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Effect of Hydrogen in the Chemisorption of n-Hexane over Platinum Black

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The chemisorption and transformation of n-hexane have been investigated over Pt black in the presence of hydrogen between 450 and 600 K. Direct gravimetric measurements have confirmed that only 3–8% of the total hydrocarbon coverage can be removed by evacuation or by purging the system with an inert gas. Hydrogenation experiments have been used to separate reactive and irreversibly bound hydrocarbons; their coverages have been measured as a function of temperature and partial pressure of hydrogen. The variation of the product selectivity with the partial pressure of hydrogen has been interpreted considering the effect of the irreversibly bound hydrocarbons on ensemble size and on availability of hydrogen.

While in the transformation of alkanes the reactivity and selectivity of various types of Pt catalysts, including films,[1] blacks,[2] supported catalysts[3–6] and single crystals,[7–9] have been systematically investigated, less attention has been directed towards the surface state of the working catalysts.[9,10] High-temperature ($T > 623$ K) reforming studies have unambiguously confirmed that the carbonaceous deposits form a component of the catalytic system.[11–13] In the low-temperature reactions, however, direct data for the hydrocarbon coverage are scarce.[8–10] Considering the negative reaction order with respect to hydrogen it has been generally assumed that the surface coverage of the hydrocarbon in a large excess of hydrogen should be negligible.[14,15] The positive hydrogen order and the deceleration of the reaction rate at low hydrogen/hydrocarbon ratios point on the other hand to the formation of trapped hydrocarbons.[16–18] Recent studies by Davis *et al.*[8,9] seem to prove that Pt single crystals even at carbon coverages $C/Pt^s = 2$–3, where Pt^s is the number of surface sites, still exhibit remarkable catalytic activity in the transformation of n-hexane. However, the results of Davis *et al.*[8,9] are at variance with the suggestions that the chemisorption of alkanes requires a large number of contiguous Pt or Pt—H sites.[14,15] The toxicity of carbon atoms[11] observed in hydrocarbon transformations over supported Pt catalysts also cannot be reconciled with the results measured on single crystals.[8,9] The temperature-independent initial carbon coverage reported by Luck *et al.*[10] does not agree with experimental results observed in other laboratories.[9,13]

The obvious discrepancies in the literature concerning activity and carbon coverage have directed our attention to a study of the nature of hydrocarbon transformations on working Pt catalysts. The work presented here is aimed at an investigation of the chemisorption of n-hexane in H_2 over Pt black using a microbalance, since in the case of gravimetric detection the analytical procedure does not influence the hydrocarbon coverage. Systematic studies have shown that the variation of the partial pressure of hydrogen significantly affects the product selectivity of the individual reaction routes.[2] It was therefore decided to pay special attention to the effect of the partial pressure of hydrogen on the coverage of the chemisorbed species formed from n-hexanes. In particular, attempts have been made to answer the following questions. (i) What are the total and reversible hydrocarbon coverages in the presence of H_2 at low temperature

($450 < T/\text{K} < 600$) for the interaction of n-hexane with Pt? (ii) What is the coverage of the reversibly bound hydrocarbons which are removed by evacuation and therefore not detected in microreactor studies?

Experimental

In order to avoid support effects the experiments were carried out with Pt black. The preparation of the black has been described in earlier papers.[17,19] In the experiments 0.265 g Pt black was used. As the black reduced by formaldehyde contains some carbon, the sample was repeatedly oxidized at 623 K in 1.33 kPa O_2 and reduced in H_2. After a few O_2–H_2 runs the amount of carbon measured by temperature-programmed oxidation (t.p.o.) was < 0.005 cm^3 (s.t.p.) CO_2 g_{Pt}^{-1}. The number of surface sites, Pt^s, inferred from O_2–H_2 titrations was 1.25×10^{19} g_{Pt}^{-1}.

All the gases were carefully cleaned: H_2 and H_2–He mixtures taken from cylinders were purified and dried over Pd/Al_2O_3 and molecular-sieve contacts. He and Ar were passed through MnO_x/Al_2O_3 and molecular-sieve columns. n-Hexane was purified by preparative gas chromatography. No impurities could be detected in the n-hexane used in the kinetic studies. In the gravimetric measurements the purity of n-hexane was 99.96%, the impurities were 3-methylpentane and traces of 2-methylpentane.

The gravimetric measurements were performed by means of a Sartorius microbalance. The 'hangdown' tubes and the upper part of the balance were separated by orifices and the upper part was purged continuously with H_2 (0.5 cm^3 min^{-1}). The hydrogen and the H_2–He–n-hexane mixture entered at the bottom of the hangdown tubes, moved upwards and left the tubes at side-ports. Prior to the measurement of n-hexane chemisorption the Pt black was oxidized (1.33 kPa O_2) and reduced in a stream of H_2 at 573 K. As soon as a stable baseline was reached in the H_2 or H_2–He stream at the temperature of the experiment the carrier gas was passed through a saturator filled with n-hexane, and the n-hexane–H_2–He stream (flow rate 6–15 cm^3 min^{-1}) was introduced into the microbalance.

The experimental set-up used for the gravimetric measurements is not suitable for determining the rate of n-hexane transformation because only part of the reaction mixture 'meets' the catalyst surface. For this reason additional experiments were performed in a microreactor working under differential conditions.

The 'free' Pt sites (surface sites which are capable of chemisorbing CO or H_2 and O_2 after hydrocarbon reaction)[19] were measured at 298 K. In the microreactor studies the amount of surface carbon was inferred from temperature-programmed oxidation.[13]

Results and Discussion

Typical gravimetric measurements are collected in fig. 1–3. Fig. 1 shows the temperature dependence, while in fig. 2 and 3 the effect of hydrogen partial pressure on the formation of the chemisorbed species are presented. Further data on the n-hexane/Pt^s ratio are summarized in table 1, while tables 2 and 3 relate to the results of the microreactor experiments.

The gravimetric measurements in fig. 1–3 show that the concentration of the chemisorbed species reaches a steady state within a few minutes. Because of back-mixing the concentration profile of n-hexane in the H_2–He stream deviates from a stepwise function. The shape of the adsorption curve, as confirmed by a mass-spectrometric analysis in the vicinity of the Pt black, follows the concentration profile of n-hexane (nH). This observation suggests that the build-up of hydrocarbon coverage is fast on Pt sites.

From the n-hexane/Pt^s ratios observed it can be concluded that under the experimental conditions investigated n-hexane effectively competes with hydrogen for

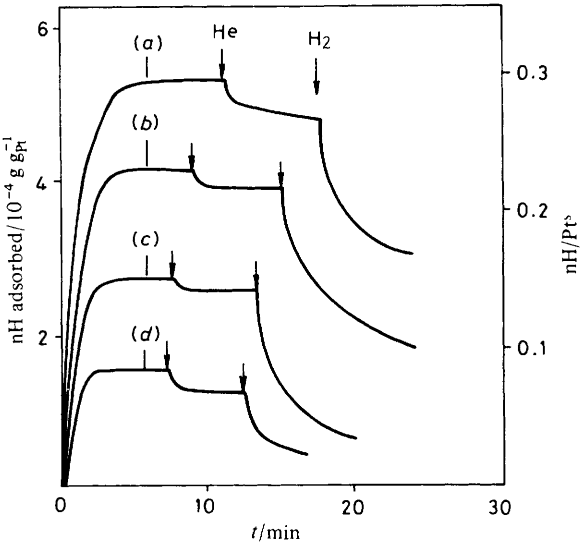

Fig. 1. Chemisorption of H_2–n-hexane as a function of temperature. $p_{H_2} = 93.5$ kPa, $p_{nH} = 4.92$ kPa. (*a*) 593, (*b*) 563, (*c*) 510 and (*d*) 453 K.

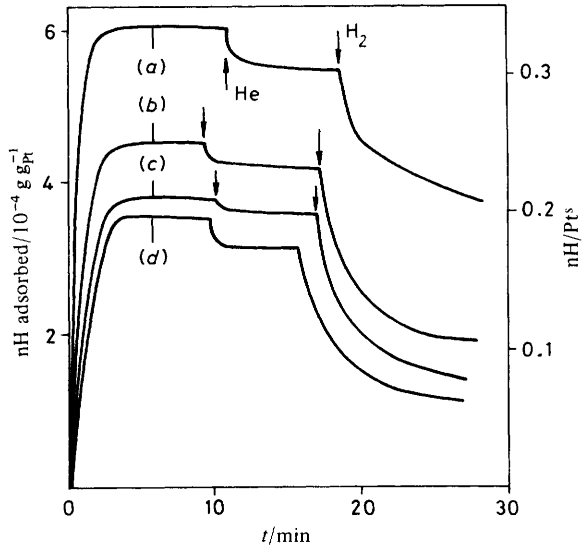

Fig. 2. Chemisorption of H_2–n-hexane as a function of the partial pressure of hydrogen at 543 K. Chemisorbed hydrocarbon was hydrogenated with 98.4 kPa H_2 after He purging. $p_{nH} = 4.92$ kPa. (*a*) $p_{H_2} = 0$; (*b*) $p_{H_2} = 4.67$ kPa; (*c*) $p_{H_2} = 18.7$ kPa and (*d*) $p_{H_2} = 93.5$ kPa.

adsorption sites. Already at -55 K with $H_2/nH = 19$ the nH/Pt^s ratio is 0.083, indicating that in the kinetic interpretations the carbon coverage of Pt sites should be considered. This suggestion is also supported by the fraction of 'free' sites, $100f = 63$, even though the chemisorption phase is obviously perturbed by the procedure used to measure the 'free' sites. In the course of the He treatment (or upon evacuation of the

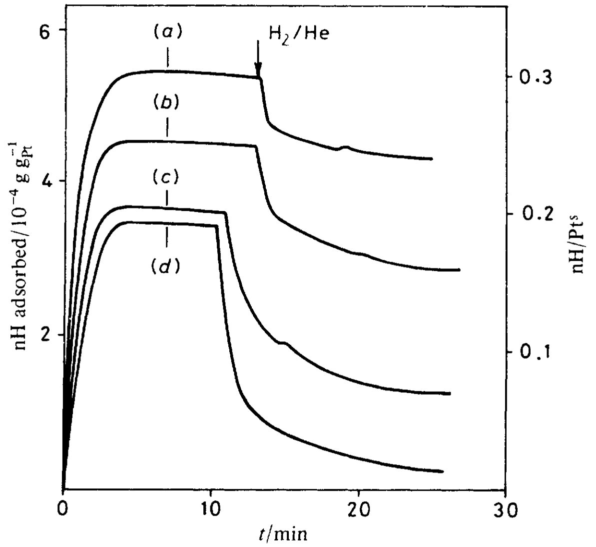

Fig. 3. Chemisorption of H_2–n-hexane as a function of the partial pressure of hydrogen at 543 K. $p_{nH} = 4.92$ kPa. (*a*) 1, (*b*) 5, (*c*) 19 and (*d*) 100% H_2/He.

Table 1. Carbon coverage and number of free sites on a Pt black as measured in a gravimetric system

experiment	T/K	H_2/nH	nH^t/Pt^s	nH/Pt^s	nH^i/Pt^s	$100f_{CO}$	$Pt^s \times (1-f_{CO})/nH$
1	453	19	0.082	0.076	0.02	—	—
2	455	19	0.080	0.075	—	65.8	4.55
3	515	19	0.148	0.135	—	55.3	3.31
4	516	19	0.151	0.143	0.023	89.9	4.36
5	563	19	0.231	0.22	0.055	81.3	3.4
6	563	19	0.236	0.22	—	38.2	2.81

$p_{nH} = 4.92$ kPa; nH^t/Pt^s = hydrocarbon coverage in equilibrium with nH/H_2; nH/Pt^s = hydrocarbon coverage after He treatment; nH^i/Pt^s = hydrocarbon coverage after 10 min H_2; f_{CO} = free fraction measured by 0.65 kPa CO (adsorption 5 min, evacuation 5 min). In experiments (4) and (5) $100f_{CO}$ and $Pt^s \times (1-f_{CO})/nH$ refer to nH^i/Pt^s, otherwise to nH/Pt^s.

H_2–nH mixture) the chemisorbed hydrocarbons transform into more firmly held forms, and thus the coverage of the free sites (this term corresponds to $1-\theta_{nH}$) might be less than the amount in equilibrium with the H_2–nH mixture.

The total hydrocarbon coverage as shown in fig. 1 and tables 1 and 2 increases with temperature in accordance with the exothermicity of hydrogen adsorption. With a decrease in the partial pressure of hydrogen (fig. 2 and 3) the hydrogen coverage decreases, so that more sites become available for n-hexane adsorption; hence the carbon coverage increases. The coverage of 'free' sites changes in the opposite direction.

Plugging the nH–H_2–He inlet and purging the balance with He permitted measurements of the reversibly bound proportion of the adsorbed hydrocarbons, which is not detected in u.h.v. systems. The reversibly bound hydrocarbons represent

Table 2. Carbon coverage (nH/Pt^s) and number of free sites on a Pt black as measured in a microreactor

experiment	T/K	H_2/nH	nH/Pt^s	$100f^a$	Pt$^s \times (1-f)$/nH
1	455	19	0.078	66.0	4.35
2	481	19	0.11	67.1	2.99
3	508	19	0.13	53.4	3.58
4	536	19	0.21	46.1	2.56
5	563	0	0.39	—	—
6	563	0.95	0.31	22.1	2.51
7	563	0.95^b	0.24	33.6	2.76
8	563	0.95^c	0.21	35.6	3.06
9	563	6.46	0.25	21.5	3.14
10	563	6.46^b	0.101	61.4	3.82
11	563	6.46^b	0.055	82.8	3.12
12	563	19	0.24	34.3	2.73
13	563	19^b	0.066	—	—

$p_{tot} = 98.42$ kPa, $p_{nH} = 4.92$ kPa; time on stream, 5 min after that 5 min in Ar. ^{a} Surface was saturated with 0.1 cm^3 H_2 pulses at 273 K, and after 10 min Ar purging O_2 titration followed. In experiments (b) and (c) the nH stream was closed and there was 3 and 15 min hydrogenation, respectively, with H_2/He [experiments (7) and (8), 31 % H_2/He; experiments (10) and (11), 5 % H_2/He].

Table 3. Product selectivity (%) in catalytic test (R) and in hydrogenation–desorption (HD)

T/K		t/s	$< C_6$	2MP	3MP	nH	MCP	B	$R_{nH}{}^a$
448	R	—	reaction is not observed						—
448	HD	20–30	0.4	1.5	0.2	61.1	36.6	0.00	—
448	HD	30–60	3.6	21.5	1.3	53.9	19.4	0.00	—
463^b	HD	20–40	0.3	0.7	0.1	89.3	9.6	0.00	—
526	R	—	85.6	9.9	3.2	—	1.3	0.00	2.51×10^{-9}
526	HD	20–40	3.9	10.5	2.3	63.2	20.1	0.02	—
541	R	—	80.9	12.4	4.7	—	2.0	0.00	1.63×10^{-8}
541	HD	15–30	2.0	4.9	1.1	20.2	70.7	0.8	—
541	HD	30–45	3.9	4.2	0.5	65.4	25.7	0.1	—
563	R	—	82.1	12.6	4.1	—	1.2	0.00	6.33×10^{-8}

$p_{nH} = 4.92$ kPa, $p_{H_2} = 93.5$ kPa; R, time on stream 6 min; HD, catalyst Ar treated for 6 min before hydrogenation flow of $H_2 = 17$ cm^3 min^{-1}.
^{a} R_{nH} = rate of n-hexane consumption in mol g_{Pt}^{-1} s^{-1}. ^{b} Sample cooled to 373 K in nH–H_2, sample heated in Ar to 463 K for 1 min and H_2 addition. $< C_6$, fragments; 2-MP, 2-methylpentane; 3-MP, 3-methylpentane; nH, n-hexane; MCP, methylcyclopentane; B, benzene.

chemisorbed species which are able to recombine with surface hydrogen. Because of the high temperature the presence of physisorbed species on the surface is not likely. With n-hexane over Pt black under the experimental conditions investigated the reversible fraction is 3–8 % of the total carbon coverage. The close similarity of nH/Pt^s values measured gravimetrically and in a microreactor by t.p.o. after Ar purging of the catalyst also confirms that the reversible fraction is only a small part of the total carbon coverage (tables 1 and 2).

In the presence of gas-phase hydrogen a considerable fraction of surface species can be hydrogenated off the surface. Two types of experiment were performed. (i) After the

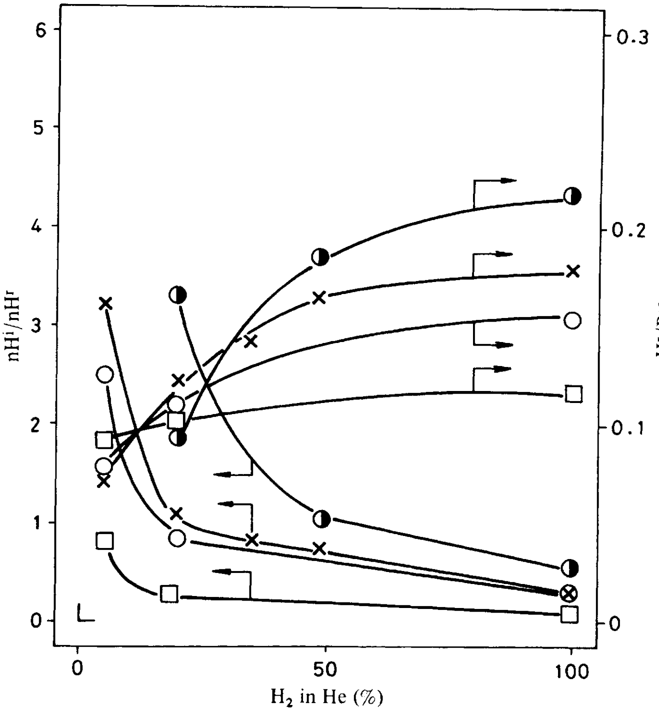

Fig. 4. Ratio of the strongly bound hydrocarbons to the reactive ones, nH^i/nH^r, and the coverage of the reactive hydrocarbon, nH^r/Pt^s, measured after 5 min hydrogenation as a function of percentage H_2 in He. $p_{nH} = 4.92$ kPa, $p_{tot} = 98.4$ kPa. ◑, 603 K (B); ○, 543 K (B); ×, 563 K (R); □, 523 K (B) (B = balance, R = microreactor test).

formation of the steady-state carbon coverage in nH–H_2–He, the n-hexane stream was closed and only the H_2–He mixture was passed through the system (fig. 3). In fig. 4 the surface coverage of the hydrocarbons hydrogenated from the surface within 5 min in the H_2–He stream and the ratio of the irreversibly to reversibly bound hydrocarbons are summarized. (ii) After He or Ar treatment of chemisorbed hydrocarbons, hydrogenation was performed with 94.5 kPa hydrogen (fig. 2). Owing to the hydrogen loss in the trapped hydrocarbons, the coverage of the irreversibly bound forms is higher than in the direct hydrogenations with H_2–He, with the exception of experiments in which the partial pressure of hydrogen in the nH–H_2–He inlet is kept low (fig. 5).

The coverage of the reversibly bound hydrocarbons, like that of the irreversibly bound ones, is a sensitive function of the temperature and the nH/H_2 ratio. The chemisorbed hydrocarbon which could be removed by H_2 might be regarded as a reactive surface intermediate which is responsible for n-hexane transformation on Pt sites. Of course a sharp dividing line cannot be drawn between reversibly and irreversibly bound forms.[20] It is likely, however, that hydrocarbons residing on the surface for 5 min or longer might contribute only to a very limited extent to the formation of the products.

The product composition measured after cooling and Ar purging of the microreactor (table 3) confirms that at low temperatures a large fraction of chemisorbed n-hexane maintains its molecular identity. This result is in accordance with the fact that below 523 K only a limited transformation of n-hexane could be detected. Previous deuterium-exchange studies with ethane,[20,21] propane,[17] n-pentane[22] and cyclopentane[22] have also shown that the rate of deuterium exchange (this reaction was regarded as a weak

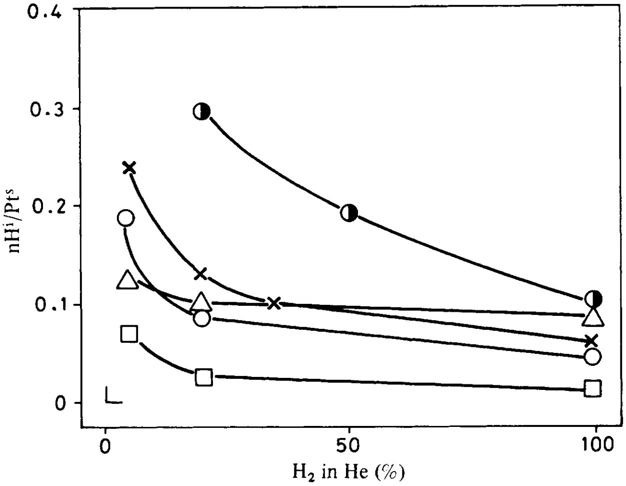

Fig. 5. Coverage of strongly bound hydrocarbons, nH^i/Pt^s, measured after 5 min hydrogenation as a function of percentage H$_2$ in He. p_{nH} = 4.92 kPa, p_{tot} = 98.4 kPa. ◑, 603 K (B); ×, 563 K (R); ○, 543 K (B); □, 523 K (B); △, 543 K (B), hydrogenation after He treatment with 98.4 kPa H$_2$.

interaction[23] of hydrocarbons with Pt sites) is at least two orders of magnitude faster than that of hydrogenolysis (strong interaction) at 10^{15} mol m^{-s} s^{-1} fission rate. The chemisorption results reported have over Pt black and the previous kinetic considerations[22] seem to support the view that in alkane transformation over poorly dispersed Pt catalyst distinction can be made between chemisorption and reaction sites, and that the chemisorbed hydrocarbons are likely to reach the reaction sites by surface migration rather than direct adsorption on reaction sites. In a recent paper Davis *et al.*[9] have argued that the low hydrogenolysis activity of Pt and Pd within the 5*d* and 4*d* series, respectively, stems from the ease of formation of carbonaceous deposits on these metals. These chemisorption results with a Pt black do not support this conclusion. The hydrogenolysis activity of Pt (and Pd) is usually measured under experimental conditions (high H$_2$/hydrocarbon ratio, low temperature) when the surface coverage of the irreversibly bound hydrocarbons is relatively small (fig. 3). The exchange activity of Pt and the ease of hydrogenation of the surface species in equilibrium with nH–H$_2$ point rather to the low concentration of surface sites being able to catalyse the hydrogenolysis of alkanes.[21,22] The conclusion of Davis *et al.*[8,9] has been based upon 'total' hydrocarbon coverages measured after evacuation of the H$_2$–nH mixture from the reactor. The 'total' hydrocarbon coverage, as is clearly shown by the results in this paper, also includes the coverage of the reactive forms.

The carbon coverage and the fraction of free sites enable an average site requirement of the chemisorbed species, Pt^s × $(1-f)$/nH, to be calculated. The site requirement has been observed to range from 2.5 to 4.5 under the experimental conditions reported. The kinetic site requirement determined from a comparison of the slope of the hydrogen isotherm and the reaction order with respect to hydrogen[14,15] has been proposed to be larger than eight. The obvious discrepancy between chemisorption and kinetic site requirement might be explained if it is assumed that the kinetic site requirement also involves the free and hydrogen adsorption sites which are required for a given reaction. One cannot exclude that the discrepancy stems from the fact that the procedure used to measure the free sites perturbs the surface state of the chemisorbed hydrocarbons. Taking for example the first row in table 2, T = 455 K, H$_2$/nH = 19, nH/Pt^s = 0.078

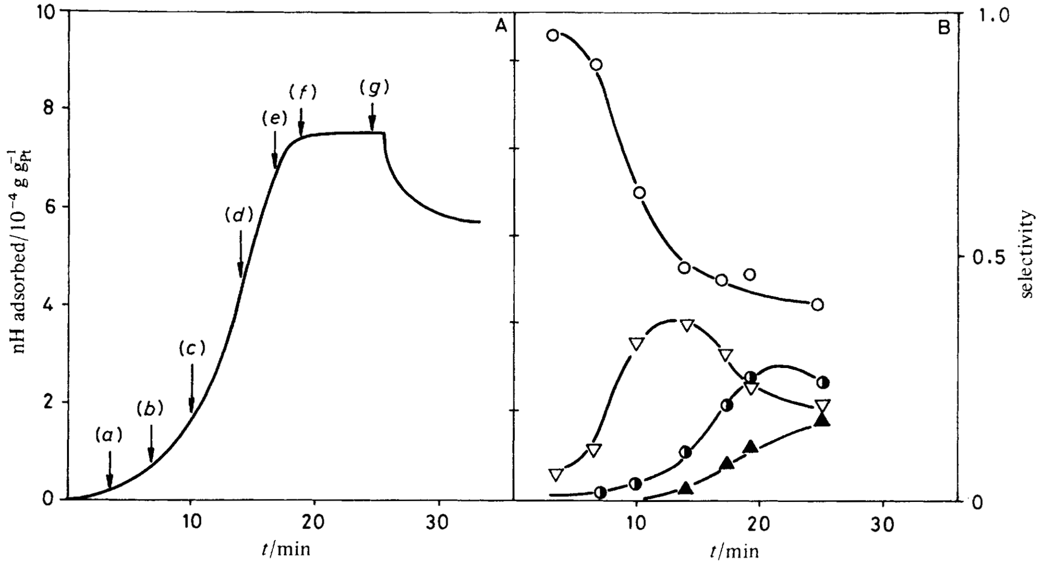

Fig. 6. n-Hexane chemisorption and product selectivity observed at 603 K in a 20% H_2/He stream, $F = 12$ cm^3 min^{-1}, $p_{tot} = 98.4$ kPa; inlet nH (*a*) 0.31, (*b*) 0.55, (*c*) 0.88, (*d*) 1.53, (*e*) 4.7, (*f*) 4.9 and (*g*) 4.8 kPa. Selectivity: ○, $S_{<C_6}$; ▽, $S_{2MP+3MP}$; ◑, S_{MCP}; ▲, S_B.

and $100f = 66$, it is observed for $100f < 37.6$ that one obtains a site requirement higher than eight. If the hydrocarbon-covered Pt sites are capable of chemisorbing a limited amount of H_2, O_2 or CO, this would increase the value of $100f$. In this particular experiment this additional adsorption would mean 3.6 O atoms for each chemisorbed n-hexane molecule, which does not seem probable. In experiments with $nH/Pt^s > 0.125$ the site requirement is less than eight, even if the fraction of the free sites is neglected. Clearly, a thorough investigation is required to clarify the problem.

The ratio of the irreversibly to reversibly bound hydrocarbons shows a systematic variation as a function of the partial pressure of hydrogen. As is illustrated in fig. 4, at 563 K the hydrocarbon species adsorb only reversibly in the presence of hydrogen with $H_2/nH > 19$. Since H_2/nH is related to the appearance of the entirely reversible adsorption of n-hexane, it shifts to lower values with a decrease in the reaction temperature: obviously the n-hexane transformation at large H_2/nH ratios is not affected by the presence of firmly held hydrocarbons. In other words, the reaction rate and product formation are governed only by the hydrogen coverage on the surface: the ensemble of surface sites can be regarded as an H–Pt system. At low H_2/hydrocarbon ratios the transformation of n-hexane takes place in the presence of firmly held hydrocarbons: it might be suggested that the catalytically active surface consists of H–Pt–C ensembles.

Systematic studies over Pt,[2] Pd,[24] Rh[25] and Ni[26] have shown that the variation of the partial pressure of hydrogen significantly influences the product selectivity. Over Pt in the transformation of alkanes, considering the rate maxima for various reactions, the hydrogen requirement of the individual reaction routes was proposed to increase in the following order:[2,25,27,28] dehydrogenation and dehydroisomerization < C_6 dehydrocyclization < hydrogenolysis < C_5 cyclic reactions < bond-shift skeletal isomerization. The hydrogen sensitivity of the product distribution has been interpreted by the inhibiting effect of hydrogen on the degree of dissociation of C—H bonds in the reacting surface intermediate[2,25,27] and by the role of hydrogen as an astoichiometric reactant. In previous papers we have shown that a remarkable change can be observed in the product selectivity when the rate of consumption of the parent compound exhibits positive hydrogen orders.[26,29] The likely connection between the product selectivity and the accumulation of the firmly held hydrocarbons on Pt sites also appears in the gravimetric measurements. A typical run is presented in fig. 6: the n-hexane partial pressure (the actual pressures denoted by arrows were calculated from the g.l.c. analysis) was continuously raised in 19% H_2–He at 593 K. In a large excess of H_2, when the reaction proceeds essentially on a 'clean' surface, the main reaction route is fragmentation. With a decrease in the H_2/nH ratio, as soon as the surface of the Pt crystallites becomes covered with trapped hydrocarbons (the H–Pt system is transformed into an H–Pt–C one) non-destructive reactions such as isomerization (2MP+3MP) and methylcyclopentane (MCP) and benzene (B) formation come into prominence. The decrease of the partial pressure of hydrogen allows the transformation of reversibly bound forms into more dehydrogenated surface species, which by blocking the hydrogenolysis sites increase the selectivity of the non-destructive reactions. The retardation of the hydrogenolysis activity has already been observed in the poisoning of Pt sites by carbonaceous deposits formed at elevated temperatures.[6,7,29] The alloying of Pt with a catalytically inactive metal to form Pt–Au,[30,31] Pt–Cu[32] and Pt–Sn[13,33,34] catalysts corroborated that hydrogenolysis is a reaction route whose selectivity is drastically reduced by the increase in the surface concentration of the second metal.

The discrepancy between product distribution observed in the activity tests and in hydrogenation–desorption of the trapped hydrocarbons at 526 and 541 K (table 3) might also be interpreted by the formation of firmly held hydrocarbons. With H_2/nH = 19 at 526 and 541 K the principal reaction is fragmentation: the selectivity of this reaction route reaches 86 and 81%, respectively. Purging the H_2–nH inlet with Ar and keeping the trapped hydrocarbons for 6 min in Ar (this time being much longer than the average residence time of n-hexane molecules in the reactor in the activity tests) allow the transformation of chemisorbed n-hexane. One of the remarkable features of the product distributions observed upon hydrogenating the trapped hydrocarbons is the very limited amount of fragments among the products. This observation emphasizes again that the surface sites, which in the presence of sufficient hydrogen produce fragments, are the most likely to be poisoned by the decrease of the partial pressure of hydrogen. In previous papers this route of poisoning, which is apparently connected with fragmentation, is referred to as the C_1 or hydrogenolysis route of site blocking.[13,34]

On the basis of the systematic variation of the carbon coverage on the catalysts it is proposed that the hydrogen affects the product selectivity through the alteration of geometric/steric and electronic properties of Pt sites caused by the transformation of a H–Pt surface to a H–Pt–C one. The partial pressure of hydrogen governs the coverage of the irreversibly held hydrocarbons; thus the lower the H_2/hydrocarbon ratio, the less the size of the working Pt ensembles. Owing to the decrease of the ensemble size the dissociation of C—H bonds becomes restricted, even though the low H_2/hydrocarbon ratio should promote the rupture of C—H bonds. Moreover, the carbon atoms on the surface might result in the formation of localised hydrocarbon–metal bonds rather than delocalised ones.[35] The presence of firmly held hydrocarbons causes crowding on Pt sites, which in turn might exert steric effects upon the configuration of the reacting species. The effect of hydrocarbon congestion has already been assumed in the reactions of alkenes[36] and in chain lengthening.[37,38] The high selectivity of α-alkene formation in an He stream might also be explained by geometric/steric effects of firmly held deposits rather than electronic ones.[39] Electronic effects are likely to contribute to the ease of product desorption.[40]

Besides ensemble size, hydrogen availability on the ensembles formed might be a factor which influences the dissociation of C—H bonds and the desorption of products. However, the ensemble size and the hydrogen availability might not be independent of each other. It might be assumed that the blocking of surface sites by deposits decreases the hydrogen coverage on the surface for geometric/electronic reasons. With the accumulation of deposits a new source of hydrogen appears on the surface as the trapped hydrocarbons, whose hydrogen content expressed by the ratio H/C is 1.2–1.5,[9] might serve as a hydrogen donor.[9] At low H_2/hydrocarbon ratios the main reaction routes are C_5 cyclisation, aromatization and alkene formation. All these reactions yield hydrogen atoms which might ensure the steady activity of Pt ensembles formed. Over highly dispersed Pt/Al_2O_3[34] and Pt/SiO_2[19] the steady-state formation of carbonaceous deposits from n-hexane at 673 K in absence of added H_2 provides evidence that the dissociated hydrogen atoms are able to maintain a constant activity of Pt sites in the formation of coke precursors and gas-phase products.

Conclusions

(1) Under the experimental conditions normally used to study the low-temperature activity of Pt catalysts n-hexane successfully competes with hydrogen for Pt sites on a Pt black sample.

(2) Hydrogenation experiments confirm that the ratio of firmly held species to reactive ones increases with temperature and with a decrease in the partial pressure of hydrogen. The reversibly bound hydrocarbons which can be directly removed by He treatment or by evacuation represent only 3–8 % of the total carbon coverage.

(3) With a change in the partial pressure of hydrogen the composition of the surface sites shows a systematic variation: the H–Pt system transforms into an H–Pt–C one upon a decrease in the hydrogen pressure. The geometric/steric and electronic effects of firmly held hydrocarbons should be considered in the interpretation of the effect of hydrogen upon product selectivity.

References

1 J. R. Anderson and Y. Shimoyama, *Proc. 5th Int. Congr. Catal.*, Miami, 1972, p. 695.
2 Z. Paál, *Advances in Catalysis* (Academic Press, New York, 1980), vol. 29, p. 273.
3 F. M. Dautzenberg and J. C. Platteeuw, *J. Catal.*, 1970, **19**, 41.
4 Z. Paál, H. Zimmer and P. Tétényi, *J. Mol. Catal.*, 1984, **25**, 99.
5 F. M. Dautzenberg and J. C. Patteeuw, *J. Catal.*, 1972, **24**, 264.
6 P. P. Lankhorst, H. C. DeJongste and V. Ponec, in *Catalyst Deactivation*, ed. B. Delmon and C. Froment (Elsevier, Amsterdam, 1980), p. 43.
7 F. Garin, S. Aeiyach, P. Legare and G. Maire, *J. Catal.*, 1982, **77**, 323.
8 S. M. Davis, F. Zaera and G. A. Somorjai, *J. Catal.*, 1984, **85**, 206.
9 S. M. Davis, F. Zaera and G. A. Somorjai, *J. Catal.*, 1982, **77**, 439.
10 F. Luck, S. Aiyach and G. Maire, in *Proc. 8th Int. Congr. Catal.*, Berlin, 1984, vol. 2, p. 695.
11 J. Barbier, P. Marecot, N. Martin, L. Elassal and R. Maurel, in *Catalyst Deactivation*, ed. B. Delmon and C. Froment (Elsevier, Amsterdam, 1980), p. 53.
12 R. Bacaud, H. Charcosset, M. Guenin, R. Torrellas-Hidalgo and L. Tournayan, *Appl. Catal.*, 1981, **1**, 81.
13 A. Sárkány, H. Lieske, T. Szilágyi and L. Toth, in *Proc. 8th Int. Congr. Catal.*, Berlin, 1984, vol. 2, p. 613.
14 A. Frennet, G. Lienard, A. Crucq and L. Degols, *J. Catal.*, 1978, **53**, 150.
15 P. Parayre, V. Amir-Ebrahimi, F. G. Gault and A. Frennet, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 1704.
16 R. S. Dowie, D. A. Whan and C. Kemball, *J. Chem. Soc., Faraday, Trans. 1*, 1972, **68**, 2150.
17 L. Guczi, A. Sárkány and P. Tétényi, *J. Chem. Soc., Faraday Trans. 1*, 1974, **70**, 1941.
18 A. Sárkány, L. Guczi and P. Tétényi, *React. Kinet. Catal. Lett.*, 1974, **1**, 169.
19 A. Sárkány, in *Catalyst Deactivation*, ed. B. Delmon and C. Froment (Elsevier, Amsterdam, 1987), p. 125.
20 L. Babernics, L. Guczi, K. Matusek, A. Sárkány and P. Tétényi, in *Proc. 6th Int. Congr. Catal.*, London, 1976, vol. 2, p. 456.
21 A. Sárkány, K. Matusek and P. Tétényi, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 1699.
22 A. Sárkány, J. Gaál and L. Tóth, in *Proc. 7th Int. Congr. Catal.*, Tokyo, 1980, vol. 1, p. 291.

23 L. Guczi and P. Tétényi, *Ann. N.Y. Acad. Sci.*, 1973, **213**, 173.
24 Z. Paál and P. Tétényi, *Appl. Catal.*, 1981, **1**, 9.
25 Z. Paál and P. G. Menon, *Catal. Rev. Sci. Eng.*, 1983, **25**, 229.
26 A. Sárkány, *J. Catal.*, 1984, **89**, 14.
27 H. Zimmer, M. Dobrovolszky, P. Tétényi and Z. Paál, *J. Phys. Chem.*, 1986, **90**, 4758.
28 H. Zimmer, Z. Paál and P. Tétényi, *Acta Chim. Hung. Acad. Sci.*, 1982, **111**, 513.
29 A. Sárkány, *J. Catal.*, submitted for publication.
30 J. R. H. Van Schaik, R. P. Dessing and V. Ponec, *J. Catal.*, 1975, **38**, 273.
31 A. F. Kane and J. K. A. Clarke, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 1640.
32 H. C. DeJongste, K. J. Kuijers and V. Ponec, in *Proc. 6th Int. Congr. Catal.*, London, 1976, p. 915.
33 F. M. Dautzenberg, J. N. Helle, P. Biloen and W. M. H. Sachtler, *J. Catal.*, 1980, **63**, 119.
34 H. Lieske, A. Sárkány and J. Völter, *Appl. Catal.*, 1987, **30**, 69.
35 M. W. Vogelzang, M. J. P. Botman and V. Ponec, *Faraday Discuss. Chem. Soc.*, 1981, **72**, 33.
36 D. McMunn, R. B. Moyes and P. B. Wells, *J. Catal.*, 1978, **52**, 472.
37 A. Sárkány, *J. Catal.*, 1986, **97**, 467.
38 A. Sárkány, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 103.
39 J. K. A. Clarke and J. J. Rooney, *Adv. Catal.*, 1976, **25**, 125.
40 A. Palazov, Ch. Bonev, D. Shopov, G. Lietz, J. Völter and A. Sárkány, *J. Catal.*, 1987, **103**, 249.

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