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Particle Size Effect in Supported Platinum: Methylcyclohexane Dehydrogenation

A. ROCHEFORT,[1] F. LE PELTIER, AND J. P. BOITIAUX

Division Cinétique et Catalyse, Institut Français du Pétrole, B.P.311, 92506 Rueil-Malmaison Cedex, France

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Dehydrogenation of methylcyclohexane has been studied over a platinum monometallic catalyst supported on α-Al_2O_3. Physical and chemical properties of platinum crystallites were studied by TPR and TPD/H_2 techniques. The hydrogen desorption profile was found to be particle size dependent. A tightly-bonded hydrogen fixed on platinum particles after high-temperature reduction was revealed by TPD/H_2. In the methylcyclohexane dehydrogenation, it was found that the reactivity of platinum crystallites is related to the activation process performed before the catalytic test. The dehydrogenation rate increased by at least a factor of 2.0 when a desorption following high-temperature reduction was performed. These results were consistent with the hydrogen desorption profiles observed by TPD/H_2.

INTRODUCTION

Supported metal catalysts are largely used in chemical transformations in refining processes (*1, 2*). Conversion of hydrocarbons into aromatics in the reforming process is usually performed on a highly dispersed noble metal such as monometallic Pt/γ_c-Al_2O_3 or bimetallic (Pt–Sn, Pt–Re) catalysts. In these systems, the transition metal is the active site for the dehydrogenation (DH) reaction. However, there is little available information about the influence of metallic particle size on turnover frequency (TOF) of this reaction.

The simplest reaction of naphtha reforming process is the dehydrogenation of cyclohexane. Attribution of structural sensitivity (*3*) in this reaction is not well established for supported platinum particles in contrast to single-crystals. Early work by Blakely and Somorjai (*4*) has shown that dehydrogenation is structure-insensitive toward an increasing kink and step density of the surface of platinum single-crystal when studied at low pressure. Further work (*5, 6*) at higher pressure has given a structure-sensitive reaction; the TOF increased when surface atom coordination decreased. Similar results were found for an iridium single-crystal (*7*).

On supported platinum catalysts, DH always seems structure-insensitive (*8–16*) when Al_2O_3 or SiO_2 are used as supports. Furthermore, the study of Abdeladim (*13*) has shown an anomalous high DH rate on very small platinum particles supported on chlorided γ_c-Al_2O_3. Over an Ni/SiO_2 catalyst, free of chlorine, a negative structure effect was observed: activity increased for particle size varying from 2.0 to 4.0 nm (*17*). In contrast to single-crystal studies, supported catalysts lead to almost all behaviors: positive, negative, or no structure effect. A new question arises with a recent single-crystal study (*6*) in which the use of a blocking site agent led to the conclusion, in agreement with the multiplet theory (*18, 19*), that cyclohexane DH needs at least eight platinum atoms. However, all other single-crystal studies prior to this showed an increasing reaction rate when surface atom coordination decreased.

An apparent size effect can sometimes be

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[1] Present address: Centre National de la Recherche Scientifique, Institut de Recherche sur la Catalyse, 69626 Villeurbanne Cedex, France.

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caused by other phenomena: chemisorbed hydrogen (*20–26*), oxygen (*27, 28*), or carbon deposit (*4, 5, 29–34*) were the most frequently represented examples cited in the literature. Maeda *et al.* (*26*) showed that a higher reduction temperature of Rh/Al_2O_3 increased the DH rate with few changes in the particle size. On other hand, adsorbed hydrogen in high-temperature (H_{HT}) conditions can also suppress the total catalytic activity (*24*). This H_{HT} was revealed by TPD/H_2 of industrial Pt/SiO_2 (*22*) and Pt/Al_2O_3 (*24*) catalysts. Carbon deposition could be structure-sensitive (*16, 29*); Mitrofanova and Boronin (*16*) have shown that the deactivation rate of a catalyst increases with particle size, and the lower stability of low dispersions is attributed to an increase in proportion of high-coordinated (111) surface.

We have studied the supported platinum particle size effect in the methylcyclohexane (MCH) dehydrogenation. The preparation of counter-ion free catalysts allowed us to focus the study on the active sites on platinum particles. We have also investigated temperature-programmed reduction (TPR) and desorption of hydrogen (TPD/H_2) techniques with the aim of correlating the "structural" effect with the physical/chemical properties of supported platinum.

EXPERIMENTAL

Catalyst Preparation

First-generation catalysts were prepared by chemical exchange techniques developed by Yermakov *et al.* (*35–37*). After a calcination at 773 K for 2 hr in an air stream (2 liter h^{-1} g^{-1}_{cat}), the α-alumina (15 m^2 g^{-1}) was added to a toluene solution of the required amount of platinum acetylacetonate ($Pt(acac)_2$). The chemical exchange was done in excess solution (five times the total pore volume or $5V_{PT}$) for a minimum period of 48 hr in order to obtain uniform metallic distribution in the pore system. The catalyst was then dried at 393 K for 16 hr, calcined in flowing air at 623 K for 2 hr, and then reduced in a hydrogen stream (2 liter h^{-1} g^{-1}_{cat}) at 723 K for 2 hr. These steps produced a highly dispersed platinum catalyst but with a low loading ($\leq$2000 ppm).

A refilling reaction technique (*38*) was used to prepare low-dispersed catalysts associated with a narrow particle diameter distribution. The first-generation catalyst (reexposed to air) and toluene solvent were placed in a glass reactor where hydrogen was allowed to bubble for 1 hr. The oxygen-free $Pt(acac)_2$ solution was then added to the catalyst. We observed a gradual bleaching of the solution during the reaction. After a single-refilling run, the catalyst was dried, calcined and then reduced in the same conditions as mentioned above. Incipient wetness was also performed, in order to obtain a higher ($\geq$0.4 wt%) platinum content, or when an ionic complex ($H_2Pt(OH)_6$) was used. This last catalyst was prepared in nitric acid/methanol solvent and calcined at 803 K rather than 623 K in order to decompose the complex.

Total platinum content was determined by X-ray fluorescence (Philips PW1404). Particle sizes were determined by either H_2–O_2 titration or electron microscopy (J.E.O.L. 120CX). Spherical shape was assumed in determining the average size in H_2–O_2 titration. Size distributions were evaluated by counting at least 200 particles. Average size and standard deviation (ϕ_m^{mic}) were calculated by the usual formulas (*39–41*). Chemical and physical properties of the reduced catalyst are reported in Table 1.

Temperature-Programmed Techniques

TPR experiments were carried out using 5% hydrogen in argon mixture and a heating rate of 5 K min^{-1} from ambient temperature to 1123 K. The temperature was held until the hydrogen consumption stopped. Before TPR experiments, reduced samples were calcined *in situ* at 623 K for 2 hr.

Prior to TPD experiments, the catalysts were reduced under flowing hydrogen at 723 K for a period of 2 hr. The samples were then cooled to ambient temperature under a

TABLE 1

Physical and Chemical Properties of Catalysts Ranked According to Metallic Dispersion

Sample	wt% Pt	D (%)	Particle size (nm)[a]
1	0.14	99	<1.0 (<1.0)
2	0.06	96	1.0 (<1.0)
3	0.11	90	1.1 (1.1)
4	0.18	84	1.2 (1.2)
5	0.16	80	1.3 (1.5 ± 0.1)
6	0.13	77	1.3 (1.4 ± 0.1)
4A	0.27	76	1.3
7[b]	0.20	71	1.4 (1.7 ± 0.1)
2A	0.11	69	1.5
2B	0.11	54	1.9 (2.1 ± 0.3)
4B	0.23	53	1.9 (1.8 ± 0.1)
8	0.46	45	2.3 (1.7 ± 0.1)
5A	0.32	33	3.1 (2.9 ± 0.2)
9	0.82	32	3.2 (2.4 ± 0.2)

Note. The second generation catalysts are indicated by the first generation number followed by a capital letter.

[a] Electron microscopy measured value indicated in parentheses.

[b] Prepared with $H_2Pt(OH)_6$.

flowing hydrogen mixture to adsorb hydrogen on the platinum surface. TPD/H_2 experiments were carried out on these samples using a pure argon flow and a heating rate of 20 K min^{-1} from ambient temperature to 1123 K and maintained until hydrogen desorption stopped.

Desorption energies were evaluated from the first-order kinetic desorption model in which readsorption is negligible (*42*). The pre-exponential factor used ($A = 10^{-3}$ cm^2 s^{-1} $H_{atom}{}^{-1}$) is taken from a single-crystal study (*43*) on Pt(111).

Catalytic Reactions

Methylcyclohexane dehydrogenation experiments were made at 573 K under atmospheric pressure in a fixed bed. The catalyst (constant platinum exposed surface, $S_{Pt} \approx$ 3000 cm^2), diluted with 10 cm^3 of quartz with the same grain size, was placed in the middle of a quartz reactor 28 mm in diameter, then reduced *in situ* during 2 hr at 723 K in a hydrogen flow of 5 liter min^{-1}. The reactant flowrates were controlled through a syringe micropump for methylcyclohexane and a rotameter for hydrogen. The H_2/MCH (or Ar/MCH) mole ratio was held at 5. The homogeneity of the reaction temperature was assured by the use of a furnace with three heating zones, such that the difference from the top to the bottom of the catalytic bed did not exceed 5 K. The temperatures were measured by three thermocouples placed in a thermometric well located along the catalytic bed.

The principal products of the reaction, mostly toluene, were separated by gas chromatography at 373 K in a 50-m WCOT Fused Silica (CP-WAX-52CB) column and analyzed by FID. The weight (w_{cat} = 0.4–1.2 g) and grain size (0.3–0.5 mm) of the catalyst were determined in order to avoid diffusion processes (*44*). The reactant flow of 15–20 cm^3 min^{-1} was used to limit conversion to 10%. The TOF represents the number of methylcyclohexane molecules transformed per initial accessible platinum atom per second. The TOF is extrapolated to zero time in the first part of the resulting deactivation curve; in the extrapolation, the decrease in reaction rate did not exceed 15% of the initial rate measured.

RESULTS

Size Distribution Measured by Electron Microscopy (EM)

With the electron microscope we were able to observe platinum crystallites larger than about 0.8 nm. On very low platinum content (≤0.1%) samples, only a few particles were observed, which precludes a relevant size distribution evaluation. However, the size of the observed platinum crystallites is in agreement with the H_2–O_2 calculated value.

For the other samples, typical size distributions are represented in Figs. 1a–1d. The samples prepared by a chemical exchange impregnation, which allows a controlled reaction between a platinum precursor and a functional group (–OH) of support, have rather small particles with a narrow distribution (see Fig. 1a). When a refilling reaction is carried out at 293 K, the particle size is displaced to a larger size (see Fig. 1b), as expected, and the shape of the distribution remains almost the same. At a higher temperature, the distribution obtained is broader and includes a small fraction of small unchanged crystallites (see Fig. 1c). For catalysts prepared by incipient wetness, distribution of particle size is broader (see Fig. 1d) than those prepared by chemical exchange for the same dispersion. As a result (see Table 1), there is a better agreement between mean diameter measured by H_2–O_2 and EM when incipient wetness is not used. Usually, the mean size of particles evaluated by EM is larger than the H_2–O_2 value because the very small (nonobservable) particles are not taken into account.

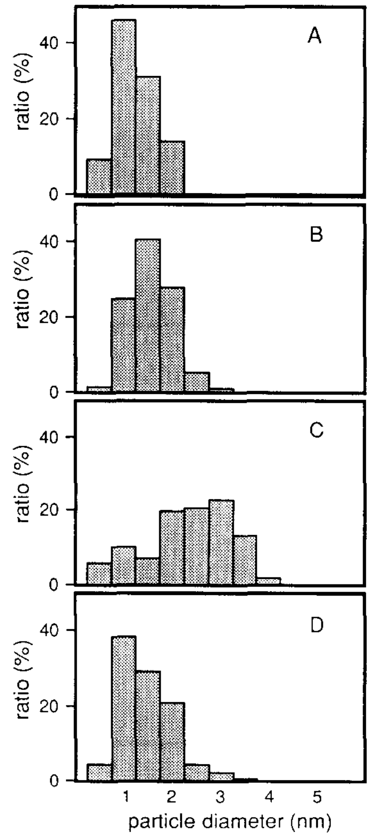

FIG. 1. Size distribution of platinum particles for a catalyst prepared by (a) chemical exchange, (b) refilling reaction at 293 K, (c) refilling at 303 K, and (d) incipient wetness.

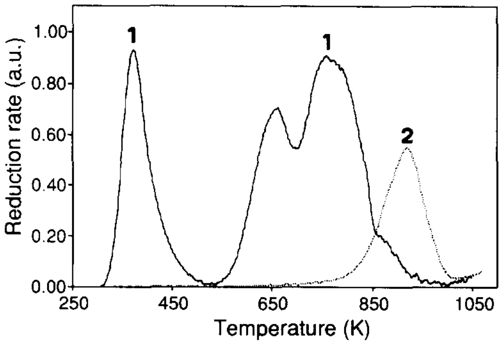

FIG. 2. TPR profiles of (1) 0.46 wt% Pt and (2) 0.0 wt% Pt catalysts for the same support weight.

TPR and TPD/H_2

The calcination performed on reduced catalysts should leave the platinum at a maximum oxidation state of 4. The theoretical stoichiometry H_2/Pt for the reduction from Pt(IV) to Pt(0) is 2. For the TPD/H_2, the generally accepted stoichiometry H/Pt_s (where Pt_s refers to surface platinum atom) is 1 (*45*).

Figure 2 shows reduction profiles of supported platinum (sample 8) and the carrier. The volume of hydrogen consumed by the support around 920 K is not negligible and must be taken into account in further considerations. The peak from the support could be attributed to the reduction of impurities. This peak does not appear in the profile of supported platinum, so we can suppose that platinum catalyzes this reduction and displaces the peak to lower temperature. In this manner, the third peak around 760 K (curve 1, Fig. 2) could correspond to the reduction of impurities. Table 2 gives experimental hydrogen consumption volumes and H_2/Pt stoichiometries for this process. The total amount of consumed hydrogen for which the support contribution was subtracted gives a H_2/Pt ratio (2.25, 1.59) close to theoretical values. The slight variation (2.25 in-

TABLE 2

Reduction Properties of Catalysts

Sample	Disp (%)	V_{H_2} ($cm^3\ g^{-1}_{cat}$)	T_R (K)	H_2/Pt
Support	—	0.280	918	—
		0.111	383	0.80
3	90	0.186	665	1.35
		0.294	822	2.13
				2.25[a]
		0.313	373	0.54
8	45	0.291	663	0.50
		0.592	763	1.03
				1.59[a]

Note. T_R, reduction temperature; H_2/Pt, hydrogen molecules per total platinum atom.

[a] Calculated with V_{H_2} (total) − V_{H_2} (impurities) (V_{H_2} (impurities) = 0.280 $cm^3\ g^{-1}$).

stead of 2.00) can be explained by the fact that the reduction of impurities is not necessarily independent of the platinum content. Furthermore, the difference in H_2/Pt ratio (2.25 and 1.59) between these two samples leads one to suppose that calcination step effected before TPR does not lead to a complete oxidation of bulk platinum in larger crystallites (sample 8).

Figure 3 shows that the profiles of hydrogen desorption are dependent on particle size. In highly dispersed samples, the profiles present two overlapping peaks: one is at a low temperature (H_{LT}) and one at a higher temperature (H_{HT}), separated by 40–50 kJ mol^{-1}, as presented in Table 3. When dispersion decreases (in other terms when particle diameter increases), the intensity of the H_{HT} peak decreases and finally disappears. For a medium dispersed catalyst (D = 71%), the H_{HT} is shifted to lower temperatures leading to a single desorption peak centered at 650 K. Globally, the small particles are able to retain on average more hydrogen than large particles with an increasing temperature. The most important point is that the total hydrogen is desorbed for temperatures between 400 and 850 K, i.e., in the same range in which dehydrogenation and aromatization reactions are usually performed. From this result we infer that the amount of chemisorbed hydrogen can vary with pretreatment conditions and affect the reactivity of platinum crystallites in methylcyclohexane dehydrogenation.

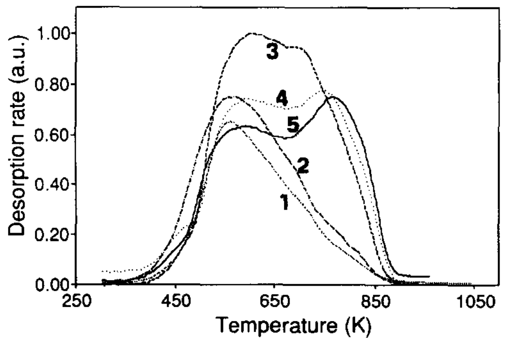

FIG. 3. Particle size effect on TPD/H_2 profiles for the same platinum amount: (1) D = 45%, (2) D = 53%, (3) D = 71%, (4) D = 77%, and (5) D = 90%.

Test Reactions

Figure 4 shows the variation of the DH rate or the TOF following two activation procedures for different dispersions of platinum. The pretreatment "A" is a single reduction at 723 K. The second, "B", refers to a reduction followed by a desorption in an argon stream also performed at 723 K. Following the "B" activation procedure, the catalytic test is performed at 573 K in flowing hydrogen ("B1") or argon ("B2"). It should be mentioned that the "B" procedure leads to higher conversion (≈ 35%), so the observed effect on TOF should only be more pronounced if tests are carried out in low conversion conditions.

For the pretreatment A, one can see that the TOF increases by a factor of around 6 when dispersion (or accessibility) is varied from 0.90 to 0.32. This observed negative structure effect is in agreement with the study of Desai and Richardson (*17*) on cyclohexane dehydrogenation over Ni/SiO_2.

The important point is that different pretreatments (A or B) lead to a much more noticeable change in TOF than the structure effect by itself. With the procedure B, a

TABLE 3

Desorption Properties of Catalysts

Sample	Disp. (%)	V_{H_2} ($cm^3\ g^{-1}_{cat}$)	T_D (K)	H/Pt$_s$	E_D (kJ mol^{-1})
3	90	0.015	297[a]	0.24	—
		0.037	580 ; 752	0.60	153 ; 208
6	77	0.027	299[a]	0.43	—
		0.044	588 ; 733	0.70	155 ; 195
7	71	0.051	299[a]	0.57	—
		0.076	652	0.85	172
4B	53	0.049	300[a]	0.64	—
		0.058	555	0.76	146
8	45	0.064	298[a]	0.49	—
		0.090	536	0.69	141

Note. T_D, desorption temperature; H/Pt$_s$, hydrogen atom per surface platinum atom; E_D, desorption energy.
[a] hydrogen chemisorption following the reduction (on cooling from 723 to 298 K).

large change in the catalytic behavior with respect to procedure A is observed. The more apparent change occurs for small particles; the DH rate increases by an order of magnitude in respect to the rate measured in procedure A. Pretreatment B leaves the particles in a state such that a positive structure effect is observed rather than a negative one. The increase in DH rate after pretreatment B is moderate for low-dispersed catalysts; both curves (A and B1) might converge to the same TOF at around $D = 25\%$ ($\phi \approx 4.0$ nm). Several tests were also repeated in an argon stream (Ar/MCH = 5) with the aim of verifying the hydrogen effect on TOF at the reaction temperature (573 K). These last results are expressed by the curve B2. Partial pressure of hydrogen ($P = 0.83$ atm) maintained in the reactor in experiment B1 decreases the DH rate as already described by the kinetic expression in previous experiments (*15*, *23*).

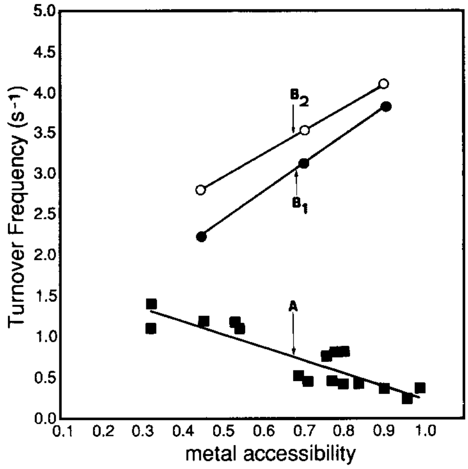

FIG. 4. Influence of activation processes of catalysts on methylcyclohexane dehydrogenation: (A) single reduction; (B1) reduction + desorption, test reaction in H_2; and (B2) reduction + desorption, test reaction in Ar.

No sulphur was detected in reactant or products and no large differences were observed by EM in the particle diameter before and after the catalytic test (see Fig. 5). The deactivation of the catalyst is principally caused by carbon deposition on metal active sites.

DISCUSSION

Temperature fixed at 293 K leads to a homogeneous refilling in the pore system. Otherwise, the use of low surface area support avoids deposition of metal on support instead of the platinum particle already fixed. The difference observed in the mean diameters (Table 1) is more pronounced for incipient wetness prepared samples. This result is in agreement with the fact that this last technique usually gives a large distribution of particle size (*1*). However, the change in particle size caused by refilling reactions is abnormally high when considering the low metal quantities which are added. Hence accurate agreement between the H_2–O_2 and EM value can only be explained by a decrease of the number of particles in the second-generation catalyst.

The hydrogen pretreatment of the platinum catalysts changes the TOF drastically. After a single reduction at 723 K, the variation of DH rate with particle size emphasizes a negative structure effect. The DH rate increases by a factor of around 6.0 when the particle size is varied from 1.0 to 3.0 nm. It was already shown that the coordination of surface atoms for a cubo-octahedral model had drastic changes between 0.0 and 3.0 nm (*17, 30*). Our findings are not in agreement with single-crystal studies (*5–7*) which claim low activity for closed-packed surfaces in respect to others containing steps and kinks. The negative structure effect observed (*17*) for cyclohexane DH over Ni/SiO_2 catalyst is not so evident. The relative increase of a factor of 2.0 does not seem significant for the attribution of structure sensitivity; an order of magnitude is more relevant. The more significant increase of 6.0 observed in our results is attributed to an "inductive" effect of hydrogen. The presence of H_{HT} on platinum crystallites at 573 K can suppress, as we see later, the accessibility to platinum atoms by the MCH molecule.

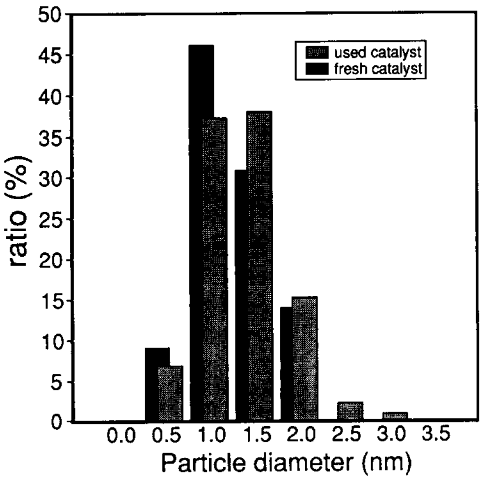

FIG. 5. Effect of catalytic test on the particle size distribution of catalyst 5.

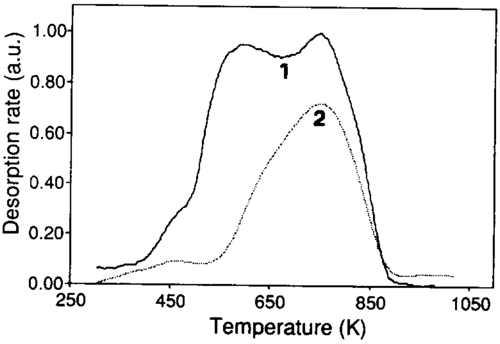

FIG. 6. Evidence of the high temperature hydrogen chemisorbed on platinum particles of sample 3: (1) reduced at 723 K and quenched in H_2 and (2) reduced at 723 K and quenched in Ar.

As shown in Fig. 3, the H_{HT} peak decreased and is displaced to lower temperature with decreasing particle size. The low H/Pt_s ratios (Table 3) obtained from TPD suggest that the high-temperature peak cannot originate from a spillover species (*22*). This H_{HT} species could be attributed to preferential adsorption sites (*17*) on small particles or related to intrinsic properties (*46, 47*) of small platinum crystallites. This H_{HT} can be isolated by quenching the sample (from 723 to 298 K) after the change of vector gas (hydrogen by argon). The TPD diagram of Fig. 6 shows the behavior of the same catalyst (0.11 wt% *D* = 90%) cooled in a different stream. The sample cooled in argon gives a single desorption peak centered at the same temperature as H_{HT} observed for the sample cooled in the H_2 stream. This means that hydrogen can be chemisorbed on small platinum crystallites at 723 K and be trapped on the surface on cooling. This trapped hydrogen is so tightly bound onto small crystallites that the reaction temperature conditions (573 K) were not sufficient to desorb all chemisorbed atoms.

The difference between the amount of hydrogen adsorbed after the reduction (on cooling from 723 to 298 K) and the total amount of hydrogen desorbed during the TPD corresponds to the quantity of hydrogen fixed on the platinum surface at 723 K, i.e., the H_{HT} species. The variation of the amount of H_{HT} as a function of the platinum accessibility is presented in Fig. 7. The variation of H_{HT} followed the inverse trend of TOF (in the A procedure) with dispersion; the amount of H_{HT} decreases as the particle size increases. This could possibly mean that the low activity of the well-dispersed catalysts is caused by the strongly bonded hydrogen which induces the poisoning of platinum surface atoms. It should be noted that this H_{HT} species is reactive toward O_2 as observed in H_2–O_2 titration. Perhaps this can be explained by the exothermic component of the H_2–O_2 reaction or by the higher reactivity of oxygen molecules on platinum particles.

Figure 8 compares the TPD profiles of the well-dispersed catalyst (catalyst 3, D = 90%) following the same activation treatments as that for "A" and "B" procedures. When the desorption for 2 hr in the "B" procedure is performed, even if the sample is re-exposed to hydrogen at 573 K (as in the test reaction), the TPD profile shows one peak at low temperature and the peak at high temperature has disappeared. Moreover, no particle size changes were observed by electron microscopy for this catalyst after both treatments (A and B).

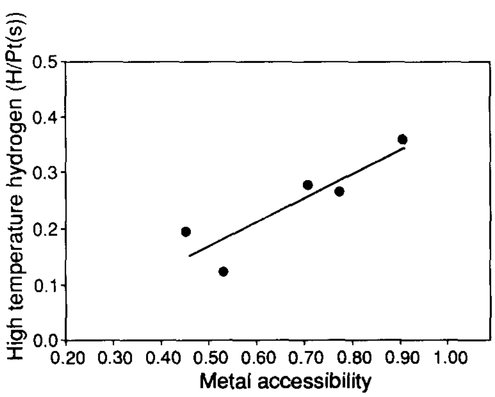

FIG. 7. Variation of the amount of high-temperature hydrogen with the metallic dispersion.

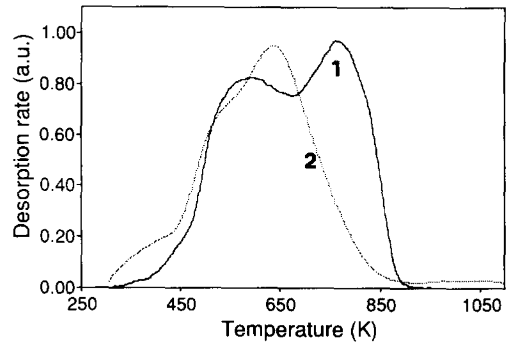

FIG. 8. Influence of pretreatments on the TPD profile of catalyst 3: (1) reduction at 723 K and (2) reduction + desorption at 723 K and re-exposure to hydrogen at 573 K.

When the H_{HT} is removed from the surface by a heat treatment in argon atmosphere, this leads to an important increase in the DH rate (see Fig. 4). The DH rate increases by a factor of around 10 for small ($\approx$ 1.0 nm) particles and only by 2 for larger ($\approx$ 3.0 nm) ones. If only pretreatment B is considered, an increase of around 2 in the DH rate is observed in either hydrogen or argon gas flow in the range of dispersion studied. This last increase does not seem meaningful for a structural effect, the type of pretreatment being much more important. The large increase observed after the desorption suggests that hydrogen chemisorbed during the reduction at 723 K is a poison for the reaction and the amount of this H_{HT} species decreases as a function of the particle size.

In summary, the methylcyclohexane dehydrogenation reaction has been found to be sensitive to the procedure in the activation process of Pt/α-Al_2O_3 catalyst. Adsorbed hydrogen in high-temperature conditions caused an important decrease of the DH rate. This H_{HT} trapped on the platinum surface appears to be unreactive and causes a strong decrease in the ability of platinum to activate the MCH molecule. It was also demonstrated that TPD/H_2 technique is a very useful tool in the understanding of particular properties of small particles.

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