

UNUSUAL CATALYTIC BEHAVIOUR OF 3% Pt/TiO₂ OVER n-HEXANE AND METHYLCYCLOPENTANE TRANSFORMATION

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ABSTRACT. Hydrogenolysis of n-hexane and MCP has been studied using Pt (3% Pt) supported on TiO₂ (Degussa), prepared by wet impregnation method from H₂PtCl₆. Reductive pretreatment (RPT: 573 K of the catalyst in H₂) produced no catalytic activity for n-hexane and MCP, however, oxidative pretreatment (OPT: 473 K of the catalyst in air followed by reduction at 573 K in H₂) gave catalytic activity of n-hexane and MCP. The loss of the catalytic activity in the absence of prior oxidation may be explained by effects analogous to SMSI-type behaviour despite this occurring at only 573 K.

INTRODUCTION

There is a wealth of experimental work on how TiO₂ affects the properties of Pt for alkanes transformation under strong metal support interaction (SMSI) conditions [1-6]. In the studies of the effects of reduction temperature on the catalytic activities [1-16], it has been shown that the high temperature reduction at 773 K (HTR) caused a strong activity suppression of hydrogenolysis (a structure-sensitive reaction) but suffer only a mild suppression of hydrogenation-dehydrogenation (structure-insensitive reactions). It is thus recognised that SMSI (defined as a reversible effect of chemisorption capacity or catalytic activity induced by HTR [17]) has great influence on structure sensitive reactions [3-5].

Hydrocarbon reactions that have been studied suggest that Pt/TiO₂ shows selectivities and activities that are different from Pt/Al₂O₃ and Pt/SiO₂ [3-6]. Selectivity is itself recognised as a probe [18-24] for structure sensitivity. Not only has selectivity been found to be a function of dispersion [18-24] but also of support used [25].

Since the discovery of structure-sensitivity for selectivity [26], hydrocarbon reactions whose activity and selectivity manifest themselves as size of metal particle dependent behaviour have been well documented [27-29]. The origin of this size effect in some of these reactions is still controversial [30,31]. However, products distribution in reactions such as MCP hydrogenolysis, which has established itself to be structure-sensitive for selectivity over Pt/Al₂O₃ catalysts [24,26] have been unequivocally shown to be a function of particle size and support [24,26-28,32,33].

In the present study the behaviour of 3% Pt/TiO₂ catalyst under reductive and oxidative pretreatments in alkanes transformation is explored with regard to the selectivity and activity of n-hexane and MCP.

EXPERIMENTAL

The 3% Pt/TiO₂ catalyst was prepared by impregnating Degussa P-25 TiO₂ (76% anatase, 24% rutile, surface area 55 m² g⁻¹) with aqueous solution of chloroplatinic acid, H₂PtCl₆·2H₂O (Johnson Matthey Chemicals, UK). After drying overnight at 373 K, the catalyst was reduced (5 K min⁻¹, 543 K, 1 h) in flowing H₂.

Hydrogenolysis at a total pressure of 101 kPa of n-hexane (>99.0%, Alfa Products; UK) and MCP (>99.0%, Fluka; Switzerland) was studied in a continuous flow apparatus using a 18:1 and 19:1 mole ratios for H₂:n-hexane and H₂:MCP, respectively.

Prior to catalytic measurements, the sample (0.5 g) was subjected to one of the following in-situ re-reduction pretreatment: (i) RPT: N₂ (573 K, 1 h), H₂ (573 K, 1 h), N₂ (423 K, 16 h) and (ii) OPT: N₂ (473 K, 1 h), air (473 K, 2h), N₂ (573 K, 15 min), H₂ (573 K, 1 h), N₂ (423 K, 16 h).

Products were analyzed by a chromosorb PAW column at 343 K. The catalyst temperature was raised at intervals of about 10 K in a stepwise manner from 573-644 K with 20 min isothermal periods, samples being analyzed after 20 min.

Products yields were expressed as selectivities, S_i, defined as the number of moles, C_i, of a product containing, i, carbon atoms formed from each mole of reactant. Hence,

$$S_i = (iC_i) / \left(\sum_1^i iC_i \right)$$

RESULTS AND DISCUSSION

When the effect of SMSI Pt/TiO₂ [1-6] was studied on the activity and selectivity of 3% Pt/TiO₂ for the skeletal rearrangement and hydrogenolysis of n-hexane and MCP, some quite remarkable effects were observed. *Reductive pretreatment (RPT)* produced no catalytic activity for n-hexane and MCP while *oxidative pretreatment (OPT)* gave catalytic activity of n-hexane and MCP. RPT may leave much residual Cl⁻ on the surface of the TiO₂; this may have some effect, positive or negative on catalytic performance. It may also suppress hydrogen spillover and hence lead to a small SMSI effect [13-16]. It is most likely that the presence of Cl⁻, partly on the Pt and partly on the TiO₂ inhibits hydrogen spillover [13-16] which is essential to the production of mobile TiO_{2-x} species and hence may account for the zero activity for n-hexane and MCP. OPT serves [13-16] to: (i) redisperse Pt particles and (ii) remove much or all of the Cl⁻ and hence may account for activity of n-hexane and MCP.

n-Hexane. Table 1 shows several reactions that have occurred between n-hexane and hydrogen (represented by unbalanced reactions 1-4) at different temperatures. Reactions

Table 1. Reactions between n-hexane and hydrogen at different temperatures.

No.	Reaction	Temperature (K)
1	C ₆ H ₁₄ + H ₂ → CH ₄ + C ₂ H ₆ + C ₃ H ₈	583
2	C ₆ H ₁₄ + H ₂ → CH ₄ + C ₂ H ₆ + C ₃ H ₈ + C ₄ H ₁₀	593
3	C ₆ H ₁₄ + H ₂ → CH ₄ + C ₂ H ₆ + C ₃ H ₈ + C ₄ H ₁₀ + C ₅ H ₁₂	604-624
4	C ₆ H ₁₄ + H ₂ → CH ₄ + C ₂ H ₆ + C ₃ H ₈ + C ₄ H ₁₀ + C ₅ H ₁₂ + 2-MP	633-644

1-3 are called multiple hydrogenolysis where several C-C bonds of n-hexane have been broken while reaction 4 is a combination of multiple hydrogenolysis and isomerisation. Table 2 shows variation of product selectivity with temperature for n-hexane hydrogenolysis over 3% Pt/TiO₂. It is clear that on going to higher temperatures, several C-C bonds of n-hexane are broken to give more fragments of hydrogenolysis products. This breaking of several C-C bonds of n-hexane may explain the drop in C₁ and C₂ selectivities between 593 K and 604 K. Again, on going from 613 K to higher temperatures, there is a significant drop in C₃ selectivity. It is most likely that the C₃ species undergo further hydrogenolysis to C₁ + C₂ as evidenced by an increase in C₁ and C₂ selectivities.

Table 2. Variation of product selectivity with temperature for n-hexane hydrogenolysis over 3% Pt/TiO₂.

T/K	Selectivity (%)					
	C ₁	C ₂	C ₃	C ₄	C ₅	2-MP
583	19	1	80	-	-	-
593	6	4	80	2	-	-
604	5	6	80	6	2	-
613	15	9	67	6	3	-
624	19	10	59	7	4	-
633	20	11	57	7	4	1
644	19	11	58	7	3	2

An earlier work [6] on n-hexane reaction over the 3% Pt/TiO₂ has revealed hydrogenolysis, skeletal isomerisation and dehydrocyclisation whereas the pattern observed here is selective to hydrogenolysis. The most unusual and intriguing result to emerge from the n-hexane reaction was: when the 3% Pt/TiO₂ catalyst was activated in air, C₁-C₃ (hydrogenolysis products) were the main products (Table 2). Again, it is interesting to wonder why Pt has a suppression of its skeletal isomerisation activity. This change of reaction mechanism may suggest the effect to be that of the support. However, the pattern of hydrogenolysis products is consistent with results described in the literature [6,34]: higher propane selectivity (main hydrogenolysis product) followed by methane, ethane, butane and pentane respectively. Traces of 2-methylpentane (2-MP) were also observed in the reaction which suggested some skeletal isomerisation activity. This is in accordance with n-hexane conversion [17] over Pt/TiO₂ (or CeO₂) where it has been observed that the catalysts exhibit high selectivity for C₁-C₃. Furthermore, Anderson [35] investigated the catalytic cracking of n-hexane over zeolite Y dealuminated with silicon tetrachloride vapour. They found C₃ to be the main product from the cracked products and proposed carbonium ion via a non-classical CR₃ species reaction mechanism to rationalise the preferential formation of C₃. Similar investigations of n-hexane conversion over Ni/SiO₂ catalysts [36] have suggested its preference for the adsorption of primary carbon atoms and its ability to form 1,2-diadsorbed species to account for the hydrogenolysis of alkanes selectivity and that 1,3- and 1,4-diadsorbed species are unlikely to be intermediates in the splitting of terminal C-C bonds. Our results reinforce the above conclusions and provide new evidence on how Pt/TiO₂ catalysts vary in their selectivity and activity in hydrocarbon reactions.

When this catalyst was tested between 573-644 K, hydrogenolysis activity of n-hexane is seen to be accompanied by suppression of skeletal isomerisation (Table 2). This was unexpected since skeletal isomerisation proceeds easily over Pt films [37-39] and over Pt on inert supports [40-45]. Whether this is a real metal-support interaction is unclear at the moment.

MCP. Hydrogenolysis of MCP (Figure 1), catalysed by Pt gives mainly n-hexane (I), 2-MP (II), and 3-methylpentane, 3-MP (III). The products of hydrogenolysis of MCP (Figure 1) have often been used [25,27,28,32,33] as a means of exploring surface morphology: on small particles (< 2.5 nm), the three possible products are formed in statistical proportions (non-selective hydrogenolysis), whereas on larger particles, n-hexane is not formed (selective hydrogenolysis).

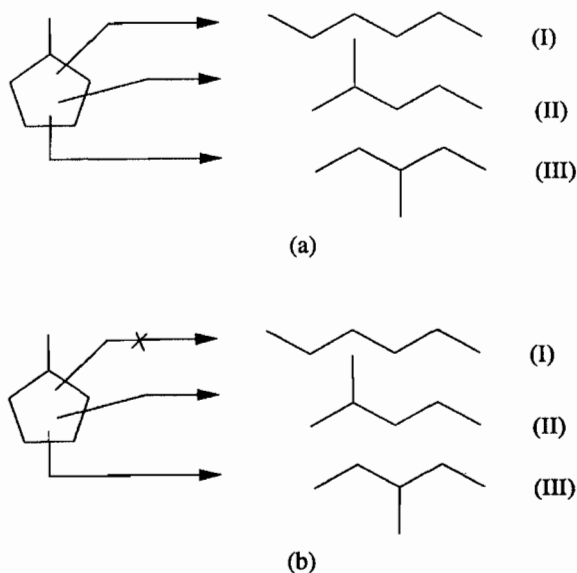


Figure 1. MCP reaction pathways (a) non-selective hydrogenolysis on highly dispersed catalysts and (b) selective hydrogenolysis on low dispersion catalysts.

Table 3 shows products distribution of non-selective hydrogenolysis of MCP. Product selectivities do not vary with temperature, indicating that the formation of these products is interlinked [6], i.e. that there is an active centre at which 2-MP or n-hexane is formed but not 3-MP.

The most remarkable result to emerge regarding the non-selective mechanism over this catalyst was the unusual enhancement of n-hexane content. This is in harmony with the finding [40-45] that small Rh particles tend to yield more n-hexane. Similarly, dispersion has been recognised to influence n-hexane selectivity although this is also a function of support. The sensitivity reported here for MCP hydrogenolysis compares favourably with the two reaction pathways suggested [13-16,30-33] previously, i.e. occurring: (i) on the Pt surface and producing mainly 2-MP and 3-MP, and (ii) at the boundary between Pt/support producing additional n-hexane.

Table 3. Variation of product selectivity with temperature for MCP hydrogenolysis over 3% Pt/TiO₂.

T/K	Selectivity (%)		
	2-MP	3-MP	n-Hexane
573	27	20	53
583	28	19	54
593	28	21	51
604	29	21	50
613	30	21	49
623	29	21	50
634	29	20	51

CONCLUSIONS

Present results suggest that Pt on TiO₂ is a good hydrogenolysis catalyst [18-23]. When the results for 3% Pt/TiO₂ are compared with those of other supported Pt catalysts [46], there seems no doubt that a real support effect has been observed. The difference in behaviour shown by n-hexane and MCP (where there is loss of catalytic activity under the same experimental conditions) from that shown by propane and n-butane [46] was real and not attributable to experimental artefacts. The nature of active sites or ensemble size involved in both n-hexane and MCP are different from those of propane and n-butane reactions [46]. These findings are very unusual and important. It is safe to assume that TiO₂ does enhance hydrogenolysis activity over other alkane reaction pathways. Thus, it may be that in 3% Pt/TiO₂, unique hydrogenolysis sites exist and that as a result, Pt/TiO₂ is a especially interesting catalyst. We do not think that SMSI is important under these conditions and hence, the loss of the catalytic activity in the absence of prior oxidation may be explained by effects analogous to SMSI-type behaviour [3-5,13-16,47,48] despite this occurring at only 573 K.

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