Specific Dehydrocyclisation of n-Hexane over Supported Platinum Crystallites Prepared from Platinum Carbonyl Cluster Anion Salts

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Summary Highly dispersed Pt-aggregates have been prepared by pyrolysis of the Pt_{15}—Pt_3 carbonyl anion salts on γ-Al_2O_3 and SiO_2 which catalyse the specific dehydrocyclisation of n-hexane.

We have tried to prepare highly dispersed Pt-crystallites by pyrolysis of well-defined Pt-cluster compounds, the particle size of which may be conveniently controlled down to <10 Å. The trigonal prismatic salts, $[\{Pt_3(CO)_6\}_n]^{2-}$-$([NEt_4]^+)_2$ (n = 1—5), were prepared by Chini's method,[1] and deposited in high dispersion (0·05—1 Pt wt %) from tetrahydrofuran solutions over silica gel, γ-Al_2O_3, or Vycor glass (no. 7930) with surface area 240—380 $m^2 g^{-1}$. The dispersed salts decomposed completely when pyrolysed *in vacuo* or under He or H_2 to produce stoicheiometric amounts of CO and NEt_3: $[Pt_{15}(CO)_{30}][NEt_4]_2$ at 150, $[Pt_9(CO)_{18}][NEt_4]_2$ at 165, and $[Pt_6(CO)_{12}][NEt_4]_2$ at 170 °C. Also, the terminal (2025—1980 cm^{-1}) and bridging (1870—1810 cm^{-1}) carbonyl absorptions in the i.r. spectra of the supported Pt-carbonyl cluster salts disappeared when the Al_2O_3 disc was evacuated at 180—250 °C for 0·5 h.

TABLE. Reaction of n-hexane over the supported Pt-aggregate catalysts; C_6 reaction products[a]

Type of catalyst[b]	Dispersion (Pt wt %)	Reaction temp. (°C)	C_6 Reaction products (mol %) 2-MP	3-MP	MCP	CH + B
$[Pt_{15}(CO)_{30}]$ $[NEt_4]_2$[c]	0·69	295	17·2	8·2	61·7	12·9
		320	15·6	6·4	65·7	12·3
,, ,, [d]	0·15	320	21·4	12·5	58·5	7·6
$[Pt_{12}(CO)_{24}][NEt_4]_2$[c]	0·54	275	15·2	6·8	64·1	13·9
$[Pt_9(CO)_{18}][NEt_4]_2$[c]	0·26	320	9·6	6·4	72·8	11·2
	0·50	320	11·4	5·2	74·4	9·0
$[Pt_6(CO)_{12}][NEt_4]_2$[c]	0·18	320	5·4	3·7	83·6	7·3
	0·25	325	5·2	2·6	87·0	5·2
$[Pt_3(CO)_3(PPh_3)_4]$	0·45	325	3·7	1·7	92·6	2·0

[a] 2-MP = 2-methylpentane, 3-MP = 3-methylpentane, MCP = methylcyclopentane, CH = cyclohexane, and B = benzene; only traces of 2,3-dimethylbutane and neohexane were detected. [b] The reaction was carried out after hydrogen reduction at 350 °C for 5 h and evacuation at 350 °C for 0·5 h. [c] On γ-Al_2O_3. [d] On Vycor glass. [e] The catalyst was prepared by hydrogen treatment at 250 °C of the dispersed $[Pt_3(CO)_3(PPh_3)_4]$ on γ-Al_2O_3 and evacuation to remove the decomposition products, such as C_6H_6 and Ph_2PH.

When H_2 (50—250 Torr at 25 °C) was admitted into supported Pt-aggregates after pyrolysis *in vacuo* [designated here as $(Pt_3)_n$], it was found that all the Pt atoms of the dispersed Pt-crystallites displayed homogeneous hydrogen adsorption (H.A.), the stoicheiometry of H per Pt atom on γ-Al_2O_3 or SiO_2 being 1·95, 1·7, 1·5, and 1·4 for Pt_{15}, Pt_{12}, Pt_9, and Pt_6, respectively. For CO adsorption on Al_2O_3, CO/Pt_{total} = 0·45, 0·37, and 0·25 for Pt_{15}, Pt_9, and Pt_6, respectively. Hydrogen titration (H.T.) of the oxygen adsorbed (O.A.) on the dispersed Pt-crystallites on Al_2O_3 after evacuation was measured and the ratios for H.A.:O.A.:H.T. were found to be 2·5—3·7:1:3·8—4·2 for Pt_{15}, Pt_9, and Pt_6. Although the Pt-aggregates here have not been proved to contain the same number of atoms as the clusters from which they are formed, the results indicate that they consist of crystallites of particle size <10 Å.[2] The H_2–O_2 titration stoicheiometries were reproduced in several runs after treatment with H_2 and evacuation at 350 °C.

The dehydrocyclisation and the skeletal isomerisation of n-hexane were measured between 250 and 340 °C in the presence of an excess of hydrogen (n-hexane:H_2 = 1:10) over the supported Pt-crystallites. For conversions of <2%, the composition of the products was determined by g.l.c. using a silicon SE-25 column at 0 °C. The dehydrogenation products (MCP + CH) were preferentially (with >75% selectivity) obtained over the Pt-aggregates prepared from Pt_{15}, Pt_{12}, Pt_9, and Pt_6 salts on γ-Al_2O_3 and Vycor glass. The smaller Pt-aggregates deposited from $[Pt_6(CO)_{12}][NEt_4]_2$ and $[Pt_3(CO)_3(PPh_3)_4]$ on γ-Al_2O_3 resulted in the formation of methylcyclopentane with 80—94% selectivity and negligible skeletal isomerisation of n-hexane occurred under these conditions. 2- and 3-methylpentanes were mainly formed from the simultaneous hydrogenolysis of the methylcyclopentane produced. It is also of interest that the skeletal isomerisation of neopentane proceeded, with less hydrogenolysis, over the Pt_{15}- and Pt_{12}-crystallites on γ-Al_2O_3 and Vycor glass at 270—340 °C under an excess of hydrogen. The ratio of isopentane: isobutane formed at lower conversion (<1%) was 5:20. In contrast, hydrocracking occurred preferentially over Pt-crystallites prepared from smaller Pt-clusters, such as Pt_6- and Pt_3-carbonyls, on γ-Al_2O_3 with negligible formation of isopentane (isopentane/isobutane = 0·1—0·01 at 310—350 °C). The results may suggest that the smaller Pt-aggregates prepared from the Pt-cluster compounds consist of lower-co-ordinated corner Pt atoms which favour the formation of adsorbed carbocyclic reaction intermediates as suggested by Anderson *et al.*[3]

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