covered by copper, it was concluded that a site consisting of 5–10 contiguous ruthenium atoms was required for the chemisorption. In a subsequent report from the same laboratory (Vickerman and Christmann 1982) on the chemisorption of deuterium on Cu/Ru(0001) surfaces prepared by deposition of copper on the ruthenium at two different temperatures (540 and 1080 K), a site consisting of 3–6 ruthenium atoms was inferred from thermal desorption spectroscopy data. The quantitative difference between this result and that from the earlier investigation was attributed to an improved determination of the coverage of ruthenium by copper.

In later work (Yates *et al.* 1985) on hydrogen chemisorption on Cu/Ru(0001), in which the surface was prepared by deposition of copper on to ruthenium maintained at a temperature of 100 K, a very different result was obtained from thermal desorption spectra. A plot of coverage of the surface by hydrogen versus coverage by copper gave a straight line with a slope of -1. Thus, the hydrogen chemisorption capacity decreased by an amount of one hydrogen atom per copper atom deposited on the surface. Annealing the Cu/Ru(0001) surface for 30 s at a temperature of 1080 K after the deposition of the copper had no effect on the results. It was concluded that the copper was present on the ruthenium surface in the form of two-dimensional (one atom thick) islands which eventually coalesce to form a complete overlayer. The fact that the results and conclusions of this investigation differ substantially from those of Shimizu *et al.* (1980) and of Vickerman and Christmann (1982) provides further evidence that differences in the details of preparation of the surface may influence the morphology of copper on ruthenium. Consequently, a very thorough characterization of the surface becomes especially important in rationalizing significant differences in the chemisorption results of different investigators.

In other studies of hydrogen chemisorbed on Cu/Ru(0001) surfaces, Feilbelman and Hamann (1986) calculated that the strength of binding of hydrogen atoms on a pseudomorphic monolayer of copper on Ru(0001) was slightly greater (by 0·05 eV) than it was on the (111) plane of a copper crystal. The calculations were made by the surface linearized augmented plane wave (SLAPW) method (Andersen 1975, Hamann *et al.* 1981, Mattheiss and Hamann 1986). However, temperature programmed desorption (TPD) studies (Goodman *et al.* 1985) indicated that the binding of hydrogen atoms to the pseudomorphic copper layer is weaker, since the TPD peaks associated with desorbing H_2 shift to higher temperatures as the coverage of ruthenium by copper increases from one to a number of monolayers. The TPD studies were made with Cu/Ru surfaces prepared by depositing copper on hydrogen-covered Ru(0001) maintained at a temperature of 100 K. It was concluded that the copper displaced the hydrogen atoms from the ruthenium and that the hydrogen was transported to the outer surface of the copper overlayer, from which desorption of H_2 occurred during the TPD experiments. Moreover, the authors concluded that the spillover of hydrogen to the copper surface occurred even after many layers of copper were deposited on the hydrogen-covered ruthenium surface.

3.3.2. *Carbon monoxide chemisorption*

The early studies on Ru–Cu catalysts (Sinfelt 1973 a) showed that the capacity for carbon monoxide chemisorption at room temperature decreased as the atomic ratio of copper to ruthenium increased. It has also been observed in thermal desorption spectroscopy studies that the amount of carbon monoxide chemisorbed on Cu/Ru(0001) surfaces decreases with increasing coverage of the ruthenium by copper (Vickerman *et al.* 1981, Houston *et al.* 1986 a, Park *et al.* 1987). Copper itself does not chemisorb carbon monoxide at room temperature (Hollins and Pritchard 1979, Richter *et al.* 1981). The measurements of carbon monoxide chemisorption capacities of the Ru–Cu catalysts and the Cu/Ru(0001) specimens also indicate that carbon monoxide is not chemisorbed at room temperature on copper which is present on the surface of ruthenium. Good evidence for this is also available from recent Fourier transform infrared spectroscopy (FTIR) studies of carbon monoxide chemisorbed on Cu/Ru(0001) surfaces (Hoffman and Paul 1987 a). When carbon monoxide is chemisorbed at temperatures higher than 250 K on Cu/Ru(0001) surfaces containing submonolayer amounts of copper, the only features observed in the spectra are attributable to chemisorption on the exposed Ru(0001) surface. As the coverage by copper increases, these features become less intense.

Chemisorption on the copper is readily observed when Cu/Ru(0001) is exposed to carbon monoxide at lower temperatures. Investigations including adsorption temperatures in the range of 85–150 K have been reported (Vickerman *et al.* 1981, Paul and Hoffmann 1986, Hoffmann and Paul 1987 a, b, Rocker *et al.* 1987). For submonolayer coverages of the ruthenium by copper, infrared spectra exhibit bands due to carbon monoxide chemisorbed on both copper and ruthenium sites on the surface. An indication of carbon monoxide chemisorbed on mixed Ru–Cu sites has been obtained from studies employing secondary ionization mass spectrometry, in which it was reported that the species $RuCuCO^+$ was present among the cluster ions emitted from the surface as a result of exposure to an argon ion beam (Harendt *et al.* 1986).

For Cu/Ru surfaces prepared by deposition of copper at 85 K, followed by annealing at 540 K, the infrared absorption band for the copper sites is observed in the frequency range of 2070–2082 cm^{-1}, while that for the ruthenium sites is found in the range of 1990–2056 cm^{-1} (Hoffmann and Paul 1987 a). These C–O stretching frequencies are characteristic of the linear form of adsorbed CO, in which the molecule is coordinated to a single metal atom in the surface. The range of frequencies for each of the bands shows the extent to which the frequency increases with increasing coverage of the surface by carbon monoxide. At constant carbon monoxide coverage of the surface, the C–O stretching frequency is independent of the degree of coverage of ruthenium by copper, at least for copper coverages in the range of 0·25–1·0. Furthermore, for this entire range of copper coverages, the frequency shift observed with changing carbon monoxide coverage is identical. On the basis of these observations, it was concluded that islands of copper are present on the ruthenium even at low copper coverages. As the amount of copper deposited on the ruthenium increases, the islands eventually coalesce to form a two-dimensional copper film which completely covers the ruthenium. When copper in excess of that required to form a complete monolayer is deposited on the surface, a layer-by-layer growth occurs.

The infrared spectrum of carbon monoxide chemisorbed on a multilayer copper film exhibits a relation between C–O stretching frequency and carbon monoxide coverage which is significantly different from the corresponding relation for a single copper monolayer. Thus, for a copper film consisting of eight layers, there is a small red shift in frequency (from 2077 to 2075 cm^{-1}) with increasing carbon monoxide coverage. This compares with a blue shift (from 2070 to 2082 cm^{-1}) for a single layer. This difference provides evidence that the first layer of copper atoms, as a consequence of its interaction with the underlying ruthenium, possesses electronic properties which are measurably different from those for the surface atoms of the multilayer film. Infrared data on C–O stretching frequencies for carbon monoxide chemisorbed on the (111) face of a copper single crystal (Hollins and Pritchard 1979, Hayden *et al.* 1985) are in close agreement with the data for the multilayer copper film on ruthenium.

Thermal desorption spectroscopy studies have shown that the first layer of copper atoms on ruthenium binds carbon monoxide more strongly than does the (111) face of a copper single crystal (Richter *et al.* 1981, Vickerman *et al.* 1981, Houston *et al.* 1986 a, Paul and Hoffmann 1986). This result is consistent with the infrared data which indicated differences in the electronic properties of copper present in the two environments. With regard to desorption of carbon monoxide from ruthenium sites in the presence of submonolayer amounts of copper on the surface of Ru(0001), it has been found that the desorption temperature decreases with increasing copper coverage, at least for some of the ruthenium sites. However, this evidence of a decrease in the strength of binding of carbon monoxide to ruthenium is not accompanied by a significant shift in the C–O stretching frequency, which indicates that the electronic properties of the ruthenium are not affected significantly by the copper (Hoffmann and Paul 1987 a). The decrease in desorption temperature at high copper coverage has therefore been attributed to an effect of copper in suppressing the formation of large ordered domains of CO molecules on the ruthenium. Attractive forces between the CO molecules lead to the domains.

Since the bonding of carbon monoxide to copper is much weaker than the bonding to ruthenium, the possibility of migration of CO from copper to ruthenium presents itself. Evidence for such a process occurring at temperatures of 150–200 K was obtained by Hoffmann and Paul (1987 a) in their studies of CO adsorbed on Cu/Ru(0001) surfaces containing submonolayer amounts of copper. The experiments involved adsorption of CO at 85 K in amounts corresponding to partial coverage of both ruthenium and copper sites, followed by annealing at temperatures of 150–200 K. The annealing temperatures were lower than the temperature (250 K) for desorption of CO from the copper. Over the range of annealing temperatures employed, the intensity of the band for CO on ruthenium increased, while the band for CO on copper became less intense and eventually disappeared.

Fourier transform infrared spectroscopy of chemisorbed CO has been shown to be a sensitive probe of the degree of dispersion of copper on Ru(0001) (Hoffmann and Paul 1987 b). A characteristic C–O stretching frequency of 2138 cm^{-1} was attributed to CO adsorbed on isolated copper atoms on Ru(0001). The latter were obtained by deposition of a very small amount of copper on the ruthenium (0·03 coverage) at a low temperature (85 K) with no subsequent annealing step. The low coverage and low temperature minimized the possibility of agglomeration of the copper atoms. At slightly higher coverages by copper (0·05 and 0·12), new features were observed at frequencies of 2135 and 2123 cm^{-1}, which were tentatively attributed to Cu_2 and Cu_3 clusters. These assignments received support from matrix isolation studies of copper clusters by Moskovits and Hulse (1976), in which CO bonded to the copper exhibited a similar range of stretching frequencies for clusters containing 2–4 copper atoms. The frequency decreased as the number of copper atoms increased.

When the copper coverage was increased to 0·35, a band was observed at an even lower frequency, 2121 cm^{-1}. This band was attributed to CO adsorbed on small two-dimensional copper aggregates. At a still higher copper coverage of 1·0, annealing the surface at a temperature of 250 K prior to CO adsorption at 85 K led to a band at 2105 cm^{-1} in addition to the one at 2121 cm^{-1}. It was attributed to CO adsorption on three-dimensional copper aggregates. Additional annealing at 350 K followed by re-exposure of the surface to CO at 85 K produced a band at 2080 cm^{-1} at the expense of the higher frequency bands at 2121 and 2105 cm^{-1}. A C–O stretching frequency of 2080 cm^{-1} is characteristic of either smooth islands of copper or a complete epitaxial monolayer of copper on ruthenium, depending on the copper coverage. For multilayer copper films prepared by deposition of the copper on ruthenium at 85 K, with no subsequent annealing, CO adsorption led to a band at 2098 cm^{-1}. This frequency is in the region characteristic of high index planes of copper single crystals, and is characteristic of a rough surface. From these various results, it is abundantly clear that Fourier transform infrared spectroscopy of adsorbed CO is an effective probe for obtaining information on the nature of the copper entities present on ruthenium surfaces.

3.3.3. *Oxygen, nitrous oxide, and methanol chemisorption*

Oxygen chemisorbs dissociatively on Ru(0001) with an initial sticking coefficient of 0·7 (Madey *et al.* 1975). On the (111) face of a copper single crystal, the initial sticking coefficient is several orders of magnitude lower (Habraken *et al.* 1979). For

Cu/Ru(0001) surfaces, the sticking coefficient decreases gradually as the degree of coverage of ruthenium by copper increases (Shi *et al.* 1981). At a copper coverage of one monolayer, the initial sticking coefficient is about one half the value for pure Ru(0001). For copper coverages as high as three monolayers, the sticking coefficient is still two orders of magnitude higher than the value of 10^{-3} for the (111) face of a copper single crystal (Shi *et al.* 1981). Thus, the interaction of the copper with oxygen is strongly influenced by the underlying ruthenium.

The interaction of a nitrous oxide molecule with Ru(0001) yields a chemisorbed oxygen atom and a molecule of nitrogen in the gas phase

$$N_2O \rightarrow O(ads) + N_2$$

The symbol (ads) signifies an adsorbed species. The reaction probability decreases with increasing temperature (Shi *et al.* 1981), presumably because the heat of adsorption of N_2O in a precursor state is greater than the activation energy for dissociation of the adsorbed N_2O. On Cu(111) the temperature dependence is the reverse of that observed for Ru(0001). In contrast to the results for the dissociative chemisorption of oxygen, data on the dissociative chemisorption of N_2O have shown that small amounts of copper on Ru(0001) lead to a precipitous decline in the initial reaction rate (Shi *et al.* 1981). At a copper coverage of 0·14, the initial rate at 520 K is only one seventh of that observed for pure Ru(0001), which suggests that a copper atom has a deactivating effect on a large number of ruthenium atoms in its vicinity. With further deposition of copper, the reaction rate continues to decline, but the influence of the additional copper is much less pronounced. At the higher copper coverages, ordered groups of copper atoms (islands) are formed, and Shi *et al.* reason that such a group of atoms would deactivate a smaller ruthenium area than would an equal number of isolated copper atoms.

When ruthenium is covered by a complete monolayer of copper, the rate of dissociative chemisorption of N_2O is three orders of magnitude higher than it is on the (111) face of a copper single crystal (Shi *et al.* 1981). Even after three monolayers of copper are deposited on the ruthenium, the rate does not fall to the value observed for pure copper. Again, there is a marked effect of the ruthenium on the properties of the copper.

Studies of the interaction of methanol with Ru(0001) and Cu/Ru(0001) surfaces have been conducted with the aid of thermal desorption and electron energy loss spectroscopies (Paul and Hoffmann 1986). On a pure ruthenium surface methoxy groups formed in the dissociative chemisorption of methanol decompose with release of hydrogen and carbon monoxide from the surface at desorption temperatures of approximately 350 and 450 K, respectively. This irreversible chemisorption process is not observed on pure copper and is insignificant on a monolayer of copper on ruthenium. However, if preadsorbed oxygen atoms are present on the copper, the interaction of methanol with the surface changes markedly. In addition to hydrogen and carbon monoxide, formaldehyde is released from the surface in thermal desorption experiments. The formaldehyde and carbon monoxide desorb at a temperature of approximately 400 K. As the coverage of ruthenium by copper increases from one to a number of monolayers, the formation of formaldehyde relative to carbon monoxide increases. At constant copper coverage, a higher oxygen coverage also increases the ratio of formaldehyde to carbon monoxide. For submonolayer coverages of ruthenium by copper, no formaldehyde is observed until the combined copper plus oxygen coverage approaches unity.

3.4. *Catalytic reactions on Cu/Ru(0001)*

In the original investigation of ruthenium–copper bimetallic cluster catalysts (Sinfelt 1973 a), several reactions were studied, the hydrogenolysis of ethane to methane, the dehydrogenation of cyclohexane to benzene, and the hydrogenolysis of cyclohexane to low molecular weight alkanes. The same reactions have recently been investigated on single crystal samples in which copper is deposited on the (0001) face of ruthenium (Peden and Goodman 1986 a, b, 1987).

When ethane hydrogenolysis was studied on such samples, Peden and Goodman (1986 a) reported that the reaction rate was approximately proportional to the fraction of the ruthenium surface not covered by copper, over the range of copper coverages from 0 to 0·3. This result contrasts with the dramatic effect of copper on the hydrogenolysis activity of ruthenium in actual catalysts, which was considered earlier in this article. The experiments with catalysts have been reported in a number of different investigations (Sinfelt 1973 a, Sinfelt *et al.* 1976, Haller *et al.* 1983, Rouco *et al.* 1983).

The copper in the single crystal samples was reported to be present as two-dimensional islands, and the effect of the copper was simply to block active ruthenium sites on a one-to-one basis. It has been concluded that the distribution of the copper on the surface of ruthenium in actual catalysts is very different from that in single crystal samples, on the basis of studies of the photoemission of electrons from xenon atoms physisorbed on the two types of surfaces (Kim *et al.* 1987). If the required site for ethane hydrogenolysis comprises an array of ruthenium atoms rather than a single atom, the probability of finding copper adsorbed on such an array would be much greater if the copper were randomly distributed as atoms or small groups of atoms than if it were present as large islands on the surface. The randomly distributed copper (which is inactive for the reaction) would therefore be much more effective in inhibiting catalytic activity. Consequently, the copper present at the surface of small Ru–Cu aggregates or clusters could have an effect on catalytic activity which is very different from that observed when copper is deposited on the smooth (0001) surface of a ruthenium single crystal.

One might also consider this matter from the point of view that defect sites on a ruthenium surface could be more active than normal sites, whether or not the reaction requires a large array of ruthenium atoms in a site. If there is preferential interaction of copper with the defects, as can be inferred from the results of the xenon photoemission studies discussed earlier, it would be reasonable for copper to have a different effect on the catalytic activity of ruthenium when defects are present. Consequently, the effect of copper on catalytic activity could well be different for a catalyst in which copper is associated with defect ruthenium sites than it is for a smooth (0001) plane of ruthenium.

In studies of cyclohexane dehydrogenation to benzene on Cu/Ru(0001), it has been reported (Peden and Goodman 1986 b) that the reaction rate is higher on a Ru(0001) surface covered by copper than it is on pure Ru(0001), despite the fact that pure copper is less active than pure ruthenium for the reaction. The rate has a maximum value when the amount of copper present is sufficient to cover three-fourths of the ruthenium surface, at which point the rate is higher than that on pure ruthenium by a factor of eight. The effect of copper on the activity of ruthenium for this reaction is very different from what it was for ethane hydrogenolysis.

Why does the deposition of Cu on Ru(0001) increase the rate of cyclohexane dehydrogenation to a level higher than that obtained with the pure ruthenium surface? The higher catalytic activity is surprising, since the ability of copper itself to catalyse the reaction is lower than that of ruthenium. One might have expected the catalytic activity to decline, since coverage of the active ruthenium surface with relatively inactive copper decreases the number of ruthenium sites available for the reaction. Contrary to this simple view, the interaction between the ruthenium and copper apparently increases the catalytic activity of one or both components.

The view is commonly held that cyclohexane dehydrogenation does not require a site consisting of a large array of active metal atoms (Sinfelt 1977). For submonolayer coverages of ruthenium by copper, exposed ruthenium atoms in the vicinity of copper could conceivably be more effective than pure ruthenium for cyclohexane dehydrogenation, possibly because of a weaker binding of the benzene product. If desorption of benzene from ruthenium were the rate-limiting step in the reaction, a weaker binding would lead to a higher rate, as suggested in early studies by the present author (Sinfelt *et al.* 1972, Sinfelt 1973 a).

One might also propose that copper on the surface of ruthenium would be more effective than the surface of pure copper as a cyclohexane dehydrogenation catalyst. It may even be more effective than the surface of pure ruthenium, according to the data reported by Peden and Goodman (1986 b, 1987). The data showed that a Cu/Ru(0001) surface prepared by deposition of an amount of copper in excess of that required to produce a complete monolayer of copper on the ruthenium is still significantly more active than the pure ruthenium surface. If a complete monolayer of copper is indeed present on the ruthenium (with no exposed ruthenium sites), we are left with the conclusion that the copper overlayer itself is a more active catalyst than pure Ru(0001) for the dehydrogenation of cyclohexane to benzene. The possibility that ruthenium could have a promotional effect on the catalytic activity of a copper overlayer for cyclohexane dehydrogenation has been suggested earlier in connection with a discussion of this reaction on typical Ru–Cu catalysts (Sinfelt 1983).

We would expect the surface species involved in the cyclohexane dehydrogenation reaction to be bound much more strongly to pure ruthenium than to pure copper. The rate-limiting step on pure copper might well be chemisorption of the cyclohexane reactant. In this case, an increase in the strength of binding could make the copper a more effective catalyst. As we have seen earlier, there is considerable evidence from thermal desorption and infrared spectroscopic studies of chemisorbed carbon monoxide that the electronic or chemical properties of copper on Ru(0001) are significantly modified by the underlying ruthenium (Hoffmann and Paul 1987 a). The change in properties could be reflected in stronger binding of hydrocarbon reaction intermediates to copper present on Ru(0001). In this regard, the thermal desorption spectrum for carbon monoxide chemisorbed on a surface consisting of a complete monolayer of copper on Ru(0001) exhibited a desorption peak at a temperature somewhat higher than the desorption temperatures characteristic of the surface of a pure copper crystal (Paul and Hoffmann 1986).

In concluding this discussion of the catalytic properties of Cu/Ru(0001), we emphasize the specificity of the surface. While the Cu/Ru(0001) surface is more active than Ru(0001) for cyclohexane dehydrogenation, it is definitely less active for such reactions as ethane hydrogenolysis and the hydrogenation of carbon monoxide to methane (Peden and Goodman 1986 a). The activity for hydrogenolysis of cyclohexane to C_1–C_6 alkanes also decreases when copper is deposited on Ru(0001), in agreement with the early data on Ru–Cu catalysts (Sinfelt 1973 a, Sinfelt *et al.* 1976). The selectivity of conversion of cyclohexane to benzene is thereby increased.

4. Concluding remarks

As can be seen from the scientific literature, the ruthenium–copper system has attracted the attention of many workers in the fields of surface chemistry and catalysis. It has become an important model system for probing fundamental questions regarding the catalytic behaviour of bimetallic systems. Moreover, the research on this system has played an additional important role in helping to bridge the gap between two camps of scientists, one working with real catalysts and the other with idealized single crystal specimens. All too frequently the two camps are isolated from each other pursuing different interests. Consequently, it is a fortunate circumstance when they both become interested in the same problem, involving a common system and the same types of fundamental questions. When this happens, there is a tendency for each camp to extend its interests and methodologies to overlap those of the other. As a consequence, there is a potential for a better understanding of the really important questions and for a greater opportunity to exploit the results of the research. These features are embodied to a very high degree in the research on the ruthenium–copper system.

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