NOTE

Reactions of Alkanes on Iridium–Gold Films

The proposal has been made (1) that addition of a Group IB metal as alloying component may cause a d-metal to act more selectively as a hydrocarbon isomerization catalyst because of the sharp reduction in the number of ensembles of contiguous "active" metal atoms of the kind needed for hydrogenolysis. We report here studies of the conversion of n-hexane and n-butane on Ir–Au films which were aimed at probing the generality of this proposal. We also thought that the experiments might enable the nature of any isomerizing activity of iridium atoms (2) to be examined.

Procedures for film formation followed essentially those used in previous studies (3, 4); iridium (99.9%) was evaporated from a plain hairpin of 0.5 mm diam wire hooked from two steel connectors in a 600 ml spherical vessel. As a result of the simple design there was a lateral variation in film composition between about ±5% in the iridium-rich deposits and about ±15% in the low-iridium films: while this could be improved by further work, film quality was considered sufficient for the present study. Films were annealed in hydrogen for 1 hr at 500°C.

X-Ray diffractometry of film samples showed peak doubling (additional to the α_1 and α_2 components of the Cu radiation) for 111 and 222 reflections for some alloy compositions (Table 1 and Fig. 1) indicating two distinct regions of composition within the metal, while widths of deconvoluted individual peak components (3) indicated homogeneity in each such region.

Phase separation is inferred for these compositions from this result and from the following additional information: (a) 1 hr annealing at 600°C gave substantially the same result as at 500°C, whereas our experience with other binary-alloy films, known from thermodynamic information to be single-phased, is that an appreciable merging of double peaks occurs after such a temperature increase, and (b) older evidence of an indirect nature (5) suggests that mutual solubility of iridium and gold is small even at 900°C. Compositions of the phases, derived on the basis of Végard's law from lattice parameters measured by the Nelson-Riley method, are given in Table 1. Clearly lattice parameters are nearly indistinguishable from those of 100% Ir and 100% Au.

TABLE 1

LATTICE PARAMETERS AND PHASE COMPOSITIONS FOR Ir–Au FILMS

Mean film composition (analysis) % Ir	Lattice constant, a (Å)	Derived composition (Végard's law: see text) % Ir
100	$3.839_9{}^a$	—
	$3.838–3.842^a$	
100	3.839	100
80–90	3.860	90–94
52	3.840, 4.076	99; 1
23	3.845, 4.074	97–98; 2
12	3.840, 4.076	99; 1
0	4.078	0
0	$4.078_6{}^a$	—

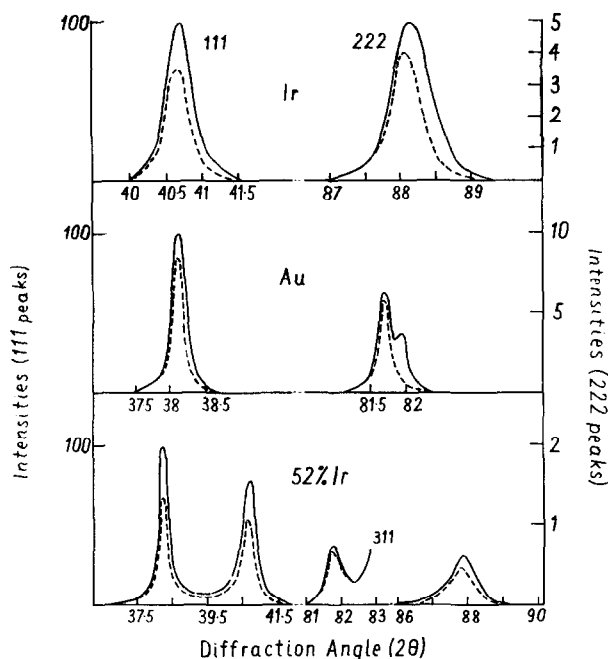^{a} Literature values (6).

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Fig. 1. X-Ray diffractometer profiles of 111 and 222 reflexions for Cu $K\alpha$ radiation. (- -) Resolved α_1 components. Intensities are normalized so that the height of each 111 peak is 100. The 311 reflexion due to the iridium-rich phase overlaps to some extent the 222 of the gold-rich phase (bottom panel).

Hydrocarbons were dried and outgassed before reactions. Hydrogen was purified by diffusion through Pd. Conversion reactions were followed in the static system by glc and mass spectrometry. The initial hydrogen/alkane pressure ratio was 10:1 with P_{alkane} = 0.81–0.85 Torr. Total conversion was less than 10% in all experiments.

n-Butane conversion was first examined, primarily as a test for bond-shift type isomerization (7). Hydrogenolysis only was observed on 100% Ir at 238°C upward and poisoning set in progressively above 260°C. No isomerization was detectable at temperatures up to 420°C. On 14% and 2% Ir, reaction commenced at about 310°C; hydrogenolysis (central scission) was the predominant process. Hydrogenolysis accounted for 100% of the product at this temperature but was accompanied at higher temperatures (~350°C) by C_3 and C_4 olefins (in the ratio ~1:2.5 by weight); the latter products were in amounts well within (>10% of) the equilibrium values.

Only on 14% Ir at 418–448°C was isobutane detected (1.2–1.3% of total products). In a single run with isobutane as reactant on a 70% Ir film hydrogenolysis was already appreciable at 270°C but no isomerization was observed at temperatures up to 415°C. The detectability limit for isomerized butane was 0.05% of total hydrocarbon, that is, about 0.5% of total products.

Reaction of n-hexane on 100% Ir gave (nonselective) hydrogenolysis as the only reaction at 180–271°C (Table 2), and the reaction already tended to self-poison in this temperature interval. At 290°C and above, benzene was formed. On 6 and 11% Ir alloys this dehydrocyclization reaction commenced at 320–330°C and, although hydrogenolysis products were still substantial, benzene was now the principal product. (The rates of benzene production were approximately equal on all the film catalysts at 400°C.) Hydrogenolysis on the alloys, clearly involving successive bond scissions, had already commenced at 200°C

TABLE 2
PRODUCT DISTRIBUTIONS IN THE n-HEXANE REACTION

Mean film composition wt% Ir	Temp (°C)	Alkane (%)[a]					Rate of hydrogenolysis × 10² % hexane/min	Benzene (%)[a]	Selectivity[b]
		C_1	C_2	C_3	C_4	C_5			
100	180	24	18	21	21	16	3.4	—	—
	203	27	18	21	19	16	4.7	—	—
	237	28	19	22	17	15	7.8	—	—
	271	26	23	21	18	12	9.7	—	—
	325	predominantly (~70%) methane					6.0	22	0.3
	364						8.0	24	0.3
	392						3.0	33	0.5
	420						8.0	37	0.6
11	334	23	12	6	—	—	0.4_4	59	1.4
	362	20	15	3	—	—	0.6_3	62	1.7
	406	8	5	4	—	—	0.6_1	83	4.9
	447	6	4	2	—	—	0.8_6	89	8.1
6	370	13	11	5	—	—	0.8_3	71	2.5
	404	11	5	3	—	—	0.7_3	81	4.3
	474	8	6	2	—	—	1.3_5	85	5.5

[a] Initial product distributions here and in the selectivity column expressed in terms of carbon content.
[b] Ratio of dehydrocyclization rate to overall rate of hydrogenolysis.

but reliable product distributions could not be measured below 300°C, essentially because there was an unusually large initial instantaneous production of hydrogenolysis products. No reaction was found below 400°C on 100% Au films; a minor amount of hydrogenolysis was detectable above this temperature. The progressive self-poisoning for hydrogenolysis of both butane and hexane, particularly for 100% Ir, leads to a greater similarity in activity between 100% Ir and alloy films for hydrogenolysis above ~250°C (Table 2) than linear portions of the Arrhenius plots, measured in different ranges of temperature, would suggest. The latter suggest an advantage for the 100% Ir of about 10³ for the n-butane reaction, and nearly 10² for the hexane reaction.

From the Sanders parameter (8), the surface migration rate of gold should be greater than of iridium. It appears justified, following the method of argument of Sachtler and Jongepier (9) and from the lattice distances in Table 1, to infer that a crystallite shell of 1-2% Ir envelops an iridium-rich core in the range of nominal film composition of 11 to at least 50% Ir. This outer "skin" represents the catalyst surface in this range although the percentage Ir at the surface would be expected to be further reduced by Gibbs enrichment.

The successive nature of the alkane hydrogenolysis tends to obscure which C–C bond is first broken, but an overall pattern can be discerned. Hydrogenolysis of n-hexane on 100% Ir was completely non-selective in the range 180-270°C, consistent with the findings of Kikuchi, Tsurumi and Morita (10) (n-pentane) and of Carter, Cusumano and Sinfelt (11) (n-heptane) on chemically prepared catalyst forms. The present n-butane results are open to a similar interpretation. Hydrogenolysis on the alloys was more selective (clearest for n-butane) tending at low temperatures to give central scission while at higher temperatures appearance of

olefin or diolefin (n-butane reaction) or increase in cyclization (n-hexane) occurs as well.

The superior selectivity for benzene production of the alloys compared to 100% Ir arises from the greater (by ~10 at 400°C) hydrogenolysis rate on the latter. There is, as noted, temperature-dependent blockage of hydrogenolysis sites by carbonaceous residues as evidenced by nonlinear Arrhenius plots. Additional indication that iridium films are more subject to such poisoning than the alloys may lie in the rather lower E_a derived for hydrogenolysis on the former at the lowest reaction temperatures (~6 kcal/mole) compared to the latter which were derived necessarily at higher reaction temperatures (8–10 kcal/mole). By contrast, site poisoning for benzene production was not noticeable, at least on the alloy catalysts, and the linear Arrhenius plots found gave E_a estimates of 10 to 15 kcal/mole. It follows that there is a positive temperature dependence of the ratio of rates dehydrocyclization/ hydrogenolysis (Table 2).

We may make the following comparisons with Ni–Cu catalysts: (i) alkane hydrogenolysis activity has been found to be several orders of magnitude less for the alloys than for 100% Ni (12–15) and this finding appears to hold irrespective of whether the reaction route is via a π-alkene, a 1,2-diadsorbed or a 1,3-diadsorbed intermediate; as stated, the 100% Ir film was only ~10 times more active than the two Ir–Au alloys at comparable temperatures; (ii) activity for n-hexane isomerization (thought to be largely carbocyclic) was nearly 10^2 times greater at 330°C for 100% Ni than for Ni–Cu alloys containing 10–30% Ni (1); rates of benzene formation are roughly equal on 100% Ir and our Ir–Au films. It is possible to adduce arguments based on surface blockage by residues to explain why the differences between 100% Ir and the Ir–Au films are so small. There is an additional influence, opposite in its effect to residues, which also merits examination. A body of evidence is now available showing that on elemental neighbor platinum both dehydro-

cyclization (16–18) and hydrogenolysis (19, 20) are surface-structure sensitive. Anderson and Shimoyama (20) have reported that, when the crystallite size was increased, the activity of platinum films for hydrogenolysis of hexane decreased more sharply than did isomerization plus dehydrocyclization. If the Ir–Au films contain less step features than the 100% Ir films this could alone be sufficient to explain that hydrogenolysis is depressed more than is dehydrocyclization on the alloys. Despite the severe heat treatment given to the present films, surface features appropriate for dehydrocyclization and (possibly also) hydrogenolysis may persist for kinetic reasons (21). More generally, it seems prudent to append to the proposition (1) that the proportion of surface ensembles of "active" metal atoms determines the participation of hydrogenolysis events in hydrocarbon conversions the caveat that surface structure changes and adsorbed residues may modify product distribution patterns.

No cyclohexane accompanied benzene production in the n-hexane reaction, consistent with the position of the dehydrogenation equilibrium at and above ca. 350°C. It is of special interest that methylcyclopentane did not appear even at the lowest levels of conversion. Its absence as an observed product is unlikely to be due to fast ring enlargement to cyclohexane and benzene because bond-shift isomerization activity is very low. We infer that the C_6-ring structure forms directly and not through a C_5-ring intermediate. A consequence is that 2-methylpentane and 3-methylpentane, both of which would arise from ring opening, are not found (> 0.5% of total products).

Finally, the preference for C_6 cyclization on iridium catalysts and steric considerations suggest that cyclization is by a π-olefin intermediate as favored for palladium by Muller and Gault (22).

benzene production through ring enlargement of methylcyclopentane cannot therefore be excluded.

REFERENCES

1. PONEC, V., AND SACHTLER, W. M. H., *Proc. Int. Congr. Catal., 5th, 1972*, 1, 645, 653–657 (1973).
2. BOUDART, M., AND PTAK, L. D., *J. Catal.* 16, 90 (1970).
3. BYRNE, J. J., AND CLARKE, J. K. A., *J. Catal.* 7, 166 (1967).
4. CLARKE, J. K. A., AND RAFTER, E. A., *Z. Phys. Chem., N.F.* 67, 169 (1969).
5. HANSEN, M., AND ANDERKO, K., "Constitution of Binary Alloys," p. 212. McGraw-Hill, New York, 1958.
6. (a) PEARSON, W. B., "Handbook of Lattice Spacings and Structures of Metals and Alloys," pp. 405, 702. Pergamon, Elmsford, NY, 1958; (b) BUCHER, E., BRINKMAN, W. F., MAITA, J. P., AND COOPER, A. S., *Phys. Rev. B* 1, 274 (1970).
7. ANDERSON, J. R., AND AVERY, N. R., *J. Catal.* 5, 446 (1966).
8. SANDERS, J. V., "Chemisorption and Reactions on Metallic Films" (Anderson, J. R., Ed.), Vol. 1, p. 1. Academic Press, New York, 1971.
9. SACHTLER, W. M. H., AND JONGEPIER, R., *J. Catal.* 4, 665 (1965).
10. KIKUCHI, E., TSURUMI, M., AND MORITA, Y., *J. Catal.* 22, 226 (1971).
11. CARTER, J. L., CUSUMANO, J. A., AND SINFELT, J. H., *J. Catal.* 20, 223 (1971).
12. PONEC, V., AND SACHTLER, W. M. H., *J. Catal.* 24, 250 (1972).
13. SINFELT, J. H., CARTER, J. L., AND YATES, D. J. C., *J. Catal.* 24, 283 (1972).
14. PLUNKETT, T. J., AND CLARKE, J. K. A., *J. Chem. Soc., Faraday Trans. I*, 68, 600 (1972).
15. BEELEN, J. M., PONEC, V., AND SACHTLER, W. M. H., *J. Catal.* 28, 376 (1973).
16. MAAT, H. J., AND MOSCOU, L., *Proc. Int. Congr. Catal., 3rd, 1964*, 2, 1277 (1965).
17. COROLLEUR, C., TOMANOVA, D., AND GAULT, F. G., *J. Catal.* 24, 401 (1972), and references cited therein.
18. JOYNER, R. W., LANG, B., AND SOMORJAI, G. A., *J. Catal.* 27, 405 (1972).
19. SINFELT, J. H., *Catal. Rev.* 3, 175 (1969).
20. ANDERSON, J. R., AND SHIMOYAMA, Y., *Proc. Int. Congr. Catal., 5th, 1972*, 1, 695 (1973).
21. BARON, K., BLAKELY, D. W., AND SOMORJAI, G. A., *Surface Sci.* 41, 45 (1974).
22. MULLER, J. M., AND GAULT, F. G., *J. Catal.* 24, 361 (1972).

T. J. PLUNKETT
J. K. A. CLARKE

Department of Chemistry
University College, Belfield,
Dublin 4, Ireland
  Received December 7, 1973;
  revised June 10, 1974