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THE EFFECT OF CARBONACEOUS DEPOSITS ON PRODUCT SELECTIVITY IN ALKANE HYDROGENOLYSIS *

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The hydrogenolysis of propane and of n-butane on Pt/Al_2O_3 and $Pt\text{-}Re/Al_2O_3$ catalysts has been studied using a stepwise temperature programme which reveals clearly the effects of carbonaceous deposits on both rate and product selectivities. On Pt/Al_2O_3 catalysts, deposits formed during the reaction of n-butane suppress C_2H_6 formation and enhance C_3H_8 formation, due solely to a decrease in the probability of central C–C bond fission. On $Pt\text{-}Re/Al_2O_3$, such deposits have little or no effect on product selectivities.

1. Introduction

There is continuing interest in the carbonaceous residues formed during hydrocarbon reactions on metallic catalysts [1]. On the one hand, carbon formation remains a problem in the operation of petroleum reforming catalysts, and research continues into its genesis and its removal [1]; on the other hand, carbonaceous species have been implicated as essential intermediates in alkene hydrogenation [2]. In the majority of publications describing alkane transformations on metallic catalysts, it is impossible to discern whether the reported results refer to the catalyst in its initial state or to that having the equilibrium coating of carbonaceous species appropriate to the conditions pertaining in the experiment. We have therefore devised a simple procedure to follow the effects of these species on the activities and product selectivities found in the hydrogenolysis of simple alkanes. We have thus been able to characterise the virgin states of Pt/Al_2O_3 and $Pt\text{-}Re/Al_2O_3$ catalysts as revealed by these structure-sensitive reactions, and to distinguish between them in terms of their response to the occurrence of carbonaceous residues.

2. Experimental

The catalysts used were 0.3% Pt/Al_2O_3 (EUROPT-3), 0.6% Pt/Al_2O_3, and 0.3% Pt-0.3% Re/Al_2O_3 (EUROPT-4), obtained from AKZO. Reactions were

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performed in a continuous flow-system at atmospheric pressure with a 10 : 1 H_2 : alkane mixture. Catalyst samples were calcined in situ at 763 K and then reduced at the same temperature; full details will be given elsewhere [3].

The temperature of the reactor furnace was programmed to rise in steps of about 10 K from 530 to 660 K with 20 min. isothermal periods at each temperature; samples were taken for analysis after 18 min. This constituted stage 1 of the reaction. The temperature was then lowered in a similar manner, giving stage 2. The cycle was usually repeated at least once, but since there was little further change in product selectivities after stage 2 the results obtained are not reported here.

Rates are expressed as mmol alkane converted per g of catalyst per h, and product selectivities are based on the number of mols of each product formed (c_j, where j is the number of carbon atoms) per mol reactant converted. Thus for n-butane

number of mols reacted $= A = (c_1 + 2c_2 + 3c_3)/4$

$S_j = c_j/A$

and $S_1 + 2S_2 + 3S_3 = 4$.

Similar equations apply to propane. Values of S_1 are not given, as they can be deduced from the above equation.

3. Results

As measured by the rates shown at 603 K, the loss of activity between the first and second stages depended more upon the alkane than upon the catalyst used (table 1). The fact that deactivation was much less with propane than with n-butane provides the first important clue to the nature of the process.

With both the Pt/Al_2O_3 catalyst, there were significant differences between the product selectivities found in stages 1 and 2 of the reactions with n-butane (see fig. 1 for an example). The selectivity to C_2H_6 (S_2) was decreased and that to C_3H_8 (S_3) was increased by the formation of the strongly-bonded carbon species; the isomerisation selectivity S_i was also lowered. The effects were greater with the

Table 1
Rates of alkane hydrogenolysis (mmol $g_{cat}^{-1}h^{-1}$) at 603 K

Catalyst	Stage	C_3H_8	n-C_4H_{10}
0.3% Pt/Al_2O_3	1	1.4	4.5
	2	1.4	3.5
0.6% Pt/Al_2O_3	1	1.1	7.8
	2	1.1	6.3
$Pt-Re/Al_2O_3$	1	1.7	9.6
	2	1.7	7.2

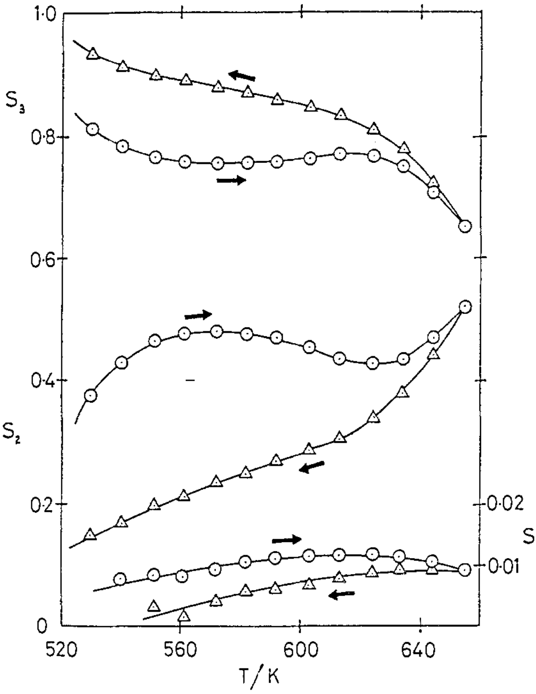

Fig. 1. Hydrogenolysis of n-butane: product selectivities obtained using 0.6% Pt/Al_2O_3 as a function of temperature.

catalyst containing 0.6% Pt, but no change in the C_2H_6 selectivity from C_3H_8 was observed with either catalyst ($S_2 \cong 0.99$).

The course of n-butane hydrogenolysis has been interpreted by a rake mechanism in which an adsorbed C_4 species can undergo either terminal fission to C_3 and C_1 fragments (probability $1 - F$) or central fission to two C_2 fragments (probability F). Each fragment (except C_1) can then either leave the surface as the corresponding alkane with rate constant k'_j (where j is the number of carbon atoms) or suffer further bond-breaking with rate constant k^*_j. The steady-state analysis of this scheme was first given by Kempling and Anderson [4]. Defining

$$T_j = k'_j / (k'_j + k^*_j)$$

the following relations hold at low conversion [5]:

$$S_2 = (1 + F - S_3)T_2$$

$$S_3 = (1 - F)T_3.$$

The three unknowns cannot be unambiguously evaluated, but a satisfactory approximation is to take the value of T_2 ($= S_2$) from the reaction of propane under the same conditions.

It will be apparent that the effect of the carbonaceous species in lowering S_2 and raising S_3 (fig. 1) could be due to changes in either T_2 or T_3, or F, or of

Table 2
Values of Kempling-Anderson parameters F and T_3 for n-C_4H_{10} hydrogenolysis at 603 K

Catalyst	Stage	F	T_3
0.3% Pt/Al_2O_3	1	0.20	0.98
	2	0.14	0.98
0.6% Pt/Al_2O_3	1	0.22	0.98
	2	0.14	0.98
$Pt-Re/Al_2O_3$	1	0.38	0.86
	2	0.38	0.86

course both. Values of F and T_3 are given in table 2, from which it appears that the effects result *entirely* from a decrease in the splitting factor F.

The $Pt-Re/Al_2O_3$ catalyst behaves quite differently. The initial deactivation leads to almost no changes in the values of S_2 and S_3, or S_i (see fig. 2) and this is reflected in the derived values of F and T_3 (table 2), which are both distinctly different from the values shown by the two Pt/Al_2O_3 catalyst. The value of S_2 for the propane reaction is also much lower than before (0.93 compared to 0.99).

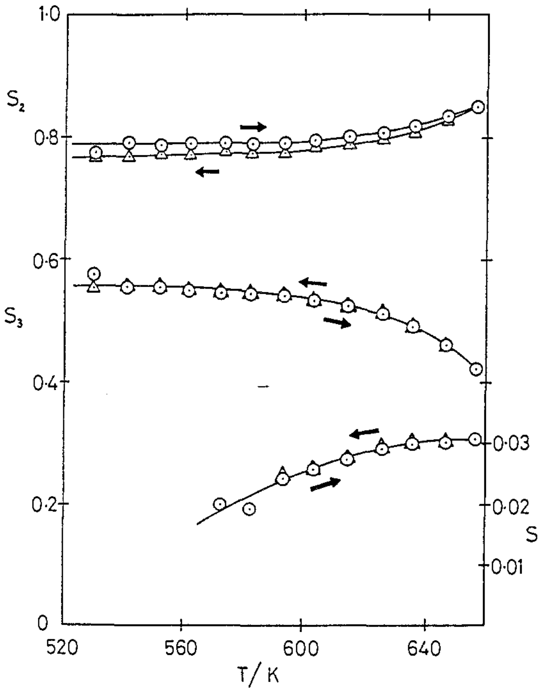

Fig. 2. Hydrogenolysis of n-butane: product selectivities obtained over $Pt-Re/Al_2O_3$ as a function of temperature.

4. Discussion

In petroleum reforming, hydrogenolysis is of course a parasitic reaction, and it is used here simply as a model, structure-sensitive reaction to probe the surface structure. Although carbon deposition in industrial conditions occurs first on the metal function and later on the acidic support, it will be evident that in this work we are only concerned with the initial stages of carbon deposition on the metal. The small amount of isomerisation observed must also occur on the metal, as it too responds to changes in S_2 and S_3.

Three principal observations have been made in this work. (1) The formation of strongly-bonded carbonaceous species on Pt/Al_2O_3 catalysts profoundly affects the mode of scission of the C_4 species formed by adsorption of n-C_4H_{10}. (2) Product selectivities are quite distinctly different with $Pt-Re/Al_2O_3$. (3) These are unchanged by the formation of carbonaceous deposits. From these findings we can conclude that there are two distinct types of site for hydrogenolysis on Pt/Al_2O_3 catalysts; they differ in the ease with which they are able to break each type of bond in a C_4 species, but they show the same kinetic parameters (i.e. T_3). Strongly-bonded species selectively deactivate the site showing the higher value of F; these species probably contain the same number of carbon atoms as the reactant alkane, since activity for propane decreases less than that for n-butane.

The quite markedly different behaviour shown by $Pt-Re/Al_2O_3$ provides clear evidence for the formation of bimetallic particles. The lack of effect of carbonaceous deposits on product selectivities suggests that there is only a single type of site that is operative; this is thought to comprise both Pt and Re atoms, and the lower value of T_3 that this catalyst shows (table 2) suggests that the intermediate species are more strongly attached to the active centres than is the case with the monometallic Pt catalysts. The effects produced by the presence of the Re, which are observed even at the lowest temperatures used, are unlikely to be due to any difference in the nature of the carbonaceous deposits, which, under our conditions, are probably just highly dehydrogenated forms of the reactant alkane.

Acknowledgements

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References

[1] J. Biswas, G.M. Bickle, P.G. Gray, D.D. Do and J. Barbier, Catal. Rev.-Sci. Eng. 30 (1988) 161.
[2] S.J. Thomson and G. Webb, J. Chem. Soc. Chem. Comm. (1976) 526.
[3] G.C. Bond and M.R. Gelsthorpe, J. Chem. Soc., Faraday Trans. I, accepted for publication.
[4] J.C. Kempling and R.B. Anderson, Ind. Eng. Chem. Process Des. Dev. 11 (1972) 146.
[5] G.C. Bond and Xu Yide, J. Chem. Soc. Faraday Trans. I 80 (1984) 769.