

Influence of Strong Metal–Support Interaction on Exchange with Deuterium and other Reactions of Hydrocarbons

Part 1.—Studies with Rh/TiO₂ and Rh/SiO₂

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The changes in the catalytic properties of Rh/TiO₂ caused by raising the reduction temperature from 473 to 773 K have been investigated for four reactions, the exchange with deuterium of methane and cyclopentane, and the hydrogenolysis of 2,2-dimethylpropane and methylcyclopentane.

The so-called strong metal–support interaction (SMSI) brought about by the high-temperature reduction had least effect on the exchange of methane but reduced the rate of hydrogenolysis of 2,2-dimethylpropane by factors of 10⁴ or 10⁵. The SMSI was reversible and its influence on each of the reactions was eliminated by oxidation of the catalyst followed by low-temperature reduction. No marked changes in the catalytic behaviour of Rh/SiO₂ resulted from increasing the reduction temperature.

The results provide further evidence for the existence of a number of kinds of catalytic sites on Rh/TiO₂. The sites for the more structure-sensitive reactions tend to be more seriously affected by SMSI and probably involve more metal atoms than the sites responsible for methane exchange.

Much interest has been stimulated in the last 15 years by the work of Tauster and co-workers^{1,2} on SMSI and Haller and Resasco³ reviewed progress in this field in 1989. The main effects are changes in the adsorptive and catalytic properties of metals, such as Rh, Pt and Ir, supported on reducible oxides (TiO₂, Nb₂O₅, V₂O₃) brought about by high-temperature reduction (HTR), typically at 773 K. The phenomena are reversible and normal behaviour is restored by oxidation, followed by low-temperature reduction (LTR) at 473 K. SMSI leads to a substantial fall in the chemisorption of H₂ or CO in the metal but, in contrast, the hydrogenation of CO is often enhanced. The influence on catalytic reactions of hydrocarbons varies but tends to be greater with the more structure-sensitive reactions. Rates of hydrogenolysis of small hydrocarbons may be reduced by factors of 10⁴ whereas hydrogenation–dehydrogenation reactions are hardly influenced and isomerisation shows intermediate behaviour. The principal causes of these effects are thought to be migration of sub-oxides of the support over the metal, and the creation of new interfacial metal/support sites as a consequence of HTR. Significant physical evidence has been reported³ for the factors described but their relative importance is still a matter of discussion.

Little work has been reported on the influence of SMSI on exchange reactions of hydrocarbons with deuterium. Clarke *et al.*⁴ studied the exchange of cyclopentane over Pt/TiO₂ and also over Pt/SiO₂. HTR of the Pt/TiO₂ for 3 h gave some reduction in rate but the nature of the exchange, as revealed by the initial product distribution, was similar to that for LTR of the catalyst. In both cases, there was substantial multiple exchange with some 35% of the D₅ compound formed initially as well as significant amounts of the D₆–D₁₀ products. HTR of the Pt/TiO₂ for 25 h led to lower activity with a marked shift in the product distribution towards the D₁ compound. Patterson and Rooney⁵ have discussed these and other results in some detail. They suggest that the active sites for exchange on Pt/TiO₂, on metal films and also on other kinds of supported Pt catalysts are possibly Pt atoms in defect sites which are present to a limited extent. They point out that SMSI Pt is catalytically akin to Pt alloyed with Cu

or Au⁶ for the reaction of hydrocarbons and they suggest that the main cause of the SMSI effects is attributable to electron donation from partially reduced TiO₂ in contact with small metal crystallites.⁷ They also draw attention to the interesting fact that extensive multiple exchange still occurs over SMSI Pt even though the capacity of the catalyst to chemisorb H₂ (or D₂) is significantly reduced and they argue that D₂ molecules must play a significant role in the reactions by mechanisms analogous to the Eley–Rideal mechanism.

For some years we have also been interested in the use of exchange reactions as a means of learning more about SMSI with various systems.^{8,9} In this paper we report results for the exchange of both methane and cyclopentane with deuterium over Rh/TiO₂ catalysts as this has been one of the most widely studied SMSI systems.³ Two other reactions were also examined to provide comparisons with the exchange reactions and with other work involving Rh/TiO₂. The hydrogenolysis of 2,2-dimethylpropane was chosen as a suitable reaction to give results which could be related to other studies of hydrogenolysis with small hydrocarbons.^{10–13} The complex reactions of methylcyclopentane were also studied since this compound has been used as a test reactant in a number of cases.^{14–18} In common with many other investigations the reactions were carried out on Rh/SiO₂ as well as on Rh/TiO₂. In a following paper, results with Nb₂O₅-supported catalysts will be reported.

Experimental

Materials

Deuterium (99.5%) was purchased from Matheson and purified by diffusion through a heated Pd–Ag alloy thimble. 2,2-Dimethylpropane was also 99.5% (Matheson) but the other three hydrocarbons were all 99.9% and obtained as follows: methane (G. T. Baker), cyclopentane (BDH) and methylcyclopentane (Koch–Light). The TiO₂ was prepared by flame hydrolysis of TiCl₄ by Tioxide International Ltd and had a BET surface area of 25 m² g^{−1}. Cylinder hydrogen was used at atmospheric pressure for catalyst reduction and pretreatment after passage through a 'Deoxo' unit (Englehard) to remove oxygen and then through traps containing 4A molecular sieve to remove water.

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The Rh/SiO₂ contained 3 wt.% Rh and was the Series C catalyst described by Rouco and Haller.¹⁹ They reported a dispersion of 89%, based on hydrogen chemisorption measurements, after reduction and evacuation at a medium temperature of 573 K, but no change in dispersion was found if the reduction was carried out at 723 K. The Rh/TiO₂ catalyst was prepared by wet impregnation of the support using a Rh(NO₃)₃ solution. It was dried for 2 days in air at room temperature and then for 24 h in an oven at 393 K. The catalyst was evacuated at room temperature and heated in flowing hydrogen for 2 h at 393 K; the temperature was raised over a period of *ca.* 2 h to 773 K and the treatment with flowing hydrogen continued for a further 16 h at this temperature. The catalyst was then evacuated for 15 min at 773 K and cooled to room temperature. It was raised to 673 K in a flow of dry air over a period of 2 h and maintained at that temperature for a further 2 h. After cooling to room temperature, the catalyst was stored in a well stoppered bottle. This procedure ensured that all experiments started with identical samples of catalyst with the TiO₂ fully oxidised. Based on the amount of the salt used in its preparation, the catalyst contained 0.6 wt.% Rh, corresponding to 3.5×10^{19} atoms Rh per g of catalyst. The Rh content was checked by plasma emission spectroscopy and found to be within 10% of the nominal value.

Exchange Reactions

The exchange reactions were carried out in a static reactor, approximate volume 200 cm³, connected by a capillary leak to a VG Micromass (MM601) mass spectrometer. The pressure of hydrocarbon in the reaction vessel for exchange of methane was 0.81 kPa, corresponding to a charge of 2×10^{19} molecules and the ratio of deuterium to hydrocarbon was 10 : 1. With cyclopentane, the pressure used was 0.68 kPa and the ratio was 20 : 1. Mass spectra were obtained using ionising electrons of 16 eV for methane and 20 eV for cyclopentane. The peak heights were corrected for naturally occurring isotopes and for fragmentation²⁰ and then used to determine the isotopic composition of the hydrocarbons at each stage of the reaction. The results were plotted according to the appropriate reversible first-order equations²¹ in order to obtain k_0 , the initial rate of disappearance of light hydrocarbon and k_ϕ , the initial rate of acquisition of D by 100 molecules of reactant. The initial product distributions were determined from plots of each of the D_i products *vs.* the percentage of the D_0 compound reacted. The value of M , the mean number of deuterium atoms entering each reacting molecule under initial conditions was obtained either from the ratio of the rate constants, k_ϕ/k_0 , or using the equation:

$$M_D = \sum_i iD_i/100 \quad (1)$$

where D_i is the percentage of the initial product with i deuterium atoms.

Other Reactions

The static reactor used for the other hydrocarbon reactions was similar to the one for exchange except that samples could be taken for analysis in one or more chromatographs. Mixtures containing hydrocarbons with < six carbon atoms were analysed in a Perkin-Elmer F33 instrument with a flame ionisation detector, using a 3 m column containing *n*-octane on 'Porasil-C', 80–100 mesh, operated at room temperature with N₂ as carrier gas at 450 kPa.

Two chromatographic systems were used in parallel to follow the reactions of methylcyclopentane. Column A was a 50 m stainless-steel capillary column coated with squalane,

operated at room temperature with He as carrier gas at a pressure of 170 kPa, and connected to a Perkin-Elmer F11 chromatograph with a flame ionisation detector. This column enabled all the products from the reaction of methylcyclopentane to be analysed except that methane and ethane were not completely separated and the benzene peak interfered with the tail of the methylcyclopentane peak. The second system had two columns connected in series by a four-way back-flush valve; column B was 2 m in length and contained *n*-octane on 'Porasil-C' and column C was 0.3 m long with 10% TCEP, 1,2,3-tris(2-cyano-ethoxy)-propane, on 'Chromasorb-P', 80–100 mesh. These columns were operated at room temperature with N₂ as carrier gas at 340 kPa and were used with an F11 chromatograph with a flame ionisation detector. The gas sample entered column B which separated methane and ethane. All saturated hydrocarbons, including methylcyclopentane, passed quickly through column C. After the methane, ethane and propane had been detected at the exit from column C, the flow of carrier gas through column B was reversed. Partially separated saturated hydrocarbons still in column B were recombined and emerged as a single pulse from column C followed by a peak for benzene which could thus be analysed without interference from methylcyclopentane. The analysis of each sample took *ca.* 20 min.

Catalyst Pretreatment

In the standard LTR treatment the catalyst sample was evacuated for 15 min at room temperature then heated to 393 K under flowing hydrogen. After 30 min the temperature was raised to 473 K and the sample maintained under hydrogen flow for 1 h. The catalyst was then evacuated for 15 min and brought to the desired reaction temperature under vacuum.

For the standard HTR treatment the catalyst was brought from 393 to 773 K under flowing hydrogen in *ca.* 2 h and maintained at 773 K for 16 h. In some experiments, longer periods were used for LTR or shorter periods for HTR, these are designated xLTR or yHTR where x and y represent the duration of the reduction in h.

Results

Characterisation

Measurement of the dispersion of the Rh/TiO₂ catalyst was made by a multiple-pulse chromatographic method using H₂ and O₂ as the titrating gases. The ratio of oxygen chemisorption: hydrogen chemisorption for the LTR catalyst was *ca.* 2 : 1 in agreement with results given by Meriaudeau *et al.*¹⁰ and assuming a 1 : 1 O/Rh stoichiometry the dispersion was 49%. HTR reduced the hydrogen chemisorption by a factor of 50 and subsequent oxygen titration showed evidence of some uptake associated with re-oxidation of the support to an extent equivalent to an oxygen deficiency of 0.4%. Some 85–90% of the chemisorptive capacity of the catalyst was restored when HTR material was oxidised and then subjected to LTR. Activities of both HTR and LTR catalysts were expressed in terms of surface Rh atoms derived from the dispersions measured after LTR. No peaks attributable to Rh were observed in an X-ray powder diffraction pattern for an Rh/TiO₂ sample, subjected to HTR. This confirmed the absence of Rh particles larger than 5 nm and was evidence against substantial particle growth due to HTR.

Exchange of Methane

The reaction was followed over LTR Rh/TiO₂ and over Rh/SiO₂ in the temperature range 423–464 K and over HTR

Rh/TiO₂ at 463–502 K. In every case the course of the exchange followed the usual first-order reversible equation. Typical rates and product distributions are given in Table 1 and Arrhenius plots in Fig. 1. At 444 K, the activity of LTR Rh/TiO₂ was seven times greater than that of LTR Rh/SiO₂. The activation energies for LTR Rh/TiO₂ and Rh/SiO₂ were 97 and 103 kJ mol⁻¹, respectively; a reliable value for HTR Rh/TiO₂ was not obtained but it appeared to be somewhat greater.

The product distributions all showed a pattern frequently found for methane exchange,²¹ i.e. with maxima for both the D₁ and D₄ products. The multiplicity of the exchange, *M*, increased with temperature and results for all experiments, except HTR Rh/SiO₂ fell on a common line, see Fig. 2. With Rh/TiO₂, the change from LTR to HTR reduced the rate of reaction by factors ranging from 3 to 13. In contrast, with Rh/SiO₂ HTR gave a three-fold increase of activity which was mainly associated with a faster stepwise exchange; this increased the percentage of D₁ product and lowered the percentages of the more highly exchanged methanes, see Table 1.

Exchange of Cyclopentane

The exchange of cyclopentane with D₂ on LTR Rh/TiO₂ at 250 K gave a rate plot, Fig. 3, which showed a marked decrease in activity over a period of 20 min with a fall by a factor of *ca.* 20; the subsequent rate was steady. In contrast, good first-order plots were observed over Rh/SiO₂ at 250 K and over HTR Rh/TiO₂ at 321 K, Fig. 4. Rates of reaction are given in Table 2; the two results for LTR Rh/TiO₂ were

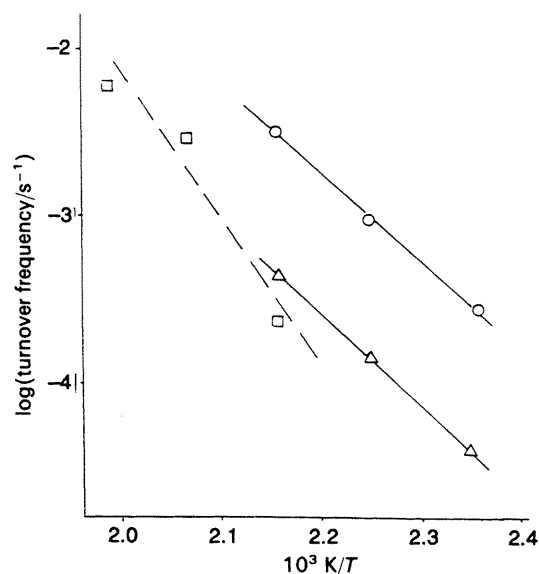


Fig. 1 Arrhenius plots for the exchange of methane with deuterium: LTR Rh/TiO₂ (○), HTR Rh/TiO₂ (□), LTR Rh/SiO₂ (△)

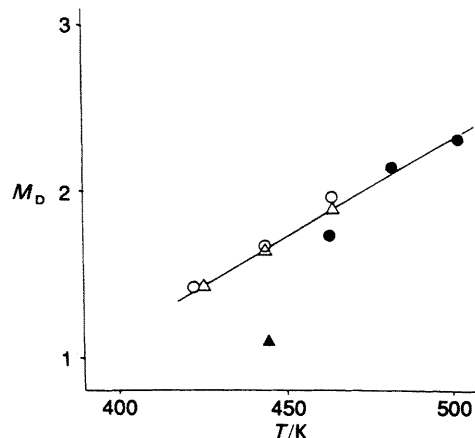


Fig. 2 Influence of temperature on the multiplicity of methane exchange; (○) and (●) for Rh/TiO₂ LTR and HTR; (△) and (▲) for Rh/SiO₂ LTR and HTR

carried out using 20.6 and 6.9 mg of catalyst respectively and the rates were the same within the limit of experimental error. An approximate activation energy of 34 kJ mol⁻¹ was obtained for HTR Rh/TiO₂. Using this value to derive an extrapolated rate at 250 K for comparison with the fast initial rate of exchange over the LTR catalyst gave a suppression

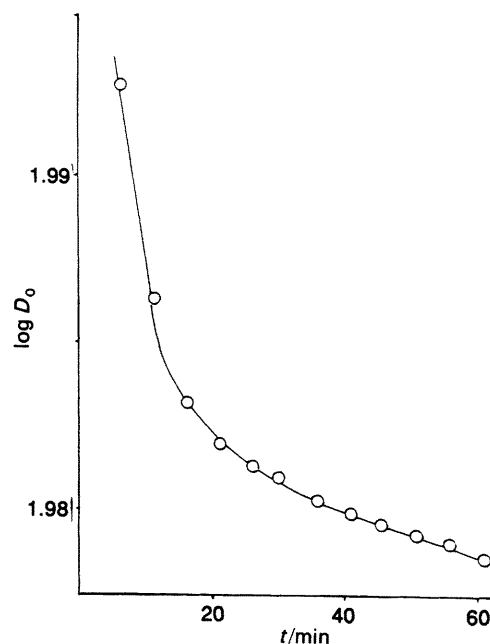


Fig. 3 First-order plot for the exchange of cyclopentane with deuterium at 250 K on LTR Rh/TiO₂; D₀ is the percentage of light cyclopentane

Table 1 Exchange of methane with deuterium

catalyst	pretreatment	T/K	turnover frequency ^a /10 ⁻⁴ s ⁻¹	products (%)				<i>M</i> _D ^b
				D ₁	D ₂	D ₃	D ₄	
Rh/TiO ₂	LTR	444	9.6	71.7	9.5	2.8	17.0	1.7
Rh/TiO ₂	LTR	464	32	58.3	11.8	5.0	24.9	2.0
Rh/TiO ₂	HTR	463	2.3	68.4	9.2	3.7	18.7	1.7
Rh/SiO ₂	LTR	444	1.4	72.8	8.9	3.5	14.8	1.6
Rh/SiO ₂	LTR	464	4.3	63.1	10.8	4.7	21.4	1.9
Rh/SiO ₂	HTR	445	6.1	89.7	3.0	1.8	5.5	1.2

^a Based on the number of surface Rh atoms. ^b Average number of deuterium atoms acquired by reacting molecules determined from the initial product distributions.

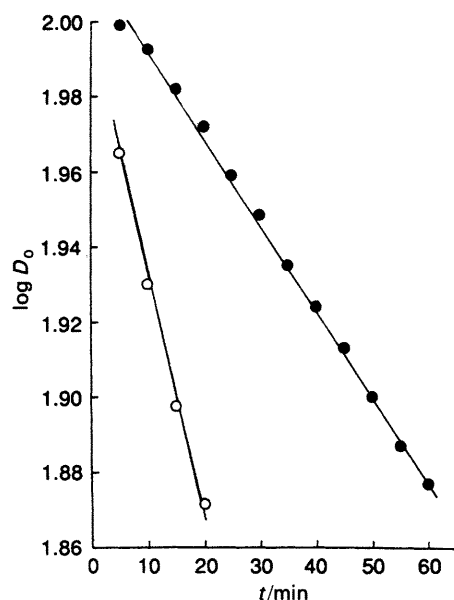


Fig. 4 First-order plots for the exchange of cyclopentane with deuterium; Rh/SiO₂ at 250 K (○), HTR Rh/TiO₂ at 321 K (●)

factor of 500 due to the SMSI. However, if the comparison was made with the subsequent steady rate, the decrease caused by SMSI was reduced to a factor of *ca.* 30. Details of initial product distributions are given in Table 3. In every case, substantial amounts of the D₁ and D₂ products were found and comparatively little in the range from D₆ to D₁₀. The smallest amounts of the latter products were observed over HTR Rh/TiO₂ despite the fact that the reaction was carried out at higher temperatures which normally increase the proportion of the highly exchanged products.²²

Hydrogenolysis of 2,2-Dimethylpropane (2,2DMP)

The hydrogenolysis was carried out on the various catalysts within the temperature range 403–625 K. Details of representative experiments are shown in Table 4 and rates of reaction for the whole range of results are summarised by the Arrhenius plots in Fig. 5. At 445 K the activity of LTR Rh/TiO₂

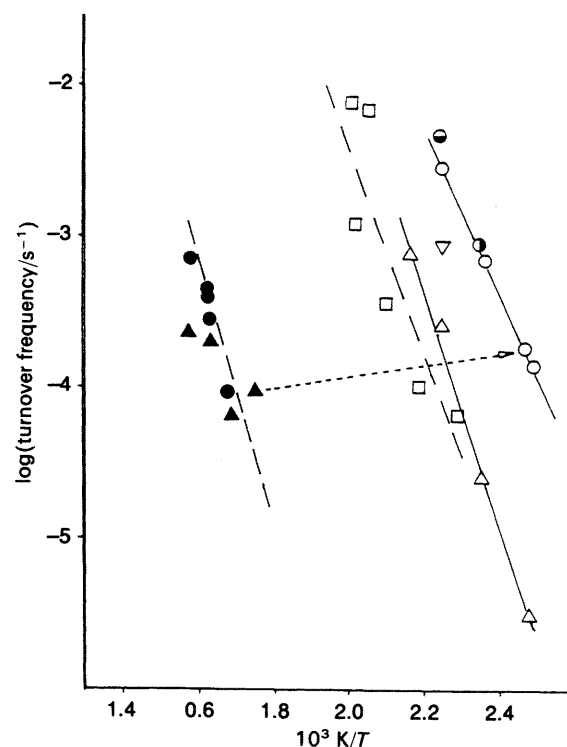


Fig. 5 Arrhenius diagram for the hydrogenolysis of 2,2DMP: Rh/TiO₂ 1LTR (○), 16LTR (●), 1LTR followed by 16 h evacuation at 773 K (⊙), 1HTR (□), 16HTR (▲), 16HTR successive runs with same catalyst sample (●), arrow denotes oxidation followed by 1LTR; Rh/SiO₂ 1LTR (Δ), 16HTR (▽)

was eight times greater than that of LTR Rh/SiO₂; this is similar to the difference found for exchange of methane. The initial product distributions were determined from the slopes, *S*, of the plots of number of molecules of each product formed for each molecule of 2,2DMP reacted. The symbols *S*₁ to *S*₄ are used for methane, ethane, propane and 2-methylpropane respectively and *S*₄ represents *n*-butane which can only be formed if rearrangement of the reactant occurs. The depth of hydrogenolysis was defined by the relationship,

$$M_b = \left(S'_4 + \sum_i S_i \right) - 1 \quad (2)$$

where *M_b* represents the number of C–C bonds broken in each reacting molecule of 2,2DMP.

Activation energies, subject to an error of ±10 kJ mol^{−1}, of 108 kJ mol^{−1} for 1LTR Rh/TiO₂ and of 146 kJ mol^{−1} for 1LTR Rh/SiO₂ were derived from the results in Fig. 5. The 1HTR treatment of Rh/TiO₂ gave an Arrhenius plot with considerable scatter so that it was not possible to obtain a reliable activation energy; the suppression of rate caused by this treatment was by factors of between 5 and 60. A much larger effect was observed when Rh/TiO₂ was subjected to 16HTR and reaction temperatures of 573 K or greater were necessary to give measureable conversion. Rates for runs

Table 2 Rates for exchange of cyclopentane with deuterium

catalyst	pretreatment	<i>T</i> /K	turnover frequency / 10 ^{−3} s ^{−1}	<i>M_D</i> ^a
Rh/TiO ₂	LTR	250	9.0 ^b	2.2
Rh/TiO ₂	LTR	250	7.3 ^b	2.1
Rh/SiO ₂	LTR	250	2.9	2.4
Rh/TiO ₂	HTR	297	0.21	1.6
Rh/TiO ₂	HTR	321	0.89	2.0
Rh/TiO ₂	HTR	341	1.2	1.9

^a Mean deuterium content of the initial products. ^b From initial stage of reaction.

Table 3 Initial product distributions for cyclopentane exchange

catalyst	pretreatment	<i>T</i> /K	products (%)									
			D ₁	D ₂	D ₃	D ₄	D ₅	D ₆	D ₇	D ₈	D ₉	D ₁₀
Rh/TiO ₂	LTR	250	37.9	32.6	12.8	8.2	6.0	1.3	0.7	0.2	0.1	0.1
Rh/SiO ₂	LTR	250	39.7	26.5	14.1	9.1	5.7	2.3	1.2	0.8	0.5	0.2
Rh/TiO ₂	HTR	341	53.4	25.3	9.8	4.7	4.4	0.7	0.5	0.4	0.3	0.4

Table 4 Results for the hydrogenolysis of 2,2-dimethylpropane

catalyst	pretreatment	T/K	turnover frequency /10 ⁻⁴ s ⁻¹	products					
				S ₁	S ₂	S ₃	S ₄	S' ₄	N _b
Rh/TiO ₂	1LTR	403	1.2	1.04	0.03	0.03	0.95	—	1.05
Rh/TiO ₂	1LTR	423	5.7	1.15	0.08	0.07	0.87	—	1.17
Rh/TiO ₂	1LTR	445	24	1.20	0.11	0.09	0.83	—	1.23
Rh/SiO ₂	1LTR	445	3.0	1.26	0.19	0.11	0.76	—	1.32
Rh/SiO ₂	16HTR	445	10	1.28	0.13	0.13	0.77	—	1.31
Rh/TiO ₂	1HTR	477	2.9	1.28	0.09	0.10	0.81	—	1.28
Rh/TiO ₂	16HTR	573	0.76	1.34	0.28	0.20	0.59	0.03	1.44
Rh/TiO ₂	16HTR ^a	614	3.7	2.00	0.59	0.25	0.22	0.05	2.11
Rh/TiO ₂	16HTR ^a	633	5.7	2.61	0.68	0.18	0.11	0.01	2.59

^a Two of the five runs on the same sample of catalyst with 15 min evacuation between experiments.

carried out with different catalyst samples varied within a factor of three but a series of successive reactions on a single sample subjected to 15 min evacuation while the system was adjusted to a new reaction temperature showed more consistent behaviour as indicated by the filled circles in Fig. 5. The suppression factors associated with 16HTR were *ca.* 10⁴–10⁵ with Rh/TiO₂. In contrast, 16HTR with Rh/SiO₂ gave a three-fold increase in activity, similar to that observed for exchange of methane. A number of other results with Rh/TiO₂ are shown in Fig. 5. No change in activity occurred by lengthening the period of LTR from 1 to 16 h or by evacuating the catalyst at 773 K for 16 h after 1LTR. Oxidation in flowing air for 16 h at 673 K followed by 1LTR fully restored the activity of a catalyst sample which had been used for a 16HTR experiment, as shown by the results linked by an arrow in Fig. 5.

The effect of temperature on the parameter, *M_b*, which corresponds to the depth of hydrogenolysis is shown in Fig. 6. For all types of catalyst there is a tendency for more C—C bonds to be broken as the temperature is raised but the position of the curve varies. Similar results were found for 1LTR

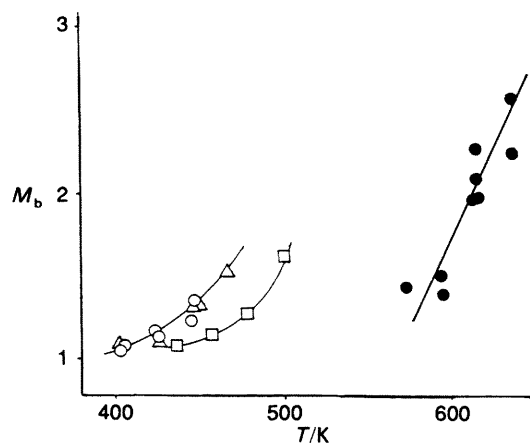


Fig. 6 Variation of the depth of hydrogenolysis of 2,2DMP with temperature; Rh/SiO₂ (mostly 1LTR but one result at 445 K was 16HTR) (Δ); Rh/TiO₂ 1LTR (○), 1HTR (□), 16HTR (●)

Rh/TiO₂ and with Rh/SiO₂, subjected to either 1LTR or 16HTR, but with Rh/TiO₂ the curve shifted slightly with 1HTR and substantially with 16HTR. These results show clearly that there are significant changes in selectivity for the hydrogenolysis of 2,2DMP associated with SMSI as well as the marked decrease in activity. No isomerised C₅ products were observed over any of the catalysts but the presence of small amounts of *n*-butane (S'₄ in Table 4) showed that some rearrangement was occurring on 16HTR Rh/TiO₂.

Reactions of Methylcyclopentane (MCP)

The reactions of MCP in the presence of hydrogen were investigated in the temperature range 473 to 573 K. A number of products were identified and six processes, listed in Table 5, contributed to the overall reaction.

Fig. 7 shows a typical experiment with LTR Rh/TiO₂ with the results presented as the percentage of MCP reacting by the various processes. There was a decrease in the rate of the overall reaction with time, see inset, indicating a progressive loss of catalytic activity. The behaviour observed for dehydrogenation, *i.e.* a fast build-up which then levelled off at a low percentage conversion was typical of most MCP reactions. The steady-state percentages of alkenes achieved over Rh/TiO₂ were 0.2% at 532 K and 1.9% at 573 K and these were thought to correspond to thermodynamic equilibria. The linear plots for the percentages of products formed in each of the other processes *vs.* the conversion of MCP showed that all reactions were equally influenced by the gradual loss of catalytic activity. No cyclohexane was detected in this or any of the experiments with Rh/TiO₂ so ring expansion was equivalent to aromatisation, linear plots were also found for the three products arising from the ring-opening process and the relative amounts were similar in most experiments with 8 ± 2% hexane, 50 ± 4% 2-methylpentane and 42 ± 4% 3-methylpentane.

Reactions over LTR Rh/SiO₂ were broadly similar to those with LTR Rh/TiO₂ with two minor differences. No alkenes were detected but cyclohexane was formed as well as benzene so the rate of ring-expansion exceeded that for aromatisation.

Table 5 Processes contributing to the overall reaction for methylcyclopentane in the presence of hydrogen on Rh catalysts

process	code	products
ring opening	RO	<i>n</i> -hexane, 2-methylpentane, 3-methylpentane
multiple hydrogenolysis	MH	methane, ethane, propane, <i>n</i> -butane, 2-methylpropane, <i>n</i> -pentane
demethanation	DM	cyclopentane, methane
ring expansion	RE	cyclohexane, benzene
aromatisation	A	benzene
dehydrogenation	DH	unsaturates other than benzene but mainly methylenecyclopentane

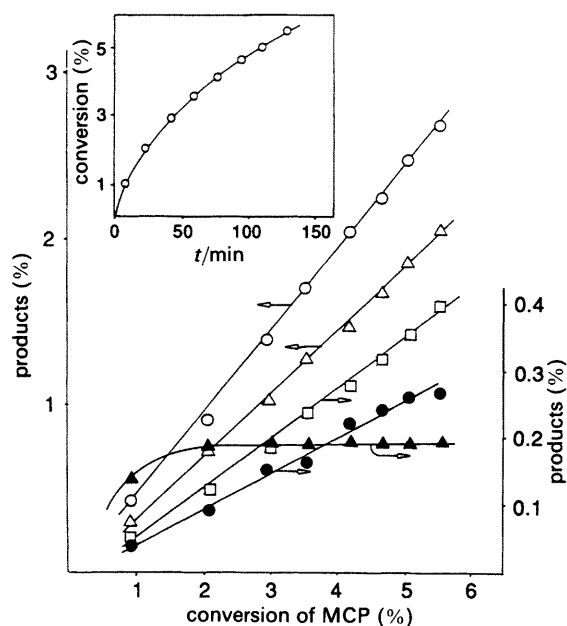


Fig. 7 Reaction of methylcyclopentane and hydrogen on LTR Rh/TiO₂ at 532 K; inset, total conversion; left-hand scale, multiple hydrogenolysis (○), ring-opening (△); right-hand scale, demethanation (□), aromatisation (●), dehydrogenation (▲)

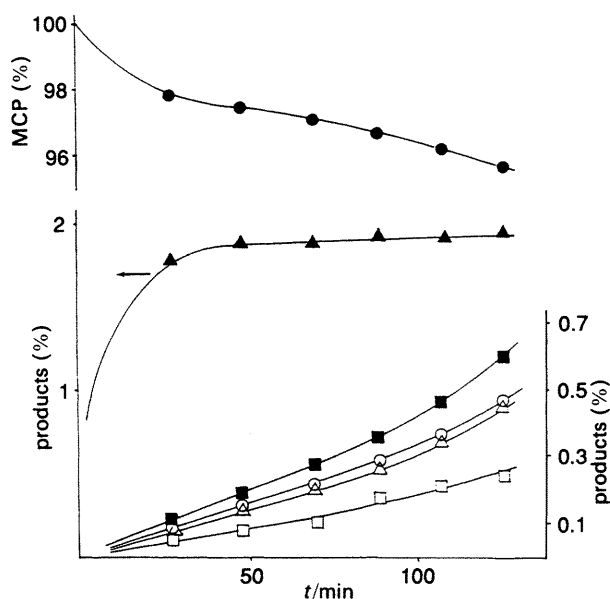


Fig. 8 Reaction of methylcyclopentane and hydrogen on HTR Rh/TiO₂ at 563 K; left-hand scale, MCP (●), dehydrogenation (△); right-hand scale, multiple hydrogenolysis (■), demethanation (○), ring opening (△), aromatisation (□)

A reaction of MCP over HTR Rh/TiO₂ is shown in Fig. 8. The initial reaction was mainly dehydrogenation, and consequently this soon slowed, but a subsequent gentle acceleration associated with increasing rates of the other processes was observed. A similar behaviour has been reported for reactions over HTR Ir/TiO₂ by Foger.²³

Rates of the various processes for typical reactions are shown in Table 6. There was relatively little increase of rate with rise of temperature and this may have been a consequence of the rapid deactivation process, possibly due to the formation of strongly adsorbed residues. Rates of reaction were similar on LTR Rh/TiO₂ and LTR Rh/SiO₂ apart from the minor differences already mentioned and with both these catalysts more multiple hydrogenolysis was found with increased temperature. A comparison of the results at 573 K for LTR or HTR Rh/TiO₂ shows that the various processes were suppressed to differing extents; DH by a factor of 2, RO, A and DM by factors of 5, and MH by a factor of 30. Normal LTR behaviour was restored by oxidation of an HTR Rh/TiO₂ catalyst. Contrary to normal procedure, some of the reactions on LTR catalysts were carried out above the pretreatment temperature but it is not likely that any substantial SMSI would have developed during the period of the reactions at temperatures which did not exceed 573 K.

Discussion

A brief review of the known features of SMSI is essential in order to relate the present results to the substantial body of published work on the subject. Many of the characteristics of SMSI and the explanations of the causes of the effects were described by Haller and Resasco³ and have been confirmed or amplified by more recent work. There is little doubt that some migration^{13,24} of oxide moieties over the surface of the metal takes place with consequential blocking of catalyst sites. At the same time, there is growing evidence for the importance of electronic interactions on the metal/oxide interface with some charge transfer or even bond formation.^{5,18,25} The similarities between the effects due to SMSI and those caused by the addition of Group 11 metals to noble metal catalysts^{3,5} provide further evidence of the role of electronic interactions. The influence of SMSI is more marked with highly dispersed catalysts³ and this correlation can be explained either in terms of oxide migration or electronic interaction.

The evidence for electronic interactions is not confined to catalysts containing the conventional SMSI oxides but is found with other oxides.^{26–28} Turlier *et al.*²⁸ reported that nickel catalysts exhibited a change in activity by a factor of 10² for the hydrogenolysis of ethane with different supports under conditions where SMSI did not occur. The critical factor was the effect of the support on the ease of reduction of the metal. Even more marked changes in activity of 10⁵ or 10⁶ were found by Gao and Schmidt^{29,30} for the hydro-

Table 6 Turnover frequencies for reactions of methylcyclopentane

catalyst	pretreatment	T/K	turnover frequency ^a /10 ⁴ s ⁻¹						
			RO	MH	DM	RE ^b	A ^b	DH	total
Rh/TiO ₂	LTR	473	10.1	3.0	0.3	0.1	0.1	0	13.5
Rh/TiO ₂	LTR	573	0.6	11.9	0.5	0.7	0.7	10.8	24.5
Rh/TiO ₂	HTR	573	0.10	0.47	0.13	0.10	0.10	5.9	6.6
Rh/TiO ₂ ^c	LTR	473	12.7	2.9	0.3	0.1	0.1	0	16.1
Rh/SiO ₂	LTR	473	11.7	3.0	0.15	0.2	0.1	0	15.0
Rh/SiO ₂	LTR	573	0.8	21.9	0.6	4.2	2.9	0	27.5

^a Processes defined in Table 5. ^b RE measured by formation of benzene and cyclohexane; A by formation of benzene. ^c Catalyst used for HTR reaction at 573 K, then oxidised in dry air for 16 h at 473 K.

genolysis of small hydrocarbons over Ru/SiO_2 or Rh/SiO_2 , subjected to various oxidation–reduction treatments. This type of behaviour was attributed to the ability of these metals to retain high-activity, low-coordination sites after oxidation and low-temperature reduction; such sites are destroyed by reduction at higher temperatures or annealing. Takehara *et al.*³¹ have reported variations in activity by factors of more than 300 for the exchange of 2,2-dimethylbutane on Rh/SiO_2 catalysts depending on the method of preparation and pretreatment. These results are of particular interest since exchange reactions are normally much less structure-sensitive than hydrogenolysis reactions.

The variations in activity quoted above for nickel, rhodium and ruthenium suggest that it is perhaps a mistake to regard SMSI as a phenomenon which is entirely distinct from other factors which influence the catalytic behaviour of metal catalysts, such as choice of support, method of preparation and pretreatment. In general, the metals which are most active for hydrogenolysis, *i.e.* ruthenium and rhodium, show the greatest variation with pretreatment and the most marked sensitivity to SMSI. Interpretation of changes in activity and selectivity often depend on the assumption of the existence of different types of catalytic sites. For instance, it has been suggested that multiatom sites will be more susceptible to inhibition by SMSI whereas sites involving a single metal atom, or perhaps a small number of metal atoms, may be less influenced by HTR.^{4,5}

Exchange of Methane

The results for the small effect of SMSI on the exchange of methane over Rh/TiO_2 show that this reaction must take place on sites which, although somewhat reduced in number, are to a large extent unaltered by HTR. The absence of any change in the multiplicity of exchange due to SMSI, see Fig. 2, is particularly interesting. This behaviour not only indicates that the catalytic properties of the sites survive HTR but also suggests that adequate supplies of deuterium must be available to give the significant amounts of CD_4 formed as an initial product, even although the chemisorption of hydrogen, or deuterium is severely curtailed. The active sites for exchange of methane may be Rh atoms which retain the normal capacity for multiple bonding with the adsorbate after HTR, although the number of such atoms may be lowered by sintering. Patterson and Rooney⁵ have suggested that such atoms may occupy defect sites so that, in contrast to the surface atoms on low-index planes, they are largely unaffected by the electronic interactions brought about by HTR of titania-supported metals. The unchanged multiplicity of the methane exchange after HTR adds support to the view of Patterson and Rooney⁵ that the reaction mechanism must include a role for gas-phase D_2 in a process essentially analogous to the Eley–Rideal³² mechanism for H_2 – D_2 exchange.

The lower activity of LTR Rh/SiO_2 compared with LTR Rh/TiO_2 and the increase resulting from HTR with Rh/SiO_2 may indicate that the reduction of the silica-supported catalyst was incomplete after treatment at 473 K.

Exchange of Cyclopentane

The decrease in rate observed at 250 K over LTR Rh/TiO_2 probably arose from the poisoning of some highly active sites. Once these had been blocked, the subsequent exchange had a steady rate and it seemed appropriate to use this lower rate as the basis for assessing the effect of SMSI.

The exchange of cyclopentane is more severely influenced by SMSI than the exchange of methane. The rate for cyclopentane fell by a factor of *ca.* 30 after HTR whereas the factors for methane lay between 3 and 13. However, there

was a significant effect on the multiplicity of the exchange with cyclopentane as shown by the results in Tables 2 and 3. It is convenient to discuss the exchanged products in three groups: D_1 and D_2 cyclopentane, the products from D_3 to D_5 cyclopentane corresponding to the completion of the exchange around the ring, and finally the D_6 to D_{10} cyclopentanes which involve propagation of the exchange to both sides of the molecule. The activation energies for these three processes increase in the order in which they are listed.^{22,23} Thus, in the absence of other effects, increase of temperature should give proportionately more of the heavily exchanged products and less of the lightly exchanged. The fact that the opposite behaviour was found for the HTR results in Table 3 shows that SMSI is having a greater effect on the multiple exchange processes, particularly the ‘turnover’ reaction which leads to products in the range from D_6 to D_{10} . There is a close similarity between the present results for Rh/TiO_2 and those reported by Clarke *et al.*⁴ for 2% Pt/TiO_2 which, after subjection to HTR for 25 h, showed a reduction in rate with a marked decrease in the proportions of multiple exchange. Clearly, it is necessary to assume that more than one type of site is involved in the exchange of cyclopentane and that those responsible for the turnover reaction are more readily eliminated by SMSI. This behaviour contrasts with that found for methane which showed no change in the proportion of multiple exchange due to SMSI.

Hydrogenolysis of 2,2-Dimethylpropane

As expected from earlier work,³ the hydrogenolysis of 2,2DMP is a highly structure-sensitive reaction with the consequence that the rate of reaction over Rh/TiO_2 was decreased by a substantial factor of *ca.* 10^4 to 10^5 after HTR. These results can be compared with data on the hydrogenolysis of *n*-butane over Rh/TiO_2 . Braunschweig *et al.*¹³ reported a fall in activity at 473 K by a factor of 10^3 due to SMSI but earlier work by Resasco and Haller¹² gave factors ranging from 10^3 to 10^6 depending on the method used to prepare the catalysts. An interesting feature of our results was the evidence that the effects of SMSI were only partially developed after reduction for 1 h and that the full influence of SMSI required a longer period of HTR, see Fig. 5. This may be associated with a slow diffusion of oxide moieties over the metal surface. The results in Fig. 6 show that the depth of hydrogenolysis was also reduced significantly by SMSI and again that there was only a partial effect after HTR for 1 h.

The restoration of activity of an HTR Rh/TiO_2 catalyst, after oxidation followed by LTR, see Fig. 5, is in agreement with other investigations.³ This reversibility of the effects of SMSI, also observed for the reactions of MCP, see Table 6, suggests that no substantial changes in the morphology of the catalysts can result from HTR.

The present results provide evidence of a parallel between the sensitivity of a reaction to SMSI and the influence on the rate of reaction by changing from a Rh to a Pt catalyst. Oliver *et al.*³⁴ showed that the exchange of methane at 463 K was five times faster over Pt/SiO_2 than over Rh/SiO_2 although the latter gave a higher proportion of multiple exchange with $M = 2.6$ compared with $M = 1.1$ for Pt/SiO_2 . In contrast, for the hydrogenolysis of 2,2DMP at the same temperature Rh/SiO_2 is a much more effective³⁵ catalyst than Pt/SiO_2 by a factor of *ca.* 200.

Hydrogenolysis of Methylcyclopentane

The critical feature associated with the reactions of this compound over both LTR Rh/TiO_2 and LTR Rh/SiO_2 is the small increase in rate associated with the rise in temperature from 473 to 573 K, see Table 6. With both catalysts, the

overall rate of reaction rises by only *ca.* 80% and this is far below the expected value for normal Arrhenius behaviour for the type of processes occurring. One factor responsible for low rates at the higher temperatures is the formation of alkene. The results in Fig. 7 show that at 532 K even 0.2% alkene is sufficient to compete for the surface and inhibit the rate of conversion of methylcyclopentane although the effect of the alkene is non-selective and all modes of reaction were equally affected. However, it is probable that self-poisoning due to the formation of carbonaceous residues is also a factor, particularly as the temperature of reaction is increased. Koscielski *et al.*³⁶ have shown that such residues can mask differences in the catalytic reactivity of C₆ hydrocarbons over silica-supported Pt/Pd catalysts. Self-poisoning, whether caused by alkene formation or carbonaceous residues, is undoubtedly obscuring the normal effects expected for SMSI. Nevertheless, some evidence of the differing structure-sensitivity of the various modes of reaction can still be discerned; as expected, dehydrogenation is only reduced by a low factor of two whereas multiple hydrogenolysis falls by a factor of 30 and other processes are influenced to an intermediate extent, see Table 6.

The present results are in accord with the other investigations of SMSI on the reactions of cyclic molecules. Haller *et al.*³⁷ found no suppression of the dehydrogenation of cyclohexane due to SMSI with Rh/TiO₂ and only a five-fold reduction in the rate of hydrogenolysis. Three investigations^{14,15,17} of the reactions of MCP over Rh/TiO₂, reduced at different temperatures, are relevant to the present work. In every case, the main process was ring-opening to form 2-methylpentane, 3-methylpentane and smaller amounts of *n*-hexane. There are, however, interesting differences in the extents of multiple hydrogenolysis to form smaller hydrocarbons. Our results are broadly similar to those reported by Schepers *et al.*¹⁴ who found that the percentage of multiple hydrogenolysis was small at 473 K but rose to over 25% for reaction at 573 K; they also reported a decrease in the overall reaction by a factor of *ca.* five for HTR at 993 K. In contrast, Anderson *et al.*¹⁵ found little reduction in rate due to HTR at 773 K but their results showed a different trend with respect to hydrogenolysis. This process represented between 10 and 49% of the overall reaction at 383 K for differently treated catalysts but never more than 4% for reaction at 423 K. Fenoglio *et al.*¹⁷ only observed ring-opening at 433 K but found with some catalysts reductions of rate of up to 10² with SMSI. The Dutch workers¹⁴ have commented on the similarities of the effects of SMSI with Rh/TiO₂ and the changes in catalytic behaviour observed when carbonaceous residues were deliberately formed on Rh/SiO₂.

Our conclusion, after consideration of these various investigations of the reactions of MCP and the present results, is that it is not a particularly suitable reactant for the investigation of SMSI. The system is undoubtedly complicated by the relative ease of formation of dehydrogenation products and the possibility that these in turn may lead to strongly adsorbed hydrocarbon residues.

Conclusions

Some, but not necessarily all, exchange reactions of hydrocarbons are less influenced by SMSI than other types of hydrocarbon reactions. Thus, in terms of structure-sensitivity, exchange reactions are comparable to hydrogenation-dehydrogenation reactions.

The full effects of SMSI on the hydrogenolysis of 2,2-dimethylpropane only develop after several hours reduction of Rh/TiO₂ at 773 K; this may be because of slow diffusion of oxide moieties over the metal surface.

The results provide further evidence for the existence of a number of kinds of sites on Rh/TiO₂ and the sites needed for the more structure-sensitive reactions may involve more metal atoms and are more seriously influenced by SMSI.

In all cases, the effects of SMSI are largely reversible and normal catalytic behaviour is restored by oxidation followed by LTR.

A.C.F. acknowledges financial support from Petrobras, Brazil.

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