Surface composition and possible rearrangement of disperse Pt and Rh catalysts: does the presence of carbon and oxygen contribute to different catalytic properties?

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The surface composition of Rh and Pt blacks (as determined by XPS) shows carbon and oxygen impurities in the untreated state. Oxygen on Pt is present as adsorbed O as well as OH/H_2O groups and oxidized carbon. Rh was partly oxidized to Rh_2O_3, in agreement with UPS showing hardly any Fermi-edge intensity in untreated Rh as opposed to untreated Pt. High Fermi-edge intensities indicated a predominant metallic surface after an *in situ* treatment with H_2 at 483 K, increasing the purity (XPS) to $\sim$90%. This treatment reduced Rh to metal and removed its C impurity. Pt, in turn, retained much carbon after H_2 treatment, present mainly as graphitic carbon. A minor amount of CO was also detected, some of the O 1s peak belonging to it. The two metals were tested in methylcyclopentane reactions. Considering the necessity of carbon for nondegradative reactions and oxygen enhancing fragmentation, a correlation is suggested between the typical impurities of Pt and Rh and their respective catalytic propensities: the high fragmentation activity of Rh and the predominant nondegradative reactions to C_6 "ring opening products" on Pt.

Keywords: rhodium black, platinum black, surface carbon, surface oxygen, methylcyclopentane

1. Introduction

The presence of carbonaceous entities has been shown to be the normal state of Pt catalysts during "skeletal" hydrocarbon reactions [1]. Somorjai and associates [1–3] distinguished three-dimensional (3D) carbonaceous polymers, individual C atoms attached to Pt atoms and attributed catalytic activity to clean Pt islands. Residual carbon on Pt black was not negligible even after customary "regeneration" with O_2 and H_2 [4]. This "chemical" regeneration produced a cleaner surface on polycrystalline foil than mere ion sputtering [4].

Counter claims have appeared concerning the form, amount and chemical state of this carbon. Webb [5] defined them as "hydrocarbonaceous deposits" indicating their character being different from "coke". Sárkány [6,7] defined Pt catalysts in their steady-state activity as "Pt–C–H" systems containing up to two C atoms per surface Pt (Pt_s). This could be hydrogenated off after reacting n-hexane. When this hydrogen flushing occurred prior to surface analysis it removed most of the chemisorbed hydrocarbons from Pt single crystals [8]. Nevertheless, photoelectron spectroscopy could provide information on the state of carbon. It was present after hydrocarbon reactions mainly as graphite and C_xH_y polymers – together with some oxygenated C species [4,9]. This may correspond to carbon in the form of 3D deposits blocking a part of the surface and leaving a sufficient fraction free and intact for catalytic reactions. "Residual C" after regeneration with O_2 and/or H_2 can be regarded as "harmless" or "invisible" carbon [10]. It contained, in turn, much "Pt/C" entities, very likely, as chemisorbed C and/or CH_x species [11]. Since this regeneration fully and reproducibly restored the activity of Pt [12] we identify these "individual C atoms" to the "C–H" entities necessary for steady-state activity in nondegradative reactions [6,7]. They may also migrate between surface and subsurface regions [13]. Indeed, the intensity of the "Pt/C" region of the C 1s peak was higher when the spectrum was measured at 603 K [14]. Their reappearance on the surface could be the first step of graphite formation [15].

Both Pt and Rh were shown to form CHM_3 surface entities after C–C bond breaking [16]. When approaching this problem, we considered the concept of "flexible surfaces" [1,17,18]. It predicts that disperse catalysts should have a more flexible surface, thus may represent a better model for real-world disperse catalysts. Electron microscopy [12] showed that our Pt black consisted of aggregates of small metal particles, becoming rounded during hydrogen treatment and/or hydrocarbon reactions, exposing thus various high-Miller-index surfaces. Adsorbate-induced surface reconstruction occurred on both Pt and Rh single crystal surfaces in the presence of ethylidyne even in near-to-monolayer amounts [16,19]. Hydrogen induced reconstruction even at low pressure with a stepped single crystal [20]. This was very pronounced with Pt(110) under the effect of O_2, H_2, and CO adsorbed at 1 bar pressure [21].

Platinum is widely applied as a catalyst for skeletal rearrangement reactions of $>C_6$ hydrocarbons such as aromatization, C_5 cyclization, isomerization, hydrogenolysis. Pure platinum showed a rather strong hydrogenolysis abil-

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ity [22]. It was lost rapidly parallel with the accumulation of “C–H” entities [6,7]. Rh is also able to catalyze analogous transformations but (i) its activity manifests itself at much lower temperatures and (ii) has a much higher tendency to promote hydrogenolysis rather than nondegradative transformations [23,24]. It preserved its high fragmentation activity during long runs, resulting mainly in “single” rather than “multiple” splitting [25]. The basic difference must lie in the different electronic structures of the two metals. One may wonder how the different amounts and states of impurities on Pt and Rh contribute to these differences. We report here a study on the surface composition of Pt and Rh after analogous treatments to monitor typical impurities and their possible role in different catalytic activities of those two metals.

2. Experimental

2.1. Catalysts

Pt black was reduced from the aqueous solution of H_2PtCl_6 by hydrazine at ca. 313 K [12] and pre-sintered in H_2 at 473 K [26]. The aqueous solution of $RhCl_3$ was reduced with HCHO in the presence of KOH [27]. Its K content was removed by washing it with diluted HNO_3, the nitric acid residues were removed by aqueous hydrazine solution at 333 K.

2.2. Electron spectroscopy

Details of electron spectroscopy have been reported earlier [4,11,28]. A Leybold LHS 12 MCD instrument was used, XPS used a Mg K_α anode, and the measurements took place in the pass energy (PE) mode (PE = 48 eV). The peaks were evaluated after satellite subtraction and Shirley background subtraction. Atomic compositions were determined from peak areas with literature sensitivity factors [29] using the homogeneous composition model. Difference spectra were obtained either by direct subtraction or after normalizing the intensities at an appropriate BE value [30]. UPS spectra were excited by He II radiation (40.8 eV), PE = 12 eV.

Dry powder samples were placed on a stainless-steel sample holder [28]. These were exposed to various gases (O_2, H_2) up to several mbar pressure in a preparation chamber and the subsequent spectra were measured without contacting the samples with the atmosphere. The XPS binding energy (BE) was calibrated to the Au $4f_{7/2}$ line (BE = 84.0 eV). Pt and Rh samples were investigated (1) as untreated samples and (2) after their treatment with 270 mbar H_2 at 483 K in the preparation chamber of the photoelectron spectrometer without exposing it to surrounding air. A survey spectrum was measured for each sample revealing the elements present. Thus, O 1s, C 1s as well as the respective Pt 4f and Rh 3d regions were monitored. Literature binding energy values were used [29], together with some values for different chemical states summarized for Pt [4] and Rh [31,32].

2.3. Catalytic reactions

Methylcyclopentane (MCP) at 13 mbar pressure was reacted in excess hydrogen in a closed-loop reactor [12,24] on pre-hydrogenated Rh and Pt black catalysts. A CP-Sil 5 capillary GC column was used for product analysis; it separated products with similar retention times such as cyclopentane and 2-methylpentane.

3. Results

3.1. Electron spectroscopy

The UP spectrum of the untreated Rh (figure 1) exhibited very low Fermi edge indicating that its state was far from being clean metal. Hydrogen treatment, in turn, produced spectra quasi-identical to those reported for clean metallic Rh [33,34]. The Fermi edge of untreated Pt pointed to the presence of metallic Pt^0 (figure 1); H_2 treatment produced a spectrum corresponding to almost pure Pt [35,36]. The He II difference spectrum (Pt(untreated) − Pt(H_2)) showed excess of carbonaceous overlayer (broad, centered at ca. 7.7 eV), some O (5 eV and higher) as well as CO (ca. 9 and 11 eV) in the untreated sample. Hydrogen removed CO from Pt but its appearance on Rh can be the

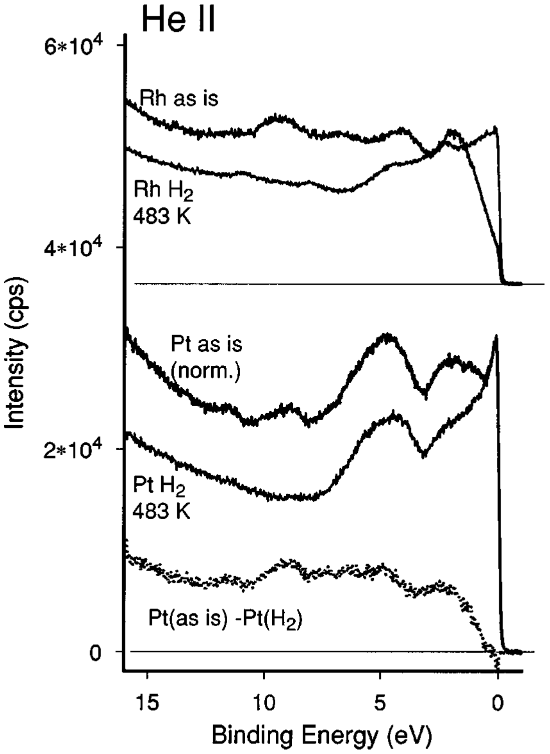

Figure 1. He II UP spectrum of Pt and Rh black in the “as received” state and after H_2 treatment at 483 K. In the case of Pt, the difference spectrum (Pt(untreated) − Pt(H_2)) is also shown, after normalizing the spectrum intensity to each other at the middle of the Fermi edge.

result of a reaction between surface C and O atoms [37]. A similar reaction was reported with Ag, but with the participation of subsurface O atoms [38].

Considerable oxygen and carbon contributions appeared in the XP spectra of untreated samples. Freshly reduced Rh retained some nitrogen component from nitric acid and hydrazine treatment which became minor after reduction. Both the O 1s and C 1s regions were subjected to line fitting in a way described earlier [4,28]. The program had to find the maximum BE values of individual components using fixed fwhm values and Gaussian–Lorentzian ratios. Figures 2–5 illustrate the self-consistency of this method: the components showed similar maximum BE values for several independent spectra.

A considerable contribution could be seen in the O 1s spectrum at ~530 eV corresponding to oxygen in direct bonding to metal (figure 2). Tolia et al. [32] attributed it to Rh_2O_3. They also found another component at ~531.7 eV that they ascribed to RhOOH or surface Rh oxide. This component appeared in our fitting procedure at ~531.3 eV. This corresponds to surface OH and/or H_2O for Pt [4,14,39] and this can be true for Rh, too. Tolia et al. tentatively assigned the third component at >532 eV to Si oxide impurity [32] or to subsurface oxygen. Due to the presence of oxidized C components (see below), it may also correspond to O bound to carbonaceous species. Pt contained similar O 1s components. Hydrogen treatment removed most of Rh_2O_3 leaving behind some "RhOOH" and about a half of the original component at highest BE (figure 3), in agreement with the possibility of reducing Rh almost completely at around 483 K [31,32]. Still, the O 1s peak on reduced Rh was much more intense than that on Pt, the latter retaining just a small component at BE ≈ 532.5 eV (figure 3).

The C 1s spectra (figure 4) could be fitted well by lines corresponding to atomically dispersed C on the metals (surface or subsurface entities) at 283–283.5 eV whereas the main body of carbon consisted of graphitic and polymeric carbon [4,28,40]. Some oxidized C (containing both C–O and C=O bonds) was also present; its abundance was higher on Pt. Hydrogen treatment left the C 1s intensity on Pt almost intact (figure 5), reduced much oxygenated carbon and increased the abundance of graphite. The graphite component corresponded to 3.5% of the whole surface in untreated Pt (figure 4), increasing to 4.8% after H_2 treatment (figure 5). The presence of hydrogen promoted the graphitization of surface polymers formed initially on Pt [15,19]. One of the most conspicuous features of H_2 treatment at 483 K was the removal of almost all carbon from Rh surface leaving a little graphite behind (figure 5).

The comparison of the Pt 4f and Rh 3d peaks corroborated the information supplied by the O 1s region. The difference spectra between reduced and untreated Rh black (figure 6) showed a rather large peak with BE shifted by ~1.3 eV. This agreed well with the BE value assigned to Rh_2O_3 [29,31,32]. An analogous difference spectrum ($Pt(H_2) - Pt(untreated)$) (figure 7) exhibited a much smaller

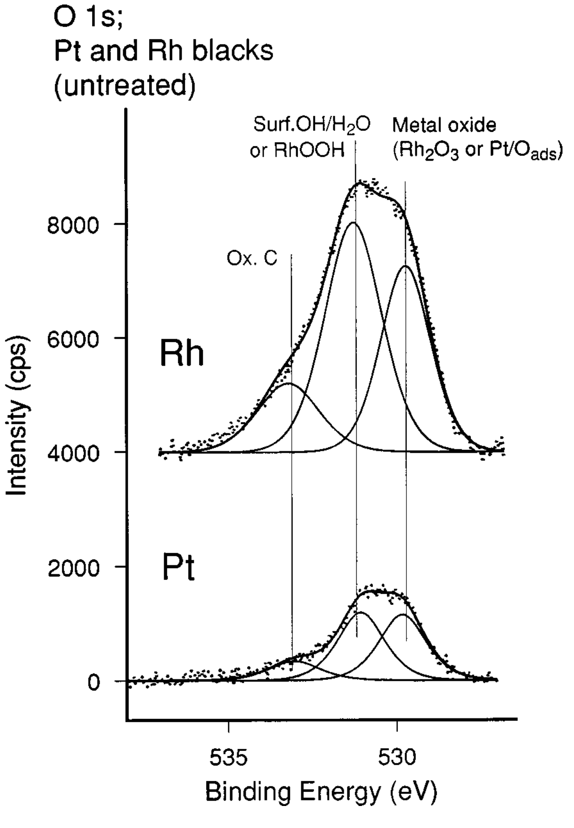

Figure 2. O 1s region of Pt and Rh black in the "as received" state. Oxygen: 20% in Rh and 13% in Pt.

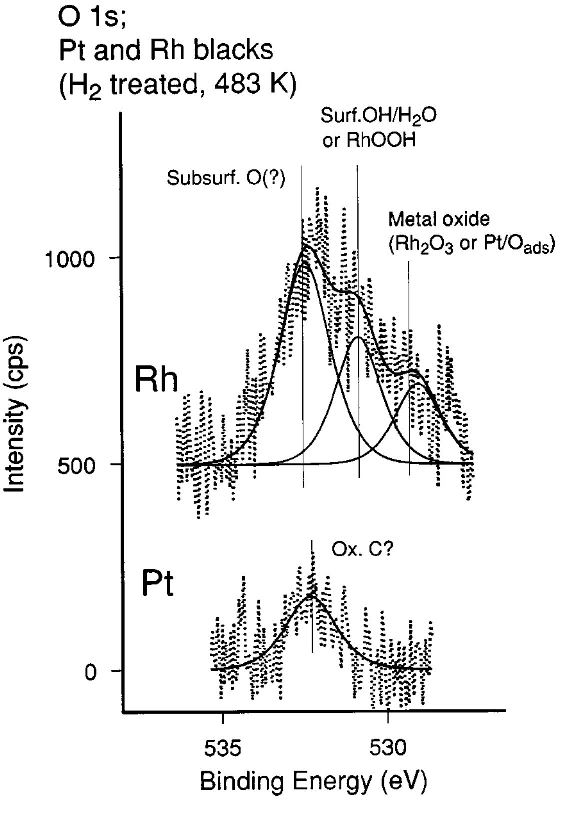

Figure 3. O 1s region of Pt and Rh black after H_2 treatment at 483 K. Oxygen: 5.5% in Rh and 0.3% in Pt.

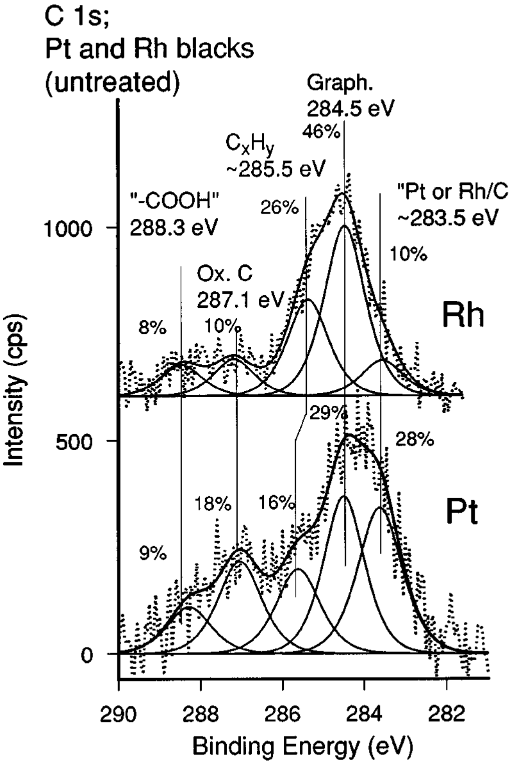

Figure 4. C 1s region of Pt and Rh black in the "as received" state. Carbon: 16% in Rh and 12% in Pt. The abundances of individual carbon components are shown on the fitted spectra.

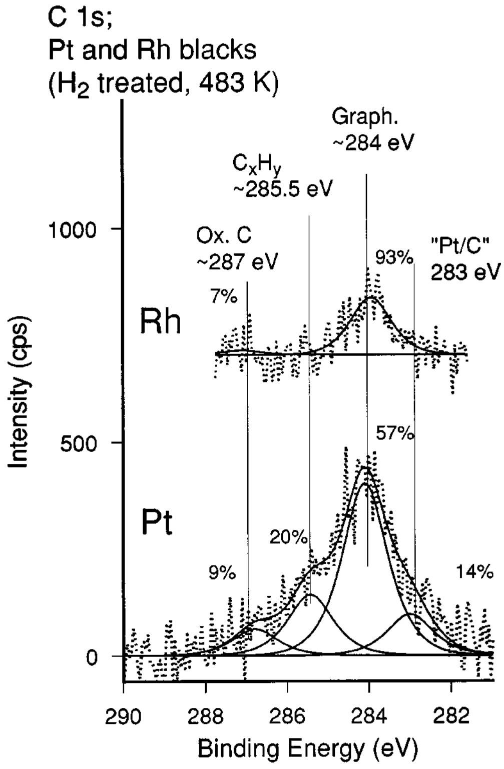

Figure 5. C 1s region of Pt and Rh black after H_2 treatment at 483 K. Carbon: 1.5% in Rh and 8.5% in Pt. The abundances of individual carbon components are shown on the fitted spectra.

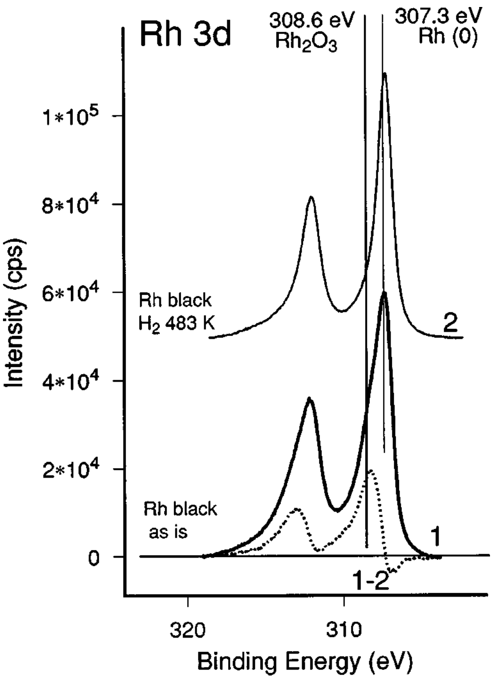

Figure 6. Rh 3d region of Rh black in the "as received" state and after H_2 treatment at 483 K. The "as received" spectrum was normalized to that of the reduced Rh black. Rhodium: 50% in the "as received" state and 92% after H_2 treatment.

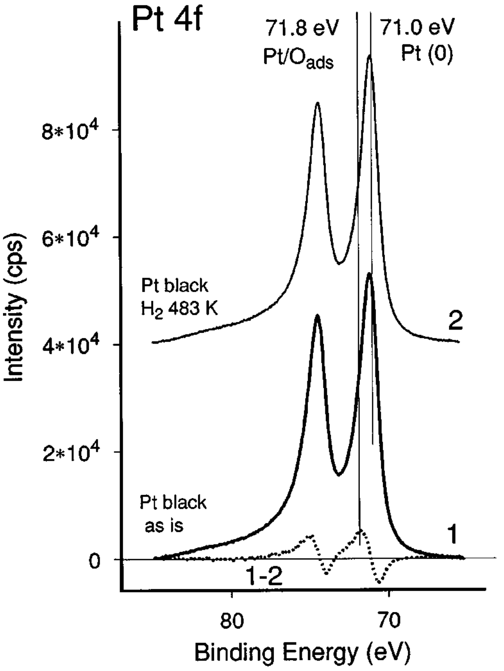

Figure 7. Pt 4f region of Pt black in the "as received" state and after H_2 treatment at 483 K. The "as received" spectrum was normalized to that of the reduced Pt black. Platinum: 64% in the "as received" state and 92% after H_2 treatment.

peak shifted by ~0.8 eV to higher BE values, corresponding to Pt with adsorbed O [7,41]. These results are in good agreement with the UPS information. The much higher C content of Pt did not seem to have been in electronic interaction with the clean metal. Keeping the samples in UHV for up to 12 h removed about 60% of the oxidized Rh component whereas the same procedure left practically no adsorbed O on Pt.

Considering the above facts, we may assume that a reduced Rh – the state of which corresponds to that applied in alkane transformation reactions carried out in excess hydrogen – still contained some oxygen but hardly any carbon. Oxygen could be removed almost entirely from Pt, but a mere reduction was not sufficient to remove carbon from its surface. It brought about, however, a marked change in the predominant chemical state of carbonaceous deposits: the abundance of the graphitic component increased at the expense of the higher BE components. An oxidative regeneration applied usually to regenerate the catalysts after alkane reactions would leave less carbon on the surface [11,13]. UPS showed the presence of metallic Pt and Rh surfaces after H_2 treatment (figure 1).

3.2. Catalytic tests

As for the catalytic activities of these metals, at comparable conversion values, the ratio $<C_7/C_7$ from n-heptane was $\sim$13 on Rh and $\sim$0.4 on Pt [23]. Similarly, the ratio $<C_6/C_6$ from 3-methylpentane was $\sim$0.2 on Pt and $\sim$45 on Rh black [25]. More C_6 alkanes were formed from MCP [24], but the difference was still there at comparable conversions: $<C_6/C_6 \approx 1.5$ on Rh and 0.03 on Pt [25]. Neopentane formed no isopentane on Rh (except for a sample heated in H_2 up to 1173 K) as opposed to Pt [42].

The test reactions of MCP transformation on the present Pt and Rh samples confirmed these expectations (table 1). Comparable conversion values were obtained at different temperatures with Pt and Rh black. The selectivities showed, however, considerable differences: Pt formed hardly any fragments but the selectivity of $<C_6$ products was remarkable on Rh, even at much lower temperature. Ring opening to C_6 alkanes occurred in a "selective" way [43], the rupture of the C–C bond near to the methyl group (resulting in n-hexane) being hindered. The values of the nH/2MP ratio was not dramatically different on these two metals. The ratio 2MP/3MP (which should be 2 in the case of random bond rupture) showed larger differences: 3MP was preferred on Rh and 2MP on Pt.

Fragment composition could not be evaluated with the fragment selectivities being $<1\%$ on Pt. The fragment distribution on Rh (table 2) showed a predominance of methane, with isopentane as the second most abundant product. This could be formed from splitting another methane from the most abundant ring opening products: methylpentanes. Higher temperatures were favorable for formation of smaller fragments, including also C_2–C_4 alkanes. The products of "single splitting" of C_6 alkanes were still present at the highest temperature, thus the complete decomposition to methane did not occur on Rh. Demethylation to cyclopentane was minor and almost disappeared at higher temperature.

Table 1
Typical reactions of methylcyclopentane (MCP) on Rh and Pt black catalysts.[a]

	Catalyst						
	Rh black (3 mg)				Pt black (20 mg)		
	423 K	443 K	463 K	483 K[b]	523 K	538 K	553 K
Conversion (%)	10.3	14.8	13.5	30	6.1	9.6	11.2
Selectivity (%)							
$<C_6$	17.4	24.7	45.5	59	0.2	0.3	0.8
C_6	82.6	75.3	54.5	41	99.8[c]	99.7[c]	99.2[c]
Ratio 2MP/nH[d]	17.3	14.3	9.3	5.9	16.5	11.4	8.7
Ratio 2MP/3MP[d]	1.6	1.5	1.3	1.3	2.9	2.7	2.5

[a] $p(\mathrm{MCP}) = 13$ mbar, $p(H_2) = 480$ mbar, sampling time 5 min.
[b] 9 mg Rh black: the activity per unit surface was the same as with 3 mg Rh.
[c] Including 0.5–1.5% benzene.
[d] 2MP = 2-methylpentane, 3MP = 3-methylpentane, nH = n-hexane.

Table 2
Fragment distribution from methylcyclopentane (MCP) on Rh black.[a]

Fragment	Distribution (%)			
	423 K	443 K	463 K	483 K[b]
CH_4	53	54	59	61
C_2H_6	3	5	6	9
C_3H_8	1	2	3	4
C_4H_{10}	8	10	12	12
i-C_5H_{12}	25	22	15	11
n-C_5H_{12}	6	5	4	3
Cyclo-C_5H_{10}	4	2	1	<1

[a] Catalyst and conditions as in table 1, $\sum(\text{fragments}) = 100\%$.
[b] See footnote b of table 1.

4. Discussion

Although catalytic reactions and surface spectroscopy were studied in separate setups, the states of Rh and Pt black after hydrogen treatments of several mbar must have been similar. Since the surface coordination number of supported Rh was reported to affect its catalytic properties [44], surface impurities must have exerted also some influence. Indeed, a high alkane hydrogenolysis activity was reported on *pure* Pt [6,7,14,45]. Hydrocarbonaceous entities were necessary to maintain steady-state activity in nondegradative reactions [6,7] ("beneficial" carbon [10]). Oxygen treatment (followed by reduction at much lower temperature) increased, a high-temperature reduction decreased the activity of Rh catalysts [46].

Apart from the inherent electronic differences, we suggest that the different levels of carbon in Rh and Pt also contribute to their activities being so different. Rh lost its carbon impurity rather easily and this carbon-free state is favorable for degradative C–C bond splitting. The marked carbon content of Pt would also contribute to prevailing nondegradative reactions on this metal [6,7]. The changes in the chemical state of carbon during hydrogen treatment were accompanied by a solid-state rearrangement of Pt, as shown by X-ray diffraction studies [11]. At the same time, subsurface C migrated to the surface [13].

Oxygen may have been less important to this respect. As opposed to the presence of Rh oxide compound, the oxidation of Pt was negligible (figures 6 and 7) and the impurities of untreated Pt did not interact chemically with the metal (figure 1). Chemisorbed oxygen (“PtO_{ads}”) transformed to chemisorbed OH and/or H_2O within a few hours [10]. Thus, Rh was more inclined to keep oxygen on its surface than Pt even after hydrogen treatment (figures 2 and 3).

Another factor to be considered is surface mobility. Somorjai [18] showed the mobility of strongly bound adsorbates under catalytic conditions. Dispersed metal blacks can be better models for probing “flexible surfaces” than single crystals. The bulk and surface rearrangement of Pt black has been studied recently [47], disclosing the mobility of carbon between surface and surface positions. Chemisorbed components, such as hydrogen, promote structural changes [21,26]. Restructuring of single Pt crystal surfaces was reported under the effect of carbon deposits [48]. Pt is more flexible than Rh which latter did not retain its original carbon content. The rearrangement of Rh and Pt in UHV occurred between 1073 and 1273 K, Rh requiring higher temperatures [49]. This restructuring influenced also the catalytic properties.

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