Selectivities for Hydrocarbon Reactions on SMSI Titania-Supported Platinum Formed by High-Temperature Reduction

J. K. A. Clarke,* R. J. Dempsey,* T. Baird,† and J. J. Rooney,‡

*Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland; †Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, United Kingdom; and ‡Department of Chemistry, The Queen's University of Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, N. Ireland

High-temperature reduced (HTR) Pt/TiO_2 catalysts exhibit strong metal-support interaction (SMSI) as inferred from negligible hydrogen chemisorption take-up and moderate activity for skeletal reactions of alkanes. Using model reactants $\alpha\gamma$, $\alpha\gamma'$ and $\alpha\delta$ hydrogenolysis routes are found whereas $\alpha\beta$ hydrogenolysis is more severely depressed. Terminal C–C bond scission in hydrogenolysis as well as suppression of bond-shift rearrangement and of SCM cyclisation indicate a strong preference for carbanionic Pt–alkyl bond formation and are compatible with an electron shift from TiO_x moieties to Pt in these HTR Pt/TiO_2 catalysts. © 1990 Academic Press, Inc.

INTRODUCTION

The phenomenon of strong metal-support interaction (SMSI) has attracted much interest and has principally been interpreted since about 1984 on the basis of decoration of metal surface, partially or largely, by support (1). More recently this simple view has been questioned and the role of electron transfer between support and metal, originally proposed by Schwab and Pietsch (2) and Solymosi (3), has been revived (4–6).

Studies of alkane reactions on SMSI Pt/TiO_2 are few. One well-known study (7) has tended to suggest that while Pt/TiO_2 shows selectivities rather different from Pt/SiO_2 these are substantially unaltered as catalyst reduction temperature is increased. In a previous report (8), we have shown that lower-temperature-reduced (≤573 K : LTR) Pt/TiO_2 exhibits rather complete selectivity for hydrogenolysis of alkanes. Tests with a range of model reactants showed that hydrogenolysis through $\alpha\gamma$, $\alpha\gamma'$, and $\alpha\delta$ intermediates was feasible. Here we present an extension of this study to the behaviour of Pt/TiO_2 catalysts prepared by reduction at higher temperatures and with the same philosophy, namely to test the activity of the now many

fewer metal sites for these and other hydrocarbon reactions.

EXPERIMENTAL

Materials and Procedures

Degussa P-25 titania was used as received for all catalyst preparations. Ammonium hexachloroplatinate [$(NH_4)_2PtCl_6$] was Johnson Matthey specpure grade. B.D.H. Aristar grade aqueous ammonia with deionized water was used for preparation of solutions. All glassware used was cleaned in turn in aqua regia, "chromic acid" solution and nitric acid and thoroughly rinsed with deionized water following each stage. Hydrocarbons were Fluka puriss grade, except for ethane (Air Liquide 99.5%) and neopentane (B.D.H. 99%).

Catalyst Preparation

The same 2% (w/w) Pt/TiO_2 catalyst batch was used for all chemisorption and catalytic experiments. It was prepared following the method used by Anderson *et al.* (9).

Reduction of catalysts and chemisorption procedure. Prior to the final reduction period, all catalyst samples were treated as

370

follows. The catalyst after removal from a vacuum desiccator was

(i) purged in a flow of oxygen-free argon (298 K, 15 h; 473 K, 3 h);

(ii) reduced in flowing hydrogen (without prior cooling) at a temperature of 473 K (3 h);

(iii) the sample was then raised to the final reduction temperature (T_{red}) and held there for 16 h;

(iv) finally, the catalyst was purged in a flow of oxygen-free argon (1 h) at a temperature lower than or equal to that of the final reduction temperature.

Hydrogen chemisorptions were carried out at 293 K and 760 Torr on all catalyst samples prior to the catalytic reactions using the hydrogen-pulse technique developed by Gruber (10). Oxidation of catalyst samples after high-temperature reduction ($T_{red} \geq 673$ K, denoted HTR in what follows), was carried out by heating to 673 K at 10 K min⁻¹ and by maintaining this temperature for 1 h under a flow of oxygen purified by passage through a molecular sieve. Samples were subsequently purged with argon for 0.5 h at 293 K before reduction and further chemisorption tests. Argon was purified by a B.O.C. rare-gas purifier Mk.4 and hydrogen was purified by diffusion through a Johnson Matthey Pd–Ag hydrogen purification unit during the reduction, chemisorption, and reaction stages. The possibility of oxygen contamination of gases used was monitored on an ongoing basis by a MnO/SiO₂ trap (11).

Catalytic Experiments

A continuous-flow reactor as previously described (12) was used for all reactions. In general a charge of 0.075 to 0.200 g of 2% Pt/TiO₂ was used. Hydrocarbon partial pressures between 8 and 17 Torr were used and achieved by surrounding a saturator with an appropriate refrigerated bath. The balance to 760 Torr pressure was hydrogen. This is referred to as the standard reactant feed. Reactants were outgassed thoroughly by repeated freeze–thaw cycles under vacuum. Solid reactants were outgassed by re-

TABLE 1

Metal Crystallite Diameters from TEM and Hydrogen Uptakes for Representative HTR Pt/TiO₂ Catalysts and for Two Catalysts Examined for SMSI reversal

Catalyst	T_{red} (K)	H/Pt[a]	TEM average diam. (Å)
2% Pt/TiO₂	673	<0.05	8 ± 2
2% Pt/TiO₂	773	<0.05	10 ± 2
2% Pt/TiO₂	473[b]	0.52	9 ± 2
2% Pt/TiO₂	473[c]	0.43	10 ± 2

[a] Total hydrogen atoms adsorbed per platinum atom in the catalyst sample.

[b] Reduction at 473 K (1 h) following 673 K hydrogen reduction (16 h) and 673 K oxidation (1 h).

[c] Reduction at 473 K following 773 K hydrogen reduction (16 h) and 673 K oxidation (1 h).

peated sublimation under vacuum before deposition onto chemically clean glass wool. The hydrogen stream was then passed though this plug of coated wool to obtain the required hydrogen/hydrocarbon feed. Reactions under conditions of greatly reduced hydrogen pressure were carried out by diluting the hydrogen stream upstream of the hydrocarbon saturator with oxygen-free argon to yield the required mixture (hydrocarbon : hydrogen : argon = 1 : 1 : 40 which is referred to as the hydrogen-lean feed).

RESULTS

Catalyst Characterisation

Results of H₂ chemisorption and TEM determinations are presented in Table 1. The final reduction temperature (T_{red}) of the 2% (w/w) Pt/TiO₂ catalyst was varied between 673 and 773 K in the series of catalytic experiments reported here. After reduction at these temperatures, no hydrogen chemisorption uptake was detectable (Table 1, column 3). TEM examination of the reduced catalysts showed that no significant increase in the average particle size resulted from these high-temperature reductions when comparison is made with results reported previously for low-temperature reduction

TABLE 2

Reaction of Ethane/Hydrogen on 2% Pt/TiO$_2$

T_{red} (K)	P_{H_2} (Torr)[a]	T (K)[b]	T.O.N.[c]
573	~700	564	14$_0$
		573	19$_7$
573	~50	555	73$_5$
		571	198$_5$
673	~700	564	0.1
		600	0.4
		633	2.2
773	~700	626	0.00$_5$
		649	0.01$_5$
		673	0.04
773	~50	615	<0.1
		633	0.1
		653	0.3

[a] P_{ethane} = 53 Torr.
[b] Reaction temperature.
[c] Units are molec. s^{-1} g$_{Pt}^{-1}$ × 10^{-18}.

(LTR) (8). In order to check the reversibility of this further decrease in hydrogen chemisorption capacity which occurred after HTR, samples of the catalyst were treated in oxygen after T_{red} of 673 K and also of 773 K. Subsequent chemisorption determinations following LTR (473 K) of the oxidised catalyst samples indicated a restoration of chemisorption capacity to close to that observed previously after LTR only. It must be stressed that even this oxidation treatment led to hydrogen uptakes which were at most about 30% less than those projected on the basis of TEM determination of the average crystallite size.

Ethane Reaction

Hydrogenolysis of ethane was observed from typically 533 K upward with the standard reactant feed on the 2% Pt/TiO$_2$ catalyst following catalyst reduction at 673 K (Table 2). The activity for this reaction was lower by a factor of ~10^2 than that reported previously (8) after reduction at 573 K. A further reduction by 2 orders of magnitude followed reduction at 773 K. Irrespective of reduction temperature apparent activation

energies were in all cases in the range 145–155 kJ mole^{-1}.

A change to the hydrogen-lean feed led, in accordance with more general experience in ethane hydrogenolysis, to an increase in the rate of reaction. Hydrogenolysis was observed to take place from 573 K upward in various runs with the hydrogen-lean feed with the 773 K-reduced catalyst: the activity after reduction at 773 K was lower by a factor of 10^3–10^4 than that observed after reduction at 573 K (see Table 2).

n-Pentane Reaction

After reduction at 773 K (Table 3) the Pt/TiO$_2$ catalyst retained the extremely high hydrogenolysis selectivity observed previously after LTR (8). The activity however was lowered by approximately 2 orders of magnitude compared with the 573 K-reduced catalyst. The high selectivity observed for hydrogenolysis prompted an investigation of the effects of hydrogen pressure. Results are presented in Tables 4 and 5 for the reaction of n-pentane at the greatly reduced hydrogen pressure of the hydrogen-lean feed over catalysts reduced at 673 and 773 K. In both cases the activity of the catalysts was similar to that observed with the standard reactant feed. However, major selectivity changes were observed. At lower reaction temperatures the 673 K-reduced catalyst retained the selectivity for

TABLE 3

Reaction of n-Pentane/Hydrogen on 2% Pt/TiO$_2$.
(T_{red}: 773 K)

Temp (K)	Conv. (%)	T.O.N.[a]	C$_1$	C$_2$	C$_3$	nC$_4$	iC$_5$	cC$_5$
543$_i$	0.1	0.1	45	7	7	41	—	—
559$_i$	0.5	0.3	40	8	7	42	1	2
573$_i$[b]	1.5	0.8	41	7	7	43	1	1
574$_f$	1.4	0.7	41	7	7	43	1	1
596$_i$	4.2	2.1	40	8	8	41	1	2
596$_f$	3.9	2.0	42	8	7	41	1	1
624$_f$	6.9	3.5	38	9	10	40	1	2

[a] Units are: molec. s^{-1} g$_{Pt}^{2}$ × 10^{-18}.
[b] (i) Indicates initial product distribution; (f) indicates product distribution after 30 min.

TABLE 4

Reaction of n-Pentane at Reduced Hydrogen Pressure on 2% Pt/TiO$_2$. (T_{red}: 673 K)

Temp (K)	Conv. (%)	T.O.N.[a]	C$_1$	C$_2$	C$_3$	nC$_4$	iC$_5$	nC$_5^{=}$[b]	cC$_5$	cC$_5^{=}$[c]
470	0.1	0.1	45	5	6	40	—	—	4	—
491	0.2	0.3	42	7	8	37	1	—	5	—
509	0.3	0.5	40	9	11	33	1	—	6	—
525	0.6	1.0	36	12	14	28	2	1	7	—
539	0.8	1.2	30	15	18	24	3	3	7	—
561	1.3	2.0	22	19	22	18	4	3	11	—
588	1.6	2.4	14	19	21	10	5	12	19	Tr[d]

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

[b] nC$_5^{=}$, n-pentene.

[c] cC$_5^{=}$, cyclopentene.

[d] Tr, trace.

hydrogenolysis observed at higher hydrogen pressure. As the reaction temperature was raised however both the selectivity for hydrogenolysis relative to the sum of bond-shift isomerisation and cyclisation and also the overall mode of hydrogenolysis altered. Internal scission of the C$_5$ chain became the predominant hydrogenolysis process and considerable cyclisation now took place. Over the 773 K-reduced catalyst (Table 5) hydrogenolysis was greatly diminished and bond-shift isomerisation and cyclisation were enhanced. Dehydrogenation was now the major reaction observed.

Neopentane Reaction

Virtually no change in selectivity for the reaction of neopentane after T_{red} 673 K was observed compared with that reported previously for T_{red} 573 K (8) (Table 6). In line with all the alkane reactions carried out at higher hydrogen pressure the tendency was toward hydrogenolysis with minor amounts of bond shift. Activity fell by approximately

TABLE 5

Reaction of n-Pentane at Reduced Hydrogen Pressure on 2% Pt/TiO$_2$. (T_{red}: 773 K)

Temp (K)	Conv. (%)	T.O.N.[a]	C$_1$	C$_2$	C$_3$	C$_4$	iC$_5$	nC$_5^{=}$[b]	cC$_5$	cC$_5^{=}$[c]
548	0.1	0.1	5	6	6	2	17	48	16	—
573$_i$[d]	0.2	0.4	3	6	6	2	15	40	28	—
573$_f$	0.2	0.4	3	5	6	1	15	43	27	—
593$_i$	0.6	1.0	2	5	6	2	10	45	29	1
592$_f$	0.5	0.9	2	4	5	1	10	46	30	2
617$_i$	1.1	1.9	2	4	4	1	6	55	24	4
618$_f$	1.0	1.7	2	3	3	1	5	57	24	5

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

[b] nC$_5^{=}$, n-pentene.

[c] cC$_5^{=}$, cyclopentene.

[d] (i) Indicates initial product distribution; (f) indicates product distribution after 30 min.

TABLE 6

Reaction of Neopentane/Hydrogen on 2% Pt/TiO_2.
(T_{red}: 673 K)

Temp (K)	Conv. (%)	T.O.N.[a]	C_1	C_2	C_3	iC_4	iC_5
535	0.1	0.1	52	2	11	35	—
553	0.1	0.1	35	1	8	39	16
569	0.2	0.3	40	1	7	39	13
585$_i$[b]	0.5	0.8	44	1	6	44	5
585$_f$	0.5	0.8	44	1	6	43	6
600$_i$	1.7	2.5	46	1	6	44	3
599$_f$	1.6	2.5	44	1	7	44	4

[a] Units are: molec. s^{-1} g_{Pt}^{-1} $\times$ 10^{-18}.
[b] (i) Indicates initial product distribution; (f) indicates product distribution after 30 min.

one order of magnitude upon increasing T_{red} from 573 to 673 K.

Neohexane Reaction

Results for the reaction of neohexane after T_{red} of 673 to 733 K are presented in Tables 7 and 8. After reduction at 673 K a remarkably high selectivity for the hydrogenolysis of neohexane to propane was observed at lower reaction temperatures (471–518 K). The selectivity for formation of neopentane and methane was also highest in this range. Above these temperatures the selectivity pattern became similar to that observed after reduction at 573 K (Table 7, last entry) and 733 K (Table 8). Similar behaviour was observed for the reaction of neohexane following T_{red} 703 K (untabulated result). As with other reactants the selectivity for bond-shift isomerisation was almost negligible except (see Discussion) at lower reaction temperatures after T_{red} 673 K where hydrogenolysis to propane occurred after a bond-shift rearrangement of the neohexane molecule. A fall in activity by 1–2 orders of magnitude was observed upon increasing the reduction temperature from 573 to 733 K.

Hexamethylethane Reaction

As reported for the 573 K-reduced catalyst (8), the reaction of hexamethylethane (2,2,3,3-tetramethylbutane) yielded mainly methane and 2,2,3-trimethylbutane with a lesser amount of central scission to isobutane (Table 9). Only trace amounts of products due to bond-shift isomerisation were observed. The activity decreased by a factor

TABLE 7

Reaction of Neohexane/Hydrogen on 2% Pt/TiO_2. (T_{red}: 673 K)

Temp (K)	Conv. (%)	T.O.N.[a]	C_1	C_2	C_3	iC_4	nC_4	$neoC_5$	iC_5	nC_5	2MP[b]	3MP
471	0.1	0.1	14	6	66	1	—	13	—	—	—	—
487	0.1	0.1	13	6	68	3	—	10	—	—	—	—
502	0.1	0.1	20	6	50	5	—	10	9	—	—	—
518	0.2	0.1	22	12	31	11	1	7	14	—	—	2
533	0.3	0.3	26	14	17	16	1	3	21	—	—	2
549$_i$[c]	1.0	0.9	31	19	4	21	1	1	22	—	1	1
548$_f$	0.9	0.8	28	20	4	20	1	1	23	—	2	1
563$_i$	1.8	1.6	30	17	4	24	1	Tr[d]	21	—	2	1
563$_f$	1.8	1.6	31	18	2	24	1	1	20	—	2	1
483[e]	0.1	0.1	37	19	—	16	—	—	28	—	—	—

[a] Units are: molec. s^{-1} g_{Pt}^{-1} $\times$ 10^{-18}.
[b] 2MP + 2,3-dimethylbutane unresolved.
[c] (i) Indicates initial product distribution; (f) indicates product distribution after 45 min.
[d] Tr, trace.
[e] Reaction of Neohexane/Hydrogen on 2% Pt/TiO_2. T_{red}: 574 K, taken from Ref (8).

TABLE 8

Reaction of Neohexane/Hydrogen on 2% Pt/TiO$_2$. (T_{red}: 733 K)

Temp (K)	Conv. (%)	T.O.N.[a]	C$_1$	C$_2$	C$_3$	iC$_4$	nC$_4$	neoC$_5$	iC$_5$	nC$_5$	2MP[b]	3MP
538$_i$[c]	0.1	0.1	30	10	4	9	1	2	39	—	3	2
559$_i$	0.3	0.2	37	15	1	14	1	1	29	—	1	1
578$_i$	1.2	0.5	41	14	1	16	1	1	22	—	3	1
579$_f$	1.1	0.5	36	15	1	18	1	Tr[d]	24	Tr	4	1
598$_i$	4.7	2.1	39	17	1	22	2	Tr	16	Tr	3	Tr
598$_f$	3.5	1.5	43	14	1	21	1	Tr	17	Tr	2	1
619$_i$	10.5	4.6	43	18	2	23	2	Tr	10	Tr	2	Tr

[a] Units are: molec. s^{-1} g$_{Pt}^{-1}$ × 10^{-18}.
[b] 2MP (2-methylpentane) and 2,3-dimethylbutane unresolved.
[c] (i) Indicates initial product distribution; (f) indicates product distribution after 45 min.
[d] Tr, trace.

of 3–4 upon increasing T_{red} from 573 K (8) to 673 K.

Methylcyclopentane Reaction

Results for the reaction of methylcyclopentane with both standard and hydrogen-lean reactant feeds are presented in Tables 10–13. At the higher hydrogen pressure there was a higher selectivity for the demethylation route leading to cyclopentane and methane over the 773 K-reduced cata-lyst than that observed with the 573 K-reduced catalyst. This was accompanied by a slight shift toward a more nonselective ring opening although overall the ratio 2MP/nC_6 remained >1.5. A fall in activity by approximately 2 orders of magnitude was observed upon increasing T_{red} from 573 to 773 K for the standard reactant feed. With the hydrogen-lean feed, ring opening became nonselective with both 673 K- and 773 K-reduced catalysts. However, precise determination

TABLE 9

Reaction of Hexamethylethane/Hydrogen on 2% Pt/TiO$_2$. (T_{red}: 673 K)

Temp (K)	Conv. (%)	T.O.N.[a]	C$_1$	C$_2$	C$_3$	iC$_4$	nC$_4$	iC$_5$ + nC$_5$	DMB[b]	TMB[c]	TMP[d]	TMP'[e]
515	0.1	0.08	39	—	—	10	—	—	—	51	—	—
533	0.4	0.3	37	—	—	16	1	—	—	46	—	—
554	2.4	1.8	40	2	1	17	1	—	2	36	Tr[f]	1
573	6.7	5.0	37	2	1	15	1	1	6	36	Tr	1
597	8.2	12.3	42	2	2	19	2	2	5	24	1	1
597	7.7	11.5	43	2	2	19	2	1	5	24	1	1

[a] Units are: molec. s^{-1} g$_{Pt}^{-1}$ × 10^{-18}.
[b] (DMB) 2, 3 and 2,2-dimethylbutane.
[c] (TMB) 2,2,3-trimethylbutane.
[d] (TMP) 2,2,4-trimethylpentane.
[e] (TMP') 2,2,3-trimethylpentane.
[f] Tr, trace.

of the $2MP/nC_6$ and $2MP/3MP$ ratios was precluded due to the low rates of hydrogenolysis under these conditions. In both cases dehydrogenation and aromatisation became the predominant reactions but particularly so with the 773 K-reduced catalyst.

DISCUSSION

General Considerations, Alkane Hydrogenolysis

Despite the many studies carried out on the strong metal-support interaction consequent on HTR (5, 13, 14), the origin and nature of the effect is still open to debate and none of the interpretations proposed taken alone would appear to explain the phenomenon. In addition, those catalytic studies of hydrocarbon rearrangements over SMSI catalysts which have been carried out have suggested that the main effect is upon activity with selectivity for various reactions being relatively unaltered (7, 14a). The effect of high-temperature reduction with hydrogen ($\geqslant 673$ K) on the present 2% Pt/TiO_2 catalyst is substantially similar to literature findings for Pt/TiO_2 formed by HTR (7, 9, 14b). A complete loss of hydrogen chemisorption capacity, partially reversed by subsequent oxidation, is observed along with a decrease in the rates of hydrogenolysis reactions (by up to 3 orders of magnitude in the ethane reaction) after reduction at temperatures up to 773 K. The high *selectivity* for hydrogenolysis of saturated hydrocarbons reported previously for low-temperature-reduced catalysts using the standard reaction feed is substantially retained after HTR. The degree of SMSI induced by HTR as indicated by decrease in catalytic action is most pronounced in the case of the ethane reaction. Reduction at 673 K leads to a decrease in TON (per unit weight of Pt) relative to our previous LTR Pt/TiO_2 (8) by a factor of about 10^2. (As discussed in fuller detail in what follows, a relatively smaller activity decrease was found with other reactants.) However, after reduction at 773 K a further decrease by two-to-three orders of magnitude in ethane

hydrogenolysis occurs (Table 2).[1] As noted in the Results section, derived activation energies remained quite constant circa 150 kJ $mole^{-1}$ as T_{red} was increased as described. This indicates that activity decreases originate in a much diminished number of surface sites.

Use of the hydrogen-lean feed following T_{red} 773 K leads to a much increased rate of hydrogenolysis of ethane, as is general experience for more conventional supported Pt catalysts (16). Parallel dehydrogenation to ethene is now comparable in rate to hydrogenolysis.

For the majority of reactants used and with the standard reactant feed mixture, the higher catalyst reduction temperatures of the present study produced little change in selectivity for the various products as compared with the previous LTR study (8). Thus, $\alpha\gamma$ and $\alpha\gamma'$ hydrogenolysis routes persisted after reduction up to 673 or 733 K although the rates of these reactions showed a general decrease with increasing reduction temperature (Tables 6–8).

On a 673 K-reduced catalyst, clearly with already strongly developed SMSI by virtue of its negligible hydrogen chemisorption take-up, hexamethylethane reacted to give moderate amounts of isobutane alongside demethylation. The former is clearly by the $\alpha\delta$ route and sets in at 515 K (Table 9). With neohexane reactant (Table 7) the rather dramatic formation of propane as a major product may be ascribed to a preliminary methyl shift from C_2 to C_3 followed by an analogous $\alpha\delta$ hydrogenolysis. Alternatively, however, and especially in view of the lower onset temperature in this case of 471 K, it is possible that dehydrogenation of the ethyl group

[1] The disparity in behaviour of $\alpha\beta$ hydrogenolysis of neohexane and ethane has been noted previously (15). We now favour the following interpretation. In the case of ethane hydrogenolysis two methylenes are formed whereas in the neohexane hydrogenolysis a neopentylidene (electron donor) and a methylene (relatively an electron acceptor) are formed. A concomitant donor–acceptor behaviour on a contiguous pair of metal atoms may be highly conducive to C–C scission.

TABLE 10

Reaction of Methylcyclopentane/Hydrogen on 2% Pt/TiO$_2$. (T_{red}: 673 K)

Temp (K)	Conv. (%)	T.O.N.[a]	C$_1$	C$_2$–C$_5$[b]	cC$_5$	2MP	3MP	nC$_6$	2MP/nC$_6$	2MP/3MP
473	0.1	0.17	19	—	18	43	20	—	—	2.1
490	0.5	0.8	18	—	17	42	18	5	8	2.3
503	1.5	2.5	18	1	18	41	17	5	5	2.4
518$_i$[c]	3.2	5.5	19	1	19	39	16	6	6	2.4
518$_f$	2.8	4.8	21	2	19	35	16	7	5	2.2
533$_i$	3.4	11.4	21	2	20	35	15	7	5	2.3
533$_f$	3.3	11.1	18	2	22	36	15	7	5	2.4

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

[b] Excluding cC$_5$.

[c] (i) Indicates initial product distribution; (f) indicates product distribution after 60 min.

takes place and then a vinyl shift to yield 2MP occurs followed by C$_2$–C$_3$ scission.

It is of interest that change of reactant feed to the hydrogen-lean mix in the n-pentane reaction (T_{red}, 773 K) (Table 5) eliminated hydrogenolysis almost completely. Thus in the 773 K-induced SMSI state, hydrogenolysis appears to be very sensitive to carburization.

Methylcyclopentane Reaction

In the following the terminology of Gault (*17*) is used to refer to three principal ring-opening mechanisms. Thus SCM indicates selective C–C bond breaking within the dimethylene group, NSCM the nonselective breaking of all the endocyclic C–C bonds and PSCM is the breaking of the ring bond adjacent to the substituent methyl group (most likely via an $\alpha\gamma$ mechanism).

Reaction on a 673 K-reduced catalyst and with standard feed shows SCM ring scission accompanied by quite considerable PSCM to methane, cyclopentane, and n-hexane. Thus the ratio 2MP/nC$_6$ displays values in the range 5–8 (Table 10). As expected (*18*) use of a hydrogen-lean feed gives NSCM scission as signalled by a ratio 2MP/nC$_6$ close to unity. PSCM is unaltered in relative amount. More significantly for the understanding of the SMSI effect, a 773 K-re-

duced Pt/TiO$_2$ with standard reaction mixture also gives a product distribution which tends strongly toward NSCM (+PSCM) modes (Table 11). This may imply removal of those sites required for SCM by the higher catalyst reduction temperature. Such removal may take the form of a greater electron donation from support to metal which would diminish SCM by organometallic analogy (*19*). Alternatively, this result may signify a greatly reduced surface hydrogen concentration at the (very few) surface sites.

Mechanistic Inferences Pertinent to SMSI

Even silica-supported platinum catalysts can show moderate-to-high selectivities for hydrogenolysis of alkanes relative to bond-shift isomerisation and cyclisation. In particular this behaviour is found with very high metal dispersion (*20*). The present Pt/TiO$_2$ HTR catalysts are of very high metal dispersion so that the high selectivity for hydrogenolysis which they show is in line with this generalisation. However, whereas platinum surfaces usually effect indiscriminate scission of C–C bonds in alkanes, the HTR Pt/TiO$_2$ causes mainly terminal scission of n-pentane alongside very little cyclisation and no bond-shift rearrangement (Table 3). This behaviour clearly indicates carbanionic Pt–alkyl attachment at the chain end leading

TABLE 11

Reaction of Methylcyclopentane/Hydrogen on 2% Pt/TiO$_2$. (T_{red}: 773 K)

Temp (K)	Conv. (%)	T.O.N.[a]	C$_1$	C$_2$–C$_5$[b]	cC$_5$	2MP	3MP	nC$_6$	MCP$^{=c}$	Bz[d]	$\dfrac{2MP}{nC_6}$	$\dfrac{2MP}{3MP}$
503$_i$[e]	0.1	0.1	6	29	16	23	13	13	—	—	1.8	1.8
523$_i$	0.2	0.2	10	8	23	29	16	14	—	—	2.1	1.8
542$_i$	0.6	0.5	11	4	24	30	14	17	—	—	1.8	2.1
543$_f$	0.6	0.5	10	3	25	30	14	18	—	—	1.7	2.1
565$_i$	1.2	1.1	14	1	24	28	14	19	—	—	1.5	2.0
563$_f$	1.2	1.2	14	1	25	28	14	18	—	—	1.6	2.0
588$_i$	4.0	3.8	10	—	26	29	13	16	2	4	1.8	2.2

[a] Units are: molec. s^{-1} g$_{Pt}^{-1}$ × 10^{-18}.
[b] Excluding cC$_5$.
[c] (MCP$^=$) methylcyclopentene.
[d] Benzene.
[e] (i) Indicates initial product distribution; (f) indicates product distribution after 60 min.

to the formation of n-butane and methane. Initial attachment is at the primary carbon followed by metallacyclobutane formation and finally selective cleaving of the latter to give C$_1$ and C$_4$ (which is itself in accord with carbanionic behaviour). The prominence of demethylation of methylcyclopentane by PSCM (Tables 10 and 11) is further indicative of carbanionic-mechanistic behaviour. Overall this carbanionic behaviour represents evidence for an electronic effect in (HTR) SMSI and would arise by electron donation from TiO$_x$ ($x < 2$) moieties toward platinum. Such an electron shift in the case of platinum mitigates against bond shift on the basis of the accepted mechanism of that reaction (21). As already noted, organometallic analogy suggests a decrease in SCM cyclisation rate from the same cause.

A large reduction of hydrogen partial pressure in the reactant feed alters the conditions substantially by generating a carburised (even carbided) surface. NSCM routes, in Gault's original terminology (17),

TABLE 12

Reaction of Methylcyclopentane at Reduced Hydrogen Pressure on 2% Pt/TiO$_2$. (T_{red}: 673 K)

Temp (K)	Conv. (%)	T.O.N.[a]	C$_1$	cC$_5$	2MP	3MP	nC$_6$	MCP$^{=b}$	Bz[c]	cC$_6$	$\dfrac{2MP}{nC_6}$	$\dfrac{2MP}{3MP}$
488	0.2	0.1	11.5	12.9	18.1	12.3	15.9	6.5	20.3	2.5	1.1	1.5
503	0.4	0.2	9.9	11.0	8.4	6.8	9.8	9.3	44.8	Tr[d]	0.9	1.2
519	1.1	0.4	3.6	4.1	5.4	3.5	5.7	10.2	67.5	—	1.0	1.7
532	1.9	0.7	1.7	1.9	2.8	1.6	2.9	11.5	77.6	—	1.0	1.7
552	4.4	1.7	0.8	0.8	1.4	1.1	1.3	12.6	82.0	—	1.1	1.3

[a] Units are: molec. s^{-1} g$_{Pt}^{-1}$ × 10^{-18}.
[b] (MCP$^=$) methylcyclopentene.
[c] Bz, benzene.
[d] Tr, trace.

TABLE 13

Reaction of Methylcyclopentane at Reduced Hydrogen Pressure on 2% Pt/TiO₂. (T_{red}: 773 K)

Temp (K)	Conv. (%)	T.O.N.[a]	C_1	cC_5	2MP	3MP	nC_6	MCP=[b]	Bz[c]	cC_6	2MP/nC_6	2MP/3MP
523ᵢ	0.2	0.1	5.2	4.9	5.0	3.1	5.7	57.3	18.8	—	0.9	1.6
525f	0.2	0.1	3.5	4.5	4.7	2.5	4.7	58.5	21.6	—	1.0	1.9
539ᵢ	0.9	0.8	1.1	1.3	1.4	0.9	1.1	24.2	70.0	—	1.3	1.6
539f	1.2	0.9	0.6	0.8	0.9	0.6	1.0	17.5	78.6	—	0.9	1.5
558ᵢ	4.2	3.2	Tr[d]	Tr	Tr	Tr	Tr	11.1	88.9	—	—	—
558f	4.3	3.3	Tr	Tr	Tr	Tr	Tr	9.9	90.1	—	—	—

[a] Units are: molec. s^{-1} g_{Pt}^{-1} × 10^{-18}.
[b] (MCP=) methylcyclopentene.
[c] Bz, benzene.
[d] Tr, trace.

now appear: there is appreciable cyclisation of n-pentane (Tables 4 and 5) and equal probabilities of ring opening of methylcyclopentane C–C bonds such as to yield the statistical ratios of hexane isomers (Tables 12 and 13). Isomerisation of n-pentane now appears, being more evident with the 773 K-reduced catalyst than with the 673 K-reduced (Table 5 vs Table 4). The latter finding strengthens the view that a free radical and substantially gas-phase pathway for bond shift becomes viable. Indeed, plausible reaction schemes can readily be drawn by which both NSCM cyclisation and bond-shift reaction can be rationalised by free-radical mechanisms having surface assistance.

The present results extend a previous report (8) in demonstrating that Pt/TiO₂ SMSI catalysts under hydrogen-rich reaction conditions give mainly hydrogenolysis of alkanes. The nature of the hydrogenolysis and the suppression of the bond-shift reaction and of cyclisation are consistent with electron transfer from support to platinum. The very few sites operative in these SMSI catalysts in hydrocarbon reactions can still bring about hydrogenolysis by αγ, αγ', and αδ routes: the αβ hydrogenolysis route is reduced more severely than the former routes when comparison is made with LTR Pt/TiO₂ or with Pt/SiO₂ catalysts having similar mass of metal. Bonding to two contiguous surface metal atoms is clearly indicated for the αβ hydrogenolysis whereas αγ, αγ', or αδ diadsorbed species may form and react further as complexes of one metal atom. We have also noted (22) that the multiple exchange of cyclopentane with D₂ at ambient temperatures is strongly suppressed relative to d_1 isomer formation using HTR Pt/TiO₂ as catalyst. This accords with the idea that multiatom active sites relative to single atom sites are reduced by SMSI on Pt/TiO₂.

ACKNOWLEDGMENTS

REFERENCES

1. Tauster, S. J., Acc. Chem. Res. 20, 389 (1987).
2. Schwab, G. M., and Pietsch, E., Z. phys. Chem. B1, 385 (1928).
3. Solymosi, F., Catal. Rev. 1, 233 (1967).
4. Belton, D. N., Sun, Y.-M., and White, J. M., J. Catal. 102, 338 (1986).
5. Herrmann, J. M., J. Catal. 118, 43 (1989).
6. Shpiro, E. S., Dysenbina, B. B., Tkachenko, O. P., Antoshin, G. V., and Minachev, Kh. M., J. Catal. 110, 262 (1988).
7. Anderson, J. B. F., Burch, R., and Cairns, J. A. J. Catal. 107, 364 (1987).

8. Clarke, J. K. A., Dempsey, R. J., and Baird, T., *J. Chem. Soc. Faraday Trans.* **86,** 2789 (1990).

9. Anderson, J. B. F., Burch, R., and Cairns, J. A., *J. Catal.* **107,** 351 (1987).

10. Gruber, H. L., *Anal. Chem.* **34,** 1828 (1962).

11. Juszczyk, W., and Karpiński, Z., *J. Catal.,* **117,** 519 (1989).

12. Kane, A. F., Clarke, J. K. A., and Baird, T., *J. Catal.* **64,** 200 (1980).

13. Sun, Y.-M., Belton, D. N., and White, J. M., *J. Phys. Chem.* **90,** 5178 (1986).

14. (a) Anderson, J. B. F., Burch, R., and Cairns, J. A., *Appl. Catal.* **28,** 255 (1986); (b) Mériaudeau, P., Ellestad, O. H., Dufaux, M., and Naccache, C., *J. Catal.* **75,** 243 (1982).

15. Clarke, J. K. A., Rooney, K. M. G., and Baird, T., *J. Catal.* **111,** 374 (1988).

16. Sinfelt, J. H., *J. Phys. Chem.* **68,** 344 (1964).

17. Gault, F. G., *Adv. Catal.* **30,** 1 (1981).

18. Finlayson, O. E., Clarke, J. K. A., and Rooney, J. J., *J. Chem. Soc. Faraday Trans. 1,* **80,** 191 (1984).

19. McDermott, J. X., White, J. F., and Whitesides, G. M., *J. Amer. Chem. Soc.* **98,** 6521 (1976).

20. Clarke, J. K. A., Creaner, A. C. M., and Baird, T., *Appl. Catal.* **9,** 85 (1984).

21. McKervey, M. A., Rooney, J. J., and Samman, N. G., *J. Catal.* **30,** 330 (1973).

22. Clarke, J. K. A., Hegarty, B. F., and Rooney, J. J., *J. Mol. Catal.,* in press.