Fischer–Tropsch Synthesis over Ru-Group Ib/SiO$_2$ Catalysts

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Reaction studies probing the catalytic activity and selectivity of the Fischer–Tropsch synthesis reaction have been performed for a series of chlorine-free, silica-supported Ru–group Ib (Ag, Au, Cu) bimetallic catalysts. The goal of this work was to isolate ensemble effects, electronic effects, or the influence of the metal particle structure on catalytic behavior.

The rate per surface ruthenium atom, or turnover frequency, was used to correlate catalytic activity with surface composition. Surface compositions were determined previously via nuclear magnetic resonance of chemisorbed hydrogen and strong hydrogen chemisorption experiments. The turnover frequencies for the series of Ru–Cu catalysts declined by a factor of about two when the relative copper composition increased from 0% to 10% (at constant ruthenium loading). Increasing the copper loading beyond this level did not affect the turnover frequency. Similar behavior was noted for the Ru–Ag catalysts where the turnover frequency declined until a silver loading of about 25% was obtained. Increased silver content did not further change the turnover frequency. The drop in turnover frequency with relatively small amounts of copper or silver is attributed to a structure sensitivity effect. As the segregating element (Ib) preferentially goes to the low-coordination, defect-like sites, the observed turnover frequency declines. Once all low-coordination sites are filled, no variation in turnover frequency with composition was observed, indicating a lack of ensemble effects. This result contrasts with previously reported investigations of the Ru–Cu system. The overall rate changed modestly and the turnover frequency did not change significantly with composition over the series of Ru–Au catalysts. The product distribution shifted to smaller molecules with increasing copper content in the Ru–Cu series but remained constant over the entire composition range for the Ru–Ag and Ru–Au catalysts. The ability of hydrogen to exchange between copper and ruthenium sites was correlated with enhanced chain termination rates. © 1990 Academic Press, Inc.

INTRODUCTION

Supported bimetallic cluster catalysts are interesting subjects of fundamental catalytic investigations because one can, in principle, vary those properties thought to influence chemisorptive and catalytic behavior simply by varying the relative content of the constituent metals (*1, 2*). The term "bimetallic cluster," coined by Sinfelt (*3*), describes supported systems composed of metals that do not form bulk alloys. The bimetallic catalysts Ru–Cu, Ru–Ag, and Ru–Au are examples of this type of catalyst where one of the elements (Ru) is catalytically active for a variety of reactions and the second metal (Cu, Ag, or Au) is relatively inactive (*2–9*).

The Fischer–Tropsch synthesis, which converts carbon monoxide and hydrogen to hydrocarbons, occurs readily on ruthenium, and a significant reduction in catalytic activity is observed, for example, when copper is added to the catalyst.

Previous investigations of silica-supported Ru–Cu catalysts have noted a drastic reduction in catalytic activity when the copper content is increased (*4–6*). Lai and Vickermann (*4*) reported a change in apparent activation energy from 19.6 kcal/mole for pure ruthenium up to 28.9 kcal/mole with increasing copper content for a series of Ru–Cu catalysts, and they suggested that copper exerts an electronic effect on ruthenium. They proposed that copper blocking

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the active sites was the dominant effect, however. Bond and Turnham (6) and Luyten *et al.* (5) observed no change in the activation energy, 21 and 30 kcal/mole, respectively, but did note a change in the preexponential factor. They proposed that no change in the mechanism occurred but that the addition of copper served to block the active sites by a geometric or ensemble effect. Various estimates of the ensemble size necessary for reaction have been given as four to five (6) and nine to thirteen (4) adjacent ruthenium atoms. These ensemble estimates are based on the assumption that copper disperses randomly over a ruthenium surface and that ruthenium surface concentrations can be accurately determined from chemisorption techniques.

The selectivity toward higher hydrocarbons is also affected by the addition of copper to ruthenium. A shift in selectivity toward methane and smaller hydrocarbons has been noted as the copper content was increased (4–6).

Peden and Goodman (7) studied copper deposited on a single-crystal Ru(001) surface. They found a linear decrease in methanation activity with increasing copper coverage, which indicates no change in turnover frequency. Their data suggest that copper merely acts as a diluent, blocking ruthenium atoms on a one-to-one basis. Consequently no ensemble effects were observed.

Fewer studies have been reported for the Ru–Ag (8) and Ru–Au (9) systems. Datye and Schwank (9) reported results for a silica-supported Ru–Au system that showed a monotonic decline in turnover frequency with increasing gold and decreasing ruthenium content. No change, within experimental error, is reported for activation energies with varying gold contents, suggesting perhaps that gold serves to dilute active ruthenium ensembles. Slight shifts in product distributions to larger molecules occurred when the ratio of gold to ruthenium was increased. Note that both gold and ruthe-

nium content of the catalyst were varied in this work.

A key to understanding catalytic behavior of bimetallic catalysts is the proper determination of the catalysts' surface composition. Characterization of single-crystal surfaces can be accomplished by using surface-sensitive techniques, such as low energy and Auger electron spectroscopies and temperature programmed desorption (10). Supported catalysts are more difficult to characterize because of their structure and heterogeneity. Supported copper, silver, or gold catalysts by themselves do not appreciably adsorb hydrogen. Therefore, it may be reasonably assumed that the amount of surface ruthenium present can be calculated from the amount of dissociatively adsorbed hydrogen and from the assumed stoichiometry of adsorption. Recently it has been shown that the presence of copper in the system causes an overestimation of surface ruthenium because hydrogen spillover from ruthenium to copper occurs (11–16). Hydrogen dissociatively adsorbs on surface ruthenium atoms and then migrates to the adjacent copper atoms. The spillover effect is not seen for the addition of gold or silver to ruthenium (17). Consequently, selective hydrogen chemisorption can be used to determine the amount of ruthenium at the surface in the Ru–Au and Ru–Ag systems; but for the Ru–Cu system, an alternative method must be used. A useful alternative method for determining Ru–Cu catalyst surface compositions employs nuclear magnetic resonance of adsorbed hydrogen (12).

Similar arguments can be made to suggest that carbon monoxide adsorption, as applied in one previous study (6), will not give the relative surface composition of Cu–Ru bimetallic particles. The use of CO adsorption to determine ruthenium dispersion has been questioned because of its tendency to form multiple adsorption bonds, the number of which depends on surface morphology (18–21). Also, the nature of CO adsorption on copper changes significantly when cop-

per is present in the form of a thin layer on ruthenium (22–25).

Monte Carlo simulations can provide interesting insights into the nature of small bimetallic particles (26). This approach can be applied to the Ru–Cu system with one modification; for the purpose of simulation, ruthenium which has a hexagonal-closed-packed (hcp) structure is assumed to be face-centered-cubic (fcc). This technique shows that copper, in low concentrations, tends to populate low-coordination edge, corner, and other defect-like sites. With further addition of copper, two-dimensional copper islands are formed on the basal planes. If this is the case, individual copper atoms could not break up ensembles; certainly, the assumption of random surface dispersion is invalid. Similar behavior is noted for simulations of the Ru–Au and Ru–Ag systems except that a greater three-dimensional clustering tendency is predicted. Kim et al. (27) report experimental evidence of copper preferentially populating ruthenium defect sites. Also, single-crystal studies with submonolayer amounts of copper deposited on ruthenium (001) surfaces show that copper is highly dispersed at 100 K. However, subsequent annealing of the sample to 300 K results in the formation of two-dimensional copper islands (7, 15, 16, 28–30).

A final factor to consider is chlorine contamination that may occur because of the metal salts used in preparing the catalysts (31–34). Lu and Tatarchuk (31, 34) report that on Ru/Al_2O_3 at 373 K chlorine causes hydrogen chemisorption to become activated. The adsorbed electronegative chlorine decreases the electron density of nearby ruthenium atoms and thereby inhibits electron donation to, and dissociative adsorption of, hydrogen. They suggest that this electronic effect serves to increase the barrier to dissociative chemisorption of hydrogen. Narita et al. (32, 33) also report that chlorine inhibits the adsorption of CO and H_2 on Ru/SiO_2 prepared from $RuCl_3 \cdot 3H_2O$.

In either case, a similar conclusion can be drawn: adsorbed chlorine causes a decrease in the chemisorptive capacity of ruthenium. Consequently, dispersion measurements made with chemisorption techniques may tend to underestimate the surface ruthenium when chlorine is present. In addition, chlorine may preferentially adsorb at catalytically distinct sites (e.g., edges and corners) (31) and thereby alter catalytic trends. The previous studies on supported systems (4–6, 9) were all performed on catalysts prepared from metal salts containing chlorine.

This paper reports the results of the study of the Fischer–Tropsch synthesis reaction over a series of chlorine-free, silica-supported Ru–Cu, Ru–Ag, and Ru–Au catalysts. Careful attention was given to the determination of the amount of ruthenium at the surface of the metal particles, and the effects of hydrogen spillover on the Ru–Cu catalysts was taken into account. The goal of our work was to isolate ensemble effects, electronic effects, or the influence of the metal particle structure on catalytic behavior.

EXPERIMENTAL

All the catalysts used were supported on Cab-O-Sil HS-5 amorphous fumed silica (with a surface area of 300 $m^2 g^{-1}$). Ruthenium loadings were 4% (by weight) in all cases. Catalysts were prepared by the coimpregnation incipient wetness technique from an aqueous solution of the metal salts. The metal salts used were $Ru(NO)(NO_3)_3$ with either $Cu(NO_3)_2 \cdot 6H_2O$ or $Ag(NO_3)$, and $RuCl_3 \cdot 3H_2O$ and $HAuCl_4 \cdot H_2O$ for the Ru–Au series. When ruthenium chloride was used, the residual chlorine was removed by washing the catalysts in warm distilled water five times (17). Detailed preparation procedures are described elsewhere (12, 17, 35). For the chlorine-contaminated catalysts, the ruthenium dispersion measured by strong hydrogen chemisorption after each wash confirmed that the apparent dispersion increased with successive wash-

ing. After five washes no further increases were observed. All catalysts were dried at 383 K overnight and reduced at 723 K in 50 sccm H_2 for two hours.

Ruthenium dispersions for the Ru–Au and Ru–Ag catalysts were measured by using strong hydrogen chemisorption (17). Reduced and evacuated samples were exposed to hydrogen (0–60 Torr) and allowed to equilibrate at various pressures in order to generate a total hydrogen adsorption isotherm. The reversible hydrogen adsorption isotherm was collected under the same conditions after a 10-min evacuation period (to 10^{-6} Torr) following the first adsorption step. The strong hydrogen uptake is taken to be the difference between values of the total and the reversible isotherms extrapolated to zero pressure.

Dispersion of ruthenium in the Ru–Cu catalysts was measured via proton NMR (12). The surface composition was obtained from the NMR of the reversibly adsorbed hydrogen rapidly exchanging between copper and ruthenium sites at the surface.

Reaction studies were carried out in a single-pass, fixed-bed, flow microreactor system described previously (36). Reactant gas, consisting of purified H_2, CO, and Ar in a molar ratio of 3/1/0.5 and a space velocity of about 10,000 hr^{-1} (STP) based on bed volume, was used in all runs. The reactor pressure was held at 1.1 MPa and the temperature at 523 K for all runs except for activation energy studies, where a range from 498 to 548 K was used. Reactor temperature was maintained with an air-fluidized sand bath. Thermocouples at the top, middle, and bottom of the sand bath plus a movable thermocouple positioned axially in the reactor assured the presence of a uniform temperature distribution.

Catalyst sample loadings were varied from 0.1 to 3.0 g, depending on activity, and conversions were kept below 10% to ensure differential operation. In all cases the catalyst bed was diluted to 10 cm^3 using 100-to-200 mesh crystalline SiO_2.

All catalysts were re-reduced at reactor temperature with 200 sccm H_2 for two hours prior to the introduction of the synthesis gas feed. Samples of the product stream were taken after approximately ten minutes on stream. This was sufficient time for the flow to fully develop with minimal catalyst deactivation. All reported values corresponded to initial rate measurements. After sampling, the catalysts were regenerated with 200 sccm H_2 for 30 min at 523 K before reactant gases were reintroduced. From three to five samples were taken for each catalyst run. Periodic blank runs with 10 cm^3 of 200-to-300 mesh crystalline SiO_2 were performed to ensure that no reactions occurred on the walls of the reactor.

On-line product analysis was performed by gas chromatography. Ar, CO, CO_2, and CH_4 were separated on a Supelco S-2 carbosieve column and detected by thermal conductivity. Organic products (up to C_{10}) were separated and analyzed with a 0.25 mm ID, 30 m Supelco SPB-1 capillary column and a flame ionization detector.

RESULTS

The dispersions of the various catalysts (determined by either strong hydrogen chemisorption or proton NMR) and their activity and selectivity are given in Table 1. Slight variations in the pure ruthenium dispersions between different systems are apparent from the data in Table 1. The series of Ru–Au catalysts, which were prepared from a chloride-containing salt, had a slightly higher total metal dispersion as evidence by the pure ruthenium catalyst. The total dispersion (surface atoms per total atoms) for all catalysts is approximately 30%.

The influence of the group Ib metals on the Fischer–Tropsch synthesis rate (expressed as moles of CO consumed per second per total mole of ruthenium) is demonstrated by the results given in Table 1 and Fig. 1. The influence of gold (Fig. 1a) appears to be rather modest. The rate drops by a factor of less than two when gold makes up 40% of the metal portion of the catalyst. The results given in Fig. 1b indicate that

TABLE 1

Atomic % Ib[a]	Ru disp[b]	Rate[c]	TOF[d]	Alpha
0-Au	0.36	0.21 ± 0.02	0.58 ± 0.06	0.57 ± 0.03
10-Au	0.35	0.20 ± 0.01	0.57 ± 0.03	0.52 ± 0.02
20-Au	0.31	0.19 ± 0.03	0.61 ± 0.08	0.51 ± 0.03
30-Au	0.29	0.18 ± 0.03	0.61 ± 0.12	0.49 ± 0.02
40-Au	0.29	0.15 ± 0.04	0.53 ± 0.12	–
0-Ag	0.29	0.21 ± 0.04	0.71 ± 0.12	0.54 ± 0.01
13-Ag	0.23	0.14 ± 0.01	0.58 ± 0.04	0.53 ± 0.02
20-Ag	0.20	0.074 ± 0.01	0.36 ± 0.02	0.55 ± 0.03
30-Ag	0.17	0.072 ± 0.005	0.42 ± 0.03	0.53 ± 0.01
40-Ag	0.11	0.043 ± 0.005	0.38 ± 0.03	–
50-Ag	0.06	0.020 ± 0.005	0.33 ± 0.03	–
0-Cu	0.29	0.17 ± 0.02	0.58 ± 0.01	0.54 ± 0.01
2.5-Cu	0.26	0.10 ± 0.01	0.39 ± 0.02	0.50 ± 0.02
6.1-Cu	0.23	0.063 ± 0.007	0.27 ± 0.03	0.52 ± 0.02
12.1-Cu	0.16	0.037 ± 0.005	0.23 ± 0.03	0.49 ± 0.02
17.9-Cu	0.07	0.016 ± 0.002	0.22 ± 0.01	0.46 ± 0.03
23.6-Cu	0.04	0.0092 ± 0.001	0.24 ± 0.01	0.43 ± 0.01
34.6-Cu	0.02	0.0048 ± 0.001	0.20 ± 0.05	0.37 ± 0.03

[a] All catalysts contain 4% by weight ruthenium.
[b] Surface ruthenium/total ruthenium. Determined via strong hydrogen chemisorption for Ru–Au and Ru–Ag, proton NMR for Ru–Cu. A one-to-one H-to-Ru ratio was assumed in all cases. (Data from Ref. (12).)
[c] Overall rate, mole CO/total mole Ru sec.
[d] Turnover frequency = rate/dispersion.

silver has a more pronounced effect on the reaction rate. At a silver content of 50%, the overall rate has dropped by a factor of ten. The most dramatic reduction of rate with the addition of the diluent Ib metals occurs in the Ru–Cu system (see Fig. 1c). When the catalyst is composed of only 3% copper in the metal phase, the rate is nearly a factor of two lower than a pure ruthenium catalyst. The rate drops by a factor of 35 by the time the copper content has reached 34%.

Turnover frequencies (mol CO consumed per second per surface mole of ruthenium) were calculated by taking the overall rate and dividing by the ruthenium dispersion. Turnover frequencies for each system are given in Table 1 and Figs. 2a–c.

For the Ru–Cu system, interesting behavior contrary to earlier reports is noted. The results given in Table 1 and Fig. 2c show an initial decline of the turnover frequency with copper addition up to about 10% copper. Over this range of copper compositions, the turnover frequency drops by a factor of 2.5. Higher copper loadings do not affect the turnover frequency. Even though the observed rate continues to decrease, the turnover frequency levels off at a constant value. Activation energies were determined for the pure ruthenium catalyst and the bimetallic catalyst containing 35% copper. Values of 20.6 ± 1 kcal/mole and 24.3 ± 4 kcal/mole were obtained, respectively.

The Ru–Ag system showed behavior similar to the Ru–Cu system. The turnover frequency (Fig. 2b) declined up to a silver loading of approximately 20%, after which it remained constant. The Ru–Au system showed a constant turnover frequency (Fig. 2a) over the entire composition range. This latter result is not surprising since the rate changed little with the addition of gold. Clearly gold and ruthenium do not form bimetallic clusters on the support.

Selectivity toward the formation of hydrocarbons was also determined. With the
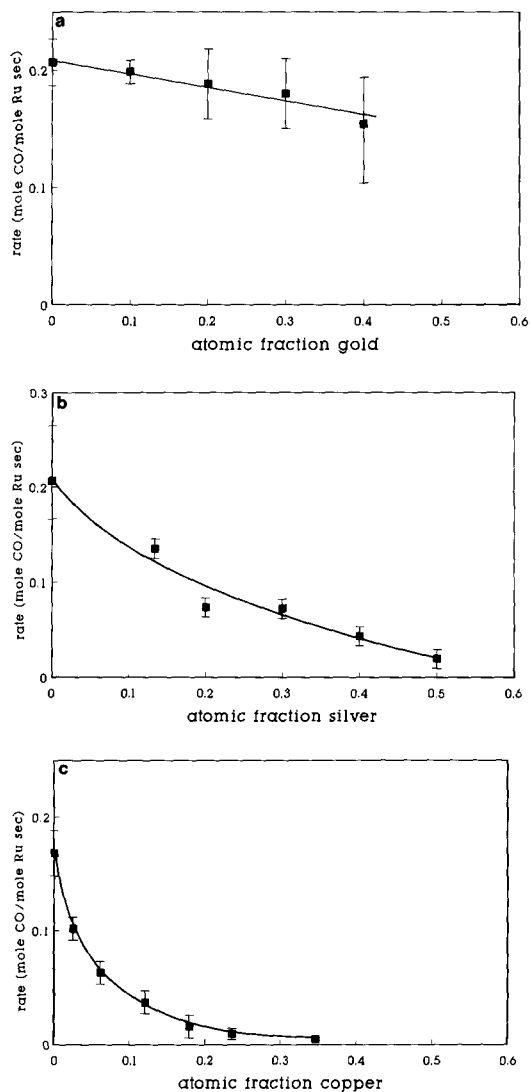
or a propagation constant. A larger value of alpha indicates that a greater proportion of higher molecular weight products are formed. The data gave a good linear relationship for C_3-C_9, with some scatter occurring for methane and ethane, as has been reported in other studies (*9, 38*). Alpha values reported here were calculated with carbon numbers three to nine. The variation in methane and ethane behavior is perhaps due

FIG. 1. The rate of the Fischer–Tropsch synthesis reaction expressed as moles of CO consumed per mole of ruthenium per second as a function of the atomic fraction of (a) gold, (b) silver, and (c) copper. All runs were at 1.1 MPa, 523 K, and $H_2/CO = 3/1$.

conversions used (<10%), we were able to observe molecules of up to carbon number nine or ten. Correlations were drawn by using Flory distribution (*37*) (i.e., a plot of the natural log of the mole percent of molecules of a given carbon number versus carbon number, Fig. 3). The inverse natural log of the slope of this line yielded the value alpha
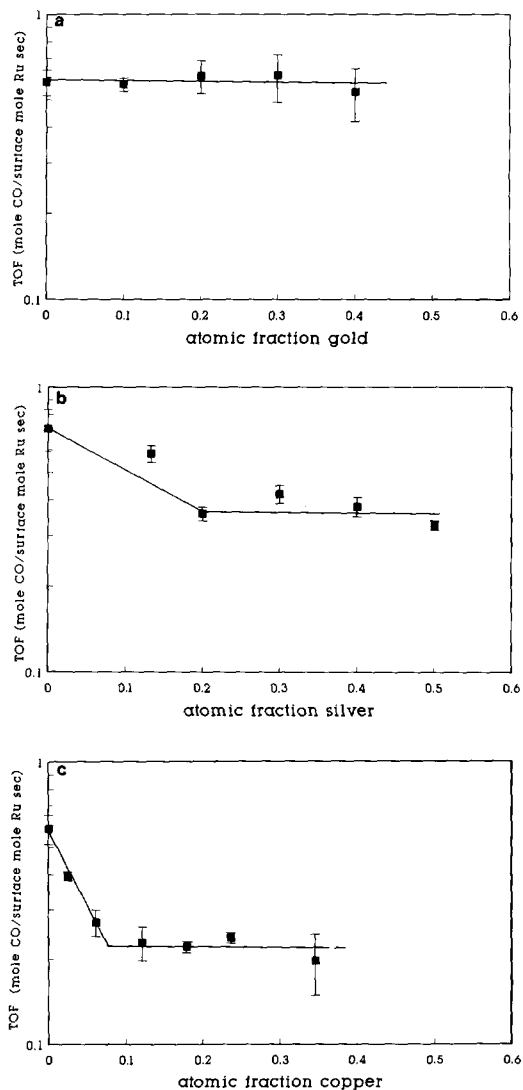
FIG. 2. The turnover frequency (moles CO consumed per mole of surface ruthenium per second) as a function of (a) gold, (b) silver, and (c) copper.
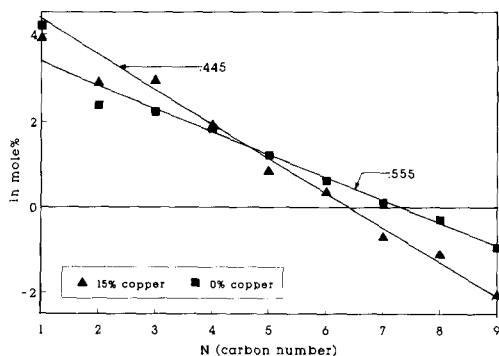
FIG. 3. Product distribution for two Ru–Cu catalysts.

to ruthenium's strong hydrogenolysis activity (2). The selectivities as given by the alphas for the various catalysts are given in Table 1 and Fig. 4.

The alphas determined for the various Ru–Cu catalysts show a monotonic decrease from pure ruthenium to the highest-loading copper catalyst investigated. The shift in the product distribution to smaller molecules occurs continuously, even after the turnover frequency has leveled off with increasing copper content. Both the Ru–Ag and Ru–Au catalysts display a product distribution that does not significantly vary with gold or silver content. For the gold catalysts this is not unexpected because the lack of change in either the observed rate or the turnover frequency indicates that gold and ruthenium are not coming into significant contact on the silica support. The results for the Ru–Ag catalysts, on the other hand, clearly show that silver was affecting the activity of the ruthenium in much the same way that copper alters the catalytic rate. Yet, unlike copper, no change in the product distribution occurred when silver was combined with ruthenium.

DISCUSSION

The results presented in Fig. 2 demonstrate behavior contrary to earlier reports. Prior studies on Ru–Cu catalysts reported a continuous decline in turnover frequency with increasing copper content (4–6). This

decrease was attributed to ensemble effects. The data given in Fig. 2c showed an initial decline in turnover frequency until copper constituted about 10 atomic percent of the metal portion of the catalyst. In this low-copper range, the turnover frequency changes rapidly from a value of about 0.58 to about 0.22 mole CO/(mole·surface Ru·sec). At compositions higher than about 10% copper, the turnover frequency remains constant. A similar trend in turnover frequencies was noted for the ethane hydrogenolysis reaction over silica-supported Ru–Cu catalysts operating in a low temperature regime (39).

The turnover frequency behavior for increasing copper content suggests that structure sensitivity may be associated with certain sites that are first populated by the relatively inactive copper atoms. With ultraviolet photoelectron spectroscopy of adsorbed xenon, Kim et al. (27) have shown that copper tends to preferentially populate defect-like, lower-coordination sites. Presumably after the defect-like sites are populated by copper, the rest of the ruthenium surface will be blocked by the copper atoms. Indeed, much previous work has indicated that copper will segregate to the ruthenium surface and cover it in nearly a monolayer fashion (12, 40, 41). This view is consistent with the data given in Fig. 1c, indicating that copper is still reducing the observed rate
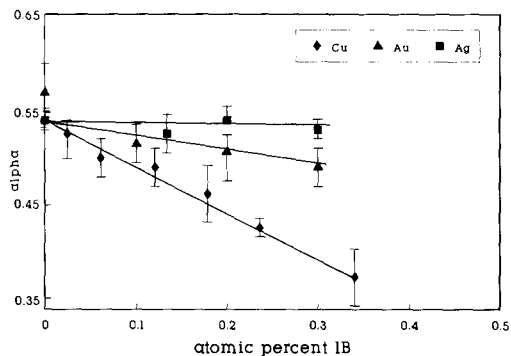

FIG. 4. Propagation constant, alpha, as a function of atomic fraction group Ib metal.

even after the turnover frequency has lev-
eled off. In addition, the fact that the activa-
tion energies for the pure ruthenium catalyst
and the ruthenium–copper bimetallic cata-
lyst are different suggests that more than
one type of site may be involved in the cata-
lytic process on the pure ruthenium catalyst.
Copper at low concentrations (less than
about 10%) has an affinity for one type of
site, and it is only when the copper content
goes above the 10% value that we see the
other site, or sites, blocked.

Clearly, for copper contents of about 10%
and larger, there is no evidence of an ensem-
ble effect. The rate per surface ruthenium
atom is invariant with copper content, indi-
cating either that the reaction is not sensitive
to ruthenium ensemble size or that copper
does not break up ruthenium ensembles.

Monte Carlo simulations can be used to
gain insight into the mixing behavior of small
bimetallic particles to help explain the be-
havior noted above (26, 39). The Ru–Cu
bimetallic system has been approximated
previously by assuming the ruthenium is an
fcc metal rather than hcp (39) for the average
particle size of the catalysts used in this
work (i.e., total dispersions of about 30%).
As with all simulation procedures, we
should be aware of limitations to the tech-
nique. The output from the simulation is an
equilibrium solution and as such does not
take the kinetics of the formation of the bi-
metallic crystallites into account. Given a
sufficiently long reduction step for our cata-
lysts, this should not restrict our use of the
model. In addition, the simulations do not,
in general, allow for modification of the cata-
lyst surface by adsorbed species. However,
simulations have been reported that allow
for an adsorbed species such as hydrogen or
carbon monoxide (26). It was found that the
presence of an adsorbate did not signifi-
cantly change the calculated crystallite mor-
phology in cases where the metal–metal
bond is much stronger than the metal–ad-
sorbate bond. A final limitation of the simu-
lations is that they are done with a rigid
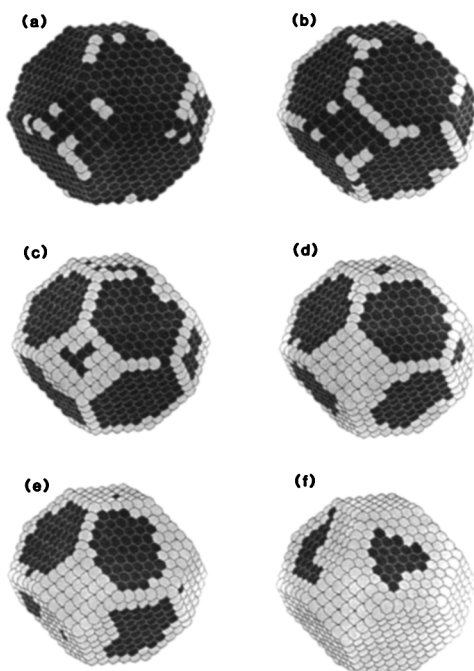lattice. The crystal structure used in the sim-

FIG. 5. Monte Carlo simulation results for Ru–Cu/
SiO₂ catalysts with a total metal dispersion of 30%; (a)
2% Cu, (b) 5% Cu, (c) 10% Cu, (d) 15% Cu, (e) 20%
Cu, (f) 30% Cu.

ulation is a face-centered cubic lattice while
ruthenium has a hexagonal close-packed
structure. Because ruthenium does not mix
with either silver or copper, but merely pro-
vides a surface for the second metal to form
aggregates, the general results are not sig-
nificantly influenced by this limitation.
Given these restrictions, we think that the
simulations can give useful qualitative re-
sults for an average particle size that can
be used to assist our understanding of the
systems we have studied. The results of the
simulation are given in Fig. 5 and Table 2.
Shown in Fig. 5 is a series of particles with
varying copper content. Two important fea-
tures are noted. First, at low copper con-
tent, copper tends to populate the low-coor-
dination edge and corner sites almost
exclusively. The edge and corner sites be-
come completely filled with copper atoms at
a copper content of about 10 to 20%. At
higher copper loadings, copper begins to

TABLE 2

Monte Carlo Simulations

Ru–Cu		
Total Atomic Fraction Cu	Surface Atomic Fraction Ru	Edge and Corner Fraction Ru
0.00	1.00	1.00
0.02	0.94	0.78
0.04	0.87	0.49
0.05	0.84	0.36
0.10	0.67	0.05
0.15	0.53	0.00
0.20	0.36	0.00
0.30	0.12	0.00
0.40	<0.01	0.00

Ru–Ag		
Total Atomic Fraction Ag	Surface Atomic Fraction Ru	Edge and Corner Fraction Ru
0.00	1.00	1.00
0.05	0.84	0.40
0.10	0.69	0.11
0.20	0.44	0.054
0.30	0.28	0.027
0.40	0.16	0.017

cover the single-crystal-like basal planes or facets. The second important feature is that when covering the facets, copper does not disperse over the surface, breaking up ruthenium ensembles. Two-dimensional copper islands grow from the edges of the facets covering the ruthenium but do not mix with it to any great extent. No small ruthenium ensembles are formed until the copper content is very high (greater than 30%). This clustering behavior is expected for bimetallic systems that have such a highly endothermic heat of mixing that bulk alloys are not formed (26). Hence, no breakup of ruthenium ensembles is expected.

The simulations in Fig. 5 show perfectly shaped cubo-octahedral structures. The initial morphology used in the Monte Carlo procedure was this shape. The algorithm allowed the particle shape to change; however, the cubo-octahedral structure represents an energetically stable configuration, and stepwise transition probabilities to other stable structures are quite low. If an unstable initial configuration such as a block structure is used (26), then the resultant particle is similar to the shape shown in Fig. 5 except that a higher degree of surface roughness is observed. That is, in addition to edge and corner sites, step and kink surface features are observed that are similar to the structures reported by Pérez et al. (42). For these rougher morphologies, copper still preferentially populates the low coordination sites (edges, corners, steps, and kinks) before covering the basal planes. The transition from populating defect-like sites to monolayer coverage of basal planes occurred in the 10-to-20% copper content range for 30% dispersion catalyst particles used in this study. The trend in population of defect-like sites with copper is very similar to that indicated in Table 2 for edge and corner sites of the cubo-octahedral structure.

This picture of the interaction of copper and ruthenium is consistent with previous work on small particles and single crystals. Kim et al. (27) experimentally observed copper tending to populate defect sites as was seen at the edges and corners with the Monte Carlo simulations. A variety of researchers have noted the formation of two-dimensional islands of copper on ruthenium single-crystal surfaces (7, 15, 16, 28–30).

Hence, we are left with a qualitative picture of Ru–Cu bimetallic particles in which copper at low concentrations preferentially occupies low coordination, defect-like sites. At higher concentrations, copper covers the basal planes in a contiguous monolayer. Because of the lack of microscopic mixing of copper and ruthenium atoms, small ensembles of ruthenium are not formed unless the surface is almost totally copper. The random-mixing models used in previous studies (4, 6) to determine apparent ensemble size are not supported by the Monte Carlo simulations or numerous single-crystal studies (7, 15, 16, 28–30).

Given this view of the morphology of small Ru–Cu particles, we can interpret the turnover frequency data for the Fischer–Tropsch synthesis reaction reported here as displaying two regimes. At copper loadings higher than roughly 10 to 20%, no ensemble effects are noted as evidenced by a turnover frequency not changing with increasing copper content. An ensemble effect is not noted because ensembles of ruthenium are not broken up by copper on the surface. Hence, even if this reaction were sensitive to ensemble effects, it would not be possible to observe it for the Ru–Cu system. This interpretation is consistent with the methanation data of Peden et al. (7) that show no ensemble effect for Cu/Ru(001) surfaces. In many ways, the small particles, at copper loadings above the point where the edge, corner, and other defect-like sites are filled with copper, look like single-crystal ruthenium surfaces.

Previous investigations that reported ensemble effects relied on methods of determining the surface composition of the metal particles that overcounted the ruthenium because of hydrogen spillover (11–16), for example. Consequently, the turnover frequency trends noted in these previous studies may not be valid. In addition, the estimation of the ensemble size needed for the methanation reaction relies on a knowledge of the surface mixing behavior. The assumption of a random dispersion of copper over the surface of the ruthenium, even if the surface composition is accurately known, is not correct.

At copper contents lower than 10%, where the turnover frequency is decreasing with increasing copper content, there is clearly an influence by the copper on the observed catalytic activity of ruthenium. A comparison of the turnover frequency data in Table 1 with the Monte Carlo data in Table 2 suggests that the rate drops off approximately linearly with the loss of ruthenium from defect-like sites. The fact that the turnover frequency drops as copper replaces ruthenium at the low coordination locations indicates that the reaction is structure sensitive. Also supporting this view is the result that the activation energy data for a partially copper-covered ruthenium catalyst (with low coordination sites occupied by copper) and a pure ruthenium catalyst are different.

One possible explanation for the structure-sensitive behavior in the low-copper content region is that the edge and corner sites are more active for the surface reactions than the basal planes. This explanation seems unlikely in view of the results of Shincho et al. (43) who found that CO dissociation occurs more rapidly on stepped Ru surfaces than on basal planes. The increased activity is associated with the ability of CO to bond with higher coordination at a step. Edges and corners offer even less opportunity for higher-order bonding than do basal planes, and hence their ability to enhance the rate is reasonably diminished.

Another, more feasible explanation is that the steps and kinks are responsible for the

enhanced activity. These structures are known to be present on supported metal particles (42), and the Monte Carlo simulation suggest that they are preferentially populated by copper in Ru–Cu bimetallic systems. In addition, the degree of surface roughness noted by Pérez *et al.* (42) is approximately independent of metal particle size. Hence, for a pure Ru catalyst as metal dispersion and ratio of active step and kink sites to inactive edge and corner sites increase, one would expect the turnover frequency to decrease. Such behavior has been reported for supported Ru catalysts (*18, 38, 44, 45*).

The Ru–Ag catalysts show behavior similar to the Ru–Cu catalysts. The turnover frequency declined with increasing silver loading up to a silver content of approximately 25%. Additional silver had no effect on the turnover frequency. The results of the Monte Carlo simulations (see Table 2) indicate that silver in lower concentrations populates low-coordination sites and completely fills these sites when the silver loading reaches 20–30 atomic percent. The results noted for the Ru–Ag catalysts indicate, by the same reasoning as used for the Ru–Cu catalysts, that the high- and low-coordination ruthenium sites have different activities. Again no ensemble effects are seen.

We observed essentially no change in the turnover frequency as gold was added to ruthenium. Monte Carlo simulations, similar to the ones reported above, suggest gold is strongly clustering and has little interaction with ruthenium. This lack of contact between gold and ruthenium is reflected in the ruthenium dispersion data given in Table 1. At 40 atomic percent gold, the dispersion has dropped by a factor of 1.24 from pure ruthenium. At similar copper or silver contents, the ruthenium dispersion drops by a factor of 11.9 and 4.9, respectively. Little change in catalytic activity is noted simply because gold and ruthenium maintain separate particles. This view of the lack of direct interaction between gold and ruthenium is

consistent with the results of Cowley and Plano (46). In a recent microdiffraction study employing scanning transmission electron microscopy (STEM) they observed no evidence for any direct association of ruthenium and gold atoms for particles in the 1 to 3 nm range. In another microdiffraction study Shastri and Schwank (47) investigated larger particles of ruthenium and gold on MgO using a TEM/STEM instrument. Again, no evidence was found for an intermetallic compound. Like copper and silver, gold does not form bulk alloys with ruthenium. However, gold has a relatively high bulk cohesive energy that inhibits its tendency to cover or "wet" a ruthenium surface (*17, 26*). Consequently, this inability of gold to alter the catalytic activity of ruthenium is not unexpected. Previous work with Ru–Au bimetallic catalysts (9) for the methanation reaction altered the relative composition by increasing the gold content at the same time the ruthenium content was decreased. A drop in the turnover frequency was observed, but this drop may have been due to increased ruthenium dispersion (see Ref. (*38*)) rather than to an interaction between ruthenium and gold.

The trends in catalyst selectivity with the addition of the group Ib metals demonstrate interesting behavior. The Ru–Cu system displays a continual decline in alpha with increasing copper content, while alpha remains essentially constant for the Ru–Au and Ru–Ag systems. It was suggested above that the low-coordination step and kink sites are more active than the basal planes at the conditions used in this work. One may then postulate that the observed alpha behavior is due to the low-coordination sites having alpha values intrinsically different from those of the basal planes. If this were the case, we would expect that the propagation constants would not change once the low-coordination sites were eliminated by being filled with copper or silver atoms. But for Ru–Cu catalysts, alpha continues to decline even once the turnover frequency has stopped declining. On the other hand, the

Ru–Ag system showed little change in alpha over the entire range of composition. Therefore, the suggestion that low-coordination sites have different alpha values than the basal planes seems invalid.

Another possibility for the observed selectivity variations is that the presence of copper facilitates termination of chain growth, while gold and silver are passive toward termination. Two proposed mechanisms for chain termination involve hydrogen (48). One mechanism suggests that termination occurs via β-hydride elimination that produces an α-olefin. The second mechanism calls for insertion of hydrogen at the α-carbon to yield a normal paraffin. In both mechanisms, a site for either accepting or donating a hydrogen atom is needed. In the systems studied, hydrocarbon chains are present only on ruthenium atoms because carbon monoxide does not react on the group Ib metals. Also, hydrogen does not appreciably adsorb on gold or silver; therefore on the Ru–Ag and Ru–Au catalysts, only ruthenium sites are involved in chain propagation and termination. No ensemble effects were observed as gold or silver was added to ruthenium; gold and silver simply covered ruthenium atoms on a one-to-one basis. Since active ruthenium sites were blocked by totally passive atoms, one cannot expect a change in alpha with either the Ru–Au or Ru–Ag bimetallic catalysts.

The spillover of dissociated hydrogen from ruthenium to copper indicates that copper could be involved in the chain termination step. Hydrogen on copper in a supported Ru–Cu catalyst is not passive but rapidly exchanges with hydrogen on ruthenium (11, 12). This observation suggests that copper could serve as a source or sink for hydrogen atoms to either attack the α-carbon or accept a hydrogen atom from the β-carbon and thereby terminate chain growth. The data presented here do not offer conclusive evidence as to which of these mechanisms predominates. Both α-olefins and normal paraffins were present in the product streams. In either case, copper aids in the termination of growth, while silver and gold do not noticeably affect chain growth. This is in agreement with previous studies of Ru–Cu catalysts that show an increase in the selectivity toward methane with increasing copper content (4–6). Earlier work on Ru–Au catalysts (9) also showed little change in product distribution in agreement with the results of this work.

CONCLUSIONS

Depending on which group Ib metal was added to ruthenium, we observed different catalytic behavior. Addition of copper and silver caused a decline in turnover frequency until defect-like sites were depleted of ruthenium. After these low-coordination sites were filled with silver or copper, no change was seen in turnover frequency. No change was seen in the turnover frequency for Ru–Au catalysts over the entire composition range.

The drop in turnover frequency at low loadings of copper or silver indicate that the Fischer–Tropsch synthesis reaction is structure sensitive over ruthenium catalysts. At copper or silver loadings sufficiently high to block all defect-like sites, the turnover frequency does not change with composition. Ensemble effects therefore are not observed. Thermodynamic simulations suggest that copper, silver, or gold cannot break up ruthenium ensembles on the surfaces of these bimetallic particles. Consequently, even if ensemble effects were important for Fischer–Tropsch synthesis over ruthenium catalysts, they could not be observed with the bimetallic catalysts used in this study.

Finally, silver and gold did not affect catalyst selectivity, while a continual decline in alpha (a shift of the product distribution to smaller molecules) was seen for increasing copper content. The ability of hydrogen to exchange between ruthenium and copper adsorption sites correlates with enhanced chain termination.

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