JOURNAL OF CATALYSIS 54, 230-242 (1978)

Preparation of Supported Platinum–Gold, Platinum–Tin, and Rhodium–Copper Catalysts and Some Tests with *n*-Hexane/Hydrogen Reactant

J. K. A. CLARKE,* I. MANNINGER,* AND T. BAIRD†

* *Department of Chemistry, University College, Dublin 4, Ireland and* † *Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland*

Received May 24, 1977; revised March 15, 1978

Studies are reported on the influence of preparative variables on the dispersion and alloying of the metals in silica-supported Pt–Au, Rh–Cu, and (in part) Pt–Sn. Tests of *n*-hexane conversion on selected catalyst samples using a pulse reactor are presented. It is shown that (i) while there is no evidence from X-ray diffraction of significant alloying in Pt–Au samples from various preparations, catalytic results show some interaction between the two metallic elements and (ii) samples of 15% Rn:85% Cu remain poorly alloyed, a rhodium-rich region remaining even with reasonably severe heat treatment prior to and during reaction: Even then, such a catalyst shows a selectivity of ~25% for $C_5 + C_6$ cyclic products whereas 100% Cu has only a small, and 100% Rh a negligible, cyclization selectivity.

INTRODUCTION

There is interest currently in the use of binary alloys as heterogeneous catalysts because these may show selective catalytic action not shown by either metallic component separately [for a review see Ref. (*1*)].

Useful information on the course of hydrocarbon and other reactions on alloys has been derived from studies of film catalysts (*2*, *3*). These, besides being convenient to prepare, are amenable to tests of homogenity using readily available instrumental techniques. Surface areas tend to be somewhat low, however, and surface topography may be different from that of practical forms of catalyst on account of the severe heat treatment needed in film preparation. In consequence, temperatures required to give conveniently measurable catalytic reaction rates on films are commonly higher than are typical for these processes.

Increasingly studied of late has been the preparation of supported alloys, particularly in regard to the effects of different preparation conditions on the physical nature of the resulting material. Success in attaining acceptable metal dispersion and, at the least, substantial metal mixing in bulk using a hydrogen reduction method, has been reported for Pt–Fe/carbon (*4*), for Pd–Ag/silica (*5*, *6*), and for Ni–Cu/silica (*7*). A 450°C sintering stage was found necessary for metal homogenization for Pt–Au/silica (*8*) and, in a later fuller study, for Pt–Cu/silica (*9*), resultant metal particle diameters in the latter case being in the range of 4.0 to 30 nm. In contrast to previous work (*10*) lattice parameters were in satisfactory agreement with Végard's law expectations for Pt–Cu. A very severe heat treatment stage was found by Sancier and Inami (*11*) and by O Cinneide and Gault (*12*) to be necessary

0021-9517/78/0542-0230$02.00/0

for bulk metal homogenization for Pd–Au/alumina catalysts: Metal particle sizes appear to have been large as a result in both studies. Illustratively of more gentle heat treatment, Pd–Ag/alumina samples prepared by impregnation followed by reduction at 400°C comprised metal crystallites too small to give X-ray diffraction patterns (*13*). Reduction by hydrazine (*14*) has been used for preparation of supported Pd–Au by Gerberich *et al.* (*15*), who, however, gave no information on the resultant metal dispersion, and also by Allison and Bond (*16*) and by Nakamura and Wise (*17*), both of which groups obtained good metal dispersion, the last-cited study reporting, however, the need for a 730°C calcination to give bulk metal homogeneity. Kulifay (*14*) reported *inter alia* successful preparations of $PtAu_3$ and of $PdCu_3$ wherein the metal was homogeneous as judged from X-ray powder photographs and had a mean crystallite size of ca. 10 nm.

The present work was designed to study the effects of preparative variables on the metal dispersion and bulk homogeneity of silica-supported Pt–Au, Pt–Sn, and Rh–Cu using mainly a hydrogen-reduction method but in addition the method employing hydrazine. There is catalytic interest in these alloy systems from previous work (*1*, *3*). Some tests of *n*-hexane/hydrogen reaction on selected catalyst samples are also presented.

EXPERIMENTAL

Materials and procedures. Joseph Crosfield i.d. Gel No. 1 [surface area 300 to 400 m^2 g^{-1}, mean pore diam 12 nm, or in a lesser number of experiments, Degussa Aerosil 200 (area 200 m^2 g^{-1}, 12-nm mean particle diam), after drying overnight at 120°C, was singly impregnated with a mixed solution of the metal salts. The primary solutions were (i) 0.1 M platinum(IV) chloride (Johnson Matthey, chemical grade) and 0.1 *M* chlorauric acid (Johnson Matthey "spectrographically standardised") for preparation of Pt–Au; (ii) 0.2 *M* tin(II) chloride and later 0.14 *M* tin nitrate (prepared from Cominco 5*N* tin), with 0.1 *M* platinum(IV) chloride for Pt–Sn, and (iii) 0.3 *M* copper(II) nitrate or copper(II) chloride (from Johnson Matthey "spectrographically standardised" copper oxide) and 0.2 *M* ammonium hexachlororhodite(III) (Johnson Matthey, "spectrographically standardised") for Rh–Cu. In each case the solution, appropriately mixed to yield the desired nominal alloy composition, was brought in contact with the carrier with vigorous stirring, the solution having a diluted total volume sufficient to bring the carrier to incipient wetness. The resulting mixtures were dried with stirring under an infrared lamp to a fine-powder condition and then dried finally in an oven. Reduction was carried out in a greaseless all-metal flow reactor (see catalytic experiments) following a purge with pure argon (B.O.C. Rare Gas Purifier 2) at room temperature (0.5 h) and then at 200°C (0.25 h) [cf. Anderson *et al.* (*10*)]. The reductant was palladium-diffused hydrogen, admixed on some occasions (Table 1) with argon.

Tests using hydrazine reduction were carried out for the Pt–Au and Rh–Cu systems. Unreduced catalyst, 0.2 g, was added to 0.6 ml hydrazine hydrate + 12 ml of water, with vigorous stirring until gas evolution ceased, the temperature of the mixture being set alternatively at either 20 or 80 to 90°C. The separated precipitate was washed 10 times with deionized water and dried by infrared lamp and oven, as before.

The details of individual sample preparations together with information from electron microscopy (JEM 100C) are given in Table 1. The catalyst code is described under Results.

Catalytic experiments. These were carried out in an all-metal flow reactor in a pulse mode. Catalyst, 0.1 g, rested on a porosity 3 sintered glass disk in a vertical 4.8-mm

TABLE 1

Sample Preparation Details and Particle Size Measurements from Electron Microscopy

Sample no.	Metal composition	Metal loading		Prepared from	Calcined		Reduced			Electron microscope data	
		I.D. gel (%)	Aerosil (%)		Temp (°C)	Time (h)	Temp (°C)	Flow (ml/min)	Time (h)	Average size (nm)	Size range (nm)
S112	100% Sn	4		Cl^-	500	6	450	20 H_2/80 Ar	4		
S122	100% Sn	4		Cl^-	600	10	450	20 H_2/80 Ar	4	64.0 ± 30	20–300
S132	100% Sn	4		Cl^-	600	10	450	20 H_2/80 Ar	4		
S302	100% Sn	4		NO_3^-	—	—	400	100 H_2	4	38.0 ± 9	15–75
S312	100% Sn	4		NO_3^-	500	15	400	100 H_2	4	37.0 ± 8	20–80
S322	100% Sn	4		NO_3^-	600	10	400	100 H_2	4	35.0 ± 7.5	15–60
S301	100% Sn	4		NO_3^-	—	—	450	100 H_2	4	37.5 ± 8.0	15–75
S402	100% Sn		4	NO_3^-	—	—	400	100 H_2	4	46.0 ± 14	15–150
PS322	5% Sn–95% Pt	4		Cl^-/Cl^-	600	10	450	20 H_2/80 Ar	4	7.9 ± 5.2	
PS102	5% Sn–95% Pt	4		NO_3^-/Cl^-	—	—	400	100 H_2	4	3.4 ± 2.6	
PS112	5% Sn–95% Pt	4		NO_3^-/Cl^-	500	15	400	100 H_2	4	3.5 ± 2.5	
PS122	5% Sn–95% Pt	4		NO_3^-/Cl^-	600	15	400	100 H_2	4	5.2 ± 3.4	
PS101	5% Sn–95% Pt	4		NO_3^-/Cl^-	—	—	450	100 H_2	4	5.0 ± 2.5	
PS402	5% Sn–95% Pt		4	NO_3^-/Cl^-	—	—	400	100 H_2	4	3.6 ± 1.6	
P201	100% Pt	4		Cl^-	—	—	200	100 H_2	3	2.2 ± 0.6	<1–10
P202	100% Pt	4		Cl^-	—	—	400	100 H_2	3	4.9 ± 3.4	8–9%>10
P222	100% Pt	4		Cl^-	600	10	450	20 H_2/80 Ar	4	4.7 ± 3.0	10%>10
P211	100% Pt	4		Cl^-	500	10	200	20 H_2/80 Ar	4	2.4 ± 0.7	1%>10
P401	100% Pt		4	Cl^-	—	—	200	20 H_2/80 Ar	3	1.5 ± 0.5	<1–5
P402	100% Pt		4	Cl^-	—	—	400	20 H_2/80 Ar	3		1–50
P230	100% Pt	4		Cl^-	—	—	80	Hydrazine	—	65.0 ± 40	
P150	100% Pt	4		Cl^-	—	—	20	Hydrazine	—	70.0 ± 40	
P231[a]	100% Pt	4		Cl^-	—	—	80	Hydrazine	—	72.0 ± 40	
AP101	50% Au–50% Pt	4		Cl^-/Cl^-	—	—	200	100 H_2	3	2.7 ± 1.1	
AP101U[a]	50% Au–50% Pt	4		Cl^-/Cl^-	—	—	200	100 H_2	3	2.9 ± 0.7	
AP201	5% Pt–95% Au	4		Cl^-/Cl^-	—	—	200	100 H_2	3	2.5 ± 1.4	
AP401	5% Pt–95% Au		4	Cl^-/Cl^-	—	—	200	100 H_2	3	8.4 ± 7.5	<1–60
AP130	50% Au–50% Pt	4		Cl^-/Cl^-	—	—	80	Hydrazine	—		10–300
AP131[a]	50% Au–50% Pt	4		Cl^-/Cl^-	—	—	80	Hydrazine	—		10–300
AP250	5% Pt–95% Au	4		Cl^-/Cl^-	—	—	20	Hydrazine	—	8.7 ± 6.0	

TABLE 1—*Continued*

Sample no.	Metal composition	Metal loading		Prepared from	Calcined		Reduced			Electron microscope data	
		I.D. gel (%)	Aerosil (%)		Temp (°C)	Time (h)	Temp (°C)	Flow (ml/min)	Time (h)	Average size (nm)	Size range (nm)
AP251[a]	5% Pt–95% Au	4		Cl^-/Cl^-	—	—	20	Hydrazine	—	12.4 ± 6.0	
AP230	5% Pt–95% Au	4		Cl^-/Cl^-	—	—	90	Hydrazine	—	10.3 ± 4.0	
A101	100% Au	4		Cl^-	—	—	200	100 H_2	3	10.0 ± 8.8	
A401	100% Au		4	Cl^-	—	—	200	100 H_2	3	10.8 ± 4.0	
A130	100% Au	4		Cl^-	—	—	90	Hydrazine	—	15.0 ± 6.0	
A150	100% Au	4		Cl^-	—	—	20	Hydrazine	—	24.5 ± 8.5	
A151[a]	100% Au	4		Cl^-	—	—	20	Hydrazine	—	13.0 ± 7.0	
C113	100% Cu	4		Cl^-	500	15	400	100 H_2	3		
C230	100% Cu	4		Cl^-	—	—	90	Hydrazine	—		20–200
R102	100% Rh	4		Cl^-	—	—	200	100 H_2	3	4.4 ± 2.0	<1–25
R102U[a]	100% Rh	4		Cl^-	—	—	200	100 H_2	3	4.7 ± 2.2	<1–25
R112	100% Rh	4		Cl^-	500	15	200	100 H_2	3	5.2 ± 3.1	<1–25
R103	100% Rh	4		Cl^-	—	—	400	100 H_2	3	6.9 ± 5.0	<1–100
R113	100% Rh	4		Cl^-	500	15	400	100 H_2	3	6.2 ± 2.4	<1–30
R401	100% Rh		4	Cl^-	—	—	200	100 H_2	3	5.2 ± 2.8	<1–30
R130	100% Rh	4		Cl^-	—	—	90	Hydrazine	—		20–300
RC102	15% Rh–85% Cu	4		Cl^-/Cl^-	—	—	200	100 H_2	3	3.4 ± 1.2	<1–500
RC112	15% Rh–85% Cu	4		Cl^-/Cl^-	500	15	200	100 H_2	3	4.0 ± 1.7	<1–12
RC103	15% Rh–85% Cu	4		Cl^-/Cl^-	—	—	400	100 H_2	3	4.8 ± 2.9	1.5–700
RC113	15% Rh–85% Cu	4		Cl^-/Cl^-	500	15	400	100 H_2	3	4.9 ± 2.4	1.5–20
RC202	15% Rh–85% Cu	4		Cl^-/NO_3^-	—	—	200	100 H_2	3		1.5–500
RC212	15% Rh–85% Cu	4		Cl^-/NO_3^-	500	15	200	100 H_2	3		1.5–5.0
RC203	15% Rh–85% Cu	4		Cl^-/NO_3^-	—	—	400	100 H_2	3		1.5–700
RC302	15% Rh–85% Cu	8		Cl^-/NO_3^-	—	—	200	100 H_2	3		1.5–700
RC303	15% Rh–85% Cu	8		Cl^-/NO_3^-	—	—	400	100 H_2	3		1.5–700
RC312	15% Rh–85% Cu	8		Cl^-/NO_3^-	500	15	200	100 H_2	3	3.5 ± 1.2	1–12
RC313	15% Rh–85% Cu	8		Cl^-/NO_3^-	500	15	400	100 H_2	3	4.6 ± 2.4	1–20
RC401	15% Rh–85% Cu		4	Cl^-/NO_3^-	—	—	200	100 H_2	3	2.5 ± 0.9	<1–5
RC230	15% Rh–85% Cu		4	Cl^-/NO_3^-	—	—	90	Hydrazine	—		25–200

[a] See the text for further treatment (P231, AP101U, AP131, AP251, A151, and R102U).

TABLE 2

n-Hexane/Hydrogen Reaction on Platinum–Gold System: Product Distributions (%)

Pulse no.	Catalyst basis	Catalyst code[a]	Temp. (°C)	Conv. (%)[b]	Turnover number[b] (molec·s^{-1} cm^{-2})	C_1, C_2	C_3	iC_4	nC_4	iC_5	nC_5	cC_5, isohexene	2MP	3MP	MCP	Bz, cC_6	$\sum C_{<6}$/total products (%)
Hydrogen reduced																	
57	Pt	P201	295	55.8	8.0×10^{13}	4.1	9.3	0.2	4.2	1.7	7.4	—	48.3	21.6	2.6	—	26.9
18	50% Pt–Au	AP101	320	60.5	1.0×10^{14}	6.7	13.3	0.5	7.7	2.4	9.2	—	34.8	15.8	4.6	4.9	39.8
269	5% Pt–Au	AP201	316	0.4	1.0×10^{13}	6.8	30.0	—	18.0	—	13.4	—	7.1	0.5	24.2	—	68.2
261	Au	A101	300	0.02	2.0×10^{12}	2.0	5.0	—	5.0	—	72.0	—	16.0	—	—	—	84.0
28	50% Pt–Au	AP101	362	88.4	—	10.3	15.7	1.8	8.3	3.9	12.0	0.1	18.0	11.2	2.5	16.2	52.1
56	Pt	P201	380	99.7	—	16.7	13.8	2.1	3.9	1.9	1.3	—	0.3	0.3	—	59.6	39.8[c]
29	50% Pt–Au	AP101	381	96.9	—	15.5	16.8	3.2	10.2	5.4	8.2	0.1	5.9	4.0	1.0	29.3	59.4
268	5% Pt–Au	AP201	378	15.2	3.6×10^{14}	0.9	5.1	—	3.0	—	3.3	—	16.3	4.1	56.7	10.5	12.3[c]
259	Au	A101	396	3.4	3.0×10^{14}	1.2	1.7	—	2.2	0.1	1.9	0.9	10.9	6.0	48.9	26.2	8.0
267	5% Pt–Au	AP201	460	50.0	1.2×10^{15}	3.4	4.6	—	2.9	0.2	3.5	0.9	9.8	6.0	34.7	33.6	16.0[c]
258	Au	A101	458	5.6	5.0×10^{14}	2.8	3.3	—	2.7	0.1	2.3	1.2	6.8	3.2	39.1	38.1	12.2[c]
Hydrazine reduced																	
43	Pt	P231	295	0.9	4.3×10^{12}	6.0	13.3	—	7.8	0.1	11.0	—	26.6	11.6	20.0	3.7	38.2
33	50% Pt–Au	AP131	305	0.15	5.0×10^{11}	0.8	8.2	0.4	43.6	0.5	38.2	—	2.0	6.5	—	—	91.7
49	Pt	P231	360	34.8	1.7×10^{14}	4.0	10.0	0.8	4.4	0.6	4.1	0.2	37.1	18.7	9.8	10.5	24.1
39	50% Pt–Au	AP131	362	0.20	6.0×10^{11}	5.4	3.1	0.2	28.4	0.1	40.7	—	6.6	13.9	1.3	0.2	79.2
48	Pt	P231	380	43.2	2.1×10^{14}	3.6	9.1	1.4	7.8	1.1	4.6	0.2	30.0	18.9	10.1	13.2	27.8
38	50% Pt–Au	AP131	380	0.25	8.0×10^{11}	4.8	3.1	Trace[d]	23.2	0.1	29.9	—	9.9	11.2	14.0	3.5	61.2
47	Pt	P231	403	56.4	2.7×10^{14}	8.6	16.5	3.8	6.5	1.7	5.5	—	21.0	11.6	9.0	15.8	42.6
36	50% Pt–Au	AP131	405	0.8	3.0×10^{12}	6.4	4.2	0.1	8.8	0.1	9.8	—	17.9	19.8	28.3	4.6	29.4

[a] Amounts, 0.1 g, of catalysts AP201 and A101; 0.4-g amounts of catalysts P201, AP101, P231, and AP131.

[b] Estimated in Tables 2 to 4 assuming metal crystallites to be spheres having diameter equal to mean diameter from electron microscopy.

[c] Balance of total product (to 100%) C_5 or C_6 dienes.

[d] Trace signifies <0.05.

i.d. glass tube. After the reduction, a flow of 80 ml/min argon and 20 ml/min hydrogen (both purified as earlier) was passed through the catalyst and then directly into the glc column. *n*-Hexane was the reactant hydrocarbon in all runs. The reactor temperature having been set, a pulse of the alkane vapor (5 ml, 17 Torr) was injected into the gas mixture upstream of the catalyst. The glc column for product analysis was 2 m squalane on Chromosorb P operated at 67°C.

Initial checks on the 50% Pt–50% Au AP101 and the 100% Rh R102 showed that neither catalyst suffered change in metal dispersion following a typical, or even a more extended, catalytic usage (3 h, >200 pulses, 200–400°C). Experiments with R102 confirmed that product distributions measured in a descending temperature sequence (from 400°C) matched those in an ascending temperature sequence, the former procedure being that followed in the runs reported here. There was a slow decline in catalyst activity with time in successive pulses even though hydrogen/argon reductant was flowed through the catalyst bed continuously. Principal attention will be given in this report therefore to selectivity differences between catalysts, but comment is possible on activity differences when these are substantial.

Product distributions for P201, A101, AP201, AP101, P231, and AP131 (platinum–gold system) are given in Table 2. The results for S302 and PS102 (platinum–tin system) are given in Table 3. Table 4 contains representative experiments for R113, C113, RC113, and some runs with R102 (rhodium–copper system).

RESULTS AND DISCUSSION

Structural Examination

The main aim of the work was to prepare supported alloys acceptable for basic catalytic work. To attain this objective in a reasonable time scale, an empirical approach was adopted in which a relatively small number of preparation conditions were varied for a given bimetallic system. These conditions were choice of salts, of supports, effects of calcination, reduction temperatures, and percentage metal loading.

The resulting metal dispersion was measured by electron microscopy while metal homogeneity was tested in appropriate cases by X-ray diffraction. Acceptable, not necessarily optimum, recipes were the goal.

The catalyst code, which is chosen for simplicity rather than precision, comprises one or two letters, signifying metal(s), followed by three digits denoting, respectively, (i) support, or metal loading, or metal composition, or precursor salt(s), (ii) calcination or hydrazine reduction condition used, and (iii) reduction conditions or further heat treatment of catalyst. For example (see later) the sample AP 131 is gold–platinum on i.d. gel prepared by hydrazine reaction and without subsequent heat treatment in hydrogen.

Pt–Sn. Tests with tin itself [derived from tin(II) chloride, 4% loading, on i.d. gel] based on color of the product showed that a moderate calcination (600°C) followed by reduction (450°C using $H_2/A :: \frac{1}{4}$) gave an acceptably dark-grey product which gave X-ray diffraction lines due to metallic tin only (S122). Metal particles were large (~20–300 nm). Similar reduction conditions preceded by a 500°C calcination gave a visibly less reduced product giving a less intense metallic tin X-ray diffraction pattern (S112). Reduction of tin(II) chloride on i.d. gel at 450°C *without* prior calcining was clearly an impracticably slow process, judging from the absence of diffraction lines (S132).

Impregnation of the carrier with tin nitrate made possible reduction to metal without including a calcining stage. Tests of the effect of *having* such a stage on final metal dispersion, now made possible,

TABLE 3

n-Hexane/Hydrogen Reaction on Platinum–Tin System: Product Distribution (%)

Pulse no.	Catalyst basis	Catalyst code[a]	Temp. (°C)	Conv. (%)	Turnover number (molec·s^{-1} cm^{-2})	C_1, C_2	C_3	iC_4	nC_4	iC_5	nC_5	cC_5, isohexene	2MP	3MP	MCP	Bz, cC_6	$\sum C_{<6}$/total products (%)
2	Pt	P201	296	77.4	1.8×10^{15}	5.5	9.8	1.2	6.5	3.5	8.6	—	40.9	21.9	2.0	0.1	35.1
274	5% Sn–Pt	PS102	315	0.6	2.1×10^{12}	4.4	19.9	—	7.5	—	15.9	0.5	20.7	8.9	16.6	5.5	48.2
254	Sn	S302	304	0.01	1.3×10^{12}	100.0	—	—	—	—	—	—	—	—	—	—	100.0
273	5% Sn–Pt	PS102	340	4.1	1.4×10^{13}	0.9	5.2	—	2.2	—	54.9	—	10.2	1.9	21.1	3.4	63.2
251	Pt	P201	400	92.4	—	13.9	12.9	2.0	5.1	3.0	6.7	—	8.8	4.9	3.6	39.3	43.6
272	5% Sn–Pt	PS102	400	81.4	—	1.7	5.4	—	1.7	0.2	3.2	—	27.4	19.5	19.7	21.1	12.2
255	Sn	S302	395	0.08	1.1×10^{13}	15.2	13.7	—	12.5	—	28.4	0.4	14.5	15.5	—	—	70.2
263	Pt	P202	440	42.8	2.2×10^{15}	10.1	11.7	0.2	6.9	1.2	5.5	0.1	6.7	5.9	15.5	36.3	35.6
271	5% Sn–Pt	PS102	436	86.4	—	4.5	7.7	Trace	2.9	0.7	5.4	0.5	15.7	7.9	28.5	26.2	21.7
256	Sn	S302	435	0.3	—	5.4	7.6	—	6.6	Trace	12.2	1.2	9.7	30.6	—	26.8	33.0

[a] One-tenth gram amount in each case except pulses 2 and 251 which refer to 0.4 g of catalyst (see text); hydrogen-reduced.

[b] See also Table 2.

TABLE 4

n-Hexane/Hydrogen Reaction on Rhodium–Copper System: Product Distributions (%)

Pulse no.	Catalyst basis	Catalyst code[a]	Temp. (°C)	Conv. (%)	Turnover number (molec·s^{-1} cm^{-2})	C_1, C_2	C_3	iC_4	nC_4	iC_5	nC_5	cC_5, isohexene	2MP	3MP	MCP	Bz, cC_6	$\Sigma C_{<6}$/total products (%)
66	Rh	R102	156	24.5	6.4×10^{14}	22.8	26.9	—	30.1	—	19.5	—	0.2	0.4	Trace	—	99.3
281	Rh	R113	174	13.2	4.9×10^{14}	19.8	22.4	—	22.9	0.2	26.7	—	7.1	0.8	—	—	92.0
280	Rh	R113	206	67.5	2.5×10^{15}	32.1	32.5	—	27.8	0.2	2.1	—	4.2	1.1	—	—	94.7
68	Rh	R102	208	95.5	—	27.4	26.9	1.0	23.4	4.1	14.8	—	1.7	0.8	Trace	—	97.6
293	15% Rh–Cu	RC113	200	0.04	$\sim 9.0 \times 10^{11}$	13.0	19.0	—	17.0	—	36.0	—	2.0	12.0	—	—	85.0
288	Cu	C113	218	0.1	$\sim 8.0 \times 10^{12}$	22.0	21.0	—	21.0	0.5	30.0	—	2.0	4.0	—	—	94.0
278	Rh	R113	300	100.0	—	100.0	—	—	—	—	—	—	—	—	—	—	100.0
292	15% Rh–Cu	RC113	300	1.8	4.0×10^{13}	24.5	13.3	—	12.5	1.0	16.3	—	5.2	2.4	1.8	22.9	67.6
286	Cu	C113	325	3.9	3.0×10^{14}	84.8	—	—	3.3	0.4	3.0	—	0.4	0.2	—	7.8	91.5
289	15% Rh–Cu	RC113	360	4.7	1.1×10^{14}	3.3	1.7	7.1	12.1	2.8	28.5	—	6.8	2.4	11.1	24.3	55.5
285	Cu	C113	372	5.7	$\sim 5.0 \times 10^{11}$	88.3	—	—	0.1	—	1.3	—	0.2	0.2	—	10.0	89.7
275	Rh	R113	416	100.0	—	100.0	—	—	—	—	—	—	—	—	—	—	100.0
290	15% Rh–Cu	RC113	410	15.7	3.5×10^{14}	41.6	5.9	—	12.1	1.3	22.3	0.1	4.2	1.3	3.9	7.6	83.3
291	15% Rh–Cu	RC113	450	26.3	5.9×10^{14}	38.0	10.0	—	11.0	0.6	11.4	0.7	3.3	2.0	1.8	21.0[b]	71.9
284s	Cu	C113	449	35.8	$\sim 3.0 \times 10^{15}$	96.4	—	—	—	—	Trace	Trace	Trace	0.1	—	3.5	96.4

[a] Catalyst, 0.1 g, in each case, hydrogen-reduced.

[b] Balance of total product to 100% consisted of C_5, C_6 diene(s).

showed that even 600°C calcination had no apparent effect on the (albeit poor) dispersion (S302, S312, S322: sizes ca. 37 ± 8 nm); S322 gave lattice parameters consistent with tetragonal tin. (Here and in subsequent work reduction to metal was with undiluted hydrogen).

Tests with platinum metal (4%, on i.d. gel) showed a 200°C reduction without prior calcination to give particles of diam <1 to 10 nm (av 2.2 ± 0.6 nm, P201). Either 500 to 600°C precalcination or reduction at 400°C without prior calcination led to poorer dispersion (P211, 1% of particles >10 nm diam, av 2.4 ± 0.7 nm; P222, <1 to 50 nm, 10% of particles >10 nm, av 4.7 ± 3.0 nm; P202, 8 to 9% of particles >10 nm, av 4.9 ± 3.4 nm). Application of a simple reduction to a 5% Sn–95% Pt sample and to a 100% Pt sample (PS102 vs P202) showed that, other factors being equal, the presence of tin renders the particles less mobile as deduced from the considerably lower average particle size exhibited by PS102. A 500°C precalcination was not injurious to dispersion in the bimetallic system (PS112 vs PS102) but a 600°C precalcination is detrimental to a significant degree (PS122), reduction being at 400°C in these cases. When tin(II) chloride was used as the source of tin (PS322) and a reduction temperature of 450°C was employed following 600°C calcination, dispersion is further worsened (7.9 ± 5.2 nm av diam). Use of Aerosil 200 as support gave marginally better dispersion (i.e., average diameter) than i.d. gel (P401 vs P201 and PS402 vs PS102, respectively). X-Ray diffraction is hardly sufficiently sensitive in the case of supported metal to reveal dissolution of Sn in Pt as α-phase alloy [maximum tin content ~7 atom% (*18*)]: Thus, a lattice parameter of 0.3922 ± 0.0003 nm was derived for PS122 while that measured for P150 was 0.3917 ± 0.0002 nm.

If similar severe heat treatment conditions are necessary for complete reduction of Pt–Sn as used for 100% Sn, the foregoing tests suggested that a 5% Sn–95% Pt on either i.d. gel or Aerosil 200 with tin from tin(II) chloride [calcined for 10 h at 600°C; 450°C reduction (*19*)] or, preferably, for greater dispersion, tin nitrate (400°C reduction, viz., PS102) represents an acceptable preparation. PS102 was selected for catalytic tests.

Pt–Au. Because gold was derived from chlorauric acid, which decomposes and then sublimes as $AuCl_3$ at 250°C, calcination was not feasible. A simple comparison of reduction temperatures of 200 and 400°C with platinum-containing catalysts showed the lower temperature to give good dispersion (P201 vs P202; AP101) even at a high percentage of Au (AP201). Dispersion is better for 100% Pt with the Aerosil 200 support (P401 vs P201); however, while the alloy AP201 showed excellent dispersion, the Aerosil-supported AP401 gave a very wide scatter of particle sizes and larger average value. Catalyst usage in hydrocarbon conversion at 250 to 380°C following the reduction (see AP101U) gave no significant loss of metal dispersion. The lattice parameter for 100% Au, measured by Mr. A. Kane, was 0.4078 ± 0.0002 nm (A101); AP201 gave a value indistinguishable from this of $0.4077 \pm 0.0001_5$ nm while AP101 yielded 0.4077 ± 0.0002 nm (only one metallic phase being represented in the X-ray diffraction pattern). The Aerosil-supported sample corresponding to AP201, designated AP401, gave 0.4077 ±0.0001 nm.

Reduction by hydrazine solution gave unsatisfactory preparations. Dispersion was always poor, even with 100% Pt. No preference could be deduced between 80 – 90°C reduction and 20°C reduction (P230 vs P150; AP230 vs AP250) except for 100% Au where the 90°C reduction gave somewhat better dispersion. There was no significant loss of dispersion (P231 vs P230; AP131 vs AP130) for 100% Pt or the 50:50 metal mixture through later reduction in hydrogen at 200°C; the 5% Pt–95% Au, however, showed a significant loss. It is clear that dispersion with either 20°C or 80 to 90°C preparation temperature was in all cases inferior to that from hydrogen reduction at 200°C and with the same support material.

A 5% Pt–95% Au from hydrazine reduction (AP250) gave a lattice parameter from X-ray diffraction of 0.4076 ± 0.0001 nm (that expected from Végard's law being 0.4070 nm), so that this method too fails to give appreciable metal mixing.

According to Dorling and Moss (*19a*) the number of crystallites of metal produced by hydrogen reduction of dry impregnated support is likely to be determined by the number of individual micropores in which the salt is trapped. The crystallite size is then fixed by the concentration of the solution used. The reduction by aqueous hydrazine is probably more complex. Other workers have succeeded in preparing well-dispersed Pt (*14*) or Pd (*16*) by this method, and factors such as solution pH which may influence crystallite size (*19b*) require further study before an assessment will be possible.

Rh–Cu. Starting from a Cl^-/Cl^- source of metals, inclusion of a 500°C calcination stage with a 400°C reduction leads to better (R113 vs R103) or only marginally better (RC113 vs RC103) dispersion. With a 200°C reduction, however, dispersion is slightly worsened (RC112 vs RC102; R112 vs R102) on precalcining. There is some indication that a Cl^-/NO_3^- source of metals with 500°C calcination and 200°C reduction gave better dispersion than the same treatment on the Cl^-/Cl^- preparation (RC212 vs RC112). When reduction was carried out at 400°C, however, metal dispersion was similar to that from Cl^-/Cl^- (RC313, ~1 to 20 nm, av diam 4.6 ± 2.4 nm vs RC113, ~1.5 to 20 nm, av diam 4.9 ± 2.4 nm). We note at this point that dispersion is not significantly altered by increasing metal loading from 4 to 8% (RC313 vs RC212; RC302 vs RC202; RC303 vs RC203).

Use of Aerosil 200 support compared to i.d. gel showed that uncalcined preparations subjected to reduction at 200°C are slightly poorer in dispersion in the former case for 100% Rh (R401 vs R102). The use of the Aerosil, however, leads to definitely better dispersion with the bimetallic situation (RC401 vs RC202 or RC102).

Hydrazine reduction at 90°C, and reverting to use of i.d. gel, led to the production of large metal crystallites for both single metals and alloys (R130, RC230, and C230). This method was not further pursued.

The nominal alloy composition 15% Rh–85% Cu was chosen so that a single metal phase might result (*20, 21*). A single set of diffraction arcs giving a lattice parameter of 0.3643 nm is expected from Végard's law for this alloy composition. In fact, two sets of reflexions appear in X-ray diffraction in the 8%-loaded "alloys" made from Cl^-/NO_3^- (RC312, RC313). The more intense, and so fuller, set of diffraction arcs gives a lattice parameter of 0.3612 nm (RC312) or 0.3617 nm (RC313) while 100% Cu gave 0.3612 nm (C230): The few extra lines, which pertain to a second metallic region, yield $a = 0.3717 \pm 0.0013$ nm (RC312; similarly for RC313) corresponding to a metal solution of about 60% Rh on Végard's law. It is clear that even the 500°C calcination/400°C reduction treatment of RC313 is inadequate in practice to bring about a homogeneous alloy. The particular compositions found for the two metal regions in these poorly alloyed samples probably reflect the mode of variation of bulk interdiffusion coefficients of Rh and Cu with atom fraction: Indeed there is a similiarity in these compositions to those noted by Soma-Noto and Sachtler (*7*) for Ni–Cu alloys of <50% Ni which are difficult to homogenize.

General Comment on Effect of Calcination (Rh–Cu, Pt–Sn)

The question whether or not a calcining stage prior to reduction is beneficial for metal dispersion does not obtain a general answer. For Rh and Rh–Cu from Cl^-/Cl^- sources calcining is beneficial for 100% Rh when the reduction stage which follows is at 400°C (R113 vs R103) and marginally better for the alloy (RC113 vs RC103). With a 200°C reduction, however, no benefit is derived from calcination, again if Cl^-/Cl^- sources are used. When, however, the Cl^-/NO_3^- starting compound combination is used, the calcination is beneficial with either the 200°C reduction (RC212 vs RC202; RC312 vs RC302) or with the 400°C reduction (RC313 vs RC303). With Pt, reduction at 200°C after calcining at 500°C appears to be only slightly less favorable compared to a simple 200° reduction (P211 vs P201). The conclusion for Pt–Sn is that a 500°C precalcination has no effect on dispersion (PS112 vs PS102) but that a 600°C precalcination has a somewhat worsening effect (PS122).

Catalytic Experiments

Pt–Au. A comparison of "hydrogen-reduced" and "hydrazine-reduced" catalysts (either for the case of 100% Pt or for 50% Pt–Au) shows that the former were appreciably more active than the latter, consistent with the greater dispersion of metal yielded by the hydrogen reduction method (Table 2). Although conversions are higher with the hydrogen-reduced catalysts so that product distributions are affected by the occurrence of successive reaction, useful comparisons are possible. The ratio of destructive/nondestructive reaction is not noticeably dependent (for 100% Pt) on whether the hydrogen reduction or hydrazine reduction route is used (see results for P201 vs P231 in Table 2). The ratio is generally greater for the 50% Pt–Au catalysts when these are prepared by hydrazine reduction: Certainly cases of very high ratios with the hydrazine-reduced alloy (e.g., at 305, 362°C) are not encouraging for utilization of such catalysts for cyclizations in organic syntheses. We may conclude also that lower ratios of destructive/nondestructive reactions are not found with the 50% Pt–Au catalyst AP101 as compared to the 100% Pt P201. From the few results available for it, the 5% Pt–Au catalyst AP201 prepared by hydrogen reduction appears to give a greater ratio of destructive/nondestructive reaction at 300 to 320°C than the ratios found with 100% Pt similarly prepared (P201); however, at 380°C upward this ratio is reduced considerably with the alloy. We shall return to the question of the structures of AP101 and AP201 later.

It is of interest that the 5% Pt–Au catalyst AP201 is notably more effective for methylcyclopentane production at 316°C than the 100% Pt catalyst P201 (both prepared by hydrogen reduction, the more acceptable method from the standpoint of chemical purity) (Table 2). This result concurs with a finding of O Cinneide and Gault (*12*) from a continuous flow reactor at 300°C for a 15% Pt–Au catalyst (which likewise represents a low-platinum single-phase alloy). These authors interpreted this result as implying a catalytic similarity between dilute-Pt-in-Au alloys and highly dispersed Pt, the latter being known to catalyze 1,5-cyclization of *n*-hexane and its reverse, nonselective ring opening. In view of the "demanding" nature of dehydrocyclization, it is of special interest that present comparison is for alloy and single-metal catalysts of closely similar metal diameter (Table 1). From a practical standpoint, the present observation represents a reassurance that the 5% Pt–Au catalyst is not merely a mechanical mixture of gold and (X-ray invisible) platinum. At the higher temperature of ~400°C, supported 100% Au (A101) has a substantial activity and methylcyclopentane and benzene are predominant products (Table 2).

The 5% Pt–95% Au catalyst AP201 has about one tenth the estimated specific activity of the 100% Pt catalyst P201 at 300°C, consistent with the former being a single-phased alloy of small percentage of Pt. For an alloy composition of 50% Pt–50% Au (AP101) two phases are present as expected (see X-ray characterization). These are a phase of ~15% Pt, ~85% Au and one of ~98% Pt, ~2% Au. It seems likely that AP101 contains the two metal phases in separate particles, or at least as separate exposed surfaces, judging from the type of product pattern (proportion of isohexanes and absence of methylcyclopentane as a major product) which shows no significant change at 300 to 320°C compared to 100% Pt (P201).

While lack of information on surface purity must discourage simplistic interpretation of the selectivity behavior of hydrazine-reduced catalysts, it seems a justifiable speculation that the 50% Pt–50% Au AP131 contains a platinum-rich phase largely enveloped by a very gold-rich phase, judging from the much lower conversions found on AP131 relative to P231. Phase envelopment (still to be substantiated by structural evidence) would come about most probably during the heat treatment in hydrogen which follows reduction by aqueous hydrazine. The hydrazine reaction places the metal nuclei in comparative juxtaposition so that growth to large crystallites, noted earlier, and envelopment of platinum with the more mobile element, gold, take place with ease compared to the situation with widely separated nuclei in samples reduced entirely in hydrogen (AP201, AP101).

Pt–Sn. There is no clear decrease observed in the ratio destructive/nondestructive reaction with Pt–5% Sn compared to 100% Pt except in the higher temperature range 400 to 440°C, where the ratio is decreased by a factor of between 2 and 5 (PS102 vs P201, P202: Table 3). The latter finding is thus the sole available evidence that the two metallic elements have alloyed to some degree during catalyst preparation. In this connection, the absence of large metal particles in PS102 (compare S302) is suggestive that, at least, the two elements are not spatially separated on the surface of the support.

We are unwilling to comment further with the present information on the Pt–Sn results but present them for their current interest. Questions such as completeness of reduction of the tin component merit further study, and work is desirable with catalysts PS112 and PS101 (Table 1) to this end.

Rh–Cu. 100% Rh-on-silica catalysts show some difference in product distribution and in activity following mild (R102) and following severe (R113) reduction conditions (Table 4, Rh catalysts, 156–208°C). It is evident, however, that in the absence of a second metallic element supported Rh acts above 200°C predominantly (or exclusively) as a hydrogenolysis catalyst, yielding only minor amounts of isohexanes and negligible cyclic products. With the 15% Rh, 85% Cu bimetallic catalyst RC113, appreciable percentages of cyclic products and also some isohexanes were formed (Table 4). Thus, at 300°C, 25% of products were C_6 cyclic and 32% of products in all were C_6. Using supported catalysts, therefore, the ratio destructive/nondestructive reaction decreases upon incorporation of 85 nominal percent of copper into rhodium. Supported 100% Cu (C113) gives approximate turnover numbers of similar magnitude to those with this bimetallic catalyst. Dehydrocyclization on C113, however, is small compared to that on RC113 (Table 4: 325, 360–370, 450°C so that production of methylcyclopentane/benzene on the latter most probably occurs on Rh centers at the metal surface. Previously, with severely annealed evaporated films (in which form 100% Cu has only a small activity) benzene was a major product even on 100% Rh, the destructive reaction/cyclization ratio being 3 to 4 at 280 to 340°C decreasing to values between 0.3 and 0.03 for Rh–Cu alloy films (*3*). There is most probably an effect due to surface–structure changes (and associated carbiding differences) involved when a comparison is made between Rh films and supported Rh so that it appears unjustified at present to invoke other bases to rationalize the further difference in catalytic behavior which follows copper incorporation.

The two bimetallic regions (Rh-rich, Rh-lean) indicated by X-ray diffraction of RC113 may both act as catalytic surfaces even if, as suggested by similarity of particle sizes to 100% Rh (R113: Table 1), there is no gross spatial separation of these from one another on the support. Further efforts to develop a preparation method giving a single low-Rh phase supported on silica would seem justified therefore in quest of a supported catalyst having a useful dehydrocyclization activity.

ACKNOWLEDGMENTS

This work was supported by the Irish National Science Council to whom thanks are offered (J.K.A.C.). The Science Research Council are gratefully acknowledged for an equipment grant for the JEM 100C (T.B.).

REFERENCES

1. Clarke, J. K. A., *Chem. Rev.* **75**, 291 (1975).

2. Moss, R. L., and Whalley, L., *Advan. Catal.* **22**, 115 (1972).

3. Peter, A., and Clarke, J. K. A., *J. Chem. Soc., Faraday I* **72**, 1201 (1975).

4. Bartholomew, C. H., and Boudart, M., *J. Catal.* **25**, 173 (1972).

5. Cormack, D., Thomas, D. H., and Moss, R. L., *J. Catal.* **32**, 492 (1974).

6. Soma-Noto, Y., and Sachtler, W. M. H., *J. Catal.* **32**, 315 (1974).

7. Soma-Noto, Y., and Sachtler, W. M. H., *J. Catal.* **34**, 162 (1974).

8. van Schaik, J. R. H., Dessing, R. P., and Ponec, V., *J. Catal.* **38**, 273 (1975).

9. de Jongste, H. C., Kuijers, F. J., and Ponec, V., *in* "Proceedings of the Sixth International Congress on Catalysis (London 1976)," p. 915. Chemical Society, London, 1977.

10. Anderson, J. H., Conn, P. J., and Brandenberger, S. G., *J. Catal.* **16**, 326 (1970).

11. Sancier, K. M., and Inami, S. H., *J. Catal.* **11**, 135 (1968).

12. O Cinneide, A. D., and Gault, F. G., *J. Catal.* **37**, 311 (1975).

13. Bond, G. C., Dowden, D. A., and Mackenzie, N., *Trans. Faraday Soc.* **54**, 1537 (1957).

14. Kulifay, S. M., *J. Amer. Chem. Soc.* **82**, 4916 (1961).

15. Gerberich, H. R., Cant, N. W., and Hall, W. K., *J. Catal.* **16**, 204 (1970).

16. Allison, E. G., and Bond, G. C., unpublished work: see Ref. 85 of the same authors in *Catal. Rev.* **7**, 233 (1973), and Bond, G. C., "Heterogeneous Catalysis," pp. 63–64. Clarendon Press, Oxford, 1974.

17. Nakamura, M., and Wise, H., *in* "Proceedings of the Sixth International Congress on Catalysis (London 1976)," p. 881. Chemical Society, London, 1977.

18. Hansen, M., and Anderko, K., "Constitution of Binary Alloys," p. 1142. McGraw-Hill, New York, 1958.

19. It remains possible that a calcination temperature of 500°C, mentioned in patents [e.g., Dautzenberg, F. M. (Shell Internationale Research Maatschappij N. V.) Ger. Offen. 2, 121, 765 (1971): *Chem. Abstr.* **76**, 37875j (1972)] allows complete reduction of Pt–Sn, prepared using platinum (IV) chloride, and, as noted in the text, it is not injurious to dispersion.

19a. Dorling, T. A., and Moss, R. L., *J. Catal.* **7**, 378 (1967).

19b. van Dillen, J. A., Geus, J. W., Hermans, L. A. M., and van der Meijden, J., *in* "Proceedings of the Sixth International Congress on Catalysis (London, 1976)," p. 677. Chemical Society, London, 1977.

20. Raub, C., Röschel, E., Menzel, D., and Gadhof, M., *Metallwirtschaft Tech.* **25**, 761 (1971).

21. Pearson, W. B., "Handbook of lattice Spacings and Structures of Metals and Alloys," p. 834. Pergamon, London, 1958.