# Influence of Metal–Support Interactions on the Hydrogenolysis of Methylcyclopentane over Supported Rh Catalysts

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Titania- and silica-supported Rh catalysts have been prepared, pretreated in various ways and their activity and selectivity for the hydrogenolysis of methylcyclopentane determined. Over Rh/silica catalysts the major products are 2-methylpentane and 3-methylpentane. When Rh/titania catalysts are reduced at low temperatures the product distribution differs from that obtained over Rh/silica. More n-hexane is formed and the temperature dependence of the product distribution is different. The results provide evidence of a real support effect. The most remarkable result obtained is that after reduction of the titania-supported catalysts at high temperatures, which leads to a suppression of hydrogen adsorption due to contamination of the Rh by  $TiO_x$ , the activity of the Rh remains high. The product distribution, in contrast, is only slightly modified. When the catalyst reduced at high temperature is partially oxidised by exposure to oxygen at 298 K ca. 50%of the Rh surface is freed from contamination. However, the activity and turnover numbers decrease as a result of this treatment. It is concluded that only a small fraction of the surface Rh atoms have high turnover numbers for the methylcyclopentane reaction. It is suggested that the active centre is a small Rh ensemble (1 or 2 Rh atoms) in a planar surface.

The importance of metal-support interactions, particularly at the metal-support interface, was first recognised by Schwab and Pietsch<sup>1</sup> almost 60 years ago. Subsequent research has confirmed that metal-support interactions are а general phenomenon.<sup>2, 3</sup> Interest in this topic has increased in recent years since it was reported by Tauster and co-workers<sup>4-7</sup> that after reduction at high temperatures metals supported on reducible oxides developed unusual properties. The term 'strong metalsupport interaction' (SMSI) was introduced to describe these effects, and the origin of the anomaly was thought to be an exchange of electrons between a small metal particle and a reduced cation in the support surface. There is now some doubt whether this effect as originally defined really exists, and the consequences of reduction at high temperatures are now generally attributed to partial encapsulation or decoration of the metal particles by  $MO_r$  species which migrate from the support.<sup>8</sup>

The main consequences of SMSI are a large decrease in the capacity to adsorb hydrogen and a dramatic loss of catalytic activity for hydrocarbon reactions. These results are easy to understand on the basis of surface contamination effects. A feature of these catalysts which is less well recognised or understood is that even after reduction at low temperatures such catalysts may exhibit anomalous behaviour. In the CO-H<sub>2</sub> reaction, for example, it has been shown<sup>9</sup> that enhanced activity occurs for titaniasupported catalysts which retain completely normal adsorption characteristics. So far

# Hydrogenolysis of Methylcyclopentane over Rh Table 1. Catalyst reduction and reoxidation

procedures

code	treatment <sup>a</sup>
Δ	<b>R 573</b> (1)
B	R773(1)
С	R773(1)/A298(1)/R573(1)
D	R773(1)/A673(1)/R573(1)
Ε	R773(16)
F	R773(16)/A298(1)/R573(1)
G	R773(16)/A673(1)/R573(1)

<sup>a</sup> 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<sup>-1</sup> and the H<sub>2</sub> flow was  $3.0 \times 10^5$  cm<sup>3</sup> g<sub>M</sub><sup>-1</sup>. 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<sub>2</sub> for 15 min.

little attempt has been made to investigate hydrocarbon reactions over catalysts in an intermediate state, *i.e.* where the metal is partially contaminated by the support. Such studies are inherently valuable because of the insight they may provide into the mechanism of hydrocarbon reactions and the nature of active centres.

A further important feature of SMSI catalysts is that each metal behaves in a distinctive manner.<sup>10</sup> Thus Pt very easily enters the SMSI state and reversal is difficult. On the other hand, it is very difficult to put Rh into the SMSI state, but reversal is comparatively facile. It is of interest to compare the catalytic properties of such metals under conditions where the activity is modified but not eliminated (partial SMSI state) and for reactions which by their complexity afford a sensitive probe of changes in the nature of the active centres as a result of various reduction treatments. The results presented here for the reaction of methylcyclopentane (MCP) over titania-supported Rh catalysts form part of a general study of metal–support interactions.

# **Experimental**

Catalysts (2% or 5% Rh by wt) were prepared by wet impregnation of silica gel (Davison grade 57, surface area 300 m<sup>2</sup> g<sup>-1</sup>) and titania (Degussa P25, surface area 50 m<sup>2</sup> g<sup>-1</sup>, 80% anatase) supports using aqueous solutions (pH 8) of rhodium(III) chloride. The silica was ground and sieved (0.25–0.5 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 and then calcined in flowing oxygen by heating at 10 K min<sup>-1</sup> to 673 K and holding at this temperature for 1 h. Prior to the catalytic measurements the catalysts were pretreated in a variety of different ways, details of which are given in table 1.

The amount of hydrogen chemisorbed by the Rh catalysts after the various reduction treatments was determined using a conventional glass volumetric apparatus. Equilibrium pressures in the range 0-5 kPa were measured using a pressure transducer (Bell and Howell) and the monolayer coverage estimated by back-extrapolation to zero pressure.

The catalytic properties of the samples were determined at atmospheric pressure using a glass microreactor. MCP was introduced into the hydrogen stream using two bubblers,

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catalyst	pretreatment	H/M	$d_{ m H}/{ m nm}^a$	$d_{\rm TEM}/{\rm nm}$
Rh2/Si <sup>b</sup>	Α	0.22	5.0	
Rh2/Si	В	0.26	4.2	
Rh2/Ti	Α	0.59	1.9	1.4
Rh2/Ti	В	0.04	c	
Rh2/Ti	С	0.30	c	
Rh2/Ti	D	0.47	2.4	1.6
Rh2/Ti	Ε	0.02	c	
Rh2/Ti	F	0.24	c	
Rh2/Ti	G	0.46	2.4	
Rh5/Ti	Α	0.27	4.2	
Rh5/Ti	В	0.04	c	

 
 Table 2. Hydrogen chemisorption and TEM data on Rh catalysts after various pretreatments

<sup>a</sup> Calculated from  $H_2$  chemisorption data assuming that the Rh particles are spherical. <sup>b</sup> The numbers indicate the Rh content (wt%), Si indicates silica support, Ti indicates titania support. <sup>c</sup> Not determined because of the uncertainty of the chemisorption data.

the second of which was held at 273 K to give an  $H_2/MCP$  ratio of *ca.* 18:1 (MCP vapour pressure of 5.37 kPa). The  $H_2$  flow rate was 1200 cm<sup>3</sup> h<sup>-1</sup> and the MCP flow was 0.57 mol  $g_{Rh}^{-1}$  h<sup>-1</sup>. Measurements were made in the temperature range 373–433 K at intervals of 10 K starting at the lowest temperature. Samples of the products were injected, using a heated gas sampling valve, into a Perkin-Elmer F33 GC fitted with an FID detector and a 6 m 20% silicone fluid on Chromosorb P column thermostatted at 353 K. Peak areas were integrated using an LDC electronic integrator and the data were corrected to take account of the different response factors of the products.

The activities of the samples are expressed as conversions of MCP, the units being mmol MCP converted  $g_{Rh}^{-1}$  h<sup>-1</sup>. 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 Measurements**

 $H_2$  chemisorption was used to monitor changes in the nature of the catalysts following the various pretreatments. These were supplemented by TEM measurements on selected samples. The results are summarised in table 2. The Rh2/Si catalysts have a low dispersion which appears to increase slightly as the reduction temperature is increased. The Rh5/Ti catalyst after R573 has a similar dispersion to the Rh2/Si catalysts and so provides a useful catalyst for comparing support effects. The Rh2/Ti catalyst has a high dispersion after R573, and the calculated average particle size compares reasonably well with the value obtained by TEM. After R773 for 1 h this catalyst still adsorbs a small amount of  $H_2$  (ca. 7%). Even after R773 for 16 h some capacity to adsorb  $H_2$  is retained (3.5%). When the catalysts are exposed to air at 298 K there is marked recovery in adsorption capacity (50% for a catalyst reduced for 1 h at 773; 40% for a catalyst reduced at 773 K for 16 h). Re-oxidation for 1 h at 673 K (treatments D and G) almost fully

						selectivity (%)		
$code^a$	H/M	$T/\mathbf{K}^{b}$	$R^c$	TON <sup>d</sup>	< C6 <sup>e</sup>	2MP	3MP	Hex
 Α	0.22	403	12.9	1.7		71.7	28.3	0.0
		423	37.3	4.4	2.1	70.0	26.3	1.6
		443	85.4	11.1	4.3	68.1	25.0	1.9 <sup>f</sup>
В	0.26	403	10.9	1.2		70.4	24.8	4.8
		423	37.5	4.2	1.1	68.4	23.6	6.9
		443	91.7	10.0	2.0	68.5	23.0	$6.1^{g}$
h	0.25	480			0.3	74.5	23.8	1.7
i	0.24	496				64.7	26.1	3.6

 Table 3. The effect of pretreatment conditions on the activity and selectivity of Rh/silica catalysts for the hydrogenolysis of methylcyclopentane

<sup>*a*</sup> See table 1 for details of catalyst pretreatment. <sup>*b*</sup> Reaction temperature. <sup>*c*</sup> Rate of MCP conversion, units are mmol  $g_{Rh}^{-1}h^{-1}$ . <sup>*d*</sup> Turnover number, units are 10<sup>3</sup> molecule MCP s<sup>-1</sup> (surface Rh atom)<sup>-1</sup>. <sup>*e*</sup> All products containing less than 6 C atoms. <sup>*f*</sup> 0.7% Benzene also produced. <sup>*g*</sup> 0.4% Benzene also produced. <sup>*h*</sup> 2% Rh/silica catalyst, after ref. (11). <sup>*i*</sup> 4.4% Rh/silica catalyst, after ref. (12).

restores the ability of the Rh to adsorb  $H_2$ . (The lower H/Rh values obtained reflect a degree of sintering. This is confirmed by the TEM results, which show the elimination of Rh particles smaller than 1 nm). The limited results available for the 5% Rh/titania catalyst show similar behaviour. For convenience we shall describe catalysts after treatments A, D or G as 'normal' and after treatments B, C, E or F as in a 'partial' SMSI state.

# **Catalytic Experiments**

#### **Rh/Si** Catalysts

Table 3 contains the activity and selectivity results for the hydrogenolysis of MCP over our Rh/silica catalysts. The major product in all cases is 2-methylpentene (2MP). Very little n-hexane (Hex) is formed, but the selectivity to Hex increases with the reaction temperature and appears to be higher for a slightly better-dispersed catalyst.

Few investigations into the hydrogenolysis of MCP over Rh catalysts have been reported, so it is difficult to make reliable comparisons. Table 3 includes some results for Rh/silica catalysts having dispersions comparable to our catalysts. These show some similarities in that 3-methylpentane (3MP) is the major product and little Hex is formed. However, the reaction temperature has a major influence on the product distribution but no consistent effect is observed. Thus as the temperature is increased we observe a decrease in the selectivity to 2MP and 3MP and an increase in selectivity to Hex. Schepers et al.<sup>11</sup> report a decrease in selectivity to 2MP and an increase in selectivity to Hex but an increase in selectivity to 3MP. Del Angel et al.<sup>12</sup> report that 'the selectivity to Hex tends to decrease when the temperature increases'.

Equally confusing are the reported effects of Rh particle size on the activity and selectivity. Del Angel *et al.*<sup>12</sup> report that the turnover number decreases with increasing particle size for Rh/silica catalysts but increases with particle size for Rh/alumina catalysts, which they attribute to a direct support effect (*i.e.* the support modifies the properties of the Rh particles). With regard to the selectivity no clear pattern emerges<sup>12</sup> other than that with Rh/alumina catalysts rather more Hex seems to be formed over highly dispersed catalysts.

					selectivity (%)			
$code^a$	H/M	$T/K^b$	R <sup>c</sup>	TON <sup>d</sup>	< C6 <sup>e</sup>	2MP	3MP	Hex
Α	0.27	383	2.4	0.3		64.7	25.5	9.8
		403	9.7	1.0	2.1	65.1	25.4	7.4
		423	30.7	3.3	3.5	65.0	26.6	4.9
В	0.04	383	0.3	0.2		69.0	28.3	3.5
-		403	2.2	1.5		67.9	24.2	7.8
		423	9.8	7.0	1.4	65.0	23.8	9.8
С		423	2.6			63.6	28.6	7.8
Ď		383	1.2			62.3	23.7	14.0
2		403	8.3			63.9	22.3	13.8
		423	29.8			64.7	23.9	11.4
E	0.02	423	0.7	0.7		75.4	24.1	0.5
Ē		423	2.2			64.9	31.4	3.7
Ġ		383	1.5			64.4	24.9	10.7
U		403	10.4			68.5	24.7	6.7
		423	33.3			68.5	24.9	5.7

 Table 4. The effect of pretreatment conditions on the activity and selectivity of 5% Rh/titania catalysts for the hydrogenolysis of methylcyclopentane

a-e See table 3.

If we compare our results with those of Schepers *et al.*<sup>11</sup> for an Rh catalyst of similar dispersion and if we allow for the differences in the reaction temperatures, we find that our catalysts produce less 2MP, more 3MP and more Hex. We have no explanation for this difference in properties. Clearly, the selectivity of Rh for the MCP reaction is dependent on the precise chemical and physical nature of the catalyst but is not related in any simple way to parameters such as particle size, type of support or reaction temperature.

## Rh5/Ti Catalysts

The activity and selectivity results for the reaction of MCP over our 5% Rh/titania catalysts are given in table 4. After treatment A this catalyst has essentially the same TON as our Rh2/Si catalyst (see table 3). Slightly less 2MP and slightly more Hex is produced over the Rh5/Ti catalyst. However, the product distributions of the two catalysts differ mainly because the selectivity to Hex increases with temperature for Rh2/Si but decreases with temperature for Rh5/Ti. Rh/titania thus behaves more like Rh/alumina<sup>12</sup> than Rh/silica.

After reduction for 1 h at 773 K (treatment B) catalyst Rh5/Ti loses much of its activity. However, the TON actually increases. After reduction for 16 h at 773 K (treatment E) when the H/Rh ratio is down to 0.02 even the TON declines. The catalyst with H/Rh = 0.04 (in a partial SMSI state) has lost 85% of its capacity to adsorb  $H_2$ , yet its specific activity is higher than that of a clean fresh Rh catalyst. In this partial SMSI state the Hex selectivity increases with temperature. (Compare Rh2/Si and contrast Rh5/Ti after treatment A.) We shall discuss later the implications of these observations as regards the active centres for the MCP reaction over Rh.

When catalyst Rh5/Ti is exposed to air at 298 K and re-reduced at 573 K (a procedure which substantially reverses the SMSI state) a remarkable transformation occurs. The activity of the catalyst actually declines by at least a factor of four. After a re-oxidation at 673 K (treatment D or G) the catalyst recovers all its original activity but the selectivity

code <sup>a</sup>	H/M	$T/\mathbf{K}^{b}$	<b>R</b> <sup>c</sup>	TON <sup>d</sup>	< C6 <sup>e</sup>	2MP	3MP	Hex
Α	0.59	383	4.6	0.22	11.0	59.4	23.5	6.1
		403	25.6	1.24	4.4	66.8	25.1	3.7
		423	71.2	3.5	3.9	67.3	25.9	2.9
В	0.04	383	0.6	0.4	49.4	23.3	23.1	4.2
		403	4.1	2.9	17.7	57.0	22.5	2.8
		423	25.6	18.3	3.5	68.3	24.9	3.3
С	0.30	403	1.2	0.1	42.0	41.1	16.6	
		423	10.3	1.0	7.2	63.1	26.1	3.6
D	0.46	383	3.2	0.2	10.9	63.3	25.8	
		403	16.5	1.0	4.4	65.5	23.9	6.2
		423	61.1	3.8	1.6	67.0	24.4	6.9
E	0.02	403	2.0	2.9	_	73.6	26.4	
		423	21.4	30.6		72.3	25.5	2.2
F	0.24	423	0.9	0.1		63.0	24.7	12.3
G	0.46	383	2.8	0.2		61.6	23.7	14.7
		403	16.2	1.0		72.4	23.6	4.0
		423	64.0	4.0	0.7	72.0	23.5	3.8

 Table 5. The effect of pretreatment conditions on the activity and selectivity of 2% Rh/titania catalysts for the hydrogenolysis of methylcylopentane

a-e See table 3.

to Hex is slightly higher. We shall discuss these changes together with the results for the Rh2/Ti catalyst.

### Rh2/Ti Catalysts

Table 5 summarises the activity and selectivity results obtained for our Rh2/Ti catalysts. Comparison with table 4 shows that after treatment A the turnover numbers of the two catalysts are identical (*i.e.* there is no particle size effect in the range of dispersions from 22-59%). Some differences in selectivity are observed, however, particularly the larger amount of hydrogenolysis and the lower selectivity to Hex. These differences need to be treated with caution, since although excellent consistency was obtained in each set of experiments, quite large variations were observed between repeat experiments with fresh catalysts. The problem of obtaining consistent patterns of results with Rh catalysts has been alluded to above.

When the catalyst is reduced for 1 h at 773 K the H/Rh ratio is reduced by a factor of 15, but the activity is only slightly lower so that the turnover number is higher (compare catalyst Rh5/Ti, see table 4). Indeed, even when the H/Rh ratio is decreased to 0.02 by reduction at 773 K for 16 h (treatment E) the activity remains very high. Resulting from this R773 treatment there is a sharp change in the product distribution. Hydrogenolysis to form smaller hydrocarbons is favoured, especially at the lower reaction temperatures, and this occurs more or less exclusively at the expense of 2MP.

When these catalysts after R773 (for 1 or 16 h) are exposed to air at 298 K (treatment C or F) the H/Rh ratio is recovered but the activity decreases dramatically. After treatment C the turnover number is 20 times lower, and after treatment F 300 times lower than after the original treatment A.

Re-oxidation at 673 K (treatment D or G) returns the catalyst to its original state, and both the activity and turnover number recover their original values. The product distribution is also essentially the same as after treatment A. The only significant change



**Fig. 1.** Compensation effect plot for the reaction of methylcyclopentane over supported Rh catalysts. Rh2/Si:  $\triangle$ , C<sub>1</sub>-C<sub>5</sub>;  $\bigtriangledown$ , 2-methylpentane;  $\bigcirc$ , 3-methylpentane;  $\bigcirc$ , n-hexane. Rh2/Ti:  $\triangle$ , C<sub>1</sub>-C<sub>5</sub>;  $\bigtriangledown$ , 2-methylpentane;  $\bigcirc$ , 3-methylpentane;  $\bigcirc$ , n-hexane. Rh5/Ti:  $\triangle$ , C<sub>1</sub>-C<sub>5</sub>;  $\bigtriangledown$ , 2-methylpentane;  $\bigcirc$ , 3-methylpentane;  $\bigcirc$ , n-hexane.

in selectivity appears to be that more Hex is formed (compare treatments A and D or A and G in tables 4 and 5). This parallels the higher selectivity to Hex observed over larger Rh particles and is consistent with the fact that a small amount of sintering occurs during the reduction/oxidation cycles.

## Activation Energies and Pre-exponential Terms

Bond<sup>13</sup> has recently discussed the significance of the compensation effect and has suggested that 'any family of catalysts exhibiting a simple compensation effect must possess active centres which are similar in their geometric and electronic architecture'. When the activation energies and pre-exponential terms for our Rh catalysts are plotted as a compensation effect plot (fig. 1) all the points lie about a single line. Consequently, no significance can be placed in the apparent variations in the activation energy terms for the different catalysts. Following Bond<sup>13</sup> it appears that the nature of the active centres for the MCP reaction over Rh catalysts is more or less independent of the support, the particle size, SMSI effects, *etc.* Of course, the proportions of different types of sites may vary, thus providing an explanation for the observed small variations in the product distribution.

# Discussion

The hydrogenolysis of MCP over supported Rh catalysts turns out to be a complex reaction and few clear-cut trends emerge. The main features of the reaction may be summarised as follows.

catalyst	code	2MP/Hex
Rh2/Si <sup>a</sup>	Α	> 72 <sup>b</sup>
,	В	44
2% Rh/SiO <sub>2</sub> <sup>c</sup>		50
Rh5/Ti <sup>a</sup>	Α	13
3% Rh/TiO <sup>c</sup>		17
Rh5/Ti <sup>a</sup>	В	7
3% Rh/TiO <sub>2</sub> <sup>c</sup>		20

**Table 6.** The influence of the support on the selectivity of the MCP reaction over Rh catalysts

<sup>a</sup> Reaction temperature 423 K. <sup>b</sup> No n-hexane detected. <sup>c</sup> After ref. (11), reaction temperature 480 K.

(a) The major products are 2MP and 3MP, formed in a ratio of ca. 2.5:1 to 3:1, *i.e.* above the statistical ratio of 2:1. Only a small amount of hexane is produced. The reaction therefore proceeds by a selective mechanism.<sup>14-16</sup>

(b) The product distribution is temperature- and also support-dependent. Over Rh/silica catalysts the selectivity to n-hexane increases with temperature, but over Rh/titania the selectivity to n-hexane decreases with temperature (cf. Rh/alumina catalysts<sup>12</sup>). Furthermore, Rh/titania is more selective then Rh/silica for the formation of n-hexane.

(c) Larger Rh particles tend to produce more n-hexane.

(d) After allowance has been made for compensation effects it is found that Rh/silica and Rh/titania catalysts have essentially identical activation energies for the formation of each type of hydrogenolysis product.

(e) There is a small change in selectivity for Rh/titania catalysts after high-temperature treatment, but no change in the activation energy for the different reactions.

(f) When Rh/titania catalysts are reduced at 773 K the 'SMSI' state is produced, but the catalysts retain much of their activity and the turnover number is actually increased substantially.

(g) When 'SMSI' Rh/titania catalysts are re-oxidised at 298 K to reverse the SMSI state the activity and turnover number decrease sharply. No clear variations in product distribution are observed to accompany these changes.

The variability of the product distribution from the MCP reaction over Rh catalysts makes it difficult to identify significant support effects. In general, we would agree with Schepers *et al.*<sup>11</sup> that the product distribution changes are relatively small. However, table 6 summarises some of our results, which indicate a real support effect. We observe that Rh/titania catalysts are more selective for the formation of n-hexane than Rh/silica catalysts of comparable dispersion. Note that the Rh5/Ti catalyst after treatment A is in the 'normal' state but still produces significantly more n-hexane than the Rh2/Si catalyst. This is further evidence of a support effect in the absence of SMSI.<sup>9</sup> Table 6 also includes some results obtained by Schepers *et al.*<sup>11</sup> at a higher reaction temperature. These are consistent with our results for catalysts reduced at low temperatures. However, when the reduction temperature is increased our catalysts produce more n-hexane, whereas Schepers *et al.*<sup>11</sup> found less n-hexane. It is possible that the differences reflect the choice of reaction temperature.

#### The Nature of the Active Centres in Rh/Titania Catalysts

The most significant result from our research is the unusual variations in the activity and

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turnover number of the Rh/titania catalysts after the various treatments. Given that there are only small changes in selectivity and no measurable variation in the activation energies accompanying these changes in activity, the questions which arise are how can the Rh retain activity when the surface is almost completely covered by contaminants and why is the activity then lost when the Rh surface is decontaminated?

It is generally accepted now that the major effect of reducing a titania-supported catalyst at high temperature is for a  $\text{TiO}_x$  species to migrate from the support on to the metal particles. There is some evidence that the  $\text{TiO}_x$  species has a stoichiometry close to  $\text{TiO}_{.17, 18}$  For Rh we have shown elsewhere<sup>10</sup> that this migration is a slow process and complete encapsulation is difficult to achieve. It is also well known that small metal particles succumb to the SMSI state more readily than large particles, an observation which is entirely consistent with a diffusion-controlled process. The particle size distribution of our Rh/titania catalysts is narrow, with a maximum at *ca*. 1.5 nm. It seems likely, therefore, that after reduction at 773 K all the Rh particles will be contaminated by TiO<sub>x</sub> to about the same extent.

Our catalytic results show that after treatment E the Rh2/Ti catalyst only adsorbs ca. 3% of the amount of hydrogen adsorbed after treatment A yet this small fraction of the Rh contributes ca. 30% of the total activity. Conversely, after treatment C almost 50% of the Rh surface is exposed, but this contributes only 15% of the total activity of a fresh uncontaminated catalyst. It seems clear that not all the Rh atoms in small particles have equal activity for the MCP reaction. We now consider possible explanations for this behaviour.

We can gain some insight into the nature of the Rh/titania after high-temperature reduction from hydrogen and oxygen chemisorption and from hydrogen/oxygen titration data.<sup>10</sup> After reduction at 573 K, H/Rh = 0.59 and after reduction at 773 K, H/Rh = 0.04. When the catalyst reduced at 773 K is exposed to oxygen at 298 K the quantity of oxygen consumed is found to be equivalent to O/Rh = 0.75. A subsequent  $H_2/O_2$  titration consumes hydrogen equivalent to H/Rh = 0.52. From the normal titration reaction:

$$\mathrm{O}_{ads}\!+\!\tfrac{3}{2}\!H_2=H_{ads}\!+\!H_2\mathrm{O}$$

this last result implies that there are 0.17 (*i.e.* 0.52/3) adsorbed oxygen atoms per surface Rh atom. Subtracting 0.17 from the total O/Rh ratio (0.75) indicates that oxygen equivalent to O/Rh = 0.58 is consumed irreversibly on exposure of an Rh/titania catalyst to oxygen at 298 K. Presumably this irreversibly retained oxygen is combined with titanium. If we accept that the TiOx species which contaminates the Rh surface after high-temperature reduction is TiO<sup>17, 18</sup> and that this is oxidised to TiO<sub>2</sub> on contact with oxygen at 298 K, then we arrive at a ratio of TiO to surface Rh of essentially unity. This supports rather well the surface contamination model of SMSI.

Some of this  $TiO_2$  which we postulate to be formed must remain on the Rh particles, because if a further reduction is performed at 573 K only 50% of the original hydrogen adsorption capacity is recovered. (This reduction temperature is too low to allow the migration of TiO from the titania support.)

Let us now consider our catalytic results in the light of this model. We suggest that after R773 our Rh/titania consists of Rh particles covered with monomeric TiO moieties, with only a few Rh atoms remaining accessible to hydrogen adsorption. It would seem likely that the strongest interaction between Rh atoms and TiO would occur at corners, edges and steps on the Rh particles, so we postulate that after the reduction at 773 K the only 'free' Rh atoms are in flat surfaces. A model of 'SMSI' Rh is shown in fig. 2(a).

The free Rh atoms, shown in fig. 2(a), give the same product distribution and have the same activation energy as that observed over uncontaminated Rh particles, so the active centre probably consists of a very small ensemble (1 or 2 Rh atoms). These active



Fig. 2. Proposed model of Rh/titania catalysts (a) after reduction for 1 h at 773 K; (b) after partial re-oxidation at 298 K and reduction at 573 K. ○, Rh atoms; 🖾 , TiOx.

centres have much higher turnover numbers than the average for a whole Rh particle. This indicates that the Rh atoms which have become contaminated by TiO would have been relatively inactive for the MCP reaction in any case. These 'low-activity' Rh atoms, if our model is correct, are the edge and corner atoms of the Rh particles. It is easy to rationalise such a possibility on the grounds that MCP may adsorb too strongly at highly coordinatively unsaturated Rh atoms for any products to desorb at the low temperatures used in our investigations.

When the catalyst shown in fig. 2(a) is exposed to oxygen at 298 K the TiO oxidises to TiO<sub>2</sub> and *ca*. 50% of the Rh becomes uncovered. We suggest that at this stage what happens is that the TiO monomers oxidise to TiO<sub>2</sub>, which then reconstructs to form a coherent two-dimensional layer as shown in fig. 2(b). At this point the oxygen adsorption results show that *ca*. two-thirds of the Rh is still covered by a titanium species. Re-reduction at 573 K exposes 50% of the Rh so during this heat treatment some of the TiO<sub>2</sub> must migrate off the Rh back to the support. This reverse migration may be facilitated by the water vapour generated in the reduction of adsorbed oxygen. After this second low-temperature reduction the 50% of the Rh still accessible to hydrogen has a very low turnover number in the MCP reaction. To be consistent with our model we would suggest that during the oxidation and/or second reduction at 573 K the TiO<sub>2</sub> having grown into a two-dimensional layer further reconstructs and, possibly in a reduced state, spreads over the planar surfaces of the Rh. This will have the effect of eliminating the majority of the active centres for the MCP reaction.

To summarise, what we propose is that after an initial high-temperature reduction TiO monomers interact strongly, but independently of each other, with edge atoms in the Rh particles, blocking these sites. The retention of a high turnover number for the MCP reaction by Rh in this state we attribute to other active centres (consisting of 1 or 2 Rh atoms) in planar surfaces not contaminated by TiO species. Oxidation at 298 K causes the TiO monomers to migrate across the Rh oxide surface and form into two-dimensional

 $TiO_2$  units. Re-reduction at 573 K causes these  $TiO_2$  particles to spread across the planar surfaces of the Rh, thus eliminating many of the active centres for the MCP reaction.

Although we have described our results in terms of a simple contamination model we cannot, and indeed would not wish to, exclude the possibility that electronic perturbations of the Rh atoms by attachment to TiO species may also contribute to changes in catalytic properties. However, the absence of any clear evidence for significant changes in the product distribution or in the activation energy seems to indicate that if Rh atoms are modified electronically by contact with TiO species then such Rh atoms have a very low activity. The observed activity in the MCP reaction seems to reside in unmodified Rh atoms, but only a small fraction of the surface Rh atoms have any significant activity.

We recognise that our model is speculative. It is, however, consistent with what is known about titania-supported metals and it does explain satisfactorily our unusual catalytic results.

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