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The Preparation and Activity for Alkane Reactions of Aerosil-Supported Rhodium–Copper "Clusters"

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Rhodium–copper "clusters" supported on Aerosil 200 were prepared from spectroscopically monitored solutions of anion precursors and from support which had been subjected to a severe heat treatment. Reaction of *n*-pentane and of neohexane in a hydrogen flow on 90 Rh : 10 Cu and 50 Rh : 50 Cu at 473–623 K was predominantly by hydrogenolysis with relatively minor amounts (5–10%) of isomerization. The $\alpha\beta$-type hydrogenolysis of neohexane (to neopentane and methane) was not decreased on copper incorporation relative to $\alpha\gamma$ and $\alpha\gamma'$, hydrogenolysis routes which are believed to require single metal atom sites only. This result suggests the possibility of a single metal atom site mechanism for the "$\alpha\beta$" process.

INTRODUCTION

There is particular interest in the catalytic properties of highly dispersed bimetallic "clusters," especially in systems in which the metallic components have limited miscibility in the bulk (*1*). An example of such a system is rhodium–copper supported on silica.

The primary aim of this work was to extend the preparation of supported bimetallic clusters of high dispersion by preparing those of Rh–Cu using the same incipient wetness technique found to be successful for the Pt–Au system (*2*). Previous work with supported Rh–Cu of moderate dispersion suggested that appreciable selectivities for isomerization of alkanes may follow incorporation of Cu into Rh (*3*). A purely structural study of Rh–Cu clusters on Aerosil has been published (*4*). A brief conference abstract reporting results for ethane reaction on Rh–Cu/silica of unstated dispersion has also appeared (*5*).

Silica (which has the advantage of catalytic inertness) is generally accepted as being a poor support on which to attempt the dispersion of a metal by impregnating with a solution of metal anion (*6*). This is due to the fact that the active exchange sites are the silanol groups which are weakly acidic. However, if silica is heated to 973 K, the concentration of silanol groups is considerably suppressed. Dale and Rooney (*7*) suggest that such silica surfaces contain Lewis acid sites. This implies that anionic exchange is now possible and it has (inferentially) been achieved in the Pt–Au system (*2*). In the present work, anionic chloride and nitrate precursors have been used.

Three alloy compositions were chosen: (i) 10% Rh, 90% Cu, (ii) 50% Rh, 50% Cu, and (iii) 90% Rh, 10% Cu. Catalytic experiments were conducted on (ii) and (iii). These would be expected for alloys in the massive form to be two-phased (*8*) but "clusters" may be presumed to contain homogeneous metal (*1*).

Initially, following Sinfelt (*1*), suppression of ethane hydrogenolysis on prepared "clusters" was sought as a criterion of intimate association between the metallic constituents. Catalysis of the reactions of *n*-pentane and neohexane over these catalysts was then examined.

EXPERIMENTAL

Materials and Procedures

Degussa Aerosil 200 (area 200 m^2/g, mean particle size 12 nm, nonporous) was pre-

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treated as follows. To remove base-metal impurities (which we have shown can be a source of spurious catalytic activity) the material was leached three times with Aristar concentrated nitric acid with constant shaking. It was then washed repeatedly (minimum of 30 washings) using deionized water, the support being retrieved by decanting and centrifugal sedimentation. Following drying at 383 K (15 h), the treated Aerosil was heated in air at 973 K (15 h) to oxidize off any organic contaminants and to condition the surface as already noted.

Primary sources of metals were rhodium trichloride (Fisher Scientific, purified grade), rhodium trichloride and rhodium nitrate (Johnson Matthey, "spectrographically standardized"), and copper chloride (Aldrich, "gold label"). Copper nitrate was prepared from cupric oxide (Johnson Matthey, "spectrographically standardized") by dissolving in Aristar concentrated nitric acid at 323 K and then evaporating the resulting solution at 313 K to obtain the nitrate trihydrate.

All glassware used was washed in (i) aqua regia (2 h), (ii) "chromic acid" cleaning mixture (15 h), and (iii) concentrated nitric acid (15 h), followed by washing thoroughly with deionized water after each stage.

Catalyst Preparation

Acres *et al.* (*6*) have argued that mixed impregnating solutions for preparing bimetallic catalysts of high dispersion should contain the following (i) it should have the same chemical form of metal precursor, viz., both chloride or both nitrate, etc., (ii) both forms should be cationic *or* anionic depending on whether the support is a cation exchanger or an anion exchanger, and (iii) (if possible) the charge on the metal complex ion should be the same for both metals. In the first phase of this work, chlorides of Rh and Cu in concentrated HCl aq. were used because this mixed solution contains $RhCl_6^{3-}$ and $CuCl_4^{2-}$ as the sole metallic species. Literature reports to this effect (*9*, *10*) were confirmed for the present impregnating solutions by the measurement of UV/Vis absorption spectra. (Absorption maxima were 402, 510 nm for Rh and 512 nm for Cu.) For reasons to be presented later, nitrates were eventually used as metal precursors for all catalytic experiments to be reported.

The impregnating solution contained the two metals in a ratio appropriate to the desired Rh–Cu "cluster" composition. The solution was diluted (as required) with concentrated HCl aq. in the case of chloride precursors and concentrated HNO_3 aq. in the case of nitrate precursors to a total volume sufficient (i) to bring the Aerosil to incipient wetness and (ii) to furnish a 0.3% (w/w) metal loading. Solution and support were brought into contact and stirred vigorously until a visually homogeneous material was achieved (~20 min). The material was dried overnight at 383 K and then stored in a vacuum desiccator.

The reduction procedure was as follows: (i) purged in oxygen-free argon (298 K, 15 h; 473 K, 3 h), (ii) reduced in hydrogen (473 K, 3 h; 673 K, 15 h), and (iii) cooled in oxygen-free argon. A British Oxygen Mk III inert gas purifier and a Johnson Matthey hydrogen diffusion unit furnished high-quality gases for these stages.

Catalytic Experiments

A continuous flow reactor was used as previously described (*11*). A catalyst charge of 0.25–0.65 g (according to activity) was used. The total feed-gas pressure was 760 Torr. Hydrocarbon partial pressure was maintained at ca. 17 Torr (55 Torr in the case of ethane) by surrounding a saturator with an appropriate refrigerated bath; the remainder was pure hydrogen. Products of ethane hydrogenolysis were analysed by glc on 10 m silicone SE30 on Chromosorb P and of *n*-pentane and neohexane reactions on 2 m squalane on Chromosorb P.

RESULTS AND DISCUSSION

Catalyst Characterization

The techniques used to estimate metal dispersion in each catalyst preparation

TABLE 1

Metal Crystallite Diameters (nm) from TEM and H_2 Chemisorption

Metal composition (at.%)	Chlorine precursor TEM[a]	Nitrate precursor TEM	H_2 chemisorption
100Rh	2.7 ± 0.9	<1.0	≤1.2–1.3[b]
90Rh–10Cu		<1.0	≤1.2–1.3[c]
50Rh–50Cu	2.4 ± 0.7	<1.0	No chemisorption
10Rh–90Cu	<1.5	—	
100Cu	<1.5	<1.0	

[a] Embedded in "Araldite" epoxy resin prior to electron microscopy to preclude oxidation by ambient air.

[b] Molecules adsorbed (8.9×10^{21}) per gram metal. Even with H/Rh = 2.5 (*16*) all Rh atoms are deduced to be surface atoms in this and in the 90 Rh–10 Cu catalyst. The upper limiting diameter stated is so based.

[c] Molecules adsorbed (7.8×10^{21}) per gram metal. Catalytic activities, more particularly for ethane hydrogenolysis (see text), suggest a minimum particle size of 0.6–0.7 nm for this catalyst in that each cluster may be presumed to contain at least one Cu atom.

were TEM and hydrogen chemisorption determination (Table 1). Chemisorptions were studied by the hydrogen-pulse technique as developed by Gruber (*12*), measurements being made at 298 K and 760 Torr. This provided an *in situ* measurement of the metal site count and hence dispersion, both being subject to qualifications now to be discussed.

Below a nominal (spherical) crystallite diameter of ~1.2–1.3 nm all rhodium atoms are surface atoms, and chemisorption cannot distinguish between differing degrees of dispersion. Further, there may be quite a large variation in the average number of hydrogen atoms adsorbed per exposed Rh atom, that is, the H/Rh stoichiometry (*13–16*). Average particle diameters may therefore be estimated only for the larger clusters and upper limits given for smaller clusters. The chloride-derived catalysts contain metal particles having an average diameter of more than 1.5 nm from TEM (Table 1). Concurrence between TEM diameters and average diameters from chemisorption would therefore be expected for these samples. Quantitative confirmation of this particle size by hydrogen chemisorption was not, however, possible, take-up being invariably several fold greater than that corresponding to TEM estimates of area, irrespective of the value assumed for H/Rh stoichiometry (*15, 16*). This was in contrast to previous work on Pt and Pt–Au clusters (*2*) where excellent agreement was found. Borrowing from a painstaking discussion of a related effect by Bond *et al.* (*17*), we believe that chlorine becomes bonded to the support surface as Si–Cl groups during the reduction step with the present samples. These bonded chlorines are then slowly removed by hydrogen spillover as

$$X\text{–Cl} + \text{H}\cdot \rightarrow \text{HCl} + X\text{–}$$

where X– represents a Lewis acid site. Even after an additional 8-h reduction period (total reduction of 23 h) of a Rh/Aerosil preparation, the tail gas still contained appreciable hydrogen chloride as indicated by AgCl precipitation in $AgNO_3$ aq. There is therefore quite strongly bound chlorine in the reduced catalyst which is only removed extremely slowly. From the large quantity of hydrogen consumed in hydrogen-pulse chemisorption, we are inclined to reject the possibility of an adlayer of chlorine on the rhodium surface alone which would give rise, at most, to about double the consumption to be expected from the estimated metal area, and indeed from existing tests (*18*) probably to less than this expected consumption. Our experiments do not allow further elaboration of this problem.

Partly because of the somewhat ill-defined nature of the chloride-derived catalysts and partly in an effort to improve the metal dispersion it was decided to make use of a nonchlorine-containing precursor and the nitrate precursor of both metals was chosen. In order to effect anion formation, impregnating solutions contained both salts dissolved in concentrated HNO_3 aq. (absorption maxima for nitrate solutions were 804 nm for Cu and 338, 380 nm for Rh). Hydrogen chemisorption results following the use of such solutions show the metal particles to be in the desired cluster range (Table 1 including footnote). No metal particles were observed by TEM for such cata-

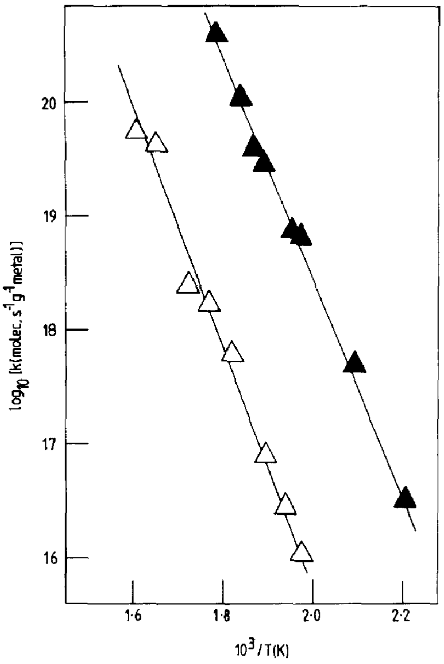

FIG. 1. Hydrogenolysis of ethane on 100% Rh and 90% Rh–10% Cu on Aerosil. (▲) 100% Rh; (△) 90% Rh–10% Cu.

lysts, as expected, because they are below the detectability limits imposed by the microcrystallinity of the support (*19*). However, in representative postcatalysis samples (which had been subjected to a temperature of ca. 673 K in reaction mixtures) a few particles of 2.0–6.0 nm diameter were observed.

Two 50 Rh : 50 Cu samples (from nitrate precursors) showed no detectable hydrogen chemisorption capacity. These catalysts, however, subsequently showed interesting catalytic behavior (see later).

Catalysis

Ethane reaction. In the "cluster" range of dispersion where X-ray diffraction is no longer feasible for monitoring metal homogeneity, Sinfelt has favored (*1*) use of ethane hydrogenolysis for this purpose for Group VIII-IB combinations. This approach is based on the need in the ethane reaction, which is demanding (*20*), for either pair sites or sites of a special degree of coordinative unsaturation, or both. A striking decrease in hydrogenolysis activity on incorporation of the inactive metallic element is taken to signify intimate association of the metallic elements. The incorporation of only 10 at.% Cu causes a fall in ethane hydrogenolysis activity of two to three orders of magnitude (see Fig. 1) suggesting that catalytic centres are minority sites and these are "blocked" preferentially by copper atoms. This result also implies that the great preponderance of clusters at 90 Rh–10 Cu contain a copper atom and this dictates that clusters comprise a minimum of seven to eight atoms (see footnote to Table 1).

Finally, we note that turnover numbers for the ethane reaction at 453–463 K match quite well those of Sinfelt and Yates (*13*) for Rh/silica but present activation energies are about one-half of theirs (see footnote later).

n-Pentane reaction. n-Pentane was chosen as the main reactant alkane because the four main types of alkane skeletal reactions which can be catalyzed by platinum metals are all possible, namely, hydrogenolysis, isomerization, cyclization, and homologation. On all catalysts (Tables 2–5), hydrogenolysis was the main reaction with minor isomerization; only trace cyclization was observed and this was for the bimetallics at higher temperatures.

Apart from the "running in" of the catalysts at the lowest reaction temperatures, hydrogenolysis was predominantly by internal C–C bond scission throughout yielding ethane and propane. Homologation was absent on all catalysts. On incorporation of 10 at.% Cu there is a much smaller decrease in turnover number for the *n*-pentane reaction (Table 3) than that found for the ethane reaction. Thus, at lower temperatures there is a 15-fold decrease; at higher temperatures there is appreciable self-poisoning with the bimetallic catalyst and turnover number comparisons are not justified. The selectivity for isomerization S_I shows a modest but significant increase from ~1–2% (100 Rh) to 5–15% for the bimetallic catalysts.

TABLE 2

Reaction of *n*-Pentane/Hydrogen over 100% Rh: Product Distribution (wt%)

Temp. (K)	Conv. (%)	Turnover no. (molec. s^{-1} g $metal^{-1}$)	C_1	C_2	C_3	iC_4	nC_4	iC_5	cC_5	S_H	S_I	S_C
419	0.01	$\sim 1 \times 10^{18}$	25	—	75	—	—	—	—	100	0	0
446	0.02	2.7×10^{18}	—	38	56	—	—	6	—	94	6	0
460	0.1	1.8×10^{19}	2	40	46	—	6	6	—	94	6	0
491	0.5	9.2×10^{19}	4	42	47	—	6	1	—	99	1	0
533	>50	1.4×10^{22}	3	47	46	Tr[a]	3	1	—	99	1	0
540	38	6.3×10^{21}	3	45	45	Tr	6	1	—	98	2	0

[a] Tr, trace.

The contrast in hydrogenolysis turnover number change on incorporation of Cu with the effect on the ethane reaction implies that the former is less demanding as to surface sites (i.e., requiring a lesser degree of coordinative unsaturation or needing only a single metal atom site). Certainly the thrust of recent publications is that not only isomerization but also hydrogenolysis of higher alkanes ($\alpha\gamma$ intermediates) takes place on a single metal atom (*21, 22*).

No major change in the character of the conversion (activity, selectivity) was found on incorporating further Cu to 50 at.% (Tables 4, 5). However, the reaction on two 50% Rh–50% Cu catalysts yielded a new and interesting feature, namely, a very rapid production of *n*-butane occurring at a low temperature (and loss of matching methane to surface carburization). In the two experiments, such temperatures were 364 and 430 K, respectively, catalyst history being different in the two cases as stated in the two tables: a further change of temperature, either in small steps upward or cyclically through a lower temperature, caused an immediate suppression of activity, not restored until the normal temperature range above 493 K was reached. At the onset temperature, it is clear that this higher Cu concentration promotes a rapid, highly specific terminal hydrogenolysis. Since the adsorbed hydrogen concentration at the surface has a large effect on the catalytic activity in view of the large difference in the two temperatures mentioned (the lower temperature referring to a run with an initially hydrogen-free surface, the higher

TABLE 3

Reaction of *n*-Pentane/Hydrogen over 90% Rh–10% Cu: Product Distribution (wt%)

Temp. (K)	Conv. (%)	Turnover no. (molec. s^{-1} g $metal^{-1}$)	C_1	C_2	C_3	iC_4	nC_4	iC_5	cC_5	S_H	S_I	S_C
479	0.01	$\sim 1.5 \times 10^{18}$	—	35	65	—	—	—	—	100	0	0
508	0.03	3.9×10^{18}	5	24	44	—	—	27	—	73	27	0
543	0.7	1.0×10^{20}	7	32	39	—	17	5	—	95	5	0
574	0.5	6.9×10^{19}	8	32	37	—	18	6	—	94	6	0
606	1.2	1.6×10^{20}	9	28	29	—	22	10	2	88	10	2
637	3.3	4.5×10^{20}	15	19	20	Tr[a]	28	14	4	81	15	4

[a] Tr, trace.

TABLE 4

Reaction of *n*-Pentane/Hydrogen over 50% Rh–50% Cu (Initially Hydrogen-Free Surface): Product Distribution (wt%)

Temp. (K)	Conv. (%)	Turnover no. (molec. s^{-1} g metal^{-1})	C_1	C_2	C_3	iC_4	nC_4	iC_5	cC_5	S_H	S_I	S_C
364	100	$>10^{22}$	—	Tr[a]	Tr	—	100	—	—	100	0	0
338–468[b]	0	—	—	—	—	—	—	—	—	—	—	—
494	0.01	5×10^{18}	29	24	47	—	—	—	—	100	0	0
527	0.1	5.6×10^{19}	8	32	34	—	14	11	—	89	11	0
555	0.3	1.3×10^{20}	5	29	36	—	20	10	—	90	10	0
595	1.3	6.5×10^{20}	9	21	30	Tr	23	12	4	83	13	4
629	1.7	9.0×10^{20}	11	16	25	Tr	28	13	7	79	14	7

[a] Tr, trace.

[b] Catalyst was tested for activity at eight temperatures in all in this range.

TABLE 5

Reaction of *n*-Pentane/Hydrogen over 50% Rh–50% Cu (Initially Hydrogen-Covered Surface): Product Distribution (wt%)

Temp. (K)	Conv. (%)	Turnover no. (molec. s^{-1} g metal^{-1})	C_1	C_2	C_3	iC_4	nC_4	iC_5	cC_5	S_H	S_I	S_C
326–388[b]	0	—	—	—	—	—	—	—	—	—	—	—
430	100	$>10^{22}$	Tr	—	—	—	100	—	—	100	0	0
445–476[b]	0	—	—	—	—	—	—	—	—	—	—	—
508	0.03	1.4×10^{19}	—	36	46	—	18	—	—	100	0	0
536	0.1	7.3×10^{19}	7	32	41	—	14	6	—	94	6	0
580	1.4	7.7×10^{20}	9	30	32	—	15	9	5	86	9	5
615	2.2	1.2×10^{21}	11	23	24	Tr	20	16	5	79	16	5

[a] Tr, trace.

[b] Catalyst was tested for activity at five temperatures in all in these ranges.

TABLE 6

Reaction of Neohexane over 100% Rh: Product Distribution (wt%)

Temp. (K)	Conv. (%)	Turnover no. (molec. s^{-1} g metal^{-1})	C_1	C_2	C_3	iC_4	nC_4	iC_5	neoC_5	cC_5	$S_{H_{\alpha\beta}}$[a]	$S_{H_{\mathrm{other}}}$
455	0.01	$1\text{–}2 \times 10^{19}$	19	—	—	—	—	17	64	—	77	23
480	1.3	2.9×10^{20}	19	1	—	2	—	21	57	—	69	31
491	4.2	9.3×10^{20}	18	1	0.2	2	—	14	64	—	77	23
506	20	4.5×10^{21}	20	1	0.4	4	0.3	11	63	—	75	25

[a] The separation of hydrogenolysis into an "$\alpha\beta$" process and into "other" ($\alpha\gamma$, $\alpha\gamma'$, cracking) processes is clearly not a rigorous one; for example, cracking to methane may initiate in an $\alpha\beta$ process. It is, however, adopted for convenience of discussion and conclusions reached (see text) do not rely on a rigorous separation.

TABLE 7

Reaction of Neohexane over 90% Rh–10% Cu: Product Distribution (wt%)

Temp. (K)	Conv. (%)	Turnover no. (molec. s^{-1} g $metal^{-1}$)	C_1	C_2	C_3	iC_4	nC_4	iC_5	neoC_5	cC_5	$S_{H_{\alpha\beta}}$[b]	$S_{H_{other}}$
451	0.01	2×10^{18}	100	—	—	—	—	—	—	—	0	100
471	0.03	5.3×10^{18}	29	—	—	—	—	44	14	13	17	83
491	0.2	3.0×10^{19}	25	1	—	4	—	7	63	—	76	24
502	1.1	1.9×10^{20}	25	1	0.2	2	—	13	59	0.4	71	29
518	4.7	8.3×10^{20}	24	1	0.4	2	2	14	56	0.1	67	33
532	19	3.3×10^{21}	21	0.3	0.1	1	0.2	7	70	Tr[a]	84	16

[a] Tr, trace.

[b] See footnote to Table 6.

temperature to one with a hydrogen-covered surface; see Tables 4, 5), it may likewise be the case that the influence of Cu incorporation is in modifying the surface hydrogen concentration and so directing the C–C scission reaction towards retrohomologation. The sensitive influence of surface hydrogen on the forward homologation reaction has been discussed (*23*). We note here too that above 493 K the hydrogenolysis reaction on 50% Rh–50% Cu reverts to the usual C–C central scission.

If it is recalled that the 50 Rh–50 Cu catalysts initially showed negligible hydrogen chemisorption capacity, the catalytic results suggest that one or more structural changes take place in the clusters as the temperature is increased. This interesting catalyst invites structural investigation.

The 100% Cu catalyst was found to be inactive in the temperature range 424–663 K in contrast to a previous finding (*3*) which might be accounted for by base metal impurities on the silica in the earlier work.

Neohexane reaction. Neohexane was used as a reactant in order to test the preference of Rh and Rh–Cu for catalytic surface intermediates involving 2C–$\alpha\beta$, 3C–$\alpha\gamma$, $\alpha\gamma'$, or 4C–$\alpha\delta$ adsorption complexes (adopting the terminology of Vogelzang *et al.* (*24*)). Conversions were kept under about 5% to ensure initial product distributions whereby the mode of attachment of reaction intermediates to the surface might be deduced.

For 100% Rh hydrogenolysis selectivity is high for the production of neopentane and methane suggesting an $\alpha\beta$ adsorption complex is the dominant entity (Table 6). $\alpha\gamma$ and $\alpha\gamma'$ complexes resulting in the production primarily of methane and isopentane with trace amounts of ethane, propane, and butanes were also evident, especially at increased reaction temperature. ($\alpha\beta$-type product may also arise from $\alpha\delta$ complexes as noted in the following paragraph.)

On incorporation of 10 at.% Cu a decrease in activity of approximately 25-fold is observed (Table 7), similar in magnitude to that found in the *n*-pentane reaction (see Table 3). It is surprising that the proportion of the hydrogenolysis by the "$\alpha\beta$" route is not noticeably reduced on Cu incorporation, the behavior to be expected if this mode of C–C bond scission took place by the same mechanism and so on the same surface sites as those of the demanding ethane hydrogenolysis.[1] This would suggest

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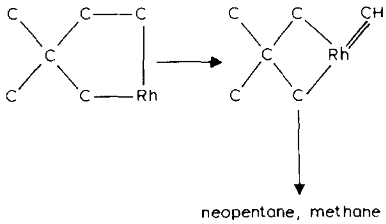
[1] Activation energies are not helpful in probing this question, being closely similar for the several reactions studied here. Approximate values derived for *E* are 92 kJ/mole for neohexane reaction on both Rh and 90 : 10 Rh : Cu, 74 kJ/mole for *n*-pentane reaction on Rh, 82 and 88 kJ/mole respectively for the ethane reaction on Rh and 90 : 10 Ru : Cu.



SCHEME 1

that the "$\alpha\beta$" process for neohexane hydrogenolysis requires only a single metal atom (Rh) site as has been argued for $\alpha\gamma$ processes. A feasible mechanism is the ring contraction of an $\alpha\delta$-diadsorbed radical to an $\alpha\gamma$ with elimination of a single methylenic carbon unit (Scheme I) (*25*). The reversible formation of an $\alpha\delta$-diadsorbed intermediate in alkane/deuterium exchange on rhodium has been shown by deuterium NMR spectrometry (*26*). An immediate difficulty is that symmetrical scission of the metallocyclopentane entity of Scheme I does not also take place to any marked extent; that is, isobutane and ethane are not substantial products (Tables 6 and 7). By contrast central scission of *n*-pentane, giving ethane and propane, is a marked feature for Rh and the Rh–Cu catalysts above the initial "run-in" temperature and this must result from such symmetrical scission. This kind of contrast is even clearer in the work of Foger and Anderson (*27*) who found for a range of IrAu "clusters," covering the complete composition range of Ir/Au ratios, that in all cases (i) there was preponderant ethane formation in the hydrogenolysis of *n*-butane whereas (ii) completely selective hydrogenolysis of neohexane by "$\alpha\beta$" scission was found giving neopentane and methane. Vogelzang *et al.* (*24*) reported a substantial "$\alpha\beta$" component in neohexane hydrogenolysis at 583 K on a 65 Ni–35 Cu alloy catalyst. Ethane hydrogenolysis is considerably suppressed at this alloy composition (*28, 29*). Both the present RhCu cluster results and those for IrAu of Foger and Anderson can be rationalized by the consideration that central scission of the metallocyclopentane surface radical is subject to different steric restrictions from those in the ring contraction reaction of Scheme I. This is because reaction fragments first form as π-alkene groups in the former (*30*) and the formation of these may be possible for ethene or propene (in reaction of *n*-butane or *n*-pentane) but not for the more bulky 2-methylprop-1-ene (in reaction of neohexane). The result of Vogelzang *et al.* can clearly also be accommodated within this interpretation.

An alternative possibility, capable of reconciling the several facts noted, is that the "$\alpha\beta$" process may take place by a mechanism similar to that for ethane hydrogenolysis but that the electronic asymmetry caused by the neopentylidyne (-ene) group may aid cracking of the "$\alpha\beta$" C–C bond, in effect rendering the reaction a less demanding one. Reaction of appropriately deuterium-labelled neopentane on rhodium and on iridium with glc/ms analysis of product neopentane would represent a test for the participation of an $\alpha\delta$-diadsorbed intermediate in the hydrogenolysis.

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