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Surface and bulk structural response of Pt black upon its hydrogen treatment and catalytic reaction with n-hexane

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Pt black has been studied by X-ray and ultraviolet photoelectron spectroscopies (XPS, UPS) and XRD after reduction, after presintering and after subjection to various *in situ* treatments. All samples contained carbon and oxygen impurities. Sintering decreased the abundance of C. Samples introduced from the air contained a large amount of oxygen whose amount dropped markedly upon keeping the Pt in UHV for several hours. XPS and UPS revealed considerable amounts of nondissociatively chemisorbed CO after this treatment. An *in situ* hydrogen treatment at 603 K decreased the O content further but *increased* the concentration of surface carbon. The Pt 4f regions showed some oxidized Pt both before and after sintering. Pt reached an almost clean metallic state after UHV treatment. This state seemed to remain unchanged after further manipulations. Hardly any electronic interaction could thus be observed between Pt and its main impurity: C, which was present mostly as graphite and C_xH_y polymer after treatment with n-hexane plus hydrogen. n-Hexane alone produced mostly “disordered” surface carbon species. The intensity of higher-order X-ray reflections of Pt was suppressed upon sintering. This anisotropy was reversed after *in situ* H_2 treatments, inducing recrystallization with preferential formation of higher Miller-index planes, (220) and (311). These reflections were again suppressed after exposure to n-hexane. Thus, adsorbate-induced solid-state rearrangement occurred as a result of the interplay of surface and subsurface impurities. The catalytic reactions of n-hexane over Pt black subjected to different pretreatments were different: abundant (220) and (311) reflections promoting isomerisation, C_5-cyclisation and also hydrogenolysis. Carbon accumulation decreased the “intrinsic” activity of the Pt fraction detected by XPS. Selectivities, in turn, were governed by the crystallite structure as well as by the presence of composite platinum–carbon sites. “Disordered” surface carbon species poisoned all skeletal reactions and favoured dehydrogenation to hexenes.

Introduction

The “flexible surface” concept[1,2] of Somorjai underlines the importance of “rough surfaces” in catalysis as opposed to close-packed, low Miller-index faces. Reconstruction induced by chemisorbed entities—including reactants of catalytic processes—can also produce “rough” surfaces.[3] O_2, H_2 or CO, each adsorbed at 1 bar pressure, generated adsorbate-specific surface reconstruction of the Pt (110) single crystal plane.[4] Thermal restructuring of Pt particles required at least 1073 K.[5]

High-surface Pt black that had been prepared by aqueous reduction of H_2PtCl_6 with formaldehyde underwent considerable sintering during its very first contact with H_2 between ~480 and ~680 K.[6] No sintering occurred in vacuum, helium or air under the same conditions.[6] Hydrogen may have removed the majority of surface impurities and promoted coalescence of particles purified in this way.[6] This sintering process resulted in agglomerates of rounded, larger crystallites.[7] When the solution of H_2PtCl_6 was reduced with hydrazine, somewhat larger, polyhedral crystallites were formed. They also became rounded upon their first hydrogen treatment without considerable crystallite growth.[8] Recent photoelectron spectroscopic and X-ray diffraction studies[9,10] confirmed the restructuring of Pt black upon its exposure to O_2, H_2 and n-hexane/H_2 mixtures. Hydrogen treatment of Pt black at 600 K resulted in “retention” of hydrogen—occupying partly subsurface positions—as shown by radiotracer studies.[11] UPS results indicated that H at 600 K penetrated into the subsurface layers and forced O to the surface. This O_{ads} reacted with hydrogen when the sample was left at 600 K overnight and produced minor but stable surface species like OH and H_2O.[12,13]

Regeneration with O_2 and H_2 is a well-established process for the restoration of the activity of dispersed Pt. Even a polycrystalline foil can be purified more efficiently by this “chemical” method than by ion sputtering alone.[12] Such treatments of Pt black bring about a stable and reproducible catalyst activity and selectivity in n-hexane model reactions.[8,13,14] The “rough” surfaces of unsupported Pt agglomerates[7,8] “do chemistry” in the sense of Somorjai’s concept.[1,2] We present here an integrated approach combining XRD to study structural changes and photoelectron spectroscopy to monitor sample composition and the valence states of the components in Pt black after its treatment in various atmospheres. Test runs with n-hexane/hydrogen mixtures after analogous treatments complete the picture. The results of the physical and catalytic measurements correlated well with each other. These experiments represent two sides of

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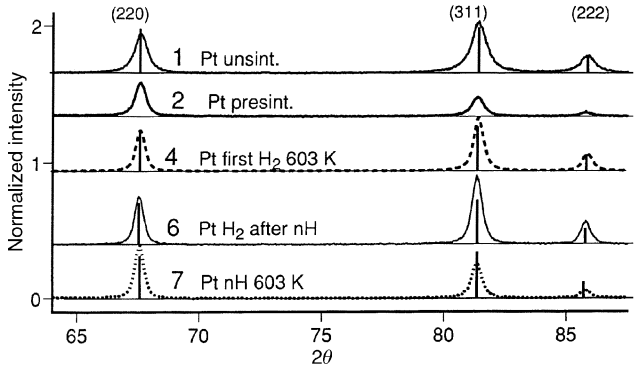

Fig. 1 X-Ray diffractograms of Pt black in different states. Intensities have been normalized to the strongest, (111), line. The thick vertical lines show the relative intensities according to the JPCD file. Note the anisotropic recrystallisation after treatments.

the "pressure gap"[15] between catalytic and surface chemical studies; its bridging being the hope of most scientists in this field.

Experimental

Catalysts and treatments

Pt black was reduced from an aqueous solution of H_2PtCl_6 by ~10% hydrazine at 313 K[8] and washed with bidistilled water (sample **1**). Its specific surface was ~10 m^2 g^{-1}. This preparation was presintered in H_2 flow at 473 K for 1 h,[6] (sample **2**). Its specific surface decreased to 2.6 m^2 g^{-1}. Photoelectron spectra of samples **1** and **2** were measured after storing them in air for a few months. Electron spectroscopy was repeated after having kept the "as-received" sample **2** in UHV for ~60 h (sample **3**). Exposure to 270 mbar H_2 followed in the preparation chamber of the electron spectrometer (sample **4**). Another Pt black sample from the same batch was exposed to a mixture of n-hexane (nH) and hydrogen ($nH/H_2 = 13 : 80$ mbar; sample **5**) and was regenerated subsequently by 27 mbar O_2, evacuation and 270 mbar H_2 (sample **6**). Sample **7** was obtained after regeneration and exposure to 53 mbar nH alone. Measurements on samples **6** and **7** were preceded by a few hydrocarbon exposures and subsequent regenerations. All treatments to produce samples **4**–**7** lasted for 20 min at 603 K.

XPS and UPS

Details of the methods of electron spectroscopy have been reported earlier.[16,17] Dry powder samples were placed on a stainless steel sample holder evacuated and treated in the preparation chamber of a Leybold LHS 12 MCD instrument. UPS spectra were excited by He II radiation (40.8 eV), pass energy (PE) = 12 eV. A Mg-Kα anode was used for XPS (PE = 48 eV). The peaks were evaluated after satellite subtraction and Shirley background subtraction. The binding energy (BE) was calibrated to the Au 4f 7/2 line (BE = 84.0 eV). Atomic compositions were determined from the peak areas with literature sensitivity factors[18] using the homogeneous composition model. Difference spectra were obtained either by direct subtraction or after normalizing the intensities at an appropriate BE value.[19]

Table 1 Surface composition of samples in various stages of their treatment

	Composition (atom%)		
Sample	O 1s	C 1s	Pt 4f
1[a]	15	18	67
2	24	12	64
3	4.5	11	84.5
4	1	15	84
5	3	27	70
6	2	23	75
7	0.5	40	59.5

[a] Disregarding the ~7% Cl and ~4% N impurity from reduction of H_2PtCl_6 by hydrazine, disappearing completely after first evacuation.

X-Ray diffraction

XRD measurements were carried out on samples taken from the spectrometer at room temperature. A STOE double-circle transmission mode diffractometer was used in Debye–Scherrer geometry, equipped with a Ge(111) primary monochromator and a position-sensitive detector, using Cu-Kα radiation, $\lambda = 154.06$ pm. XRD measurements were recorded for samples **1**, **2**, **4**, **6** and **7**, interim states between *in situ* treatments (**3** and **5** in our case) could not be measured. The intensities of individual reflections were normalized to that of (111).

Catalytic reactions

The catalytic behavior of Pt black was tested by reacting a standard mixture of n-hexane (nH) and hydrogen at $p(nH) : p(H_2) = 13 : 160$ mbar. A closed-loop reactor was used. Sampling took place after 5, 20, 35 and 50 min reaction time. The catalyst pretreatments in the photoelectron spectrometer were simulated as closely as possible. In one run the reactor volume was kept in vacuum at 603 K for several hours and the hydrogen-rich reaction mixture was introduced directly afterwards (analogous to preparation of **3**). Catalytic runs were also carried out after the first H_2 exposure (as after preparation of **4**). These were compared with results corresponding to the preparation of **6** (sample regenerated several times, with well-reproducible activity and selectivity). The catalytic properties were also checked after two exposures to n-hexane: with or without H_2, as in the preparation of **5** and **7**, respectively. Turnover frequencies were calculated using "nominal" Pt_s values obtained from hydrogen–oxygen titration results, after treating the presintered catalysts with hydrogen (corresponding to sample **4**).

Results

Structure of different samples

Fig. 1 shows the high-angle sections of X-ray diffractograms obtained on five catalyst samples. The X-ray diffraction pattern of the unsintered Pt (**1**) showed a slight line broadening (crystallite size ~20 nm, *cf.* the value of 23 nm reported for an analogous preparation[8]). Sintering increased crystallite size only slightly (~25 nm), as opposed to the behaviour of Pt reduced by formaldehyde.[6] Results on those samples have been reported recently.[10] The relative intensities of individual reflections of the unsintered sample (sample **1**) were close to literature values for bulk Pt.[20] The X-ray diffractogram of presintered Pt (**2**) showed a marked decrease in the intensities of higher-order reflections. This agrees with earlier electron micrographs revealing that this process changed the polyhedral contours of the crystallites to a rounded shape rather than promoting particle growth. The loss of specific surface must have been due to agglomeration of the crystallites.[8] The first H_2 treatment (sample **4**) increased the relative intensities of the (311) and (220) reflections. This anisotropy was enhanced when the regenerative treatment followed an exposure to nH/H_2 at 603 K. (sample **6**). When the Pt black was exposed to 53 mbar n-hexane without hydrogen (sample **7**), rearrangement in the opposite direction took place, the higher-order reflections were suppressed again. Repeated

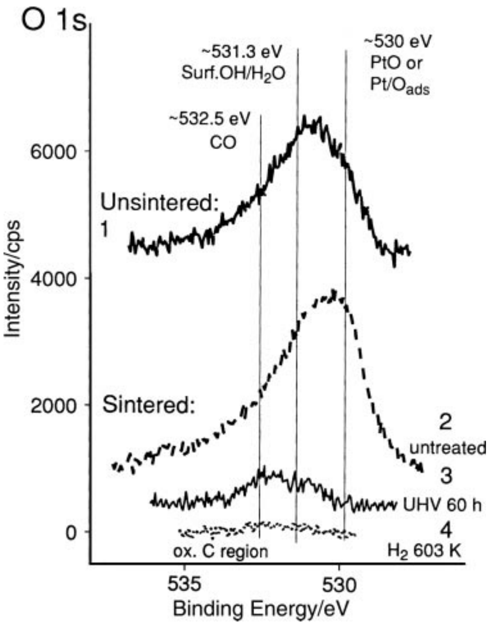

Fig. 2 O 1s region of Pt black in different states. The Pt 4f 7/2 intensities were normalized and the same factor used for the O 1s intensities.

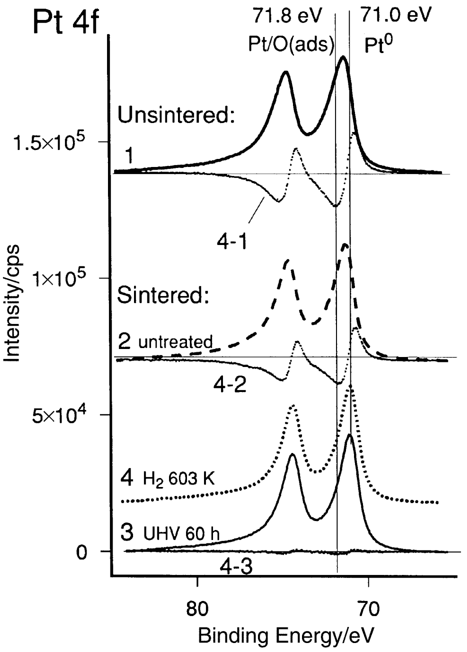

Fig. 4 Pt 4f region Pt black samples in different states, together with their difference spectra. Intensities were normalized at the peak position of the Pt 4f 7/2 line.

exposure to n-hexane at different temperatures produced reflections analogous to sample **7**.[9] The lattice constants (0.3920 to 03924 nm) were very close to the bulk Pt state (0.3923 nm). Very small lattice strain values (up to 0.08%) were observed. They showed no correlation with the crystal anisotropy.

Photoelectron spectroscopy after different treatments

Initial treatments of Pt black. Table 1 shows the compositions of samples **1** to **7** determined from XPS line intensities. Considerable oxygen and carbon contributions appeared in both untreated samples. Evacuation (sample **3**) removed from sample **2** most of the oxygen that had accumulated during storage in air. Subsequent treatments reduced the percentage of oxygen still further.

To compare the individual XPS regions of samples **1** to **4**, the intensities of the Pt 4f 7/2 peaks were normalized to the peak height measured after H_2 treatment (sample **4**). The same normalization factor was applied thereafter to the intensities of the other regions. The major component of the O 1s region of untreated Pt samples (Fig. 2) was at ~530 eV corresponding to oxygen bound directly to the metal, accumulated during lengthy storage in air. Its chemical state is not clear: it may be adsorbed oxygen or—as observed[21] with a highly disperse Pt/SiO_2—a nearly monomolecular surface layer of PtO. Its amount was larger in sample **2** than in sample **1**. Leaving the sample in UHV for ~60 h (sample **3**) removed ~85% of the oxygen, as estimated from peak areas (Fig. 2). In addition to surface OH/H_2O, a component in the O 1s region at BE ≈ 532.5 eV appeared. This can be assigned to chemisorbed CO.[12] Hydrogen treatment (sample **4**) completed the oxygen removal. Carbon was the major impurity in all cases. It appeared[12] mainly as graphitic C, poly-C_xH_y and oxidized C (Fig. 3). Narrower peaks appeared upon UHV and hydrogen

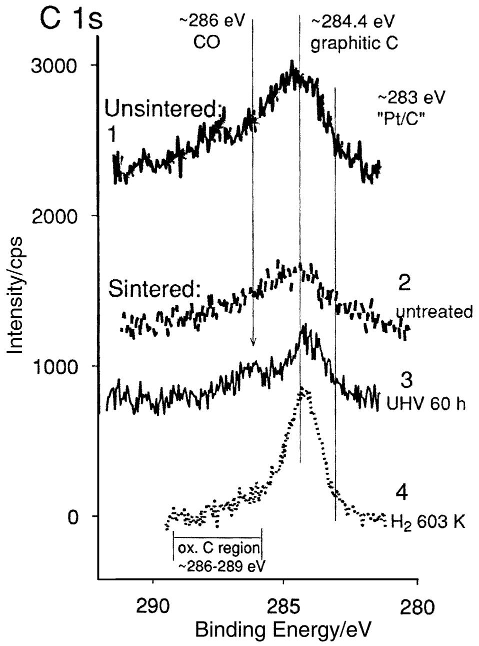

Fig. 3 C 1s region of Pt black in different states. The Pt 4f 7/2 intensities were normalized and the same factor used for the C 1s intensities.

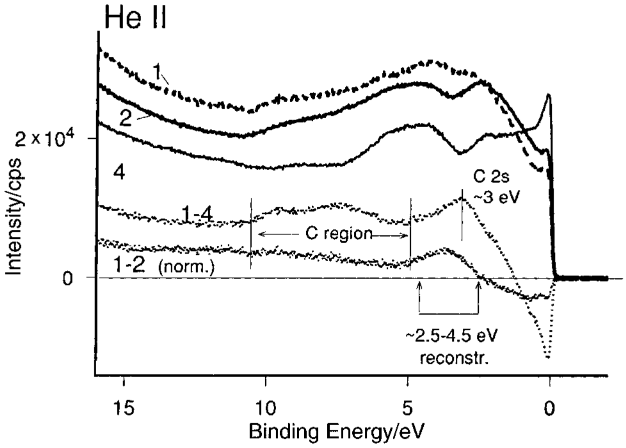

Fig. 5 He II UP spectrum of the unsintered (**1**), sintered (**2**) and H_2-treated (**4**) Pt black samples together with their difference spectra (intensity normalization at 2.45 eV).[13]

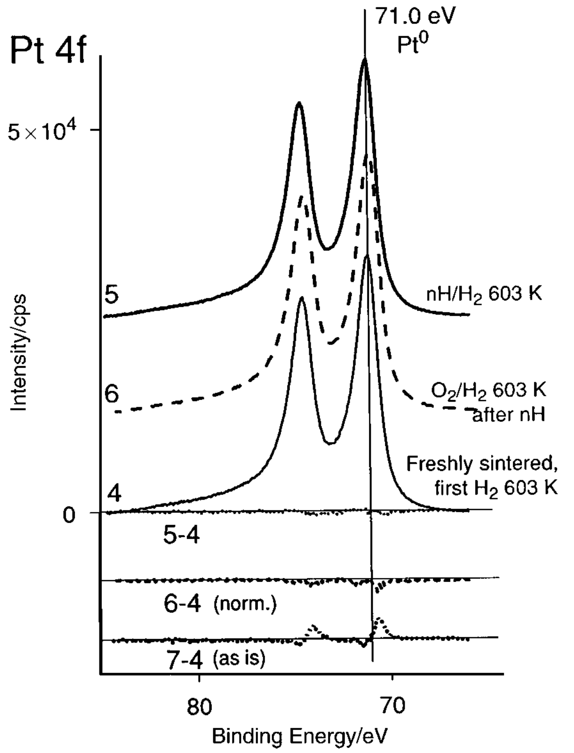

Fig. 6 Pt 4f region of Pt black samples subjected to H_2 treatment for the first time (**4**), after exposure to n-hexane/H_2 (**5**) and after a subsequent regeneration (**6**). All difference spectra were calculated after intensity normalization.

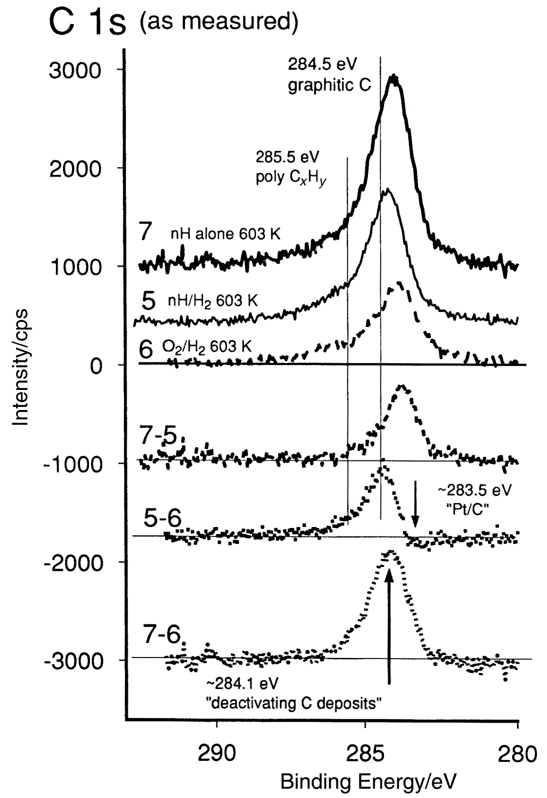

Fig. 8 C 1s region of Pt black samples **4**, **6**, **7** and their difference spectra calculated as measured.

treatments (**3** and **4**) pointing to advancing graphitisation. The marked component at BE ≈ 286 eV in sample **3** (Fig. 3) agrees well with that reported by Belton and Schmieg for adsorbed CO.[22] The C 1s intensity *increased* after contacting the vacuum-treated Pt with H_2 (from sample **3** to **4**) graphitic C (BE ≈ 284.3 eV) being the main component. The Pt 4f 7/2 peaks were similar in both samples **1** and **2** with maxima shifted to higher BE values than that corresponding to Pt^0. The Pt 4f peak did not change much upon presintering. The negative peak in the difference spectra **4** − **1** and **4** − **2** with ΔBE *ca.* +0.8 eV corresponds to "PtO_{ads}".[23] This confirmed that adsorbed oxygen was the main impurity in the untreated samples.[24] Even UHV treatment was sufficient to remove most of the oxygen. These experimental data are not sufficient to attribute any definite structure to this oxygen species, which may not be identical with the atomically chemisorbed O that would desorb from Pt single crystal surfaces at higher temperatures.[25] The difference spectrum **4** − **3** appeared as a nearly straight horizontal line (Fig. 4) indicating that hydrogen treatment did not purify Pt further.

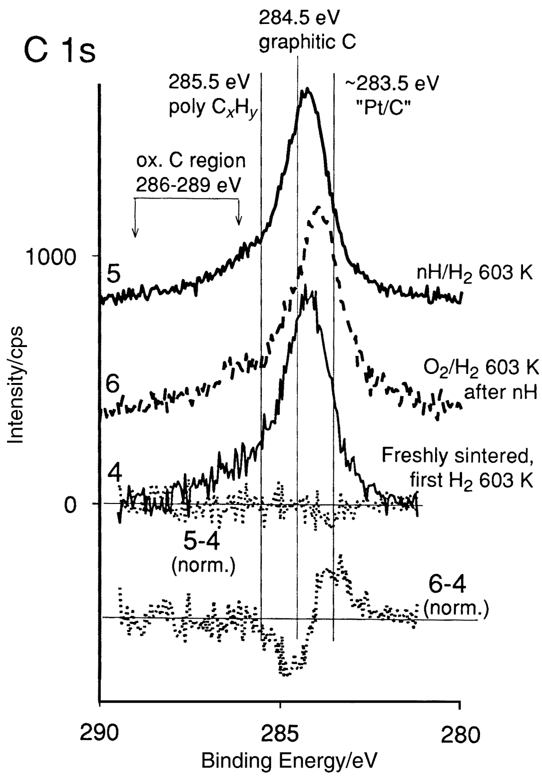

Fig. 7 C 1s region of Pt black samples **4**, **5**, **6**. Treatments, see Fig. 6. Difference spectra were calculated after intensity normalization.

The He II UP spectra of untreated catalysts (Fig. 5) showed rather low Fermi-edge intensities. The normalized difference spectrum **1** − **2** was rather featureless, except for a broad intensity excess in the unsintered Pt between 2.5 and 4.5 eV. An increased intensity in this region was attributed to *restructuring* of a Pt (100) single crystal surface.[26] This would be in agreement with the *loss* of some irregularities of the freshly reduced crystallites upon sintering in H_2[6–8] as shown also by XRD (Fig. 1). The Fermi-edge intensities confirmed the considerable purification of Pt after UHV and H_2 treatments (sample **4**). Nondissociatively adsorbed CO appeared in spectrum **3** (not shown). Its origin cannot be established without doubt, hence it will not be discussed further. The small amount of other adsorbed species at BE ≈ 5 and ~7–8 eV may be tentatively assigned to various surface oxygenates, such as O, OH or H_2O.[12,13,27]

Exposure to n-hexane and regeneration. Contacting Pt black with n-hexane (nH) plus H_2 modeled what might happen to the catalyst during alkane reaction in a closed system. The Pt 4f region in sample **5** was identical to that observed after the

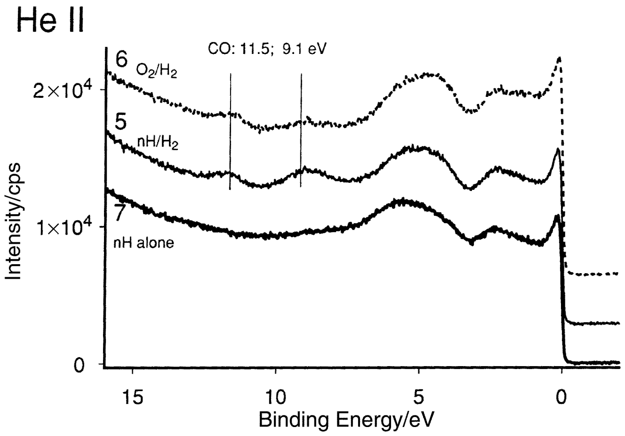

Fig. 9 He II UP spectra of sintered Pt black samples **5**, **6** and **7**.

first contact with H_2 (Fig. 6, spectrum **5** − **4** calculated without intensity normalization). The Pt 4f doublet indicated a predominant Pt^0 state, hence there was hardly any chemical interaction between Pt and its major impurity, C.[28] The difference spectrum **6** − **4** (Fig. 6) indicated some PtO_{ads} in sample **4**, this excess being less in sample **7** (spectrum **7** − **4**), in agreement with the surface Pt composition.

Carbon intensities were markedly different in samples **4**, **5**, **6** and **7** (Table 1). The C 1s spectra of samples **5** and **6** (Fig. 7) were similar to those reported earlier.[9,10] The normalized difference spectra between the carbonized and regenerated catalysts showed that O_2/H_2 treatment—removing relatively little carbon (Table 1)—decreased the amount of graphitic C component. At the same time the contribution due to "atomic C" in surface or subsurface positions increased. The distribution of C 1s components in sample **4** (first contact with H_2) was more similar to that in sample **5** (exposed to nH/H_2) than to that in sample **6**. This means that there was some graphite present after the first contact of Pt with H_2 (Fig. 3) as opposed to more "Pt/C" after repeated regenerations (*cf.* the difference spectra **5** − **4** in Fig. 7). Exposure to n-hexane without H_2 (sample **7**) not only produced more carbon but also its BE appeared at a lower value. Difference spectra in Fig. 8 calculated without intensity normalization confirm the presence of "atomic C" in the regenerated sample (**5** − **6**). A high amount of C 1s component at BE ≈ 284.1 eV appeared in sample **7**.

The related He II UP spectra (Fig. 9) indicate rather marked Fermi-edges after each treatment, pointing to the presence of metallic Pt (as in Fig. 6). The peak doublet at 9.1 and 11.5 eV indicated the presence of adsorbed CO in samples **5** and **6**.[29] The increased intensity in the region 5.5–10 eV in spectrum **7** confirms the presence of a high amount of carbon after exposure to 53 mbar nH.

Table 2 n-Hexane transformation (13 mbar) in 160 mbar hydrogen on various catalysts[a]

	Reaction time/min			
	5	20	35	50
First run after evacuation (sample **3**):				
TOF/h^{-1}	23	12	9	7
Selectivity (%): $<C_6$	30	29	29	30
Isomers[b]	18	19	19	19
MCP[c]	27	27	26	26
Benzene	20	20	21	21
Hexenes	5	5	5	4
Run after first H_2 treatment (sample **4**):				
TOF/h^{-1}	29	13	9.5	7.5
Selectivity (%): $<C_6$	25	25	24	24
Isomers[b]	19	22	23	23
MCP[c]	29	30	29	29
Benzene	19	19	19	19
Hexenes	8	4	5	5
After exposure to n-hexane/H_2 at 603 K (sample **5**):				
TOF/h^{-1}	12	5.5	4	3
Selectivity (%): $<C_6$	37	37	37	38
Isomers[b]	16	17	17	16
MCP[c]	16	17	17	17
Benzene	24	26	26	26
Hexenes	7	3	3	3
Regenerated, H_2/O_2 603 K (sample **6**):[d]				
TOF/h^{-1}	20 ± 0.82	10	7	5.5
Selectivity (%): $<C_6$	40 ± 1.5	39	39	40
Isomers[b]	18 ± 0.9	19	19	19
MCP[c]	16 ± 0.8	16	15	14
Benzene	24 ± 0.7	24	25	26
Hexenes	2 ± 0.5	2	2	1
After exposure to n-hexane without H_2 at 603 K (sample **7**):				
TOF/h^{-1}	2	1.2	1	0.8
Selectivity (%): $<C_6$	25	32	34	35
Isomers[b]	8	11	11	11
MCP[c]	10	13	14	14
Benzene	22	24	26	26
Hexenes	35	20	15	14

[a] Treatments analogous to those performed in the photoelectron spectrometer. Catalyst mass: 16 mg for **3** and **4**; 50 mg for **5**, **6**, **7**. Typical conversions were 3 to 15%; somewhat higher for **6** and lower for **7**. [b] Sum of methylpentanes. [c] Methylcyclopentane. [d] The TOF and selectivity values at 5 min have been averaged from 21 independent runs after the same regeneration carried out after various test reactions with nH + H_2 mixtures on the same charge of catalyst. Values for longer times have been taken from one long run.

Catalytic results

"Skeletal" reactions of n-hexane in mixtures with hydrogen at ~600 K involve aromatization, C_5-cyclisation and isomerisation as well as hydrogenolysis.[8,13,14] Table 2 summarises the catalytic results. The turnover frequencies (TOF) for the three catalysts treated in vacuum or in hydrogen prior to the run (samples **3**, **4** and **6**) were rather close to each other. The table contains average values for the 5 min run on the "regenerated" sample **6**, indicating the good reproducibility of the catalytic properties of this state.

The selectivities (*S*) were also well-reproducible after standard regeneration (Table 2). The differences after various pretreatments were rather pronounced. Sample **6** produced most fragments. The most active catalysts after vacuum and first H_2 treatments (samples **3** and **4**) produced most isomers ($S \sim 20\%$) and methylcyclopentane (MCP) up to $S \sim 30\%$. The fragmentation selectivity was highest with the "steady-state" regenerated Pt (sample **6**). The benzene selectivity was rather constant (20–25%), that of hexenes remained low (2 to 5%), but its standard deviation was largest. Deactivation during a test run caused an approximately fourfold decrease in the initial TOF value during 50 min reaction time. The selectivities were, in turn, constant during this period (Table 2).

Deactivation with nH/H_2 (sample **5**) increased the surface carbon concentration and also decreased the TOF by about 50% but caused hardly any selectivity changes as compared to sample **6**. The highly deactivated sample **7** was, however, in a class of its own. Its carbon percentage was about twice that of the regenerated sample **6** (Table 1) but its activity was lower by an order of magnitude. It produced initially mainly hexenes (up to 35%), at the expense of C_6 saturated products and fragments, but with hardly any change in the benzene selectivity. The selectivity changes during longer runs indicated a slow reactivation of skeletal processes, as shown also by the TOF value at the end of run.

The number of surface Pt atoms used for calculating the TOF values in Table 2 was measured in a state corresponding to sample **4**. XPS indicated 84% Pt on its surface. Table 3 contains corrected TOF values of other samples by considering the ratio of their actual Pt percentages measured by XPS to the value observed for sample **4**. Sample **3** showed the same percentage of Pt, so no correction was necessary. It was less active than sample **4**. In all other cases the percentage of Pt shown by XPS was lower, therefore, fewer Pt atoms were responsible for the transformation measured and thus their corrected TOF values were higher than those in Table 2. The overall corrected activity of samples **5** and **7** also proved to be lower with this calculation method, indicating that the likely number of "working" active sites was *lower* than estimated from the XPS Pt signal. This lower catalytic activity (sample **5** and especially sample **7**) was concomitant with the accumulation of (graphitic or disordered[30,31]) surface carbon entities that were, likely, not thick enough to suppress the Pt signal but deactivated the active Pt ensembles in their vicinity. In spite of the known difficulties of transforming directly XPS data for *real* surface compositions, their correlation with activity data is remarkable. As for the activities of individual reactions, n-hexane pretreatment decreased first processes involving formation and/or rupture of C–C bonds. All activities dropped to a disproportionately high degree for sample **7.** However, the dehydrogenation activity to hexenes even increased and remained constant in both deactivated samples (**6** and **7**) in agreement with the suggestion that single-atom Pt atoms (or "PtC" ensembles) can be the appropriate active sites.[32,33]

Table 3 Normalized turnover frequencies (TOF) of various n-hexane reactions[a]

Sample	Overall	$<C_6$	Iso	MCP	Benzene	nH$^{=}$
"Fresh" catalysts						
3	23	6.9	4.2	6.2	4.6	1.1
4	29	7.2	5.5	8.5	5.5	2.3
"Used" catalysts						
6	22.5	9	4	3.6	5.4	0.5
5	14.5	5.4	2.3	2.3	3.5	1
7	2.8	0.7	0.22	0.28	0.6	1

[a] The TOF values of Table 2 normalized to the Pt% measured in sample **4** (analogous to the pretreatment for H_2–O_2 titration) on the basis of the Pt percentages of Table 1. TOF for individual reactions were calculated from the initial selectivities of Table 2.

Discussion

Surface spectroscopy and catalytic measurements represent two sides of the "material and pressure gap", as pointed out by Bonzel.[15] Nevertheless, the catalytic properties and active sites on single crystals, metal films and unsupported metal powders can essentially be discussed in an analogous way.[34] The necessity of leaving "the comfortable world of single crystals" has been pointed out recently.[35] Unsupported Pt black may be a unique model catalyst, its study being complementary to rather than competing with single crystal investigations. (i) Its particles are certainly more "flexible" than that of macroscopic single crystals. (ii) The size of individual crystallites is large enough to carry out XRD but small enough that this bulk method can also monitor the reconstruction of a few surface layers.[10] (iii) It exposes different crystal planes like catalysts of practical importance. (iv) The absence of carrier facilitates electron spectroscopy. (v) Interactions between very small metal particles and the support, arising from chemical bonds present on the metal/support interface[36] are also eliminated—remember that the catalytic behaviour of 0.2% Pt/Al_2O_3 ($Pt \approx 1$ nm) could *not* be modeled by single crystal faces, in contrast to catalysts with 2 to 10% Pt loading.[37]

The (rounded) crystallites of our Pt black expose a great variety of surface microfacets.[38] It has been pointed out already by Taylor[39] that the reactant itself may "select" the appropriate active sites. Surface reconstruction may be a significant step in creating those sites, in agreement with the "flexible surface" concept.[1,2] It may occur largely as a result of the effect of chemisorbed species.[4] All these may agree with the earlier idea (postulated then on a rather intuitive basis[40]) that the catalyst, the reactant and other components present create together the active "catalytic system".

Rather marked changes occurred on the surface of the "as-received" sample **2** during its first treatment in the spectrometer (samples **3** and **4**). In spite of various amounts of impurities present, a reasonably clean Pt^0 state appeared after these treatments (Fig. 4). Surface O entities were easily removed. The residual O appeared mainly as adsorbed OH and H_2O (Fig. 2), being, likely, the reaction products between hydrogen and oxygen.[12,13]

Although the effect of O may be more conspicuous with large single crystal surfaces,[4] the most important component inducing reconstruction of unsupported catalyst particles was found to be hydrogen.[6] Exposing a 6(111) × (100) stepped Pt single crystal surface to H_2 caused a, reversible, doubling of step height and terrace width.[41] A surface H : Pt ratio as low as 1 : 1 was sufficient to induce reconstruction of Pt(100).[42] A highly enhanced mobility of [Pt–H] complexes was reported as compared to single Pt atoms.[43] The XRD of "as-reduced" Pt black (**1**) compared with that measured upon first sintering in H_2 (**2**) confirms the considerable hydrogen-induced restructuring.[6,8,10] Higher-index reflections: (220), (311) and (222) were favoured after H_2 treatments in the electron spectrometer (samples **4** and **6**). Contacting Pt with hexane (sample **7**) caused a reverse reconstruction which also appeared after long storage in air. The less pronounced anisotropy after the first contact of Pt with H_2 (sample **4** *vs.* sample **6**) indicates that movement of H and C atoms (present in ample amount after nH treatments) between different positions can be important in crystallite reconstruction. These atoms were reported to be more stable on the Pt surface above 250 K than CH_x entities.[44]

The reconstruction demonstrated by XRD after H_2 treatment may have been related to penetration of hydrogen atoms into subsurface layers.[11,13] These might obviously have mobilized other subsurface entities. One of the possible explanations for the increased C 1s intensity after H_2 treatment (Fig. 3) could be their agglomeration into three-dimensional (possibly graphite-like) carbon promoted by hydrogen.[45] Indeed, the Pt signal in ion scattering spectroscopy of a carbon-covered Pt black increased by about 6 times, at the same time, the percentage of Pt calculated from the Pt 4f XPS signal only increased from 56 to 70%.[16] This points to the presence of thin C deposits permitting the underlying Pt to appear in XPS. This reconstruction of surface carbon may be the reason why sample **4** was more active than the apparently "cleaner" sample **3**. The hydrogen-induced migration of subsurface C atoms to the surface, however, cannot be excluded.

Exposure to n-hexane resulted in accumulation of surface C, present, in part, as three-dimensional overlayers:[12,46] graphite as well as poly-C_xH_y. The BE values for carbon species likely present on the Pt surface have been summarized recently.[30] More graphite was formed from nH/H_2 (sample **5**) than with n-hexane alone (sample **7**). Nongraphitic carbon (BE $\approx$ 284.1 eV) was present in the latter case. Counter claims can be found concerning its structure—we may identify them with the "disordered carbon overlayer"[47] or with the "several hydrocarbon fragments intermediate between ethylidyne and a dehydrogenated C_2 species".[48] This particular BE can arise from several, single and/or multiple bonds between C and Pt, more numerous than in the case of graphite and different from that of "Pt/atomic C" entities. The latter was more abundant after H_2 treatment. Its presence can point to (a) hydrogen forcing some C atoms from subsurface layers to the surface and/or (b) splitting up of a fraction of polymerized surface entities. This latter process may be important in regeneration and can lead to carbon removal as methane.[49]

Skeletal reactions of n-hexane reportedly require various active sites. They are ensembles of threefold symmetry for benzene formation,[50] two neighbouring atoms for C_5 ring closure and opening[51] while larger ensembles may possibly be active for fragmentation.[52] The importance of "ledge structures" (or five-coordinated "B_5 sites") as the active sites of C_5-cyclisation, isomerisation and single hydrogenolysis was also pointed out.[37] The selectivity of these four main reactions was roughly equal on samples **3** to **6**, the most active sample **4** showing the highest selectivity for C_6 saturated products, especially MCP (Table 2). The promoting effect of hydrogen in the gas phase[7,8,53] was explained in terms of much surface hydrogen favouring their not too deeply dehydrogenated intermediates.[54] In addition, hydrogen treatment enhanced the (220) and (311) reflections (*e.g.* in sample **6**). This can also contribute to the high isomerisation *and* hydrogenolysis selectivities,[55] since the so-called "B_5-sites", with (311) or (110) structure, reportedly favoured the related skeletal reactions: isomerization and single hydrogenolysis.[37] The almost constant benzene selectivity may point to the stability of three-atom ensembles[50] during reconstruction. They may possibly be in step or kink configuration.[3,55]

Surface (hydro)carbonaceous adsorbates ensured optimum conditions for nondegradative reactions.[56] This would explain the high and reproducible activity of sample **6**, even in the presence of 20–25% "invisible carbon".[57] The pronounced amount of disordered carbon (BE $\approx$ 284.1 eV) was most deleterious to all skeletal reactions. Dehydrogenation activity increased in carbonized catalysts. In addition, the treatment with n-hexane in the absence of hydrogen (sample **7**) resulted not only in the accumulation of much carbon but also in suppression of the (311) and (222) reflections. Thus, the *activity* of Pt black is governed not only by its purity but also by its restructuring under the effect of H_2.

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