

Modification of the Activity of Pt/Al₂O₃ Catalysts for Reactions of *n*-Pentane by High-Temperature Treatment

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The activity and selectivity of Pt/Al₂O₃ catalysts, containing 0.3 and 1.0% Pt, for the conversion of *n*-pentane have been determined as a function of pretreatment, using a pulse technique. The results show that the initial hydrocracking activity is dependent on the age of the catalyst, and on whether or not it is precalcined before storage. Data for freshly prepared catalysts agree well with published data. The loss of hydrocracking activity with increasing temperature of reduction has been determined and found to be dependent on whether the initial state of the Pt is the oxide or the metal. Only a small decrease in activity is observed for prereduced samples after annealing in hydrogen at high temperatures. It is proposed that the loss of activity is due to changes in surface morphology which result in a reduction in the number of low-coordinate Pt atoms exposed on the surface. Data for catalysts heated in argon are presented to show that the loss of activity is not related to the presence of hydrogen. It is concluded that the loss of activity is not due to PtAl alloy formation, nor to retention of strongly adsorbed hydrogen. The transformation of exposed Pt surfaces into Pt(111) planes may be a contributing factor, but evidence is presented which shows that the major loss of activity occurs very rapidly.

INTRODUCTION

The activity and selectivity of catalysts are both important parameters in determining the efficiency of an industrial catalyst. Higher activities are generally associated with higher metal dispersions, and in the case of Pt catalysts, dispersions approaching 100% are desirable and often obtained. However, it is apparent that for such small metal particles there may be important changes in selectivity with particle size. The concept of structure-sensitive and structure-insensitive reactions has been introduced (1) and general guidelines to the active site requirements of various model reactions have been established (2). For instance, hydrogenation (3) and isomerisation (4) may occur on a single metal atom site, whereas hydrogenolysis is believed to require multiplet sites (5).

Recently attention has focussed on the sensitivity of Pt catalysts to pretreatment

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conditions. Otero-Schipper *et al.* (6) have shown how the activity and selectivity of Pt/silica catalysts are affected by pretreatment. Various authors have commented on the problem of obtaining reproducible data for Pt catalysts (7). Furthermore, hydrogen chemisorption data, used to determine Pt dispersions, have displayed unusual effects. Dautzenberg and Wolters (8) have found that after high-temperature reduction the ability of Pt to adsorb hydrogen is reduced, but not because of sintering. They propose the formation of a PtAl alloy species with reduced affinity for hydrogen. Menon and Froment (9), on the other hand, suggest that the loss of hydrogen chemisorption capacity is due to self-poisoning of the Pt surface by hydrogen adsorbed at high temperatures. It is rather difficult to visualise a surface site of Pt at which H atoms could be adsorbed irreversibly at 900 K, because, although there is some evidence for strong H adsorption with Pt black (10-12), experiments on single-crystal Pt surfaces show that there is only a small increase in the enthalpy of adsorption at

surface defects (steps, vacancies, etc.) as compared with a flat surface (13–15). If adsorbed H is present after high-temperature treatment, it is more probable that it is in a subsurface position. Although the solubility of hydrogen in bulk Pt is very low (16), Inoue *et al.* (17) have pointed out that the solubility of H in mesoclusters of Pt may be significantly higher. Thus, although very strongly adsorbed *surface* hydrogen seems unlikely, the presence of H in subsurface sites, either within the Pt lattice or at lattice defects, could reduce the amount of H which can adsorb on the surface. Vannice *et al.* (18) have discussed just such problems of consistency in Pt dispersion determinations.

In a similar vein the loss of hydrogenolysis activity of Pt catalysts after high-temperature reduction has been attributed to PtAl alloy formation (19), or to the retention of strongly adsorbed hydrogen (9). On the other hand, Dutartre and Martin (20), by analogy with earlier work on nickel (21), prefer a model in which loss of activity parallels a transformation into (111) planes at the surface. We decided to investigate reactions of *n*-pentane over Pt/Al₂O₃ catalysts because of this uncertainty as to why there is a loss of activity after high-temperature reduction, and because of the implications which such an effect has on the determination of Pt dispersions from H adsorption.

EXPERIMENTAL METHODS

Materials

The base catalyst used in this work (Pt03) was a commercial Pt on γ -alumina reforming catalyst, CK303, supplied by Akzo Chemie B.V., Amsterdam. The catalyst contained 0.3% Pt, had a surface area of 187 m² g⁻¹, and a pore volume of 0.5 cm³ g⁻¹. The chlorine and sulphur contents were 0.66 and 0.02%, respectively. Before use the catalyst extrudate was crushed and the 0.25- to 0.5-mm fraction was taken, dried at 370 K for 16 h, and stored in a desiccator.

A second catalyst (Pt10) containing 1% Pt was prepared from the crushed base catalyst (Pt03) by adding the appropriate amount of a solution of chloroplatinic acid to a known weight of base catalyst. The solution was evaporated to dryness in a rotary evaporator over a period of about 2 h. The impregnated catalyst was dried and stored as before.

n-Pentane (B.D.H. 99.8% purity), hydrogen and argon (both B.O.C. 99.999% purity) were used without further purification.

Apparatus and Experimental Procedure

The catalytic experiments were performed in a quartz U-tube microreactor (i.d. 8 mm, length 20 cm) with the catalyst powder (usually 300 mg) supported on a sintered disc. Gases flowed downstream through the catalyst bed at a rate controlled by a precision flow controller (Negretti and Zambra). The flow was measured with a bubble flowmeter. Pulses of *n*-pentane (2 μ l) were injected upstream from the reactor through a silicone rubber septum into a heated stainless-steel tube. The hydrogen flow was 750 cm³ h⁻¹ at atmospheric pressure, and during injection of *n*-pentane the hydrogen/hydrocarbon ratio always exceeded 5:1. Products were collected by withdrawing samples (100 μ l) from the outlet of the reactor with a gas syringe, and analysed by injection into a Perkin-Elmer F33 F.I.D. detector gas chromatograph fitted with a silicone fluid column. Product concentrations were determined by an Infotronics electronic integrator. The microreactor was heated by a small electric furnace (stability 0.5 K), the temperatures were monitored continuously by means of a thermocouple situated in a thermowell adjacent to the catalyst bed.

Catalyst pretreatment generally involved an initial *in situ* calcination in flowing air (750 cm³ h⁻¹) at 773 K for 1 h, followed by flushing with argon during which time the temperature was adjusted to the desired reduction temperature. Hydrogen was introduced and the catalyst was reduced for 0.5

h. The furnace temperature was lowered to 673 K ready for activity testing. Several pulses of *n*-pentane were introduced (at 0.25-h intervals) until reproducible analyses were obtained. Typically, three or four pulses were injected. After testing, the catalyst was heated to the next desired temperature and the above procedure repeated, i.e., reduction for 0.5 h, cooling to 673 K, and testing of activity.

A single, more complicated experiment was performed to differentiate between the various possible mechanisms of deactivation and this will be described under Results.

RESULTS

Preliminary experiments were designed to limit the total conversion of *n*-pentane to avoid diffusion problems and to restrict the reaction to the formation of initial products only. Figure 1 shows results for the formation of methane (C_1) and isopentane (iC_5) over catalyst Pt03 (111-mg sample). Table 1 shows how the selectivity for hydrocracking versus isomerisation is affected by reduction temperature. The results indicate a much lower hydrocracking activity (as measured by the methane content in the products) than was observed

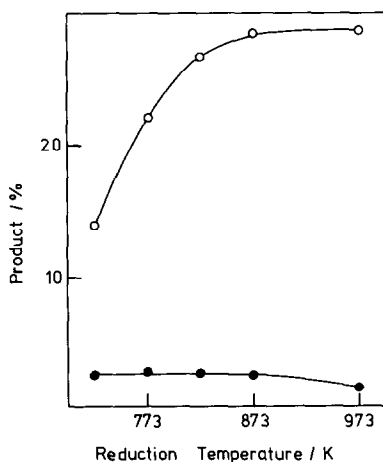


FIG. 1. Rate of formation of methane (●) and isopentane (○) over catalyst Pt03 as a function of the temperature of reduction.

TABLE 1

Variation in Product Selectivity with Temperature of Reduction

Cracked products ^a × 10 ²	Isomerised products ^a × 10 ²	Reduction temperature (K)
6.4	14.1	723
6.5	22.1	773
6.5	26.7	823
6.2	28.5	873
3.6	28.7	973

^a Calculated as the fraction of *n*-pentane converted.

by Menon and Froment (MF) (9) using a similar catalyst. (The catalyst used by MF contained 0.6% Pt and was also supplied by Akzo Chemie.) The rate of formation of methane, calculated on an equivalent weight of Pt basis, was five times lower with our catalyst. Furthermore, the decline in hydrocracking activity with increasing reduction temperature for our catalyst was negligible up to 873 K and then decreased by a mere 40% at 973 K. In contrast, MF observed a rapid decrease in cracking activity above 723 K with the methane concentration in the products decreasing from 30% to almost zero after reduction at 823 K. The isomerisation of *n*-pentane to isopentane also shows significant differences between the two catalysts. Our results show a sharp rise in isomerisation activity between R723 and R873³ at which point the activity stabilises. MF, on the other hand, observe a fairly steady isomerisation activity up to R823 followed by a sharp increase at R873. Our isomerisation activity is also much higher; for example, at R823 we obtain 25% conversion as compared with their 2% conversion.

Our catalyst differs, therefore, from that of MF in three important respects. First, it has a much lower hydrocracking activity after reduction at 723 K. Second, it has a much higher isomerisation activity at all

³ R873 indicates a reduction at 873 K for 0.5 h.

temperatures. Third, the activity for isomerisation increases sharply and the hydrocracking activity decreases very little with reduction temperature.

Our catalyst, and our experimental procedure differ from that of MF in that our catalyst contains less Pt (0.3 as compared with 0.6%), and we omit the calcination step between each reduction stage. Since differences in the catalysts are already apparent after reduction at 723 K, up to which point we have used a procedure similar to that of MF, intermediate reoxidation cannot account for all the differences although it may be a contributing factor. The Pt loading may be important, particularly if our low loading of Pt leads to significantly smaller (or less perfect) Pt crystallites. We have examined the influence of Pt loading by testing a second catalyst Pt10 (see previous section for details of preparation) containing 1% Pt. A sample of this catalyst (200 mg) was calcined and reduced as before, and the activity tested after each reduction treatment. The results are shown in Fig. 2. This sample contains 6 times more Pt than the sample of Fig. 1 but its activity for the formation of methane is about 40 times higher after R723, but decreases sharply with increasing temperature of reduction. However, it does not deactivate sig-

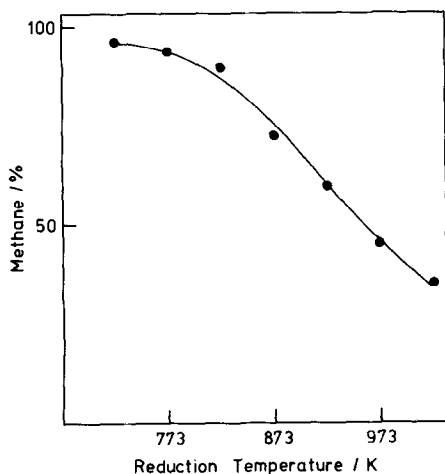


FIG. 2. Rate of formation of methane over catalyst Pt10 as a function of the temperature of reduction.

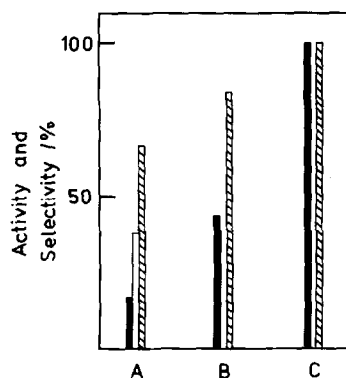


FIG. 3. Total activity \blacksquare , and selectivity for the formation of isopentane \square , or cracked products \blacksquare , over catalyst Pt03 as a function of pretreatment (see text for details).

nificantly below R823, so it still differs from the MF catalyst. This suggests that the greater loss of activity observed by MF on raising the reduction temperature is associated with the intermediate reoxidation steps. Of course, this cannot account for the difference in activity between the catalysts after R723. On an equivalent weight of Pt basis the order of hydrocracking activity is Pt10 > MF 06 > Pt03. Moreover, our own two catalysts give inconsistent results, the Pt10 catalyst being about seven times more active per milligram Pt than the Pt03 catalyst after R723. We have investigated our catalysts further because of this lack of consistency and a most interesting effect has been discovered.

Figure 3 shows the total activity, and the selectivity for cracked or isomerised products over different samples of catalyst Pt03. The three samples were, respectively, a sample of as-received catalyst (A), a sample of as-received catalyst dried overnight at 370 K and stored in a desiccator for several weeks (B), and a sample of as-received catalyst dried overnight and used immediately (C). We observe that the "driest" sample has the highest activity and highest selectivity for hydrocracking, the dried and stored sample has lower activity, lower hydrocracking activity, and higher selectivity for isomerisation, and the "wettest" sam-

ple has even lower activity and higher isomerisation selectivity.

During activation of these catalysts, which involves calcination *in situ* in flowing air at 773 K, followed by reduction at 723 K many things may happen to affect the nature of the Pt crystallites ultimately formed. Since water will be expelled from the catalyst during calcination it is probable the water is present, and affects the formation of the crystallites of Pt oxide from the precursor oxochloro complex initially present, rather than affecting the subsequent reduced material. It would appear that the surface morphology of the final Pt crystallites (possibly manifested as a variation in particle shape, size distribution, or degree of surface imperfection) is strongly dependent on the nature of the initial oxide. Surjo and Christoffel (7) have reported recently that the activity and selectivity of Pt catalysts for simultaneous hydrocracking and isomerisation of *n*-hexane are dependent on the moisture content of the reactants and on the history of the catalyst. Yao *et al.* (22)

have commented also on the variability of the behaviour of Pt oxides after different pretreatments.

It seems possible that some of the activity loss observed by MF after high-temperature reduction arises not because of the effect of hydrogen but by the cumulative effect of repeated reoxidation in air and reduction in hydrogen. In our experiments, in which there was no intermediate reoxidation step, we observe a much smaller loss of activity. We note also that on a dry sample of Pt03 the activity is quite similar to that observed by MF who precalcined their samples before use.

We have investigated further the storage properties of these catalysts by preparing a fresh batch of Pt10, drying overnight at 370 K, and then determining its activity (using 90-mg samples) after calcination at 773 K and reduction at 723 K. The activity after reduction at 973 K was also determined. These tests were repeated over a period of 5 weeks on new samples of this same batch of catalyst stored in a desiccator. (The des-

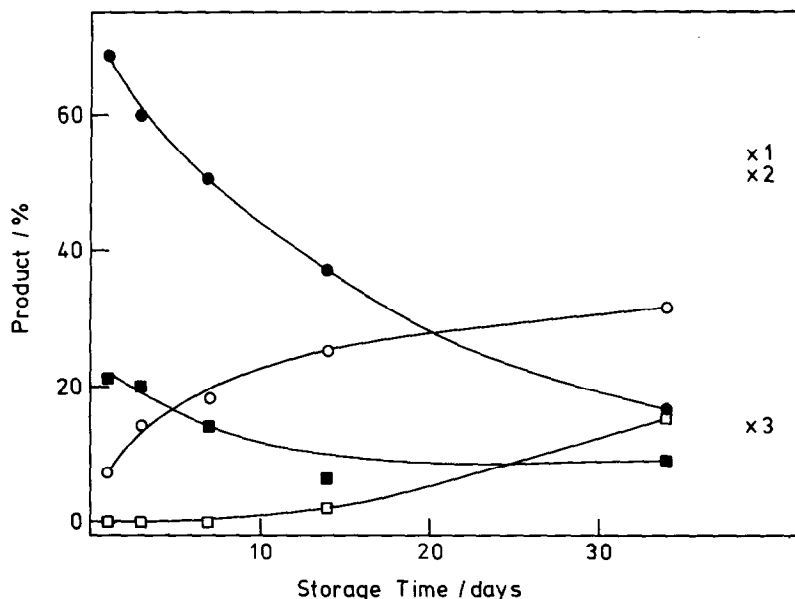


FIG. 4. Variation with storage time of the rate of formation of methane and isopentane over catalyst Pt10 after reduction. ●, Methane after reduction at 723 K; ■, methane after reduction at 973 K; □, isopentane after reduction at 723 K; ○, isopentane after reduction at 973 K. Single points 1, 3, and 2 (see text) refer to new Pt03, old Pt03, and to the Pt06 catalyst of Menon and Froment (9) respectively.

icator was opened often to remove or replace other samples.) The results are shown in Fig. 4. The hydrocracking activity after R723 was very high for a fresh sample, but each successive sample became less active, and even after 34 days the activity was probably still declining. The individual points on the right-hand side of Fig. 4 show for comparison the hydrocracking activity after R723 for new and old Pt03 samples and for the MF Pt06 catalyst.

The ratio of the hydrocracking activity after R973 to the activity after R723 is 0.31 for the fresh sample but 0.56 for the 34-day-old sample.

The data plotted in Fig. 4 refer to samples stored in a dried, but uncalcined form. To determine the effect of calcination a further batch of Pt10 was prepared and divided into two portions. One portion (Pt10C) was dried at 370 K for 1 h and then calcined at 773 K for 6 h. The other portion (Pt10D) was dried for 16 h at 360 K. After the standard *in situ* calcination and reduction the two catalysts gave the results shown in Table 2.

For the fresh catalysts precalcination is only of marginal importance. The activities and the product distributions are very similar both after R723 and R973, although the precalcined catalyst is slightly more selective towards isomerisation. After storage for 7 days the activity of the dried sample

has declined to 78% of its initial activity (based on methane formation), whereas the activity of the precalcined catalyst is still 98% of its initial activity. We assume that in the precalcined catalyst any moisture taken up is adsorbed as OH groups on the alumina support, so that little loss of activity occurs on storage. The uncalcined catalyst, on the other hand, can either adsorb moisture, or has retained sufficient residual moisture for changes to occur either during storage or during the subsequent calcination.

To test the various hypotheses which have been proposed to account for the loss of activity after high-temperature reduction, a further experiment was performed. (The alternative possibilities are (i) formation of PtAl alloy particles, (ii) retention of strongly adsorbed hydrogen, (iii) formation of Pt(111) surfaces.) A sample of catalyst Pt03 was dried at 370 K for 16 h, cooled in a desiccator, and a 300-mg portion weighed into the reactor. It was calcined at 773 K for 1.0 h, flushed with argon, cooled to 723 K, and reduced in hydrogen at 723 K for 0.5 h. The sample was cooled to 673 K and *n*-pentane injected. The results are given in Table 3 (Expt. 1). The sample was then heated to 823 K in hydrogen for 0.5 h, cooled to 673 K, and the activity measured again (Expt. 2, Table 3). There is a decrease in hydrocracking activity between R723 and R823.

TABLE 2

Effect of Pretreatment and Storage on the Activity and Selectivity of Pt Catalysts

Catalyst	Age (days)	Reduction temperature (K)	Products (%) ^a						
			C ₁	C ₂	C ₃	iC ₄	C ₄	iC ₅	C ₅
Pt10D	1	723	71.2	27.8	0.9	—	—	—	—
Pt10C	1	723	64.3	34.3	1.3	0.1	0.1	—	—
Pt10D	1	973	22.2	26.5	22.6	2.2	8.8	7.1	10.5
Pt10C	1	973	16.0	20.3	18.1	2.3	8.5	13.8	20.2
Pt10D	7	723	55.3	28.3	12.2	0.5	2.3	0.1	0.3
Pt10C	8	723	62.7	35.7	1.6	—	—	—	—
Pt10D	7	973	15.1	17.0	15.3	2.3	7.9	18.3	23.3
Pt10C	8	973	18.1	22.5	19.7	2.2	8.5	10.9	17.4

^a Calculated as molar concentrations of products.

At this point the sample was flushed with argon and two 1-cm³ pulses of air were passed over the catalyst at 673 K. This represents sufficient oxygen to remove several complete layers of adsorbed hydrogen, so it should remove any residual hydrogen remaining from the R823 treatment. After this air treatment, hydrogen was introduced and the activity measured (Expt. 3). The effect of the oxygen is to *reduce* the hydrocracking activity rather than increase it as would be expected if the original loss of activity was due to retained hydrogen.

This result was confirmed by reducing the sample at 923 K, cooling to 673 K, and measuring the activity (Expt. 4). The cracking activity has decreased as expected. However, after flushing with argon and injecting two 1-cm³ pulses of air, reintroducing hydrogen, and measuring the activity, the activity is hardly altered (Expt. 5). We conclude that it is most improbable that

adsorbed hydrogen is responsible for the loss of activity on reduction at high temperature.

The next stage in the sequence was to reoxidize the catalyst at 773 K. This was followed by reduction at 723 K, and activity testing at 673 K. The results are given in Table 3 (Expt. 6). There is a very good recovery of the catalyst activity, the results being almost identical to those obtained with the fresh sample. The catalyst was cooled to room temperature and stored in a very slow flow of hydrogen overnight. The catalyst was then reheated to 673 K and the activity checked (Expt. 7). For reasons unknown the activity had declined, particularly for methane formation.

In order to determine how quickly changes occurred during heat treatment in hydrogen at 923 K, the sample was heated rapidly (1.2 K s⁻¹) to 923 K, held for 60 s, cooled quickly to 673 K, and the activity

TABLE 3
Variation in Product Distribution with Catalyst Pretreatment

Experiment	Pretreatment	Products (%) ^a						
		C ₁	C ₂	C ₃	iC ₄	C ₄	iC ₅	C ₅
1	R723 ^b	52.8	28.9	16.2	0.9	1.2	0.07	0.02
2	R823	39.5	25.1	20.8	4.5	6.7	2.4	1.2
3	Air pulses at 673 K	30.6	21.0	19.1	4.0	10.3	7.3	7.6
4	R923	7.9	9.9	9.8	1.7	5.7	38.0	27.0
5	Air pulses at 673 K, calcine at 773 K for 0.5 h	7.5	9.3	9.7	1.5	5.1	36.1	30.7
6	R723	57.6	29.0	14.8	1.0	1.0	0.05	0.02
7	Stored 24 h	43.2	25.3	21.7	2.4	5.4	1.2	0.8
8	R923/60 s, oxidize at 673 K for 300 s	15.5	16.9	16.4	3.4	9.0	22.3	16.6
9	R673, oxidize at 673 K for 0.5 h	18.8	15.2	15.2	2.2	10.4	12.7	25.7
10	R673, oxidize at 773 K for 0.5 h	18.5	15.8	14.8	2.0	10.1	12.8	26.1
11	R723, heat in argon at 923 K for 60 s	29.0	20.2	18.8	3.2	11.6	7.1	10.1
12	R673	16.9	18.1	18.0	3.0	9.0	17.8	18.1
13	R923/60 s	13.8	18.0	17.4	2.9	8.3	22.9	16.7

^a All data refer to the average of three to four pulses of *n*-pentane injected into flowing hydrogen with the catalyst at 673 K.

^b R723 indicates reduction in hydrogen at 723 K for 0.5 h.

determined (Expt. 8). There is a large change in activity. The rate of formation of methane is much smaller. During this very short heat treatment we think it is most unlikely that PtAl alloy formation could occur. Strong H adsorption could occur, but we have already established that this is unlikely to account for the loss of activity. This latter conclusion was further confirmed by the next experiment. The sample was flushed with argon, air was introduced at 673 K, and the sample oxidized for 300 s. The sample was flushed with argon, hydrogen was introduced, and reduction continued for 0.5 h at 673 K. The activity was determined (Expt. 9). There is hardly any change in hydrocracking activity, so adsorbed hydrogen cannot be responsible for activity loss.

A further oxidation for 0.5 h at 673 K, followed by reduction at 673 K for 0.5 h, gives the results in Table 3 (Expt. 10). This further more prolonged oxidation and reduction has had almost no effect on the catalyst. Strongly retained hydrogen cannot make a significant contribution to the activity loss.

The catalyst was now reoxidized for 0.5 h at 673 K, followed by reduction at 723 K. The activity data are given in Table 3 (Expt. 11). There is quite a significant recovery in hydrocracking activity after this treatment, but by this stage the catalyst has lost irreversibly some activity.

The final parts of this experiment were designed to determine whether a loss of activity would occur if the catalyst was heated not in hydrogen but in an inert atmosphere. The catalyst was heated rapidly in argon to 923 K, held for 60 s, cooled rapidly to 673 K and heated in hydrogen for 0.5 h, and tested (Expt. 12). A significant loss of activity is observed, very similar to that found previously when the sample was heated to 923 K in hydrogen for 60 s. Finally, the sample was heated rapidly to 923 K in hydrogen, held for 60 s, cooled to 673 K, and tested (Expt. 13). The change is marginal, indicating once again the limited

extent to which H adsorption can possibly affect the activity.

DISCUSSION

The objective of this work was to understand the changes in hydrogenolysis activity which accompany the annealing of Pt catalysts in a hydrogen atmosphere at high temperatures. In the course of our work it became apparent that the activity of these catalysts was strongly dependent on the conditions of storage and pretreatment. The activity for hydrocracking can vary by almost an order of magnitude depending on whether the initial catalyst is dry or wet. We have suggested that this is because activity changes for these catalysts are closely linked to changes in surface morphology. We consider that the hydrocracking activity is mainly determined by the number of low-coordinate Pt atoms on the surface. Our later experiments, summarised in Table 3, are consistent with this proposal.

Our data show that strongly adsorbed hydrogen cannot be responsible for the loss of activity. Similarly, the formation of PtAl alloy particles cannot be responsible because large activity decreases are observed when samples are heated for very short times even in argon. Furthermore, the fact that similar activity losses are found with silica as well as alumina as support, and with Ni as well as Pt, argues for a more general explanation. Yao *et al.* (22) have also argued against the alloy model.

Moreover, we do not think that transformation of all exposed Pt surfaces into Pt(111) planes is a satisfactory explanation for the following reasons. First, about 40% of the hydrocracking activity is lost after heating for only 60 s at 923 K: we do not think that 40% of the exposed Pt surface could transform into Pt(111) so quickly. Second, various authors (21, 23, 24) have found that the rate of hydrocracking over Pt(111) or Ni(111) planes is at most an order of magnitude lower than that over other surfaces. The activity losses of three to four

orders of magnitude discussed earlier cannot be due, therefore, to changes to (111) surfaces.

Our data support a model (23, 25–27) in which hydrocracking occurs at a single surface Pt atom via a π -adsorbed surface intermediate. Following Foger and Anderson (23) and Somorjai (28) we would identify these single Pt atoms as special atoms in low coordination at corners, edges, steps, or kinks, on the surface.

A rapid decrease in surface "roughness" on annealing at 923 K would account for the loss of activity. The further, much slower loss of activity on extended annealing (> 15 h) could be a continuation of this process, or may be due to the gradual elimination of very small, very active Pt particles or clusters (22). Dutartre and Martin (20) find for well-annealed Pt/SiO₂ samples that the hydrocracking activity is three orders of magnitude lower than that for a poorly annealed surface. We suggest that this large decrease in activity is due to the near absence of special sites on the well-annealed surfaces.

Finally, we reiterate our observation that the activity is strongly dependent on whether the initial state of the Pt is the oxide or the metal. It is possible that when the oxide is reduced at a sufficiently low temperature (< 723 K) the removal of oxygen gives a highly defective metallic structure which experiences only a small amount of rearrangement (723 K is just below the Tamman temperature for Pt). This defective structure would contain many sites active in hydrocracking. After "soaking" for 0.5 h at 723 K the structure would be stabilised, become less amenable to rearrangement, and be less affected by annealing at high temperatures. On the other hand, if the oxide is reduced directly at a high temperature, rearrangement will be possible, and so the number of special sites will be small.

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