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Modification of the Properties of Pt–Al_2O_3 Catalysts by Hydrogen at High Temperatures

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The activity of Pt–Al_2O_3 catalysts for hydrogenolysis of *n*-pentane and *n*-hexane at about 400°C can be attenuated markedly by a pretreatment of the catalyst in H_2 in the temperature range 450 to 600°. The effect is similar to that of chloriding or mildly sulfiding the catalyst, as shown from reactivity data, H_2 chemisorption on the pretreated catalyst, and temperature-programmed desorption (TPD) of H_2 from it. The stronger chemisorption of H_2 occurring at higher temperatures seems to render a fraction of the surface Pt atoms so unreactive that they cannot react with H_2 and O_2 in surface titrations at 20°C or with the paraffins at 300 to 400°C. It also decreases H_2 desorption in the 50 to 300°C range and shifts the main desorption peak to higher temperatures by 100 to 200°C in the TPD spectrum of H_2. An air oxidation at 500°C followed by reduction at 400°C restores most of the original activity and characteristics of the catalyst. This shows the reversibility of the attenuation and the absence of any sintering or permanent structural changes during these pretreatments. Since high-temperature H_2 attenuates the properties of platinum black also in a manner similar to those of Pt–Al_2O_3 catalysts, this effect seems to be specific to the platinum metal and not caused by any metal–carrier interaction. The profuse desorption of H_2 from the catalyst in the 50 to 300°C range during TPD is an indication of the strong hydrogenolysis activity of the catalyst. The Pt sites responsible for the hydrogenolysis may be the same ones which also get modified during the above pretreatments.

INTRODUCTION

In a recent investigation of the stoichiometry of H_2–O_2 titrations on Pt–Al_2O_3 catalysts, Prasad *et al.* (*1*) have proposed that the gas uptakes on freshly reduced samples should not be the starting point for characterization of the state of Pt on the catalyst surface. They attribute the reason for this to the complexity of the interaction of H_2 and O_2 with irreproducible fresh catalyst surfaces. Dautzenberg and Wolters (*2*) have just reported that during heat treatment of Pt–Al_2O_3 catalysts in H_2 a certain fraction of surface Pt atoms becomes "inaccessible" and causes the usually observed decrease in H/Pt ratio, hitherto often interpreted as due to sintering of Pt. Den Otter and Dautzenberg (*3*) suggest that this inaccessible part of Pt may be due to a reversible surface combination between reduced Pt and reduced Al; a mild air oxidation at 400–500°C can restore the catalyst back to its original state with all the surface Pt atoms once again accessible for chemisorption of H_2. Gonzalez-Tejuca *et al.* (*4*) have observed this decrease in Pt dispersion, as measured by H_2 chemisorption, on exposure of Pt–Al_2O_3, Pt–silica, and Pt–NaY zeolite catalysts to H_2 even at 300–450°C and the

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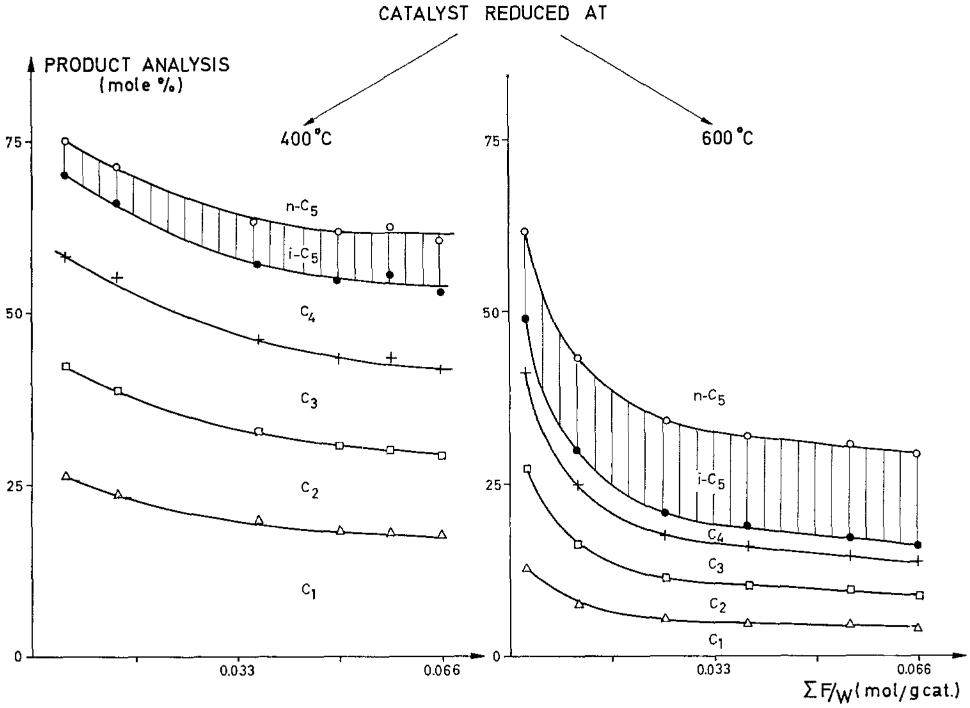

FIG. 1. Hydrogenolysis and isomerization of *n*-pentane in a continuous-flow reactor at 400°C on $Pt-Al_2O_3$ catalyst reduced at 400 and 600°C. Catalyst wt. 1.59 g. Pentane feed rate 0.0525 mole/hr. Mole ratio H_2/pentane 6.2.

restoration of the original dispersion on oxidation at 300°C and reduction at 0°C. They ascribe this loss of dispersion and the loss of a number of catalytic centers (for hydrogenation of ethylene) to a decomposition of Pt particles or clusters into an "atomic" form of Pt incorporated into the alumina support, or into molecular forms involving Pt diads on silica.

In continuation of earlier work in this laboratory by Hosten and Froment (5) and De Pauw and Froment (*6*) on the kinetics of isomerization of *n*-pentane on $Pt-Al_2O_3$ reforming catalysts, we have now investigated the effect of H_2 pretreatment on the activity and selectivity of the catalyst for hydrogenolysis and isomerization of *n*-pentane and *n*-hexane. Hydrogen chemisorption on the catalysts and temperature-programmed desorption (TPD) of H_2 from them after various pretreatments have been employed to get an insight into the changes undergone by the catalyst. The results are compared to those obtained by us for the same catalyst from other pretreatments like sulfiding and chloriding (*7*).

EXPERIMENTAL

A small stainless-steel reactor with a temperature-programmed tubular heater and connected to a gas chromatograph (gc) through a gas-sampling valve was used for most of the present work. With some changes in the connections, the reactor could be used as a pulse microreactor or as a continuous flow reactor with an on-line gc. For H_2 chemisorption and TPD measurements, the gc column was shortcircuited and an external column or capillary tube was connected after the katharometer to give a line pressure of 1.1 to 1.5 bar. For TPD, a U-tube cooled in liquid air was introduced between the

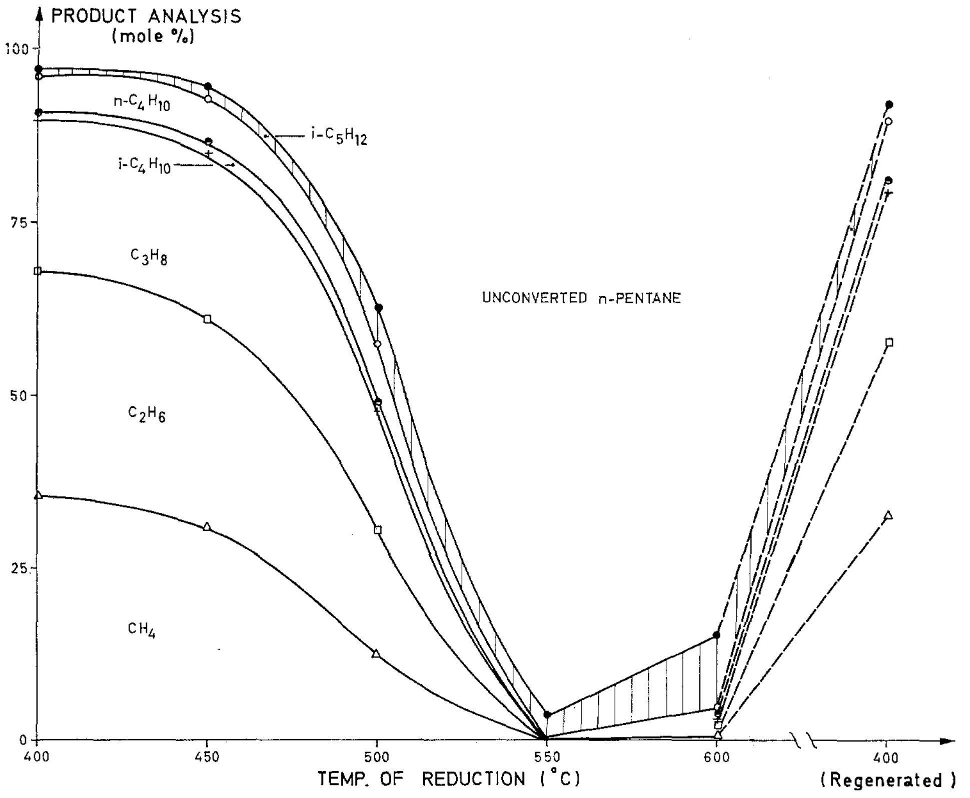

FIG. 2. Effect of catalyst reduction temperature on the conversion of *n*-pentane at 400°C. Catalyst: 0.4725 g of CK 306. Pulses of 2 μl *n*-pentane. Carrier gas: 60 cm^3/min of H_2.

reactor and the detector to trap any moisture or HCl vapor.

A quartz tube, 8 mm o.d. × 6 mm i.d. and 20 cm long, with an axial quartz thermocouple pocket, was used as the reactor for the TPD work, since earlier experiments showed considerable distortion or magnification of TPD spectra due to the up-take of H_2 by the empty stainless-steel reactor and the desorption of H_2 from it at higher temperatures. The empty quartz reactor, on the contrary, did not show any up-take or desorption of H_2 during blank TPD runs. Details of this experimental set-up have been given elsewhere (*7*).

The H_2 chemisorption measurements on the catalysts were carried out by the O_2–H_2 titration method of Benson and Boudart (*8*), adapted to the faster gc pulse technique proposed by Freel (*9*) and Menon *et al.* (*10, 11*).

The catalyst used was the commercial CK 306 grade (0.6% Pt on γ-Al_2O_3) of Ketjen Catalysts, Amsterdam. Its characteristics are: surface area 180 m^2/g, pore volume 0.5 cm^3/g, Cl 0.67%, and S 0.03% by weight. Another commercial reforming catalyst containing 0.75 wt% Pt on γ-Al_2O_3 was also tried in all the present series of experiments. The results with it are very similar to those with CK 306. Hence they are not reported here separately.

The catalyst, originally in the form of 1.5-mm-diameter extrudates, was crushed to 0.1 to 0.4 mm size, calcined in air at 500°C for 1 hr, and cooled in a desiccator. A weighed quantity of the catalyst was then taken in the reactor, calcined in a stream of air at 500°C for 1 hr, reduced at

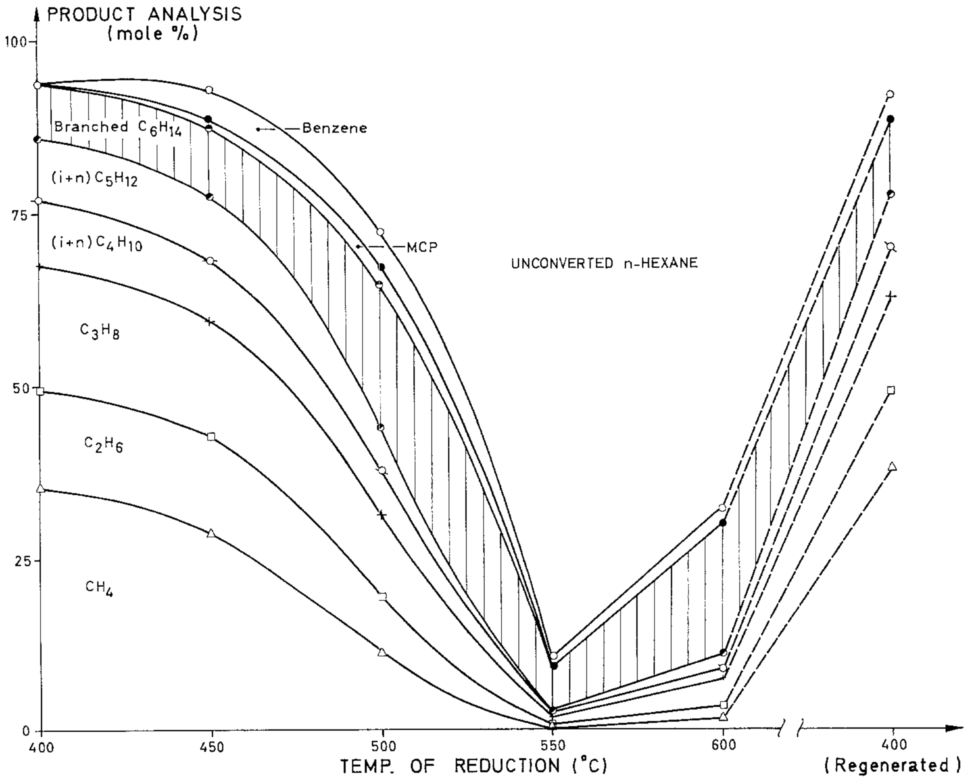

Fig. 3. Effect of catalyst reduction temperature on the conversion of *n*-hexane at 400°C. Pulses 2 μl *n*-hexane on 0.4725 g of catalyst. Carrier gas flow: 60 cm^3/min of H_2.

the desired temperature for 30 min, and then brought to 400°C in a stream of H_2 for reactivity studies or to 20°C for H_2 chemisorption and TPD measurements. Since the effects of exposure to H_2 at 600°C and to air at 500°C for these short periods did not produce any permanent or irreversible change in the properties of the catalyst, it was possible to use one and the same catalyst charge in the reactor for a few series of measurements in attenuation–regeneration cycles.

The gases used were the ultrahigh pure grades of L'Air Liquide, Belgium. The *n*-pentane and *n*-hexane were pro-analyse grades of Union Chimique Belge.

RESULTS AND DISCUSSION

Typical data for reactions of *n*-pentane in the continuous flow reactor are shown in Fig. 1. For the catalyst reduced at 400°C, hydrogenolysis is the main reaction, whereas for that reduced at 600°C, the hydrogenolysis is considerably suppressed and isomerization has become very prominent. These experiments were conducted at 1 atm pressure. Naturally, due to coke lay-down on the catalyst the activity of the catalyst declines rapidly at first and slowly thereafter.

To avoid this complication due to coke lay-down, the pulse microreactor technique was employed to get an idea of initial activities with practically no coke on the catalyst. The catalyst was air oxidized at 500°C for 1 hr and reduced for 30 min at 400°C. Then its activity for the catalytic conversion of 2 μl pulses of *n*-pentane and *n*-hexane was determined in the pulse reactor at 400°C. The catalyst was again

TABLE 1

Reactions of n-Pentane and n-Hexane on Pt–Al_2O_3 in Pulse Reactor[a, b]

Catalyst pretreatment	n-Pentane					n-Hexane				
	a	b	c	d	e	a	b	c	d	e
CH_4	0.28	36.8	0.2	0.2	32.5	0.8	28.7	3.4	0.7	27.6
C_2H_6	0.24	37.3	0.5	0.4	31.0	1.2	16.5	4.8	1.5	16.9
C_3H_8	0.28	22.8	0.7	0.5	25.7	1.3	21.0	5.9	1.8	25.1
i-C_4H_{10}	0.23	0.9	0	0	1.5	0.3	2.5	2.5	0.5	2.6
n-C_4H_{10}	0.06	1.9	0.2	0.2	5.9	0.7	8.1	2.3	0.9	8.8
i-C_5H_{12}	16.2	0.1	53.7	25.8	0.7	0.1	3.6	1.6	0.3	2.4
n-C_5H_{12}	82.7	0.2	44.7	72.7	2.8	0.2	5.6	0.9	0.3	4.8
2,2DMB						1.6	0.4	8.2	3.0	0.2
2,3DMB + 2MP						15.6	3.5	30.3	21.5	2.3
3MP						11.7	2.0	16.8	14.5	1.6
n-C_6H_{14}						64.9	2.9	22.4	52.9	4.0
MCP						1.1	0.2	0.9	1.1	0.3
Benzene						0.5	5.0	0	0.8	3.3

[a] Catalyst wt., 0.4728 g; temperature, 410°C; H_2 flow, 65 ml/min; 2μl pulses of the hydrocarbon; analysis of reaction product in mole%.

[b] Pretreatments: (a) H_2 at 550°C for 1 hr; (b) catalyst from (a) air oxidized at 500°C and then reduced at 410°C; (c) catalyst from (b) treated with 20 μl CCl_4 in H_2 at 410°C; (d) catalyst from (b) treated with 1 μl thiophene at 410°C; (e) catalyst from (c) reoxidized in air at 500°C, followed by reduction at 410°C.

oxidized at 500°C for 1 hr and reduced in turn at 450, 500, 550, and 600°C and the catalytic activity was determined as a function of the temperature of reduction of the catalyst (Figs. 2 and 3). The strong hydrogenolysis activity of the catalyst reduced at 400°C is rapidly suppressed with increasing temperature of reduction. On reduction at 550°C, it is practically zero and only isomerization takes place. If the catalyst is now oxidized in air at 500°C and reduced at 400°C, the original strong hydrogenolysis activity of the catalyst is fully restored. Thus the suppression of hydrogenolysis on exposure to H_2 at high temperature is a reversible phenomenon which can be reversed by a reoxidation; it does not involve any sintering of Pt or of Al_2O_3, or any such permanent change of the catalyst surface.

Table 1 gives the pulse microreactor conversion data at 410°C for n-pentane and n-hexane on the catalyst exposed to attenuation by high-temperature reduction at 550°C, chloriding and sulfiding (columns a, c, and d respectively in the table) and intermediate regenerations (columns b and e) by air oxidation at 500°C followed by reduction at 410°C. There is a remarkable similarity in the behavior of the catalyst after pretreatments a, c, and d: The conversion is moderate, hydrogenolysis to C_1–C_4 (for n-pentane) and C_1–C_5 (for n-hexane) products is effectively suppressed, while isomerization to branched paraffins is the main reaction. On regenerating the catalyst (b and e), the conversion shoots up to over 95%, mostly because of enhanced hydrogenolysis while the isomerization is no longer appreciable (probably due to the ready hydrogenolysis of the isoproducts formed as well). This suggests that *the Pt sites becoming progressively unreactive on exposure to H_2 at higher temperatures are precisely the same ones which are responsible for the strong hydrogenolysis*

TABLE 2

Effect of Pretreatment on the Chemisorption of H_2 on the Catalyst at 20°C and the Desorption of H_2 from it up to 600°C during TPD[a,b]

Pretreatment	H_2 chemisorbed (μmol/g catalyst)	Relative area of TPD curve up to 600°C
(a) Air 500°C, H_2 400°C	9.72	100
(b) Air 500°C, H_2 500°C	9.7	100
(c) Air 500°C, H_2 550°C	8.7	103
(d) Air 500°C, H_2 600°C	8.3	96
(e) Again air 500°C, H_2 400°C	9.7	98
(f) (a) + 20 μl CCl_4 in H_2 at 400°C	7.9	62
(g) (a) + 10 μl CS_2 in H_2 at 400°C	3.0	44

[a] Catalyst, 1.59 g.

[b] Pretreatment in air/H_2, for 30 min each at a gas flow rate of 150 cm^3/min.

activity and which can also be readily inhibited or selectively poisoned by chloriding or sulfiding.

In the case of chloriding with CCl_4, we have found (*7*) that some coke deposition actually occurs on the catalyst; this may be responsible for the decrease in hydrogenolysis activity. Chloriding has also the additional effect of enhancing the acidity of alumina, thereby accelerating the relatively slower carbonium-ion reactions at the acid sites, as in typical bifunctional catalysis (cf. Weisz, *12*; Sinfelt, *13*).

The conditions of the pulse-reactor experiments were modified to check the selectivities for hydrogenolysis and isomerization at comparable conversion levels on the catalyst reduced at different temperatures. Then also the suppression of demethanation in particular is quite noticeable, e. g., for n-pentane at 400°C, the selectivities for formation of C_1, C_2, C_3, $(i + n)C_4$, and iC_5 paraffins were respectively 101, 63, 47, 20, and 10 at a conversion of 62% on a catalyst reduced at 400°C, and 40, 57, 55, 21, and 20 at 61% conversion on catalyst reduction at 500°C (Selectivity = moles C_i formed per 100 moles of n-pentane converted).

The H_2 chemisorption and desorption data given in Table 2 show that exposure to H_2 above 500°C renders a fraction of the Pt surface inaccessible for subsequent chemisorption of H_2. Air oxidation at 500°C followed by a reduction at 400°C makes all the surface Pt atoms again available for H_2 chemisorption. These results also show the similarity of the high-temperature H_2 treatment to chloriding or sulfiding the catalyst. The catalytic activity and the H_2 chemisorption on the catalyst can both be restored to the prechlorided levels by the same oxidation–reduction procedure as above (7). With the sulfided catalyst, the restoration of activity on reoxidation was not quite complete, however. Hence the sulfiding experiment was always done as the last in a series with any catalyst sample.

The change in H_2 chemisorption capacity of the catalyst after H_2 pretreatment at 500 to 600°C may actually be much more pronounced than indicated in Table 2, because the O_2–H_2 cycles at 20°C used in the chemisorption measurement already neutralize part of the effect of high temperature H_2 pretreatment. This has been observed by us from both catalytic activity studies and TPD spectra. Den Otter and Dautzenberg (*3*) have also reported that, for catalyst samples reduced at 550 and 650°C, the chemisorption capacity is initially much lower for H_2 than for O_2, indicating the presence of sites which accept O_2 but not H_2; during gas titrations these sites are partly converted (in O_2 at 0°C) into sites which adsorb both gases, while in O_2 at 300°C the conversion is complete, i.e., the catalyst is back in its initial state. The results of Gonzalez-Tejuca *et al.* (*4*) are also very similar.

Figure 4 shows the TPD of H_2 from the catalyst after exposure to 20, 100, 200, 300, 400, 500, 550, and 600°C for 1 hr, as also after chloriding and sulfiding at 400°C, and cooling the catalyst to 20°C in the H_2 stream in all cases. The desorption was complete before 500 to 600°C. The heating was stopped at 600°C and the catalyst was cooled (in the same N_2 stream as for the TPD experiment) to the temperature for the next H_2 exposure. Though the quantities of H_2 desorbed from the catalyst for the various TPD runs with H_2 exposures at 400 to 550°C are practically the same, there is a progressive shift of the TPD curves to higher temperatures: The higher the temperature of exposure of the catalyst to H_2, the higher is the temperature at which H_2 can be desorbed from it. Thus a stronger chemisorption of H_2 seems to intervene at higher temperatures. Most of the Pt atoms, which are covered by strongly chemisorbed H_2, cannot be determined by the usual volumetric adsorption method of evacuation of the catalyst followed by its exposure to H_2 at 20°C, or even by the H_2–O_2 titration method. A part of them, however, can react with O_2 at 20°C and behave normally again toward H_2, thus

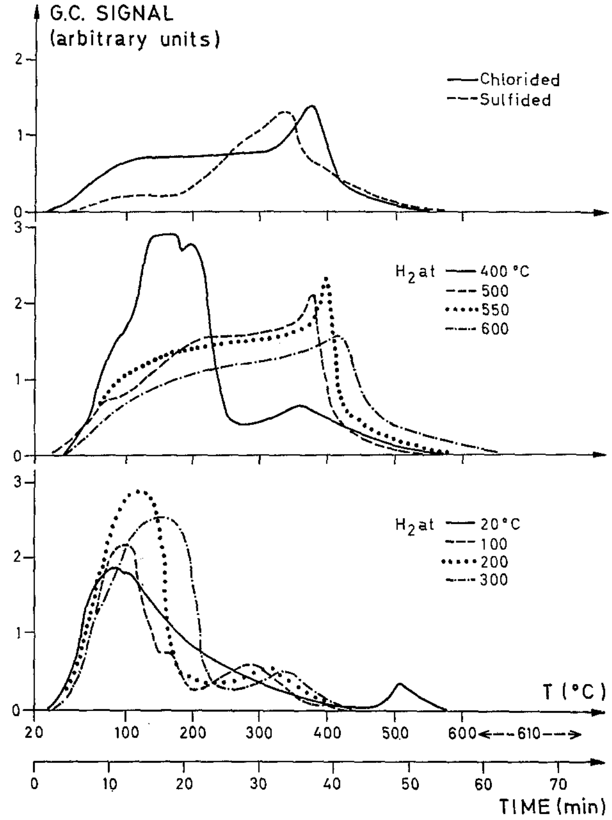

FIG. 4. TPD of H_2 from the catalyst exposed to H_2 at various temperatures for 1 hr and cooled in H_2 to 20°C, and after chloriding and sulfiding in H_2 at 400°C. Catalyst: 0.84 g. N_2 flow 17 cm³/min. Heating rate 10°C/min, gc attenuation 4 X.

TABLE 3

Reactions of *n*-Pentane on Platinum Black in Pulse Reactor[a]

Pretreatment		Reaction temperature (°C)	Product analysis (mol%)						
Air at (°C)	H_2 at (°C)		C_1	C_2	C_3	iC_4	nC_4	iC_5	nC_5
500	400	400	46.0	3.5	3.8	0.14	1.1	4.1	41.3
500	450	400	17.0	1.0	0.44	0	0.2	0.8	80.6
500	500	400	0	0	0	0	0	0.4	99.6
500	500	500	41.9	20.8	7.6	0.26	4.3	0.75	24.3
500	550	500	13	4.8	2.4	0	1.5	0.6	77.6
500	600	500	10.5	5.6	4.0	0	2.3	0.9	76.7
500	400	400	43.0	13.0	10.2	0.79	2.6	7.6	22.8

[a] Catalyst wt., 0.5 g; H_2 carrier flow, 50 cm^3/min.

explaining the homogenizing effect of air–H_2 cycles at 20°C observed by Prasad *et al.* (*1*) and also by us in the present work, and the acceptance of O_2, but not H_2, by these sites, reported by Den Otter and Dautzenberg (*3*). All the strongly chemisorbed H_2 can react with O_2/air during the oxidation at 500°C, making all the surface Pt atoms once again available for chemisorption of both H_2 and O_2.

A comparison of the TPD spectra of Fig. 4 with the data of Table 1 shows that only the catalyst reduced at 400°C or below, from which H_2 is desorbed mainly in the 50 to 300°C region, has strong hydrogenolysis activity. From the catalyst samples pretreated with H_2 at higher temperatures, or by chloriding, or by sulfiding, the desorption of H_2 occurs profusely only at 300 to 500°C; they also have little or no hydrogenolysis activity. Thus there seems to be a direct correlation between the profuse desorption of H_2 in the 50 to 300°C region during TPD and the hydrogenolysis activity of the catalyst for *n*-pentane and *n*-hexane. A similar correlation of a low-temperature H_2 desorption (at about −20°C) in the TPD spectra of $Pt-Al_2O_3$ catalysts with their hydrogenation activity for benzene at 50°C was reported earlier by Aben *et al.* (*14*).

In the literature of chemisorption of H_2 on Pt, stronger and weaker forms of chemisorption of H_2 have been reported or discussed in the past by several investigators, e.g., de Boer (*15*), Boudart (*16*), Mignolet (*17*), Suhrman *et al.* (*18*), Sachtler and Dorgelo (*19*), Toya (*20*), Eley *et al.* (*21*), and others. Perhaps the most direct proof for the existence of different chemisorbed forms of H_2 on Pt, without possible complications from hydrogen spill-over on to the carrier, can be seen in the TPD of H_2 from platinum black reported by Tsuchiya *et al.* (*22*) and the radio-tracer studies of the interaction of H_2 and platinum black by Paál and Thomson (*23*). On introducing a tritium pulse to platinum black at 360°C (*23*), a "hydrocarbon-accessible" region (I) was first created on the surface, a part of which was transformed into a "hydrogen-accessible but hydrocarbon-inaccessible" region (II):

$$H_{2(g)} \rightleftharpoons 2H_I \rightleftharpoons 2H_{II}$$

The two peaks or regions in the TPD spectra of H_2 on $Pt-Al_2O_3$ in the present work, in particular the growth of the high-temperature peak at the expense of the low temperature one when the catalyst was exposed to H_2 at higher temperatures, may be the two types of chemisorption of H_2 on Pt, as postulated by Paál and Thomson (*23*). Very similar behavior as shown in Fig. 4 for the 0.6% $Pt-Al_2O_3$ catalyst was also seen in the present

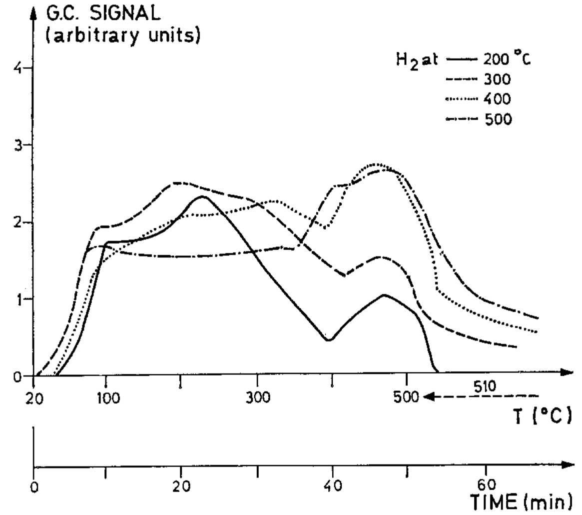

FIG. 5. TPD of H_2 from 0.5 g of platinum black exposed to H_2 at various temperatures for 1 hr and cooled in H_2 to 20°C. N_2 flow 16 cm^3/min. Heating rate 10°C/min, gc attenuation 1 X.

studies for the TPD spectra of H_2 for two samples of a 2% Pt–Al_2O_3 catalyst, one with a Pt dispersion of 35% and the other with only 7%. Though other workers have reported the desorption of H_2 from the carrier alumina while working at lower temperatures and pressures, e.g., Charcosset *et al.* (*24*) and Kramer (*25*), under the present conditions of TPD (at 1.1 bar N_2 pressure up to 600°C), the alumina carrier itself, exposed to H_2 at 400 to 600°C and cooled in H_2 to 20°C, did not show any detectable desorption of H_2 during TPD runs.

To confirm that the attenuation effect of high-temperature H_2 on the Pt–Al_2O_3 catalyst is specific to platinum and does not involve any metal–carrier interaction, the experiments were also carried out with platinum black (Johnson Matthey, London). The platinum black after reduction at 400°C had a surface area (calculated from H_2 chemisorption) of 1.0 m^2/g, but it sintered strongly in H_2 at 600°C for 30 min to an area of 0.28 m^2/g. All measurements were taken after this initial strong sintering given as a preliminary pretreatment. Pulse-reactor data for the reactions of *n*-pentane on the platinum black at 400 and 500°C, given in Table 3 show the attenuation of catalytic activity on exposure to H_2 at higher temperatures and the restoration of this activity on air oxidation at 500°C followed by reduction at 400°C, just as in the case of the Pt–Al_2O_3 catalyst (Table 1). The TPD spectra of H_2 from platinum black, exposed to H_2 at 200, 300, 400, and 500°C for 1 hr and cooled in H_2 to 20°C, shown in Fig. 5, also exhibit a behavior similar to that of the Pt–Al_2O_3 catalyst (Fig. 4).

Thus, the attenuation of hydrogenolysis by high-temperature H_2 pretreatment of the catalyst may be a consequence of the stronger chemisorption of H_2 on Pt, a typical case of self-inhibition by one of the reactants. It need not necessarily involve a surface alloy formation between reduced Pt and reduced Al, as proposed by Den Otter and Dautzenberg (*3*), or a decomposition of Pt particles into an atomic form of Pt incorporated into the alumina support, as suggested bv Gonzalez-Tejuca *et al.* (*4*). The exact mechanism of such attenuation of hydrogenolysis will be clear only from further studies. Work in this direction is in progress in our laboratory.

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