J. King Saud Univ., Vol. 7, *Science* (1), pp. 89–103 (A.H. 1415/1995).

High-temperature Pretreatment of Alumina-supported 0.6% Platinum Catalysts: Methylcyclopentane Hydrogenolysis

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(Received 28 September 1993; Accepted for publication 18 June 1994)

Abstract. The activity of 0.6% Pt/Al_2O_3 catalysts pretreated at different temperatures were determined on the hydrogenolysis of methylcyclopentane (MCP). It was found that high-temperature pretreated catalyst (Pt 973) gave more substantial amounts of CH_4 than its lower counterpart. On this catalyst hydrogenolysis is suppressed. This was possibly caused by the surface morphology change during its pretreatment when moisture was removed. This produced a number of low-coordinate Pt atoms exposed on the surface which are responsible for its hydrocracking activity. This was conifrmed during the chemisorption measurements. High-temperature pretreated catalysts (Pt 673 and Pt 973) become less amenable to H_2 adsorption. That change in surface morphology coupled by annealing – which decreased surface roughness responsible for some special sites for efficient activity – gave the catalysts their poor performance. Poorly-annealed catalyst (Pt 523), in comparison, had the usual efficiency for MCP hydrogenolysis. Expectedly, it gives large surface area (210 m^2/gm) during chemisorption. Rearrangement of its structure was not possible, and it is less affected by annealing. Kinetic measurements were made on the catalysts at different reaction temperatures (503, 533, 573 K), H_2 (200-800 mm Hg) and MCP (20, 41.7, 135 torrs) partial pressures. A comparison between them is discussed to the extent of hydrogenolysis and hydrocracking reactions. In summary, activity of the catalysts follows the sequence Pt 523 > Pt 673 > Pt 973. High-temperature pretreatment lowers the surface area and activity of 0.6% Pt/Al_2O_3 catalysts.

Introduction

Studies on the sensitivity of platinum catalysts to pretreatment conditions have varied and the effect on specific reactions was attributed to the particle size of the catalyst. With platinum catalysts, high metal dispersion (low-Pt loading) are generally associated with higher activities which may have significant changes in selectivity with respect to its particle size [1–7].

Investigators have shown how pretreatment affects the activity and selectivity of alumina-supported Pt catalysts [8–13]. Burch and Garla [8] have pointed out that loss

of hydrocracking activity (on n-pentane) with increasing temperature of reduction is dependent on factors such as whether its initial state is the oxide or the metal. The hydrocracking activity depends on how long the catalyst was stored before being used. It was observed that the driest catalyst had high hydrocracking activity compared to the one received and used as-is without oven-treatment prior to its testing. Meanwhile, Dutartre and Martin's [9] investigation attributed the loss of activity to a transformation into (111) planes at the surface. A (111) plane had been found to give 1/2 the rate of formation of methylpentanes [10] compared to the (100) surface. But this was contested by Burch and Garla (BG) based on their experiments, and they alleged that this could not give convincing explanation. On the other hand, Dautzenberg and Wolters [11; 12] stated that an alloy of PtAl formed after high-temperature treatment hinders H_2 uptake of the catalyst due to the reduced affinity to the adsorbate. However, investigations of BG denied their proposals owing to the fact that a transformation into (111) planes and formation of PtAl alloy would not occur quickly enough. Results of their experiments could attest to this [8]. Another proposal was suggested by Menon and Froment [13]. During their chemisorption measurements, they got low values on H_2-adsorbed for high-temperature treated catalysts. It was proposed that loss of chemisorption capacity was caused by poisoning by the adsorbate gas (H_2) itself on the surface of the metal. At high-temperature treatment the catalyst adsorbed some H_2 on its surface, and hence, there was a loss of H_2 uptake during its measurements. It also remarkably lowered its activity. A loss of activity could not be accounted for by the effect of H_2 on high-temperature reduction, but BG had suggested that it may be possible that it was due to the cumulative effect of their repeated reoxidation in air and reduction in H_2 during its testing.

Since hydrogenolysis of methylcyclopentane is known to be a structure-sensitive reaction the effect of highly-dispersed Pt/Al_2O_3 catalysts which undergo high-temperature treatment was studied. This catalytic reactoin is a chemical test for particle size of Pt where selectivity and product distribution depends on the size [14; 15, p. 30; 16]. This study involves kinetic measurements of 0.6% Pt/Al_2O_3 catalysts pretreated at different reduction temperatures and their chemisorption capacity is being explored. MCP hydrogenolysis and hydrocracking activity are discussed at different temperatures and partial pressures of H_2 and the hydrocarbon.

Experimental Methods

The catalysts were prepared from chloroplantinic acid (BDH) and contained 0.6% Pt. After evaporation with the support and drying, they were treated at different desired tempertures (523, 673, 973 K). N_2 flow was introduced after H_2 was stopped. The resulting catalysts were labelled Pt 523, Pt 673 and Pt 973, respectively.

MCP (Riedel de Haen, 99%) showed no detectable impurities on a chromatographic analysis while H_2 gas was further purified through silica gel and a molecular sieve.

Kinetic measurements were done using a pulse-technique. The reactor was enclosed in an electric furnace where the reaction temperatures were monitored by a thermocouple placed adjacent to the catalyst bed. A sintered disc inside the reactor supported the catalyst. A precision flow controller (Aalborg instruments) controlled the gases flowing through the catalyst bed, and manometers were installed before and after the reactor. The reactions were taken at different H_2 pressures and reaction temperatures (200-800 mm. Hg and 523-573 K, respectively). The flow was measured with a bubble flowmeter. Methylcyclopentane (5.0 ul) was injected via a silicone rubber septum in a coiling U-tube passing through a TCD situated before the reactor, and the products were collected by withdrawing the samples with a gas syringe (2000 ul) from the outlet located after the reactor. A Varian FID gas chromatograph fitted with DC-220 in chromosorb at 333 K was employed to analyze the withdrawn samples.

Preceeding the catalytic experiments was a reduction overnight of the catalysts under H_2 flow at 573 K. The experiments were performed at their desired reaction temperature and H_2 pressure.

Chemisorption measurements were done using the conventional method [17, p.113]. The temperature used was 473 K.

Results and Discussion

Table 1 shows the effect of temperature on the rate of MCP hydrogenolysis on various Pt/Al_2O_3 catalysts. It was noticed that for catalysts Pt 523 and 673, increase of the rate for the formation of 2MP, 3MP and n-hexane was proportional to temperature. But using Pt 973 the rate of formation of n-hexane was almost constant at different temperatures while 3MP appearance had diminished and formation of 2MP was only possible at higher temperature. Increasing to each new temperature doubled the rate for 2 MP and 3MP formation on Pt 523. Noticeable was the rate of n-hexane and 2MP production which was equal. At lower temperature, n-hexane formation was favorable, and increase of temperature made 2MP formation compete with the rate of n-hexane formation (Fig. 1).

The production of n-hexane predominates at lower temperature (<533 K), but at high reaction temperature, 2MP formation is more pronounced. Arrhenius plots for the catalysts can be found in Fig. 2. The activation energy of this catalyst (Table 2) clearly shows that n-hexane and 2MP have closer values than 3MP (19.75, 24.87 and 32.64 kcal/mole, respectively). But for Pt 673 n-hexane becomes low (13.09), while the MP's have increased its values. Furthermore, for Pt 973 n-hexane becomes significantly low, while 2MP increased further, and 3MP was not observed. Generally, a rupture of a secondary-tertiary carbon bond is achieved more easily than a secondary-secondary bond on Pt catalysts, especially for a high-temperature pretreated

Table 1. Effect of temperature on the rate of MCP hydrogenolysis over Pt/Al_2O_3 catalysts; P_{HC} = 135 torrs, PH_2 = 710 torrs

		503 K ($\times 10^{-3}$)	518 K ($\times 10^{-3}$)	533 K ($\times 10^{-3}$)	548 K ($\times 10^{-3}$)	563 K ($\times 10^{-3}$)	573 K ($\times 10^{-3}$)
Pt523							
MCP	→2MP	2.94	4.55	8.80	19.50	29.30	65.40
	→3MP	–	1.36	3.20	7.75	14.20	31.90
	→n-Hex	4.36	5.87	6.53	12.30	24.90	55.50
Pt673							
MCP	→2MP	0.38	1.86	5.69	9.29	14.20	30.90
	→3MP	–	0.14	2.61	4.46	5.95	13.40
	→n-Hex	2.32	4.97	9.49	7.82	8.14	17.70
Pt973							
MCP	→2MP	–	–	–	0.88	1.46	4.91
	→3MP	–	–	–	–	–	–
	→n-Hex	–	2.09	2.01	2.82	2.75	3.64

Table 2. Activation energy (kcal/mole)

	2MP	3MP	N-hexane
Pt523	24.87	32.64	19.75
Pt673	33.10	42.46	13.09
Pt973	40.76	–	5.85

one. That would correspond to the statistical ring opening responsible for n-hexane which follows a non-selective mechanism. In addition, the activity of Pt 973 had lowered considerably, Kramer and Zuegg's findings [18] of phase-boundary may hold true since for this catalyst, during its high-temperature pretreatment, annealing may have occurred which lost its activity affecting greatly the MP's (3MP had vanished), but then n-hexane production was still possible. There is a shift of selectivity here from a non-selective mechanism into a mechanism where only n-hexane is favored. High-temperature pretreatment of catalysts thereby produced Pt particles which were well-annealed and less reactive to MCP hydrogenolysis which might be due to the decrease of the Pt surface exposed for the reaction to occur on.

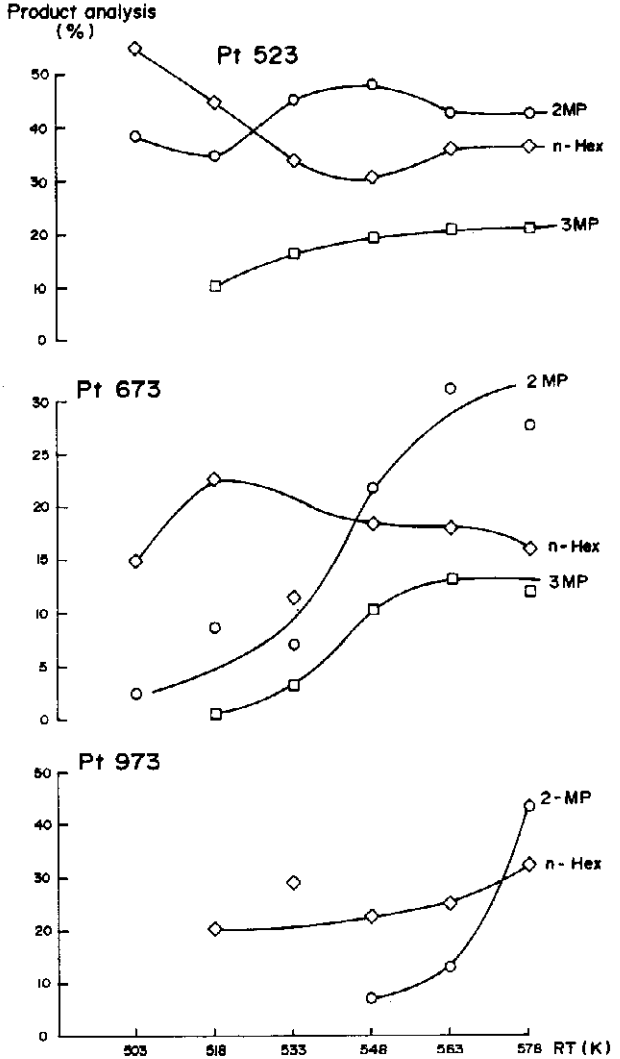

Fig. 1. Rate of formation of 2MP (○), 3MP (□) and n-Hex. (◇) as a function of reaction temperature.

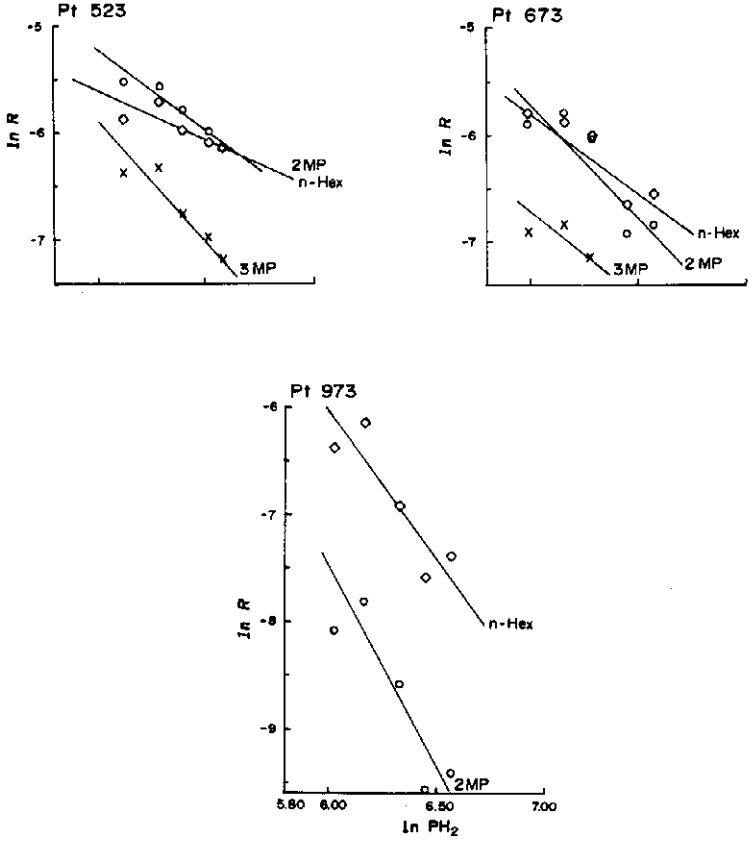

Fig. 2. Arrhenius plots

To know the extent of hydrocracking on the activity of Pt/Al_2O_3 catalysts to MCP, they were exposed to different reaction temperatures (503, 533, 573 K), hydrocarbon pressures (20, 41.7, 135 torrs) and H_2 pressures (200-800 mm. Hg.). Using Pt 523 at any reaction temperature doesn't allow hydrocracking to occur; whereas Pt 973 gave a substantial amount of CH_4 at the lowest temperature, but tended to decrease when the temperature of the reaction was increased (Fig. 3 and Table 3). Pt 673 gave exceptional high CH_4 yield at 503 K. Methane production holds stable to low percentage for all temperatures, but a threshold to a very high percentage is achieved below 518 K. Lowering the MCP pressure to 41.7 torr (Table 4) doesn't affect hydrocracking activity (the same at 135 torr), but at 20 torr of MCP, hydrocracking could not occur at a temperature of 523 K, but appears at higher temperature (573 K). This was the opposite of using a higher MCP pressure. On this catalyst, methane only accounted for about 5-10% of the products. For the other two catalysts, hydrocracking was more pronounced (especially at higher H_2 pressure), except at 20 torr of MCP and higher reaction temperature (573 K), where hydrocracking activity did not occur. During high-temperature pretreatment of these catalysts, a single surface Pt atom occurs through a ll-adsorbed surface intermediate [8] which was responsible for methane production. These special, single Pt atoms had been identified by Foger and Anderson [19] and Somorjai [20, p. 1] in low coordination on the surface (corners, kinks, edges or steps).

Table 5 shows the effect of H_2 pressure on the rate of MCP hydrogenolysis over the catalysts. The order of catalytic activity and the order of formation of products are of the same magnitude. It was observed that for all the catalysts, the order of catalytic activity and 2MP, 3MP and n-hexane formation followed the sequence Pt 523>673>973. Rate of MCP hydrogenolysis is at its maximum at a H_2 pressure of @ 450 mm Hg when reaction temperatures being used are 523 K and 548 K. High reaction temperature (573 K) yields a maximum rate at a H_2 pressure of @ 700-750 mm Hg. Generally an increase in the H_2 pressure made hydrocracking prominent. An increase of H_2 pressure increases CH_4 production which suppressed hydrogenolysis. Overall, the order of reaction with respect to H_2 is negative (Table 6) comparable to the results of Zaera, *et al.* [13] on MCP hydrogenolysis. Clearly, n-hexane had higher negative values at Pt 523 and Pt 673 which makes its formation favorable (at lower temperature).

On focussing at a lower MCP pressure (20 torr) and a reaction temperature of 523 K (Table 4), hydrogenolysis of MCP occurred at Pt 523, whereas on the other two catalysts, hydrogenolysis activity was suppressed and hydrocracking became prominent. An assumption would be that high-temperature pretreatment of these catalysts produced a well-annealed platinum catalyst thereby reducing its activity and suppressing hydrogenolysis. At small crystallites (Pt 523) two reaction pathways competed between the phase-boundary support of Pt and the support and the Pt surface (Kramer and Zuegg). The former accounts for the n-hexane production, while the

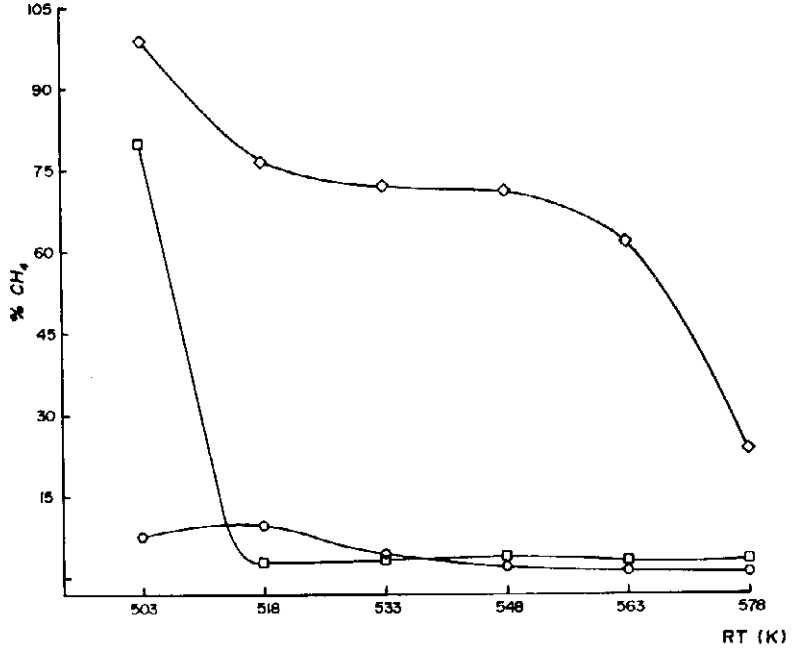

Fig. 3. Rate of formation of (CH_4 over Pt 523 (○), Pt 673 (□) and Pt 973 (◇) as a function of the temperature of reaction. PHC = 135 torr, PH_2 = 710 torr.

Table 3. (%) Methane production

	503 K	533 K	573 K
Pt 523	0.077	0.126	0.110
Pt 673	1.526	0.353	0.409
Pt 973	27.743	0.638	0.388

Table 4. Reaction occurring over 0.6% Pt/Al_2O_3 at different MCP partial pressure and reaction temperature

	20 torr MCP		41.7 torr MCP		135 torr MCP	
	523 K	573 K	523 K	573 K	523 K	573 K
Pt 523	Hydrogenolysis	Hydrocracking :6–6% (CH_4)	Hydrocracking (6–10% CH_4)	Hydrogenolysis	Hydrocracking (5–10% CH_4)	Hydrogenolysis
Pt 673	Hydrocracking (30–70% CH_4)	Hydrogenolysis	Hydrocracking (26% CH_4)	Hydrocracking (5–10% CH_4)	Hydrocracking (10–40% CH_4)	Hydrocracking (5–10% CH_4)
Pt 973	Hydrocracking (30–60% CH_4)	Hydrogenolysis	Hydrocracking (20% CH_4)	Hydrocracking (5–10% CH_4)	Hydrocracking (5–40% CH_4)	Hydrocracking (8–50% CH_4)

Note: A high percentage of CH_4 accounts to the high H_2 partial pressure.

Table 5. Effect of hydrogen pressure on the rate of MCP hydrogenolysis over Pt/Al_2O_3 catalysts; P_{HC} = 20 torr, RT = 523 K.

Pt 523	446 mm Hg ($\times 10^{-3}$)	592 mm Hg ($\times 10^{-3}$)	616 mm Hg ($\times 10^{-3}$)	753 mm Hg ($\times 10^{-3}$)	805 mm Hg ($\times 10^{-3}$)
MCP → 2 MP	4.90	2.60	3.50	1.40	1.50
→ 3 MP	2.00	1.20	1.40	0.60	0.60
→ n-Hex	2.50	1.80	1.80	1.10	1.10

Pt 673	413 mm Hg ($\times 10^{-3}$)	514 mm Hg ($\times 10^{-3}$)	592 mm Hg ($\times 10^{-3}$)	672 mm Hg ($\times 10^{-3}$)
MCP → 2 MP	1.20	0.70	0.40	0.30
→ 3 MP	0.40	0.20	0.10	0.06
→ n-Hex	0.60	0.40	0.30	0.30

Pt 973	398 mm Hg ($\times 10^{-3}$)	463 mm Hg ($\times 10^{-3}$)	546 mm Hg ($\times 10^{-3}$)	610 mm Hg ($\times 10^{-3}$)	700 mm Hg ($\times 10^{-3}$)
MCP → 2 MP	0.90	0.80	0.50	0.40	0.20
→ 3 MP	0.30	0.30	0.20	–	–
→ n-Hex	0.80	0.80	0.80	0.30	0.20

Table 6. Order of reaction with respect to hydrogen, HCpressure = 20 torr at 523 K

	2MP	3MP	n-Hexane
Pt 523	–0.41	–0.41	–0.63
Pt 673	–0.32	–0.28	–0.65
Pt 973	–0.38	–0.39	–0.39

latter for 2MP and 3MP. Using Pt 673, the hydrocracking was pronounced especially at higher H_2 pressure, and loss of hydrogenolysis activity was evident as H_2 pressure was increased. It is concluded then that the factor responsible for producing a well-annealed catalyst at high-temeprature pretreatment is also the one which is responsible for the loss of hydrogenolysis activity and the emergence of CH_4.

The product distribution (Table 7) showed that increasing the reaction temperature increases the 3MP/n-hexane ratio. The larger the ratio generally means a larger Pt particle size [1; 3; 14; 15; 21]. Pt 673 gave a substantial amount of n-hexane compared to Pt 523. When Pt 673 was treated at high temperature it produced an annealed catalyst. Further annealing of the catalyst (Pt 973) hinders the selective mechanism (only n-hexane is possible). The Pt 973 catalyst gave a very low activation energy for n-hexane (5.85 kcal/mole) compared to Pt 523 and Pt 673 ctalysts (see Table 2). The 2MP activation energy became greater for Pt 523-673 and 3MP was not obtained for Pt 973.

Chemisorption measurements (Table 8) had shown that the surface area of Pt 973 was almost 16 and 10 times those of Pt 523 and 673, respectively. Pt 673 has about 54% more surface area than that of Pt 523. Pt 973 gave a lower H_2 uptake during the measurement. Menon and Froment [12] suggested that during high-temperature treatment of the catalyst, it adsorbed some H_2 on its surface and during the adsorption measurements, the H_2-saturated catalyst can't take up more H_2 on its surface, thus giving a low H_2-adsorbed value. In a similar vein Dautzenberg and Wolters [11] had mentioned a possible PtAl alloy formation which made the catalyst not amenable to H_2 adsorption, but Burch and Garla investigations lead to neither conclusions [8]. It may be that extended annealing of the Pt had slowly eliminated very small and active platinum particles, thereby reducing some active sites on the well-annealed surfaces [22]. A high-temperature pretreatment produces a number of low-coordinate Pt atoms on the surface. This is responsible for the hydrocracking activity of Pt973 which has an Π-adsorbed surface intermediate [1; 4; 19]. On the contrary, the other two catalysts involve the arrangement of cyclic Π-adsorbed olefins to a dicarbene species (for n-hexane production) and a rearrangement of a αααββ-tetraadsorbed species for 2MP and 3Mp [18; 23].

Table 7. Product distribution

	518 K				533 K				548 K				563 K			
Pt	**2MP**	**3MP**	**n-Hex**	**3MP/ n-Hex**	**2MP**	**3MP**	**n-Hex**	**3MP/ n-Hex**	**2MP**	**3MP**	**n-Hex**	**3MP/ n-Hex**	**2MP**	**3MP**	**n-Hex**	**3MP/ n-Hex**
523	38.61	11.58	49.82	0.23	47.50	17.27	35.23	0.49	49.25	19.60	31.15	0.63	42.87	20.81	36.33	0.57
673	19.44	9.27	71.29	0.13	31.96	14.66	53.37	0.28	43.05	20.68	36.27	0.57	50.22	21.02	28.77	0.73
973	–	–			–	–			23.75	–	76.3		34.75	–	65.25	–

Table 8. Chemisorption of 0.6% Pt/Al_2O_3 at 200°C.

Sample	Vol. H_2 ads. (ml gm^{-1} - cat)	S_{Pt} (m^2/gm)
Pt 523	0.2934	210.00
Pt 673	0.1905	136.00
Pt 973	0.0185	13.24

A high-temperature pretreatment of catalyst lowers the activity of the Pt catalysts. This may be caused by annealing which produced a decrease in surface "roughness" as pointed out by Burch and Garla and thus lack of some special sites needed for efficient activity. When these catalysts were reduced directly at high tempeatures as in the case of Pt 973, some rearrangement of their structures may have occurred, and thus special sites that usually occur on poorly-annealed catalysts (which are responsible for their good activity) were not possible giving a low performance.

It was also true during the chemisorption measurements. The lower uptake of H_2 gas by the catalysts Pt 673 and Pt 973 could be accounted for by the rearrangement of their structures which made them less amenable to adsorption during the measurements. These special sites which were responsible for good activity had somewhat diminished upon chemisorption; a low value for H_2-absorbed was obtained because of the near absence of the special sites on the well-annealed surfaces of these catalysts compared to a poorly-annealed one as for Pt 523.

The hydrocracking activity of high-temperature treated catalysts may be traced to the surface morphology change as a result of moisture being removed during the pretreatment. These changes had in turn produced a number of low-coordinate Pt atoms exposed on the surface. These atoms via an Π-adsorbed surface intermediate enhanced hydrocracking to be observed on Pt 673 and Pt 973 at any pressure of the hydrocarbon and H_2.

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المعالجة الحرارية العالية لحفّاز ٠,٦٪ بلاتين/ ألومينا: تفكيك ميثيل البنتان الحلقي بوجود الهيدروجين

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قسم الكيمياء، كلية العلوم، جامعة الملك سعود، ص.ب. ٢٢٤٥، الرياض ١١٤٥١، المملكة العربية السعودية

(استلم في ١٤١٤/٦/١٢هـ؛ قُبل للنشر في ١٤١٥/١/٩هـ)

ملخص البحث. تمّ تحديد فعاليّة حفّاز ٠,٦٪ بلاتين/ ألومينا المعالج عند درجات حرارة مختلفة في تفكيك ميثيل البنتان الحلقي بوجود الهيدروجين. ووجد أن الحفّاز المعالج عند درجات حرارة عالية (بلاتين ٩٧٣) يعطي كميّة من الميثان أكبر من المعالج عند درجة حرارة منخفضة. ففيه تحمد عملية التفكيك بوجود الهيدروجين، وذلك ممكن بسبب التغيرات المورفولوجية للسطح خلال المعالجة الحرارية حين إزالة الرطوبة. وقد أدى ذلك إلى إنتاج العديد من ذرّات البلاتين ذات التناسق المنخفض على السطح والتي تكون مسؤولة عن حدوث عملية التكسير الهيدروجيني. وقد تأكد ذلك من خلال قياسات الامتزاز الكيميائي. فالحوافز المعالجة عند درجات حرارة عالية (بلاتين ٦٧٣ وبلاتين ٩٧٣) أصبحت متدنية من حيث امتزاز الهيدروجين. وقد جعل هذا التغير في مورفولوجية السطح إضافة إلى التكتل المؤقت للذرّات ـ الذي خفض خشونة السطح المسؤولة عن وجود المواقع المتميزة بالكفاءة ـ الحوافز ذات أداء ضعيف. أما الحفّاز (بلاتين ٥٢٣) فقد كان بالكفاءة المعتادة لتفكيك ميثيل البنتان الحلقي بوجود الهيدروجين. فقد كانت مساحة سطحه ـ كما هو متوقع ـ كبيرة (٢١٠م^2/جم) خلال الامتزاز الكيميائي، ولم تكن إعادة تنظيم سطحه ممكنة، ولم يتأثر كثيرًا بعملية التكتل المؤقت للذرّات. كما عُملت قياسات حركيّة على الحوافز عند درجات حرارة مختلفة (٥٠٣، ٥٣٣، ٥٧٣ كالفن)، وعند ضغوط مختلفة للهيدروجين (من ٢٠٠ إلى ٨٠٠ ملم زئبق) وليثيل البنتان الحلقي (من ٢٠ إلى ١٣٥ ملم زئبق). وقورنت نتائج ذلك وكانت تسير فعاليّة الحوافز، باختصار، وفق الترتيب بلاتين ٥٢٣ > بلاتين ٦٧٣ > بلاتين ٩٧٣. فالمعالجة الحرارية العالية تخفض من الفعاليّة ومن مساحة السطح لهذا الحفّاز.