The Influence of Metal–Support Interactions on the Reaction of n-Hexane over Supported Pt Catalysts

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The hydrogenolysis and skeletal rearrangement reactions of n-hexane have been investigated on Pt catalysts supported on silica and titania. The results show that the product distribution is dependent on the choice of support but that Pt/titania catalysts in the "normal" state are similar to Pt/titania catalysts in the "strong metal–support interaction" (SMSI) state. It is observed that in the SMSI state, when more than 99% of the Pt is inaccessible to hydrogen, the activity is only slightly reduced. Surprisingly, the selectivity for hydrogenolysis versus skeletal isomerisation is almost the same in normal and in SMSI catalysts. The results provide evidence that the same active centre is involved in both the hydrogenolysis and the skeletal rearrangement reactions, and do not support the contention that hydrogenolysis requires a larger ensemble of Pt atoms than skeletal rearrangement. The results are interpreted in terms of an active centre consisting of a single Pt atom located in the planes of the small Pt crystallites. The precise selectivity observed may depend on the local environment of the Pt atom during the sojourn of the n-hexane molecule on the active centre. © 1987 Academic Press, Inc.

INTRODUCTION

Many catalysts are prepared by depositing metal salts on high surface area oxide supports. Subsequent reduction leads to the formation of highly dispersed metal catalysts. It is tacitly accepted that the properties of small metal particles may be different from those of the bulk metal and may be affected by interaction with the support. The special importance of the interface between a metal particle and the support with regard to catalytic properties was first discussed many years ago by Schwab and Pietsch (1). Subsequent studies of the influence of the support on the catalytic properties of metals has concentrated mainly on essentially irreducible oxides (2, 3). Some support effects have been identified and these have been attributed to electronic interactions. Recently, investigations of metal–support interactions have

developed a new momentum following the observation (4–7) that metals supported on reducible oxides (e.g., TiO$_2$, Nb$_2$O$_5$, V$_2$O$_3$) developed strange properties after reduction at moderately high temperatures. The capacity to adsorb hydrogen or carbon monoxide is greatly diminished and in many cases the catalytic activity is suppressed, sometimes almost totally (8). TiO$_2$ has received particularly close attention. It was believed initially that these so-called strong metal–support interactions (SMSI) were due to the exchange of electrons between the metal particles and the reduced support. Now, however, the favoured explanation involves the migration of TiO$_x$ species onto the surface of the metal during reduction at high temperature. There is good experimental evidence in support of this migration model (9–17). However, the electronic model cannot be discounted (18–22), and at least in terms of localised interactions some degree of electronic modification of metal atoms at the metal–

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support interface must be considered a possibility. The situation is, of course, further complicated by the fact that if TiO_x migrates onto a metal particle this creates a new "interface" which may make an important contribution to the changes in the overall catalytic properties.

The dramatic changes in adsorption and catalytic properties generated by reduction at high temperatures have tended to overshadow the smaller, but nevertheless significant, differences in catalytic properties between titania-supported metals and, for example, silica-supported metals, which are observed even after reduction at low temperatures. There is now good evidence that titania-supported metals in a "normal" state, i.e., having normal adsorption properties, may have unusual catalytic properties. For example, it is well established that normal titania-supported metals have a higher activity for the CO/H_2 reaction (23, 24). Recently, it has also been shown that Rh/titania catalysts have a high activity for *n*-hexane conversion (25, 26) and give quite different product distributions in the *n*-hexane (26) and methylcyclopentane (27) reactions. Similarly, it has been shown for the methylcyclopentane reaction that Pt/titania catalysts give quite different product distributions to Pt/silica catalysts (26).

None of these support effects are dependent upon SMSI. However, after high temperature reduction further unusual effects are observed (26, 27). For example, in the methylcyclopentane reaction Rh/titania catalysts develop a higher turnover number whereas Pt/titania catalysts become totally inactive. When the SMSI state is partially destroyed by oxidation at 298 K, Pt/titania catalysts recover their original turnover numbers whereas Rh/titania catalysts become much less active. This contrasting behaviour of titania-supported Rh and Pt catalysts parallels the differences already reported for these two metals (28). Thus, we have shown that Pt enters the so-called SMSI state much more easily than Rh and with Pt it is more difficult to recover the

original adsorption capacity. The purpose of the present paper is to describe the influence of "normal" support effects and SMSI effects on the properties of titania-supported Pt catalysts for the skeletal isomerisation and hydrogenolysis of *n*-hexane.

EXPERIMENTAL

Catalysts (2% Pt by wt) were prepared by wet impregnation of silica gel (Davison Grade 57; surface area, 300 m^2 g^{-1}) and titania (Degussa P25; surface area, 50 m^2 g^{-1}; 80% anatase) supports using aqueous solutions (pH = 8) of ammonium hexachloroplatinate. The silica was ground and sieved (0.25- to 0.5-mm fraction retained) before use. The excess water was removed by rotary evaporation at 340 K, after which the catalysts were lightly ground and dried in an air oven at 393 K for 16 h. The catalysts were calcined in flowing oxygen by heating at 10 K min^{-1} to 673 K and holding at this temperature for 1 h. The samples will be referred to using the code Pt2/Si or Pt2/Ti where the number is the weight percent Pt, and Si and Ti refer, respectively, to the silica and titania supports. Prior to the catalytic measurements the catalysts were given a variety of different pretreatments, details of which are given in Table 1.

The quantity of hydrogen chemisorbed by the Pt catalysts after the various reduction treatments was determined using a conventional glass volumetric apparatus (29).

The catalytic properties of the samples were determined using a glass microreactor operating at atmospheric pressure (29). *n*-Hexane (Hex) was introduced into the hydrogen stream using two bubblers, the second of which was held at 273 K to give a H_2:Hex ratio of about 15:1 (Hex vapour pressure of 6.17 kPa). The H_2 flow rate was 1200 cm^3 h^{-1} and the Hex flow was 0.64 mol g_{Pt}^{-1} h^{-1}. Measurements were made in the temperature range 503–593 K at intervals of 10 K starting at the lowest temperature. In all experiments the conversion was kept

TABLE I

Catalyst Reduction and
Reoxidation Procedures

Code	Treatment[a]
A	R573(1)
B	R773(1)
C	R773(1)/A298(1)/R573(1)
D	R773(1)/A673(1)/R573(1)
E	R773(16)
F	R773(16)/A298(1)/R573(1)
G	R773(16)/A673(1)/R573(1)

[a] Reduction treatments are summarised by the code $RT(x)$ where T is the final temperature (K) and x is the time (h) at the final temperature. In all cases the heating rate was 10 K min^{-1} and the H_2 flow was 3.0×10^5 cm^3 g$_M^{-1}$. $AT(x)$ indicates a treatment in pure flowing air at a temperature T for x (h). Each change in procedure was preceded by flushing the sample with N_2 for 15 min.

below 10% so that only primary products were formed in significant quantities. It was also observed that after the first few minutes on stream the activity decreased only very slowly. This slow deactivation is to be expected given the low temperatures used in our experiments.

The activities of the samples are expressed as conversions of n-hexane, the units being millimoles n-hexane converted per gram Pt per hour. Product yields are expressed as selectivities S_i, defined as the number of moles, c_i, of a product containing "i" carbon atoms formed from each mole of reactant. Thus,

$$S_i = 6c_i \bigg/ \sum_1^6 ic_i.$$

For convenience the products are referred to as $<C_6$, indicating all products containing less than six C atoms, and 2MP, 3MP, MCP which refer to the C_6 products 2-methylpentane, 3-methylpentane, and methylcyclopentane, respectively.

RESULTS

Pt/Silica Catalysts

The n-hexane reaction is difficult to analyse because of the wide range of products formed and because of the importance of taking into account apparently minor variations in selectivity. For brevity we shall tabulate only a small selection of the results obtained and where appropriate we shall supplement these with additional comment in the text.

Although there have been many investigations (30–39) of the n-hexane reaction over Pt catalysts, it is known that the product distribution is dependent on the hydrogen partial pressure (39) so direct comparison with our results is impossible in most cases. Table 2 summarises the results obtained for our Pt/silica catalysts and compares these with typical results from the literature. There are some variations in the turnover number of our Pt/silica catalysts after the various treatments but otherwise the reduction conditions have little effect. The selectivity for hydrogenolysis is always close to 55% and the selectivity for the formation of each of the C_6 products (2MP, 3MP, and MCP) remains essentially constant. MCP is the main C_6 product, followed by 2MP.

Comparison with the results of Lankhorst et al. (31) (see Table 2) shows that the turnover number which we obtain is similar to their value. The apparent difference in selectivity for hydrogenolysis is due to the different method used to calculate the selectivity and can be ignored. However, there is a significant difference in the relative proportions of the C_6 products. Lankhorst et al. obtain a (2MP + 3MP):MCP ratio of 5.2:1 whereas we obtain an average ratio of 1.0:1. We have no unambiguous explanation for the higher selectivity of our catalysts for the formation of MCP. One possible reason may be found by considering the results obtained by Davis et al. (39) for Pt single crystals. (Note, however, that a hydrogen partial pressure effect

TABLE 2

The Activity and Selectivity of Pt Catalysts for the Isomerisation and
Hydrogenolysis of n-Hexane

Catalyst	Code[a]	H/Pt	Rate[b]	TON[c]	Selectivity[d]			
					$<C_6$	2MP	3MP	MCP
Pt2/Si	A	0.12	16.1	7.3	55.5	18.0	6.6	19.9
	B	0.17	4.8	1.5	55.2	15.5	6.5	22.8
	C	0.17	5.6	1.8	54.1	15.6	6.2	24.1
	D	0.17	8.3	2.7	52.5	16.8	6.6	24.1
Pt/SiO$_2$[e]				2.5	19	—68—		13
Pt(111)[f]					26	—42—		26
Pt(100)[f]					25	—29—		41

[a] See Table 1 for details of treatment.
[b] Rate at 563 K, units are millimoles n-hexane per gram Pt per hour.
[c] Turnover number, units are $10^3 \times$ molecules n-hexane per second per surface Pt atom.
[d] Expressed as percentage of all products formed.
[e] After Ref. (31), reaction temperature was 568 K.
[f] After Ref. (39), reaction temperature of 573 K.

needs to be taken into account since the single-crystal experiments were performed at low pressure.) These results, shown in Table 2, indicate that the selectivity for the formation of MCP is structure sensitive. More MCP is produced over Pt(100) surfaces than over Pt(111). Note also that the selectivity for the formation of all C_6 products (2MP + 3MP + MCP) is constant, an observation which may be significant with regard to our Pt/titania results (discussed later).

The variations in the product distribution as a function of temperature for our Pt/silica catalysts are shown in Fig. 1. At all temperatures propane is the major hydrogenolysis product although this is closely followed by methane with roughly equal amounts of ethane, butane, and pentane being formed. As the temperature is increased the selectivity for hydrogenolysis decreases and the selectivity for the formation of C_6 products increases. The selectivity for the formation of MCP increases most rapidly with temperature to the extent that MCP becomes the single most dominant product above about 550 K.

Pt/Titania Catalysts

Table 3 summarises the results obtained for the n-hexane reaction over our Pt/titania catalysts after the various treatments. After treatment A the Pt has a high dispersion. However, there is no clear evidence in the literature of a significant particle size effect for the n-hexane reaction over Pt catalysts so it is not surprising that this catalyst has a turnover number similar
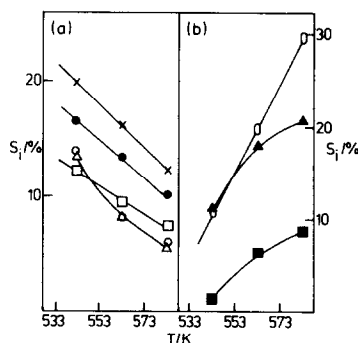

Fig. 1. Variations in the product distribution from the n-hexane reaction on Pt/silica catalysts as a function of the reaction temperature. (a) ●, C_1; ○, C_2; ×, C_3; △, C_4; □, C_5. (b) ▲, 2MP; ■, 3MP; 0, MCP.

TABLE 3

The Activity and Selectivity of Pt2/Ti Catalysts for
the Isomerisation and Hydrogenolysis of n-Hexane

Code[a]	H/Pt	Rate[b]	TON[c]	Selectivity[d]			
				<C_6	2MP	3MP	MCP
A	0.59	18.9	1.7	61.1	24.2	7.9	6.8
B	0.00	3.6	—	63.1	6.7	8.9	21.3
C	0.16	5.5	1.9	72.0	9.9	1.4	16.7
D	0.56	19.4	1.9	60.5	25.0	7.4	7.1
E	0.00	2.7	—	59.2	9.8	2.0	29.0
F	0.06	3.8	3.4	59.2	14.8	3.5	22.5
G	0.56	15.2	1.5	55.0	30.7	8.2	6.1

[a] See Table 1 for details of treatment procedures.

[b] Units are millimoles n-hexane per gram Pt per hour; the reaction temperature was 553 K.

[c] Turnover number, units are $10^3 \times$ molecules n-hexane per second per surface Pt atom.

[d] Expressed as percentage of all products formed.

to that of the Pt/silica catalysts shown in Table 2. On the other hand the product distribution is significantly different. After treatment A catalyst Pt2/Ti has a much higher selectivity for the formation of 2MP and a much lower selectivity for the formation of MCP. The (2MP + 3MP) : MCP ratio is 4.7 : 1 (compare 1.0 : 1 for our Pt2/Si catalyst). The selectivity of Pt2/Ti for the formation of hydrogenolysis products is only slightly higher (61% as compared with 55%).

After treatment A (Table 1), catalyst Pt2/Ti adsorbs hydrogen in a normal way. The H/Pt ratio corresponds to an average particle size of 1.9 nm which agrees well with the average particle size measured by TEM. Therefore, this catalyst contains "normal" Pt, i.e., there is no evidence of SMSI effects. This is further substantiated by the fact that the turnover number is the same as for the Pt/silica catalysts which are accepted as being free from SMSI. Nevertheless, our Pt/titania catalyst behaves differently from a Pt/silica catalysts studied under the same experimental conditions. The product distributions are sufficiently different to indicate the possible existence of a real support effect.

Further evidence of a support effect is found by comparing the effect of reaction

temperature on the product distribution for the Pt2/Ti catalyst (Fig. 2) with the corresponding results for the Pt2/Si catalyst (Fig. 1). Although there is a decrease in the selectivity for the formation of hydrogenolysis products as the temperature is increased this trend is much less obvious with the Pt2/Ti catalyst. Furthermore, propane is now by far the most important hydrogenolysis product and much less methane is produced. The relative proportions of the various C_6 products are also significantly different. At all temperatures 2MP is now the dominant C_6 product followed by 3MP and MCP in that order. It seems fairly clear that although the nature of the active centres in our Pt/silica and Pt/titania catalysts may not be very different (see activation energy data later) there is a substantial variation in the number of each type of active centre present.

Table 3 also contains the results obtained for catalyst Pt2/Ti after the various pretreatments. For simplicity we shall consider only the major changes in activity and selectivity. We note in passing only that although there are some variations in the selectivity for the formation of hydrogenolysis products as the treatment of the catalyst is changed the distribution of hydrogenolysis products, and the temperature dependence of the product distribution, are
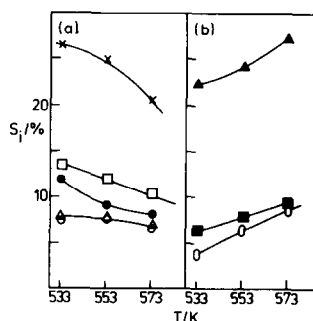

Fig. 2. Variations in the product distribution from the n-hexane reaction on Pt/titania catalysts, after treatment A (Table 1) as a function of the reaction temperature. (a) ●, C_1; ○, C_2; ×, C_3; △, C_4; □, C_5. (b) ▲, 2MP; ■, 3MP; 0, MCP.

in all cases very similar to those shown in Fig. 2a for catalyst Pt2/Ti after treatment A.

When the Pt2/Ti catalyst is reduced for 1 h at 773 K (treatment B) the capacity to adsorb hydrogen is totally eliminated. This catalyst is described by convention as being in the SMSI state. In this state metals generally become inactive for hydrocarbon reactions, particularly for hydrogenolysis reactions (8). This is indeed precisely what we have observed previously (26) for these same catalysts in the reaction of MCP where the activity declined by at least three orders of magnitude after treatment B.

Table 3 shows a remarkable result; namely, that after treatment B our Pt2/Ti catalyst retains a high activity for both hydrogenolysis and skeletal rearrangement reactions. Although the catalyst adsorbs no hydrogen, and therefore presumably has no Pt atoms accessible in the surface of the Pt particles, its activity is still 19% of its original value after treatment A. This retention of activity is paralleled by a retention of the selectivity for the formation of hydrogenolysis products. The only significant change in selectivity is in the formation of C_6 products. The catalyst after treatment B has a much lower selectivity for the formation of 2MP, a much higher selectivity for the formation of MCP, and essentially the same selectivity for the formation of 3MP.

Figure 3a shows the selectivity for the formation of each of the C_6 products as a function of reaction temperature for four different treatments. MCP is the major product and increases in importance as the reaction temperature is increased whereas 2MP and 3MP are minor products whose formation is almost independent of temperature. This should be contrasted with Fig. 2b which shows the strikingly different selectivity obtained after a prereduction at 573 K.

Some recovery of the capacity to adsorb hydrogen, and hence a partial reversal of the SMSI state, are achieved by exposing the catalyst after treatment B to oxygen at 298 K, followed by re-reduction for 1 h at
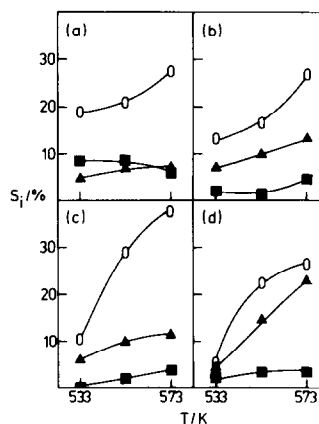

FIG. 3. Variations in the distribution of C_6 products from the n-hexane reaction on Pt/titania catalysts, after various treatments (Table 1), as a function of the reaction temperature. (a) After treatment B; (b) after treatment C; (c) after treatment E; (d) after treatment F. (▲) 2MP, (■) 3MP, (0) MCP.

573 K (treatment C). Table 3 shows that compared with treatment A this catalyst has recovered 27% of its hydrogen adsorption capacity and 29% of its activity. In consequence, the turnover number is again similar to its original value. In this intermediate state the catalyst has a slightly higher selectivity for hydrogenolysis but the major change is in the distribution of C_6 products (see Table 3 and Fig. 3b). MCP is still the major product but this is now followed by 2MP with only a small amount of 3MP being formed.

Treatment D is designed to return the catalyst to its original state after treatment A and Table 3 shows that this is indeed the case. The activity, turnover number, and product distribution all return to close to their original values.

When the catalyst is reduced at 773 K for 16 h (treatment E) it has characteristics similar to those obtained after treatment B (reduced for 1 h at 773 K). The adsorption of hydrogen is totally suppressed and yet the activity is still 14% of its value after treatment A. Table 3 and Fig. 3c show that the main effect of the longer reduction at 773 K is to increase the temperature depen-

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dence of the MCP selectivity and to sup-
press the selectivity for the formation of
3MP (compare Figs. 3a and 3c, treatments
B and E).

When the catalyst reduced at 773 K for
16 h is partially reoxidised by exposure to
oxygen at 298 K and then re-reduced for 1 h
at 573 K (treatment F) there is a smaller
recovery in the H/Pt ratio (10%) than that
found after the reoxidation/reduction of a
catalyst reduced for only 1 h at 773 K
(treatment C). Nevertheless, the same
trend in selectivity is observed in that the
formation of 2MP is increased mainly at the
expense of MCP (compare Figs. 3c and 3d).
Comparison of Figs. 3b and 3d shows that
the two catalysts in an intermediate state
(in terms of H/Pt ratios) have similar but
not identical selectivities for the formation
of each of the C_6 products.

Finally, when the catalyst is reoxidised at
673 K and re-reduced at 573 K, i.e., treat-
ment G, it returns to a state which is
substantially the same as that observed
after treatment A. The only significant dif-
ference is that rather more 2MP (30.7% as
compared with 24.7%) and rather less hy-
drogenolysis products (55.0% as compared
with 61.1%) are formed.

Activation Energies and Preexponential Terms for the n-Hexane Reaction

Some indication of how metal–support
interactions affect the nature of the catalyti-
cally active centres can occasionally be
obtained by an analysis of the activation
energies for the various types of reaction
under investigation. However, it is neces-
sary to consider the possible existence of a
compensation effect between the activation
energy and the preexponential term since
this can cancel out apparent differences in
the activation energy.

Figure 4 shows a compensation effect
plot for the n-hexane reaction over Pt cata-
lysts. It is clear for all the catalysts that all
the points for both the isomerisation and
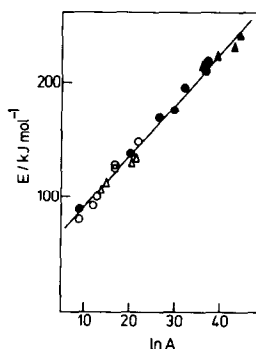hydrogenolysis reactions lie on the same

FIG. 4. Compensation effect plot of activation
energy versus preexponential term for the various
reactions over Pt catalysts. Hydrogenolysis reactions:
(△) Pt2/Si, (○) Pt2/Ti. Skeletal rearrangement reac-
tions: (▲) Pt2/Si, (●) Pt2/Ti.

straight line. The only conclusion which
may be drawn from these activation energy
data is that there is no significant change in
the nature of the active centres when Pt is
supported on titania rather than silica. The
variations in the product distributions ob-
tained with our Pt/silica and Pt/titania cata-
lysts, or brought about as a result of the
different treatments of the Pt/titania cata-
lysts, must arise because of a variation in
the relative numbers of active centres in
each case rather than in the character of the
active centres.

DISCUSSION

The main points to emerge from the
present investigation of the n-hexane reac-
tion over supported Pt catalysts are as
follows:

(a) The selectivity of our Pt/silica cata-
lysts for the formation of the various prod-
ucts (2MP, 3MP, or MCP) differs very
significantly ((2MP + 3MP) : MCP = 1 : 1)
from the selectivity previously reported
(31) for apparently equivalent catalysts
((2MP + 3MP) : MCP = 5 : 1). These differ-
ences in selectivity indicate the existence of
a support effect even with silica-supported
Pt catalysts. Comparison with the results
obtained (39) with Pt single-crystal surfaces

suggests a possible explanation, namely, that the reaction is structure sensitive and that the morphology of the Pt particles is dependent on the method of preparation and/or on the pretreatment of the catalysts. Caution is required, however, in applying this reasoning too rigidly because of the fact that small metal particles have such a small proportion of their surface atoms in flat planes. Other factors, such as a direct involvement of the support, need to be considered (see later discussion).

(b) Titania-supported Pt catalysts reduced at low temperatures have similar turnover numbers to Pt/silica catalysts. However, the product distribution is quite different, showing a higher selectivity for hydrogenolysis, especially for the formation of propane, and a much lower selectivity for the formation of MCP ((2MP + 3MP) : MCP = 4.7 : 1). Comparison with our Pt/silica catalysts shows the existence of a support effect. However, since the selectivity of our Pt/titania catalysts is similar to that of the Pt/silica catalysts studied by Lankhorst et al. (31) it is possible that the main effect of the support is to change the morphology of the Pt particles.

(c) When our Pt/titania catalysts are reduced at 773 K for 1 or 16 h to induce the SMSI state (total loss of hydrogen adsorption capacity) much of the activity for the n-hexane reaction is retained and the selectivity for the formation of hydrogenolysis products is hardly affected. The only significant change in catalytic properties is a sharp decrease in the selectivity for the formation of 2MP and a corresponding increase in the selectivity for the formation of MCP.

(d) Low temperature oxidation of the SMSI Pt/titania catalysts, which is designed to partially reverse the SMSI state, produces only a small increase in activity but further significant changes in selectivity. As compared with the SMSI catalyst, the catalyst in this intermediate state produces less MCP, more 2MP, and very much less 3MP.

The Mechanism of the Skeletal Rearrangement of n-Hexane over Pt Catalysts

Experimental evidence has demonstrated that the n-hexane reaction is unaffected by the Pt particle size in the range 1.5 to 8 nm (30, 31). However, with Pt catalysts containing very small (1-nm) Pt particles (33) or with ultrathin films (34) a higher activity is observed. These changes in catalytic behavior with the Pt particle size have been interpreted in terms of "C$_5$-cyclic" (40–42) and "bond-shift" mechanisms (42–45) which are thought to prevail, respectively, on very small and on large Pt particles.

The predominant mechanism operating with our Pt/silica and Pt/titania catalysts appears to be a C$_5$-cyclic rather than a bond shift mechanism.

The crucial point about the cyclic mechanism in the context of the present work is that this mechanism is believed to require only a single Pt atom (46, 47). The critical question then concerns the environment of the active Pt atom centre. Is it situated in a planar surface, or at an edge, or does it really not matter? We shall now consider how our results can provide some insight into the nature of the active centre required to catalyse the skeletal rearrangement of n-hexane by the nonselective cyclic mechanism.

A Model of the Active Centre for the n-Hexane Reaction over Pt Catalysts

The most remarkable observation made in the present work is that a Pt/titania catalyst which is totally incapable of adsorbing hydrogen (H/Pt reduced by at least two orders of magnitude) retains 19% of its activity both for the hydrogenolysis and the skeletal rearrangement of n-hexane. It seems highly probable, therefore, that the active centre must consist of only one Pt atom. (The number of larger groups of Pt atoms available must be exceptionally small.) It also seems very likely that this Pt atom is special and that in the original Pt

catalyst it was one of only a very few such atoms. It is difficult otherwise to understand how such a large fraction of the activity could be retained when such a small fraction of the Pt atoms is accessible. (It is worth noting here that separate experiments have confirmed that no additional Pt atoms become available to hydrogen even after exposure to the hydrogen/n-hexane mixture at the reaction temperature.)

A further important observation in the present work is that the selectivity for hydrogenolysis versus skeletal rearrangement, and the distribution of hydrogenolysis products, are unaffected by the treatment which leads to the loss of hydrogen adsorption capacity. The only significant change is in the relative proportions of the various C_6 products formed (see Table 3). This suggests to us that the active centre for all these reactions is one and the same single Pt atom. However, this is an atom whose precise catalytic properties are modified in a very subtle and delicate way by its local environment.

Figure 5 shows schematically why this may be possible. It is postulated that an n-hexane molecule adsorbs at a single Pt atom. If bond (1) forms and this is followed by desorption the product is MCP. Formation of bond (1) and simultaneous rupture of bond (2) or (3) lead, after desorption, to the
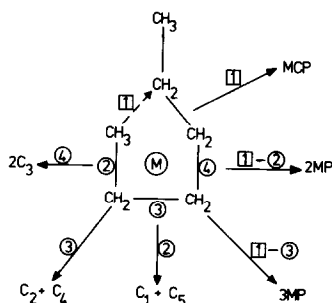
formation of 2MP or 3MP, respectively. Rupture of bond (2), (3), or (4) prior to the formation of bond (1) ultimately results in the formation of hydrogenolysis products. Which of the reactions shown in Fig. 5 occur will, we believe, be determined by the secondary influence of the environment of the central Pt atom.

There are a number of different ways in which the environment of a central, active Pt atom could modify its catalytic properties. These include allowing access even in a transitory way to an adjacent metal atom; the presence of a blocking layer of carbonaceous matter or, in the SMSI catalysts, of TiO_x species; and the direct involvement of an adsorbed or deposited species in binding the reactant molecule. However, since there is so little difference in the selectivity of Pt for hydrogenolysis versus isomerisation-plus-cyclisation irrespective of whether Pt is supported on silica or titania, or whether it is in the normal or in the SMSI state, we conclude that the factor which determines the catalytic properties of a central Pt atom must be essentially independent of the support, the degree of cleanliness, etc. However, the selectivity for the formation of MCP versus 2MP + 3MP is dependent on the pretreatment and on the support. This could be due to the influence of metal ions at the Pt–support interface, as discussed in the companion paper (29).

Paál and Menon (48) have demonstrated that there is a very strong hydrogen effect in hydrocarbon reactions. They have shown that the product distribution is dependent on the hydrogen partial pressure. We believe that a hydrogen effect offers the best explanation for our results. Examination of the reaction steps shown in Fig. 5 shows that the formation of MCP requires the removal of two H atoms, formation of 2MP or 3MP requires no net loss or gain of H atoms, and hydrogenolysis requires the addition of H atoms. What we propose, therefore, for our catalysts is that via the cyclic mechanism all these products may be formed but that the product(s) produced

Fig. 5. A possible mechanism for the reactions of n-hexane on a single Pt atom. Numbers indicate either the formation ([1]) or rupture ((2), (3), (4)) of C–C bonds. (M) indicates a single metal atom on which the n-hexane molecule is adsorbed in an unspecified manner.

from a specific n-hexane molecule depend on the availability of hydrogen atoms during the sojourn of the n-hexane molecule on the active centre. The availability of hydrogen would be determined by the local environment around the Pt atom of the active centre. For example, a carbonaceous deposit or a blocking layer of TiO_x could act as a reservoir of H atoms.

The final point to be considered is the location of the single active Pt atom. From the fact that almost all the surface Pt atoms can be prevented from adsorbing hydrogen without destroying the activity we suggest that the active centre consists of a Pt atom in a flat surface on a small Pt particle. We base this mainly on the expectation that TiO_x species will tend to bind most strongly at the highly coordinatively unsaturated edge sites of a small particle, with the result that these Pt atoms will be the most completely contaminated. In a small "spherical" particle (2 nm in diameter) the largest flat surface will consist of an equilateral triangle of close-packed atoms containing no more than four or five atoms along each side. This means that about 80–90% of the exposed Pt atoms is located in edges and only 10–20% in planes. It seems relevant that when our Pt/titania catalysts are reduced at 773 K for 1 h about 20% of the activity is retained. The most reasonable explanation of this result is to attribute the activity to isolated Pt atoms in the planes which are not covered by TiO_x. Many planes will contain only a single Pt atom which is not in an edge. This Pt atom could act as an active centre for the n-hexane reaction but because it consists of only a single Pt atom it may not be able to dissociate hydrogen at room temperature. Support for the proposal that the active centre comprises a Pt atom in a *plane* is found in the work of Somorjai and co-workers (*39, 49*).

When the SMSI catalyst is oxidised at 298 K and re-reduced at 573 K about 27% of the hydrogen adsorption capacity is recovered but the activity only increases by a small amount (see Table 3, treatments C and D). We believe that the recovery of adsorption capacity is due to the removal of some TiO_x from edge atoms on Pt particles. However, if these Pt atoms are not active for the n-hexane reaction there will be only a small recovery of the activity which, in fact, is what we observe.

The main conclusion from this research is that the active centre for the conversion of n-hexane into any product is probably a single Pt atom. The product(s) formed from each individual n-hexane molecule which adsorbs on this active centre depends on the balance between bond-making and bond-breaking reactions. It seems that a single Pt atom may be capable of performing all the reactions of n-hexane, including hydrogenolysis, but the product which is formed depends on the local environment of the Pt atom, which may sometimes include other Pt atoms, a carbonaceous residue, or a blocking layer of TiO_x.

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