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Pt/MgO as Catalyst for Hydrogenolysis Reactions of C_5 and C_6 Hydrocarbons: Evidence for Metal–Support Interactions

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Pt/magnesia catalysts having high metal dispersion (av. dia. 21 Å) have been prepared employing nonaqueous impregnating solutions and an incipient wetness technique. Both chlorine-free and residual-chlorine-containing catalysts were studied, the latter being prepared from platinum (IV) chloride. Both types of catalyst are of negligible sulphur content (<2 ppm). Comparison of hydrogen chemisorption and transmission electron microscopy results for both "chlorine-free" and chlorine-containing Pt/MgO catalysts showed that (i) chemisorption capacity was substantially as expected from TEM-derived particle size following a reduction temperature of 593 K (LTR), and (ii) chemisorption was depressed to 40% or less of expectation when a reduction temperature of 753 K (HTR) was used. Reactions of saturated hydrocarbons in a flow of hydrogen ($p_{\mathrm{hydrocarbon}}$ = 8–16 Torr, balance to 760 Torr hydrogen) showed hydrogenolysis to be a prominent reaction. With LTR chlorine-free catalysts, hydrogenolysis of *n*-pentane was almost exclusively by central scission. The chlorine-containing HTR catalyst yielded largely terminal scission. HTR chlorine-free catalysts and LTR chlorine-containing catalysts gave an intermediate behaviour. Thus, both higher reduction temperature and presence of chlorine act to move scission of the C–C chain from the centre to the ends. Hydrogenolysis of neohexane showed increased direct demethanation to give *n*-butane with the presence of chlorine in the catalyst. Ring scission of methylcyclopentane gave an enhanced production of 2-methylpentane on all the Pt/magnesia catalysts. The considerably depressed hydrogen chemisorption and the carbanionic reactivity in these cracking reactions are interpreted in terms of a moderately strong metal–support interaction with a shift of negative charge from the magnesia O^{2-} ions to the platinum. This interaction is increased by the presence of chlorine in the catalysts.

INTRODUCTION

The phenomenon of strong metal–support interactions (SMSI) was first reported for the Pt/titania system in 1978 (*1*). In the intervening years, the study of the interactions which may occur between metal and support has intensified. Many metal–support systems have now been shown to exhibit SMSI characteristics. A support which has recently become the subject of debate in this regard is magnesium oxide, strong metal–support interactions in the Pt/magnesia system having been both claimed and counterclaimed.

The anomalous hydrogen adsorption behaviour exhibited by the Pt/MgO system was first reported by Wanke and his group in 1981 (*2*). A 0.5% Pt/MgO catalyst, established to be of high dispersion both from TEM studies and hydrogen uptake following LTR (573 K), was reported to have negligible chemisorption capacity after an HTR treatment (773 K). Further work with a higher metal loading showed the same effect to a lesser degree. The behaviour was attributed to a metal–support interaction (*3*). The same group reported (*4*) losses in activity and a small and reproducible shift in the infrared absorption frequency of linearly ad-

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sorbed CO with increase in reduction temperature on a 0.5% Pt/MgO catalyst. The results were interpreted in terms of a platinum–magnesia complex in which electron transfer occurred from metal to support.

Gold supported on magnesia was studied by EXAFS by Bassi *et al.* (*5*), who reported that the supported metal was present in two distinct phases, one exhibiting bulk metallic characteristics and the other atomically dispersed. In Au/MgO (*d* = 20 Å) samples a longer Au–Au distance was observed than is found in the bulk metal. This was tentatively attributed to a lattice distortion due to interaction with the support. In turn, this was considered to bring about removal of an electron from each of a number of gold atoms, resulting in stabilized Au^+ found on the support surface. On the other hand, infrared spectral frequencies of chemisorbed CO on gold have led to the conclusion that Au is electron-enriched from the magnesia support (*6*).

Haller's group (*7*) concluded from a study of the related Rh/MgO system that sulphate in the support acted as a poison precursor. The resulting strong Rh–S bonds weakened the interaction of the supported metal with other adsorbates, thereby causing reduced chemisorption. They reported that there was no diminution of hydrogen chemisorption when an ultrapure magnesia was used. Recent work by Wanke's group (*8*) confirmed that the presence of sulphate causes suppression of hydrogen chemisorption in the Pt/MgO system. However, a diminution in hydrogen uptake was observed even for a sulphur-free Pt/MgO (HTR) catalyst. An ultrapure magnesia support (>99.999%) was used as a norm in this study.

In the present work, apart from use of best grade materials, much care was given to ensuring that no adventitious impurities were introduced during any stage of catalyst preparation or support pretreatment. FTIR spectroscopy and energy dispersive X-ray microanalysis (EDX) were employed to monitor catalyst purity. It is argued that any effect observed may be attributed to a real interaction between metal and support and is not a result of some extraneous influence. The study concentrates on catalytic hydrogenolysis reactions of selected alkanes on such Pt/magnesia samples.

EXPERIMENTAL

Materials

Premier Periclase magnesia type PC-210G (stated to have <10 ppm S and <20 ppm Cl) was used as support throughout. Hydrocarbons were Fluka puriss grade and were further checked for impurities by gas chromatography prior to all catalytic reactions. Platinum (IV) chloride and hydrogen hexahydroxyplatinate (IV) were supplied by Johnson Matthey plc. BDH Analar acetone, Hi-Per-Solv methanol, Aristar nitric acid, and Merck pro-analysi absolute ethanol were employed in catalyst preparations. All solvents were dried prior to use by refluxing over BDH molecular sieve type 13X activated by heating in a flow of nitrogen.

Procedures

Support pretreatment. The magnesia was given the following pretreatment prior to impregnation:

(i) 3–4 g of as-received magnesia was suspended in boiling conductance water (1×10^{-7} mho at 298 K) and the suspension heated with stirring until the water was almost evaporated. The resultant thick slurry was transferred to an air-oven for a short preliminary drying (3 h, 338 K). The solid obtained was then dried more completely overnight in a furnace at 383 K;

(ii) calcined in air (19 h, 973 K);

(iii) pretreated in palladium-purified hydrogen (3 h, 773 K, 30 ml min^{-1});

(iv) stored in a vacuum desiccator over regenerated molecular sieve (BDH type 4A) until required.

The initial part of procedure (i), boiling of the supplied magnesia in water suspension following Ueda *et al.* (*9*), resulted in substantially increased surface area for the final derived magnesia. Procedures (ii) and (iii) were carried out to stabilize the support structurally and hence minimise the possibility of surface area reduction and consequent encapsulation of the metal (*7*) during the later heat treatment and during reduction; they further ensured the decomposition of any residual magnesium carbonate (*10*). After the above pretreatment the BET surface area of the support, as determined by N_2 adsorption, was 42–43 $m^2 g^{-1}$.

Catalyst preparation. All catalysts studied were 1% w/w Pt/MgO and were prepared by one of two methods:

Chlorine-containing catalysts: Platinum/magnesia catalysts containing residual chlorine were prepared using methanolic solutions of platinum (IV) chloride and an incipient wetness technique. The solution of metal salt was added dropwise to the support with stirring until a visually homogeneous slurry was obtained (~20 min). The catalyst was dried in an air-oven (3 h, 338 K) before being dried overnight in a furnace (16 h, 383 K).

Chlorine-free catalysts: Because the available halogen-free platinum compound $H_2Pt(OH)_6$ was insoluble in all organic solvents tested it was converted into a soluble (non-halogen containing) form as follows. A known weight (~0.2 g) of $H_2Pt(OH)_6$ was treated three times with Aristar grade conc. nitric acid (20–30 ml) and each time evaporated to dryness on a steam-bath. The resultant material, which was red in colour, was dissolved in dry absolute ethanol and the resultant solution was used to impregnate a sample of magnesium oxide in the way already described. The mixture was homogenized and dried as before. The catalyst was stored in a vacuum desiccator until required.

Apparatus

The flow-reactor system used was a modification of that previously described (*11, 12*). It was constructed entirely of metal, Teflon, and glass except for Viton seals which were replaced on a regular basis to avoid unwanted retention of hydrocarbons. Nupro bellows stopcocks and Nupro metering valves were used to control the flow of gas streams.

All hydrocarbons were outgassed prior to reaction studies by means of repeated freeze–pump–thaw cycles in vacuo. The catalyst under examination was supported on a sintered-glass disk of porosity 3 sealed within a 12-mm-o.d. pyrex tube fitted with 6-mm o.d. ends to suit Cajon Ultratorr vacuum fittings. Hydrocarbons were introduced to the gas flow over the catalyst by means of a saturator thermostatted at a suitable temperature. Hydrogen and argon were purified by means of a Johnson–Matthey EP28/1 hydrogen purifier employing a palladium/silver membrane and a BOC Rare Gas Purifier Mark IV, respectively. The rigorous exclusion of oxygen in the gases used in all runs was visually monitored on a continuous basis by means of a tube of freshly reduced 1% w/w MnO/SiO_2 (*13*) which had been positioned at the exit of the reactor tubulation.

Reduction and Chemisorption Procedure

A standard procedure was adopted for all catalysts. It included an oxidative redispersion stage principally because this was found to be necessary in the case of chlorine-free Pt/MgO catalysts to produce a high platinum dispersion. A charge of ~0.25 g catalyst was used in each catalytic run and was subjected to the following pretreatment prior to hydrogen chemisorption determination:

(i) argon purge: 16 h, 293 K, 50 ml min^{-1};

(ii) argon purge: 3 h, 473 K, 50 ml min^{-1};

(iii) hydrogen reduction: 3 h, 473 K, 30 ml min^{-1};

(iv) hydrogen reduction: 16 h, 593 K, 30 ml min^{-1};

(v) oxidative redispersion (O_2): 1 h, 793 K, 50 ml min^{-1};

(vi) hydrogen reduction: 16 h, 30 ml min^{-1}, at the final reduction temperature (LTR 593 K; HTR 753 K);

(vii) argon purge: 1 h, 50 ml min^{-1} at the temperature of the final reduction temperature.

The hydrogen pulse technique pioneered by Gruber (*14*) was employed in the determinations of hydrogen uptake.

Catalytic Reaction Procedure

The reactor system was operated in the continuous mode under differential conditions (conversions <10%). Following the chemisorption determination, the hydrogen stream was diverted via the hydrocarbon saturator and the resulting mixed stream was passed through the catalyst bed. A high partial pressure of hydrogen (1 atm) was used throughout in order to minimise formation of carbonaceous residues on the platinum surface and to optimise the conditions for uncovering SMSI effects. The reactor furnace was raised to the desired temperature. Samples of the reactor exit gas were injected by means of a 6-port gas sampling valve into a Perkin–Elmer F11 gas chromatograph fitted with a flame ionization detector. Products were separated on a 3-m column packed with 15% squalane on Chromosorb P.

Particle Size Measurements by TEM

Catalysts selected for particle size analysis were finely ground between glass slides and suspended in distilled water. The suspension was dried down on to carbon-filmed specimen grids and very thin areas were examined in either a JEOL 1200 EX or Akashi 002B TEM. Electron micrographs were recorded at 200,000 × and measurements of the diameters of 300–400 Pt particles were made from prints of 1,000,000 ×. The TEMs were calibrated using 3.35 Å lattice fringes from graphite. Pt particles down to about 6 or 7 Å could be detected in very thin areas; below this size contrast from the support material confused particle identification.

EDX Analysis

Three catalysts were examined by EDX: 1% w/w Pt/MgO prepared from chlorine-free precursor compound (code Pt-M-19-91), 1% w/w Pt/MgO *ex* Pt(IV) chloride (Pt-M-11-91) and a reference 1% w/w Pt/Aerosil (Pt-S-1-91). Samples for study were prepared by lightly crushing the powder in propan-2-ol and drying a drop of the suspension on a lacey carbon film. The samples were analysed in a VG HB5 scanning transmission electron microscope (STEM) operating at 100 kV and equipped with a field emission gun. With this equipment areas down to ~10 $Å^2$ could be probed. A horizontally mounted solid-state energy dispersive X-ray spectrometer with a Be window was used for this study. An annular dark-field detector allowed easy visibility of the small Pt particles on the MgO support. Pt, Mg and Cl were the major elements detected. Low levels of Si were occasionally found in both the Pt/MgO catalysts and low levels of Ca were sometimes detected in the chlorine free Pt/MgO.

RESULTS AND DISCUSSION

EDX Analysis

The aims of the present programme have been to determine whether a magnesia support in the absence of superposed influences affects the H_2 chemisorption capacity and the catalytic action in alkane skeletal reactions on platinum microcrystallites. The Pt/MgO catalysts prepared from multiple treatment of $H_2Pt(OH)_6$ with hot concentrated nitric acid are deemed to be chlorine-free. EDX analysis showed that chlorine was zero to within the experimental error (~0.2% w/w) (combustion-flask analysis using a mixture with benzoic acid gave 0% w/w to within ±0.01% w/w). The Pt/MgO catalyst prepared from Pt(IV) chloride exhibited a range of chlorine contents in different regions from 0.3 to 0.8% w/w (with a mean of 0.5% w/w). These values agree well with combustion-flask analyses which showed typically a chlorine content of 0.7–0.8% w/w. Chlorine was not detected by EDX (to within experimental error) in the Pt/SiO_2 catalyst (see Fig. 1).

Neither set of catalysts showed evidence of S–O bonds in FTIR (and no definite evidence of S by EDX) and both were notable for their high platinum dispersion. The FTIR

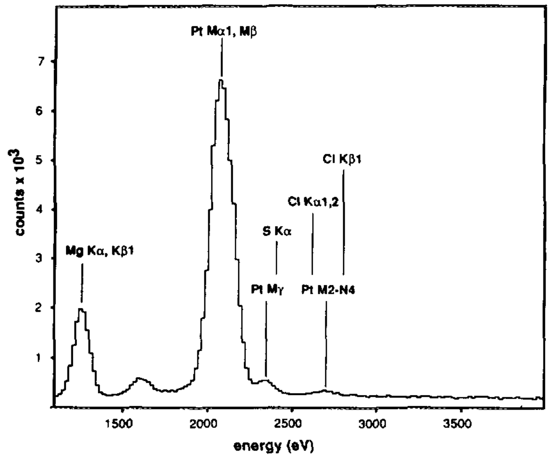


FIG. 1. Region of the X-ray spectrum from a single platinum particle showing the Pt*M* peaks. If sulphur and chlorine are present, their *K* peaks overlap with the *M*γ and *M*2–*N*4 peaks of the platinum as indicated.

examination is sufficiently sensitive to permit the conclusion that sulphur impurity is <2 ppm. Clearly the chlorine-free catalysts are of the highest quality particularly from the standpoint of chemical purity (from EDX Zn, Pb, and Sn are absent completely) and represent our ultimate standard for the catalytic evaluation of this supported-metal system. In turn, the chlorine-containing Pt/magnesia catalysts permit the effect of adventitious chlorine content on catalytic and chemisorptive behaviour to be examined: this information was considered to be of practical as well as fundamental interest.

In the following short section hydrogen chemisorption and TEM results are presented for the catalysts of the present program and these are discussed. Then a longer section follows which presents and treats the catalytic results found for these catalysts with *n*-pentane, neohexane, and methylcyclopentane as reactants and includes a short study on particle size variation.

Characterization of Pt/MgO Catalysts by Chemisorption and Electron Microscopy

For catalysts reduced at 593 K (LTR), excellent agreement was found between particle sizes calculated from chemisorption determinations and those calculated from TEM measurements. Table 1 shows a typical set of such data. A representative electron micrograph is shown in Fig. 2. Following reduction in hydrogen at elevated temperature (753 K) a marked reduction in chemisorptive uptake in the Pt/magnesia catalysts was noted (HTR).

TABLE 1

Average Platinum Particle Diameter Estimated from Hydrogen Chemisorption Compared with Values Derived from TEM for Selected Pt/Magnesia Catalysts (LTR)

Catalyst code	$d_{\text{chemisorption}}$ (Å)[a]	d_{TEM} (Å)[b]
Pt-M-7-91	24	21 ± 6
Pt-M-11-91	25	21 ± 3
Pt-M-19-91	22	21 ± 8

[a] Assuming spherical metal clusters of equal size.
[b] Averaged (see text).

Table 2 shows the effect of HTR on the hydrogen adsorption capacity of several chlorine-containing and chlorine-free catalysts. It can be seen that the chemisorption capacity is decreased by 60–80% following HTR (relative to LTR) in chlorine-containing Pt/MgO catalysts, while the decrease in chlorine-free catalysts was generally around

TABLE 2

The Effect of HTR on the Hydrogen Adsorption Capacity of Selected Chlorine-Containing and Chlorine-Free Pt/MgO Catalysts

Catalyst	Reduction temp. (K)	H atoms adsorbed[e] / Total Pt atoms	d_{TEM} (Å)[f]
Pt-M-4-91[a]	593[c]	0.39	21 ± 4
Pt-M-4-91[a]	753[d]	0.16	21 ± 5
Pt-M-11-91[a]	593[c]	0.42	22 ± 3
Pt-M-11-91[a]	753[d]	0.09	20 ± 4
Pt-M-19-91[b]	593[c]	0.50	21 ± 8
Pt-M-19-91[b]	753[d]	0.20	19 ± 6
Pt-M-20-91[b]	593[c]	0.45	21 ± 8
Pt-M-20-91[b]	753[d]	0.16	19 ± 6

[a] Chlorine-containing.
[b] Chlorine-free.
[c] LTR.
[d] HTR.
[e] Thus, a value of 0.50 implies a platinum dispersion of 50% on the basis H/Pt = 1 and no metal–support interaction.
[f] Averaged (see text).

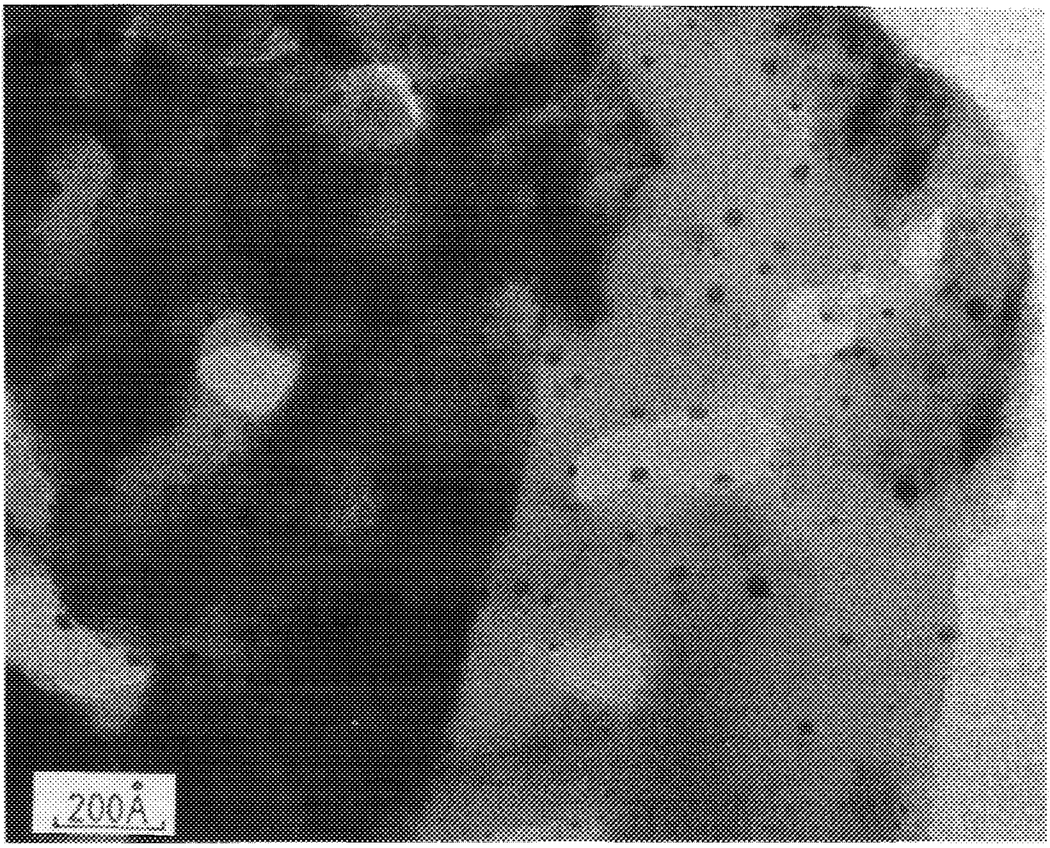


FIG. 2. Transmission electron micrograph showing small particles of Pt on magnesia. Sample Pt-M-7-91 (LTR).

60%. Average particle diameters showed no significant change from LTR to HTR and indeed from chlorine-containing to chlorine-free (column 4). The possibility of bimodal particle size distributions in the catalysts under study was also investigated. Figures 3 and 4 show the particle-size distribution from TEM for Pt-M-19-91 after LTR and HTR treatments, respectively. In neither case was a bimodal pattern found.

In conclusion, a decrease in chemisorptive uptake of 60–80% was found after high-temperature reduction in all the Pt/MgO catalysts examined. The absence of significant impurities such as sulphur in the materials employed in this work (see the Experimental section) would appear to eliminate any role which they could play in the lowering

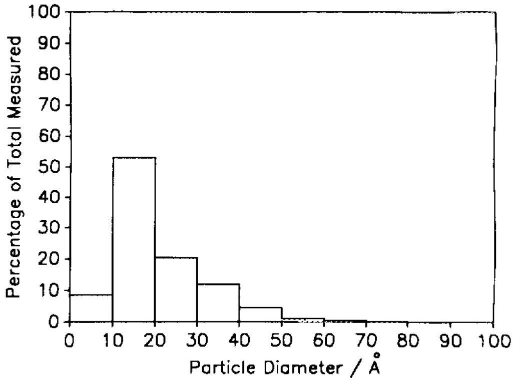


FIG. 3. Particle size distribution from TEM for chlorine-free Pt/magnesia following LTR (catalyst code Pt-M-19-91).

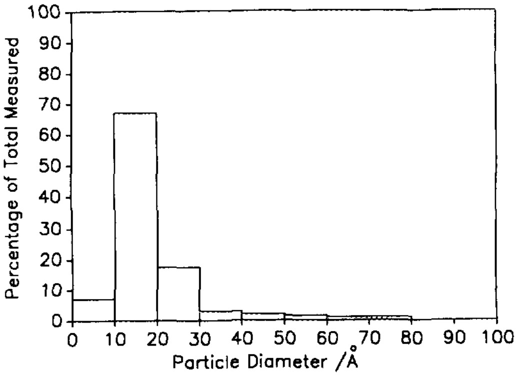


FIG. 4. Particle size distribution from TEM for chlorine-free Pt/magnesia following HTR (catalyst code Pt-M-19-91).

of chemisorption capacity. Incomplete reduction of the metal as a possible cause of decreased hydrogen chemisorption can be disregarded because, as already noted, satisfactory agreement was found between TEM-derived particle size and hydrogen uptake following reduction at the lower temperature (LTR). We note that the similarity in depression of chemisorption found both in chlorine-containing and chlorine-free catalysts mitigates against the theory of decoration by $MgCl_2$ moieties proposed by Murata and Aika (*15*). Also, we have found a similar depression of hydrogen chemisorption with Pt/MgO catalysts prepared by aqueous impregnation (not tabulated). This rules out any effect arising from the nature of the impregnating solvent per se in the diminution of chemisorptive capacity, i.e., the depressed chemisorption capacity is not a result of the choice of impregnating solvent. From the evidence presented, it would appear that reduced chemisorption following HTR is a genuine manifestation of an interaction between metal and support in the Pt/MgO system.

Catalytic Results

n-Pentane reaction. Hydrogenolysis is a prominent reaction path (Table 3) consistent with the high metal dispersion (*11*). Isomerisation, found with chlorine-free Pt/magnesia, is suppressed with HTR chlorine-containing Pt/magnesia. The choice of high hydrogen partial pressure to minimise coking and highlight any SMSI, and also made necessary by the very strong self-poisoning effects with chlorine-free Pt/magnesia discussed later, does, however, cause cyclisation to be moved into the region of thermodynamic control: tabulated results for the always considerable cyclopentane formation therefore represent merely minimal values.

In hydrogenolysis, chlorine-containing LTR Pt/magnesia is clearly more active than the chlorine-free LTR counterpart (×50–100); the corresponding HTR catalysts are similar to one another in hydrogenolysis activity. Both the Pt/silica comparison catalysts (Table 4A) are intermediate in hydrogenolysis activity between the LTR chlorine-containing and LTR chlorine-free catalysts, being about 10–20 times more active than the latter. Chlorine-containing LTR Pt/magnesia and the Pt/silica comparison catalysts are not noticeably different in activity from the chlorine-free LTR Pt/magnesia.

Chlorine-free Pt/magnesia (HTR) shows more random scission of C–C bonds in hydrogenolysis than does the LTR chlorine-free catalyst which showed largely central scission (Table 3 C vs 3A). Scission is wholly random with Pt/silica. The HTR chlorine-containing Pt/magnesia shows a more noticeable preference for terminal scission than the chlorine-free (Table 3D vs 3C). This repeats a tendency noted for the LTR catalysts, namely, that the presence of chlorine promotes a greater contribution of terminal scission. Hydrogenolysis may take place through either a metallacyclobutane or a metallacyclopentane intermediate or by both routes in parallel. There are undoubtedly a number of influences which determine the dominance of one rather than the other of these paths. Engstrom *et al.* (*16*) reported that a high index surface favours the latter route over the former for iridium.

TABLE 3

Reaction of *n*-Pentane/Hydrogen on Cl-Free and Cl-Containing Pt/MgO

T (K)	Flow rate (ml min^{-1})	Conv. (%)	T.O.N.[a]	C_1	C_2	C_3	nC_4	iC_5	cC_5[b]
A. Cl-free Pt/MgO (LTR: T_{red} = 593 K); d_{TEM} = 21 ± 8 Å									
536	30	0.33	0.26	Tr[c]	20	30	6	24	20
545	30	0.72	0.56	Tr	18	29	6	27	20
558	30	4.6	3.6	Tr	18	31	7	36	8
B. Cl-containing Pt/MgO (LTR); d_{TEM} = 21 ± 4 Å									
520	50	0.87	1.31	3	31	43	14	5	4
536	100	5.0	14.9	5	31	45	15	1	3
542	170	3.7	19.0	5	32	45	11	2	5
C. Cl-free Pt/MgO (HTR: T_{red} = 753 K); d_{TEM} = 19 ± 6 Å									
577	30	0.60	0.5	3	10	14	8	32	33
587	30	1.5	1.2	3	9	12	8	45	23
599	30	2.7	2.1	4	11	14	8	48	15
D. Cl-containing Pt/MgO (HTR); d_{TEM} = 21 ± 5 Å									
558	30	0.07	0.05	15	12	14	45	—	14
567	30	0.13	0.10	9	12	17	37	—	25
578	30	0.16	0.12	12	11	15	34	—	28

[a] Units are molecules s^{-1} g_{Pt}^{-1} × 10^{-18}.
[b] Minimum values (see text).
[c] Tr signifies trace.

Foger and Anderson (*17*) reported that small crystallites of iridium, particularly of <20 Å, gave several-fold more central then terminal scission in *n*-butane: this corresponds to a preference for the metallacyclopentane route. There is a lesser but still pronounced tendency for the same route on platinum (*16*). It may be presumed that small particle size of platinum, or more fundamentally, highly coordinatively unsaturated platinum, favours this process.

We interpret the behaviour of the chlorine-free Pt/magnesia catalysts here as effecting the metallacyclopentane route through the action of the proportion of the platinum present in high coordinative unsaturation. This leads to central scission, most noticeable for the LTR catalyst (Table 3A). The movement towards random C–C scission is noticeable with the HTR chlorine-free catalyst already (Table 3C) and with the chlorine-containing LTR Pt/magnesia (Table 3B). Eventually with HTR chlorine-containing Pt/magnesia there is marked terminal scission (Table 3D). More than one factor is likely to contribute to these changes, but on the experimental evidence the metallacyclobutane route becomes, in stages, more competitive. The preference for terminal scission on the HTR chlorine-containing catalyst is the fullest instance of carbanionic behaviour (*12*). It requires participation of a metallacyclobutane intermediate of the (C_1, C_3) type and, further, its preferential scission to give $CH_2{=}$ fragments rather than $CH_3CH{=}$ species. To anticipate, this feature will be matched closely in the neohexane reaction results which follow later. Electron shift from the MgO to the platinum by relay through chlorine bridges (*18*) seems probable.

In the *n*-pentane reaction the chlorine-free catalysts are much more prone to self-poisoning than are the chlorine-containing ones, and this holds for the reactions (discussed later) of neohexane and of methylcy-

TABLE 4

Reactions on Pt/SiO_2[a]

T (K)	Flow rate (ml min^{-1})	Conv. (%)	T.O.N.[b]	C_1	C_2	C_3	iC_4	nC_4	$neoC_5$	iC_5	nC_5	cC_5[c]	2MP	3MP	nC_6	S_H	S_I
A. Reaction of *n*-pentane/hydrogen																	
530[d]	30	3.5	1.9	10	28	34	—	24	—	2	—	2	—	—	—	—	—
544[d]	70	4.5	3.5	10	23	32	—	28	—	4	—	3	—	—	—	—	—
536[e]	40	2.1	3.6	7	23	30	—	32	—	3	—	5	—	—	—	—	—
547[e]	40	2.8	4.8	8	19	28	—	32	—	6	—	7	—	—	—	—	—
B. Reaction of neohexane/hydrogen																	
548[e]	20	6.8	2.3	9	14	8	30	2	Tr[f]	30	Tr	—	5	2	—	93	7
573[e]	30	9.8	6.0	6	14	9	25	4	2	29	1	—	8	2	—	90	10

[a] T_{red} 673 K.

[b] Units are molecules $s^{-1}\,g_{Pt}^{-1} \times 10^{-18}$.

[c] minimum values (*n*-pentane reaction).

[d] EuroPt-1 (6.3% w/wPt): $d_{chemisorption} = 18 \pm 5$ Å.

[e] 1% w/w Pt/SiO_2 in-house prepared, Cl-free by combustion flask analysis: $d_{chemisorption} = 23 \pm 5$ Å.

[f] Tr signifies trace.

TABLE 5

Reaction of Neohexane/Hydrogen on Cl-Free and Cl-Containing Pt/MgO

T (K)	Flow rate (ml min^{-1})	Conv. (%)	T.O.N.[a]	C_1	C_2	C_3	iC_4	nC_4	$neoC_5$	iC_5	nC_5	2MP	3MP	nC_6
A. Cl-free Pt/MgO (LTR); d_{TEM} = 21 ± 8 Å														
573	30	0.37	0.19	5	12	5	14	25	—	11	2	8	12	6
587	30	1.2	0.61	4	14	4	17	25	—	13	3	12	4	4
B. Cl-containing Pt/MgO (LTR); d_{TEM} = 22 ± 3 Å														
545	30	0.21	0.12	10	9	3	11	27	—	—	—	28	12	—
570	30	5.2	3.1	14	14	7	17	30	5	5	—	5	3	Tr
580	70	4.7	6.5	13	14	5	20	34	3	4	—	5	1	1
C. Cl-free Pt/MgO (HTR); d_{TEM} = 19 ± 6 Å														
586	30	0.20	0.10	—	11	Tr	17	7	—	13	4	37	11	—
598	30	0.50	0.40	2	13	2	18	5	—	13	Tr[b]	34	8	5
619	30	1.0	0.70	1	15	3	19	5	—	15	3	33	3	3
D. Cl-containing Pt/MgO (HTR); d_{TEM} = 20 ± 4 Å														
571	20	1.6	0.54	6	7	4	10	7	2	16	1	36	7	4
583	30	5.8	3.0	10	10	9	13	6	3	21	5	18	3	2

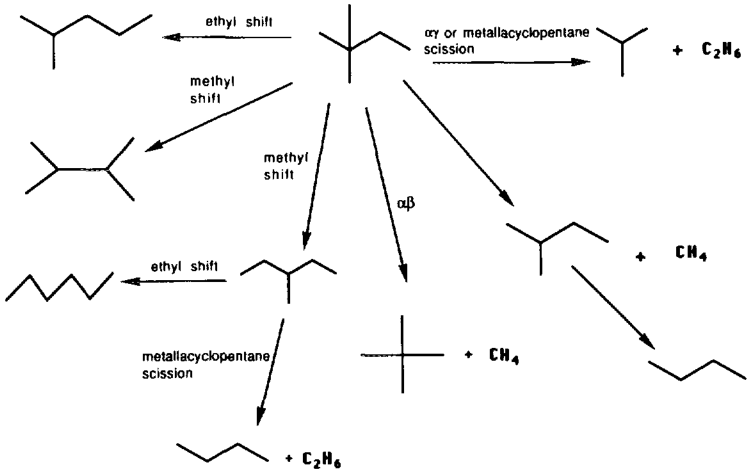
[a] Units are molecules s^{-1} g$_{Pt}^{-1}$ × 10^{-18}.

[b] Tr signifies trace.

clopentane. We suggest tentatively that a proportion of the chlorine in the latter catalysts remains associated with the platinum surface. Chlorine adatoms then act to break up pairs of adjacent bare Pt sites leading to a preponderance of single platinum atom sites. The alkane fragment $-CH_2-$ which forms on pair sites is a poison in that it converts to the more strongly bound $=C-$ and single carbon atoms (carbide); $CH_2=$ species on single metal atoms are, by contrast, reactive and add hydrogen to give methane (*19*). Availability of multiplet Pt sites may then be the main cause of self-poisoning on platinum/magnesia.

Neohexane reaction. These results (Table 5) in turn yield information both on the metal–support interaction and on the effect of chlorine. Hydrogenolysis is again a major process with all catalysts. However, bond-shift isomerisation on Pt/magnesia (Scheme 1) plays a more prominent part than was the case with the n-pentane reactant. The activity of the LTR chlorine-free Pt/MgO catalysts is 30–90 fold less than that of the in-house prepared Pt/SiO_2 although bond-shift activity is only fourfold less (Table 5A vs Table 4B). The metal–support effect is therefore reflected catalytically principally in the hydrogenolysis reactions and shows up as a diminution in rate. Chlorine-containing Pt/MgO catalysts are 10–20 fold more active than the chlorine-free (Tables 5B and 5D vs Tables 5A and 5C).

Comparing the LTR chlorine-containing catalyst (Table 5B) with LTR chlorine-free (Table 5A), bond shift is greater for the former by a factor of $\sim$10. This ratio holds roughly also for the HTR chlorine-containing (Table 5D) and HTR chlorine-free catalysts (Table 5C). Thus, both hydrogenolysis and isomerisation are promoted by the presence of chlorine and about equally so. The Pt/magnesia catalysts give broadly the same kind of product pattern whether or not chlorine is a constituent. There is major production of isobutane which matches the ethane production and is a comparable fraction of the total reaction for both chlorine-free and chlorine-containing catalyst. Formation of 2-methylpentane by bond-shift is always prominent. Its mode of subsequent hydrogenolysis parallels that shown in the n-pentane reaction, already discussed, terminal scission yielding methane being favoured with the chlorine-containing catalysts and more internal scission giving ethane with the chlorine-free. 2,3-Dimethylbutane, which was not resolvable from 2-methylpentane with the glc columns used, was judged to be only a minor product of bond-shift isomerisation because its expected symmetric



SCHEME 1. Neohexane reactions.

scission product propane was not found (see later and also Clarke *et al.* (*12*)). A kinetic barrier to formation of 2,3-dimethylbutane in bond-shift isomerisation has been noted by Sinfelt (*20*).

A notable feature of the hydrogenolysis product distributions is that the Pt/magnesia catalysts all give a large production of *n*-butane, whereas the Pt/silica (Table 4B) does not. In all cases isopentane is produced in substantial amount and in the case of chlorine-containing Pt/magnesia (Tables 5B and 5D) it undergoes further demethylation to yield *n*-butane and methane; it appears that for chlorine-free Pt/magnesia *n*-butane is formed instead or additionally by reaction of 3-methylpentane through an $\alpha\delta$-diadsorbed intermediate (the Pt/silica product pattern is accommodated in this rationalisation in that virtually no *n*-butane is produced even though isopentane is adequately produced, i.e., demethylation here is weak). We suggest that chlorine-free Pt/magnesia shows preference for hydrogenolysis by a route not involving break-up of a metallacyclobutane to a carbene of the type $CH_2{=}Pt$. Instead, translation of the metallacyclobutane to a metallacyclopentane (*21*) is preferred, and the symmetric scission of this ring structure (*22*) is signalled by the predominance of ethane over methane in the products (Tables 5A and 5C). It seems clear from comparison of rates and products of hydrogenolysis with chlorine-free Pt/magnesia and also with Pt/silica that the presence of chlorine enhances demethylation. Chlorine-free Pt/magnesia rather resembles Pt/silica as to the manner of hydrogenolysis but, as noted, the rate is of the order of 50 times less for the former.

Methylcyclopentane reaction. Chlorine-containing Pt/magnesia catalysts exhibit an overall catalytic activity greater by a factor of 2 than the 'chlorine-free' Pt/magnesia samples (Tables 6A and 6C vs 6B and 6D). Thus, the promoting influence of chlorine found in the *n*-pentane reaction (and to a lesser extent with neohexane) is significantly reduced when methylcyclopentane is the reactant. The strong self-poisoning with time noted for *n*-pentane and neohexane reactants on chlorine-free Pt/magnesia is again observed, chlorine-containing catalysts being free of this effect.

Although the ratios of ring-opening products are broadly those to be expected for nonselective (NSCM (*23*)) ring opening,

TABLE 6

Reactions of Methylcyclopentane/Hydrogen on Cl-Free and Cl-Containing Pt/MgO

T (K)	Flow rate (ml min^{-1})	Conv. (%)	T.O.N.[a]	$<C_6$	2MP	3MP	nC_6	$\frac{2MP}{3MP}$	$\frac{2MP}{nC_6}$	2MP : 3MP : nC_6
A. Cl-free Pt/MgO (LTR); d_{TEM} = 21 ± 8 Å										
523	50	1.9	2.8	—	51	18	31	2.8	1.6	2.8 : 1 : 1.7
545	50	7.7	11.0	—	50	17	33	2.9	1.5	2.9 : 1 : 1.9
B. Cl-free Pt/MgO (LTR); d_{TEM} = 22 ± 3 Å										
496	20	1.0	0.80	1	45	19	35	2.4	1.3	2.4 : 1 : 1.8
515	20	7.6	5.7	Tr	47	18	35	2.6	1.3	2.6 : 1 : 1.9
C. Cl-free Pt/MgO (HTR); d_{TEM} = 19 ± 6 Å										
528	30	0.50	0.50	—	56	17	27	3.3	2.1	3.3 : 1 : 1.6
550	30	4.1	3.8	—	51	17	32	3.0	1.6	3.0 : 1 : 1.9
D. Cl-containing Pt/MgO (HTR); d_{TEM} = 20 ± 4 Å										
528	30	0.93	1.1	—	52	16	32	3.2	1.6	3.2 : 1 : 2.0
550	30	3.9	4.7	Tr	47	20	33	2.3	1.4	2.3 : 1 : 1.6
E. Cl-containing Pt/MgO (LTR); d_{TEM} = 21 ± 6 Å. Hydrogen diluted with argon[b]										
495	420	0.92	0.52	3	44	21	32	2.1	1.4	2.1 : 1 : 1.5
507	420	0.44	0.25	9	36	19	36	1.9	1.0	1.9 : 1 : 1.9

[a] Units are molecules s^{-1} g_{Pt}^{-1} × 10^{-18}.

[b] H_2 : A : 1 : 20 (column 2 indicates flow rate of this mixture).

there is (i) a markedly greater 2-methylpentane and (ii) a slightly lesser *n*-hexane production than corresponds to the statistical expectation of 2 : 1 : 2 for 2-methylpentane:3-methylpentane:*n*-hexane. There are reports (*24, 25*) of similar product ratios to these on highly dispersed platinum, one example cited (*24*) being for a platinum film evaporated onto a pyrex wall. This type of product ratio is not, it seems, special to a magnesia- supported platinum and, indeed, it is readily understandable on mechanistic grounds. A preferred route of C_5-ring opening by NSCM, particularly at higher hydrogen partial pressures as here, is a retro-alkene/alkyl insertion route (*26–28*). Whether or not the statistical 2 : 1 : 2 ratio of hexane isomers is realised depends on the initial point of attachment of the methylcyclopentane molecule to the surface (*29*). Examination of a molecular model shows that a methylcyclopentane chemisorbed at C_6, the exocyclic carbon atom, is sterically quite constrained from converting through C_1–C_2 (=C_1–C_5) bond scission to *n*-hexane. Conversion of this initially chemisorbed form through a π-methylenecyclopentane intermediate ($\alpha\beta$ process (*32*)) to methylcyclopentyl chemisorbed at C_1 will then take place. By the retroalkene/alkyl cracking process this species can only give 2-methylpentane. Further migration of the point of attachment round the ring in the methylcyclopentyl species to C_2(=C_5), C_3(=C_4) is necessary before the retro-alkene/alkyl cracking process can afford *n*-hexane and 3-methylpentane. A bias in the initial point of attachment to the surface can change the ratio of products in favour of 2-methylpentane. Although platinum in the form of an evaporated film appears to break primary, secondary and tertiary C–H bonds with roughly equal rates (*30*) platinum of atomic dispersion may discriminate. Direct experimental information does not appear to be available on other forms of platinum. Nickel has long been known to break tertiary C–H bonds more rapidly than primary (*31*). Electron enrichment or depletion may affect the preference for a given metal (*12*): the several observations already discussed point to carbanionic behaviour on Pt/MgO and thus to electron-enriched platinum. Preferred initial chemisorption of MCP at the methyl group, i.e., primary carbon, is then the most reasonable basis for interpreting the observed ring-opening products and those of Kramer and Zuegg (*25*) for Pt/MgO.

It is significant that the ratio of ring-opening products at reduced hydrogen partial pressure fits more closely the statistical one of 2 : 1 : 2 (Table 6E). Here the relevant surface radicals are the more completely dehydrogenated cyclopentenyl and pentadienyl (*28*). In the interconversion of these species steric distinctions are much less marked between the several positions of C–C scission within the ring.

To summarise, the methylcyclopentane reaction shows again the strong self-poisoning effect with the chlorine-free catalysts (LTR, HTR) and confirms the promoter effect of chlorine (LTR, HTR). There is further indication of the action of electron-enriched platinum shown by carbanionic reactivity.

Particle-size variation. A short study was conducted with a number of chlorine-containing Pt/magnesia catalysts having different metal particle size from the standard and with either *n*-pentane or methylcyclopentane as reactant. Essentially this was to check whether deductions reached in the main program required to be qualified on account of particle-size dependence of rates of individual reaction routes.

In the *n*-pentane reaction hydrogenolysis was predominantly by central scission on both a catalyst of 21 Å average Pt diameter (Table 3C) and one of 38 Å (Table 7A), both being catalysts subjected to LTR treatment prior to reaction. As has been widely reported in the literature (*32*), T.O.N's for isomerisation by bond-shift are relatively insensitive to particle size variation even though isomerisation selectivity increases with particle diameter. The activity for hydrogenolysis is depressed by a factor of

TABLE 7

Reactions on Cl-Containing Pt/MgO (LTR) of Larger Platinum Particle Size[a]

T (K)	Flow rate (ml $\min^{-1}$)	Conv. (%)	T.O.N.[b]	C_1	C_2	C_3	nC_4	iC_5	cC_5	2MP	3MP	nC_6
						A. Reaction of *n*-pentane/hydrogen						
534	30	0.14	0.11	4	18	21	8	21	28	—	—	—
546	30	0.47	0.38	3	16	23	9	29	20	—	—	—
555	30	1.9	1.5	3	13	20	8	41	15	—	—	—
						B. Reaction of methylcyclopentane/hydrogen						
508	30	6.5	5.8	—	—	—	—	—	—	52	16	32
513	70	4.9	10.3	—	—	—	—	—	—	53	16	31

[a] $d_{\text{chemisorption}} = 38$ Å, known to be a reliable estimate of metal diameter because this is an LTR catalyst (see Table 1).
[b] Units are molecules $s^{-1}\, g_{Pt}^{-1} \times 10^{-18}$.

about 80 as particle size is increased from 21 to 38 Å. Hydrogenolysis activity therefore shows extreme sensitivity to increase in particle size in harmony also with the now considerable body of literature results (e.g., (*33*)).

In the methylcyclopentane reaction there is close correspondence in ring scission preference for catalysts of average diameter 38 Å (Table 7B) with one of 22 Å (Table 6B). Even with the larger diameter metal catalysts, *n*-hexane is not appreciably reduced relative to the two isohexanes. There are no grounds therefore for believing that the selective (SCM (*23*)) ring opening route begins to play any significant part at the platinum particle size present in the catalysts of Table 6. This conclusion justifies the discussion of the methylcyclopentane reaction on the latter catalysts wholly on the basis of NSCM ring scission.

CONCLUSIONS

(i) Whereas hydrogen chemisorption on both LTR chlorine-free and LTR chlorine-containing catalysts was of the level expected from the TEM-derived average platinum particle diameter, chemisorption was depressed to 40% or less of this level for both HTR chlorine-free and HTR chlorine-containing Pt/magnesia.

(ii) Reactions of *n*-pentane and of neohexane on chlorine-free Pt/magnesia show the hydrogenolysis rate to be reduced by at least one order of magnitude compared to that on Pt/silica of comparable platinum dispersion. Scission of C–C bonds in *n*-pentane is markedly central on LTR chlorine-free Pt/magnesia and follows the normal random behaviour for Pt (*34*) on HTR chlorine-free Pt/magnesia. Chlorine in all cases increases rates of hydrogenolysis as compared to the chlorine-free Pt/magnesia counterpart. The tendency towards terminal C–C scission in *n*-pentane is strong for the HTR catalyst.

In the neohexane reaction isobutane and ethane are major and linked products on all catalysts as is frequently reported in the literature for highly dispersed platinum (*22*, *35*). However, whereas double demethylation to *n*-butane through isopentane is prominent in chlorine-containing Pt/magnesia, there is evidence for competition from an alternative route via 3-methylpentane (formed by methyl shift) by an $\alpha\delta$ hydrogenolysis intermediate. Thus reactions of *n*-pentane (principally), of 2-methylpentane intermediate product in the neohexane reaction and the formation of *n*-butane from neohexane indicate a lessened tendency for hydrogenolysis by demethanation on chlorine-free Pt/magnesia catalysts, and also on Pt/silica, than on chlorine-containing Pt/magnesia. Rather there is a trend towards internal hydrogenolysis for which central scission of an $\alpha\delta$ intermediate is the probable mechanism. Tentatively we suggest that there are two types of platinum site and judging from organometallic analogy (*36*) the $\alpha\delta$ are the more electron-enriched, the

$\alpha\gamma$ (for which even a degree of electron depletion appears beneficial (*37*)) less so. The work of Engstrom *et al.* (*16*) suggests that there may be a difference in extent of coordinative unsaturation between the two kinds of site. Results suggest that HTR serves to eliminate the former sites more than the latter but whether this is a result of advancing magnesia decoration is not known.

(iii) The reactions of all three hydrocarbons showed strong self-poisoning on chlorine-free Pt/magnesia and not on chlorine-containing Pt/magnesia. The simplest interpretation, assuming that chlorine is adsorbed on the Pt, is that the chlorine adatoms reduce the proportion of pair sites on which σ-diadsorbed methylene radicals can form on the platinum surface. These species are catalyst poisons which convert to surface carbide and are likely to form extensively on the chlorine-free catalysts. It is possible that the chlorine prevents the accumulation of σ-diadsorbed methylene, which is the poisoning agent on the surface. A satisfactory interpretation of the more general promoter action of chlorine on hydrogenolysis rates remains elusive. One possibility meriting examination is that it owes its origin to morphological changes in the metal clusters. Such changes have been inferred from infrared spectra of chemisorbed CO on supported platinum (*38*).

(iv) Study of particle-size variation reveals no new features in catalytic action which qualify conclusions already reached. There is confirmation that rates of hydrogenolysis are sensitive to particle diameter and the SCM does not intervene in the reaction of methylcyclopentane.

(v) The several effects of the magnesia support on chemisorption and on the individual skeletal reactions studied suggest some shift of negative charge from the oxide ions to the platinum cluster. The basicity of magnesia samples depends on their mode of formation (*39, 40*). Other magnesia preparations may be expected to show quantitative differences from that used in the present work in the extent of support–metal interaction realised.

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