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A Comparative Investigation of Silica-Supported Ru–Cu and Ru–Ag Catalysts

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A series of silica-supported ruthenium catalysts with varying amounts of either silver or copper have been examined by hydrogen chemisorption, X-ray diffraction, and X-ray photoelectron spectroscopy, and tested for the exchange of methane with deuterium and the hydrogenolysis of ethane and 2,2-dimethylpropane. All catalysts contained 3 wt% of ruthenium which was highly dispersed. The silver was thought to be present on the ruthenium crystallites mainly as islands and not atomically dispersed because its effect on hydrogen chemisorption and catalytic activity were broadly similar. The addition of copper had little influence on hydrogen chemisorption and some spillover from ruthenium to the group IB metal may occur. Even though hydrogen chemisorption suggested that little copper was dispersed on the ruthenium there was a significant reduction in catalytic activity which was believed to result from a combination of electronic and geometric effects. Not all reactions were influenced to the same extent by the addition of copper but the effects on the multiple exchange of methane and the hydrogenolysis of 2,2-dimethylpropane were similar.

INTRODUCTION

Sinfelt's original investigation of immiscible group VIII–group IB bimetallic catalysts opened up a very productive area of new research (*1*). The Ru–Cu system has been the subject of several chemical and physical investigations (*2–9*). The variation of hydrogen chemisorption and activity for ethane hydrogenolysis with catalyst composition found by Sinfelt (*1*) gave evidence of direct metal–metal interaction between Ru and Cu although the miscibility of these metals in the bulk state is extremely low (*10*). Sinfelt emphasized these facts by referring to the Ru–Cu catalysts as bimetallic clusters instead of alloy catalysts. In a series of papers utilizing a comparative study of highly dispersed supported Ru–Cu and unsupported Ru–Cu (*2*), electron microscopy (*3*), X-ray photoelectron spectroscopy (XPS) (*4*), and extended X-ray absorption fine structure (EXAFS) (*5*), Sinfelt and co-workers built up a picture of Ru–Cu interactions which essentially involved chemisorption of Cu on the surface of Ru particles. From the electron microscopy, there was found evidence for very thin clusters with raft-like shapes. However, the EXAFS results which confirm the Cu surface deposition on Ru particles also shows an average Ru coordination number of 11 ± 1, clearly indicating that Ru–Cu rafts cannot be the dominant particle shape unless these are several atoms thick.

No direct evidence for an electronic interaction between Ru and Cu was found in the XPS core level binding energies (*4*). However, the work function of clean Ru(0001) increases upon Cu deposition, indicating a slight electron transfer from Ru to Cu which was interpreted in terms of an almost covalent bond between Cu and Ru (*6*). The UPS spectra for increasing submonolayer coverage of Cu on (0001) Ru first develops a peak 2.75 eV below the Fermi level (E_F), and this peak shifts upward in energy and develops a broad and

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relatively intense shoulder at ~4.2 eV below E_F as the coverage of Cu approaches four monolayers, the latter spectrum being that of bulk (111) Cu (*9*). No simple interpretation in terms of electron transfer was given and indeed is probably not possible, since the shift in the main *d*-band feature is probably more a result of a narrowing of the Cu *d*-band than net electron transfer. It is now realized that such changes in *d*-band shape can lead to electron transfer quite in contradiction to expectation of simple rigid band theory (*11*). Using CO chemisorption as a probe, both Vickerman *et al.* (*8*) and Richter *et al.* (*9*) find evidence for mutual electronic perturbation of the two metals. Not surprisingly the perturbation of the minor constituent Cu seems to be greater than that of Ru. The bond strength of CO to Cu appears to be about 12 kJ mol^{-1} stronger on the Cu in submonolayers than on bulk Cu (*9*), and at ~150 K isolated Cu atoms are capable of forming $Cu(CO)_2$ complexes as well as CuCO. Vickerman *et al.* interpreted the more efficient adsorption of CO on Cu deposited on Ru as due to increased back-donation, made possible by transfer of charge from Ru to Cu, but this is probably an oversimplification given the change in the band shapes seen in the ultraviolet photoelectron spectrum. Both CO and H_2 chemisorption on Ru are strongly perturbed by Cu. Based on reduction in the amount of strong chemisorption by Cu, it was suggested that an ensemble of 3 Ru atoms participate in the binding of 1 CO molecule (*8*), and ensembles of up to 5–10 adjacent Ru atoms are involved in H_2 chemisorption (*7*). Such large apparent ensemble effects may be an indication of an electronic perturbation of Ru by Cu.

While it is clear that Cu interacts with Ru and that it is effectively a surface bonding of Cu to Ru, the question of whether the Cu at low coverage spreads out randomly or forms islands or indeed begins three-dimensional Cu structures before completion of the first monolayer appears not to have a simple answer. Using thermal desorption, Christmann *et al.* found the Cu on Cu interaction to be about 16 kJ weaker than the Cu on Ru interaction. However, in a later investigation from the same laboratory, Vickerman *et al.* (*8*) find that Cu deposition on Ru(0001) at 540 K leads to statistically distributed nuclei, which grow to three-dimensional clusters, but deposition at 1080 K gives a more dispersed and strictly two-dimensional Cu atom distribution. Using unsupported Ru–Cu catalysts, there is evidence from H_2 chemisorption, ethane hydrogenolysis, and XPS for the effective spreading of Cu over Ru with increased temperature in H_2 in the region of 473–873 K, but it is not clear from this work whether the Cu spreads out as a moving front or if Cu interaction with Ru is strong enough for isolated atoms, pairs, or other small aggregates to move out across the Ru surface from a macroscopic Cu source (*2, 4*).

To the best of our knowledge, the catalytic properties of Ru–Ag have not been previously described except in the patent literature (*12*). Also, by way of comment on the effect of group IB metals on group VIII metals hydrogenolysis activity, Sinfelt mentioned Ru–Cu, Ru–Ag, and Os–Cu implying similar behavior (*13*). The third group IB metal, Au, in combination with Ru has been extensively investigated and is distinctly different from other Ru-group IB systems when supported on MgO, but comparable to Ru–Cu when supported on the more inert SiO_2 (*14*).

The purpose of the present work was to compare the properties of a series of Ru–Ag catalysts with a series of Ru–Cu catalysts prepared by identical methods in order to determine how activity depended on the ratio of the group IB metal to ruthenium. One reason for choosing Ag was recent evidence (*15*) that for a series of Rh–Ag catalysts the activity for ethane hydrogenolysis expressed in terms of sites for hydrogen chemisorption did not vary with composition. A possible interpretation of these results was that Ag on Rh may tend to form islands in contrast to the Ru–Cu system where the Cu tends to be more widely spread out. Clearly it was of some interest to discover whether the Ru–Ag and Ru–Cu systems were similar to catalytic behavior.

The reactions chosen to probe the Ru-group IB interaction were the hydrogenolysis of ethane, the hydrogenolysis of 2,2-dimethylpropane and also the exchange of methane with deuterium.

EXPERIMENTAL

Preparation of catalysts. The catalysts were prepared by impregnation following the incipient wetness procedure. According to this procedure, the ratio of the volume of impregnating solution to weight of support is such that the support is just wetted by the impregnating solution. For the support used in this study (Davison silica grade 923, 600 m^2/g), the amount of impregnating solution to bring about incipient wetness was 1 cm^3/gram of support. The drying of the supports was carried out in an oven at 393 K for about 12 h after which the dried supports were stored in a dessicator. The impregnating solutions were prepared by dissolving the salts, $AgNO_3$, $Cu(NO_3)_2 \cdot 6H_2O$, and $RuNO(NO_3)_2 \cdot H_2O$, obtained from Alfa Products, in distilled water. The impregnating solutions containing the two metal salts were put in contact with the support simultaneously, the solutions of each salt having been pre-mixed in a Petri dish and then the support added to it while stirring. For all the catalysts prepared, the amount of the noble metal was maintained constant at 3% by weight, based on metal plus dry support. The volume of the solution containing the group IB metal added to the support was varied, depending on the amount of group IB metal required for a given metal composition.

After impregnation, the catalysts were dried for 2 days at room temperature and then for 2.5 h in air at 393 K. The dried catalysts were stored in a dessicator. The reduction procedure was as follows: 1 to 3 g of dried catalyst was further dried by flowing He at 393 K for 1 h, after which He was replaced by H_2 and the temperature raised at 2 K/min to 723 K. The catalyst was maintained in flowing H_2 for two additional hours at that temperature and then cooled in flowing He. The H_2 used was AirCo grade 4.5, which had been further purified by passage through a Pd–Ag diffusion cell. Helium (AirCo CP grade) was used as received.

Chemisorption of hydrogen. The apparatus used for adsorption measurements was a conventional volumetric adsorption system. Adsorption isotherms at room temperature were measured by admitting a known quantity of gas to the adsorption cell and waiting overnight before reading the equilibrium pressure for the first point. The range of pressure used was 0–0.4 kPa, measured with a differential pressure gauge provided by MKS Instruments, Inc. Prior to any measurement the catalyst (approximately 0.6 g) was reduced *in situ*. With the sample in flowing H_2, the temperature was raised at 5 K/min to 593 K and maintained at that level for 1 h after which the adsorption cell was sealed and pumped at the same temperature for 5 h. An increase in temperature and time of pumpout to 723 K and 8 h did not lead to a change in the amount of gas adsorbed.

The total hydrogen chemisorbed was obtained by extrapolating the isotherm to zero pressure. In order to determine the amount of strong chemisorption, the sample was evacuated for 10 min at room temperature and a second isotherm measured. The difference between the total chemisorption (first isotherm) and the isotherm obtained after room temperature evacuation was taken as a measure of strong chemisorption, i.e., chemisorption irreversible at room temperature.

X-Ray diffraction. The reduced catalysts were examined by X-ray diffraction using a Norelco diffractometer with Cu*Kα* radiation. Instrumental line broadening was determined in the angular range of interest from the width of the diffraction lines of metal foils.

X-Ray photoelectron spectroscopy. X-Ray photoelectron spectra (XPS) were taken on a Hewlett–Packard 5950A spectrometer using monochromatic Al $K\alpha$ radiation. The samples were ground and pelletized before examination. The reduction was carried out *in situ* at temperatures around 573 K in a H_2 atmosphere at pressures in the range of 0.004–0.27 kPa. The Ru/Si and group 1B metal/Si XPS intensity ratios were determined from the height of the Ag $3d_{5/2}$, Cu $2p_{3/2}$, Ru $3d_{5/2}$, and Si $2p_{1/2}$ lines using 20-eV sweeps. The sample was irradiated with an electron flood gun (0.3 mA, ~0 V) to minimize charging effects. All reported XPS intensities are the average of three independent measurements made on three different samples of the same catalyst.

Catalytic activity measurements. The activity measurements for ethane hydrogenolysis reaction were performed in a microcatalytic pulse reactor already described (*15*). Purified (Pd–Ag diffused) hydrogen was used as the carrier gas and ethane was used as received from AirCo (CP grade). The differential rate of reaction was calculated based on the conversion and a residence time assumed to be the reactor (catalyst bed) volume ratioed to the carrier flow rate and converted to units of molecules converted per surface Ru atom per second (turnover frequency) based on an assumed H : surface Ru stoichiometry equal to one for hydrogen chemisorption.

The hydrogenolysis of 2,2-dimethylpropane and the exchange of methane with deuterium were carried out in static systems using procedures which have already been described (*16*). The usual weight of catalyst was 0.05 g and before each run the sample was purged with hydrogen for 20 min at room temperature and then the temperature was increased manually at ~5 K/min to 623 K. After reduction for 1 h at this temperature the catalyst was evacuated for a further hour before decreasing the temperature to the value selected for reaction. Hydrogen used for reduction was passed through a Deoxo unit, molecular sieves and a liquid nitrogen trap. Hydrogen and deuterium (99.5%, Cambrian Gases) used for reaction were purified by diffusion through Pd–Ag thimbles. Both methane (99.97%) and 2,2-dimethylpropane (99%) were supplied by Cambrian Gases and except for degassing were used as received.

The charge of 2,2-dimethylpropane used for hydrogenolysis was 1.93×10^{19} molecules admitted to the reaction vessel (185 cm^3) with a 10 : 1 ratio of hydrogen : hydrocarbon. Samples (0.2 cm^3) were withdrawn periodically and analyzed by gas chromatography, using a 3-m column of n-octane on Porasil C, operated at room temperature with nitrogen as carrier gas and a Perkin–Elmer flame ionization detector.

For the exchange of methane with deuterium the charge in the reaction vessel (265 cm^3) was 2.55×10^{19} molecules with a 10 : 1 ratio of deuterium : methane. There was a direct capillary leak from the reaction vessel to a Vacuum Generators MM601 mass spectrometer so that analyses could be made at any stage of the reaction. The methane was ionized using 16-eV electrons and corrections made for natural isotopes present and for fragmentation. Standard methods (*17*) were used to calculate the initial rates of exchange of methane and the mean number of deuterium atoms (M) entering each molecule reading under initial conditions.

RESULTS

Characterization of the Catalysts

X-Ray diffraction experiments gave no lines corresponding to Ru, Ag, or Cu particles with any of the catalysts nor were there detectable diffraction lines corresponding to the oxides RuO, Ru_2O, Ag_2O, CuO, etc. It follows that the metals were highly dispersed and present only in small crystallites.

Results for hydrogen chemisorption on

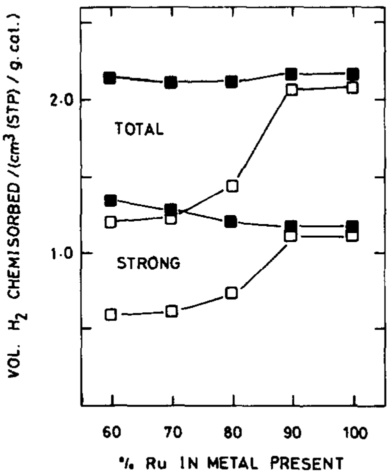

FIG. 1. The specific H_2 adsorption at room temperature as a function of the percentage Ru in the total metal present: ■, Ru–Cu; □, Ru–Ag. The curve labeled strong indicates the H_2 that could not be removed by evacuation at room temperature.

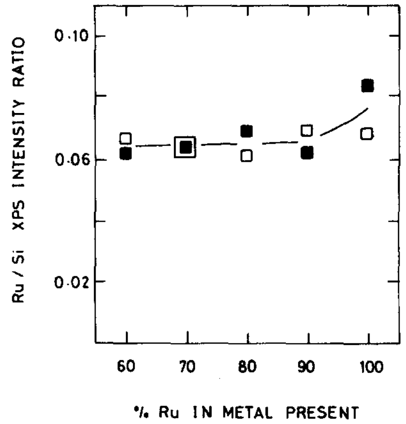

FIG. 2. XPS intensity ratio (Ru $3d_{5/2}$/Si $2p_{1/2}$) as a function of the percentage Ru in the total metal present: ■, Ru–Cu; □, Ru–Ag.

the catalysts are shown in Fig. 1 which gives both the total adsorption and the amount not readily reversible at room temperature. The values of H/Ru based on the total hydrogen adsorption and the total ruthenium present in the catalysts are given in Tables 1 and 2 for the two series of catalysts. The labeling of the catalyst gives the atomic percent of the total metal as Ru, i.e., the metal fraction of 90-Ru–Ag was 90% Ru and 10% Ag, but the amount of ruthenium was maintained as 3 wt% for all catalysts.

The results of the XPS experiments are given in Figs. 2 and 3. Within experimental error the Ru/Si intensities in Fig. 2 were not influenced by amount of the group IB metal present and the ruthenium appeared to be

TABLE 1

Results for Ru–Ag Catalysts

Catalyst	100-Ru–Ag	90-Ru–Ag	80-Ru–Ag	70-Ru–Ag	60-Ru–Ag
H/Ru	0.63	0.62	0.44	0.37	0.37
Methane exchange (398 K)					
10^4 r_1 (molecule s^{-1} $site^{-1}$)	8.1	6.6	4.7	5.6	5.1
Value of M[a]	1.24	1.21	1.14	1.21	1.10
2,2-Dimethylpropane hydrogenolysis (398 K)					
10^4 r_2 (molecule s^{-1} $site^{-1}$)	1.8,1.9	1.2	0.87	0.55	0.15
% Multi-bond hydrogenolysis	24,21	15	14	11	(35)[b]
Ethane hydrogenolysis (478 K)					
10^3 r_3 (molecule s^{-1} $site^{-1}$)	16	9.5	8.3	8.3	7.0
E[c] (kJ mol^{-1})	167	167	163	163	159

[a] The mean number of deuterium atoms entering each reacting methane molecule initially.

[b] Rate too low to measure accurately.

[c] Error ±5 kJ mol^{-1}.

TABLE 2

Results for Ru–Cu Catalysts

Catalyst	100-Ru-Cu	90-Ru-Cu	80-Ru-Cu	70-Ru-Cu	60-Ru-Cu
H/Ru	0.65	0.65	0.64	0.63	0.64
Methane exchange (398 K)					
$10^4 r_1$ (molecule s^{-1} site^{-1})	8.8	6.2	8.7,6.4	5.5,6.3	2.2,2.0
Value of *M*[a]	1.17	1.18	1.14,1.11	1.09,1.02	1.06,1.02
2,2-Dimethylpropane hydrogenolysis (398 K)					
$10^4 r_2$ (molecule s^{-1} site^{-1})	2.8,2.7	0.61	0.71,0.82	0.58,0.48	0.04,0.06
% Multi-bond hydrogenolysis	23,24	10	11,9	9,13	45,[b]20[b]
Ethane hydrogenolysis (478 K)					
$10^3 r_3$ (molecule s^{-1} site^{-1})	14	4.5	3.7	2.7	2.2
E[c] (kJ mol^{-1})	167	163	151	151	130

[a,b,c] See footnotes to Table 1.

equally accessible to XPS in all the catalysts. Thus, in agreement with the X-ray diffraction results, there is no evidence for an increase of metal particle size to values greater than the electron escape depth of 1.5 nm (*18*) as the composition of the catalysts was altered. The values of the group IB/Si XPS intensities increased steadily with the amount of group IB metal in the catalysts but, as shown in Fig. 3 the change was linear with Cu but slightly curved with Ag. Catalysts containing the same amount of Ag or Cu as in the 60-Ru-Ag or 60-Ru-Cu but without ruthenium gave identical group IB/Si intensities to the mixed metal catalysts.

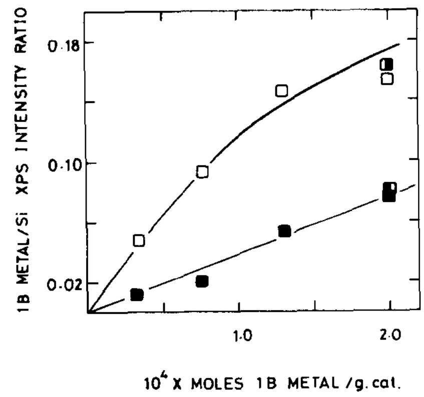

FIG. 3. XPS intensity ratios (Ag $3d_{5/2}$/Si $2p_{1/2}$) or (Cu $2p_{3/2}$/Si $2p_{1/2}$), as a function of moles group IB metal/grams catalyst: ■, Ru–Cu, □, Ru–Ag; catalysts containing only group IB metal at the same loading as in the 60% Ru bimetallic catalysts: ◧, Cu, ◨, Ag.

Catalytic Reactions

In all cases the rates of reaction were expressed as turnover frequencies i.e., molecule s^{-1} site^{-1}, where the number of sites was assumed to correspond to the total number of hydrogen atoms adsorbed by the catalysts.

The rates of exchange of methane with deuterium at 398 K are given in Tables 1 and 2 for the Ru–Ag and Ru–Cu series of catalysts and the values of *M* which provided an indication of the extent of the multiple exchange are also included. Even on the 100% Ru catalysts there was only a relatively small amount of multiple exchange with about 10% of the reacting molecules emerging as CH_2D_2, CHD_3, and CD_4.

The rates of hydrogenolysis of 2,2-dimethylpropane at 398 K are also given in Tables 1 and 2. The main reaction on all catalysts involved the splitting of one C–C bond to give 2-methylpropane and methane as products but some multi-bond splitting yielding propane, ethane, and additional methane also occurred. Typical product

TABLE 3

Initial Products from the Hydrogenolysis of 2,2-Dimethylpropane

Catalyst	Initial products (mol%)			
	Methane	Ethane	Propane	2-Methylpropane
100-Ru–Ag	51	10	5	34
70-Ru–Ag	50	4	3	43
100-Ru–Cu	51	11	4	34
70-Ru–Cu	47	5	3	45

distributions are shown in Table 3 and the percentage of the molecules undergoing multi-bond hydrogenolysis are recorded in Tables 1 and 2.

The results for the hydrogenolysis of ethane at 478 K are shown in Fig. 4 and activation energies determined over a limited temperature range of about 30 K are given in Tables 1 and 2.

DISCUSSION

Ruthenium–Silver Catalysts

The presence of increasing amounts of silver with the Ru–Ag series of catalysts blocked up to 40% of the Ru hydrogen chemisorption sites (Fig. 1 and Table 1). But there was comparatively little additional effect of the silver on the activities of the catalysts for the reactions studied. The rate of exchange of methane decreased by less than a factor of 2 as the atomic percentage of ruthenium was decreased to 60%. The rate of hydrogenolysis of ethane also decreased by a factor of 2 but there was no significant change in the activation energy as the percentage of silver increased. The reaction of 2,2-dimethylpropane was influenced rather more substantially by the addition of silver to the ruthenium, the rate falling by a factor of 3 as the percentage of ruthenium decreased to 70% and by a similar factor for the further 10% decrease to 60%.

The simplest interpretation of these results is that the silver is present on top of the ruthenium crystallites but probably concentrated into islands and not dispersed over the surface of the group VIII metal to an appreciable extent. The results for the Ru–Ag system are broadly similar to those already reported for some series of Rh–Ag catalysts (*15*). However, the results for the XPS studies shown in Fig. 2 suggest that part of the silver may be aggregated into crystallites which are sufficiently large to give the curvature for the intensity of the Ag/Si peaks against amount of silver but not large (Fig. 3) enough to lead to observable X-ray diffraction patterns. Such crystallites are probably not directly associated with the ruthenium because the constant ratio of Ru/Si peak intensities (Fig. 2) is evidence that the thickness of the silver on top of the ruthenium is not sufficiently great to reduce the intensity of the Ru peak.

Ruthenium–Copper Catalysts

Our Ru–Cu catalysts do not reflect the same extent of interaction as reported by Sinfelt (*1*) in either the hydrogen chemisorption or ethane hydrogenolysis. We have reproduced Sinfelt's results and traced the different behavior of our catalyst to the combination of impregnation salt of Ru and silica support (*19*). In brief, $Ru(NO)(NO_3)_3$ in combination with microporous, high area (600 m^2/g) Davison silica results in a higher dispersion of Ru (and a

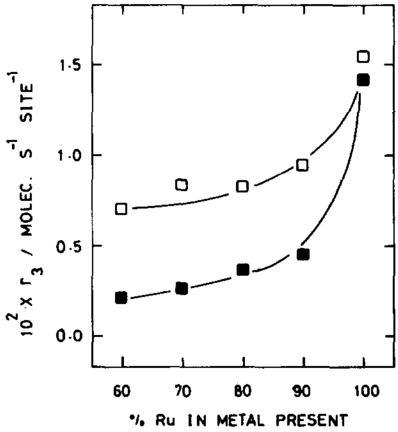

FIG. 4. The turnover rate for hydrogenolysis of ethane at 478 K as a function of the percentage Ru in the total metal present: ■, Ru–Cu; □, Ru–Ag.

consequent smaller degree of interaction with Cu (*2*)) than does $RuCl_3$ in combination with relatively low area, non-porous Cab-o-Sil. Our choice of $Ru(NO)(NO_3)_3$ was made to avoid precipitation of AgCl in the preparation of Ru–Ag catalysts. It was also used in the preparation of the Ru–Cu in order to minimize differences in preparation variables between the two catalysts series.

Two different interpretations can be given for the results for hydrogen chemisorption on the Ru–Cu catalysts reported in Fig. 1. First, there is the possibility that some uptake of hydrogen occurs on copper perhaps assisted by spillover from hydrogen more readily adsorbed on ruthenium. The main features about adsorption of hydrogen on copper are that the strength of adsorption is not large and also, and perhaps more significantly from our point of view, the rate of establishment of equilibrium for adsorption and desorption is slow (*20*). The results in Fig. 1 show that the proportion of the reversibly adsorbed hydrogen on the catalyst fell as the percentage of copper increased. This would rule out spillover if the establishment of the adsorption equilibrium with copper was rapid but does not exclude spillover if the processes of adsorption and desorption of hydrogen on copper are slow. Thus, although it is customary to refer to hydrogen not removed by evacuation at room temperature as strongly adsorbed it is more accurate to describe such adsorption as not readily reversible adsorption. In most cases the two descriptions may be equivalent but for copper the distinction may be important. If spillover was important with our catalysts it is easy to understand why the total adsorption of hydrogen is not reduced by the presence of copper in the same way as it was by the presence of silver. Previous workers (*8, 9*), have presented evidence that carbon monoxide is adsorbed more rapidly and more strongly on copper which is present as a submonolayer on ruthenium than on bulk copper. The effect was attributed to an interaction between the two metals and such an effect might also be expected to enhance the adsorption of hydrogen on copper dispersed on ruthenium, in agreement with the spillover hypothesis. On the other hand, the detailed investigations of hydrogen adsorption on Ru/Cu catalysts by Shimizu *et al.* (*7*) did not provide any evidence for adsorption by the copper under the low pressures which they used. Our results by themselves are not sufficiently detailed to establish clearly that hydrogen spillover does occur with the Ru–Cu system but it is important to note that if such a phenomenon occurs even to a limited extent the derivation of the number of ruthenium metal sites from the total hydrogen adsorption becomes questionable.

The other interpretation of the results in Fig. 1, neglecting spillover, is to assume that the dispersion of the ruthenium is somewhat greater in the catalysts rich in copper and that the amount of copper on the surface of the ruthenium is not sufficient to give an appreciable decrease in the hydrogen adsorption. The previous work (*7*) established clearly that even as little as 5% of a Cu monolayer was sufficient to reduce hydrogen adsorption by 50% and suggested that such adsorption might involve an ensemble of 5 to 10 adjacent Ru atoms. The apparently poor coverage of the Ru by Cu with our catalysts may be described by one of two simple models. The first of these postulates that the two metals are mainly present as isolated crystallites with only a small amount of Cu deposited on the surface of the Ru particles. The second model assumes that while the bulk of the two metals is still present in separate crystallites, these two kinds of crystal are frequently in contact. If the latter hypothesis was correct, it should be possible to increase the surface coverage of the Ru particles by Cu by prolonged exposure to high temperature (*4*). In order to test this hypothesis, the 60-Ru–Cu sample was held at 723 K under flowing hydrogen for 24 h and then the hydrogenolysis of 2,2-dimethylpropane was repeated. No change in rate was observed and since 723 K is well above the minimum temperature at which Vickerman *et al.* (*8*) observed Cu mobility on Ru we conclude that the first model constitutes a better representation of our catalysts.

The results presented in Table 2 are based on the assumption that hydrogen adsorption provides a measurement of Ru sites and that spillover to the Cu is unimportant. There are some significant effects of the addition of copper to the ruthenium catalyst despite the evidence already discussed that the amount of Cu atoms dispersed on the group VIII metal must be strictly limited. The effect of Cu on the exchange of methane with deuterium is not greatly different from the effect of Ag; there is a tendency for the exchange to become more predominantly stepwise (M decreasing toward 1.0) with Cu and there is a marked drop in activity for the 60-Ru–Cu catalyst. The results for the hydrogenolysis of 2,2-dimethylpropane are broadly similar to those for addition of Ag but again the difference between 70-Ru–Cu and 60-Ru–Cu is particularly noticeable. Rates of ethane hydrogenolysis fall by a factor of 5 across the Ru–Cu series and again the 60-Ru–Cu catalyst exhibited a rather lower activation energy.

The general conclusion for Ru–Cu series is that although the amount of Cu on the Ru surfaces may be very small there is an undoubted influence of the group IB metal on the catalytic activity particularly for the hydrogenolysis reactions. We suggest that this may, in part, arise from an electronic interaction between Cu and Ru which is more significant than with Ag and Ru. The Allred–Rochow electronegativities (*21*) are 174, 142, and 142, respectively, for Cu, Ag, and Ru. Thus, one might expect some charge transfer from Ru to Cu, as was observed by work function measurement (*6*) but very little with the Ru–Ag system. We do not wish to imply that geometric effects are unimportant for the Ru–Cu system because they have been clearly demonstrated by Sinfelt (*1*) for his series of such catalysts where there was evidence from hydrogen chemisorption of a reasonable coverage of Cu on the Ru and for which he observed a more significant fall in activity for ethane hydrogenolysis over a range of catalyst compositions similar to those used by us. But if we relied simply on geometric arguments to explain our results we should have to assume an unreasonably large ensemble of Ru atoms to be necessary for hydrogenolysis of ethane. So we believe that the results for the Ru–Cu system are best explained by a combination of electronic and geometric effects which together contribute to a larger suppression of rate than might be explained by either effect considered alone.

Comparison of the Catalytic Reactions

The results in Tables 1 and 2 show that on all catalysts the rate of exchange of methane with deuterium was faster than the rate of hydrogenolysis of 2,2-dimethylpropane at the same temperature. This means that the rate-determining step of the hydrogenolysis reaction is C–C bond breaking and not the rate of product desorption. The same conclusion applies even more strongly to the hydrogenolysis of ethane which had to be studied at a substantially higher temperature to achieve reasonable rates of reaction. It is possible to use the Arrhenius parameters to estimate a rate of reaction of ethane at 398 K and for the 100% Ru catalysts the calculated rate is 3×10^{-6} molecule s^{-1} $site^{-1}$, i.e., about a factor of 10^2 slower than the rate of reaction of 2,2-dimethylpropane.

The two catalysts labeled 100-Ru–Ag and 100-Ru–Cu were prepared by similar methods and were expected to show the same activities for all catalytic reactions. Good agreement was found for methane exchange and ethane hydrogenolysis but the latter catalyst was 50% more active for the hydrogenolysis of 2,2-dimethylpropane. However, the character of this reaction was the same on both catalysts as shown by the similarity of the product distributions in Table 3. An analysis of these product distributions raises a question about the mechanism of formation of ethane and propane from the reactant. The simplest assumption is that successive demethylation occurred on adsorbed intermediates and this would have given 2-methylpropane + 1 CH_4, propane + 2 CH_4, and ethane + 3 CH_4. But the amount of methane formed was insufficient to accord with such a process of multi-bond hydrogenolysis. We believe that some isomerization of the C_5-hydrocarbon probably occurred and that the iso-C_5 or normal-C_5 intermediates so formed underwent rapid hydrogenolysis to give C_2 and C_3 products. The formation of such products was reduced significantly by the presence of either group IB metal as shown by the distributions in Table 3 for the 70-Ru–Ag and 70-Ru–Cu catalysts for which the reaction was predominantly cleavage of one C–C bond to form 2-methylpropane with methane.

It is interesting to compare the patterns of activity against catalyst composition for the Cu series using the two reactions studied at 398 K. Two ways of making such a comparison are given in Table 4—using (A) the total rate of exchange of methane with deuterium or (B) the rate of multiple exchange of methane. The first method does not give a constant ratio of activities but the second does. The obvious conclusion is that the sites which are important for the multiple exchange of methane are also important for the hydrogenolysis of 2,2-dimethylpropane and are influenced significantly by the addition of copper to ruthenium. This type of comparison is valuable because it is not subject to any possible uncertainty about the meaning to be attached to the hydrogen chemisorption data for the Ru–Cu series of catalysts. This point is particularly significant in light of our observation that Ru–Cu catalysts may exhibit almost no depression in either strong or total hydrogen chemisorption (as measured using our long equilibration times) relative to pure Ru but still show a 10^3 depression in ethane hydrogenolysis activity (*19*). It is also worth noting that the 60-Ru–Cu catalyst falls into line with the other catalysts when 2,2-dimethylpropane activity is normalized to methane multiple exchange whereas from the turnover numbers based on hydrogen chemisorption it appeared to be of low activity. The general conclusions obtained by comparing the catalytic reactions are (a) that the stepwise exchange of methane is not greatly influenced by the presence of either group IB metal and (b) that the multiple exchange of methane and the hydrogenolysis of 2,2-dimethylpropane are inhibited to similar extents by the addition of copper.

TABLE 4

Comparison of Reaction Rate/Ratios at 398 K on the Ru–Cu Catalysts

Catalyst	(A) Hydrogenolysis of C_5H_{12}[a] / Exchange of CH_4	(B) Hydrogenolysis of C_5H_{12}[a] / Multiple exchange of CH_4
100-Ru–Cu	0.31	3.1
90-Ru–Cu	0.10	1.6
80-Ru–Cu	0.12	2.2
70-Ru–Cu	0.08	2.1
60-Ru–Cu	0.025	1.8

[a] 2,2-Dimethylpropane.

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