Effect of Silica Support on Ru–Cu Cluster Morphology As Determined by Catalytic Activity

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Several silica supports impregnated with 1% Ru and a 1:1 atomic ratio of Ru:Cu in the bimetallic catalysts have been characterized by H₂ chemisorption, temperature programmed desorption and re-reduction, and several catalytic reactions of varying structure sensitivity. Clusters of Ru-Cu on one of the silicas, Cab-O-Sil HS5, is distinguished by the fact that only on this support is hydrogen chemisorption suppressed by added Cu. It is postulated that the morphology of the Ru-Cu clusters on HS5 involves a Cu-rich mixture of Ru and Cu on a Ru core. Clusters of Ru-Cu on other silicas appear to be more heterogeneous and have an associated pure Cu phase. Hydrogen spillover occurs with the latter morphology and both hydrogen chemisorption and spillover are suppressed by the morphology of clusters on HS5.

Introduction

Over the past decade, few areas of catalysis have been more productive for the development of concepts and practical aplications than that of bimetallic catalysts.¹ Among those bimetallic catalysts that have been repeatedly investigated, the Ru-Cu system stands out as one that has been well studied by classical chemisorption and catalytic probes as well as a wide variety of physical techniques (XPS, EXAFS, NMR, etc.)²⁻¹² for Ru-Cu clusters supported on high-area oxides. Model systems of Cu films on single-crystal Ru have also been intensively studied by a variety of surface science techniques (TPD, work function measurements, Auger, UPS, etc.).¹³⁻²¹ These two kinds of Ru-Cu catalysts, dispersed particles on silica support and films on single crystals, appeared to be converging to a consistent and satisfying picture (outlined below) of how Cu, the inactive component, affects the active component, Ru, for reactions of hydrocarbons under reducing conditions.

The global understanding of the Ru-Cu interaction, as conceived and elucitated by Sinfelt in a series of systematic and characteristically elegant papers,¹⁻⁷ is surely correct. However, the detailed description of these catalysts has been challenged in two important ways, one each evolving from reinvestigation of the Cu film/Ru single crystal models 1^7 and from reinvestigation Ru-Cu supported on silica.¹⁰ In both instances, the questions that are raised by the new work involve the effect of Cu addition on hydrogen adsorption. In the former case of the model systems, there is strong evidence that hydrogen may spill over onto Cu, and, as pointed out by Goodman, this will surely change the estimate of site density and may thereby lead to a reinterpretation of metal-metal interaction or its effect on catalysis. In the latter case of dispersed bimetallic clusters on silica, it has been found that depression of hydrogen chemisorption by addition of Cu to Ru, as originally reported by Sinfelt,² cannot be generalized to other silicas.⁹⁻¹¹ The fundamental question of how the silica support affects the interaction of the two metals cannot be answered yet, but this article will elaborate on the chemisorption and cataytic consequences of the different kinds of interaction and offer possible models for morphologies that result on different silicas

The Ru-Cu system exhibits very little bulk miscibility, yet small particles containing both metals can be obtained on high surface area supports. The most direct evidence for this statement comes from the observation that chemisorption, e.g., of H₂, and catalysis, e.g., ethane hydrogenolysis, which occur on pure Ru particles but not Cu, are changed when both metals are impregnated onto the same support. From a comparative study of silica supported and unsupported bimetallic Ru-Cu catalysts, Sinfelt developed the

hypothesis that the Cu effectively chemisorbed on the surface of Ru and, in the case of well-dispersed supported catalysts, these could be considered bimetallic clusters forming a Ru core with Cu more-or-less uniformly spread over the surface. This hypothesis has been strengthened and made quantitative by an extended X-ray absorption (EXAFS) analysis of the structure of Ru-Cu clusters supported on silica.⁸ Accordingly, the strong decreases in catalytic activity observed for several reactions after addition of Cu are usually ascribed to the disruption of active ensembles caused by the presence of Cu on the surface.²¹ Local electronic, or "ligand", effects have also been proposed.²²

In this paper we will relie on conventional catalytic probes of the degree of interaction of Ru and Cu supported on different silicas. While a wide variety of silica supports has been surveyed, we will concentrate on the comparative behavior of Cab-O-Sil HS-5 and Cab-O-Sil M-5. The HS-5 silica is that used by Sinfelt for all of his work and M-5 is representative of several silicas which result in a different Ru-Cu interaction. The Cab-O-Sil silicas are nonporous, submicron particles of different surface area and, because both silicas are manufactured by the same process and by the same supplier, they are expected to have similar impurities. We have investigated their effect on Ru-Cu interaction using H₂ chemisorption and several reactions of varying structure sensitivity (ethane hydrogenolysis, cyclohexane hydrogenolysis and dehydrogenation, and benzene hydrogenation). Temperature pro-

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grammed desorption (TPD) and temperature programmed rereduction (TPR) have also been used to characterize the Ru-Cu interaction, but aside from X-ray diffraction, which has not been very informative, we have not yet attempted a more sophisticated characterization by physical techniques, e.g., EXAFS.

Experimental Section

Catalyst Preparation. A series of silica-supported monometallic 1 wt % Ru and bimetallic Ru-Cu (Ru/Cu = 1, mole ratio) catalysts were prepared by impregnation following the incipient wetness procedure. Several different silica supports were investigated: Cab-O-Sil M5 (200 m²/g), Cab-O-Sil HS5 (325 m²/g), Cab-O-Sil EH5 (385 m²/g, Cab-O-Sil L90 (90 m²/g), Davison 62 (300 m²/g), Davison 952 (300 m²/g), and Davison 923 (600 m²/g). The amount of impregnating solution was 2.5 cm³/g for the Cab-O-Sil supports and 1.0 cm³/g for the Davison supports.

The effect of varying the anion of the ruthenium salt in the aqueous impregnating solution was also investigated. A series of catalysts was prepared using RuCl₃ while a second series was prepared using Ru(NO)(NO₃)₃. In both cases the Cu salt was Cu(NO₃)₂. The three salts were obtained from Alfa Products.

Two different impregnation methods were followed. In the co-impregnation procedure the solutions containing the two metal salts were premixed in a Petri dish and then placed in contact with the support. The sequentially impregnated bimetallic catalysts were prepared by impregnating the prereduced ruthenium catalyst with the $Cu(NO_3)_2$ aqueous solution.

After the impregnation step, the catalyts were dried at room temperature and then placed in an oven at 393 K. Finally, they were reduced in flowing H_2 at 723 K for 2 h. Before each experiment they were further reduced "in situ" at 723 K for 2 h. In the next section the catalysts are identified as follows: A indicates pure Ru; B, Ru-Cu; 1, co-impregnation; 2, sequential impregnation. The type of support and the anion of the Ru salt are also indicated for each catalyst.

Chemisorption Measurments. The chemisorption experiments were carried out in a static volumetric Pyrex glass system equipped with a Baratron MKS pressure gauge. Adsorption isotherms at room temperature were obtained by admitting a known amount of gas to the adsorption cell. The first adsorption point was obtained after 12 h, and the subsequent ones after a 2-h period. The total hydrogen chemisorption values were calculated by extrapolating the isotherms to zero pressure.

Temperature Programmed Desorption. Temperature programmed desorption (TPD) of preadsorbed hydrogen were carried out in a Pyrex cell directly connected to a thermal conductivity detector. After reduction in hydrogen at 723 K, the sample was cooled to room temperature in a hydrogen atmosphere. It was then flushed with pure argon until a flat background was sensed in the thermal conductivity detector. At this point, the heating program was initiated at a constant rate of 15 K/min.

Subambient hydrogen flash desorption spectra were obtained by performing the adsorption at room temperature followed by immersion in a cold bath (176 K). The nonprogrammed desorption spectra for the temperature range 176-298 K were then obtained by removing the cold bath and letting the sample warm to room temperature.

Catalytic Activity Measurements. Activity measurements for the hydrogenolysis of ethane, the hydrogenation of benzene, and the dehydrogenation/hydrogenolysis of cyclohexane were obtained in an atmospheric pressure, continuous flow system. The gas mixtures of hydrogen and hydrocarbon were kept at a ratio 1:6 for ethane hydrogenolysis, 1:10 for benzene hydrogenation, and 1:20 for the cyclohexane reactions. The total flow rates were 20, 75, and 20 cm³/min, respectively. Constant activity levels were obtained after 30 min on stream. The reaction rates were measured at various temperatures in a 40 K range.

Temperature Programmed Re-Reduction. In order to further probe the surface structure of the Ru-Cu bimetallic clusters we performed temperature programmed re-reduction (TPR) experiments. In this case, the Ru-Cu clusters were first formed during

TABLE I: Hydrogen Uptakes on Silica (Cab-O-Sil) Supported Ru and Ru-Cu Catalysts

catalyst	Cu/Ru molar ratio	anion of Ru salt	Cab-O-Sil support	impregnation procedure	H/Ru
A1-HS5-Cl	0	CI	HS5	co-impregn	0.29 ·
B2-HS5-Cl	1	CI	HS5	sequential	0.26
A1-HS5-NO B1-HS5-NO B2-HS5-NO	0 1 1	NO NO NO	HS5 HS5 HS5	co-impregn sequential	0.57 0.50 0.41
A1-M5-Cl B1-M5-Cl B2-M5-Cl	0 1 1	C1 Cl Cl	M5 M5 M5	co-impregn sequential	0.09 0.21 0.06
A1-M5-NO B1-M5-NO B2-M5-NO	0 1 1	NO NO NO	M5 M5 M5	co-impregn sequential	0.16 0.24 0.15
A1-EH5-Cl B1-EH5-Cl	0 1	Cl Cl	EH5 EH5	co-impregn	0.20 0.41
A1-L90-Cl B1-L90-Cl	0 1	Cl Cl	L90 L90	co-impregn	0.04 0.06

TABLE II: Hydrogen Uptakes on Silica (Davison) Supported Ru and Ru-Cu Catalysts

catalyst	Cu/Ru Molar ratio	anion of Ru salt	Davison support	impregnation procedure	H/Ru
A1-62-Cl	0	Cl	62	co-impregn	0.06
B1-62-Cl	1	Cl	62		0.10
A1-62-NO	0	NO	62	co-impregn	0.16
B1-62-NO	1	NO	62		0.24
A1-952-Cl	0	Cl	952	co-impregn	0.07
B1-952-Cl	1	Cl	952		0.09
A1-952-NO	0	NO	952	co-impregn	0.18
B1-952-NO	1	NO	952		0.21
A1-923-Cl	0	Cl	923	co-impregn	0.10
B1-923-Cl	1	Cl	923		0.23
A1-923-NO	0	NO	923	co-impregn	0.30
B1-923-NO	1	NO	923		0.36

the initial high-temperature reduction and then mildly oxidized at 373 K in air. We try to avoid bulk oxidation which causes the disruption of the Ru and Cu phases. Under these mild oxidation conditions we expect that only a thin layer on the surfaces of both metals would be oxidized.

The TPR spectra were obtained by flowing a mixture of 5% hydrogen in pure argon while the catalyst sample (50 mg) was heated at a rate of 8 K/min. The sample cell was directly connected to a thermal conductivity detector which monitored the hydrogen consumption during the reduction.

Results

Hydrogen Chemisorption. Table I summarizes the total hydrogen chemisorption data, expressed as H/Ru, obtained for the monometallic and bimetallic catalysts supported on the nonporous Cab-O-Sil silica supports. Similarly, Table II shows the chemisorption data obtained on Ru and Ru-Cu catalysts supported on the porous Davison silicas.

When comparing the uptakes on the catalysts prepared by coimpregnation, two opposite trends were immediately obvious. On the Cab-O-Sil HS5 silica-supported catalysts, the presence of copper made the hydrogen uptakes decrease as compared to the uptake obtained for the pure Ru catalysts. On the other hand, for all the other supports the uptakes on the bimetallic catalysts were higher than on the monometallic ones.

The extent of increase in hydrogen uptake on the Ru–Cu catalyst compared to that on the pure Ru catalyst depends on Ru dispersion. This dependence is illustrated in Figure 1 which shows the ratio between the hydrogen uptakes on the Ru–Cu and on the pure Ru catalysts as a function of ruthenium dispersion (H/Ru) in the monometallic catalyst. Besides our own data, we have



Figure 1. Hydrogen chemisorption on Ru-Cu bimetallic catalysts relative to that on pure Ru catalysts on various silica supports as a function of hydrogen uptake (H/Ru) on the pure Ru catalyst. Squares correspond to Cab-O-Sil silica supports. Empty squares, HS5. The triangle represents unsupported catalsyt: (a) ref 9; (b) ref 2; (c) ref 5; and (d) ref 11.

included those from ref 2, 5, 9, and 11. Most of the silica-supported systems follow the same trend. The $(H/Ru)_{Ru-Cu}/(H/Ru)_{Ru}$ ratio is greater than one but it rapidly decreases with increasing $(H/Ru)_{Ru}$ and approaches one at high Ru dispersions.

An opposite trend is observed in the case of unsupported catalysts and HS5-supported catalysts. The $(H/Ru)_{Ru-Cu}/(H/Ru)_{Ru}$ ratio is less than one and it increases as $(H/Ru)_{Ru}$ increases. As before, it approaches one at high Ru dispersions.

Even though the two observed trends oppose each other, both are consistent with the presence of copper on the ruthenium surface. As was first proposed by Sinfelt et al.,⁵ the effect of Cu addition is more pronounced on poorly dispersed ruthenium particles because it is mainly located on the ruthenium surface. Similar amounts of copper will have a more noticeable effect on larger particles.

These trends appear too be independent of the type of salt used for the impregnation. As we have proposed in a previous work,¹⁰ the type of Ru salt used may only affect the resulting ruthenium dispersion. On a given support, the Ru catalysts prepared from $Ru(NO)(NO_3)_3$ are better dispersed than those prepared from $RuCl_3$. The Ru dispersion may, in turn, indirectly affect the extent of Ru-Cu interaction. But, as demonstrated here, the anion used in the impregnating solution is not the main cause of the increased hydrogen chemisorption observed on Ru-Cu catalysts. This observation contradicts the hypothesis of other workers¹¹ who ascribe these high H₂ uptakes to the presence of chloride on the catalysts.

The impregnation procedure seems to have a more important influence on the resulting chemisorptive properties. In the case of sequentially impregnated catalysts, it is observed that, independent of the support, the chemisorption capacity is lower on the bimetallic catalysts. However, in most of these catalysts the decrease in hydrogen chemisorption was very modest.

Therefore, our chemisorption results would indicate that primarily the type of silica support used and, to a lesser extent, the impregnation procedure play a crucial role in the resulting metal-metal interaction. We will focus our attention on two silica supports, Cab-O-Sil HS5 and M5, which have very similar physical characteristics but cause strikingly different effects on the chemisorption capacities of the catalysts.

Temperature Programmed Desorption. The TPD (298-773 K) for the Ru only catalysts are shown in Figure 2a. That part of the total H_2 chemisorption which is irreversible at room temperature is stronger on HS5 than M5. This may only be an indirect effect of the support, i.e., the smaller particles on HS5 may account for this difference. In Figure 2b, we show the flash desorption (nonprogrammed) between 176 and 298 K and the TPD for four catalysts: M5 and HS5 supports with Ru only (labeled A) and Ru-Cu (labeled B). Note that the stronger hydrogen chemisorption observed on A1-HS5-Cl is not apparent



Figure 2. TPD of H_2 (a, top) from Ru only A1-M5-Cl and A1-HS5-Cl, and (b, bottom) from Ru-Cu catalysts B1-M5-Cl and B1-HS5-Cl. In b, the Ru only catalysts (labeled A) are repeated for comparison. The low-temperature desorption from 196 to 298 K is shown as a function of warming time because this temperature change was not programmed.

on B1-HS5-Cl. This could imply a growth in particle size, but because we do not see any change in the X-ray diffraction we attribute it to Cu blocking more energetic H_2 chemisorption sites. On both supports, the bimetallic catalysts show a decreased hydrogen desorption, in the range 298-773 K, compared to the corresponding pure Ru catalyst. These results do not parallel the opposite behavior exhibited in the static adsorption measurements. We must keep in mind that in these TPD measurement the catalysts are flushed with a carrier before the heating program is initiated. This may cause the desorption of weakly held hydrogen, which would be counted in the volumetric adsorption experiment. On the other hand, the low temperature desorption results (176-298 K) show a closer correlation with the volumetric adsorption data, i.e., a slight increase in the H₂ uptake on the Ru-Cu/M5 catalyst relative to the pure Ru catalyst, but a decrease on the bimetallic catalyst supported on HS5 silica.

Catalytic Activity Measurements. We have investigated the effect of Cu addition on catalytic activity of several Ru monometallic and Ru–Cu bimetallic catalysts for various hydrocarbon reactions. In particular, we have performed a comparative study on the two contrasting silicas, HS5 and M5, for two different Ru salts and for two different impregnation procedures. Table III summarizes the reaction rates measured in the continuous flow reactor over these catalyst for ethane hydrogenolysis, benzene hydrogenation, and cyclohexane dehydrogenation/hydrogenolysis reactions. To avoid the potential problem of overcounting surface ruthenium atoms by H_2 chemisorption, we have expressed the rates per total Ru atoms in the catalysts in units of molecules/(min Ru).

In agreement with previous investigations,² profound decreases in ethane hydrogenolysis activity were found for the bimetallic Ru-Cu on either HS5 or M5 compared to the pure Ru catalysts, but the activation energy remained about constant around 30 kcal/mol for all the catalysts. No significant differences were observed between the two supports. However, the activity depression was more pronounced for the bimetallic catalysts prepared

TABLE III: Catalytic Activity of Ru and Ru-Cu Catalys	TABLE III:	Catalytic /	Activity o	f Ru and	Ru-Cu	Catalysts
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	C ₂ H ₄	C_6H_{12} reaction rates at 473 K		C, H,	
catalyst	hydrogenolysis rate at 473 K	hydro- genolysis	dehydro- genation	hydrogenation rate at 323 K	
A1-HS5-Cl	10.7	0.01	0.08	1.40	
B1-HS5-Cl	0.06	0.001	0.03	0.26	
B2-HS5-Cl	3.12				
A1-HS5-NO	11.4				
B1-HS5-NO	0.11				
B2-HS5-NO	0.86				
A1-M5-Cl	8.90	0.13	0.003	6.0	
B1-M5-Cl	0.04	0.00016	0.006	0.06	
B2-M5-Cl	0.07				
A1-M5-NO	12.1				
B1-M5-NO	0.32				
B2-M5-NO	4.95				

^aRates are in units of molecules per min per total number of Ru atoms. Specific rates normalized to hydrogen site density may be obtained by using the results in Table I.



Figure 3. Temperature programmed re-reduction of (a) Ru and (b) Ru-Cu catalysts supported on HS5 Cab-O-Sil silica support.

from ruthenium chloride. As previously proposed,¹⁰ this effect may be related to a poorer Ru dispersion.

In parallel to the behavior exhibited in the chemisorption experiments, it was observed that, independent of the support, the sequentially impregnated catalysts exhibited a modest decay in ethane hydrogenolysis activity. The greatest activity decay was observed for the B2-M5-Cl catalyst. However, this effect may be ascribed to the very low Ru dispersion. In any case, the sequential impregnation appears to result in a poor metal-metal interaction.

Only modest decreases in activity were observed for the cyclohexane hydrogenolysis and benzene hydrogenation reactions over the HS5-supported Ru-Cu catalyst compared to the pure Ru catalyst. The cyclohexane dehydrogenation reaction was much less affected. By contrast, on the M5-supported catalyst, the addition of Cu caused a strong activity depression (three orders of magnitude) for cyclohexane hydrogenolysis, which was accompanied by a slight increase in the dehydrogenation activity. On the other hand, the benzene hydrogenation reaction was very much affected by the addition of Cu. It dropped tow orders of magnitude, an effect not expected for a structure insensitive reaction (see Discussion).

Temperature Programmed Re-Reduction. Figure 3 shows the TPR spectra obtained for HS5-supported Ru and Ru-Cu catalysts after oxidation at 373 K. In both cases, a single reduction peak



Figure 4. Temperature programmed re-reduction of (a) Ru and (b) Ru-Cu catalysts supported on M5 Cab-O-Sil silica support.

was evident, indicating that the ruthenium and copper phases are reduced simultaneously. Obviously, the reduction of copper must have been assisted by ruthenium since pure Cu only gets reduced at temperatures above 520 K. A slight shift to higher reduction temperatures was observed for the B1-HS5-Cl catalyst, which indicates that copper, in turn, may modestly inhibit the reduction of ruthenium.

The TPR spectra of M5-supported catalysts are shown in Figure 4. For these catalysts, the reduction patterns of the monometallic and bimetallic catalysts are decidedly different. In this case, the temperature shift observed for the C1-M5-Cl catalyst compared to the A1-M5-Cl catalyst was more pronounced. In addition, the bimetallic catalyst B1-M5-Cl exhibited a high temperature reduction shoulder on the main peak at about 470 K which was not present for the B1-HS5-Cl catalyst. This high temperature reduction shoulder may be ascribed to a separate copper phase. However, its reduction occurs at a much lower temperature than that observed for pure Cu. Thus, the reduction of this pure copper phase must also be assisted by ruthenium.

Discussion

The most obvious conclusion from this work is that Cab-O-Sil HS-5 silica results in substantially different Ru-Cu clusters than do the other silicas in so far as this is reflected in the effect of Cu addition on th sign of the relative amount of H₂ chemisorption compared to pure Ru/SO_2 (see Figure 1). It is also evident that the metal-metal interaction is very dependent on dispersion and that the unique properties of HS-5 are most obvious at low dispersion. It seems that this is not a result of the silica influencing the final Ru-Cu cluster that results from the series of steps: impregnation, drying, etc., but an effect of the silica on the genesis of the cluster, i.e., the interaction of the precursors of the metals or other steps in the cluster formation has an effect on the degree or kind of metal-metal interaction. We are not in a position to explain just how the silica works its will during cluster genesis, but we will try to use the catalytic consequences to make deductions about the structure of the resulting Ru-Cu clusters.

We begin with the working hypothesis that the morphology of the final Ru–Cu cluster on HS-5 is different from M-5 (and all other silicas we have investigated). Then we will attempt to construct a qualitative morphological model that conforms to all of our experimental observations. First, consider the relative effect of added Cu on three reactions, ethane hydrogenolysis, cyclohexane hydrogenolysis, and benzene hydrogenation. From a large number of investigations of catalysts in which the average size of available surface atom ensembles (sites) on group VIII (group 8)³² metals is decreased by addition of an inert grup 1b (group 11) metal,²⁰ a poison such as S,²¹ coke formed by side reactions,²³ or other means, it is generally agreed that the effect will be greatest on

⁽²³⁾ Ponec, V. Mater. Sci. Eng. 1980, 42, 135.

ethane hydrogenolysis and least on benzene hydrogenation.²⁴ Put another way, the order of structure sensitivity for these reactions is ethane hydrogenolysis > cyclohexane hydrogenolysis > benzene hydrogenation. Indeed, this is the order observed when the ratio of $\{(Ru/SiO_2)/(Ru-Cu/SiO_2)\}_{HS5}$ is calculated from Table III, i.e., the ratio is 250:10:5. This suggests that the overall morphology of the Ru-Cu clusters on HS-5 must be one in which Cu atoms (or small islands) are spread out over the Ru particles effectively breaking up large Ru ensembles and thus having a relatively greater effect on the more structure-sensitive reaction (ethane hydrogenolysis) and relatively little effect of the least structuresensitive reaction (benzene hydrogenation). This behavior has to be constrasted with the ratio of $\{(Ru/SiO_2)/Ru-Cu/SiO_2)\}_{M5}$ calculated from Table III, i.e., the ratio 160:810:100. The inherent structure sensitivity of the three reactions is not evident here, but there is a relatively large effect for all reactions. This suggests to us that Ru particles on M-5 are covered by comparatively large (and probably thick) islands of Cu with only small patches of Ru showing through between the islands.

If the two pure-Ru catalysts (A1-HS5-Cl and A1-M5-Cl) are compared, rather large differences in activity and selectivity are immediately obvious. The rates, on a per total Ru atom basis, for cyclohexane hydrogenolysis and benzene hydrogenation over the Ru catalyst supported on M5 are, respectively, 13 and 4.3 times as high as those over the HS5-supported catalyst. In addition, the selectivity toward dehydrogenation for the cyclohexane reactions is 90% on Ru/HS5 but only 2.2% on Ru/M5. These differences however, must be contrasted with the almost identical rates observed for ethane hydrogenolysis on the two pure-Ru catalysts. We may note that the metal dispersion of these two catalysts are significantly different, i.e. 29% for Ru–HS5 and 9% for Ru/M5. According to the order of structure sensitivity described above, the greater particle size effects should be observed for the ethane hydrogenolysis reaction. But, this is not true in this case. We may explain this apparent contradiction in terms of the extent of carbon deposition, which may strongly depend on the type of reaction being studied. We have observed that, in the case of cyclohexane and benzene reactions, a rapid deactivation takes place during the first few minutes before a steady-state activity level is reached. We ascribe this activity decay to the presence of carabonaceous deposits on the metal surface. On the other hand, no deactivation is observed in the case of ethane hydrogenolysis reaction. Thus, the differences observed for the cyclohexane and benzene reactions over the two pure-Ru catalysts might be related to different extents of C buildup. As shown by Lankhorst et al.,²⁵ larger particles are more resistant to carabon deposition than smaller ones. This would mean that our Ru/HS5 catalyst would be more affected by carbon deposition than Ru/M5. In that case, we should expect a lower activity for benzene hydrogenation and cyclohexane hydrogenolysis but a higher selectivity toward dehydrogenation on Ru/HS5. When two parallel reactions, like cyclohexane hydrogenolysis/dehydrogenation, occur simultaneously, a partial blocking of the surface affects the selectivity by preferentially deactivating the more "demanding" reaction, i.e. hydrogenolysis.

We note that there may be a correlation between the stronger hydrogen chemisorption on Ru/HS5 than on Ru/M5 (as evidenced by TPD, see Figure 2a) and the greater propensity for these smaller particles to become covered by carbon during reaction. Somorjai et al.²⁶ have shown that stepped and kinked surface are more effective at breaking C-C bonds that smooth surfaces. Kim et al.⁷ have shown that Cu preferentially goes to the most coordinately unsaturated (step or defect) sites on model Ru single crystals. When Cu is added to Ru on HS5, the strongly bonded hydrogen chemisorption is removed (see Figure 2b). Thus, strong hydrogen bonding and propensity for C poisoning appear to be associated with the same sites on A1-HS5-Cl. One caution must be added here. A 29% dispersion does not imply that Ru particles are all that small, so it may be that HS5 produces a Ru morphology which has more rough surfaces. The particle size itself would not be then the governing factor.

A situation similar to the carbon deposition effect is encountered in the case of bimetallic catalysts. At first glance, the fact that added Cu decreases the rate of dehydrogenation relative to pure Ru on HS-5 and increases this rate on M-5, entirely in parallel with the behavior of H_2 chemisorption, might suggest that there was in these results an important clue. We believe this not to be the case because of the probable kinetic coupling between cyclohexane dehydrogenation and hydrogenolysis. In the case of M-5, addition of Cu depresses hydrogenolysis by about three orders of magnitude. Because there is so little consumption of adsorbed cyclohexane via hydrogenolysis, the dehydrogenated precursor to both dehydrogenation and hydrogenolysis must increase in surface coverage. Put another way, the kinetically derived virtual pressure of cyclohexane will be so increased by blocking of the route to hydrogenolysis that one might say it was surprising that the apparent cyclohexane dehydrogenation rate only increases by a factor of two. It should be noted that Sinfelt² also saw a modest increase in cyclohexane dehydrogenation on Ru-Cu/SiO₂ (HS-5) when hydrogenolysis was greatly inhibited by addition of Cu. He suggested that this might be a result of Cu decreasing the bond energy between the product (benzene) and the site. We discount this possibility because TPD of benzene always has the same temperature of maximum desorption rate with or without Cu on both HS-5 and M-5 (but, of course, the amount of adsorbed benzene depends on the silica support, dispersion, and added Cu). This interpretation would predict that the apparent absolute rate of cyclohexane dehydrogenation as a function of progressively covering a particle (or surface) of Ru with Cu would be a gradual increase in the rate as the structure-sensitive hydrogenolysis was selectively poisoned in preference to dehydrogenation but the dehydrogenation rate would pass through a maximum as the surface of Ru became completely clogged with Cu. This may be an alternative explanation for Peden and Goodman's recent results¹⁹ for Cu deposits on Ru(0001) which behaved just this way and was interpreted as a "modified activity of the strained Cu overlayer" or, alternatively, "a mechanism whereby the two metals cooperatively catalyze different steps of the reaction"

The differing carbon deposition on A1-HS5-Cl and A1-M5-Cl is clearly a complicating factor in the interpretation of the effects of added Cu. However, there is one observation which makes it clear that carbon deposition does not have an overriding effect. Smaller particles result on A1-HS5-Cl, and, therefore, there is a larger carbon effect. However, this effect is not so great that the expected ordering of structure sensitivity, i.e., C_2H_6 hydrogenolysis > C_6H_{12} hydrogenolysis > C_6H_6 hydrogenation, is not apparent when catalysts with and without Cu are compared. In contrast, this expected ordering does not prevail when pure Ru and Ru-Cu supported on M5 are compared even though the carbon deposition effect is smaller, i.e., the change in order of activity can clearly be attributed to an effect of Cu.

When a significant amount of carbon deposits is present on a group VIII (group 8) metal surface under reaction conditions, the addition of a less-active group Ib (group 11) metal, such as Cu, may not only affect the primary reaction only but also the extent of carbon buildup. The presence of Cu on the group VIII (group 8) metal surface strongly affects C-C bond breaking, but only modestly C-H bond breaking. Thus, if the primary reaction involves the rupture of C-H rather than C-C bonds the two opposite effects of Cu addition may cancel to some extent. As shown by van Barneveld and Ponec,²⁷ the addition of Cu to Ni causes a decrease in the rate of benzene hydrogenation at low reaction temperatures, but an increase in rate at high temperatures. The competing effects of Cu to decrease carbon buildup (increase rate) and directly inhibit the rate (modestly for structure insensitive

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reactions) appear to be evident in the relative rates of benzene hydrogenation shown in Table III. On A1-HS5-Cl, the rate is low (due to C deposition) but, because of the competing effects, the change in rate is small when compared to B1-HS5-Cl after Cu addition. In the case of M5 support, the dominant effect appears to be a massive blocking of the Ru surface by Cu (compare A1-M5-Cl to B1-M5-Cl) to give rise to a two order of magnitude depression in the rate of this structure-insensitive reaction.

All the sequentially impregnated catalysts, independent of the support, exhibited modest depressions in catalytic activities and chemisorption capacities compared to the pure Ru catalysts. This behavior indicates that by the sequential impregnation method little metal-metal interaction is achieved. In every case, small amounts of Cu appear to be well spread over the Ru surface. The support does not affect the resulting cluster structure, which suggests that its main effect would operate at the first stages of the catalyst genesis. Thus the differences between the two silica supports are only evident when coimpregnated catalysts are compared.

To further elaborate on the morphology difference of Ru-Cu clusters formed on HS-5, we next consider the temperature programmed re-reduction results in Figures 3 and 4. In these experiments we are attempting to probe the metal-metal interaction between Ru and Cu by the ease with which chemisorbed oxygen can be removed. That is, the Ru-Cu clusters were first formed during the initial high temperature reduction and then mildly oxidized (373 K) with the expectation that the surfaces of both metals would be oxidized. (Bulk oxidation and consequent phase separation¹¹ would destroy all memory of the initial morphology.) The temperature programmed re-reduction clearly shows that hydrogen is transported between the two metals on both supports in the sense that bimetallic clusters on both supports reduce well below that temperature where pure Cu would be reduced, 520 K. However, beyond this generalization, the Ru-Cu clusters are quite dissimilar on the HS-5 amd M-5 supports. On HS-5 the Ru–Cu clusters reduce at a temperature only slightly above that of pure Ru, indicating a very intimate contact of the two metals and reasonably direct access of hydrogen to the Ru surface (see Figure 3). In contrast, the Ru-Cu clusters on M-5 reduce at a substantially higher temperature than pure Ru on M-5 and there is evident a shoulder on the high temperature side of the reduction peak. These results are entirely consistent with the general outline of the morphology deduced from the activity depression above, i.e., well spread out Cu on Ru particles on HS-5 and both massive coverage of the surface of Ru by Cu (resulting in a somewhat impervious copper oxide layer) and probably a separate Cu particulates phase in contact with the copper covered Ru particles on M-5. This general picture of cluster morphology does not violate mass conservation for the 1:1 atomic ratio of Cu:Ru sued for M-5, but it is difficult to account for all the Cu on HS-5. That is, H_2 chemisorption indicates that approximately one-third of the Ru is exposed on the surface of Ru particles on HS-5 (see Table I). Using the factor by which benzene hydrogenation is depressed, 5, one finds that at least 20% of the Ru must remain exposed in the Ru-Cu cluster. If all of the Cu were spread out over the remaining 80% of the surface Ru atoms to get the intimate contact required by the TPD results, the average thickness of the Cu layers covering Ru would be four atomic layers. The above reasoning suggests that this is a minimum average thickness. It seems difficult to have all the Cu in intimate contact with the Ru and at the same time well spread out without picturing the unlikely structure of Cu whiskers bristling on the surface of Ru particles. We will return to this apparent contradiction after we consider our last chemical probe of cluster morphology, H₂ chemisorption.

We are obliged to account for the fact that added Cu decreases H₂ chemisorption on HS-5 but increases H₂ chemisorption on M-5 at the same 1:1 Cu-to-Ru ratio. In the case of M-5, the recent results of Goodman on hydrogen spillover from Ru to Cu in the model system would appear to allow a straightforward rationalization for M-5. We believe that the Ru particles on M5 are massively covered, nearly encapsulated by Cu (with very limited access to Ru) and these are in contact with or connected to separate Cu particles (or perhaps pure Cu halos) resulting from the migration of Cu precursors to the edge of Ru particles where they were catalytically reduced. There is an unpublished report that H₂ spillover from Ru to Cu on silica supported bimetallic clusters has been confirmed by NMR.⁷ The combined surface area of the Cu clad Ru particles and the associated Cu halo exposes an area greater than that of the Ru particles alone and, given H₂ spillover following dissociation on the Ru (of very limited exposure), we can account for the increase in H_2 chemisorption when Cu is added to Ru on M-5.

The decrease in H₂ chemisorption on HS-5 is more difficult to explain unless a lower Ru dispersion is contemplated for the bimetallic catalyst. If all of the Cu were in intimate contact with the Ru particles on HS-5 and hydrogen spillover were also to occur here, then at best there would be no change in the H₂ chemisorption on addition of Cu. One way of accounting for both the mass balance problem outlined above and the decrease in H_2 chemisorption would be to postulate a limited mixing (let us call it a surface alloying) for the clusters of Ru-Cu on HS-5, which would alter the normal properties of copper. Recent TPD spectra of H_2 from Cu on Ru (0001)¹⁸ suggest that Cu in intimate contact with Ru or within one or two atomic layers of the Ru might have weaker H_2 chemisorption. The amount of hydrogen retained at room temperature when less than a monolayer of Cu is deposited on Ru(0001) is about half of that held by the clean Ru(0001)crystal.

One must ask if there is any precedent for the formation of mixed clusters or partial alloying in small particles for a system which is immiscible in the bulk. The answer is that this has been observed for the Rh-Ag system supported on TiO2.28 Rhodium-silver is an immiscible bimetallic system quite similar to ruthenium-copper. An EXAFS analysis of Rh-Ag/SiO₂ is consistent with the usual picture of Ag chemisorbed on the surface of Rh particles, but the EXAFS of Rh-Ag/TiO₂ can only be understood if Rh atoms are mostly surrounded by Ag and Ag is mostly surrounded by Rh, i.e., that there is something approximating alloying. In this case one has the chemical out that a species from the support, TiO_x , gives rise to direct Rh-Ti bonding²⁹ and this species may act more or less like a flux to allow the Rh and Ag to mix or approximate an alloy. Could it be that there is some impurity or surface property of HS-5 which plays this role? We cannot answer this question at the present time, but see little alternative if we are to retain the qualitative morphological structure that is demanded by the catalytic activity and TPR reduction results and at the same time rationalize the H₂ chemisorption.

During the process of revision of this paper, an analytical electron microscopy study of Ru-Cu/SiO₂ catalysts was published.³⁰ The support used in that study is a silica Davison 951. The bimetallic catalysts, containing only 34 and 8 mol %~Ru(compared to 50 mol % used in our work), exhibited a drastic suppression of H_2 chemisorption, which would suggest that these catalysts behave like the HS5-supported systems. In qualitative agreement with the model that we have proposed for the bimetallic clusters supported on Cab-O-Sil HS5, the authors propose that atomic interdispersion of Ru and Cu occurs on the surface of the bimetallic clusters. On the other hand, they observe the presence of pure Cu particles which in every case are larger than 4 nm in diameter. However, both the high Cu/Ru ratios used and the microporosity (about 5-nm average pore diameter) of the very high surface area Davison 951 would tend to result in metal phase separation and large Cu particles. One must also be aware of the effects of pore blockage when the particle size is comparable to the pore diameter. Using a similar silica, in a Rh-Ag investigation³¹ we found evidence for pore blockage at all Ag/Rh ratios

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greater than one.

Summary

Hydrogen chemisorption may be increased or decreased, depending on the support, by Cu addition to Ru (Figure 1). Ethane hydrogenolysis is always depressed (Table III). Therefore, one must conclude that there is no direct correlation between room temperature equilibrium chemisorption of H₂ and ethane hydrogenolysis, as was originally suggested.²

It appears reasonably certain that Ru-Cu clusters on Cab-O-Sil HS5 silica have a significantly different morphology than Ru-Cu clusters on other silicas, Cab-O-Sil M5 in particular. The deduced morphology on M5 suggests an almost completely encapsulated Ru particle (with a pure Cu halo) such that both structure-sensitive and structure-insensitive reactions are inhibited to about the same extent. The morphology of Ru-Cu clusters on HS5 is such that there is an efficient breaking up of ensembles of surface Ru atoms and therefore a selective suppression of structure sensitive reactions. To account for intimate contact of all the Cu with Ru on HS5 as demanded by the TPR we postulate that the outer layers of the clusters form a Cu-rich mixture that does not form on other silicas nor in the bulk.

Note Added in Proof. We have recently obtained X-ray absorption spectra of catalysts which were prepared by a procedure identical with that used for A1-HS5-C1, B1-HS5-C1, A1-M5-C1, and B1-M5-C1, the four principal catalysts discussed here. Analysis of the near edge and EXAFS of Ru and Cu should allow us to paint a more quantitative picture of the difference in morphology of Ru-Cu clusters on the HS5 and M5 silicas. For example, above we assumed that oxidation at 373 K for the TPR experiments resulted only in surface oxidation of Cu and/or Ru. We can now say that the Cu in both B1-HS5-C1 and B1-M5-C1, is essentially oxidized at 373 K, that Ru is partially oxidized B1-M5-C1, and that Ru is effectively completely passivated toward oxidation at 373 K on B1-HS5-C1. We also note that, based on EXAFS coordination numbers, Ru in the bimetallic catalyst B1-M5-C1 is better dispersed than in B1-HS5-C1. For pure Ru, just the opposite was observed by H₂ chemisorption (and confirmed by EXAFS) on A1-M5-C1 and A1-HS5-C1 catalysts. This possibility was not taken into account in the above analysis and suggests that it may not be necessary to invoke H_2 spillover from Ru to Cu to account for the increase in H₂ uptake when chemisorption A1-M5-C1 and B1-M5-C1 are compared. A manuscript on the near edge and EXAFS of Ru and Cu for these four catalysts which will refine the morphological model is in preparation.

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Registry No. H₂, 1333-74-0; Cu, 7440-50-8; Ru, 7440-18-8; ethane, 74-84-0; cyclohexane, 110-82-7; benzene, 71-43-2.

Covered Clusters: The Composition of Hydrogenated Iron and Nickel Clusters

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The composition of hydrogenated and deuteriated iron and nickel clusters are reported for clusters in the 6 to 260 atom size range. Full surface coverage (i.e., one adsorbate atom for every surface metal atom) is found for iron clusters up to about 80 atoms, while larger clusters show decreasing coverage with increasing cluster size. In contrast, full coverage is found for the larger nickel clusters. These results are discussed in terms of cluster structure, and a possible connection is made to the different catalytic behavior seen for these two metals.

Introduction

In recent years studies of the physical and chemical properties of isolated transition-metal clusters have been providing us with fascinating insights into these unique species. Techniques have been developed to measure cluster chemical reactivity, 1-3 adsorbate binding energies, 36,4 ionization potentials,5 electron affinities,6 and magnetic properties.⁷ However, an important cluster property has remained elusive—their geometrical structures. Aside from high-resolution optical spectroscopy on the smallest clusters,8 direct techniques for determining isolated metal cluster structure do not yet exist. With the intense interest in clusters sparking rapid development of the field, this situation will probably not continue for long. In the meantime, the one general experimental probe of structure that we have is to measure the ability of clusters to bind simple molecular adsorbates. Experiments analogous to gas uptake measurements of catalytic preparations give us some idea of the number and nature of binding sites on cluster surfaces. As our body of data in this area grows, hopefully some consistent picture of cluster structure will emerge.

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In a previous publication,⁹ we reported on the composition of iron clusters saturated with hydrogen. In general, the results could be interpreted in terms of roughly spherical clusters that, at least

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