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The Reconstruction of Supported Platinum Particles Monitored by Methylcyclohexane Dehydrogenation and H_2 TPD

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Alteration of the dehydrogenation activity of α-alumina-supported platinum particles induced by a high-temperature (723 K) treatment in argon atmosphere has been investigated. The methylcyclohexane dehydrogenation rate over reduced platinum particles is highly dependent on the argon treatment applied at 723 K after hydrogen treatment at the same temperature. With an increasing exposure time to the argon stream, the reaction rate increases sharply to a maximum and gradually diminishes afterwards to a stable value for a prolonged exposure time. This change is the result of two modifying actions induced by inert gas: (1) the desorption of tightly bound hydrogen species, responsible for the low initial activity, and (2) the reconstruction of the platinum crystallite surface toward a more stable active surface. The presence of "high-temperature hydrogen" is systematically observed on small particles after hydrogen treatment at 723 K and seems to be related to the specific electronic properties of small particles and not to their surface structure. The reconstruction of the surface of the particles is by contrast very important for obtaining stable catalytic activity. Highly dispersed (80–90%), restructured catalysts were found to be similar in stability to mediumly dispersed (45%) catalysts.

INTRODUCTION

The influence of the metallic structure either for single-crystal or supported catalysts on the catalytic activity and selectivity of different hydrocarbon transformations has been the subject of many investigations (1, 2). Studies concerning the structural effect of supported platinum generally consider the particle size rather than the surface structure to explain the catalytic behaviour of the metal. Geometric and/or electronic changes are claimed to be due to changes in the particle size. However, these two possibilities are not necessarily independent; it is possible to observe a modification in the surface topology and simultaneously a change in the electronic structure with increasing particle size. Another factor which might influence both electronic and geometric properties is the metal-support interaction and more specifically the type of bonding between the particle and the surface of the support (3). Thus, the extrapolation of the catalytic behaviour with single-crystals to that obtained with supported catalysts could be quite difficult and even futile. Nevertheless, the single-crystal studies lead to a better understanding of the surface structure dependence in catalytic transformation.

The difference between supported metal and single-crystal catalysts can be emphasized by the example of cyclohexane dehydrogenation. This reaction is usually considered structure-insensitive with supported metal catalysts (4–7) whereas a dehydrogenation rate difference due to structural sensitivity is emerging from studies during the last decade with single-crystals (8, 9). Herz *et al.* (8) have shown that at atmospheric pressure the cyclohexane dehydrogenation rate increases with surface roughness. Furthermore, using a site blocking additive (bismuth) on Pt{111} single-crystal, Rodriguez and Campbell (9) have shown, with respect to the multiplet theory (10, 11), that an ensemble containing at least eight platinum atoms is required to dehydrogenate cyclohexane. Therefore, cyclohexane dehydrogenation tends to occur preferably on a rough surface composed of isolated terraces of at least eight platinum atoms. If this trend applied to supported catalyst, small particles could present different activities due to differences in crystallite morphology.

The topology or the surface structure of the supported metal particles was shown to be strongly dependent on the cluster size. In the case of an octahedral or a cubo-octahedral model, it was demonstrated that the coordination number of surface atoms changes significantly with a decrease in particle diameter below 3.0 nm (12). The small particles are made up of low-coordinated surface sites (kinks, steps) and their proportions decrease with increasing particle size. The more open the surface, the larger the freedom of the surface atoms which may move until the surface is reconstructed. For example, the reconstruction of the close-packed Pt{111} and Pt{100} surfaces

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is strongly disadvantaged by comparison with an open surface such as the Pt{110}. The low-coordinate surface of the small particles could be compared with an open surface single-crystal which is easy to rebuild. Furthermore, in respect to the thermodynamic driving force, the small particles are more inclined to a structure modification than the large particles because they are simply more flexible than the latter (13).

The reconstruction of single-crystal surfaces is a well known phenomenom in heterogeneous catalysis. The surface structure modification is usually induced by adsorbed species such as hydrogen, oxygen, sulphur (14–17), or carbon monoxide (18). More recently, it has been shown that the Pt{110} surface may be reconstructed by sputtering with argon ions (19) under high temperature conditions.

In a previous paper (20), we have shown that the reactivity of various dispersed supported platinum catalysts is related to the activation process applied at 723 K before methylcyclohexane dehydrogenation reaction at 573 K. Flores *et al.* have shown that benzene hydrogenation strongly depends on the pretreatment of Pt/Al_2O_3 (21). The present paper addresses the effect of the pretreatment using alternatively hydrogen and argon treatments on the initial reactivity and on the deactivation of supported platinum particles toward methylcyclohexane dehydrogenation. The surface properties of the particles were concurrently studied by H_2 temperature programmed desorption (TPD).

EXPERIMENTAL

Catalyst Preparation

After air calcination at 773 K, the α-alumina support ($15\ m^2\ g^{-1}$) was added to a solution containing the required amount of precursor bis-acetylacetonate platinum II ($Pt(acac)_2$). The chemical exchange (22) was performed in excess solution at a ratio equal to five times the total pore volume ($V_{TP} = 0.60\ cm^3\ g^{-1}$) for a minimum period of 48 h. The catalyst was then dried at 393 K for 16 hours, calcined in air at 623 K and reduced under a hydrogen stream at 723 K for 2 h (gas flow = 2 liter $h^{-1}\ g_{cat}^{-1}$). Two different catalysts have been prepared which are referenced with respect to metal dispersions: Pt90 (0.11 wt% Pt, D = 90%) and Pt71 (0.20 wt% Pt, D = 71%). The particle sizes, evaluated by either H_2–O_2 titration (23) (performed at 295 K) or electronic microscopy (JEOL 120cx), are in agreement for both techniques. The average particle sizes are 1.1 and 1.4 nm for Pt90 and Pt71, respectively.

The catalyst Pt45 was prepared by incipient wetness with the same platinum precursor in order to obtain a catalyst with a lower dispersion (0.46 wt% Pt, D = 45%). The heat treatments applied to this catalyst were the same as those used on the catalyst Pt90. The particle size determined by electronic microscopy (1.7 nm) is not in agreement with that calculated from H_2/O_2 titration (2.3 nm). This difference is explained by the broadness of the size distribution of Pt45 (size from 0.5 to 3.5 nm) by comparison with the distribution of the catalyst Pt90 (size from 0.5 to 1.5 nm) (24).

Temperature-Programmed Desorption

Sample pretreatments and TPD experiments were performed using a geomecanique X-SORB apparatus. Prior to the TPD experiments, the samples were reduced in-situ using 5% (±0.1%) hydrogen in argon mixture with a heating rate of 5 K min^{-1} from ambient temperature to 723 K. The temperature was held at 723 K for 2 h in order to assure the reduction of all oxidized platinum without sintering (20). Following this last reduction, the sample was cooled to ambient temperature under flowing 5% H_2/Ar mixture in order to adsorb hydrogen on platinum until the hydrogen consumption stopped. This quenching in 5.0% H_2/Ar mixture between 723 and 303 K leads to the adsorption of hydrogen which has been previously described (20). Then, the catalyst was purged under a pure argon (Air Liquide, 99.995%) flow at 303 K for 1.5 h. The TPD/H_2 experiments were carried out on this sample using pure argon and a heating rate of 20 K min^{-1} from 303 to 1200 K. The temperature was held at 1200 K until the hydrogen desorption, followed by a catharometric detector, were completed.

Catalytic Reactions

The methylcyclohexane (MCH) dehydrogenation test reaction was performed at 573 K under atmospheric pressure in a fixed bed reactor. The catalyst (w_{cat} = 1.1 g), diluted with 10 cm^3 of quartz of the same grain size (0.3–0.5 mm), was placed in the middle of a quartz reactor (28 mm diameter), then reduced *in situ* at 723 K under a pure hydrogen (Air Liquide, 99.999%) flow (5000 $cm^3\ min^{-1}$) for 2 h. This highly pure hydrogen was treated before the gas line intake of the catalytic unit through a Deoxo unit for O_2 and H_2O removal. Argon or hydrogen treatments (gas flow = 5000 $cm^3\ min^{-1}$) at different exposure times were applied to the reduced samples prior to catalytic testing. All the pretreatments were applied *in situ* and were composed of one or more consecutive treatments at 723 K. The sequence of the treatments is expressed according to the notation X^Y (where X represents the atmosphere and Y the duration of the treatment in hours).

The flow rates of reactants were controlled by a syringe micropump for methylcyclohexane (MCH) and by a rotameter for hydrogen or argon. The H_2/MCH mole ratio was fixed at 5. The homogeneity of the reactor temperature was assured by the use of a furnace with three heating zones and the temperature difference from the top to the bottom of the catalyst bed did not exceed 5 K. The temperatures were measured by three thermocouples placed in a thermocouple well located along the catalytic bed.

The reaction products (selectivity to toluene = 99.9%) were separated by gas chromatography at 373 K on a 50-m WCOT Fused Silica (CP-WAX-52CB) column and analyzed by a flame ionization detector (FID). The reactant flow rate (18–20 cm^3 min^{-1}) was selected to avoid diffusion limitations (25) and to limit the conversion to 30%.

The dehydrogenation rate v_{DH} is expressed in moles of methylcyclohexane transformed per surface platinum atom per second. The catalysts deactivate with time; thus the platinum dispersion is considered as the initial dispersion obtained from H_2/O_2 titration and the turnover frequency, TOF, is extrapolated to zero time on the resulting deactivation curve. The first dehydrogenation rate was recorded starting from 12 min after initial injection of the reactants up to 1.0 h after the first analysis. The decrease in activity in this short period did not exceed 15% of the initial value and allowed us to evaluate the TOF accurately. The reproducibility of the reaction rates has been evaluated by repeated measurements with the same catalyst. These experiments gave a reproducible reaction rates within 15% error.

RESULTS AND DISCUSSION

As shown previously (20), the removal of a hydrogen H_{HT} species from the surface of the platinum particles by a high temperature treatment under argon atmosphere results in an important increase in the dehydrogenation (DH) rate. This H_{HT} phase was shown to be fixed on small platinum particles during the hydrogen treatment at 723 K and its proportion decreases with increasing particle size (20). This result may be interpreted in terms of the auto-inhibition concept already mentioned by Menon and Froment (26) for an alumina-supported Pt catalyst.

Behaviour of Reduced Catalysts

Figure 1 presents the deactivation profiles of Pt90, Pt71 and Pt45 catalysts after a single hydrogen treatment (Fig. 1a) and followed by an additional heat treatment which consists of a flushing with an argon flow (Fig. 1b) at 723 K. After a single hydrogen treatment ($H_2^{2.0}$) the activity of the Pt90 catalyst is quite low and the deactivation profile is characterized by a flat curve. This low activity is consistent with the presence of the H_{HT} species and the flatness of the deactivation profile is simply explained by the fact that platinum particles "work" very little in the formation of toluene. In connection with the presence of a low quantity of H_{HT} phase on the reduced Pt45 (20), the observed rate on the large-particle catalyst is higher at the beginning (see Fig. 1a, curve Pt45), and diminishes with reaction time giving after 4 h of test nearly the same final activity as the reduced Pt90 catalyst. The catalyst Pt71 shows a compromise between the behaviour of the two Pt90 and Pt45 catalysts.

Behaviour of Desorbed Catalysts

After the high-temperature treatment under argon flow (see Fig. 1b), a large increase in the TOF is observed (from 0.4 to 4.0 s^{-1}) for the Pt90 catalyst. The Pt45 catalyst shows a less contrasting behaviour than for small particles: the gain (from 1.3 to 2.3 s^{-1}) in TOF is moderate with respect to the increase observed on small platinum particles. The behaviour of the Pt71 catalyst following the flushing treatment is again intermediate between those of the Pt90 and Pt45 catalysts. As previously shown (20), these measured rates after an argon treatment are quite reproducible; small variations of TOF were observed when argon was used as a vector gas rather than with hydrogen (mainly caused by the hydrogen pressure maintained in the catalytic bed).

The shape of the deactivation profile of the Pt90 catalyst drastically changes after the argon flushing and three distinct zones could be distinguished (see curve Pt90, Fig. 1b) on this profile:

(1) the dehydrogenation rate is important and it gradually diminishes during the first 2 h of work;

(2) the v_{DH} decreases sharply over a very short period of time;

(3) the low v_{DH} (similar to the $H_2^{2.0}$ rate) diminishes slowly until there is complete deactivation of the catalyst.

Except for a sharp difference with single reduced catalyst on the initial activity, the deactivation of the $H_2^{2.0}Ar^{2.0}$ pretreated Pt90 catalyst leads to a final catalytic activity which is about the same as previously noted for the reduced Pt90 and Pt45 catalysts.

The important point is a clearly higher activity of the desorbed Pt45 than the Pt90 catalyst at the end of the catalytic test. The activity of the desorbed Pt45 catalyst did not reach the observed value when it was reduced and, as we have shown (20), the small amount of H_{HT} fixed on those particles does not interfere drastically with their catalytic properties. Thus these results (high initial and final activities of the desorbed Pt45 sample) suggest an additional effect induced by the argon treatment at 723 K. In order to define on the one hand the role of the H_{HT} phase and on the other hand the

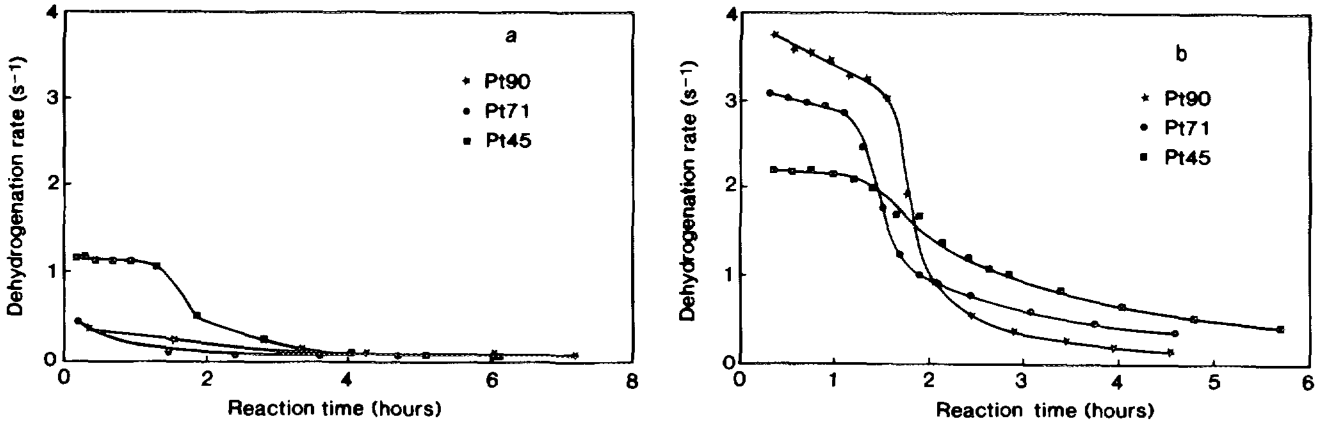

FIG. 1. Deactivation of the various dispersed Pt/Al$_2$O$_3$ catalysts following (a) single reduction ($H_2^{2.0}$) and (b) reduction + flushing in argon ($H_2^{2.0}Ar^{2.0}$) at 723 K. Reaction conditions: T = 573 K, P = 1 atm, H_2/MCH = 5).

additional effect of the argon treatment, we have studied the reversibility of the H_{HT} species and the duration of the argon treatment on the most sensitive Pt90 catalyst.

Reversibility of the High-Temperature Species

Figure 2 presents the effect of this further hydrogen treatment on the hydrogen desorption profile of the Pt90 catalyst. As already described (20), the $H_2^{2.0}$ profile shows the H_{LT} and H_{HT} phases, and this latter H_{HT} phase disappears after the argon treatment ($H_2^{2.0}Ar^{2.0}$). The second hydrogen treatment ($H_2^{2.0}Ar^{2.0}H_2^{2.0}$) restores the H_{HT} species but the shape of the profile is quite different from the $H_2^{2.0}$ profile: the intensity of the H_{LT} peak is lower and the intensity of the H_{HT} peak is higher. The H/Pt$_s$ ratios obtained from these three experiments 0.6, 0.5, and 0.7, respectively. The agreement between these H/Pt$_s$ ratios suggests that the exposed platinum surface remains almost the same for all pretreatments applied. This is confirmed by the electron microscopy observations; the particle size increases slightly from 1.1 nm ($H_2^{2.0}$) to 1.2 nm ($H_2^{2.0}Ar^{2.0}H_2^{2.0}$).

If the H_{HT} species were the only species responsible for the low activity of undesorbed catalysts, the TOF would decrease from 4.0 (after argon treatment) to 0.4 s^{-1} (the activity of the undesorbed catalyst) after such a further hydrogen treatment. As reported in Table 1, the TOF actually decreases with this latter hydrogen treatment but the final value of the TOF is 1.8 s^{-1}. The presence of the H_{HT} species is surely a cause of the lower activity of the undesorbed catalysts ($H_2^{2.0}$ and $H_2^{2.0}Ar^{2.0}H_2^{2.0}$) compared to the desorbed catalyst ($H_2^{2.0}Ar^{2.0}$). However, it is not sufficient to explain the difference in their resulting TOF: the catalyst with the higher quantity of H_{HT} species ($H_2^{2.0}Ar^{2.0}H_2^{2.0}$) leads to a higher TOF (1.8 s^{-1})

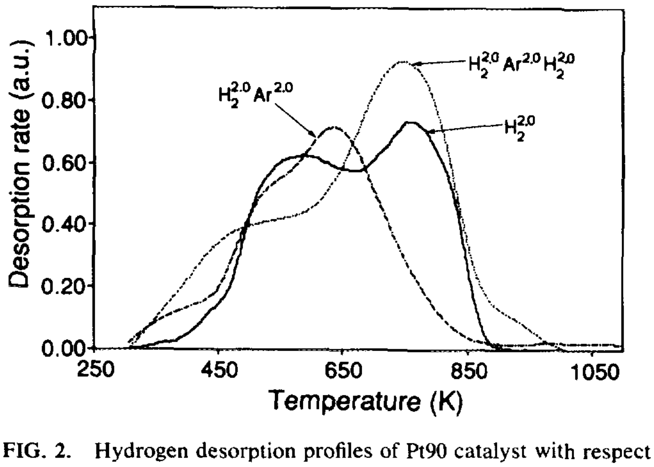

FIG. 2. Hydrogen desorption profiles of Pt90 catalyst with respect to the pretreatment applied (the sample was reexposed to hydrogen at 573 K before the TPD experiment in the $H_2^{2.0}Ar^{2.0}$ treatment).

TABLE 1

Initial Activity of the Investigated Pt/Al$_2$O$_3$ Catalysts for Methylcyclohexane Dehydrogenation Following Various Pretreatments

	TOF (s^{-1})		
Pretreatment[a]	Pt90	Pt71	Pt45
$H_2^{2.0}$	0.4	0.6	1.3
$H_2^{2.0}Ar^{0.5}$	2.8	—	—
$H_2^{2.0}Ar^{2.0}$	4.0	3.3	2.3
$H_2^{2.0}Ar^{4.0}$	2.3	—	—
$H_2^{2.0}Ar^{6.0}$	2.6	—	—
$H_2^{2.0}Ar^{2.0}H_2^{2.0}$	1.8	—	—
$H_2^{2.0}Ar^{2.0}H_2^{2.0}Ar^{0.5}$	3.5	—	—
$H_2^{2.0}Ar^{2.0}H_2^{2.0}Ar^{2.0}$	2.3	—	—

[a] Atmosphere$^{\text{duration in hours}}$.

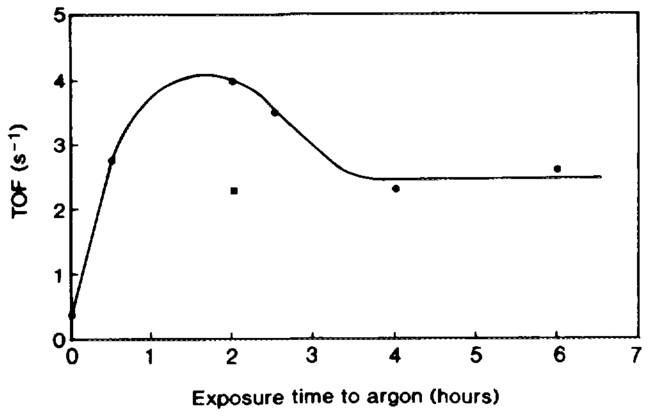

FIG. 3. Variation of initial activity (TOF) of the catalysts as a function of the flushing time under argon stream (○, Pt90; ■, Pt45).

than the reduced ($H_2^{2.0}$) catalyst (0.4 s^{-1}). The argon treatment does not only desorb the H_{HT} phase, the platinum particles appear more deeply affected by this heat treatment.

Effect of Argon Treatment on the TOF

Figure 3 shows the behaviour of Pt90 catalyst after various exposure times to an argon stream preceding the catalytic tests. The TOF is very sensitive to this exposure time: it increases sharply from 0.4 s^{-1} up to a maximum around 4.0 s^{-1} between 0 and 1.5 h then diminishes gradually to a stable value around 2.4–2.6 s^{-1} for a prolonged exposure time (>4.0 h). One can see that the stable rate for Pt90 is nearly the same as for Pt45 catalyst after $H_2^{2.0}Ar^{2.0}$ treatment. The argon treatment results in an evolution of the platinum particles towards a stable state.

The TOFs after alternative further H_2 and Ar treatments are reported in Table 1. This indicates the respective role of argon towards the desorption of H_{HT} species and towards the modification of the platinum particles. A short desorption of 0.5 h following the $H_2^{2.0}Ar^{2.0}H_2^{2.0}$ treatment leads to a TOF increase from 1.8 to 3.5 s^{-1} which shows the cleaning of the fixed H_{HT} species from the platinum surface. This latter value of 3.5 s^{-1} is nearly the same as the measured one on the desorbed catalyst ($H_2^{2.0}Ar^{2.0}$ pretreatment). As already observed, longer argon treatments allow the TOF to decrease until a stable value which is identical to the TOF measured for the desorbed ($H_2^{2.0}Ar^{2.0}$) Pt45 catalyst.

All these experimental features in initial activity concur to suggest a reconstruction of the platinum particles; an argon treatment modifies the surface structure of small particles originally made up of low-coordinate atoms. In respect to Fig. 3, the evolution of the smaller particles of Pt90 (1.1 nm) slowly reaches a stable form at prolonged exposure times. The behaviour of Pt71 and Pt45 catalysts also suggests a reconstruction for particles size of 1.6 and 2.0 nm, respectively, but the stable state is more quickly reached than for the small particles (1.0 nm) of Pt90.

The effect of the hydrogen treatment at 723 K is to induce the chemisorption of the H_{HT} species which poisons the platinum particles. This high-temperature hydrogen was already mentioned by several authors and was attributed either to a strongly bound species (26, 27), to a subsurface hydrogen phase (28) or to a spillover activated species (29, 30). In our case, we did not take these two last hypotheses into consideration due to the fact that, contrary to our results, they give a higher H/Pt_s ratio than the generally accepted (H/Pt_s = 1) value (26). The attribution of the H_{HT} species to a specific site on a small particle is very delicate when assuming the reconstruction of the surface of the particle because this H_{HT} phase appears before and after the argon treatment, or, in other words, on the original and on the reconstructed particles. The H_{HT} is probably related to the electronic properties of small particles and/or to those platinum atoms present at the periphery of the particle in intimate contact with the support (31).

From a thermodynamic point of view, small particles are unstable in comparison with large particles; the surface of small particles is composed of low-coordinate platinum atoms which are less stable than the surface atoms of a large particle. The surface structure of the large particle is similar to a close-packed surface such as the {111} or the {100} face (13). The change in TOF observed with the exposure time to an argon flow could be compatible with a "topological surface composition" change from an open surface to a more stable structure like the surface of large particles without any sintering. In this manner, the stable form of the small particle is a "large-like" structure.

Effect of Argon Treatment on the Deactivation Profile

The poisoning effect of the H_{HT} phase is clearly demonstrated and the "proposed reconstruction" under argon not only changes the TOF but also changes the deactivation profile. The comparison of the desorbed but not reconstructed Pt90 with the already reconstructed Pt45 of Fig. 1b emphasizes a drastic difference in terms of deactivation: the initial rate of the Pt90 catalyst is far above the Pt45 but after a couple of hours of operation, the reverse is true.

Figure 4 shows the deactivation profiles of Pt90 catalyst following different H_2-Ar cycle treatments. After the $H_2^{2.0}Ar^{2.0}$ treatment, the TOF increases sharply with respect to the $H_2^{2.0}$ treatment, in agreement with the elimination of the H_{HT} species, and the low activity at 4 h could be compatible with a slight reconstruction of the surface of the particles. An additional H_2 treatment (curve $H_2^{2.0}Ar^{2.0}H_2^{2.0}$) on the catalyst brings the H_{HT} phase on the

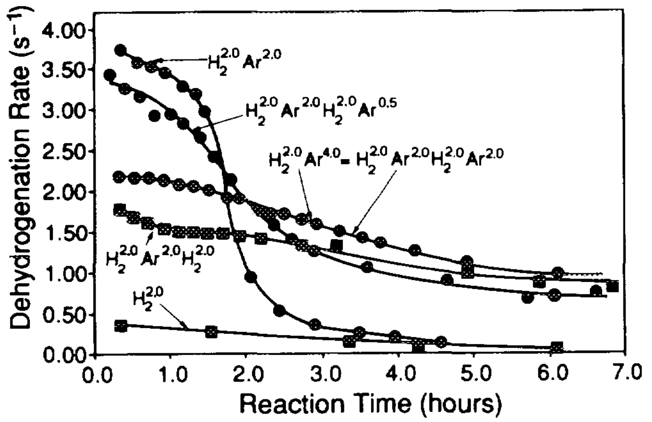

FIG. 4. Effect of the pretreatment on the deactivation profiles of the Pt90 catalyst (atmosphere$^{\text{duration in hours}}$). Reaction conditions: T = 573 K, P = 1 atm, H_2/MCH = 5.

particles to decrease the initial rate and the final activity increases with respect to the $H_2^{2.0}Ar^{2.0}$ treatment. This last increase suggests that the reconstruction of the platinum surface is initiated even under a hydrogen flow. The short desorption in $H_2^{2.0}Ar^{2.0}H_2^{2.0}Ar^{0.5}$ allows one to clean the surface of the H_{HT} species and its initial activity is close but lower than the $H_2^{2.0}Ar^{2.0}$ pretreated catalyst. This result, including the fact that final activity reaches the same level as the previous pretreatment, allows one to suppose that the reconstruction is partially complete. Finally, the prolonged treatments under argon ($H_2^{2.0}Ar^{4.0}$, $H_2^{2.0}Ar^{2.0}$ $H_2^{2.0}Ar^{2.0}$) allow the stabilization of the TOF as well as the final activity, which can be easily compared with the results obtained on large and stable particles of Pt45 catalyst (see Fig. 1b). At this point, the Pt90 catalyst with 1.1-nm particles is "catalytically equivalent" to the 2.3 nm particles of Pt45. Again, we can conclude that the proposed reconstruction of small particles could be made towards a surface structure which is similar to the surface structure of larger particles, the reconstruction being achieved without real sintering.

The platinum of the small particles is probably composed of a small proportion of highly-coordinate atoms (A sites) and a large majority of low-coordinate atoms (B sites) (12). The reconstruction of the platinum surface could lead to a modification of the proportion of the two types of site and appears as a disappearance of the highly unsaturated B sites. The lower TOF obtained with the desorbed Pt45 catalyst with respect to Pt90 suggests that the coordinatively unsaturated sites are more active than the others. However, this activity improvement of highly dispersed catalysts is not permanent because the final activity is much lower than for the totally reconstructed catalyst. This last result suggests that highly active B sites are quickly and irreversibly deactivated by carbon deposition.

Assuming a deactivation mechanism by a nucleation and growth of carbonaceous deposit, these results could be compatible with the conclusions of single-crystal studies (32). For cyclohexane as reactant, it was claimed that the carbonaceous deposit mainly participates as a nonselective poison, the platinum surface sites being simply blocked. However, it was also shown that a small concentration of uncovered platinum surface sites always persists in the presence of this carbon deposit. These sites, which exist in the form of ensembles containing several contiguous surface atoms, remain available for hydrogen adsorption and rehydrogenation of a part of the carbon deposit. In our case, the argon treatment should diminish the proportion of very active B sites of the highly dispersed catalysts. In the same manner, it is possible that the increasing proportion of high-coordinate atoms (A sites) of the "reconstructed" particles could favour the presence of ensembles or multiatomic sites previously described (32) and then it could induce a better stability of the active phase.

In summary, the methylcyclohexane dehydrogenation appears to be insensitive to the dispersion but sensitive to the structure of the supported platinum particles. The presence of the H_{HT} phase appears to be sensitive not to the structure but to the size of the particles. This H_{HT} phase is more probably related to the specific properties of small particles and/or to those platinum atoms located at the particle–support interface. Although experimental efforts such as EXAFS and HREM should lead to a better understanding of the proposed processes, this study gives an alternative explanation of reactivity changes following high-temperature treatments which did not lead to a significant sintering of the platinum particles. The original unstable small particles created were probably stabilized by a reconstruction of platinum surfaces facilitated by the thermodynamic driving force.

REFERENCES

1. Bond, G. C., *Surf. Sci.* **156,** 966 (1985).
2. Che, M., and Bennett, C. O., *Adv. Catal.* **36,** 55 (1989).
3. Haller, G. L., and Resasco, M., *Adv. Catal.* **36,** 173 (1989).
4. Kraft, M., and Spindler, H., *in* "Proceedings, 4th International Congress on Catalysis, Moscow 1968", Vol. II, p. 286. Akadémiai Kiadó, Budapest, 1971.
5. Cusumano, J. A., Dembinski, G. W., and Sinfelt, J. H., *J. Catal.* **5,** 471 (1966).
6. Guenin, M., Breysse, M., and Frety, R., *J. Mol. Catal.* **25,** 119 (1984).
7. Guenin, M., Breysse, M., Frety, R., Tifouti, K., Marecot, P., and Barbier, J., *J. Catal.* **105,** 144 (1987).
8. Herz, R. K., Gillespie, W. D., Petersen, E. E., and Somorjai, G. A., *J. Catal.* **67,** 371 (1981).
9. Rodriguez, J. A., and Campbell, C. T., *J. Phys. Chem.* **93,** 826 (1989).
10. Balandin, A. A., *Adv. Catal.* **10,** 96 (1958).
11. Dalmon, J. A., Candy, J. P., and Martin, G. A., *in* "Proceedings,

6th International Congress on Catalysis, London, 1976", p. 203. Chemical Society, London, 1977.

12. van Hardeveld, R., and Hartog, F., *Adv. Catal.* **22,** 75 (1972).
13. Somorjai, G. A., *Catal. Lett.* **9,** 311 (1991).
14. Lanzillotto, A. M., and Bernasek, S. L., *J. Chem. Phys.* **84,** 3553 (1986).
15. Lindauer, G., Legaré, P., and Maire, G., *Surf. Sci.* **126,** 301 (1983).
16. Maire, G., Lindauer, G., Garin, F., Legaré, P., Cheval, M., and Vayer, M., *J. Chem. Soc. Faraday Trans.* **86,** 2719 (1990).
17. Lang, B., Legaré, P., and Maire, G., *Surf. Sci.* **47,** 89 (1975).
18. Hu, P., Morales de la Garza, L., Raval, R., and King, D. A., *Surf. Sci.* **249,** 1 (1991).
19. Lin, B. C., and Shern, C. S., *Chin. J. Phys. (Taipai)* **28,** 355 (1990); *Chem. Abstr.,* No. 238675t, **113,** 459 (1990).
20. Rochefort, A., Le Peltier, F., and Boitiaux, J. P., *J. Catal.* **138,** 482 (1992).
21. Flores, A. F., Burwell, R. L., and Butt, J. B., *J. Chem. Soc. Faraday Trans.* **88,** 1191 (1992).
22. Yermakov, Yu. I., and Kuznetsov, B. N., *J. Mol. Catal.* **9,** 13 (1980).
23. Boudart, M., Aldag, A., Benson, J. E., Dougharty, N. A., and Harkins, C. G., *J. Catal.* **6,** 92 (1966).
24. Rochefort, A., and Le Peltier, F., *Rev. Inst. Fr. Pet.* **46,** 221 (1991).
25. Andreev, A. A., Shopov, D. M., and Kiperman, S. L., *Kinet. Catal.* **7,** 941 (1966).
26. Menon, P. G., and Froment, G. F., *J. Catal.* **59,** 138 (1979).
27. Davis, S. M., and Somorjai, G. A., *Surf. Sci.* **91,** 73 (1980).
28. Nagy, F., Moger, D., Hegedus, M., Mink, Gy., and Szabo, S., *Acta. Chim. Acad. Sci. Hung.* **100,** 211 (1979).
29. Kramer, R., and Andre, M., *J. Catal.* **58,** 287 (1979).
30. Frennet, A., and Wells, P. B., *Appl. Catal.* **18,** 243 (1985).
31. Modica, F. S., Miller, J. T., Lane, G. S., Meyers, B. L., Vaarkamp, M., and Koningsberger, D. C., "Symposium on Developing the Understanding of Heterogeneous Catalyst Systems, San Francisco, 1992, p. 1009. (Private communications)
32. Davis, S. M., Zaera, F., and Somorjai, G. A., *J. Catal.* **77,** 439 (1982).