IMPORTANCE OF SURFACE MORPHOLOGY
IN n-PENTANE REACTIONS OVER Pt/ALUMINA
CATALYSTS

R. Burch and L. C. Garla*

Department of Chemistry, The University, Whiteknights, Reading, England

The hydrocracking activity of a Pt/alumina catalyst has been determined and found to depend on surface morphology. Observed differences in thermal stability depend on whether the Pt is initially in a reduced or oxidized form. Various models proposed to account for the loss of hydrocracking activity are re-examined in the light of the new data.

Была определена активность катализатора Pt/Al$_2$O$_3$ в гидрокрекинге и было найдено, что она зависит от морфологии поверхности. Различия, наблюдаемые в термической стабильности, зависят от того, что Pt в исходной форме находится в окисленном или восстановленном состоянии. В свете новых данных пересматриваются различные модели, предложенные для объяснения потери активности в гидрокрекинге.

INTRODUCTION

Platinum-alumina catalysts represent one of the most important types of industrial catalysts, and have been the subject of many investigations. Nevertheless, there are still features of Pt catalysts which are poorly understood. While it is known /1/ that some reactions (e.g. hydrogenation) are insensitive to the particle size of the metal, whereas other reactions (e.g. hydrocracking) are affected by particle size, it is also known that this is a second order effect. Thus, whereas the specific activity may vary by many orders of magnitude between one metal and another, the variation in activity with particle size rarely changes by more than a factor of ten /2/. Therefore, it is very significant that various authors have reported activity changes of 3 or 4 orders of magnitude in the hydrocracking of ethane /3/ or n-pentane /4/

*Present address: Depto Quimica Faculda de Filosofia de Ribeirao Preto, U. S. P., Brasil

over Pt catalysts sintered in hydrogen at high temperatures. Since hydrocracking is undesirable in reforming reactions, a better understanding of this effect could be of technical importance.

Several models have been proposed to explain these activity data. These are (i) formation of PtAl alloy particles /5/, (ii) retention of strongly adsorbed hydrogen /4/, (iii) formation of Pt(111) surface planes /3/. The objective of our work was to differentiate between these models. In fact, none of the models appear entirely satisfactory, and we have identified a further parameter which we believe to be related to changes in surface morphology. The observation of such an effect raises questions about the relevance of hydrogen chemisorption measurements as a means of determining specific activity data.

EXPERIMENTAL

(a) Materials. The catalyst used in this work was a commercial 0.3% Pt on γ-alumina catalyst (code CK303) supplied by Akzo Chemie B. V. Amsterdam. The catalyst had a surface area of 187 m^2g^{-1}, a pore volume of 0.5 cm^3g^{-1}, and Cl and S contents of 0.66 and 0.02% respectively. Before use the catalyst was crushed and sieved and the 0.25–0.5 mm fraction taken, dried at 370 K overnight and stored in a desiccator. n-Pentane (British Drug Houses 99.9% purity), hydrogen and argon (both British Oxygen Co. 99.999% purity) were used without further purification.

(b) Apparatus and experimental procedure. The catalytic experiments were performed in a silica U-tube reactor fitted with a sintered disc to support the catalyst. Samples of catalyst (300 mg) were placed in the reactor, flushed with air and calcined by raising the temperature to 770 K while maintaining a constant flow of air (750 cm^3 h^{-1}) downstream through the catalyst. Gas flows were controlled accurately with a Negretti and Zambra flow controller, and measured with a bubble flowmeter. After calcining for 1 h at 770 K the reactor was flushed with argon and the temperature reduced to 723 K, hydrogen was introduced (750 cm^3h^{-1}) and the catalyst reduced for 0.5 h at 723 K. To determine the activity for n-pentane reactions the temperature was lowered to 673 K, and 2μl pulses of n-pentane injected (at 0.25 h intervals) upstream from the reactor through a silicone rubber septum into a heated stainless steel tube. Products were analyzed by collecting gas samples from the outlet of the reactor (100 μl) and injecting into a Perkin Elmer F33 gas chromatograph fitted with a silicone fluid column. Complete separation of all products was obtained and areas were determined with an Infotronics electronic integrator.

316

This experimental procedure was chosen to reproduce the conditions used by Menon and Froment /4/. However, for the sake of convenience we omitted intermediate calcination treatments and simply reheated our samples in hydrogen to progressively higher temperatures. This turned out to be a fortunate choice as will become apparent later. After each fresh "reduction" in hydrogen the catalyst was cooled to 673 K and the activity redetermined as before.

RESULTS AND DISCUSSION

Figure 1 shows the variation of the activity and product selectivity with the temperature of reduction. The data differ in a number of important respects from the data in Ref. /4/. First, the activity (per unit weight of Pt) is much lower for our catalyst. Second, the loss of activity is very gradual, and only becomes significant for reduction temperatures above 820 K. Third, the isomerisation activity is high and increases sharply for catalysts reduced at 773 to 823 K. The lower activity of our catalyst, even after reproducing the pretreatment used by Menon and Froment /4/ (723 K reduction) is unexpected. The explanation turns out to be related to the age of the catalyst samples. Table 1 presents data for different batches of the catalyst which had been dried immediately prior to testing (catalyst X), or had been dried and stored for 30 days before use (catalyst Y), or had not been dried by us at all (catalyst Z). Each catalyst was calcined in situ at 773 K, reduced at 723 K, and tested at 673 K. There is a clear effect due to storage. The activity for hydrocracking, represented by the amount of methane produced, decreases by an order of magnitude and the activity for isomerisation increases by 2 orders of magnitude. (The latter increase, of course, is exaggerated because high hydrocracking activity means that iso-pentane formed as an initial product is liable to undergo further hydrocracking.) The effect of storage may be associated with the residual water content of the alumina. During calcination any water present may catalyse sintering or surface annealing of Pt oxide particles so that subsequent reduction results in the formation of less defective metal particles. We consider that the degree of surface imperfection is an important factor, not fully appreciated hitherto, in determining the hydrocracking activity of these catalysts.

Variations in the surface morphology would account also for the large difference between our data and that of Menon and Froment, after high temperature reduction. We observe only a small decrease in activity as compared with a decrease of 2–3 orders of magnitude reported by Menon and Froment. (Compare our Fig. 1 with Fig. 2 in Ref. /4/). The most obvious difference between our work and Menon and Froment's is the absence of intermadiate reoxidation stages in our work. We
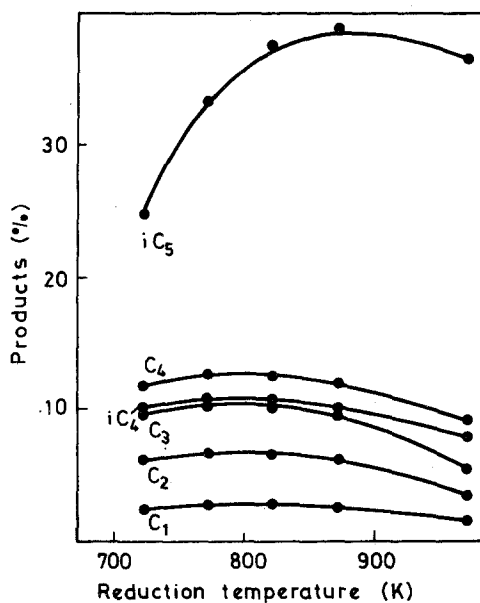
Fig. 1. Variations in the product distributions as a function of the temperature of reduction for the reaction of n-pentane

Table 1

Effect of age on activity of Pt/Al$_2$O$_3$ catalysts

Catalyst	Age (days)	Products (%)						
		C$_1$	C$_2$	C$_3$	iC$_4$	C$_4$	iC$_5$	C$_5$
X	1	52.8	28.9	16.2	0.9	1.2	0.07	0.2
Y	30	14.8	15.2	13.1	19.3	6.6	14.6	15.8
Z	100+	6.5	10.0	9.7	0.5	4.6	35.4	33.3

conclude that the amount by which the activity decreases is critically dependent on the initial state of the Pt. If, as is the case in our work, the initial state is Pt metal, reduced and stabilised (structurally) by reduction at low temperatures (673 K) the rate at which this disordered structure can convert into a more stable ordered structure on heating to higher temperatures will be very slow. On the other hand if, as in Menon and Froment's work, the initial state is Pt oxide, direct reduction at high temperature may result in formation of more stable, less defective Pt particles.
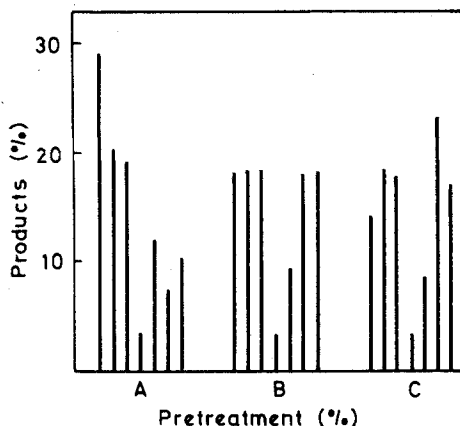
Fig. 2. Variation in the product distribution for different catalyst pretreatments. (A) calcined at
773 K/0.5 h, reduced 723 K/0.5 h; (B) annealed in argon 923 K/60 s; (C) annealed in hydro-
gen 923 k/60 s. Lines in figure represent from left to right C_1, C_2, C_3, iC_4, C_4, iC_5, and C_5
products

Our results indicate that the most active sites for hydrocracking are Pt atoms at
surface defects. Fassaert et al. /6/ have noted that strong M-C bonding is required
in order to break C-C bonds and that this is most likely to occur at corners, edges,
steps, etc. on a metal surface. Our results are consistent with such a model.

Since changes in the surface morphology should occur just as readily in the ab-
sence of hydrogen, providing the temperature is high enough for surface annealing
to occur, we performed a further experiment designed to determine whether the
hydrocracking activity was reduced by heating a prereduced sample in argon. A
sample of catalyst was dried, calcined, reduced at 723 K, and the activity de-
termined at 673 K. The reactor was then flushed with argon and the sample heat-
ed rapidly (1.2 Ks^{-1}) to 923 K, held for 60 s, and cooled rapidly to 673 K. Hydro-
gen was introduced and the activity determined. The catalyst was then heated rapid-
ly to 923 K in hydrogen, held for 60 s, cooled to 673 K and the activity determin-
ed. The results are shown in Fig. 2. It is clear that the major change in activity oc-
curs even when hydrogen is absent. The activity and the product distribution are
very different after heating to 923 K. However, the activity and product distribu-
tion are very similar irrespective of whether hydrogen is absent or present during
high temperature annealing.

We conclude from our data that the observed loss of activity cannot be due to
the formation of PtAl alloy particles /5/, nor to the retention of strongly adsorbed
hydrogen /4/. Furthermore, we conclude that although the formation of Pt(111)

319

surfaces /3/ may be a contributing factor, there must be a high probability that the surface morphology dominates the activity. Thus, if we take the activity after reduction at 723 K to be 100, the activity after 60 s at 923 K is 60, after 1800 s at 923 K is 15, and after 15 h at 923 K is 4. The rate of loss of activity is very fast initially, and then becomes quite slow. We doubt that significant amounts of new Pt(111) surface could be created in such a short time interval. It is possible that the proposed formation of Pt(111) surfaces /3/ parallels a more important surface rearrangement which reduces the number of very active, low-coordination sites.

Finally, the possible existence of a surface morphology effect raises questions about the value of using H chemisorption data to determine specific activities for *very small* metal particles. It seems highly probable that a Pt atom having low co-ordination would adsorb more than 1 H atom, so that a "rough" surface would appear to consist of smaller particles (higher apparent Pt dispersity). On "sinter-ing" a decrease in roughness would be seen as an apparent increase in particle size. Moreover, even allowing that a decrease in H adsorption represents a loss of metal surface area, how reliable are specific activity determinations if, as happens in n-pen-tane reactions, the Pt surface area decreases by only 10% and yet the activity de-creases by almost 3 orders of magnitude /4/. It seems that H chemisorption data are reliable only for quite large, well crystallised metal particles, and can only be used to determine specific activities in special cases.

*

REFERENCES

1. M. Boudart: Advan. Catal., *20,* 153 (1969).
2. M. Boudart: Proc. VI Inter. Cong. Catalysis, Eds. G. C. Bond, P. B. Wells, and F. C. Tompkins, p. 1. Chemical Society, 1977.
3. R. Dutartre, G. A. Martin: Compt. Rend. *288C,* 65 (1979).
4. P. G. Menon, G. F. Froment: J. Catal., *59,* 138 (1979).
5. G. J. den Otter, F. M. Dautzenberg: J. Catal., *53,* 116 (1978).
6. D. J. M. Fassaert, H. Berbeek, A. van der Avoird: Surface Sci. *29,* 501 (1972).