

The Influence of Metal-Support Interactions on the Reaction of Methylcyclopentane over Supported Pt Catalysts

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Silica- and titania-supported Pt catalysts have been prepared and their reactivity in the hydrogenolysis of methylcyclopentane has been studied as a function of pretreatment. The Pt/silica catalysts are little affected by an increase in reduction temperature. When the Pt/titania catalysts are reduced at low temperature they have normal chemisorption properties. However, although the activity is similar to that of the Pt/silica catalysts, the product distributions are substantially different. In particular the Pt/titania catalysts are more selective for the formation of *n*-hexane. After reduction at high temperature the Pt/titania catalysts no longer adsorb hydrogen and the catalytic activity is totally eliminated. When a reoxidation is performed at 298 K there is a partial recovery of the hydrogen chemisorption capacity and the turnover number of the Pt returns to its original value. However, in this "intermediate" state the catalyst produces even more *n*-hexane and less 2-methylpentane. From an analysis of the activation energy data it is concluded that the nature of the active centres is not affected by reduction and reoxidation treatments. Instead, the change in product distribution appears to parallel a variation in the relative proportions of the various types of active centre present. The results are discussed in terms of various mechanisms for the methylcyclopentane reaction. It is concluded that the increased selectivity for the formation of *n*-hexane is consistent with a reaction at the metal-titania interface, possibly involving adsorption at a Pt-Ti³⁺ site. This site is believed to exist even in Pt/titania catalysts reduced at low temperatures. © 1987 Academic Press, Inc.

INTRODUCTION

The interaction between small metal particles and supposedly inert supports has been known for some time. The particular importance of the interfacial region as a centre of catalytic activity was first identified by Schwab and Pietsch (1) almost 60 years ago. After this original work there followed a succession of studies in which the importance of metal-support interactions was recognised (2, 3). In recent years interest in this topic has accelerated largely as a result of the studies by Tauster and co-workers (4-7) on metals supported on reducible oxides such as titanium dioxide. The concept of a strong metal-support interaction (SMSI) introduced by Tauster *et*

al. has become established in the vocabulary of catalysis even though there is now considerable doubt as to whether the effect as originally defined really exists. There is, nevertheless, indisputable evidence (8) that after reduction at high temperatures titania-supported metals have anomalous properties. This is attributed to partial encapsulation or decoration of the metal particles by TiO_x moieties which migrate from the support when heated in hydrogen at high temperatures (8).

The existence of these rather dramatic changes in character with heat treatment has tended to overshadow the fact that even after reduction at low temperatures titania-supported catalysts may have unusual catalytic properties. It has previously been shown (9, 10) for the CO/H₂ reaction that an enhanced activity occurs for cata-

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lysts which have normal chemisorption characteristics. In the case of hydrocarbon reactions the effect of creating the "full" SMSI state is generally to reduce or eliminate the catalytic activity (8). However, little attempt has been made to study hydrocarbon reactions over metals in a "partial" SMSI state, that is, where the metal is partially contaminated by TiO_x . Furthermore, few studies have been devoted to investigating the properties of titania-supported metals in the "normal" state after reduction at low temperatures. The work presented here is part of a wider investigation into the influence of metal-support interactions on the properties of titania-supported Pt group metals for reactions of hydrocarbons. A more detailed survey of the relevant literature is given in the succeeding paper (11).

EXPERIMENTAL

Catalyst Preparation

Catalysts were prepared using as supports silica gel (Davison Grade 57, surface area $300 \text{ m}^2 \text{ g}^{-1}$) and titania (Degussa P25, surface area $50 \text{ m}^2 \text{ g}^{-1}$, 80% anatase). The silica was ground and sieved (0.25- to 0.5-mm fraction retained) before use. The Pt catalysts (2% by wt) were prepared by wet impregnation using solutions of ammonium hexachloroplatinate, $(\text{NH}_4)_2\text{PtCl}_6$, in water, the pH of which was raised to 8 with 2 M NH_4OH solution to facilitate dispersion of the Pt. 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.

Catalyst Reduction and Reoxidation Procedures

Several different pretreatments were performed on the catalysts prior to the catalytic investigations. Table 1 gives the details.

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)

^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 $3.0 \times 10^5 \text{ cm}^3 \text{ g}_M^{-1}$. $AT(x)$ 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.

Chemisorption Measurements

The quantity of hydrogen chemisorbed by the Pt catalysts was determined after the various reduction treatments using a conventional glass volumetric apparatus. Equilibrium pressures were measured in the range 0–5 kPa and the monolayer coverage was estimated by back-extrapolation to zero pressure.

Catalytic Measurements

The catalytic properties of the samples were determined using a glass microreactor operating at atmospheric pressure. Methylcyclopentane (MCP) was introduced into the hydrogen stream using two bubblers in series. The first, held at room temperature, was filled with MCP; the second, held at 273 K, was filled with glass beads. Saturation of the hydrogen with MCP at 273 K gave a H_2 :MCP ratio of about 18:1 (MCP vapour pressure of 5.37 kPa). The H_2 flow rate was $1200 \text{ cm}^3 \text{ h}^{-1}$ and the MCP flow was $0.57 \text{ mol g}_{\text{Pt}}^{-1} \text{ h}^{-1}$. Measurements were made in the temperature range 483–563 K at intervals of 10 K starting at the lowest temperature. Samples of the products were

taken periodically and injected using a heated gas sampling valve into a Perkin-Elmer F33 gas chromatograph fitted with an FID detector. Separation of the reactant and products was achieved using a 6-m-long 20% silicone fluid on Chromosorb P column at 353 K. Peak areas were integrated using an LDC electronic integrator and the data were corrected to take into account the different response factors of the products using calibration factors previously determined with pure compounds. Conversions were kept below 10% to avoid problems due to the formation of secondary products.

The activities of the samples are expressed as conversions of MCP, the units being millimoles MCP 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,

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

RESULTS

Chemisorption and TEM Experiments

Table 2 summarises the results of the H_2 chemisorption experiments and the values of the average Pt particle sizes obtained from the chemisorption measurements and from TEM experiments. Figure 1 shows the particle size distribution obtained by TEM for the Pt/Ti catalysts after treatments A and D specified in Table 1. For the Pt/Si catalysts the results show that the Pt dispersion is relatively low after R573 and increases somewhat after R773. These catalysts were chosen to have low dispersions in order to minimise as far as possible any support effect due to the silica.

After R573 the Pt/Ti catalyst has a high dispersion (59%) and the calculated average particle size agrees quite well with the value obtained by TEM. Reduction at 773 K (treatment B) results in a catalyst which

TABLE 2
Hydrogen Chemisorption and TEM Data on Catalysts after Various Pretreatments

Catalyst	Pre-treatment	H/M	d_H^a (nm)	d_{TEM} (nm)
Pt/Si ^b	A	0.12	9.4	
Pt/Si	B	0.17	6.7	
Pt/Ti	A	0.59	1.9	1.4
Pt/Ti	B	<0.02	— ^c	
Pt/Ti	C	0.16	— ^c	
Pt/Ti	D	0.56	2.0	1.6

^a Calculated from H_2 chemisorption data assuming that the Pt particles are spherical.

^b Si indicates silica support, Ti indicates titania support.

^c Not determined because of the uncertainty of the chemisorption data.

adsorbs no detectable amount of H_2 even when the sample is left in contact with H_2 for 16 h. The catalyst is in the so-called SMSI state. After exposure to air at 298 K followed by R573 (treatment C) there is a partial recovery in the capacity to adsorb H_2 . A similar catalyst heated in air at 673 K followed by R573 (treatment D) almost totally recovers the H_2 adsorption capacity of the original fresh sample. The TEM results show (see Fig. 1) that there is a small shift in average particle size and particles smaller than 1 nm are no longer observed. Overall, however, there is little change in the dispersion or particle size as the catalyst is cycled through R773, reoxidation, and R573 treatments.

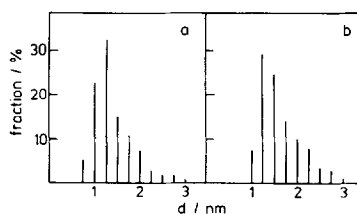


FIG. 1. Particle size distributions for Pt/Ti catalysts (a) after treatment A and (b) after treatment D.

TABLE 3
The Effect of Pretreatment Conditions on the Activity and Selectivity of Silica-Supported Pt Catalysts for the Hydrogenolysis of Methylcyclopentane

Code ^a	H/M	T ^b (K)	R ^c	TON ^d	Selectivity (%)			
					<C ₆ ^e	2MP	3MP	Hex
A	0.12	503	2.83	1.28	—	65.5	20.2	14.3
		523	9.74	4.40	—	62.5	21.6	15.9
		543	27.5	12.4	1.1	58.0	21.2	19.7
		553	41.94	18.94	1.0	55.7	21.3	22.0
B	0.17	503	2.66	0.85	—	62.6	20.0	17.6
		523	9.27	2.95	—	60.1	21.1	18.8
		543	24.1	7.68	0.9	58.2	20.8	21.0
		553	31.4	10.0	1.2	56.8	20.9	22.3
<i>f</i>	0.59	520	—	—	—	38	18	44
<i>f</i>	0.15	520	—	—	—	57	26	17
<i>f</i>	0.10	520	—	10	—	61	27	12

^a See Table 1 for details of catalyst pretreatment.

^b Reaction temperature.

^c Rate of MCP conversion, units are millimoles per gram Pt per hour.

^d Turnover number, units are $10^3 \times$ molecules MCP per second per surface Pt atom.

^e All products containing less than six C atoms (mostly methane).

^f After Refs. (12, 13).

Catalytic Experiments

Pt/Si. The activities and selectivities of the Pt/Si catalysts for the hydrogenolysis of MCP following treatments A and B are summarised in Table 3. Results very similar to those for B were obtained after treatments C and D so these have not been included in the table. Some results obtained by Kramer and Zuegg (12, 13) on model Pt/silica catalysts have been included for comparison. The turnover numbers (TON) of our catalysts agree within a factor of 3 with the value reported by Kramer and Zuegg. These differences are unlikely to have any real significance.

Table 3 also shows that the product distribution obtained with our catalysts is temperature dependent. As the temperature is raised the selectivity to 2-methylpentane (2MP) decreases and the selectivity to *n*-hexane (Hex) increases. There is little

change in the selectivity to 3-methylpentane (3MP).

The literature is somewhat confusing on the question of the temperature dependence of the selectivity. Table 4 summarises some relevant results. Gault (14) observed no temperature dependence in the temperature range 523–623 K for Pt/Al₂O₃ catalysts containing from 0.15 to 6% Pt, whereas Maire *et al.* (15) observed a strong temperature dependence for Pt/Al₂O₃ catalysts containing 1 or 10% Pt but no temperature dependence for a catalyst containing 0.2% Pt. Pt films (16) exhibit a significant effect of temperature with more hexane being produced at the higher temperature (see Table 4). The rationale for these apparent inconsistencies is believed to be related to particle size effects. Very small Pt particles have selectivities which are independent of temperature whereas large Pt particles have selectivities which vary with

TABLE 4

Variations in the Selectivity of Pt Catalysts in the Methylcyclopentane Reaction

Pt content	T^a (K)	Selectivity (%)			Reference
		2MP	3MP	Hex	
0.15	523-623	52.6	21.1	26.3	14
1	523-623	60.3	25.1	14.6	14
6	523-623	67.0	27.9	5.0	14
0.2	523-583	41.7	20.7	37.6	15
1	483	65.9	17.5	16.6	15
	514	61.2	19.5	19.3	15
	574	50.4	24.1	25.5	15
10	506	78.3	21.7	0.0	15
	548	71.7	24.1	4.2	16
	573	64.7	26.9	8.3	16
Film ^b	545	58.1	30.3	11.6	
	600	51.2	29.6	19.2	

^a Reaction temperatures.^b Normalised by setting all C₆ products = 100%.

temperature. Alternatively, the temperature dependence of the selectivity may reflect variations in the coverage with hydrogen as the temperature is increased (17).

The activation energies and preexponential terms obtained for each individual reaction over the Pt/Si catalysts are given in Table 5. There are some apparently significant variations in the activation energies, e.g., from 143.6 to 124.9 kJ mol⁻¹ for Hex formation as a function of catalyst pretreatment. There is, however, a compensating decrease in the preexponential term (see later discussion).

Pt/Ti. The activity and selectivity results obtained for the hydrogenolysis of MCP over titania-supported Pt catalysts are given in Table 6. It is immediately apparent that the method of pretreatment has a significant effect on the properties of the catalysts, unlike the silica-supported catalysts described above.

After reduction at 573 K (treatment A) the titania-supported catalyst has a TON which is the same within a factor of 2 of the TON of the silica-supported catalysts even though the dispersions of the two catalysts are very different (59 and 10%). From the limited amount of published work on the MCP reaction over Pt catalysts it appears

that the activity is essentially independent of particle size. Thus, Kramer and Zuegg (12, 13) observed only a factor of 2 change in TON when the dispersion of Pt on silica was varied from 10 to 59%. The direction of the change in activity was the same as that which we observe for our Pt/titania catalysts compared with our Pt/silica catalysts; i.e., the more highly dispersed Pt was found to be the most active.

This similarity between titania- and silica-supported Pt catalysts is restricted to the total activity for there are substantial differences in the product distribution over the two types of catalyst. In general, as compared with the Pt/Si catalyst the Pt/Ti catalysts produce rather less 2MP (about 8%) and more Hex (about 5% at 503 K). This can be attributed partly, but not entirely, to particle size effects (12, 13). Furthermore, the temperature dependence of the product distribution is exactly the reverse of that observed with Pt/Si. With Pt/Ti the selectivity to Hex decreases and the selectivity to 2MP increases as the reaction temperature is increased.

Figure 2 shows how the selectivity to Hex varies with temperature for various supported Pt catalysts. The unusual trend

TABLE 5

The Effect of Pretreatment on the Activation Energy and Preexponential Term for the Hydrogenolysis of Methylcyclopentane over Pt/Silica Catalysts

Product		Pretreatment			
		A	B	C	D
<C ₆	E^a	135	128	134	129
	$\ln A^b$	16.7	16.1	16.5	16.2
2MP	E	117	114	115	121
	$\ln A$	17.9	17.6	17.7	18.5
3MP	E	132	136	128	136
	$\ln A$	20.3	20.7	20.4	20.5
Hex	E	144	136	140	125
	$\ln A$	22.8	21.5	22.1	18.2

^a Activation energy, units are kilojoules per mole.^b Preexponential term.

TABLE 6

The Effect of Pretreatment Conditions on the Activity and Selectivity of Titania-Supported Pt Catalysts for the Hydrogenolysis of Methylcyclopentane

Code ^a	H/M	T ^b (K)	R ^c	TON ^d	Selectivity (%)			
					<C ₆ ^e	2MP	3MP	Hex
A	0.59	483	10.7	0.98	1.7	54.0	22.1	22.2
		503	36.4	3.34	1.8	57.3	21.5	19.4
		523	86.4	7.94	1.7	57.5	21.1	19.7
B	<0.01	523	0.0	—	—	—	—	—
C	0.16	483	3.95	1.34	2.6	45.0	18.9	33.5
		503	8.09	2.74	2.6	48.3	20.4	28.7
		523	23.9	8.08	2.7	51.9	20.3	25.1
D	0.48	483	7.19	0.72	4.9	52.9	18.7	23.5
		503	25.8	2.59	4.3	56.9	19.8	19.0
		523	72.5	7.27	3.3	57.8	20.5	18.4

^a See Table 1 for details of catalyst pretreatment.

^b Reaction temperature.

^c Rate of MCP reaction, units are millimoles per gram Pt per hour.

^d Turnover number, units are $10^3 \times$ molecules MCP per second per surface Pt atom.

^e All products containing less than six C atoms (mostly methane).

with Pt/Ti is apparent. It is clear that the MCP reaction over Pt is, in fact, a reaction which is essentially structure insensitive as regards total activity (the normal test of structure sensitivity) but may be structure sensitive as regards selectivity. We shall discuss these various points in detail later.

When Pt/Ti is reduced at 773 K (treatment B) the activity at 523 K for the MCP reaction is totally eliminated. This is the catalyst in the SMSI state; i.e., it is incapable of adsorbing H₂, so it might be expected to have a low activity. However, it would be dangerous to assume that this is always the case because this is an effect which is dependent on the type of reactant being studied. Thus, although MCP does not react over SMSI Pt the same catalyst retains a very substantial activity (about 20%) for the reaction of *n*-hexane (11). This fact needs to be taken into account when considering the mechanism of hydrocarbon reactions over Pt in the SMSI state.

When the SMSI catalyst is exposed to air at 298 K and then re-reduced at 573 K

(treatment C) there is a partial recovery in the H₂ chemisorption capacity (H/M = 0.16) and the catalytic activity also in-

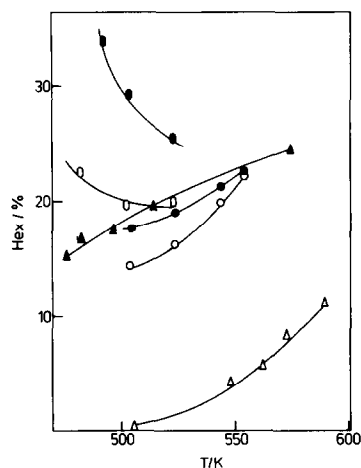


FIG. 2. Variation in the selectivity to *n*-hexane as a function of temperature for supported Pt catalysts. (●) Pt/Si after treatment A (this work); (○) Pt/Si after treatment B (this work); (●) Pt/Ti after treatment A (this work); (○) Pt/Ti after treatment C (this work); (▲) 1% Pt/alumina (Ref. (15)); (△) 10% Pt/alumina (Ref. (15)).

creases to the extent that the TON is now virtually identical to that of the original catalyst after treatment A (see Table 6). However, the product distribution is significantly different. After treatment C the Pt/Ti catalyst produces much more Hex and much less 2MP than the original fresh catalyst. The trend in selectivity with reaction temperature remains the same as that for the fresh Pt/Ti catalyst but the changes are now more apparent.

The activity and selectivity data for the MCP reaction following treatment D are essentially identical to those obtained following treatment A. This is to be expected since after treatment D the Pt/Ti has almost fully recovered its capacity to adsorb H_2 . However, these results provide a useful confirmation both that the original selectivities are reproducible after a reduction/oxidation/reduction cycle and also that the peculiar selectivity observed after treatment C is not an artefact due to some irreversible change in the nature of the Pt.

The activation energies and preexponential factors obtained from the Arrhenius plots for each type of reaction are given in Table 7 and compared with the correspond-

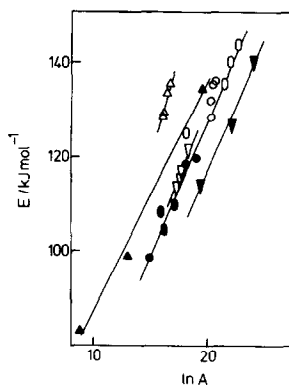


FIG. 3. Compensation effect plot for supported Pt catalysts in the MCP reaction. Pt/Si catalysts for (Δ) $<C_6$, (∇) 2MP, (\circ) 3MP, (\square) Hex. Pt/Ti catalysts for (\blacktriangle) $<C_6$, (\blacktriangledown) 2MP, (\bullet) 3MP, (\bullet) Hex.

ing data for the Pt/Si catalysts in Fig. 3. A compensation effect clearly exists. However, for most reactions the results for the Pt/Si and Pt/Ti catalysts lie on distinctly different lines. Thus, in the formation of cracked products ($<C_6$), 2MP or Hex, in each case the points for the Pt/Si catalysts lie above those for the Pt/Ti catalysts. For the conversion of MCP to 3MP the points lie approximately on the same line. This presumably reflects the fact that the selectivity to 3MP is the same for both types of catalyst and is independent of pretreatment or reaction temperature.

Comparison of the activation energies at constant values of $\ln A$ shows that for hydrogenolysis to form smaller hydrocarbon products and for the formation of 2MP the activation energy for Pt/Si is about 10 kJ mol^{-1} higher than for Pt/Ti. For the formation of Hex the activation energy for Pt/Si is about 5 kJ mol^{-1} higher. We draw two conclusions from these results. First, since the points for the different reactions over the Pt/Ti catalysts lie on three distinctly different lines (the 3MP and Hex points are indistinguishable) there are presumably at least three different types of active centre responsible for the reaction of MCP. Second, since the Pt/Si and Pt/Ti points lie on different lines, the nature of

TABLE 7

The Effect of Pretreatment on the Activation Energy and Preexponential Term for the Hydrogenolysis of Methylcyclopentane over Pt/Titania Catalysts

Product		Pretreatment			
		A	B	C	D
$<C_6$	E^a	83	— ^c	134	99
	$\ln A^b$	8.7	—	19.8	12.9
2MP	E	114	—	140	127
	$\ln A$	19.5	—	24.1	22.3
3MP	E	99	—	120	119
	$\ln A$	14.9	—	19.1	18.2
Hex	E	105	—	108	110
	$\ln A$	16.2	—	16.0	17.1

^a Activation energy, units are kilojoules per mole.

^b Preexponential term.

^c Values could not be calculated due to suppression of activity.

these active centres is different in the two types of catalyst. Finally, it is significant that for *each type of reaction* the points for all the Pt/Ti catalysts lie on the same compensation effect line. This suggests that the nature of the active centres in Pt/Ti is not affected by reduction at high temperatures. However, since the product distribution does vary with changes in the treatment procedure it would appear that the relative proportions of the various types of active centre vary with the pretreatment.

DISCUSSION

The MCP reaction provides a sensitive probe of metal-support effects because of the variety of products which may be formed. At the same time, however, the complexity of the reaction makes it particularly important to establish the characteristics of the reaction over normal catalysts before attempting to attribute changing patterns of selectivity to specific metal-support interactions. It is appropriate, therefore, to discuss first particle size effects and then support effects in the case of relatively inert supports before considering titania-supported Pt catalysts.

Particle size effects in the MCP reaction over Pt films (see Table 4), which presumably contain large Pt particles, produce relatively small amounts of Hex and large amounts of 2MP, and the selectivity to Hex increases with temperature. Comparison with a Pt/Si catalyst having a low dispersion (10%) (see Table 3, last row) shows that large Pt particles on silica give a very similar product distribution at a similar temperature. The consistency between these two types of Pt indicates that large Pt particles on silica are essentially unaffected by the support. When the Pt particle size is reduced the selectivity to Hex increases continuously to a value of 44% at 59% dispersion (see Table 3, row 9). There is a problem in interpreting this trend, however, because it is impossible to differentiate totally between a true particle size effect due to the inherent properties of

small particles and an apparent particle size effect due to effects at the metal-support interface as proposed by Kramer and Zuegg (12, 13, 18).

Support Effects in the MCP Reaction over Pt Catalysts

Figure 4 shows the variation in the selectivity for the formation of Hex from MCP as a function of Pt dispersion for various types of supported catalysts. The change in selectivity with particle size already referred to for Pt/SiO₂ catalysts is also observed for Al₂O₃- and MgO-supported Pt. As the dispersion is increased there is initially a rapid increase in selectivity but above a dispersion of about 50% the selectivity remains constant at about 40–45% Hex. However, for any chosen dispersion it is also clear that the Hex selectivity depends on the type of support. Kramer and Zuegg (12, 13, 18) have attributed this support effect to reaction at the metal-support interface with the acidity of the support affecting the proportion of Hex formed. By using different methods of preparation they have increased the acidity of the support and observed a parallel increase in the selectivity to Hex.

Support Effects over Pt/Titania Catalysts

Two observations from our work clearly indicate that titania influences the selectivity of Pt in the MCP reaction. It should be

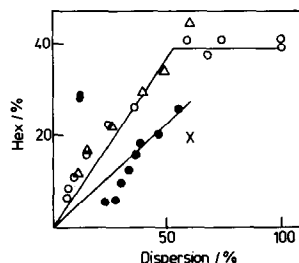


FIG. 4. Selectivity for the formation of *n*-hexane from MCP over supported Pt catalysts. (Δ) Pt/silica (after Ref. (13)); (\circ) Pt/alumina (after Ref. (27)); (\bullet) Pt/magnesia (after Ref. (13)); (\times) Pt/Ti after treatment A (this work); (\bullet) Pt/Ti after treatment C (this work).

emphasised that this statement holds for Pt/titania catalysts which are not in the SMSI state. The first observation is that the temperature dependence of the selectivity for the formation of Hex is exactly the opposite of that found with Pt film, Pt/SiO₂, or Pt/Al₂O₃ catalysts. The second unusual effect of titania is on the selectivity for the formation of hexane as a function of particle size. Figure 4 has shown that for a Pt dispersion of 59% (equivalent to our fresh Pt/Ti catalyst) the Hex selectivity would be expected to exceed 40%. Only over Pt/MgO catalysts is a selectivity below 40% observed. As indicated above, Kramer and Zuegg have associated these support effects with the acidity of the support. However, it is difficult to imagine that titania would be more basic than MgO so a more subtle support effect seems to operate.

As far as is known our Pt/Ti catalyst after treatment A (R573 for 1 h) is not affected by SMSI. Nevertheless, the Pt is only about half as selective at forming hexane as any other Pt catalyst of equivalent dispersion. If Kramer and Zuegg are correct in attributing the formation of hexane to reaction of MCP at the Pt-support interface (the adlineation theory—see later discussion), then the Pt-titania interface is singularly inefficient at forming hexane.

When our Pt/Ti catalyst is reduced at high temperatures to induce the SMSI state all activity is lost. When the SMSI state is partially removed by oxidation at 298 K the catalyst then has the same turnover number as originally. However, the selectivity to hexane is increased significantly. If we assume for the moment that the H/M ratio of this catalyst is a measure of the apparent dispersion of the Pt after treatment C we would find that the hexane selectivity (25%) lies above the lines for all other Pt catalysts (see Fig. 4). On the other hand if we take account of the trend in hexane selectivity with particle size we see that after treatment C the Pt/Ti catalyst appears to have a higher dispersion; i.e., it has a higher hexane selectivity. If hexane is produced pre-

dominantly at the Pt-titania interface then this increase in selectivity would be consistent with the currently accepted model of SMSI in which a TiO_x species is believed to migrate over the metal surface. This would create more new "interfaces" on top of the Pt particles. Even though after treatment C about 70% of the Pt in our catalyst is inaccessible for hydrogen adsorption the remaining 30% will retain its activity. However, the proportion of Pt atoms at the interface will be increased and so, therefore, will the selectivity for the formation of hexane.

The Mechanism of the MCP Reaction over Pt Catalysts

Much work has been performed on the hydrogenolysis of MCP over Pt catalysts, both supported (12–21) and unsupported (16, 17, 22, 23). Kazanskii *et al.* (24–26) have shown that over Pt/charcoal catalysts the cyclic bonds of a number of substituted cyclopentanes are broken selectively. Gault (14) has investigated the effect of metal loading for Pt/Al₂O₃ catalysts on the selectivity. On catalysts with a high metal content (6% or above) selective hydrogenolysis occurred, giving mostly 2MP and 3MP (the selective mechanism). However, when the metal content was low (0.6% or less) the five cyclic bonds were almost equally easily broken (nonselective mechanism). On catalysts with metal loadings between 0.6 and 6% intermediate behaviour was observed and attributed to a mixture of both mechanisms. Subsequent work led to the belief that this difference in selectivity was due to a particle size effect. It was postulated that several MCP molecules were adsorbed simultaneously on larger particles so that adsorption at the secondary-tertiary C–C bonds was sterically hindered thus favouring selective hydrogenolysis.

The relative proportions of 3MP and Hex ($R = 3MP/Hex$) in the products are taken as an indication of the amounts of selective and nonselective mechanism occurring.

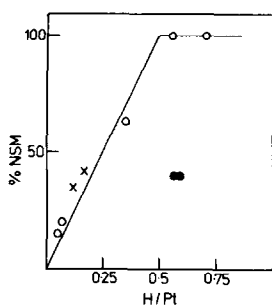


FIG. 5. Variation in the percentage nonselective mechanism as a function of Pt dispersion. (○) Pt/alumina (after Ref. (20)); (×) Pt/Si (this work); (●) Pt/Ti (this work).

Luck *et al.* (27) have extended the earlier work on Pt/Al₂O₃ catalysts to include a wide range of particle sizes and have derived a relationship which allows the percentage of nonselective hydrogenolysis (x) to be calculated from the 3MP/Hex ratio:

$$x = (0.22 \times 100)/(0.43R + 0.05).$$

In these studies the interpretation of the different mechanisms was given in terms of simple geometric effects related to particle size distributions. The support was not believed to affect the reaction.

However, as discussed above, Kramer and Zuegg (12, 13, 18) have observed a support effect and have proposed that the nonselective formation of *n*-hexane occurs at the metal-support interface. The previous suggestion by Maire *et al.* (19) that the product distribution was essentially independent of the type of support was correct but incomplete because it was based on the fact that the catalysts studied had either very high or very low dispersions. At these extremes the percentages of selective mechanism are 0 and 100%, respectively, for all supports, so it is not surprising that support effects were not detected. Figure 5 shows the variation in the percentage of nonselective mechanism with Pt dispersion over Pt/Al₂O₃ catalysts (20) and over our Pt/Si and Pt/Ti catalysts, calculated using the relationship derived by Luck *et al.* (27).

Both our Pt/Si catalysts fit closely on the curve through the Pt/Al₂O₃ points. However, with the "normal" Pt/Ti catalysts the nonselective mechanism makes a much smaller contribution than would be expected for Pt catalysts having this dispersion.

Gault and co-workers (15, 20, 28) have postulated three mechanisms (A, B, and C) for the hydrogenolysis of MCP over Pt catalysts (see Fig. 6). Mechanism A, the nonselective reaction, produces 2MP, 3MP, and Hex in the statistical ratios 40:20:40. To account for the equal probability of breaking each of the five cyclic bonds the proposed mechanism (Fig. 6a) involved an α - β diadsorbed species (an adsorbed π -olefin) as an intermediate. It was proposed that this intermediate was bonded to a single Pt atom so that the reaction could proceed on very small Pt particles.

Mechanism B, the selective mechanism, leads only to the formation of 2MP and 3MP (Fig. 6b). To account for the absence of *n*-hexane the mechanism postulates the formation of an $\alpha\alpha,\beta\beta$ -tetraadsorbed species (or 1,2-carbene) as an intermediate. For certain catalysts of intermediate dispersion Maire *et al.* (15) found that the product distribution could not be accounted for by a simple combination of mechanisms A and B. A third mechanism (C), the partially

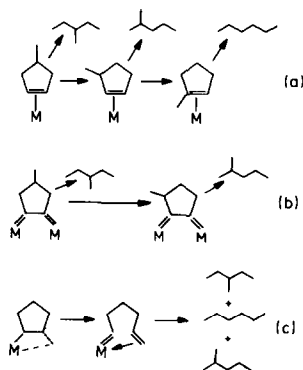


FIG. 6. Reaction mechanisms for the hydrogenolysis of MCP (15, 20, 28).

selective mechanism, was postulated (Fig. 6c). This mechanism involves breaking mainly di-secondary bonds but also some secondary-tertiary bonds giving mainly 2MP and 3MP and a little Hex. The proposed mechanism involves an $\alpha\gamma$ -diadsorbed species (or metallacyclobutane) as an intermediate.

All these mechanisms were deemed to occur on the Pt metal surface, and the active centres were described in purely geometric terms. Mechanisms A and C were thought to occur on corner atoms and mechanism B on edge atoms. However, from the work of Kramer and Zuegg previously mentioned it is evident that the support does play a role in directing the MCP reaction. Kramer and Zuegg have considered only two mechanisms (A and B as above) but have suggested that the former (which produces *n*-hexane) occurs at the metal-support interface and the latter on the surface of the Pt particles. The activity of the interface site appears to depend on the acidity of the support in that more *n*-hexane is formed when acidic supports are used. As an alternative to the purely geometric model discussed earlier Kramer and Zuegg reintroduced the concept of adlineation, originally advocated by Schwab and Pietsch (1), to account for the apparent particle size effects. In support of this model it has been observed that the fraction of *n*-hexane produced increases linearly with the metal dispersion over wide ranges (see Fig. 4). Above a dispersion of about 55% the nonselective mechanism is completely dominant. This has been explained on the basis that this threshold corresponds to Pt particles with an average diameter of only 1.8 nm and that mechanism B (which occurs via an $\alpha\alpha,\beta\beta$ -tetraadsorbed intermediate) requires particles of at least this size for the reaction to proceed.

Possible Mechanisms over Titania-Supported Pt Catalysts

Let us first reiterate the fact that all our Pt/Ti catalysts are different from any other

Pt catalysts. The creation of the SMSI state and its partial reversal modifies the properties of the catalyst but this is not an essential prerequisite. Even a catalyst reduced under mild conditions behaves quite differently from, say, a Pt/silica catalyst of similar dispersion.

Of all the mechanisms and models proposed for the MCP reaction over Pt the adlineation model suggested by Kramer and Zuegg appears to explain most satisfactorily our results with titania-supported catalysts. To take account of our results we need only to modify their model and attribute the special activity of sites at the metal-support interface to the influence of a cationic rather than an acidic site on the support. This circumvents the problem of having to classify titania as more basic than MgO (see earlier discussion).

This model, which is similar to one which we have proposed previously to account for the enhanced activity of titania-supported catalysts for the CO/H₂ reactions (9, 10), places special emphasis on interfacial sites comprising a metal atom and a Ti³⁺ cation exposed in the surface of the support adjacent to a metal particle. Figure 7a illustrates the proposed model. It is, of course, impossible to differentiate between a direct interaction as shown and an indirect effect brought about by a perturbation of the geometric structure or electronic properties of the metal atoms at the interface which

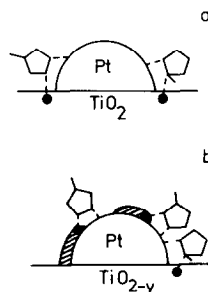


FIG. 7. Proposed mechanism for the nonselective hydrogenolysis of MCP over Pt/Ti catalysts. (a) Pt in the non-SMSI state; (b) Pt in the SMSI state. (●) Ti³⁺; (▨) TiO_x.

would cause the metal atoms themselves to acquire different characteristics.

Evidence in support of the influence of the titania in the MCP reaction can be summarised as follows. When compared with Pt/silica we find for Pt/titania catalysts that the selectivity is different, the dependence of the selectivity on particle size is different, the dependence of the product distribution on temperature is different, and the activation energy for the formation of each type of product is different. There seems little doubt that a real support effect exists in these catalysts.

When one of our catalysts is reduced at high temperature, partially oxidised at 298 K, and then reduced at 573 K only a part (30%) of the Pt recovers its original capacity to adsorb H_2 . Undoubtedly this intermediate state comprises several different types of Pt particle. Some particles may still be fully covered by TiO_x , others may be completely uncovered, while still others may be partially contaminated. The overall effect would be expected to be an increase in the proportion of metal-support interface since any TiO_x on top of a Pt particle creates new "interface." Figure 7b illustrates how this might occur. According to the adlineation model this should result in an increased contribution from the nonselective reaction leading to the formation of proportionately more *n*-hexane. This is, in fact, precisely what we observe. Our catalysts after treatment C appear to consist of smaller Pt particles than the original catalyst after treatment A even though there is TEM evidence that the particle size is largely unaffected by treatment C.

Another interesting feature of the Pt/Ti catalysts is that the turnover number is the same for clean and TiO_x -contaminated Pt even though the selectivity is different, which indicates that the TiO_x does not simply totally poison a fraction of the Pt leaving the remainder unaltered. Since it seems likely that TiO_x moieties will be well dispersed over the Pt surface this implies that the various active centres for the MCP

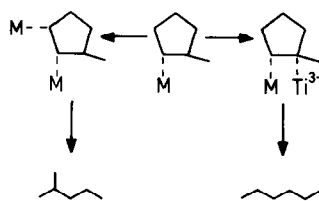


FIG. 8. Possible mechanism to explain the interrelationship of the formation of *n*-hexane and 2-methylpentane over Pt/titania catalysts.

reaction consist of small numbers of Pt atoms (perhaps one or two at most).

The one remaining question is to ask how and why the formation of hexane is facilitated by an interfacial site. From our results we observe that the selectivity to (2MP + Hex) is almost constant for all catalysts at all temperatures. This suggests that the formation of these two products is interlinked, i.e., that there is an active centre at which either 2MP or Hex is formed but not 3MP. One way in which this might occur is shown in Fig. 8. A MCP molecule first adsorbs by forming an $M-C$ bond to the C atom adjacent to the C attached to the methyl group. A second bond then forms to a second C atom, either the tertiary C atom (if the first metal atom is adjacent to a cation in the support) or the next secondary C atom (if a second metal atom is available adjacent to the first). Kramer and Zuegg have already suggested a reason why the H atom attached to the tertiary C atom should be most easily removed by an acidic site (13). This H atom is the most easily ionised so it will be most susceptible to attack by an acidic or cationic site on the support. The tendency to produce *n*-hexane will depend on the relative proportions of $M-Ti^{3+}$ and $M-M$ sites available to the MCP. One can easily envisage the initially monoadsorbed MCP oscillating from side to side until one or other of the second bonds is formed.

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