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The surface state and catalytic properties of Pt black after O₂-H₂ cycles

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XPS and UPS of a Pt black catalyst after customary H₂-O₂ regeneration shows considerable amounts of residual C as well as surface OH/H₂O species. Surface C could not be removed even by O₂ at 800 K. Oxygenates are stable even after H₂ treatment up to 750 K. Their chemical state has been tentatively identified by comparing XPS and UPS results. Catalytic transformations of n-hexane on Pt black treated analogously is reported and the effect of surface species on catalytic properties discussed. Possible consequences of the presence of stable surface OH/H₂O species on H₂-O₂ titrations are mentioned.

Keywords: XPS of Pt black catalyst; UPS of Pt black catalyst; surface state of Pt black; catalytic properties of Pt black

1. Introduction

The surface of a Pt single crystal has been regarded to consist of three parts during hydrocarbon catalysis: clean Pt sites, Pt-C ensembles and fractions covered by three-dimensional (3-D) carbonaceous islands [1]. Catalytic activity has been attributed to the first two species. It has been claimed that really clean Pt sites catalyze hydrogenolysis only [2]; to obtain nondegradative products, it is necessary to add other components to it. This is in accordance with the customary industrial practice to pretreat Pt reforming catalysts after regeneration with oxygen by a “selective, controlled poisoning procedure with sulfur to reduce its initial hydrogenolysis activity” [3]. The accumulation of carbonaceous residues from hydrocarbon reactants [4] or the addition of another catalyst component (e.g., Re, Sn or Sb [4]) are alternative ways to suppress excessive degradative activity.

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A photoemission study has been performed in order to obtain direct information on the surface state and composition of a Pt black catalyst surface after various treatments with oxygen and/or hydrogen similar to those applied during catalyst regeneration. Our aim was to correlate those with catalytic results obtained after analogous treatments.

2. Experimental

2.1. APPARATUS AND PROCEDURE

Experimental details are reported separately [5,6]. The excitation sources were MgK_{α} (1253.6 eV) for XPS ($PE = 50$ eV) and HeI (21.2 eV) for UPS ($PE = 4$ eV); a Leybold EA-12 SCD energy analyzer was used. XPS spectra were smoothed and, after background subtraction, areas were integrated [5]. Difference spectra were obtained by direct subtraction of smoothed XP and unsmoothed UP spectra. A fwhm of 1.7 eV taken from a study on thin polymer layer studies was used for line fitting to the O 1s band [7]; similar polymer thin films studies [8] gave a fwhm of 1.3 eV for C 1s line fitting. A self-consistency approach was used producing sets of individual components with nearly identical BE maxima (see in detail, [5,6]).

2.2. SAMPLE PREPARATION AND PRETREATMENT

The powder sample was pressed *very gently* to cover the cavity of a stainless steel sample holder entirely; the latter was screwed to a manipulator rod. The temperature was measured inside the rod, a few mm below the sample itself [5,6].

All treatments followed each other in the given sequence in the preparation chamber of the UHV apparatus, with sample transfer to and from the measurement chamber without interim exposure to atmosphere. The same Pt black sample presintered *ex-situ* at 633 K and used for several runs of hydrocarbon reactions (**Pt/633**) was used [9]. Its spectra were recorded first in the "as received" state (**A**). Then a "standard regeneration" by static O_2 of 27 mbar for 3 min, evacuated for 5 min and contacted with static H_2 of 267 mbar for 10 min was applied (state **R**).

The following additional treatments were carried out subsequently:

- (i) repeating the standard 600 K regeneration 4 times;
- (ii) standard regeneration at 700 K;
- (iii) 267 mbar H_2 for 5 min at 600 K;
- (iv) 13 mbar oxygen treatment for 10 min at 850 K followed by a flashing in UHV at 900 K;
- (v) 133 mbar hydrogen treatment for 1 min at 750 K.

Table 1
Composition of Pt black after various treatments ^a

Sample and treatment	Composition, atom %			
	O	K	C	Pt
Pt/633, as received (“A”)	20	0.4	47	33
Pt/633, regenerated (“R”)	19	2	29	51
Pt/633-II, as received	22	1	46	31
Pt/ox, as received	26	–	26	48

^a As calculated from O 1s, K2p, C1s and Pt4f line intensities of XPS.

All XP and UP spectra were recorded at 300 K after cooling the sample within 10 minutes with simultaneous evacuation. Since UHV was not reached during this procedure, a likely readsorption (first of all, that of water as a product of $O_2 + H_2$ reaction) took place. UP spectrum (iii)/A was recorded at 600 K, immediately after hydrogen treatment. This spectrum was followed by another hydrogen treatment (267 mbar), and the sample cooled in hydrogen. Spectra denoted by (iii) were recorded after this procedure.

Measurements with an electron flood gun (to study inhomogeneous electrostatic charging) were carried out with the same sample, in the “as received” (A) state but at another occasion.

Two additional samples are also mentioned in this paper. Another portion of the same presintered batch (Pt/633-II) which has not undergone the above treatments in UHV was used in catalysis. XPS spectra of a Pt black covered with a PtO overlayer (Pt/ox) were also recorded, as a reference for PtO identification. Surface compositions of all three Pt samples (that of Pt/633 also after standard O_2-H_2 regeneration) are shown in table 1. K impurity originates from reduction in the presence of KOH.

2.3. HYDROCARBON CATALYSIS

A mixture of 10 Torr n-hexane and 120 Torr H_2 at 603 K was reacted in a glass static-circulation system [9] with the same catalyst sample as used previously in electron spectroscopy. All treatments corresponding to R as well as (i) to (v) were applied (three times) prior to each catalytic run, followed by standard regeneration (with O_2 , evacuation and H_2 , as described above) to remove carbonaceous deposits formed during catalysis.

n-Hexane reactions were also studied in a pulse-microcatalytic reactor [10], over Pt/633-II.

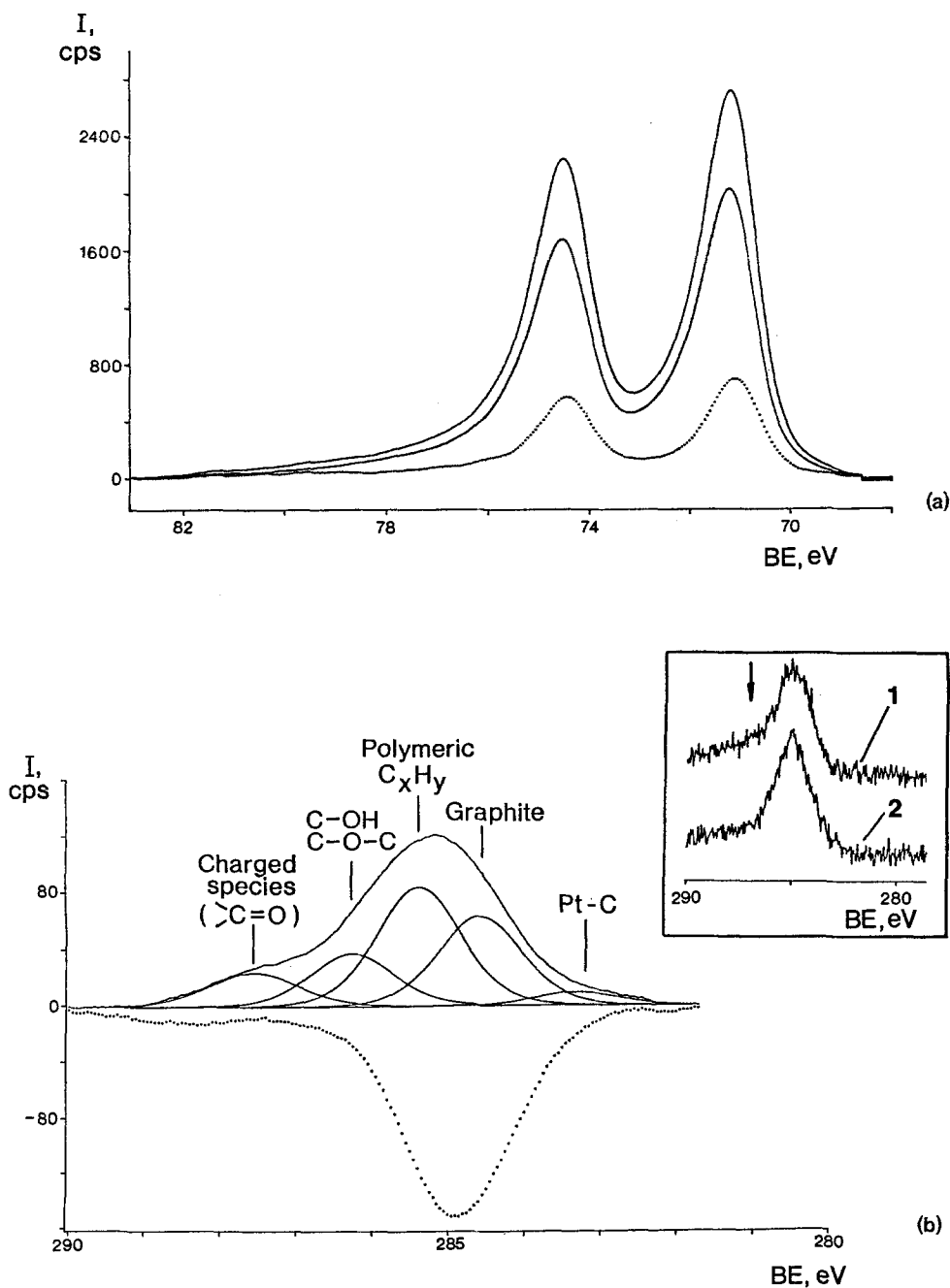


Fig. 1. XP Pt 4f (a), C 1s (b) and O 1s (c) spectra of a Pt black after standard regeneration (Pt/R), together with peak line fitting and identification of contributions of C 1s and O 1s. Difference spectra (R - A) are shown with dotted line in all three cases. Insets in panels b and c show spectra in the as received state without (curve 1) and with (curve 2) electron flood gun at 100 A. The high BE shoulder denoted by an arrow (charged species) disappears with flood gun.

3. Results and discussion

3.1. SURFACE ELECTRON SPECTROSCOPY

Fig. 1a shows that standard regeneration enhanced the intensity of the Pt 4f doublet without changing the position of the *BE* maxima at 71.1 and 74.4 eV, those values being in fair agreement with literature results [12,13]. This indicates the removal of overlayers *shielding* the metallic fraction from photoelectron spectroscopy. These impurities were, however, in *no chemical interaction* with Pt: the *BE* maxima in the difference spectrum ($R - A$) agree with those of pure Pt.

The decomposition of the C1s (fig. 1b) and O1s (fig. 1c) region into individual line components offers a semiquantitative information of the likely chemical character of those species. Individual lines arise from signals of related chemical species lumped together [6]. Thus, "graphite" means carbon signals from sp^2 carbon atoms while " C_xH_y hydrocarbon polymer" summarizes those from sp^3 C atoms. These two species prevail; in addition, some oxidized and charged carbon species and minor amounts of Pt-carbide are also detected. The difference spectrum ($R - A$) indicates that regeneration removed mainly polymeric C and, to lesser extent, graphite; the differences of about 10 cps in the oxidized carbon region are already in the range of experimental error, due to background noise.

The line fitting of O1s (fig. 1c) points to the presence of surface OH and water [13], various oxidized carbon [8,14] and also "charged" species which may

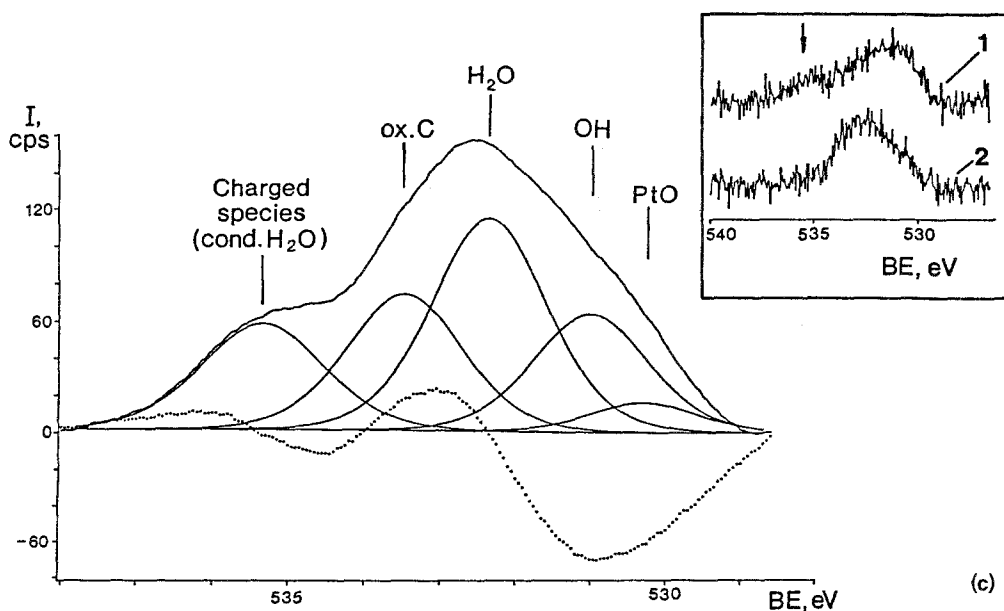


Fig. 1. (continued).

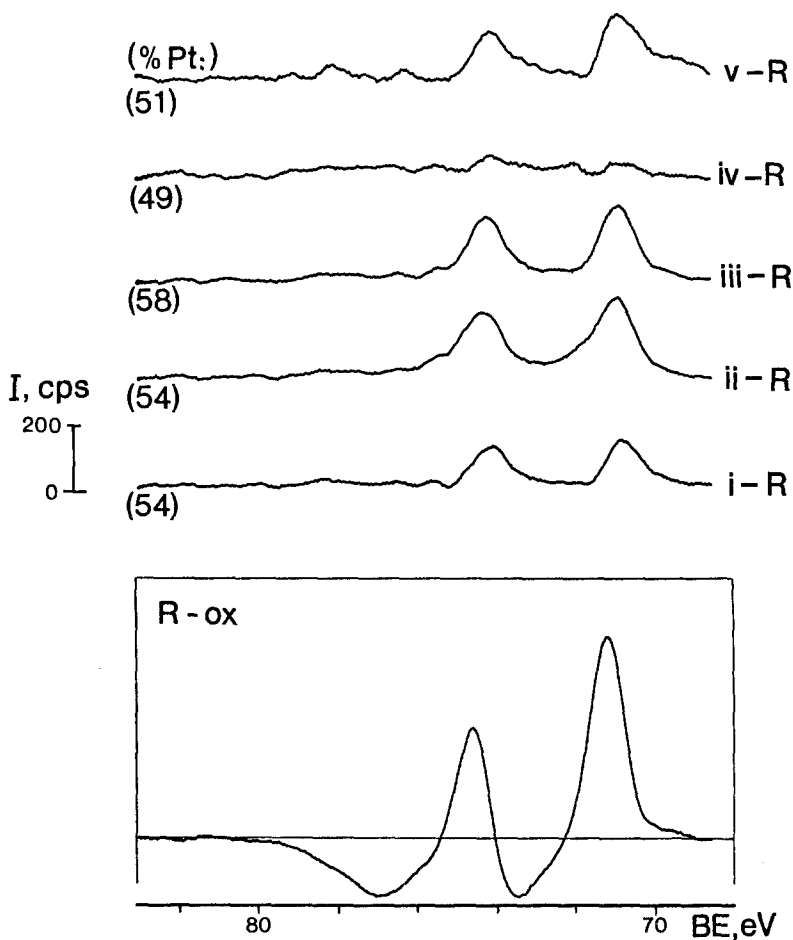


Fig. 2. Pt 4f XP difference spectra after treatments (i) to (v) with respect to the standard treatment ((i)-R to (v)-R). The per cent Pt contents after each treatment are shown in brackets. The framed bottom panel shows difference spectra between regenerated state and another, oxidized Pt ("R-ox").

include some water adsorbed on contiguous carbon islands [15]. The difference spectrum (**R** - **A**) shows that regeneration decreases considerably the amount of Pt-oxide and surface OH, while increases the amount of oxidized C. The effects in the band edge regions (above *BE* 534 eV) are in the error range here, too.

The presence of inhomogeneous electrostatic charging was evidenced by special flood gun experiments which removed most of the high *BE* shoulder of O 1s (and, to a lesser extent, that of C 1s), the total oxygen and carbon percentage remaining almost unchanged. The insets in figs. 1b and c indicate somewhat more charged oxygen species than carbon. This supports the theory on adsorbed water islands.

The effect of treatments (i) to (v) is demonstrated by XP (figs. 2-4) and UP (fig. 5) difference spectra produced by subtracting **R** from (i), (ii), (iii), (iv) and

(v). The respective per cent Pt, C and O surface contents are shown on each curve (the remainder being up to 2% K). Various treatment changed the surface composition rather insignificantly, the amount of carbon decreasing, those of Pt and surface O increasing as compared with the values shown in table 1.

The Pt 4f intensity (fig. 2) increased uniformly along the doublet region, the peaks above 75–76 eV being again due to noise. Various Pt oxides would shift the *BE* maxima by 1.5 to 4 eV towards higher energies [11]. The lowest framed panel shows a difference spectrum of the Pt black in state **R** minus the spectrum of the oxidized reference Pt sample (**R** – **ox**). The Pt⁰ bands of **Pt/R** are much more intense; the presence of (likely Pt²⁺) in **Pt/ox** is demonstrated by the negative peaks in the 72–74 and 75.5–79 eV region. No analogous intensity loss or gain can be identified in any of the other difference spectra, indicating that the uptake of O gave rise no detectable Pt oxidation.

Not all components of surface oxygen increased uniformly with increasing total oxygen content (fig. 3). Treatment (i) added mainly to surface water. The increase of the intensity of bands of PtO and OH groups was more pronounced after treatment (ii). Hydrogen at 600 K (iii) enhanced the intensity of O signal although one would expect surface reduction by hydrogen. Similar phenomenon was reported with Pd black: sorbed hydrogen atoms diffusing into subsurface positions “pushed” dissolved O atoms to the surface where they were detected by UPS [16]. The same took place upon hydrogen treatment at 750 K (v). The H₂O band intensity was also higher in both cases. The OH intensity was also enhanced by treatment (v). The most dramatic increase of spectral features belonging to Pt-oxide and OH groups were seen after O₂ at 850 K (iv).

The framed lowest panel in fig. 3 shows the O 1s region of the difference spectrum **R** – **ox**. This exhibits very pronounced excess of Pt-O and Pt-OH in **Pt/ox**. The intensities of surface water and oxidized C species, in turn, were higher on **Pt/R**. As opposed to the unchanged Pt 4f region, small PtO intensity losses ((ii), (iii), (v)) and gains ((i), (iv)) are seen in the O 1s band. This clearly demonstrates the formation and decomposition of small amounts PtO during various oxidative treatments. The sensitivity of its detection is higher in the O 1s than in the Pt 4f region [6] where the inherent asymmetry of the Pt band [17] suppresses minor changes.

All treatments removed first of all *polymeric* carbon, together with some graphite (fig. 4). Various oxidized carbon species were rather resistant but some of them is removed by O₂ at 800 K (iv).

Sections of corresponding He I UP difference spectra are seen in fig. 5. All spectra exhibit features at *BE* values around 5–5.5 eV attributed to water and/or OH groups attached to Pt/K entities [13]. A second, broad band at around 7.5 eV may be attributed to OH/H₂O species interacting with pure Pt species [11] containing also the other band of OH on Pt/K, one band of adsorbed O and any C-derived orbitals. Detailed spectrum evaluation has been given in another paper [6]. In addition, broad bands appear at or above 10 eV

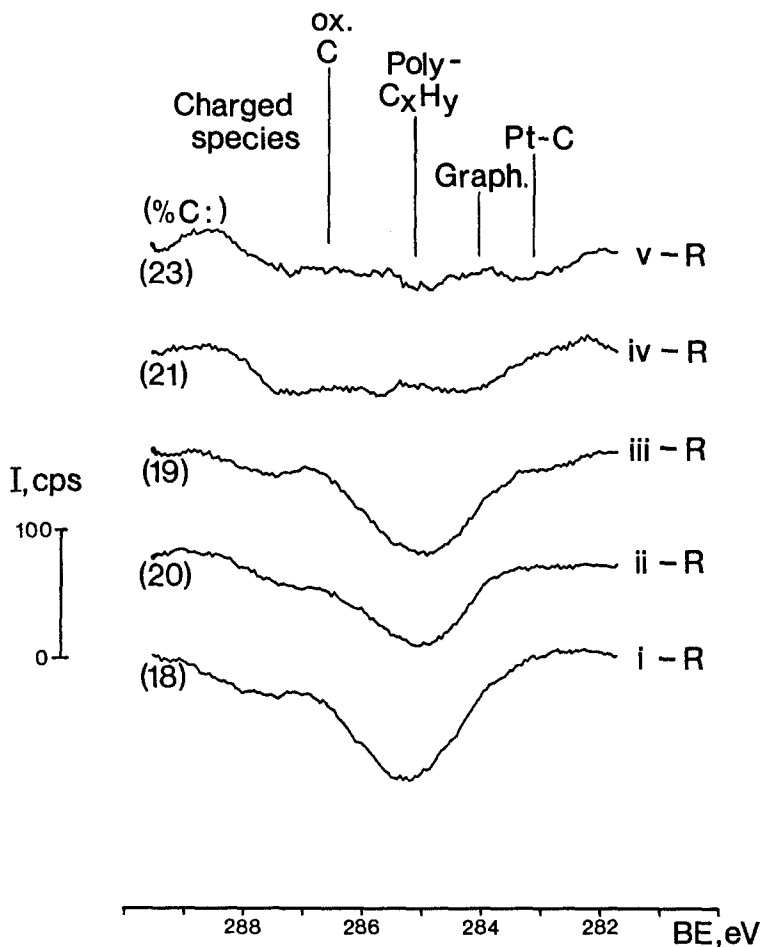


Fig. 3. C 1s XP difference spectra ((i)–R to (v)–R), together with the per cent C content (in brackets on each curve).

(sometimes overlapping with the secondary electron background) that can be attributed to oxygen atoms and one molecular orbital from water/OH. Possible C-derived orbitals (if any) cannot be identified, partly due to their weak cross sections in He I and their overlap with OH, partly due to the three-dimensional character of the carbonaceous overlayer [6] which shields the Pt-C bands from detection. Very weak carbon signals were reported for a residual carbonaceous overlayer after annealing adsorbed aromatic adlayers [18]. Individual UP spectral features have their counterparts in the O 1s XP spectral region (compare figs. 3 and 5). An intense H₂O XPS signal (treatment (i)) is concomitant with a broad UPS feature arising from overlayer-like adspecies. Increased OH signals after (ii), in turn, correspond to sharp UPS features arising from well-separated surface entities. The very intense UPS bands at BE 4.5 and 6 eV after treatment (iv) can be attributed to O⁻ and mixed OH/O₂⁻ species [6] and these are

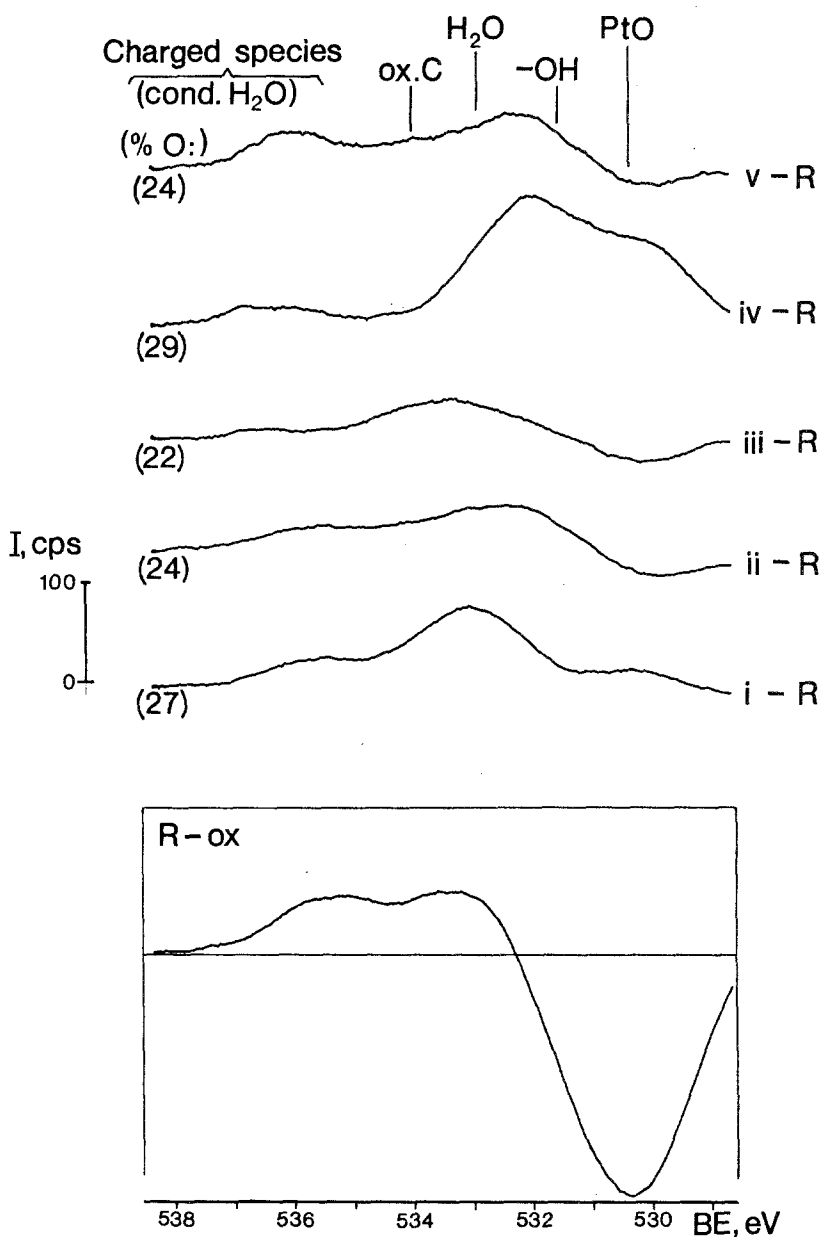


Fig. 4. O 1s XP difference spectra ((i)–R to (v)–R) together with the per cent O content (in brackets on each curve). The bottom panel shows R–ox, as in fig. 2.

concomitant with the increase of the PtO and also PtOH contribution in XPS. These species transform into OH/H₂O ones after treatment (v). The spectrum measured at 600 K ((iii)/A) indicates that features similar to those measured at 300 K are present at this temperature, too, hence their appearance is *not* due to readsorption during cooling. The “hydrogen-induced feature” at BE 3.5 eV

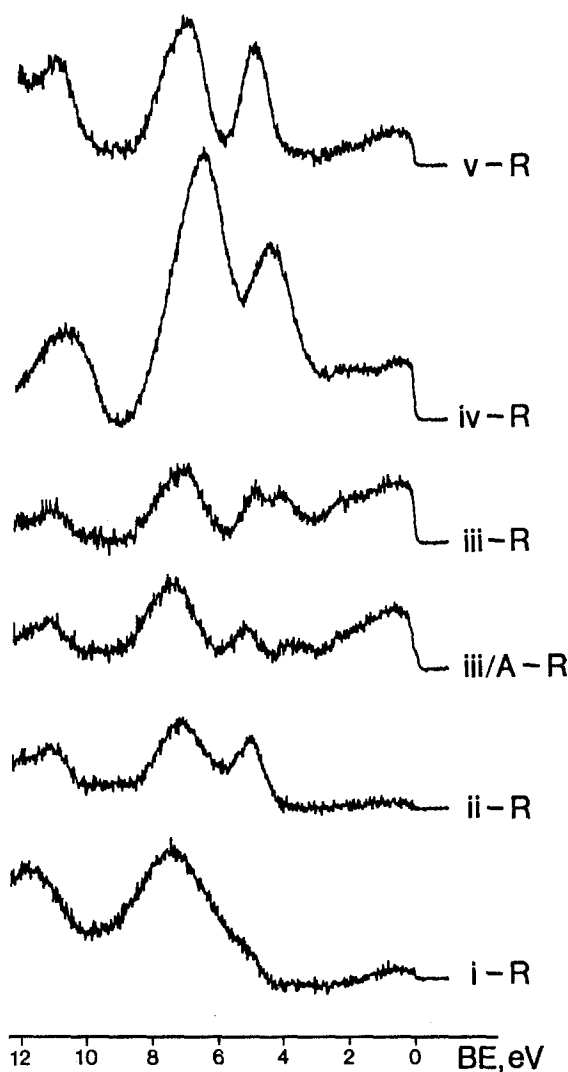


Fig. 5. Low BE sections of UP He difference spectra of Pt black subjected to various O_2 - H_2 cycles, related to the spectrum of standard regeneration ((i)-R to (v)-R). Curve (iii)/A was measured at 600 K, immediately after hydrogen treatment.

becomes more intense after cooling in hydrogen (cf. spectra (iii)/A and (ii)) and may be attributed to surface rearrangement [19].

The key feature in the UP spectra is the *increase in Fermi-edge (E_F) intensity* (treatments (iii) to (v)) pointing to an increase in metallic character of the surface layer of the polycrystalline catalyst upon regeneration with O_2 and H_2 , in spite of the relatively weak effect of the treatments on overall surface composition. One of the main messages of these measurements for catalysis is that the surface of Pt black after customary regenerations consists of predomi-

nantly *metallic platinum* (as far as the electronic state is concerned), but this catalyst is not a *clean platinum* (meaning the absence of other atoms).

The other main message of the paper is that – in spite of general belief – *oxygen does not remove carbon and hydrogen treatment does not remove surface oxygen* entirely. Considerable amounts of surface species (mainly three-dimensional carbon islands) can be assumed which are not in chemical interaction with Pt. Carbon agglomeration contributes to exposing a higher fraction of Pt metal and to the increase of the Fermi-edge intensity. The metallic fraction of the surface which is considered to be active in hydrocarbon reactions [1] *contains OH and H₂O even after high temperature hydrogen treatment*. The presence of K as “anchoring” centers for these oxygenates may be important.

3.2. CATALYTIC n-HEXANE TRANSFORMATIONS

The results discussed so far mean that a hydrocarbon reactant meets a Pt surface containing clean Pt atoms as well as *certain amounts of surface oxygenates*. The question arises how these species influence catalytic properties. Single crystal Pt [1] and Pt black [20] pretreated by oxygen have been reported to show enhanced fragmentation selectivity. Also the selectivity of methane formation from n-hexane on Pt/SiO₂ approached 100% with a few seconds of contact time [21]. The same could also be observed with Pt black [6]. The question can be put this way: are surface oxygenates responsible for the high fragmentation activity reported in the introduction (being thus the species that have to be replaced by controlled poisoning)? Alternatively, can this high hydrogenolysis activity be attributed to *clean* (or, rather, hydrogen saturated) catalyst surfaces [2]?

The catalytic activity of Pt / 633 has been probed after analogous treatments as carried out during surface analysis. Contact with hydrocarbons between treatments produced, of course, surfaces different from those studied in UHV; nevertheless, the differences between catalytic properties observed after each treatment were fairly reproducible.

Selectivities with short contact times (table 2A) may supply information on the prevailing reaction pathway(s) of the fresh catalyst. All treatments of the present Pt black resulted in mostly hydrogenolysis products, together with *hexene isomers, skeletal isomers, methylcyclopentane* and also some *benzene*. The differences observed upon various pretreatments in overall activities and selectivities were within a factor of two. Another set of experiments could produce still higher initial hexene selectivities (up to 70%), with hydrogenolysis selectivities decreasing no further than 30%. Thus, an inherent primary hydrogenolytic *and* dehydrogenation property can be attributed to this Pt black catalyst.

In longer runs (table 2B) hydrogenolysis selectivity increased only slightly. The selectivities of nondegradative products showed a much more pronounced increase, at the expense of olefins. Although in some cases also a primary

Table 2
Initial (A) and steady-state (B) selectivity of n-hexane reaction over Pt black ^a

Treatment	Conv., %	Selectivity, %				
		< C ₆	Isomer	MCP ^b	Olefin	Bz ^b
<i>A. Time-on-stream, 1.5 min.</i>						
R	0.9	39	21	15	11	14
(i)	1.3	38	19	10	23	10
(ii)	0.9	30	23	10	28	9
(iii)	0.8	32	23	13	29	8
(iv)	1.0	38	19	9	26	14
(v)	1.2	33	22	9	28	8
<i>B. Time-on-stream, 25 min.</i>						
R	5.2	40	21	15	11	14
(i)	5.7	41	21	16	7	16
(ii)	4.4	36	25	15	10	14
(iii)	3.6	37	24	13	14	12
(iv)	4.2	42	21	13	10	14
(v)	4.4	40	24	12	11	13

^a Catalyst, 28 mg Pt/633; static/circulation system, *p*(n-hexane): *p*(H₂) = 10:120 Torr.

^b MCP = methylcyclopentane; Bz = benzene.

isomerization activity (like with Pt/SiO₂ [21]) seems likely, C₆ saturated products and also benzene, can be and are actually formed from hexenes which are simultaneously consumed.

The relative amount of hydrogenolysis products was highest when surface spectroscopy following an analogous treatment indicated highest oxygen content (treatments (i) and (iv)), although the nearly 100% fragmentation activity observed with Pt/SiO₂ [21] has never been reached (like also in [2]). Highest overall activity and highest initial aromatization selectivity was observed in those cases, too. Thus, we can state tentatively that oxygenates attached to clean Pt surface (in particular, those being present as water and/or surface O) are, indeed favorable for hydrogenolysis. The *direct* participation of oxygenates in this reaction is not proven; it is not excluded that the oxygenates present prevent accumulation of deactivating coke precursors on the active sites. The amount of carbon was also lowest after those treatments. At the same time, high temperature hydrogen treatment (v) produced rather inactive catalysts as reported also earlier [22]. The lower activity observed after H₂ treatment at 600 K (iii) is different from that work, although UP spectra indicate similar surface states in these two cases. All the differences mentioned are not dramatic and the correlation is not strict (cf. the high activity of state R).

Excessive methane formation with shorter contact times (about 1.5 seconds [10]) were obtained in pulse experiments over Pt/633-II (table 3). In the case of that catalyst containing initially also some PtO, a lengthy exposure of the

Table 3
Selectivity of n-hexane reaction over Pt black ^a

Pulse No	Conv., %	Selectivity, %			
		CH ₄	C ₂ -C ₅	C ₆ sat. ^b	O1 ^c
I	0.9	32	63	4	1
II	0.3	23	44	31.5	2.5
III	0.2	25	47	25.5	4.5

^a Catalyst, 40 mg Pt/633-II. Pretreatment, 0.5 h H₂ at 600 K, reaction: 1 μl pulses of n-hexane into 30 ml min⁻¹ H₂.

^b Isomers (2- and 3-methylpentane) plus methylcyclopentane.

^c O1 = n-hexene isomers. No benzene formation was observed.

catalyst to the hydrogen carrier gas prior to reaction must have reduced that phase and, by doing so, influenced the results.

The coexistence of OH/H₂O and hydrogen on a *metallic platinum surface* may shed new light on metal surface characterization by H₂/O₂ chemisorption and titration [23,24]. The present discovery may help find a reasonable explanation for “conflicting surface stoichiometries” (depending on the temperature of pretreatment, gas pressure, number of cycles etc. [25]). Our findings contradict to the earlier conclusion that on unsupported Pt “the water formed in the reaction of hydrogen with adsorbed oxygen leaves the surface at room temperature” [23]; at the same time, it may be valid that water does not interfere with the adsorption of hydrogen [23]. The possible presence of Pt(OH)_{surf} (proven by the present results) has been postulated without drawing further conclusions. Further studies are required to clarify the consequences on titration stoichiometries.

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Note added in proof

The excessive hydrogenolysis activity with predominant methane production of a Pt foil containing oxygen as a consequence of an O₂ treatment at 773 K was described in the still unpublished thesis of F. Luck (Thèse d'Etat, University of Strasbourg, 1983). Thanks are due to Prof. G. Maire for this information.

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