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Reaction of Alkanes and Cycloalkanes on Silica-Supported Platinum and Platinum–Gold Alloy Catalysts

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The reactions of a range of cyclic and acyclic alkanes in excess hydrogen on silica-supported Pt and 10% Pt 90% Au were examined in a continuous-flow reactor. Catalysts were characterized by X-ray diffraction, electron microscopy, and hydrogen chemisorption measurement. Alloy homogenization required heat treatment at 700°C following reduction in hydrogen. From a negligible hydrogen chemisorption capacity the alloy catalyst is inferred to have a surface platinum content of $<0.4\%$. In the 300–400°C temperature range the alloy catalyst was found to have good bond-shift activity and also to be quite active in the ring enlargement of methylcyclopentane to benzene. It was found to be inactive for 1,5- and 1,6-cyclization, the hydrogenolysis of neopentane and of ethane, and also for the ring opening of cyclopentane. Absence of cyclization activity is ascribed to a surface topography of the dilute-Pt alloy unsuited to this demanding reaction on account of the severe heat pretreatment used. Bond-shift activity of such a surface is evidence for a single-site mechanism for this reaction.

INTRODUCTION

There is interest, both theoretical and practical, in the action of alloy catalysts in hydrocarbon reactions. Effects of incorporating a B-subgroup metal into a Group VIII metal which may be recognized in principle include bringing about a substantial decrease in the numbers of multiplet sites of active atoms, electronic influences, and selective "poisoning" of particular surface regions. Improved selectivity for desired reaction routes might be hoped for as a result of suitable alloy catalyst design. It seems reasonable to say that such a program is at an early stage both in the required theoretical understanding and in the realization (for reviews see (*1–3*)).

There is special interest in the Pt–Au system because of the wide applicability of platinum as a catalyst metal. In a previous study (*4*) homogeneous Pt–Au films were examined in test reactions of a series of hydrocarbons selected for mechanistic reasons. In key respects results appeared to be at variance with the small amount of published information for chemically prepared Pt–Au alloy catalysts (*5, 6*). It was decided to extend work with silica-supported Pt–Au which had already been begun in a limited way (*7*) to see if activity and selectivity patterns found with the film catalysts were matched with the supported alloys.

It had been noted (*7*) that neither a simple 200°C hydrogen reduction nor an aqueous hydrazine reduction at 80°C was effective in procuring homogeneous alloy although catalytic results suggested some interaction between the two metallic elements following either preparation method. To allow a meaningful comparison to be made with the film results it was felt necessary to develop a procedure which would ensure metal homogeneity even if the inevitably severe preparation conditions needed led to substantial loss of metal dispersion.

This report describes the preparation and characterization of well-alloyed silica-supported Pt–Au and of a Pt comparison catalyst, the reaction of a range of simple cyclic and acyclic hydrocarbons on them in a flow reactor, and a comparison of ob-

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served patterns with those found previously in a static system for Pt–Au films.

EXPERIMENTAL

Catalyst Preparation

Two types of silica were used, namely, Joseph Crosfield I.D. Gel No. 1 (surface area 300 to 400 m^2 g^{-1}, mean pore diam 12 nm) and Degussa Aerosil 200 (area 200 m^2 g^{-1}, 12-nm mean particle diam). In both cases the silica was dried overnight at 120°C and was singly impregnated with a mixed solution of the metal salts. The primary solutions were 0.1 *M* platinum(IV) chloride (Johnson Matthey, chemical grade) and 0.1 *M* chlorauric acid (Johnson Matthey, spectrographically standardized).

A 10% Pt–90% Au composition was chosen so that the alloy would be single phased since the phase boundaries are 18 and 98% Pt at temperatures in the 500°C region (*8*). In each case the solution containing the appropriate metal ratio to yield a 10% Pt–Au 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. Initial drying with stirring under an infrared lamp was followed by drying to a fine-powder condition in a rotary evaporator. Catalysts were stored in this form in an evacuated desiccator.

A hydrogen reduction was preferred to a hydrazine reduction on the grounds that the former yielded smaller crystallites and a catalyst at least as well alloyed as that resulting from the hydrazine reduction (*7*). Consequently reduction was carried out in a hydrogen flow at 200°C for 15 h following a purge with pure argon at room temperature (2 h) and then at 200°C (2 h).

In order to achieve satisfactory bulk metal homogeneity (see Catalyst Characterization) it was found necessary to subject the 10% Pt–Au catalyst to a 700°C postreduction calcination in air for 12 h. The reduction in metal surface area was considerable as a result of this severe heat treatment so that the activity of the 10% Pt–Au catalyst for the *n*-pentane hydrogen reaction, after a 3-h hydrogen reduction, was only measurable at and above 370°C. The introduction of a 500°C oxidation step for 0.25 h followed by a 3-h hydrogen reduction increased the activity such that reaction was observable from 300°C upward. The pretreatment procedure adopted for all catalysts (both single metals and alloys) on the foregoing basis was as follows:

(1) purge with argon (25°C, 2 h; then 200°C, 2 h);
(2) reduction in hydrogen (200°C, 15 h);
(3) calcination in air (700°C, 12 h);
(4) purge with argon (25°C, 0.5 h; then 200°C, 0.25 h);
(5) treatment in oxygen (500°C, 0.25 h);
(6) reduction in hydrogen (200°C, 3 h).

Catalytic Reactor

The reactor (Fig. 1) was designed to examine hydrocarbon reactions in either a pulse or a continuous-flow mode and also to estimate the metal area of supported catalysts by hydrogen chemisorption. The apparatus was constructed entirely of metal, Pyrex, and Fluon seals and contained no grease or mercury. The reaction tube was a 12-mm i.d. U-tube containing a fitted sintered-glass disk (porosity 3 or 4) on which the catalyst rested. The 100% Pt catalyst (0.1 g) was diluted with sufficient support material to give a total volume equal to that of the 1.5 g of alloy catalyst. A chemically clean glass-wool plug located upstream served to preheat the reactant gases. Hydrogen was palladium-diffused and oxygen was passed through an activated molecular sieve before use. Argon was purified by passing through a heated titanium bed at 700–800°C, followed by hot copper/copper oxide, and finally a molecular sieve.

Procedure for Catalytic Runs

The reactor was operated in a pulse mode (*7*) for rapid assessment of different cata-

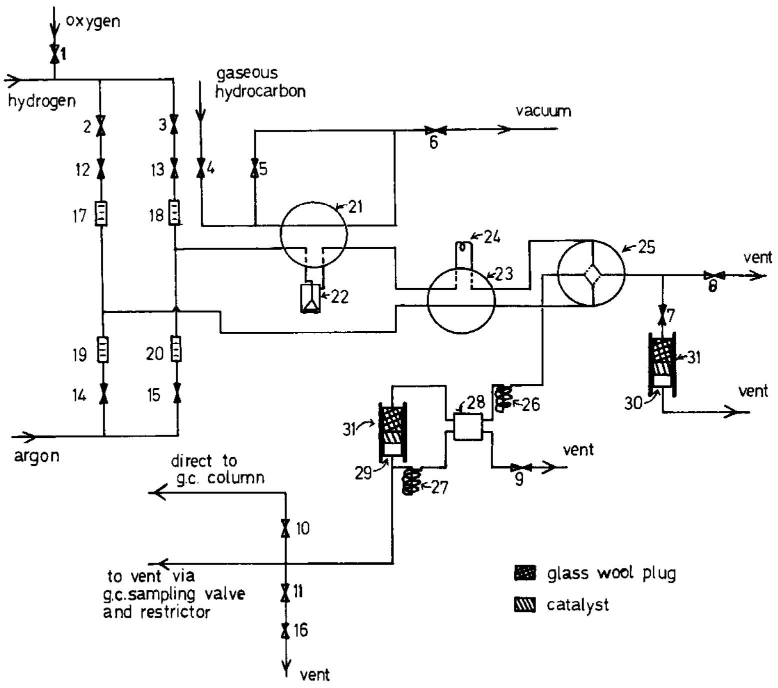

FIG. 1. Flow reactor. (1–11) On–off valves; (12–16) needle valves; (17–20) rotameters; (21) multiport valve; (22) hydrocarbon saturator; (23) 6-port valve; (24) calibrated loop; (25) 4-way valve; (26, 27) temperature equilibrating coils; (28) thermal conductivity detector; (29) reactor 1; (30) reactor 2; (31) furnace.

lyst preparation conditions. An H_2/Ar stream at slightly greater than 1 atm (reactor feed) was passed through, in order, valves 23 and 25, the thermal conductivity detector, reactor 1, and then via valve 10 directly to glc column. Simultaneously a second H_2/Ar stream was passed through the hydrocarbon saturator attached at valve 21, through loop 24 on valve 23, valve 25 to valve 8 to vent. As required, a pulse of this hydrocarbon-containing gas stream (loop 24) was injected into the H_2/Ar reactor feed and thus through the reactor to the glc.

All experimental results to be reported here were obtained from continuous-flow operation. Here hydrogen at slightly greater than 1 atm was passed through the saturator at valve 21, through valves 23 and 25, and via the thermal conductivity detector to reactor 1. The tail gas now passes through a gas-sampling cock and through a restrictor to vent. The cock allows a sample for analysis to be injected to the glc at any stage during the reaction. The saturator was held at a temperature which yielded a partial pressure as near to 17 Torr as possible. A hydrogen flow rate in the range 30–125 ml/min was chosen so as to maintain the conversion below 10%.

After the final (200°C, 3 h) reduction of the catalyst the hydrogen feed was diverted through the saturator and the temperature of the catalyst bed increased to that where activity was observable. The catalyst activity was monitored initially at each reaction temperature (within 30 min) and then allowed to attain a steady state over a 3 to 6-h period. Product analysis was effected on a Perkin–Elmer Model F11 glc using a 2-m squalane-on-Chromosorb P column or a 10-m SE30 on Chromosorb P column and flame ionization detector.

A second reactor (item 30) allowed simultaneous reduction of a further catalyst sample for characterization purposes.

Hydrogen Chemisorption Determination

The thermal conductivity detector (item 28) permits hydrogen take-up to be measured by a pulse technique. A hydrogen pulse (loop 24, 0.18 ml, 1 atm) is injected into an argon flow upstream of the detector. The pulse passes through one limb of the detector, through the catalyst bed, and then through the other limb of the detector. A difference in the two signals corresponds to the amount of chemisorption. The hydrogen take-up was measured at room temperature after the catalyst had been reduced (200°C, 3 h) and "evacuated" in an argon flow (180°C, 0.25 h). The T/C detector was held in a room-temperature water bath.

Materials

Reactant hydrocarbons (ethane, Phillips research grade; *n*-pentane, cyclopentane, *n*-hexane, neopentane, methylcyclopentane, Fluka puriss grade) were outgassed by freeze–thaw cycles and by bubbling argon through the liquid in the saturator for 0.5 h.

Catalyst Characterization

In the development of a preparation procedure which would result in good alloy homogeneity, catalysts were examined by X-ray powder diffraction. Metal crystallite sizes were determined with a JEM 100C electron microscope and a restricted number of samples were examined using the hydrogen chemisorption technique. These results and details of catalyst calcination are presented in Table 1.

Samples of the 10% Pt–Au catalyst which had been calcined for 12 h at 400, 500, 600, 700, 750, and 800°C were submitted to X-ray diffraction. As the calcination temperature was increased the lattice parameter decreased as it approached a value corresponding on Végard's law to 10% Pt 90% Au. Because any difference in lattice parameter found for samples calcined at 700, 750, and 800C agreed within the experimental error, we choose 700°C as the optimum calcination temperature. The lattice parameter (0.4065 ± 0.00005 nm) obtained

TABLE 1

Details of Catalyst Pretreatment and Results from X-Ray Diffraction, Electron Microscopy, and H_2 Chemisorption

Sample No.	Metal composition	Metal loading		Calcined		Lattice parameter (nm)	Average diameter	
		I.D. Gel (%)	Aerosil (%)	Temp. (°C)	Time (h)		Electron microscopy (nm)	H_2 chemisorption (nm)
1	100% Au		4	—	—	0.4078 ± 0.0001	25.0 ± 8.0	
2	100% Au		4	700	12	0.4078 ± 0.0001	65.0 ± 15.0	
3	100% Pt		4	—	—	not measurable[a]	2.7 ± 0.9	2.1 ± 0.6
4	100% Pt		4	700	12		18.0 ± 7.0	12.0 ± 0.6
5	10% Pt–Au		4	—	—	0.40745 ± 0.00005	7.0 ± 2.5	—
6	10% Pt–Au		4	400	12	0.40715 ± 0.0001	29.5 ± 11.0	—
7	10% Pt–Au		4	500	12	0.40705 ± 0.0002	65.0 ± 40.0	—
8	10% Pt–Au		4	600	12	0.4068 ± 0.0001	70.0 ± 30.0	—
9	10% Pt–Au		4	700	12	0.4065 ± 0.00005	90.0 ± 47.5	not measurable[b]
10	10% Pt–Au		4	750	12	0.40635 ± 0.00005	90.0 ± 38.0	—
11	10% Pt–Au		4	800	12	0.40645 ± 0.0001	105.0 ± 35.0	—
12	100% Pt	4		—	—	—	2.0 ± 0.5	—
13	100% Pt	4		700	12	—	20.0 ± 10.0	—
14	10% Pt–Au	4		—	—	—	4.0 ± 3.0	—
15	10% Pt–Au	4		700	12	—	100.0 ± 27.5; 7.0 ± 5.5	—
16	10% Pt–Au		10	—	—	—	7.5 ± 3.5	—
17	10% Pt–Au		10	700	12	—	75.0 ± 20.0	—

[a] Small crystallite size (see Column 9) precludes measurement: bulk platinum has a lattice parameter of 0.3920 nm (*6*).

[b] No chemisorption of hydrogen was detected within sensitivity of the technique (see text).

from the 700°C sample corresponded according to Végard's Law to a composition of 8% Pt. The Pt–Au catalyst so prepared can be taken to be reasonably homogeneous *in the bulk*.

The presence of gold in the catalyst leads to large particles when a calcination step is employed (Table 1). A gradual increase in the average (e.m.) particle size of the alloy catalyst is observed with increase in calcination temperature.

H_2 chemisorption tests were carried out on three catalyst samples (3, 4, and 9). In the case of sample 9 no H_2 take-up was apparent from 0.18-ml (1 atm) $H_2 : Ar$ 1 : 50 pulse. Agreement between the two methods for estimating crystallite size is seen to be reasonable as indicated by samples 3 and 4.

RESULTS AND DISCUSSION

Preliminary tests revealed that the use of Aerosil as support produced a platinum catalyst that was four times more active for the *n*-pentane/hydrogen reaction at 300°C than the corresponding I.D. Gel-supported catalyst. On this basis Aerosil was chosen as support for all catalysts. In deciding upon an optimum metal loading the activities of a 4% and a 10% Pt-on-Aerosil catalyst were compared for the *n*-pentane/hydrogen reaction. The activities of the two catalysts were found to be very similar and a 4% loading was adopted in all cases. No activity in the *n*-pentane/hydrogen reaction was observed at temperatures up to 460°C for the 100% Au catalyst.

In any experiment, comparison of initial and final activities (see earlier) can provide an indication of the extent of self-poisoning and how it may affect the different hydrocarbon processes.

n-Pentane

The *n*-pentane/hydrogen reaction was examined on 100% Pt in the temperature range 300–380°C, 300°C being the lowest temperature at which activity was measurable (see Table 2). At the three temperatures examined activity is seen to decrease during the equilibration period due to self-poisoning. However, a steady state of reaction was achieved in each case. The predominant nondestructive process was cyclization at 300°C but isomerization became comparable at 380°C.

On the 10% Pt–Au alloy the reaction was examined in the temperature range 340–400°C. In contrast to 100% Pt, activity was maintained during the equilibration period and a steady state of reaction was easily achieved at each temperature. Surprisingly the predominant process on the alloy catalyst was isomerization with no detectable cyclization activity. This result is in marked contrast to the low-Pt alloy films that were active for cyclization and inactive for isomerization of *n*-pentane (*4*). However, Van Schaik, Dessing, and Ponec (*5*) found with silica-supported Pt–Au alloys that very low percentage Pt catalysts (1 and 2.5% Pt) were active for isomerization exclusively but that a 12.5% Pt catalyst showed activity for both cyclization and isomerization of *n*-pentane.

Cyclopentane

The cyclopentane/hydrogen reaction was examined on 100% Pt at 280 and 340°C (Table 3). At 280°C the initial reaction yielded *n*-pentane (from ring opening) as almost the sole product. However, during the equilibration period self-poisoning was very severe and the production of *n*-pentane dropped sharply such that after 2 h it was no longer found. The decline in the rate of formation of *n*-pentane was accompanied by a gradual increase in the production of cyclopentene. At 340°C the activity pattern was the same but the rate of reaction had increased by an order of magnitude. A steady state of reaction was not reached at either temperature due to the severe self-poisoning.

On the 10% Pt–Au alloy the reaction was examined at 340 and 370°C. The sole process occurring was dehydrogenation to

TABLE 2

Reaction of *n*-Pentane/Hydrogen: Product Distributions (wt%)

Temp. (°C)	Conversion (%)	Turnover number[b] (molec s^{-1} cm^{-2})	C_1, C_2	C_3	iC_4	nC_4	iC_5	cC_5	S_H[c]	S_I	S_C
100% Pt											
298_i[a]	0.21	1.35×10^{12}	6.19	5.71	—	5.71	20.95	61.43	0.18	0.21	0.61
299	0.15	9.36×10^{11}	4.61	5.26	—	1.97	20.39	67.76	0.12	0.20	0.68
337_i	3.05	1.96×10^{13}	13.80	11.86	0.13	5.77	46.02	22.42	0.32	0.46	0.22
342	1.49	9.53×10^{12}	8.28	7.27	0.07	2.62	40.24	41.52	0.18	0.40	0.42
383_i	7.26	4.66×10^{13}	15.57	13.26	0.43	6.08	43.83	20.83	0.35	0.44	0.21
380	3.22	1.98×10^{13}	8.26	7.08	0.16	3.57	45.37	35.56	0.19	0.45	0.36
10% Pt–90% Au											
338_i	0.01	1.35×10^{10}	16.67	8.33	—	—	75.00[d]	—	0.25	0.75	—
346	0.02	2.37×10^{10}	42.86	4.76	—	—	52.38	—	0.48	0.52	—
368_i	0.06	7.00×10^{10}	12.90	1.61	—	—	85.48	—	0.15	0.85	—
366	0.06	6.54×10^{10}	8.62	1.72	—	—	89.66	—	0.10	0.90	—
403_i	0.18	2.01×10^{11}	8.99	1.12	—	—	89.89	—	0.10	0.90	—
400	0.15	1.70×10^{11}	8.61	1.32	—	—	90.07	—	0.10	0.90	—

[a] "i" indicates that the product analysis was in the initial stages of reaction; all other analyses were following a 3 to 6-h period.

[b] Estimated in Tables 2–7 per square centimeter of metal assuming metal crystallites to be spheres with diameter equal to the mean diameter from electron microscopy.

[c] S_H, S_I, and S_C are selectivities for hydrogenolysis, isomerization, and cyclization expressed as the percentage *n*-pentane consumed in the designated process divided in each case by total consumption.

[d] iC_5 column includes iC_5H_{10} in results for Pt–Au alloy.

TABLE 3

Reaction of Cyclopentane/Hydrogen: Product Distributions (wt%)

Temp. (°C)	Conversion (%)	Turnover number (molec s^{-1} cm^{-2})	C_1, C_2	C_3	nC_4	iC_5	nC_5	cC_5H_6	cC_5H_8	S_H	S_{RO}[a]	S_D
283_i	2.2	7.02×10^{13}	0.05	0.05	—	0.05	99.54	—	0.32	—	1.00	—
283	0.01	4.55×10^{11}	7.14	—	—	—	—	—	92.86	0.07	—	0.93
346_i	26.2	7.82×10^{14}	0.1	0.1	—	0.1	99.4	—	0.3	—	1.00	—
339	0.14	4.68×10^{12}	1.39	—	—	—	—	—	98.61	0.01	—	0.99
10% Pt–90% Au												
338_i	0.18	4.16×10^{11}	—	—	—	—	—	7.69	92.31	—	—	1.00
340	0.21	4.85×10^{11}	—	—	—	—	—	5.66	94.34	—	—	1.00
367_i	0.59	1.34×10^{12}	—	—	—	—	—	2.39	97.61	—	—	1.00
370	0.54	1.24×10^{12}	—	—	—	—	—	1.11	98.89	—	—	1.00

[a] S_{RO} and S_D are selectivities for *n*-pentane production and dehydrogenation both defined in the manner indicated in Table 2.

form cyclopentene and cyclopentadiene. At both temperatures self-poisoning was very slight and a steady state of reaction was reached in each case.

Methylcyclopentane

The methylcyclopentane/hydrogen reaction was examined on 100% Pt in the temperature range 280–380°C (Table 4). At 280°C the predominant reaction is ring opening to form *n*-hexane, 2-methylpentane, and 3-methylpentane. From the proportions of these three products it would appear that both the selective and nonselective ring-opening mechanisms (*9*) are in operation. At 340 and 380°C the ring-enlargement-product benzene is formed together with a product corresponding in glc retention time to either methylcyclopentene or methylcyclopentadiene. As found with cyclopentane, self-poisoning at all three temperatures was severe and so a steady state of reaction was not reached.

On the 10% Pt–Au catalyst the reaction was examined at 340 and 380°C, no activity being found below 340°C. At both temperatures only two products were formed, benzene and the dehydrogenated ring product found on 100% Pt. Self-poisoning did not occur and a steady state of reaction was reached at each temperature. This result matches closely the findings with the evaporated films (*4*) where the low-Pt alloys gave only two products, benzene and either methylcyclopentene or methylcyclopentadiene.

There is also qualitative agreement with the result of Van Schaik, Dessing, and Ponec (*5*) who found that the reaction of methylcyclopentane on a 2.5% Pt-in-Au alloy supported on silica gave virtually only ring enlargement at 359°C. However, both the present results and those of Van Schaik *et al.* are in contrast to the findings of O Cinneide and Gault (*6*) who reported that a 15% Pt–85% Au alloy on alumina was active for nonselective ring opening of methylcyclopentane at 280°C.

n-Hexane

The reaction of *n*-hexane/hydrogen on 100% Pt was examined in the temperature range 300–380°C (Table 5). Self-poisoning occurred at each of the three temperatures examined with the result that a steady state of reaction, while achieved at 300°C, was not achieved at 340 or 380°C. As is seen from the product distribution the selectivity for the isomerization products (2MP and 3MP) increases during the equilibration period in contrast to the selectivity for methylcyclopentane production, which falls.

On the 10% Pt–Au catalyst the reaction was examined in the 340–400°C temperature range. Self-poisoning did not occur and a steady state of reaction was reached at the three temperatures examined. The sole reaction occurring at 340 and 370°C was isomerization with 3-methylpentane as the major product. At 400°C a trace of hydrogenolysis occurred as well. An unusual feature of the action of the alloy catalyst is that no methylcyclopentane or benzene was produced up to 400°C; a check made at 450°C revealed that both products were being produced at this temperature.

The dominance of the isomerization process on the alloy catalyst agrees with the findings for the *n*-pentane/hydrogen reaction. Since the alloy catalyst appears to be inactive for both the formation of the C_5 ring (*n*-pentane results; *n*-hexane results) and its opening (cyclopentane and methylcyclopentane results) it would appear that isomerization occurs via the bond-shift and not the carbocyclic route. A feature of the evaporated films (both Pt and Pt–Au), which does not appear to extend to the supported catalysts, is the predominance of benzene as a product of the *n*-hexane/hydrogen reaction.

Neopentane

The reaction of neopentane/hydrogen on 100% Pt was examined in the temperature

TABLE 4

Reaction of Methylcyclopentane/Hydrogen: Product Distributions (wt%)

Temp. (°C)	Conversion (%)	Turnover number (molec s^{-1} cm^{-2})	C_1, C_2	C_3	iC_4	nC_4	iC_5	nC_5	cC_5	2MP	3MP	nC_6	CPD[a]	CPE[b]	Bz	S_H	S_{RO}[c]	S_D	S_{RE}
100% Pt																			
282_i	10.38	1.43×10^{14}	0.12	0.04	0.01	0.01	—	0.13	—	75.76	20.13	3.81	—	—	—	—	1.00	—	—
279	1.76	2.42×10^{13}	0.23	—	—	—	—	0.23	—	74.59	20.53	4.42	—	—	—	—	1.00	—	—
342_i	12.48	1.72×10^{14}	0.22	0.20	0.14	0.06	0.03	0.12	0.02	66.15	23.79	6.91	—	0.04	2.32	0.01	0.97	—	0.02
341	2.05	2.82×10^{13}	0.24	0.10	0.05	—	—	0.19	—	56.55	21.48	5.80	4.58	0.24	10.76	0.01	0.83	0.05	0.11
381_i	15.36	2.11×10^{14}	0.68	0.85	0.74	0.33	0.16	0.27	0.14	50.96	27.85	11.44	—	0.17	6.40	0.03	0.91	—	0.06
379	2.96	4.06×10^{13}	0.24	0.14	0.10	0.03	0.03	0.14	0.27	25.79	9.98	3.81	14.84	0.20	44.43	0.01	0.40	0.15	0.44
10% Pt–90% Au																			
335_i	0.38	4.62×10^{11}	—	—	—	—	—	—	—	—	—	—	24.08	—	75.92	—	—	0.24	0.76
342	0.43	5.23×10^{11}	—	—	—	—	—	—	—	—	—	—	25.64	—	74.36	—	—	0.26	0.74
378_i	1.78	2.15×10^{12}	—	—	—	—	—	—	—	—	—	—	23.60	—	76.40	—	—	0.24	0.76
383	2.26	2.74×10^{12}	—	—	—	—	—	—	—	—	—	—	23.91	—	76.09	—	—	0.24	0.76

[a] CPD = cyclopentadiene.

[b] CPE = cyclopentene.

[c] S_{RO} and S_{RE} are selectivities for ring opening and ring enlargement both defined in the manner indicated in Table 2.

TABLE 5

Reaction of *n*-Hexane/Hydrogen: Product Distributions (wt%)

Temp. (°C)	Conversion (%)	Turnover number (molec s^{-1} cm^{-2})	C_1, C_2	C_3	iC_4	nC_4	iC_5	nC_5	2MP	3MP	MCP	Bz	S_H	S_I	S_5[a]	S_6
							100% Pt									
300_i	3.66	2.20×10^{13}	6.01	10.66	—	6.83	—	4.10	36.89	22.40	10.66	2.46	0.28	0.59	0.11	0.02
305	0.18	1.08×10^{12}	5.55	9.44	—	5.00	—	—	40.00	32.78	4.44	2.78	0.20	0.73	0.04	0.03
340_i	0.94	5.66×10^{12}	2.87	5.84	0.21	2.86	0.11	—	29.22	18.60	27.63	12.65	0.12	0.48	0.27	0.13
340	0.48	2.91×10^{12}	3.10	6.20	—	3.93	—	—	38.22	29.75	13.84	4.96	0.13	0.68	0.14	0.05
350_i	3.99	2.40×10^{13}	3.73	6.66	0.48	3.33	0.23	2.73	32.10	22.05	20.05	8.64	0.17	0.54	0.20	0.09
382	0.79	4.74×10^{12}	3.30	4.57	0.13	2.66	0.13	1.90	32.36	32.36	17.01	5.58	0.13	0.65	0.17	0.05
							10% Pt–90% Au									
338_i	0.01	1.72×10^{10}	—	—	—	—	—	—	—	100.00	—	—	—	1.00	—	—
340	0.01_4	1.85×10^{10}	—	—	—	—	—	—	—	100.00	—	—	—	1.00	—	—
368_i	0.05	6.48×10^{10}	—	—	—	—	—	—	4.08	95.92	—	—	—	1.00	—	—
371	0.06	7.28×10^{10}	—	—	—	—	—	—	3.64	96.36	—	—	—	1.00	—	—
403_i	0.19	2.49×10^{11}	0.53	1.06	—	—	—	—	6.38	92.02	—	—	0.02	0.98	—	—
401	0.16	2.14×10^{11}	0.62	0.62	—	—	—	—	4.94	93.83	—	—	0.01	0.99	—	—

[a] S_5 and S_6 are selectivities for 1,5- and 1,6-cyclization both defined in the manner indicated in Table 2.

range 320–390°C (Table 6). Self-poisoning occurred at the three temperatures examined and a steady state of reaction, while achieved at 320 and 360°C, was not achieved at 380°C. Isomerization to produce isopentane and *n*-pentane is the main process occurring to the extent that the isomerization selectivity is always above 0.88. In contrast to the 100% Pt film of the earlier study, the selectivity for isomerization is independent of temperature and the overall reaction seems much less prone to self-poisoning.

The neopentane/hydrogen reaction was examined on the 10% Pt–Au catalyst at temperatures in the 340–450°C range. No activity was observed at temperatures up to and including 420°C. At 450°C signs of activity were apparent with the production of trace amounts of cracking products. This compares very well with previous experience of the neopentane/hydrogen reaction on Pt–Au films where no activity was found with <89% Pt up to 400°C.

Ethane

The reaction of ethane/hydrogen on 100% Pt was examined at 400 and 440°C,

TABLE 6

Neopentane/Hydrogen Reaction on 100% Pt:[a] Product Distributions (wt%)

Temp. (°C)	Conversion (%)	Turnover number (molec s^{-1} cm^{-2})	C_1, C_2	C_3	iC_4	iC_5	nC_5	S_H	S_I
318_i	0.16	1.17×10^{12}	3.70	0.62	4.32	91.36	—	0.09	0.91
321	0.14	9.96×10^{11}	1.45	—	4.35	94.20	—	0.06	0.94
358_i	2.63	1.90×10^{13}	2.51	0.49	7.76	84.78	4.45	0.11	0.89
360	1.38	1.06×10^{13}	1.30	0.22	5.57	90.67	2.24	0.07	0.93
388_i	17.03	1.18×10^{14}	3.88	1.50	6.20	78.31	10.11	0.12	0.88
386	1.11	8.32×10^{12}	1.81	0.18	4.15	90.07	3.79	0.06	0.94

[a] 10% Pt–Au was inactive for the neopentane/hydrogen reaction up to 450°C.

the catalyst being inactive at temperatures below 400°C (Table 7). At each temperature self-poisoning occurred but a steady state of reaction was reached. The rate of reaction was particularly low compared to that obtained previously on the corresponding 100% Pt film.

No activity was observed even at 500°C for the reaction of ethane/hydrogen on 10% Pt–Au. This is in agreement with the Pt–Au alloy film study in which catalysts containing <92% Pt were inactive up to 450°C.

In efforts to test whether altered reduction conditions might increase catalyst activity for the ethane/hydrogen reaction, a 0.5-h 500°C hydrogen reduction was included in the procedure with the normal 3-h, 200°C hydrogen reduction and following the 0.25-h oxidation. Surprisingly the 100% Pt catalyst was found to have lost its activity completely up to 460°C. The only way found to restore the activity was to avoid exposure of the catalyst to hydrogen at high temperatures. In order to see whether this effect was peculiar to the ethane/hydrogen reaction we examined the methylcyclopentane/hydrogen reaction on 100% Pt having included a 500°C hydrogen reduction in the pretreatment. It was found that the activity at 280°C was approximately half of that obtained earlier. It would appear then to be a more general phenomenon that exposure of the catalyst to a hydrogen atmosphere at elevated temperature has an adverse effect on the activity of the catalyst. A similar finding was reported by O Cinneide and Gault who found that the activity of 15% Pt–85% Au on alumina decreased with the duration of exposure of the catalyst to hydrogen at temperatures above 250°C.

TABLE 7

Ethane/Hydrogen Reaction on 100% Pt[a]

Temp. (°C)	Conversion (%)	Turnover No. of $C_2H_6 \rightarrow CH_4$ (molec s^{-1} cm^{-2})
399_i	0.010	1.46×10^{11}
400	0.013	9.18×10^{10}
438_i	0.193	1.36×10^{12}
440	0.024	1.70×10^{11}

[a] 10% Pt–Au was inactive for the ethane/hydrogen reaction up to 500°C.

GENERAL COMPARISONS AND CONCLUSIONS

In Table 8 we have compared the results obtained presently from the supported catalysts in terms of selectivity to those obtained previously on evaporated films. To facilitate discussion, headings give reference to the particular process which has been isolated for test in each reaction. From the table it is obvious that both catalyst types behave very similarly as to activity patterns. There are, however, two occasions where they behave differently. First, the supported alloy catalyst exhibits excellent bond-shift activity with *n*-pentane but is inactive for 1,5-cyclization whereas the converse is the case for the low-percentage Pt evaporated film. The second point of dissimilarity is that the supported alloy is inactive for benzene formation in the *n*-hexane reaction in the 340–400°C range whereas this is the sole process occurring on the low-percentage Pt evaporated film.

The present support catalyst contains Pt–Au of surface composition <0.4% Pt as inferred from negligible hydrogen chemisorption capacity. Similarity of product distributions in reaction of *n*-pentane and of *n*-hexane to those reported by Van Schaik *et al.* (*5*) for a series of Pt–Au/silica catalysts derived by the hydrazine reduction method is consistent with this conclusion. Specifically the absence of cyclization activity (Tables 2 and 5) resembles the action of either a 3% or 4% Pt-in-Au on silica described by these authors (Table 8, last two columns) and is dissimilar to that of either their 8% or 13% Pt-in-Au on silica. It has been noted earlier that preparation of Pt–Au alloy of more than about 10% Pt can yield two phases with necessarily less sim-

TABLE 8

Comparison of Catalytic Results for Supported Catalysts with Those (*4*) for Evaporated Films

Hydrocarbon process	100% Pt film		Pt–Au film, % Pt < 12%		100% Pt supported		10% Pt-in-Au supported		2.5% Pt-in-Au supported[b] (*5*)		3.7% Pt-in-Au supported[b] (*5*)	
	T (°C)	*S*[a]	*T* (°C)	*S*[a]	*T* (°C)	*S*[a]	*T* (°C)	*S*[a]	*T* (°C)	*S*[a]	*T* (°C)	*S*[a]
Bond shift of nonquaternary center (*n*-pentane)	304	0.09	380	—	299	0.20	346	0.52	350	1.00	[c]	
	340	0.03	405	—	342	0.40	400	0.90	400	0.97		
1,5-Cyclization of *n*-pentane	304	0.38	380	0.73	299	0.68	346	—	350	—		
	340	0.36	405	0.92	342	0.42	400	—	400	—		
Ring opening of C_5 ring (cyclopentane)	170	1.00	284	—	283	1.00–0.00[d]	340	—				
	320	0.44	381	—	343	1.00–0.00[d]	370	—				
Dehydrogenation of C_5 ring (cyclopentane)	320	0.32	284	1.00	283	0.00–0.93[d]	340	1.00				
	358	0.76	381	1.00	343	0.00–0.99[d]	370	1.00				
Ring enlargement of methylcyclopentane	250	0.19	260	0.84	279	—	342	0.74	359	1.00		
	335	0.75	345	0.76	379	0.44	383	0.76	—	—		
1,5-Cyclization of *n*-hexane	252	0.28	342	—	305	0.04	340	—	305	—	318	—
	382	—	381	—	382	0.17	401	—	395	—	349	—
Benzene formation from *n*-hexane	252	0.19	342	1.00	305	0.03	340	—	305	—	318	—
	382	0.81	381	1.00	382	0.05	401	—	395	—	349	—
Bond shift of quaternary center (neopentane)	232	0.85	250	—	321	0.94	320	—				
	402	—	400	—	386	0.94	450	—				
Hydrogenolysis of ethane to methane (1,2-diadsorbed intermediate)	330	2.69[e]	300	—	400	0.92[e]	300	—				
	400	289[e]	450	—	440	1.70[e]	500	—				
Hydrogenolysis of neopentane (1,3-diadsorbed intermediate)	232	0.15	250	—	321	0.06	320	—				
	402	—	400	—	386	0.06	450	—				

[a] *S* = selectivity expressed in style adopted in Tables 2–6.
[b] Prepared by hydrazine reduction technique.
[c] All blank spaces = no report.
[d] Due to self-poisoning the selectivity varied over the period of reaction monitored.
[e] Turnover number (molec s^{-1} cm^{-2} × 10^{-11}) is given in place of selectivity.

ple interpretation of catalytic action. Access to other surface compositions may therefore require a different preparative principle and Van Schaik and colleagues' work suggests that hydrazine reduction may be a suitable one to pursue in future work. We return now to the interpretation of such catalytic differences as exist between the present supported alloy and the evaporated alloy films of the previous study.

There are two possible factors which might underlie these differences. First, the topography of the surfaces may be different due to their quite different modes of preparation: we shall examine this presently. Second, the surfaces may be carbided to different extents. It has been argued that differences in the extent of carburization of a metal surface during a hydrocarbon reaction can dictate to some extent the reaction routes followed (*10*). Specifically, operating conditions which favor carbiding lead to 1,6-cyclization of *n*-hexane rather than 1,5-cyclization. The evolution of the carbided condition may be seen for Pt surfaces where the latter condition changes to the former at high reaction temperatures (*10*). There are some grounds for believing that film catalysts are more carbided under equivalent conditions than supported catalysts. Thus, in Table 8, supported Pt sustains 1,5-cyclization of hexane to temperatures well above 300°C where Pt films have already adopted the 1,6 mode of cyclization. However, the failure of the 10% Pt-in-Au supported alloy to catalyse 1,5-cyclization of *n*-pentane, in contrast to the action of the low-percentage Pt-in-Au films previously (*4*), is clearly opposite to what would be found if this influence were determining. We therefore believe that the principal origin of the difference in 1,5-cyclization activity and possibly also in bond-shift activity (see a caveat later) between the two forms of alloy and between the supported 100% Pt and supported 10% Pt 90% Au lies in surface topography, that is, in the relative extents of exposed crystal faces. On this basis absence of 1,5-cyclization on the 10% Pt 90% Au supported alloy is a result of the severe heat treatment and the blocking of such suitable step sites as remain by attachment of Au atoms (*11*). Differences in surface regions exhibited by films and supported metal may be the cause also for the self-poisoning of the bond-shift reaction that leads to inactivity of the <12% Pt-in-Au film at the temperatures required for inherent bond-shift activity. The exposed faces on the supported metal (including alloy) are those with a lesser chemisorption affinity for alkane so that it may still be possible for a catalytic steady state to operate. There is still some question whether special sites may be required for the bond-shift reaction (*12*). Further, bond-shift activity found with the supported alloy (high Pt dilution) is good evidence for a single-site reaction mechanism such as advanced by Rooney (*10*). The greater carbiding of films leads to suppression of bond-shift activity on the latter mechanism because of a buildup of negative charge on the metal centers (*10*).

A particularly significant result is that the supported 10% Pt 90% Au alloy, which shows good dehydrogenation activity, is inactive for C_6 ring formation from *n*-hexane (≤400°C). This result argues for a more specific type of 1,6-cyclization mechanism than is provided by simple hexatriene ring closure (*13*) which should be a facile reaction. Perhaps the hexatriene requires to be chemisorbed to a particular type of surface metal atom to permit its cyclization. Other cyclization intermediates have been discussed (*10*) which are possible for direct 1,6-cyclization and which would imply surface structure sensitivity. The present result is consistent with the finding (*14*) that certain step sites on a Pt single crystal have a high and sustained activity in conversion of *n*-heptane to toluene.

It is of interest to compare the results obtained with the present chemically prepared Pt–Au catalysts to those obtained previously by O Cinneide and Gault (*6*) and also (further) to those of Van Schaik, Dessing, and Ponec (*5*). The former workers subjected their alumina-supported catalysts to a 770°C calcination in air, a 400°C oxidation in air, followed by reduction in flowing hydrogen at 350°C. They found that their 15% Pt–85% Au catalyst behaved very similarly to a highly dispersed Pt catalyst in that isomerization of hexanes occurred via the carbocyclic route and that methylcyclopentane underwent nonselective ring opening.

The latter workers concluded that on their hydrazine-reduced alloy catalysts containing 3–4% Pt, isomerization was occurring via the bond-shift route, the carbocyclic route (for hexanes) being precluded by the absence of cyclization activity. They also found that Pt–Au alloys of low-percentage Pt produced only benzene and cyclohexane from methylcyclopentane, that is, they were inactive for ring opening, a necessary step in isomerization via a cyclic intermediate. Our 10% Pt 90% Au catalyst behaves very similarly to the 3–4% Pt alloy catalysts of Van Schaik *et al.* in that it exhibits good bond-shift activity and does not open the methylcyclopentane ring.

In the preparation and pretreatment of the present catalysts we have adopted a procedure which is almost identical to that used by O Cinneide and Gault. Hence differences in preparation are unlikely to be responsible for the difference in behavior. An explanation is suggested by the fact that the catalysts which behaved similarly, namely, those of Van Schaik *et al.* (*5*) and of the present work, were both silica supported, whereas the unique catalyst, namely, that of O Cinneide and Gault (*6*), was alumina supported. There must remain some doubt whether alumina can be treated as an inert support to the same extent as silica.

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