Effect of Hydrogen on the Sintering
of Pt-Black Catalyst and on its Activity
in Skeletal Hydrocarbon Reactions*

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Pt-black samples were sintered in hydrogen at 473 and 633 K.
Their surface composition and electron micrographic images are discussed
together with their catalytic activity in reactions of n-hexane and
methylcyclopentane. Pt-473 is more active in n-hexane reactions than
Pt-633; also a different hydrogen pressure sensitivity is observed.
Methylcyclopentane transformations show much less differences; thus
these two reactants exhibit different structure sensitivities. Hydro-
carbons and hydrogen compete for active sites, the availability and hyd-
rogen content of which may be lower on the - more carbonized -
Pt-633.

Introduction

Group VIII metals - in particular Pt – are typical catalysts of
hydrocarbon transformations /1/. Hydrogen is a stoichiometric partner
in hydrogenation reactions; however, the presence of hydrogen is
also necessary for dehydrogenation reactions, e.g. in naphtha refor-
ming where alkanes and cycloalkanes give aromatics. The Pt-containing
catalysts (supported alone or together with other metallic additives on

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Al_2O_3) lose rapidly their activity without hydrogen /2/. Several such nonstoichiometric effects of hydrogen in metal catalyzed reactions have been recognized; they were summarized recently /3,4/. Their common characteristic is that hydrogen actively participates in the formation of the catalytically active entity. In addition, hydrogen present during catalytic processes can considerably influence the actual catalytic properties.

The main problem in these hydrogen effects is the determination of how much hydrogen is present on and/or in the catalyst in various stages of its life, where it is situated and what is the likely form of its binding to the metal. No accurate answer can be given to these problems so far. Temperature-programmed desorption (TPD) studies detected three to five types of adsorbed hydrogen on Pt-black and Pt/SiO_2 /5-8/. It is also debated what is the temperature at which all desorbable hydrogen leaves the catalyst. The most strongly bonded type of hydrogen may be situated in subsurface layers as demonstrated for Pt /9/ and Pd-blacks /10/; on Pt this hydrogen may be exchanged with hydrogen atoms of hydrocarbon reactants /9/. Maybe the penetration of hydrogen into subsurface layers is the reason why hydrogen dramatically accelerates the reconstruction of a high-surface freshly reduced Pt-black when heated in hydrogen atmosphere between 470 and 750 K /11/. A "quasi-liquid hydrogen-platinum surface over-layer" has been proposed during sintering process /12/.

When hydrocarbons are reacted in the presence of hydrogen on Pt-catalysts, it is more correct to regard the catalyst as a "Pt-H system". Presintering in hydrogen will determine the crystallite size /11/, the surface morphology of Pt, this latter being decisive in de-termining the character of active sites as shown by single-crystal studies /13/. Presently we attempt at comparing two samples, presin-tered at 473 and 633 K. Earlier studies reveal that the former sample has smaller crystallites /11/, less surface carbon and oxygen impurity /14/. The chemical state of carbon corresponds to individual C-atoms on Pt-473 while a more polymeric carbon is present on Pt-633 /15/. The former sample contains more hydrogen /16/. Surface analysis, electron microscopy and catalytic activity in model reactions as a function of the actual hydrogen pressure ("hydrogen sensitivity") will

be reported.

Experimental

The catalysts were reduced from aqueous solution of H_2PtCl_6 by HCHO in the presence of KOH, between 273 and 278 K /17/. They were sintered according to a "standard thermal cycle" as described by Baird et al. /11/, at 473 and 633 K (Pt-433 and Pt-633, respectively).

Secondary Ion Mass Spectrometry (SIMS) was carried out in a Balzers instrument, using Ar^+ primary ions (3 keV, $1.2x10^{-5}$ A cm^{-2}); for more detail, see ref. /16/.

Specimen preparation for electron microscopy was carried out by dispersing the metal powder samples in water or methanol; after ultra-sonic treatment, they were dried on carbon coated grids in air. A JEOL 200 CX microscope operated at 200 kV, equipped with an ultra-high resolution objective pole piece was used.

Catalytic runs were carried out in a static-circulation reactor /18/. n-Hexane (nH) and methylcyclopentane (MCP) were used as feeds at a pressure of 10 Torr (1 Torr = 0.133 kPa). Feed purity was better than 99.5%. Hydrogen pressure varied between 50 and 500 Torr. Cata-lytic activities are expressed as "turnover numbers", meaning the amount of product formed, molecules per surface Pt-atom per second.

Results

In agreement with previous data /14-16/, sintering at 473 K resulted in some cleaning of the "as reduced" surfaces. Sintering at 633 K gives more surface cluster ions, presumably, owing to the poly-merization of surface carbon which is bound more firmly to the metal. This is illustrated by Fig. 1. It has to be remarked that the residual hydrogen content of the catalysts decreased in the order Pt-fresh > > Pt-473 > Pt-633 /16/.

Electron micrographs show a gradual increase of particle sizes (Figure 2) as the temperature of sintering increases. These were estimated to be 5-10 nm for Pt-fresh, 20-30 nm for Pt-473 and around 100 nm for Pt-633. This latter value is higher than that reported earlier /11,19/. The high-resolution electron micrograph of Pt-473 shows agglomeration of rounded particles with well-ordered lattice
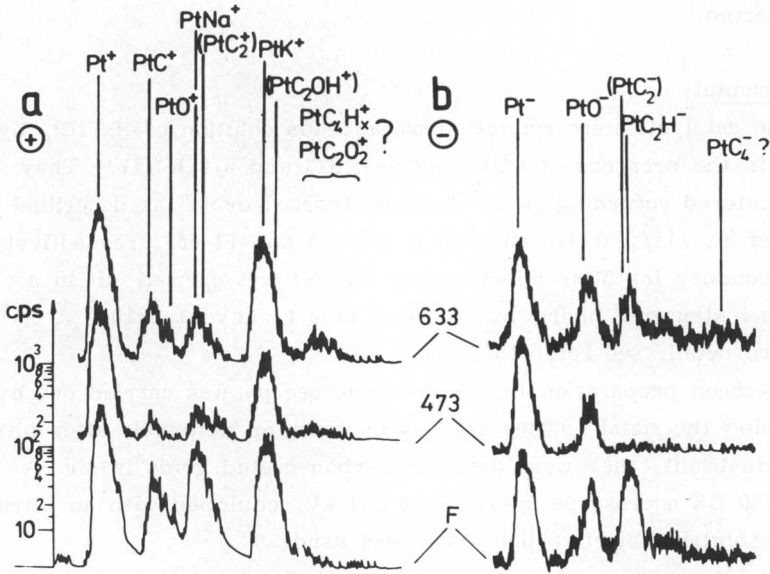
Figure 1. Secondary Ion Mass Spectra of fresh and two sintered Pt-black samples in the cluster ion range.
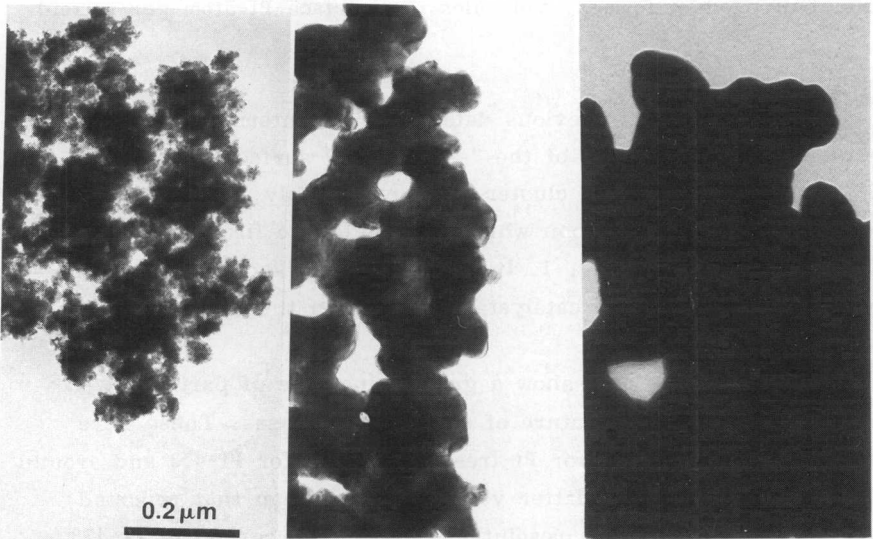

Figure 2. Electron micrographs of Pt-black samples. From left to right: Pt-fresh; Pt-473; Pt-633.
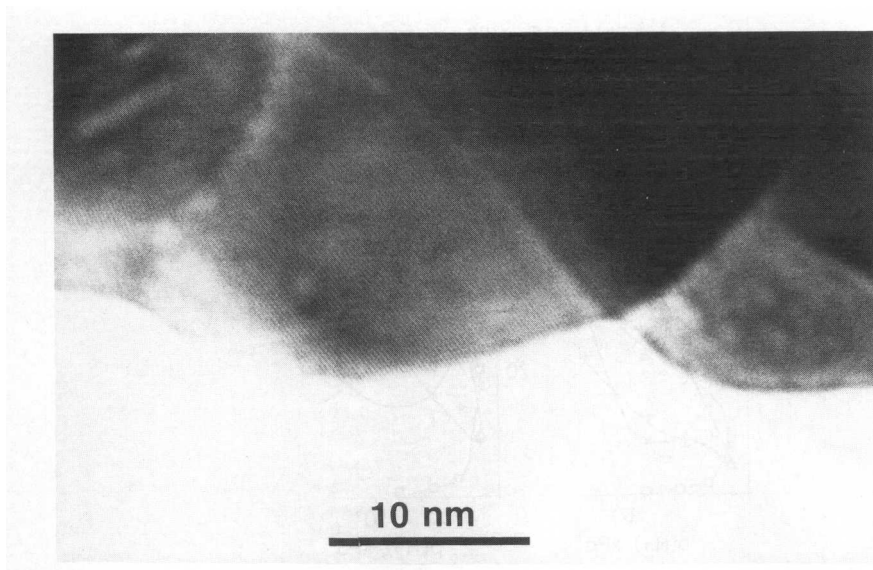
Figure 3. High resolution electron micrograph of Pt-473 /4/.

fringes (Figure 3). Pt-633 was not transparent for the electron beam; the rounded character of the particles can be seen in Fig. 2.

Various reactions of n-hexane and methylcyclopentane require surface intermediates of various degree of dehydrogenation. The amount of surface hydrogen available controls the extent of dehydrogenation of hydrocarbons bound to the active sites and, by doing so, determines which reaction will prevail /3,4/. That is the reason why maxima are observed in the yields of individual product classes /18,20,21/. These maxima are not well-defined with Pt-473 (Figure 4) and appear clearly with Pt-633 (Figure 5). In the former case, the yields of isomers, fragments increase monotonically with $p(H_2)$ whereas minima are seen in MCP and benzene yields. No olefin is detected on Pt-633 while its amount decreases with $p(H_2)$ over Pt-473. The overall activity of samples shows drastic differences: Pt-473 is more active by about an order of magnitude. The comparison of selectivities reveal that fragmentation is most important over Pt-633 whereas Pt-473 is a better catalyst for nondegradative reactions, first of all, isomerization. MCP selectivities have maxima in both cases and benzene selectivity
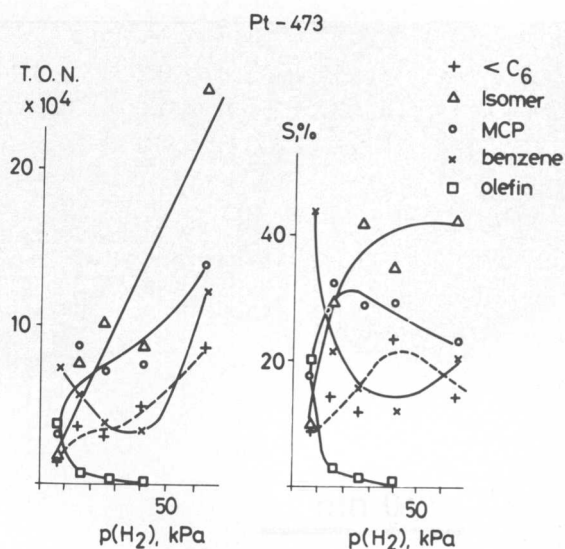
Figure 4. Activity (in terms of turnover number, T.O.N.) and selectivity, S% of Pt-473 in n-hexane transformations , as a function of hydrogen pressure, $p(H_2)$. T = 603 K, 0.1 g catalyst, 4.9×10^{18} surface Pt-atom (Pt_s).
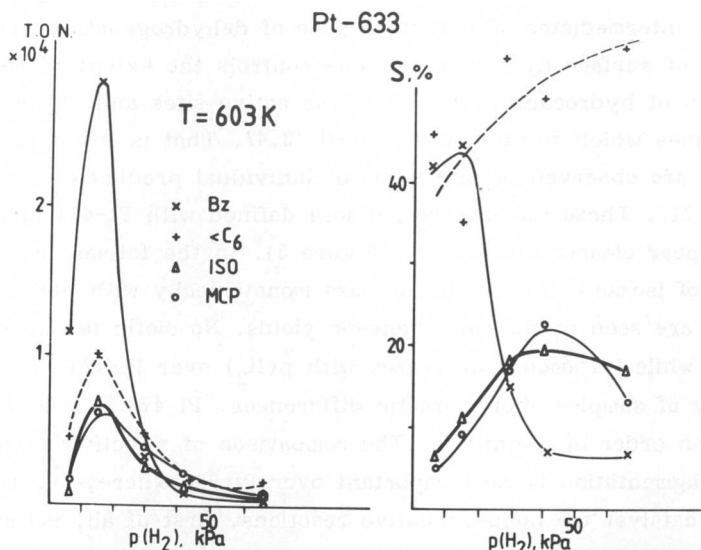

Figure 5. Activity and selectivity of Pt-633 in n-hexane transformations. T = 603 K, catalyst: 0.1 g; Pt_s: 2.25×10^{18} atom. Data were taken partly from Ref. /22/.

decreases at higher $p(H_2)$. Again, a minimum is seen in the latter value on Pt-473; the absolute values are also higher on that catalyst.

No differences in overall activity were observed in MCP reactions (Figure 6). Ring opening reaction prevailed over both Pt-samples, enormously increasing with $p(H_2)$. At low $p(H_2)$, olefins were also of importance over Pt-633 and - like with n-hexane - benzene over Pt-473. Fragmentation was unimportant in both cases.
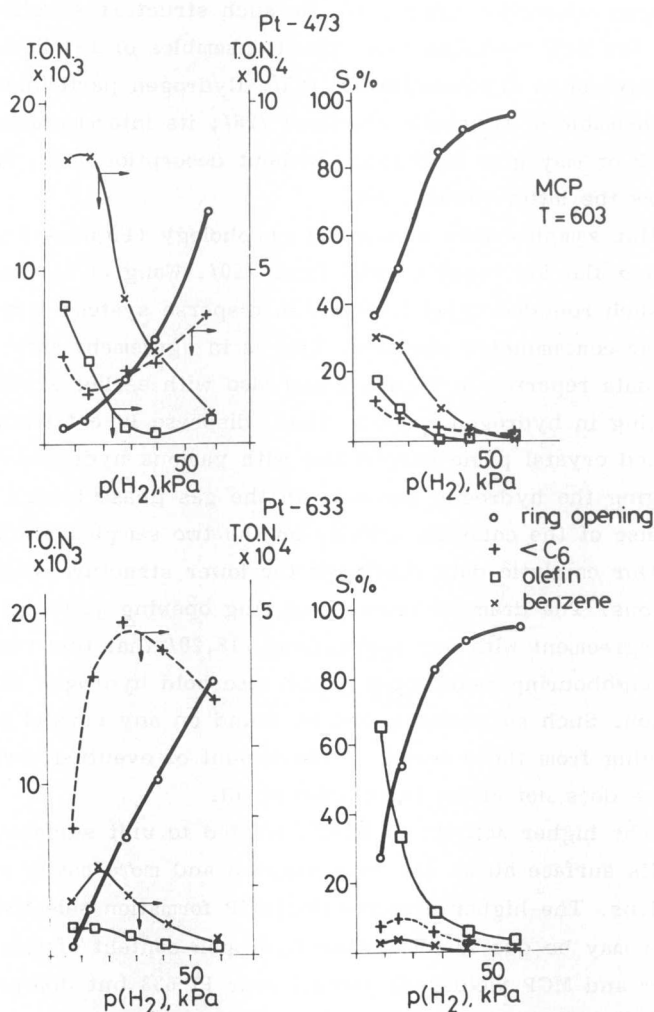

Figure 6. Activity and selectivity of Pt-473 and Pt-633 in methylcyclopentane transformations. T = 603 K.

Discussion

Surface geometry, hydrogen availability and the eventual presence of impurities determine the actual catalytic properties of Pt. Single crystals with hexagonal symmetry - (111), (322) and (10,8,7) faces - were more active in nH aromatization than those with tetragonal - (100) - symmetry /13/. Five-coordinated B_5 sites were claimed to be active in hydrogenolysis /23/. Such structures also represent peculiar hydrogen adsorption sites /24/. No such structure-sensitivity was found for MCP reactions /23/. Small ensembles of 1-3 Pt-atoms were the active sites of aromatization /25/. Hydrogen participates in the active ensemble of C_5-cyclic reactions /28/; its intermediates may desorb as MCP or may give isohexanes without desorption /26/. More hydrogen favours the latter process /4/.

Our samples show a rounded morphology (Figures 2 and 3) not exposing flat low index crystal faces /20/. Wang et al. suggested /27/ that such rounded crystal shapes in disperse systems may arise owing to their contaminated surfaces. This is in agreement with surface analysis data reported in Figure 1 and also with earlier studies /14-16,19/. Sintering in hydrogen creates, thus, disperse Pt-catalysts with ill--defined crystal plane shapes and with various hydrogen content. Changing the hydrogen pressure in the gas phase brings about various response of the catalytic activity on the two samples studied.

Our catalytic data confirmed the lower structure-sensitivity of MCP reactions. The dramatic increase of ring opening yields at higher $p(H_2)$ is in agreement with our suggestions /18,20/ that this reaction requires two neighbouring metal atoms which also hold hydrogen during the reaction. Such an ensemble can be found on any crystal plane and - judging from these results - the amount of eventual carbon on the surface does not affect these sites at all.

The higher activity of Pt-473 related to unit surface indicates that its surface atoms are more exposed and more easily available for reactions. The higher isomerization/MCP formation selectivity over Pt-473 may be due to the higher hydrogen content of this catalyst /16/. Isomer and MCP yields are parallel over Pt-633 but distinctly more isomer is formed on Pt-473 at higher $p(H_2)$ (cf. Figs. 4 and 5), that is the "hydrogen utilization" is better on the former sample /4,21/.

This can be attributed to hydrogen retained and the facility of its interaction with the hydrocarbon reactant.

Both benzene and fragments require deeply dehydrogenated surface intermediates. Obviously, aromatization is favoured over Pt-473. With increasing $p(H_2)$, the competition between hydrogen and hydrocarbons first decreases aromatization activity; thereafter, however, a strong increase is seen (Fig. 5). Hydrogen must either be able to remove individual carbonaceous species blocking active sites or there must be a possibility that under these conditions "H-Pt-C" sites are created which are favourable for nondestructive reactions /28/. Pt single crystal faces with rather large carbon coverages have also been found to be active, the hydrogen attached to C being able to interact with hydrocarbon reactants /29/.

A more prominent competition between hydrogen and hydrocarbons is observed over Pt-633. Here the partly polymerized carbonaceous overlayer leaves free a fraction of the surface only for catalysis. Of all reactions, fragmentation seems to be least affected: its selectivity remains high, like in the case of partly coked Pt/SiO_2 catalyst /21/ and Pt(111) single crystal face /29/. The presence of extra B_5- -sites is not confirmed by our results.

Acknowledgement

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