

Supported Metal Catalysts; Preparation, Characterisation, and Function

Part VI. Hydrogenolysis of Ethane, Propane, n-Butane and iso-Butane over Supported Platinum Catalysts

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The catalytic properties of three supported platinum catalysts, 0.75 wt% Pt/SiO₂, 0.89 wt% Pt/Al₂O₃, and 0.48 wt% Pt/MoO₃, are reported for the hydrogenolysis of ethane, propane, n-butane, and iso-butane. The reactions were carried out in a flow reactor at atmospheric pressure. The apparent activation energies, E_{app} , for the hydrogenolysis reactions and the isomerisation reactions of n-butane and iso-butane, all show a compensation effect with the corresponding values of $\ln A_{app}$. This compensation effect can be accounted for by the dehydrogenative chemisorption of the alkanes as the first step in the reaction mechanisms to both hydrogenolysis and isomerisation. No apparent structure sensitivity was demonstrated by the three catalysts for the hydrogenolysis of ethane. The Pt/Al₂O₃ catalyst showed the highest activity of the three catalysts for the hydrogenolysis of propane. This high activity can be related to the strong adsorption of alkane fragments on platinum sites on the Pt/Al₂O₃ catalyst which exhibit δ^+ polarisation. Over the Pt/SiO₂ and Pt/Al₂O₃ catalysts the isomerisation of n-butane and iso-butane can be explained by a metal-only catalysed isomerisation route. Very high levels of isomerisation over the Pt/MoO₃ catalyst agree with a bifunctional mechanism involving acid sites on the MoO₃ support.

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INTRODUCTION

This work is a continuation of a series of papers in which catalytic activity and selectivity have been related back to an extensive study of catalyst preparation and characterisation (1–5). A series of platinum and nickel catalysts were prepared using a variety of methods (impregnation, coprecipitation and metal vapour deposition) and were characterised using a wide range of physical and chemical techniques (electronic spectroscopy, TGA, TPR, XPS, HRTEM, EXAFS, CO/O₂/hydrocarbon chemisorption). Paper V in this series investigated the hydrogenation of ethene, 1,3-butadiene, and 2-butyne and the hydrogenolysis

of cyclopropane over three of these catalysts, a 0.75 wt% Pt/SiO₂, a 0.89 wt% Pt/Al₂O₃, and a 0.48 wt% Pt/MoO₃ all made by impregnation. This paper investigates the hydrogenolysis reaction of ethane, propane, n and iso-butane over the same three platinum catalysts² and attempts to relate the catalytic properties to the known physical properties of the catalysts and to the previous reaction studies.

The hydrogenolysis reaction of simple alkanes over metal catalysts has been known for many years and has been incorporated into many reviews of hydrocarbon reactions (6–10). Hydrogenolysis can be defined as, “the breakage of carbon–carbon bonds with the uptake of hydrogen.” As each hydrogenolysis reaction involves the rupture of one carbon–carbon bond and the formation of two carbon–hydrogen bonds they are always exothermic.

The hydrogenolysis of alkanes over supported metal catalysts maintains its interest both for the theoretical aspects of this most fundamental hydrocarbon reaction and also because of its industrial applications. Defined by Boudart as a “structure sensitive reaction,” the specific rates of alkane hydrogenolysis reactions are often highly dependent on the metal particle size of the active phase (11). In the reforming of light hydrocarbons (in the range C₅–C₁₁) hydrogenolysis has to be minimised to achieve a better selectivity of production of aromatics. Therefore a greater understanding of the hydrogenolysis mechanism, and the identification and removal of the reactive sites responsible for the reaction should lead to more highly selective reforming catalysts (12).

The metal function of supported catalysts has a large influence on the hydrogenolysis characteristics. The group VIII metals show a clear tendency for hydrogenolysis

² These catalysts were denoted as Pt/silica(I), Pt/alumina(I), and Pt/molybdena(I) in Parts I–III, where (I) denotes preparation by impregnation; this distinguished them from catalysts prepared by coprecipitation which were denoted (C). This annotation is not used in this paper because all catalysts used were prepared by the impregnation method.

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activity to decrease when proceeding from right to left across a period (6). Within the 4d series (Ru, Rh, Pd) maximum activity is found at Ru for the 5d series (Os, Ir, Pt) at Os. In the first transition series Co and Ni both exhibit comparably high activity (10). The metals also vary in their depth of hydrogenolysis, that is, in how many carbon-carbon bonds broken per visit of a reactant hydrocarbon to the catalyst surface. Single hydrogenolysis is defined as the breakage of a single carbon-carbon bond per visit to the catalyst surface. Multiple hydrogenolysis involves the breakage of more than one bond per visit. The metals Pt and Pd have a high selectivity for single hydrogenolysis. On the other hand, W, Ta, Fe, and Co all have a high tendency for total degradation to methane. The metals Ir, Rh, Os, Re, Ru, and Ni all lie somewhere between these two extremes. This depth of hydrogenolysis, however, has no relation to the selectivity of the reaction, that is, the tendency for particular bonds to be broken. Ni, Pd, and Rh show high selectivity for terminal bond splitting (demethylation). Other 4d and 5d group VIII metals (particularly Pt and Ir) show less selective cracking, leading to a largely statistical spectrum of primary products. Under hydrogenolysis conditions isomerisation of alkanes can also take place (10). Most of the group VIII metals exhibit activity, in at least one alkane isomerisation reaction. The order of activities usually follows the sequence $Rh > Ir > Pt > Pd > Ni$.

Simple alkanes such as ethane, propane, n-, and iso-butane can be used as "archetype" molecules for studying hydrogenolysis reactions as they allow the comparison between possible 1,2; 1,3; and 1,4 adsorptions of hydrocarbons on the catalyst surface (5). Iso-butane and n-butane are also useful molecules for studying bond shift isomerisation reactions.

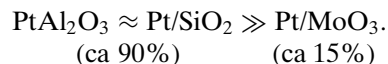
This paper reports on the hydrogenolysis of these alkanes over three well characterised supported platinum catalysts, using two traditional supports alumina and silica and one less conventional material molybdenum trioxide. The relative activities and selectivities of these catalysts illustrate important mechanistic aspects of the hydrogenolysis reaction over platinum catalysts and highlights the major influence of the support on the reaction characteristics.

EXPERIMENTAL

The preparation and characterisation of these catalyst has been reported in detail in previous papers (1-3). The catalysts were prepared by the impregnation of hexachloroplatinic acid, H_2PtCl_6 (Johnson Matthey Chemicals Ltd.) on to three support materials namely alumina (Degussa Aluminium Oxid C, surface area $102 \text{ m}^2 \text{ g}^{-1}$), silica (Cab-O-Sil, surface area $203 \text{ m}^2 \text{ g}^{-1}$), and molybdenum trioxide (BDH Analar grade 99.5%, surface area $2.1 \text{ m}^2 \text{ g}^{-1}$). The platinum contents of these catalysts were determined by ICP-MS as follows, 0.89 wt% Pt for the Pt/alumina 0.75 wt% Pt for

the Pt/silica, and 0.48 wt% Pt for the Pt/molybdenum trioxide catalyst. Before use the finely divided catalyst powders were pressed into discs, crushed, and sieved between 180 and $500 \mu\text{m}$ meshes.

A summary of the characterisation work carried out on these catalysts is as follows (1-4). After reduction the Pt/SiO₂ catalyst was shown to be chloride free with the platinum metal present in the zero oxidation state (by XPS) with a large fraction of very small metal particles ($\leq 0.7 \text{ nm}$) and minimal metal-support bonding (as judged by Pt L₃-edge EXAFS spectroscopy). After reduction the Pt/Al₂O₃ catalyst retained a significant amount of chlorine (1.01 wt%) which was associated with the support, the platinum was shown to be present as Pt^{δ+} (by XPS), the metal was again highly dispersed and there was substantial metal-support bonding evident from the EXAFS spectrum (coordination number of O about Pt was 0.8). The Pt/MoO₃ catalyst showed minimal chlorine content after reduction. Under the reduction conditions the support formed the molybdenum bronze H_xMoO₃, where x was ca 1.0 (by TGA, TPR, and XPS). The platinum retained a δ+ character in the reduced state (by XPS). This is consistent with hydrogen bronze formation or the formation of MoO_x species (where $x < 3$). This material had a wide distribution of Pt particles ranging from 0.7 to 20 nm. From the chemisorption of carbon monoxide and dioxygen the following platinum dispersions were calculated for the three catalysts:



The hydrogenolysis reactions of ethane, propane, n-, and iso-butane were carried out in a stainless steel microreactor, designed to produce a controlled flow of helium, dihydrogen, and hydrocarbon over a small charge (approx. 0.15 g) of catalyst. The He (Grade A, B.O.C.), H₂ (B.O.C.), and hydrocarbon (all B.O.C., Grade N.2.0) feeds were purified before use by passing through dioxygen filters and molecular sieves (Prolab 4A). The reactor was operated at atmospheric pressure. The catalysts were reduced by heating to 693 K at a heating rate of 10 K per minute in a flow of dihydrogen of 40 ml min^{-1} . The samples were then held in flowing dihydrogen at 693 K for 3 h to complete the reduction. After reduction the samples were cooled in flowing dihydrogen to the reaction temperature before introducing the He/H₂/hydrocarbon (approx. 4:4:1 ratio) mixture. The flows of He, H₂, and hydrocarbon were controlled by mass flow controllers.

In order to reach steady state conditions in the reactor, the reactant gases were flowed through the catalyst for 20 min before analysing the reaction products, after the analysis He/H₂ was flowed through the catalysts for 15 min; after this process the He/H₂/hydrocarbon mixture was again introduced into the reactor in order to study the

reaction at different temperatures. Using this process reproducibility of reaction rates was observed even after temperature cycling. The reaction products were analysed by gas chromatography (Perkin Elmer 8500) using a Poropak QS packed column and a flame ionisation detector.

Treatment of Results

The following treatment of the raw data was used to derive the product selectivities and activities.

(a) Fractional conversion. The following equations were used to calculate the moles of reactant hydrocarbon (denoted as A) which had undergone hydrogenolysis: for ethane $A = C_1/2$; for propane $A = (C_1 + 2C_2)/3$; for n- and iso-butane $A = (C_1 + 2C_2 + 3C_3)/4$, where C_i is the mole fraction of the products formed containing i carbon atoms ($i < 3$).

For ethane and propane the fractional hydrogenolysis conversions (X_{HYD}) were then calculated from the equations: for ethane $X_{\text{HYD}} = A/(A + C_2)$; for propane $X_{\text{HYD}} = A/(A + C_3)$.

For n-butane and iso-butane, as isomerisation can also take place, the fractional conversions were calculated from the equation

$$X_{\text{HYD}} = \frac{A}{A + \text{iso-C}_4 + \text{n-C}_4},$$

where iso-C₄ = mole fraction of iso-butane and n-C₄ = mole fraction of n-butane.

(b) Selectivity. For propane and the butanes, where there is a choice of hydrogenolysis products, the selectivity to each product is denoted by S_i , where $S_i = C_i/A$.

For propane hydrogenolysis it can be shown that $S_1 = 3 - 2S_2$ and for the hydrogenolysis of butanes that $S_1 = 4 - 3S_3 - 2S_2$.

The selectivity of isomerisation over hydrogenolysis for the butanes can be calculated from the equations: for n-butane $\text{ISOM}/\text{HYD} = \text{iso-C}_4/A$; for iso-butane $\text{ISOM}/\text{HYD} = \text{n-C}_4/A$.

(c) Turnover. The reaction rates and turnover frequencies for the hydrogenolysis reactions were calculated as

$$r_{\text{HYD}} = \frac{F \cdot X_{\text{HYD}}}{W}, \quad t_{\text{HYD}} = 1.451 \times \frac{F \cdot X_{\text{HYD}}}{W \cdot L \cdot d},$$

where

r_{HYD} = reaction rate (ml min⁻¹ g_{cat}⁻¹)

t_{HYD} = hydrogenolysis turnover (molecules s⁻¹ surface platinum atom⁻¹)

F = flow rate of hydrocarbon (ml min⁻¹)

X_{HYD} = fractional conversion

W = weight of catalyst (g)

L = % Pt loading of catalyst

d = % dispersion of Pt

1.451 = conversion factor (converts ml min⁻¹ g_{cat}⁻¹ to molecules s⁻¹ surface platinum atom⁻¹) (13).

A similar set of equations was used to calculate the isomerisation turnovers by replacing X_{HYD} in the equation above with X_{ISOM} , where for n-butane

$$X_{\text{ISOM}} = \frac{\text{iso-C}_4}{A + \text{iso-C}_4 + \text{n-C}_4}$$

and for iso-butane

$$X_{\text{ISOM}} = \frac{\text{n-C}_4}{A + \text{iso-C}_4 + \text{n-C}_4}.$$

RESULTS

(i) Nonsteady State Condition

In order to reach steady state conditions the reactant gases were flowed through the catalyst samples for 20 min before analysing the reaction products. Analyses taken during this initial 20-min period demonstrated a hydrogenolysis activity rising to a maximum after 5 min before falling to a steady state value. This initial activation of the catalyst (found for all test alkanes over all the catalysts) only occurred during the first contact of the catalyst with the reactant alkane. After the analysis a He/H₂ stream was passed over the catalyst for 15 min. During this time no products were detected and, on resumption of the reaction at the next temperature, no comparable rise and fall in activity before reaching steady state conditions was shown.

(ii) Ethane Hydrogenolysis

The fractional conversions for the hydrogenolysis of ethane (X_{HYD}) over the three catalysts are shown in Table 1. The apparent activation energies for the reaction are in the range 201 to 253 kJ mol⁻¹. This is consistent with literature values for this reaction (6, 14). The Pt/Al₂O₃ and Pt/SiO₂ catalysts showed very similar behaviours for this reaction in terms of turnover and activation energies. The Pt/MoO₃ catalyst, however, showed a steeper activation energy plot. Both the Pt/MoO₃ and Pt/SiO₂ catalysts showed a loss of linearity in their activation energy plots at higher temperatures.

(iii) Propane Hydrogenolysis

The most marked difference in the reaction of propane over the three catalysts, as compared to ethane, was that the catalysts no longer reacted with similar turnovers in the same temperature range (Fig. 1). For comparison purposes Table 2 shows the temperature at which the hydrogenolysis turnover = 0.02 molecules s⁻¹ surface platinum atom⁻¹.

TABLE 1
Hydrogenolysis of Ethane, Propane, n-, and Iso-Butane over Pt/Al₂O₃, Pt/SiO₂, and Pt/MoO₃ Catalysts

Catalyst	Alkane	Temp. (K)	Hydrogenolysis			Isomerisation		
			X _{HYD}	E _a (kJ mol ⁻¹)	ln A	X _{ISOM}	E _a (kJ mol ⁻¹)	ln A
Pt/Al ₂ O ₃	C ₂ H ₆	683–763	2.8 × 10 ⁻³ –0.125	219	32.9			
	C ₃ H ₈	603–673	6.3 × 10 ⁻³ –0.15	150	25.1			
	n-C ₄ H ₁₀	693–753	0.017–0.10	135	19.3	1.4 × 10 ⁻³ –9.3 × 10 ⁻³	161	24.8
	iso-C ₄ H ₁₀	643–713	0.016–0.12	105	15.7	2.1 × 10 ⁻³ –0.019	116	19.4
Pt/SiO ₂	C ₂ H ₆	683–763	2.3 × 10 ⁻³ –0.058	201	30.2			
	C ₃ H ₈	653–733	7.1 × 10 ⁻³ –0.11	142	21.8			
	n-C ₄ H ₁₀	593–673	7.1 × 10 ⁻³ –0.033	94	13.8	4.6 × 10 ⁻³ –0.033	102	15.1
	iso-C ₄ H ₁₀	653–733	5.1 × 10 ⁻³ –0.051	123	17.2	7.3 × 10 ⁻³ –0.085	148	26.3
Pt/MoO ₃	C ₂ H ₆	683–763	1.2 × 10 ⁻³ –0.068	253	41.4			
	C ₃ H ₈	683–763	7.9 × 10 ⁻⁴ –0.085	297	46.7			
	n-C ₄ H ₁₀	693–753	8.4 × 10 ⁻³ –0.020	66	6.5	8.5 × 10 ⁻³ –0.13	274	45.4
	iso-C ₄ H ₁₀	633–733	5.6 × 10 ⁻³ –0.030	85	10.5	6.7 × 10 ⁻³ –0.20	179	28.9

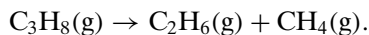
Note. Units of A-molecules s⁻¹ surface platinum atom⁻¹.

From this table the three catalysts had the following reaction temperatures,

$$\text{Pt/Al}_2\text{O}_3 \text{ 622 K} < \text{Pt/SiO}_2 \text{ 665 K} < \text{Pt/MoO}_3 \text{ 707 K.}$$

The Pt/Al₂O₃ and Pt/SiO₂ catalysts showed similar activation energies for the hydrogenolysis of propane (150 and 142 kJ mol⁻¹, respectively). The Pt/MoO₃ catalyst demonstrated a steeper activation energy plot (E_a = 297 kJ mol⁻¹). None of the activation energy plots showed a loss of linearity at higher temperatures.

Figure 2 shows the selectivity for methane (S₁) during the hydrogenolysis of propane over the three catalysts. If S₁ = 1 then the single hydrogenolysis of 1 mole of propane to 1 mole of ethane and 1 mole of methane is taking place,



At values of S₁ > 1 the multiple hydrogenolysis reaction of

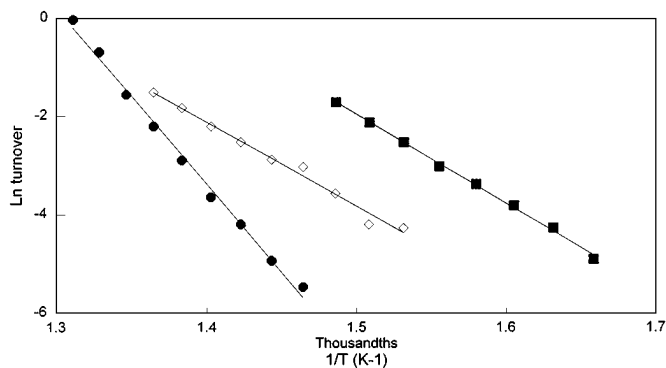
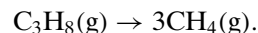


FIG. 1. Hydrogenolysis of propane over Pt/Al₂O₃ (■), Pt/SiO₂ (◇), and Pt/MoO₃ (●).

propane to form methane, is increasingly taking place,



Between 603 and 633 K the Pt/Al₂O₃ catalyst showed S₁ values slightly less than 1. At higher temperatures the Pt/Al₂O₃ catalyst showed S₁ values slightly higher than 1, suggesting that a small amount of multiple hydrogenolysis was taking place. In the temperature range of overlap between the Pt/Al₂O₃ and Pt/SiO₂ catalysts (653–673 K) the selectivities shown by the two catalysts were very comparable. The Pt/SiO₂ catalyst showed S₁ values slightly higher than 1 at all temperatures.

The Pt/MoO₃ catalyst showed S₁ values which rose with temperature from 0.96 at 683 K to 1.27 at 673 K.

TABLE 2
Temperature at Which Hydrogenolysis Turnover = 0.02
Molecules s⁻¹ Surface Platinum Atom⁻¹

Catalyst	Alkane	Temp. (K)
Pt/Al ₂ O ₃	C ₂ H ₆	715
	C ₃ H ₈	622
	n-C ₄ H ₁₀	698
	iso-C ₄ H ₁₀	644
Pt/SiO ₂	C ₂ H ₆	707
	C ₃ H ₈	665
	n-C ₄ H ₁₀	636
	iso-C ₄ H ₁₀	698
Pt/MoO ₃	C ₂ H ₆	700
	C ₃ H ₈	707
	n-C ₄ H ₁₀	753
	iso-C ₄ H ₁₀	703

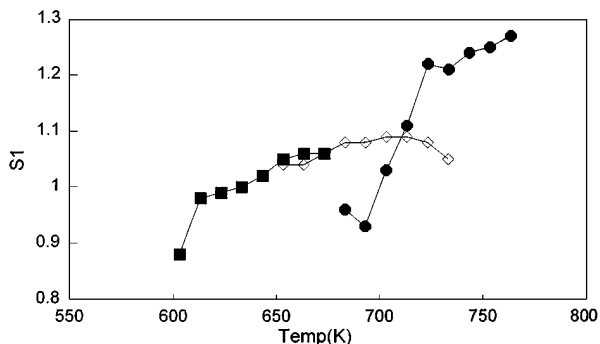


FIG. 2. Selectivity of propane hydrogenolysis over Pt/Al₂O₃ (■), Pt/SiO₂ (◇), and Pt/MoO₃ (●).

(iv) *n*-Butane and Iso-Butane Hydrogenolysis

With the reactions of *n* and iso-butane over the catalysts, in addition to the hydrogenolysis reaction, bond shift isomerisation reactions also take place. Figure 3 shows the activation energy plots for the hydrogenolysis and isomerisation of the butanes over the Pt/Al₂O₃ catalyst.

With the Pt/Al₂O₃ catalyst (Fig. 3) it is clear that there is a close relationship between the hydrogenolysis and isomerisation reactions of both the butanes. Although there is considerably more hydrogenolysis than isomerisation taking place the activation energies for the reactions are obviously very similar.

With the Pt/SiO₂ catalyst there is also a good correlation between the activation energies of the hydrogenolysis and isomerisation reactions (Table 1). With the Pt/SiO₂ catalyst there is much more isomerisation taking place than over the Pt/Al₂O₃ catalyst. For the two isomerisation reactions there is a loss of linearity shown in the activation energy plots at higher temperatures.

The Pt/MoO₃ catalyst shows the largest amount of isomerisation activity. The activation energy plots for the

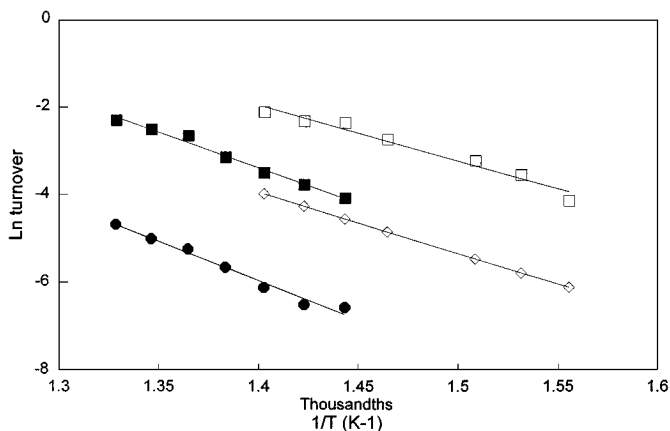


FIG. 3. Hydrogenolysis and isomerisation of *n* and iso-butane over Pt/Al₂O₃ (*n*-butane hydrogenolysis (■), *n*-butane isomerisation (●), iso-butane hydrogenolysis (□), and iso-butane isomerisation (◇)).

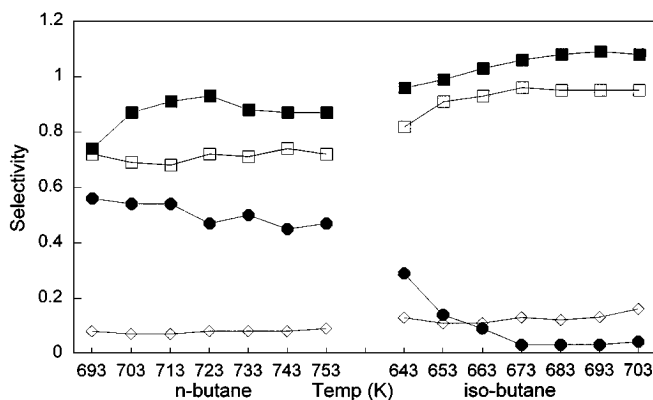


FIG. 4. Selectivity of *n* and iso-butane hydrogenolysis over Pt/Al₂O₃ (S₁ (■), S₂ (●), S₃ (□), and ISO/HYD (◇)).

isomerisation and hydrogenolysis reactions have very different gradients for both *n* and iso-butane. For both the butanes the isomerisation reaction has a higher activation energy than the hydrogenolysis reaction (Table 1). The activation energy plots for both of the isomerisation reactions show a loss of linearity at higher temperatures.

In terms of comparing hydrogenolysis activity (Table 2) for the reaction of *n*-butane the order for the catalysts were as follows:

$$\text{Pt/SiO}_2 \text{ 636 K} < \text{Pt/Al}_2\text{O}_3 \text{ 698 K} < \text{Pt/MoO}_3 \text{ 753 K.}$$

With the reaction of iso-butane the order changes:

$$\text{Pt/Al}_2\text{O}_3 \text{ 644 K} < \text{Pt/SiO}_2 \text{ 698 K} < \text{Pt/MoO}_3 \text{ 703 K.}$$

From a comparison of Figs. 4, 5, and 6 it is clear that the three Pt catalysts have very different selectivities towards isomerisation over hydrogenolysis. For the Pt/Al₂O₃ catalyst the ISO/HYD ratio is around 0.08 for *n*-butane and 0.13 for iso-butane (Fig. 4). Over the Pt/SiO₂ catalyst the ISO/HYD ratio is considerably higher at around 0.75 for *n*-butane and up to values over 2 for iso-butane (Fig. 5). The

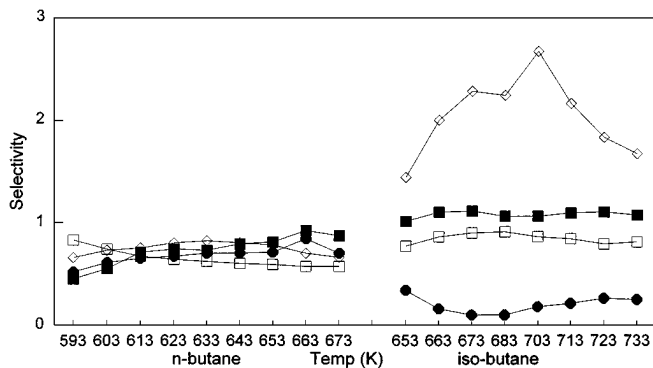


FIG. 5. Selectivity of *n* and iso-butane hydrogenolysis over Pt/SiO₂ (S₁ (■), S₂ (●), S₃ (□), and ISO/HYD (◇)).

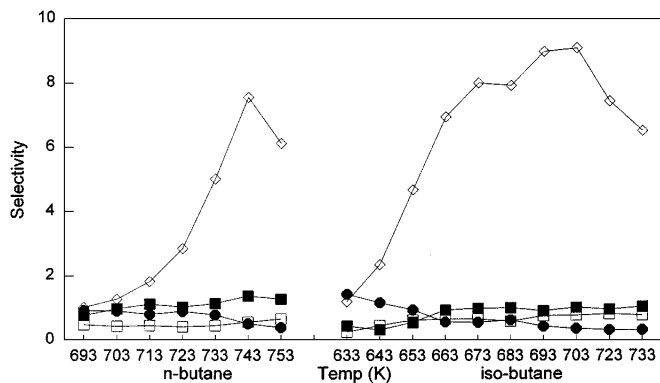
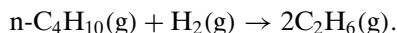
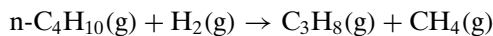


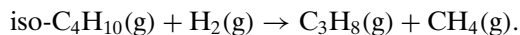
FIG. 6. Selectivity of *n* and iso-butane hydrogenolysis over Pt/MoO₃ (S₁ (■), S₂ (●), S₃ (□), and ISO/HYD (◇)).

Pt/MoO₃ catalyst shows considerable isomerisation under reaction conditions, with ISO/HYD values as high as 7.5 and 9.1 for *n* and iso-butane, respectively (Fig. 6).

The selectivities of the reactions of *n* and iso-butane over the three catalysts are shown in Figs. 4, 5, and 6. The single hydrogenolysis reaction of *n*-butane can be expressed by the following two reactions:



The selectivity towards single hydrogenolysis can be followed from the S₁/S₃ ratio: if S₁/S₃ = 1 then only single hydrogenolysis is taking place; if S₁/S₃ > 1 then multiple hydrogenolysis is taking place. For iso-butane the only single hydrogenolysis reaction that can take place is



Any ethane that is formed from iso-butane must be produced by the breakage of two carbon-carbon bonds. The value of S₂ can therefore be used to follow the multiple hydrogenolysis of iso-butane as well as the S₁/S₃ ratio above. The values of S₁/S₃ for the reactions of the butanes over the three catalysts are shown in Fig. 7.

The reactions of *n*- and iso-butane over the Pt/Al₂O₃ catalyst (Fig. 7) show only small amounts of multiple hydrogenolysis as shown by the S₁/S₃ ratio being slightly >1 in both cases and the small amount of ethane formed at low temperature with iso-butane.

With the reaction of *n*-butane over the Pt/SiO₂ catalyst (Fig. 7) there is a crossover between S₁/S₃ < 1 in the temperature range 593–613 K and S₁/S₃ > 1 from 613 to 673 K. The highest value of S₁/S₃ over the Pt/SiO₂ catalyst (S₁/S₃ = 1.61) is higher than the highest value over the Pt/Al₂O₃ catalyst (S₁/S₃ = 1.29). With the reaction of iso-butane over the Pt/SiO₂ catalyst S₁/S₃ values are slightly higher than 1 and more ethane is formed than over the Pt/Al₂O₃ catalyst.

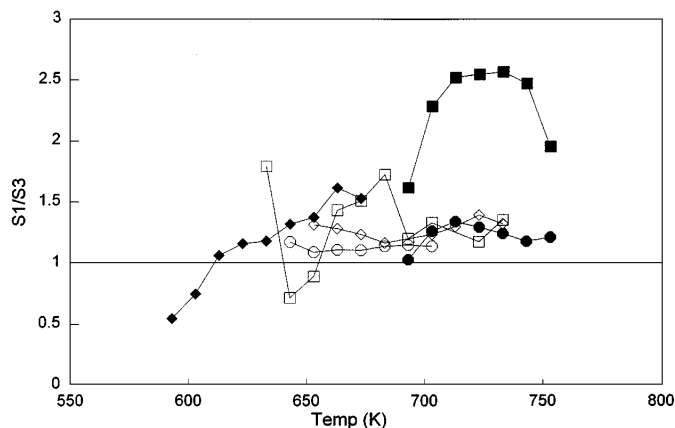


FIG. 7. S₁/S₃ ratio during hydrogenolysis of *n* and iso-butane. (Pt/Al₂O₃ *n*-butane (●), Pt/Al₂O₃ iso-butane (○), Pt/SiO₂ *n*-butane (◆), Pt/SiO₂ iso-butane (◇), Pt/MoO₃ *n*-butane (■), and Pt/MoO₃ iso-butane (□)).

The reaction of *n*-butane over the Pt/MoO₃ catalyst (Fig. 7) shows the highest values of S₁/S₃ of the three catalysts, with S₁/S₃ values as high as 2.57. The Pt/MoO₃ catalyst also shows a high selectivity towards ethane during iso-butane hydrogenolysis, particularly at lower temperatures.

(v) Compensation Effect

The Arrhenius parameters and turnover frequencies for all the hydrogenolysis and isomerisation reactions are summarised in Table 1. Plotting the ln A values against the apparent activation energies gives a convincing compensation effect plot (Fig. 8). The equation for the line obtained is

$$\ln A = 0.1711E_a - 2.587.$$

DISCUSSION

A nonsteady state behaviour was noted for the first contact of each of the reduced catalysts with the reactant gases.

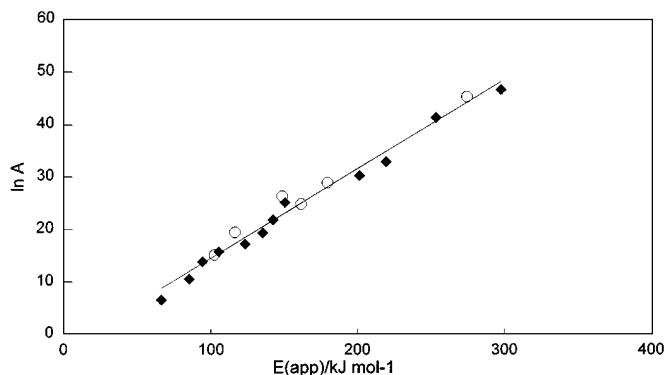
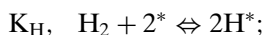


FIG. 8. Compensation effect of alkane hydrogenolysis and isomerisation (hydrogenolysis (◆) and isomerisation (○)).

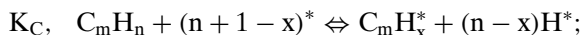
This took the form of an initial activation process followed by a deactivation. A similar nonsteady initial state has been demonstrated for the hydrogenolysis of ethane over Os and Ru clusters (15, 16). The initial activation/deactivation of the catalyst before reaching steady state is probably due to the formation of a reactive carbonaceous overlayer on the platinum surface. Subsequent treatment of the catalyst with the He/H₂ stream does not appear to remove this overlayer or “clean” the surface back to its original state. The reactive catalyst surface that is carrying out the hydrogenolysis reactions is therefore generated *in situ* and contains a carbonaceous component. The involvement of this carbonaceous component is therefore significant in any consideration of the active site for the hydrogenolysis reaction.

Several kinetic models for hydrogenolysis reactions over metal catalysts have been suggested previously (17–22). Many of the models agree with the following general reaction mechanism (22). Step (iii), the C–C bond breakage step, is generally agreed to be the rate determining step:

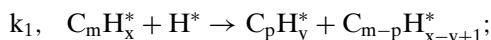
- (i) dissociative chemisorption of dihydrogen,



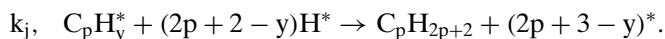
- (ii) dehydrogenative chemisorption of the alkane,



- (iii) fragmentation of this dehydrogenated species,



- (iv) rehydrogenation and desorption of the products,



The compensation behaviour noted (Fig. 8) for this set of reactions has previously been shown for alkane hydrogenolysis over Pt catalysts (23) and other metals (24). Compensation behaviour has also been shown by many other heterogeneous and homogeneous catalytic processes (25, 26). Various theories have been proposed to explain the compensation effect, including enthalpy–entropy relationships, energetically heterogeneous catalyst surfaces, and variations in the availability of surface reactants. These theories and others are discussed at considerable length in a review by Galwey (24). The compensation effect plot (Fig. 8) is in very good agreement with the compensation effect plot derived by G. C. Bond *et al.* from the hydrogenolysis and isomerisation reactions of ethane, propane, n-butane, n-pentane, n-hexane, and n-heptane over EUROPT-1 (14). From a study of alkane hydrogenolysis (22) G. C. Bond proposed that the compensation effect was a result of the apparent activation energies (E_{app}) as measured from rate data being much higher than the true activation energies (E_t) for the reactions. This discrepancy between apparent and actual activation energies arises from a positive contribution

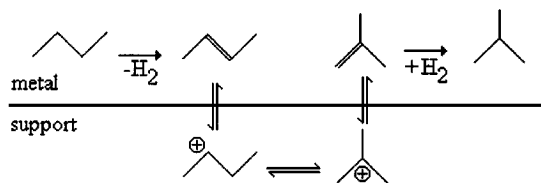
to the apparent activation energy from the dehydrogenative chemisorption of the alkane (step (ii) in the hydrogenolysis mechanism). In other words, at higher temperatures there is an increase in the surface concentration of the reactive form of the alkane ($C_mH_x^*$) which leads to higher rates of reaction. One implication of the existence of a compensation effect is that it is doubtful if any useful mechanistic information about the rate determining step can be gained by comparing overall activation energies. On the other hand, several important observations can be made from inspection of the compensation plot itself. For instance, ethane is often found to have a lower hydrogenolysis reactivity than the longer alkanes and a higher apparent activation energy (14, 22, 27). This has been explained (22) as being due to the difficulty of dehydrogenating ethane, as compared to higher alkanes (i.e., the kinetic parameters are a consequence of the thermochemical stability of the reactant alkane). This holds for the Pt/Al₂O₃ catalyst and the Pt/SiO₂ catalyst where ethane has a lower reactivity than the other alkanes and a higher activation energy. Over the Pt/MoO₃ catalyst however the highest activation energy is for the hydrogenolysis of propane, not ethane.

Another interesting observation is that the isomerisation reactions lie on the same compensation effect plot as the hydrogenolysis reactions. For the bond-shift isomerisation reactions of n- and iso-butane three possible mechanism can be envisaged:

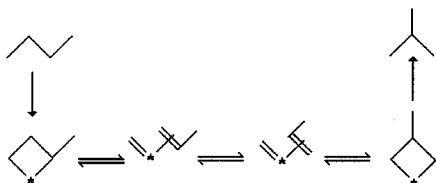
- (i) a bifunctional mechanism involving acid sites on the support,
- (ii) a metal-only catalysed rearrangement,
- (iii) a support-only catalysed rearrangement.

These three mechanisms are shown in Fig. 9. Mechanisms (i) and (ii) both involve a dehydrogenation step on the metal. The dehydrogenation gives these two mechanisms something in common with the general mechanism of hydrogenolysis discussed earlier, that is, the formation of a dehydrogenated organic intermediate on the metal function of the catalyst. The formation of a common intermediate (i.e., a dehydrogenated alkane) that leads to both hydrogenolysis and isomerisation may explain why both reactions lie on the same compensation energy plot. Over the Pt/Al₂O₃ and Pt/MoO₃ catalysts all three mechanisms of isomerisation are possible as both of these supports have acid sites available for isomerisation. On the Pt/SiO₂ catalyst only a metal-only catalysed rearrangement (ii) is possible as there are no acid sites on the silica support strong enough to carry out isomerisation reactions. Various reaction mechanisms have been suggested for metal-only bond shift isomerisation reactions (28–31). A common feature of all these mechanisms is that they all invoke 1,3 diadsorbed alkane intermediates. The mechanism shown in Fig. 9 for the metal-only isomerisation follows the work by Garin *et al.* and differs from the other suggested mechanisms in that the alkane

(i) bifunctional mechanism involving acid sites on the support



(ii) metal-only catalysed rearrangement



(iii) support only catalysed rearrangements

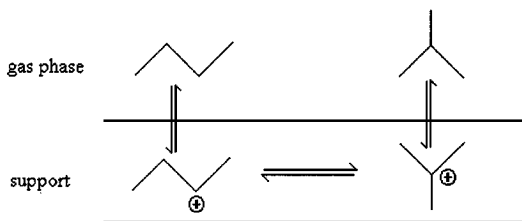


FIG. 9. Isomerisation mechanisms of n and iso-butane.

intermediate is diadsorbed on a single platinum atom. The correlation that is shown between the activation energies for the hydrogenolysis and isomerisation of the butanes over the Pt/SiO₂ catalyst supports the theory that the isomerisation, as well as the hydrogenolysis reaction, is taking place on the metal function of the catalyst. Compared to the Pt/SiO₂ catalyst very little isomerisation activity is shown by the Pt/Al₂O₃ catalyst. As discussed previously, the isomerisation that does take place over the Pt/Al₂O₃ catalyst can either take place via acid sites on the support (Figs. 9(i) and (iii)) or by the metal-only route. The close correlation between the activation energies for the hydrogenolysis and isomerisation reactions of the butanes over the Pt/Al₂O₃ catalyst does suggest that both reactions are taking place on the metal function of the catalyst; i.e., the isomerisation is also taking place by a metal-only route on the Pt/Al₂O₃ catalyst. The Pt/MoO₃ catalyst shows the highest selectivity towards isomerisation with the reactions of the butanes. Unlike the reactions over the Pt/SiO₂ and Pt/Al₂O₃ cata-

lysts the activation energies for the isomerisation reactions are considerably higher than for the hydrogenolysis reactions. The Arrhenius parameters of the isomerisation reactions still fit, however, on the compensation effect plot (Fig. 8). These two observations put together point toward an isomerisation mechanism which, although it still involves the metal function of the catalyst, does not have the same rate-determining step as the hydrogenolysis reaction. This would fit more closely to an isomerisation taking place by a bifunctional mechanism involving the support (Fig. 9(i)) rather than by a metal-only reaction on the platinum. The MoO₃ support itself will have acidic sites present (34). Under the standard reduction conditions the support is known to form the molybdenum bronze H_xMoO₃, where x is ca 1.0 (1-3). The formation of hydrogen molybdenum bronzes from spillover hydrogen can lead to structural modifications of the MoO₃ (32). When the hydrogen atoms enter the MoO₃ lattice there is a tendency for the oxide to cleave in planes parallel to its c crystallographic axis. This may lead to the formation of defect sites on the support and increase the number of acidic sites present. The high multiple hydrogenolysis activity of the Pt/MoO₃ catalyst with propane, n, and iso-butane and also the high isomerisation activity of this catalyst with the butanes may all be related to reactions taking place on acid sites on the support. These reactions may all follow a bifunctional mechanism with the transfer of adsorbed organic intermediates from the platinum to the support. The activation of propane over the Pt/MoO₃ catalyst is more difficult than the activation of ethane, which is contrary to the results derived from the Pt/Al₂O₃ and the Pt/SiO₂ catalysts and literature results (14). This, coupled with the multiple hydrogenolysis activity, suggests that the transfer of organic intermediates from the metal to react on the support is a more activated process than a reaction solely on the metal.

Hydrogenolysis of small alkanes over supported metal catalysts are often found to be structure sensitive in terms of activity (35-38), or in some cases in terms of selectivity (39). For the hydrogenolysis of ethane the three catalysts reacted with similar turnover numbers in the temperature range tested. There was no obvious structure sensitivity shown for these catalysts, or therefore, for the hydrogenolysis of ethane. Any discussion of surface sensitivity when comparing these three platinum catalysts is complicated, however, by factors such as the existence of the δ⁺ polarised sites on the Pt/Al₂O₃ and Pt/MoO₃ catalysts and in the case of the Pt/MoO₃ catalyst the existence of a wide distribution of platinum particle sizes (from 0.7 to 20 nm). The wide distribution of the platinum particles on the Pt/MoO₃ catalyst make the detection of structure sensitivity particularly difficult as the smallest particles may be responsible for the majority of the reaction (5). A turnover number as calculated from an averaged platinum particle size may not therefore be applicable.

For the hydrogenolysis of propane the three catalysts showed a range of activities; i.e.,



comparing in the first instance the activities of the Pt/Al₂O₃ catalyst and the Pt/SiO₂ catalysts. Although the Pt/Al₂O₃ catalyst has a marginally higher dispersion, as shown by EXAFS, than the Pt/SiO₂ catalyst, such a large difference in activity appears to be too large to be accounted for solely in terms of platinum particle size differences between the two catalysts. In a previous paper the hydrogenolysis reaction of cyclopropane was carried out over all three platinum catalysts (5). The hydrogenolysis of cyclopropane was shown to follow the Bond-Newham rate equation (33). The rate coefficient for the reaction was considerably higher for the Pt/Al₂O₃ catalyst ($k = 43.9$) than for the Pt/SiO₂ catalyst ($k = 10.6$). Other results from this study showed that cyclopropane adsorbed much more strongly on the Pt/Al₂O₃ catalyst than on the Pt/SiO₂ catalyst. This stronger adsorption was related to the existence of platinum sites which exhibited $\delta+$ polarisation on the Pt/Al₂O₃ catalyst, sites which then interacted strongly with the incipient π -system of the strained hydrocarbon (5). The Pt/SiO₂ catalyst, on the other hand, did not show any evidence for the existence of Pt ^{$\delta+$} sites. In the case of the Pt/Al₂O₃ catalyst the enhanced activity it demonstrated, as compared to the Pt/SiO₂ catalyst, in the hydrogenolysis of cyclopropane appears to be as a consequence of the $\delta+$ polarisation of the platinum sites, rather than the presence of marginally smaller platinum particles. The strong adsorption properties of the Pt/Al₂O₃ catalyst for dehydrogenated C₃ fragments may also explain its higher activity for propane hydrogenolysis as compared to the Pt/SiO₂ catalyst. Several crystallographic models have been proposed that relate the structure sensitivity to the existence of particular sites on very small metal crystallites (40–43). The structural sensitivity shown in this case is not due to the existence of special sites on crystallites but rather on the electronic perturbation of the platinum crystallites that takes place with the Pt/Al₂O₃ catalyst. This electronic root of structure sensitivity may explain why certain reactions are either structure sensitive or insensitive. Rate enhancement will only occur if the electronic perturbation of the site in some way promotes the reaction (i.e. by interacting with the incipient π -system of the strained cyclopropane). It is difficult to compare the relative activities of the three catalysts for the hydrogenolysis of the butanes due to the large amount of isomerisation that takes place during these reactions, particularly over the Pt/SiO₂ and Pt/MoO₃ catalysts. It is worth considering, however, the relative isomerisation activities of the Pt/Al₂O₃ and Pt/SiO₂ catalysts. The isomerisation appears to take place by a metal-only route over both catalysts, yet the Pt/SiO₂ catalyst demonstrates a considerably higher isomerisation selectivity over hydrogenolysis than the Pt/Al₂O₃ catalyst.

The metal-only isomerisation of butanes involves the following process (Fig. 9):

- (i) the breakage of a carbon–carbon bond
- (ii) skeletal rearrangement, followed by
- (iii) reformation of a carbon–carbon bond.

The $\delta+$ polarisation of the platinum sites on the Pt/Al₂O₃ catalyst would appear to have the effect of suppressing either step (ii) or step (iii) in this process relative to the Pt/SiO₂ catalyst. The stronger adsorption of the dehydrogenated C₃ fragments that would be involved in steps (ii) and (iii) on the $\delta+$ sites on the Pt/Al₂O₃ catalyst may inhibit isomerisation and favour, instead, the hydrogenolysis reaction pathway. Although the polarisation of the platinum on the Pt/Al₂O₃ catalyst is strong enough to have an effect on the isomerisation selectivity it does not appear to be strong enough to produce other effects such as increased multiple hydrogenolysis. This would manifest itself as high S₁/S₃ ratios for the reactions of both n and iso-butane and high S₂ figures for the reaction of iso-butane. This is not the case, however, on the Pt/Al₂O₃ catalyst relative to the Pt/SiO₂ catalyst.

CONCLUSIONS

A clear compensation effect is shown between the apparent activation energies and preexponential factors for the hydrogenolysis reactions of ethane, propane, n, and iso-butane over the three platinum catalysts. This effect may be due to the dehydrogenative chemisorption of the alkanes prior to the carbon bond breakage step. There is a close relationship between the mechanisms of hydrogenolysis and isomerisation of the butanes over the Pt/Al₂O₃ and Pt/SiO₂ catalysts. Both the isomerisation and hydrogenolysis reactions appear to take place on the platinum functions of the catalysts. Many of the characteristics of the Pt/MoO₃ catalyst are not typical of a platinum catalyst, i.e. multiple hydrogenolysis and large amounts of isomerisation. These characteristics are consistent with reactions taking place over acid sites on the support and bifunctional reaction mechanisms. The higher activity of the Pt/Al₂O₃ catalyst as compared to the Pt/SiO₂ catalyst for the hydrogenolysis of propane appears to be linked with the $\delta+$ polarisation of the platinum sites on the Pt/Al₂O₃ catalyst.

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