

The Kinetics and Mechanism of Carbon Monoxide Hydrogenation over Silica-Supported Ruthenium-Copper Catalysts

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The activity of Ru-Cu/SiO₂ catalysts for CO hydrogenation between 530 and 670 K decreases with increasing Cu content, while the activation energy remains essentially constant at 21 kcal mol⁻¹; the turnover number (molecules per Ru surface atom s⁻¹) for an equimolar Ru:Cu ratio is about 50 times less than for pure Ru. Simultaneously the order in H₂ becomes less positive and for CO more positive. The catalyst containing 1% Ru and 0.32% Cu initially produces less ethane and propane than does the pure Ru catalyst. The results are interpreted with a modification of the kinetic analysis due to Vannice and Ollis (7). Cu atoms are believed to segregate at the surface of Ru particles, and it is concluded that the active site for the reaction on pure Ru is an ensemble of about four Ru atoms.

INTRODUCTION

Much interest has recently been shown in the structure and activity of bimetallic catalysts. For systems exhibiting complete miscibility, it is, of course, well appreciated that the surface at equilibrium will be enriched in the component having the lower surface energy. Burton *et al.* (1, 2), for example, have proposed a model which correlates the surface composition of a series of Cu-Ni powder catalysts with their activity for ethane hydrogenolysis (3). However, it is worth noting that for very small particles, such as are found in supported catalysts (i.e., less than 10 nm in size), the surface concentration of the lower surface energy component can be limited by the composition of the alloy to a level below that predicted by this model.

The Ru-Cu and Os-Cu systems, which show a large miscibility gap in the bulk, have been shown by Sinfelt (4) to exhibit

symptoms of interaction when highly dispersed on SiO₂: the term "bimetallic cluster" was applied to distinguish them from normal alloys. He found that the activity per surface Ru or Os atom decreased with increasing Cu content for hydrogenolysis of ethane and cyclohexane, but not for cyclohexane dehydrogenation.

Vannice (5, 6) and Vannice and Ollis (7) have recently investigated the kinetics and mechanism of CO hydrogenation over supported Group VIII metals, and have presented models that apparently account for the different orders of reaction with respect to H₂ and CO for the various catalysts. Dalla Betta *et al.* (8) have also shown that this reaction is structure insensitive over Ru catalysts in the particle size range of 1.0 to 9.0 nm (dispersion 100 to 9%). This paper reports a study of CO hydrogenation over a series of Ru-Cu/SiO₂ catalysts similar to those of Sinfelt (4), to determine if Vannice's concepts are applicable to a bimetallic cluster system. The effect of

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adding Cu to Ru on the yields of higher hydrocarbons has also been briefly studied.

EXPERIMENTAL

Kinetic studies were carried out in a static reactor attached to a conventional vacuum system capable of producing dynamic pressures down to 10^{-5} Torr (1 Torr = 133.3 N m⁻²). The apparatus was grease-free, the taps (G. Springham and Co.) being equipped with Viton diaphragms. British Oxygen Company H₂ and CO were stored in 5-liter bulbs attached to the apparatus. H₂ was purified by passage through a 5% Pd/Al₂O₃ catalyst at room temperature followed by a liquid nitrogen trap; CO was used without further purification. The 30-mm o.d. × 160-mm Pyrex reactor was mounted horizontally and the catalyst (50 to 100 mg) was distributed along the length of the cylinder.

Reaction rates were determined from the rate of pressure decrease, measured by a mercury manometer. Typical reactant pressures were 20 Torr CO and 60 Torr H₂, introduced simultaneously to the reactor from a 1-liter mixing bulb. Product distributions could be measured by transferring samples directly from the reactor into a Perkin Elmer F11 gas chromatograph fitted with a 2-m Porapak N column.

Catalysts were prepared by simultaneous impregnation of Davison 70 silica gel (H₂O pore volume 0.8 cm³ g⁻¹) with aqueous solutions of RuCl₃·3H₂O (Johnson Matthey and Co.) and Cu(NO₃)₂·3H₂O (Hopkins and Williams "Analar"). They were then vacuum-dried at 273 K and reduced in a stream of H₂/N₂ for 4 hr at 673 K. Catalysts were re-reduced for 0.5 h *in situ* and evacuated for 0.25 h at the reaction temperature before introduction of the reactants. They were also stored in H₂ between experiments.

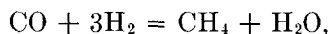
The reduced catalysts were characterized by CO chemisorption at room temperature after re-reduction in static H₂ at 523 K and evacuation overnight at 573 K. The

amount of CO chemisorbed was taken to be the difference in the intercepts of two isotherms carried out consecutively with a 900-s evacuation at room temperature between them (4).

RESULTS

The catalysts used in this study are described in Table 1. They all contained 1% Ru with varying amounts of Cu up to a 1:1 Ru:Cu molar ratio and, thus, are similar in composition to those used by Sinfelt (4), though they are less well dispersed. Linear CO bonding was assumed in the calculations of the fraction of Ru at the surface, as has been done by others (4, 8). Powder X-ray diffraction studies gave no information regarding the state of the Ru-Cu catalysts since no diffraction lines at all were apparent.

Hydrogenation rates were determined from rates of pressure decrease, assuming that CH₄ and H₂O were the only products and, thus, that the reaction might be represented as



where $\Delta P_{\text{CO}} = -\Delta P_{\text{CH}_4} = \frac{1}{2}\Delta P_{\text{total}}$. This assumption is reasonable since subsequent analyses showed that significant quantities

TABLE 1
Ru-Cu/SiO₂ Catalysts for CO Hydrogenation

Catalyst	Ru:Cu atomic ratio	CO uptake/ μmol g ⁻¹	Ru _s /Ru _t ^a
1% Ru/SiO ₂	—	20.4	0.206
1% Ru-0.016% Cu/SiO ₂	40:1	31.6	0.319
1% Ru-0.063% Cu/SiO ₂	10:1	25.0	0.252
1% Ru-0.32% Cu/SiO ₂	2:1	37.0	0.374
1% Ru-0.63% Cu/SiO ₂	1:1	19.2	0.194

^a Ru_s: Number of surface Ru atoms; Ru_t: total number of Ru atoms.

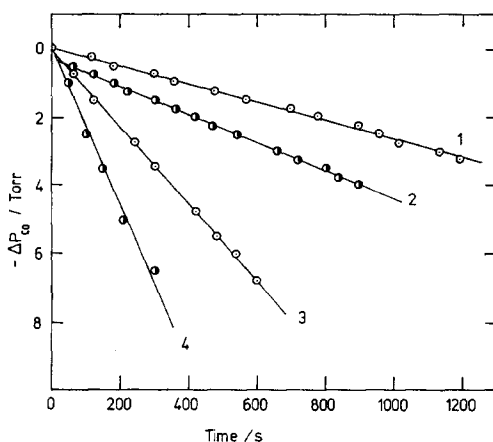


Fig. 1. Plots of ΔP_{CO} vs time for CO hydrogenation over 1% Ru-0.016% Cu/SiO₂ at various temperatures ($H_2 = 60$ Torr, $CO = 20$ Torr). Curve 1, 555.5 K; curve 2, 564 K; curve 3, 595 K; curve 4, 624 K.

of higher hydrocarbons were formed only at temperatures much below those used for the kinetic experiments. Especially at low reaction rates, plots of ΔP_{CO} versus time were linear even up to 50% or higher conversions. After allowing for an initial slow pressure decrease evident in many experiments, the rate of reaction was taken to be the slope of the first linear part of the ΔP_{CO} versus time curves. Examples of such curves taken from experiments on the 1% Ru-0.01% Cu/SiO₂ catalyst are shown in Fig. 1.

The kinetic parameters for each catalyst are tabulated in Table 2. The orders were obtained from the slopes of $\log(\text{rate}/\text{Torr s}^{-1})$ versus $\log(P_{CO}/\text{Torr})$ or $\log(P_{H_2}/\text{Torr})$ plots, and then with the pressure converted to molecule cm^{-3} and the rates to turnover numbers (N , in molecules CH_4 per surface Ru s^{-1}), they were used to calculate the rate constant, k , defined as

$$k = N/C_{H_2}^X C_{CO}^Y,$$

where X and Y are the orders of reaction in H_2 and in CO , respectively. Activation energies and pre-exponential factors were then calculated from the plots of $\log k$ versus $1/T$,

In the last column of Table 2 are listed the turnover numbers calculated at 600 K, 1×10^{13} molecules $H_2 \text{ cm}^{-3}$ and 0.33×10^{18} molecules $CO \text{ cm}^{-3}$ (62.1 and 20.7 Torr, respectively).

A 0.63% Cu/SiO₂ catalyst prepared in the same manner as the others had no measurable activity for CO hydrogenation at the highest temperature used in this study, viz., 672 K.

The results of the product analyses are shown in Fig. 2 for the 1% Ru/SiO₂ at 533 K, and for the 1% Ru-0.32% Cu/SiO₂ at 538 K. The product distributions are presented as a function of CO conversion in two forms: as mole% CH_4 of total hydrocarbon products, i.e.,

$$100 \times (CH_4) / [(CH_4) + (C_2H_6) + (C_3H_8)],$$

and as atom% of CO converted found as CH_4 , i.e.,

$$100 \times (CH_4) / [(CH_4) + 2(C_2H_6) + 3(C_3H_8)].$$

Only C_2 and C_3 hydrocarbons (predominantly ethane and propane) were found besides CH_4 . Analyses at 556 K showed no C_3 hydrocarbons and the initial atom% CH_4 had increased to 93% for both catalysts.

DISCUSSION

Activities and Orders of Reaction

The activities of our catalysts for CO hydrogenation, as given by the turnover numbers calculated *per surface Ru atom* at 600 K, decrease by a factor of about 50 on passing from the pure Ru to the 1:1 Ru-Cu catalyst (see Table 2).² This reaction is thus similar to the hydrogenolysis of ethane and of cyclohexane (4) in that the activity per surface Ru atom is de-

² This decrease would not be so marked if there were a proportion of bridge-bonded CO on pure Ru, and if the ratio of linear to bridged CO were to increase on progressive alloying with Cu.

TABLE 2
 CO Hydrogenation over Ru-Cu/SiO₂ Catalysts

Catalyst	Experimental conditions			<i>E</i> /kcal mol ⁻¹	log <i>A</i>	H ₂ order	CO order	<i>N</i> / molecules Ru ₄ ⁻¹ s ⁻¹
	<i>T</i> /K	<i>P</i> _{H₂} / Torr	<i>P</i> _{CO} / Torr					
1% Ru/SiO ₂	584	80	12.5-42				-0.43 ± 0.12	
	575	26-70	8.75			1.24 ± 0.28		
	555	55-160	20			1.09 ± 0.30		
	556-610	45	10	20.4 ± 3.7	-7.396			3.32 × 10 ⁻²
	529-601 ^a	60	20	20.6 ± 2.0	-7.089			5.73 × 10 ⁻²
1% Ru-0.016% Cu/SiO ₂	584	100	10-33				-0.19 ± 0.06	
	584	60-130	20			0.66 ± 0.07		
	556-624	60	20	21.6 ± 2.0	-2.490			1.49 × 10 ⁻²
1% Ru-0.063% Cu/SiO ₂	575	100	7.5-25				-0.36 ± 0.03	
	575	60-150	20			0.89 ± 0.14		
	560-620	100	20	21.3 ± 2.9	-3.488			3.41 × 10 ⁻²
	560-620 ^a	60	20	21.1 ± 2.8	-3.590			3.34 × 10 ⁻²
1% Cu-0.32% Cu/SiO ₂	622	80	12.5-44				-0.29 ± 0.11	
	629	35-108	12			0.73 ± 0.24		
	622	48-137	15			0.56 ± 0.21		
	590-650	45	10	19.0 ± 3.1	-2.322			1.57 × 10 ⁻³
	605-655 ^a	60	20	23.1 ± 6.2	-0.479			3.46 × 10 ⁻³
1% Ru-0.63% Cu/SiO ₂	662	100	9-28				+0.14 ± 0.15	
	662	80-200	20			0.75 ± 0.15		
	635-670	100	20	26.6 ± 9.2	-9.224			1.05 × 10 ⁻³
	564-670 ^a	60	20	22.6 ± 7.0	-10.673			1.11 × 10 ⁻³

^a Determined after CO chemisorption measurement.

pressed by the addition of Cu, although the effect is not so marked. Inspection of Table 2 further shows that the differences in activities are not caused by changes in the apparent activation energies, which are the same (about 21 kcal mol⁻¹) within experimental error for all catalysts excepting possibly that containing 1% Ru-0.63% Cu/SiO₂. The major source of the activity variation is therefore to be found in the pre-exponential factors. These vary by 10 orders of magnitude (see Table 2), but this is in consequence of (i) expressing reactant concentrations as molecules cm⁻³ and (ii) the different orders of reaction, which serve to exaggerate the differences. These observations suggest that the mechanism of the reaction is basically unaffected by the

addition of Cu, but that the number of active sites is thereby diminished. In this respect also CO hydrogenation resembles hydrocarbon hydrogenolysis (4).

The addition of Cu, however, does have a measurable effect on the orders of reaction (Table 2). The first small increment of Cu causes the order in H₂ to decrease, but thereafter it does not change significantly. The order in CO becomes progressively less negative with increasing Cu content, and for the catalyst containing equimolar amounts of Ru and Cu it is in fact slightly positive. The presence of Cu must therefore modify the detailed mechanism of the reaction in some way.

The only comparisons possible with previous work are with the results obtained

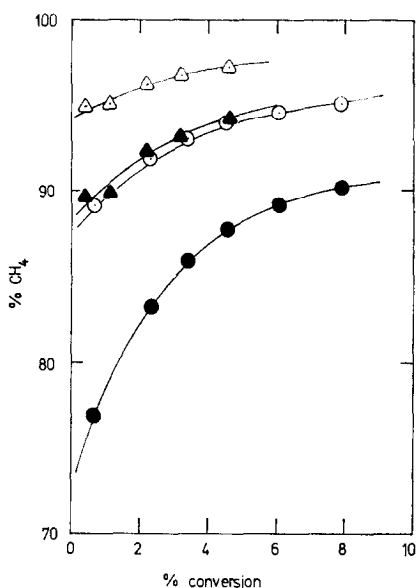
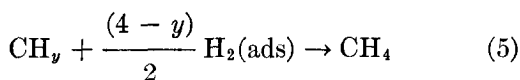
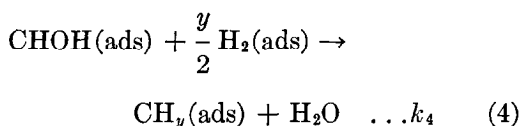
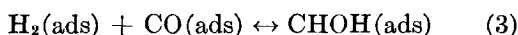


Fig. 2. Variation of % CH₄ with percentage conversion for 1% Ru-0.32% Cu/SiO₂ at 538 K (triangles) and for 1% Ru/SiO₂ at 533 K (circles): open points represent molar percentages and filled points represent atomic percentages (see text).

by Vannice (5) and by Dalla Betta *et al.* (8) for pure Ru catalysts. Extrapolating Vannice's results (5) obtained with a 6% Ru/Al₂O₃ catalyst (dispersion 6%) in a flow system using his kinetic parameters to the conditions under which our turnover numbers are expressed gives a value for CH₄ production of 0.14 s⁻¹, in fair agreement with our values of 0.03 to 0.06 s⁻¹. With various supported Ru catalysts having dispersions between 9 and 100% in a flow-recycle system, Dalla Betta *et al.* (8) found a turnover number for CH₄ production which when converted to our conditions by means of their kinetic parameters gives a value of 0.025 s⁻¹. Our activation energy for CO removal (20.5 kcal mol⁻¹) is close to their values of 17 (5) and 18.3 kcal mol⁻¹ (8); both record values of close to 24 kcal mol⁻¹ for CH₄ production. Their orders of reaction are qualitatively similar to ours, being negative in CO and exceeding +1 in H₂, but the actual values differ considerably.

Reaction Mechanism

Vannice (6) and Vannice and Ollis (7) have proposed reaction schemes such that the various orders of reaction exhibited by different metals (5) have their origin in various numbers of hydrogen molecules reacting with a CHOH(ads) species in the rate-determining step. The modified scheme (7) may be summarized as follows.



The following assumptions were then made.

(i) The first three steps, being faster than step 4, can be combined into one equation, viz.,



(ii) CHOH(ads) is the most abundant surface intermediate, the dependence of whose surface coverage θ_{C} on reactant pressures may be represented by the power law relationship

$$\theta_{\text{C}} = \frac{K P_{\text{CO}} P_{\text{H}_2}}{1 + K P_{\text{CO}} P_{\text{H}_2}} \simeq (K P_{\text{CO}} P_{\text{H}_2})^n;$$

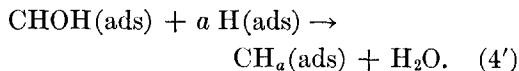
(iii) step 4 is rate-determining and step 5 is rapid. The following rate expression then results:

$$\text{Rate} = k_4 K^{n+[(n-1)y/2]} K_{\text{H}_2}^{y/2} \times P_{\text{CO}}^{n+[(n-1)y/2]} P_{\text{H}_2}^{[n+ny/2]},$$

where the experimentally obtained orders in H₂ and CO (X and Y) can be given as $X = n + ny/2$, and $Y = n + ny/2 - y/2 = X - y/2$. The value of n was found (7)

to vary between 0.38 and 0.50 for the various metals, and of y between 1.0 and 4.4, the latter being the value for Ru. According to this treatment, between one-half and two H₂ molecules react with the CHOH complex in the rate-determining step, leading to the formation of M≡CH, M=CH₂, M-CH₃ or M···CH₄ species.

We feel, however, that the use of adsorbed H₂ molecules, rather than of H atoms, is not justifiable, and we find the concept of having one-half or three-halves of a H₂ molecule in the slow step difficult to comprehend. We have therefore reformulated the reaction scheme in terms of dissociative adsorption of H₂ molecules, and the rate-determining step then becomes



With the same assumptions as before, the rate expression then becomes

$$\text{Rate} = k_4 K^{n+na-a} K_{\text{H}_2}^a P_{\text{CO}}^{n+na-a} \times P_{\text{H}_2}^{n+na-a/2},$$

where $X = n + na - a/2$, and $Y = n + na - a = X - a/2$. Application of this new treatment to Vannice's results (6, 7) leads to values of a identical to those of y , but the average value of the exponent n is increased from 0.5 (7) to 0.65. Use of this higher value of n to back-calculate orders of reaction for integral value of a or y leads to orders not much different from those which Vannice calculated, except perhaps for Ru where the high positive order in H₂ is not so well reproduced.

We have applied both treatments to our own results for Ru and Ru-Cu catalysts, with results which are shown in Table 3. The average value of n_1 , calculated on the Vannice-Ollis model, is close to 0.4, and of n_2 , calculated on our modification, is about 0.6. The back-calculated orders for integral values of y or a are also given, and again there is little difference between the orders derived from the two treatments.

TABLE 3
Observed and Calculated Kinetic Parameters^a

Catalyst	Observed		Derived		
	X	Y	n ₁	n ₂	y = a
1% Ru-0.63% Cu/SiO ₂	0.75	0.15	0.47	0.61	1.2
1% Ru-0.32% Cu/SiO ₂	0.65	-0.30	0.33	0.55	1.9
1% Ru-0.063% Cu/SiO ₂	0.90	-0.35	0.40	0.61	2.5
1% Ru-0.016% Cu/SiO ₂	0.70	-0.20	0.37	0.57	1.8
1% Ru/SiO ₂	1.15	-0.45	0.45	0.65	3.1
Calculated					
	n ₁ = 0.4		n ₂ = 0.6		
y = a	X	Y	X	Y	
1	0.6	0.1	0.7	0.2	
2	0.8	-0.2	0.8	-0.2	
3	1.0	-0.5	0.9	-0.6	

^a Values of n_1 are derived from the Vannice-Ollis treatment (7), and those of n_2 from the modification described in the text.

On the basis of this type of mechanistic analysis, we conclude that our results for Ru fit best with $y = a = 3$; for the catalysts containing 0.016, 0.063, and 0.32% Cu with $y = a = 2$; and for that having 0.63% Cu with $y = a = 1$. Increasing additions of Cu would therefore seem to diminish the number of hydrogen atoms reacting with CHOH(ads) in the rate-determining step. The value of $y = a = 3$ for Ru is more reasonable than that of 4 obtained by Vannice, as this would imply that CHOH(ads) is converted directly to CH₄ in the rate-determining step. We must also note that the orders observed by Dalla Betta *et al.* (8) lead on this analysis to the ridiculously high value for a or y of 7.

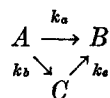
The near-constant values of n derived either by the Vannice-Ollis treatment or our modification thereof for the Group VIII metals or for the Ru-Cu catalysts used here

merit further comment. A constant value of n , no matter what its value, implies a constant coverage by $\text{CHOH}(\text{ads})$: this would seem likely only if its coverage were close to unity and not just much higher than θ_{CO} and θ_{H} . Kraemer and Menzel (9) have recently observed that the complex formed from CO and H_2 on polycrystalline Ru was more tightly bound than either CO or H_2 separately: it was stable under UHV conditions at 700 K, and was completely removed without evidence of carbon deposition at 1000 K. This observation lends some support to the basis of the mechanistic interpretation for CO hydrogenation.

Formation of Higher Hydrocarbons

Besides affecting the activity and orders of reaction, the addition of Cu to Ru also changes the selectivity towards the formation of higher hydrocarbons. However, only C_2 and C_3 hydrocarbons were observed, probably due to the high temperature required to obtain measurable conversions. Figure 2 demonstrates that the 1% Ru-0.32% Cu/ SiO_2 catalyst initially produces more methane than does the pure Ru catalyst. For both the percentage of methane increased with conversion, probably because of the subsequent hydrogenolysis of the C_2 and C_3 hydrocarbons to methane, a reaction known (4) to occur below the temperature used in this experi-

ment. The results in Fig. 2 can be described empirically by a combination of Type II and Type III selectivities (10), viz.,



where B represents CH_4 and C , collectively, the higher hydrocarbons, with $k_a/k_b \sim 6.4$ and $k_c/k_b \sim 40$ for the pure Ru catalyst. However, Dalla Betta *et al.* (8) have shown that hydrogenolysis of higher hydrocarbons does not contribute to CH_4 formation under the conditions of their experiments, and attribute this to the poisoning effect of high CO coverages. It appears that with the lower CO pressures used by us (20 Torr compared with 140 Torr) hydrogenolysis is faster than direct CO hydrogenation ($k_c/k_a \sim 7$), but this treatment is only approximate as it is based on first-order kinetics which do not in fact obtain.

Surface Composition of Ru-Cu Catalysts

It now remains to explore what light our results cast on the mechanism of CO hydrogenation catalyzed by Ru. The evidence of the changes in activity, in orders of reaction, and in selectivity of CH_4 on adding Cu to Ru strongly suggests that the properties of surface Ru atoms are modified by the presence of Cu atoms: the effect may be an electronic one or a geometric one if

TABLE 4
Surface Compositions and Particle Sizes of Ru-Cu/ SiO_2 Catalysts Calculated Assuming Either No Segregation or Complete Segregation of Cu at the Surface

Catalyst	Ru _s /Ru _t	No segregation		Complete segregation	
		d/nm	Surface composition (% Ru)	d/nm	Surface composition (% Ru)
1% Ru/ SiO_2	0.206	7.0	100	7.0	100
1% Ru-0.016% Cu/ SiO_2	0.319	4.3	97.6	4.0	92.7
1% Ru-0.063% Cu/ SiO_2	0.252	5.6	90.9	4.2	71.6
1% Ru-0.32% Cu/ SiO_2	0.374	3.6	66.7	2.1	42.8
1% Ru-0.63% Cu/ SiO_2	0.194	7.5	50.0	2.0	16.2

an ensemble of two or more Ru atoms constitutes the active site, or indeed some combination of the two. There can be no doubt from our results that Ru and Cu atoms occur partially, if not wholly, in the same particles. Arguments have been adduced (11-13) to show that miscibility may be possible in small particles with pairs of metals immiscible in the bulk. Burton *et al.* (1) have concluded that in such systems, of which Ru-Cu is an example, the component having the lower surface energy (Cu) will segregate at the surface, and specifically at sites of lowest coordination number (i.e., edges and corners). In the limit all the Cu might be at the surface and the core might contain only Ru, although a complete monolayer of Cu can only result if its mole fraction exceeds the dispersion based on both components. This limiting assumption allows us to estimate a surface composition, and also an approximate particle size, for our Ru-Cu catalysts, since the fraction of the total Ru which is present at the surface is known from the CO chemisorption measurements. Thus, the equation for the overall dispersion D becomes

$$D = \frac{Ru_s + Cu_s}{Ru_t + Cu_t},$$

where Ru_s is the number of surface Ru atoms, Ru_t and Cu_t are, respectively, the total numbers of Ru and Cu atoms present, and Cu_s is equivalent to Cu_t . Surface compositions follow directly, and these are listed in Table 4 together with those obtained by assuming complete miscibility and no surface segregation whatsoever. The true situation must lie between these two limits, and probably closer to the former.

We suppose that Cu atoms are quite inert and that all adsorbed species reside solely on Ru atoms. From the evidence of the Arrhenius parameters and from the mechanistic analysis of the orders of reaction, we are led to the qualitative

conclusion that CO hydrogenation on Ru requires an ensemble of more than one Ru atom, perhaps as many as four or five, with a central atom bonding the CHOH complex and the neighboring ones bonding H atoms. This conclusion does not contradict that of Dalla Betta *et al.* (8) that the reaction is structure insensitive, since we do not assign any particular coordination number requirement to the atoms of the ensemble. Progressive dilution of the surface of the particles with Cu atoms then reduces the average number of Ru atoms surrounding a given one bonding the CHOH complex, thus changing the number of H atoms participating in the rate-determining step and hence the kinetics. This average number does not of course have to be integral and, for example, with the 1% Ru-0.063% Cu/SiO₂ catalyst the value of $y = a = 2.5$ may have real significance. We must also conclude that the level of activity, as expressed by the turnover number and (with reservations) the pre-exponential factor, also decreases with the average number of Ru atoms surrounding a central one. It would also appear that to make a higher hydrocarbon requires a larger ensemble of Ru atoms than is needed to produce methane.

We do not feel able to take this interpretation further in a quantitative sense, as Burton and Hyman have done (2) for ethane hydrogenolysis over Ni-Cu alloys. Reasons for this include a lack of understanding of the disposition of the Cu atoms on the surface of the Ru particles, and some minor inconsistencies in the trends shown by the kinetic parameters with increasing Cu content. Thus, for example, the catalyst having 0.016% Cu behaves as if it had a higher Cu surface coverage than that containing 0.063% Cu (see Table 2); it is possible that in the latter case some of the Cu has crystallized separately from the Ru. It is also noteworthy that the orders of reaction correlate better with turnover numbers than with Cu content.

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