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Intentional carbonization of Pt black: a model spectroscopic and catalytic study

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Abstract

Pt black was exposed to *trans-trans*-2,4-hexadiene at two different pressures at 603 K. The surface composition and valence state of carbon upon carbonization and after regeneration were monitored by XPS. Exposure to hydrocarbon brought about mainly accumulation of contiguous carbon: graphite as well as C_xH_y polymers. Less than half of this carbon was removed by O_2 and H_2. "Atomic C" was more abundant after regeneration. The residual catalytic activity in test runs with n-hexane $+ H_2$ was 8–12% of that of the regenerated catalyst. Slightly more graphite and/or polymeric carbon after exposure at higher hexadiene pressure caused a more severe deactivation, manifesting itself mainly in shifting the selectivities. Partial self-regeneration under the effect of H_2 in the test mixture was also slower in the latter case. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Pt surfaces are usually covered by C-rich entities during hydrocarbon reactions [1]. Webb [2] described these as "hydrocarbonaceous deposits" during alkane reactions. They may be identical to "Pt–C–H" deposits claimed to be necessary for steady-state catalytic activity of Pt catalysts [3]. Gradual carbon accumulation on Pt/SiO_2 and Pt black poisoned alkane reactions selectively [4]. Isomerization of *n*-hexane was deactivated first, followed by hampering the activity for hydrogenolysis and methylcyclopentane (MCP) formation [5,6]. Aromatization selectivity decreased parallel to the overall activity [5]. The selectivity of dehydrogenation to hexenes — requiring presumably single Pt atoms or Pt–C ensembles [7], increased with gradual deactivation up to nearly 100%. In addition to the increased amount of surface carbon, the chemical state of carbon was more dehydrogenated on a deactivated catalyst. More than one C atom per surface Pt was present in this, "Pt–C" state [3,8]. The amount of carbon accumulated during catalytic reaction can be quite substantial and could be identified by XPS [9]. It can be present in various chemical states [10–12].

Alkanes may undergo stepwise dehydrogenation before C_6-ring closure to aromatic products. *Trans*-dienes or triene (provided their isomerization is hindered by hydrogen-deficient conditions) may serve as precursors for coke [13]. That may be the reason why *trans-trans*-2,4-hexadiene (2,4HD) can be an appropriate hydrocarbon for accelerated coking studies (as opposed to *n*-hexane [8] or the other two geometric isomers of 2,4-hexadiene). For the present study we used Pt black as a model catalyst with no metal-support interaction [14]. The amount and valence state of carbon accumulated on the catalyst after its treatment with 2,4HD at two pressures in a

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pre-chamber of an ESCA apparatus, as well as the possibility of its removal were monitored by XPS. Samples of the same catalyst were exposed in an analogous manner to 2,4-hexadiene within a catalytic reactor and the activity and selectivity changes obtained from such experiments were compared to the results of surface analysis, with the aim of finding a correlation between the amount and valence state of surface carbon and its deactivating effect.

2. Experimental

We reduced Pt black from H_2PtCl_6 by applying HCHO/KOH, the residual K removed by washing with nitric acid [5]. It was pre-sintered in H_2 at 473 K [5]. The specific surface of the sample (determined by H_2–O_2 titration) was 3.8 m^2/g. XPS was carried out in a Leybold LHS 12 MCD instrument, equipped with X-ray source (MgKα or AlKα anode) [15]. Dry powdered samples were placed on a stainless steel sample holder with the provision for exposure to various gases (2,4HD, O_2, H_2) up to several mbar pressure in a preparation chamber and the XPS measured without contacting the samples with the atmosphere. Regions of O 1s, C 1s and Pt 4f were measured in the pass energy (PE) mode (PE $=$ 48 eV). Quantitative evaluation involved Shirley background subtraction and integration. The overall surface composition of a powdered sample with a very rough outer surface could be well approximated with a homogeneous model [16]. The same exposures with 2,4HD and O_2–H_2 regeneration could be repeated in a closed-loop glass reactor [5,10,15]. Test runs with a mixture of *n*-hexane and H_2 (nH:H_2 $=$ 13:160 mbar) were carried out on the regenerated and carbonized samples.

3. Results

3.1. Surface composition

Table 1 shows the sample compositions after various stages. A standard regeneration of a fresh sample left very little oxygen and more carbon on the surface. Two exposures to 2,4HD were carried out at 13 mbar (**a**) and 53 mbar (**b**) pressures. Carbon covered almost half of the Pt surface after these treatments, its amount was practically independent on the pressure of 2,4HD (**a** and **b**). Subsequent regenerations with O_2 and H_2 removed less than 50% of the carbon deposit. This value was well-reproducible after the two exposures of different severity.

Table 1
Composition of Pt black in various stages of its treatment

Treatment	Composition (at.%)		
	O 1s	C 1s	Pt 4f
Regenerated (**R**)[a]	4	18	77
13 mbar 2,4HD (**a**)[c]	1.5	47.5	51
Regenerated (**R/a**)[b]	4	28	68
53 mbar 2,4HD (**b**)[c]	1.5	48.5	50
Regenerated (**R/b**)[b]	2	29	69

[a] Sample introduced from surrounding air, no treatment.

[b] Treatment by 26 mbar O_2, 5 min evacuation, then 270 mbar H_2, 10 min, at 603 K.

[c] Exposure with 2,4HD at 603 K.

3.2. Valence state of platinum and carbon

Fig. 1 shows nearly identical peak shapes and maximum peak binding energies (BE) for Pt 4f, close to metallic Pt^0 (BE $\approx$ 71.1 eV) after all treatments indicating that oxygen O must have been present mainly in the form of chemisorbed OH, H_2O with BE $\approx$ 532.5 eV [9] and to a lesser extent, as oxidized carbon species, BE $\approx$ 533.5 eV (Fig. 2). The latter species were slightly more abundant after 2,4HD exposure. No PtO component (BE $\approx$ 530 eV) was observed. The C 1s peak maxima were at BE $\approx$ 284.2 eV after both carbonization and regeneration treatments (Fig. 3).

The valence states of Pt and C were monitored by creating difference spectra. Whenever peak intensities measured were close to each other, difference spectra could be created between the unprocessed spectra. This feature is illustrated by Fig. 3a between the C 1s regions measured after 2,4HD exposures **a** and **b**. Peak integration procedures revealed that the difference between C 1s in **a** and **b** was about 4–4.5% of the total carbon. This figure confirms the existence of excess carbon after treatment **b**. The difference spectrum **b**$-$**a** appears as a broad peak incorporating both graphitic carbon (BE $\approx$ 284.5 eV) and “polymeric C_xH_y” (BE $\approx$ 284.9–285.2 eV) forms (their percentage being 60 and 40%, as shown by a line fitting,

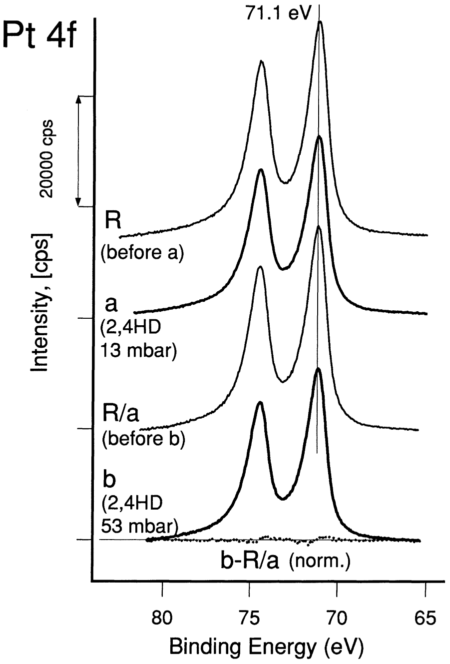

Fig. 1. Pt 4f regions of Pt black after different treatments (as described in Table 1). Spectra are shown after Shirley background subtraction and have been shifted in the direction of the *Y*-axis (scaling given separately). The difference spectrum of a carbonized and a regenerated sample (bottom) has been calculated by normalizing the intensities to each other at the maximum of the Pt 4f 72 peak at 71.1 eV (those normalized spectra are not shown).

Fig. 3a). All these carbon types have been described on different metals [12].

A refinement of this method would involve normalizing peak intensities (reasonably at maximum BE) to each other before subtracting the two spectra. Although, this is not a quantitative method, it permits one to compare peaks of different intensities with a fairly good sensitivity to small differences in the valence states [17]. A difference spectrum nearly parallel to the abscissa indicates the existence of identical valences states in the two measurements. This was the case for Pt 4f measured after carbonization and regeneration showing minimum fluctuation of intensities near to BE_{max} (Fig. 1). The C 1s region of two regenerated states, before and after exposure “**a**” to 2,4HD was treated similarly (Fig. 3b). The difference spectrum was rather noisy but showed no peaks in either direction at any BE value. Thus, the distribution of all carbon components was nearly identical

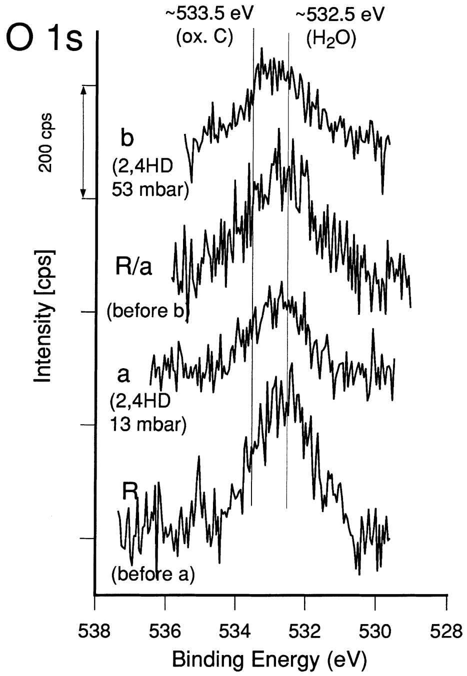

Fig. 2. O 1s regions of Pt black after different treatments (as described in Table 1).

in spite of the different overall carbon percentages (**R**:C = 18% and **R/a**; C = 28%).

So far, difference spectra between C 1s regions of samples after identical treatments were shown. The variation between carbonized and regenerated catalysts was, however, quite different. Fig. 4 shows such a difference for the C 1s spectra after exposure **a** and the regenerated sample, **R** and their difference. An excess of graphite (BE ≈ 284.5 eV) is seen after carbonization (positive peak) which carbon may also include C_xH_y entities (Fig. 5). At the same time, a higher abundance of “atomic carbon” (BE ≈ 283.3 eV) appears as a negative peak on the difference spectrum **a**−**R** after the regeneration treatment. The shallow minimum in spectrum **a**−**R** at BE ≈ 286–287 eV indicates that during regeneration O_2 could oxidize carbon mainly to species containing C–O groups.

3.3. *Catalytic properties of regenerated and carbonized Pt blacks*

Exposures **a** and **b** were carried out in sequence. Regenerated and carbonized Pt blacks were probed in

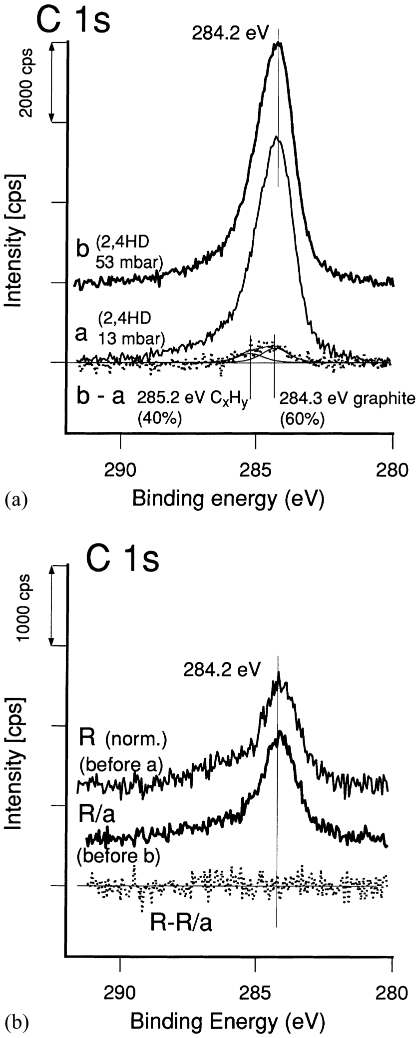

Fig. 3. C 1s regions of Pt black after different treatments (as described in Table 1): (a) spectra of carbonized samples (**a** and **b**) together with their difference spectrum **b**−**a**. A line fitting [9,16] was attempted for the difference spectrum to show the abundance of graphitic and polymeric carbon; (b) two spectra of regenerated samples (**R** and **R**/**a**). The intensity of the smaller spectrum **R** has been normalized at 284.2 eV to that of **R**/**a** before calculating the difference spectrum.

n-hexane test runs. The residual activity after exposures **a** and **b** was 8–12% of that measured with the regenerated catalyst (Fig. 5). Some self-reactivation was observed during a run of 50 min with repeated intermediate sampling. Exposure **b** caused a stronger deactivation and in this case the self-reactivation was much slower. Regenerations after both exposures restored the catalyst to ~92–95% of the original activity.

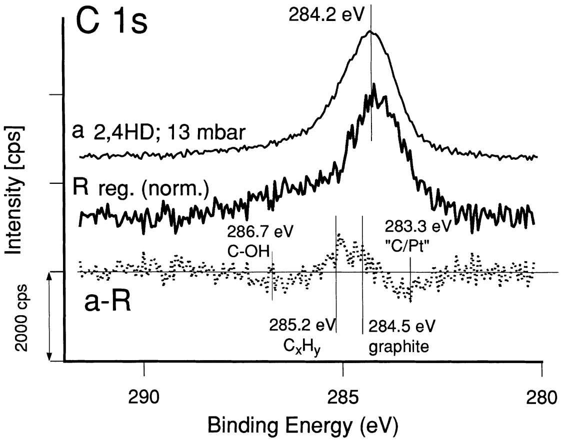

Fig. 4. C 1s spectrum after exposure to 2,4HD of 13 mbar (**a**) as measured; a normalized spectrum of a regenerated sample before exposure (**R**) and their difference spectra (**a**−**R**).

More dramatic changes appeared in the selectivities (Fig. 6). Isomerization C_5-cyclization (to methylcyclopentane, MCP) and hydrogenolysis were most suppressed. Aromatization was hardly affected, while the selectivity of dehydrogenation into hexenes increased considerably. Hydrogenolysis selectivity increased slightly at the expense of saturated C_6 products (isomers + MCP) in extended runs on a regenerated catalyst. Self-regeneration brought about

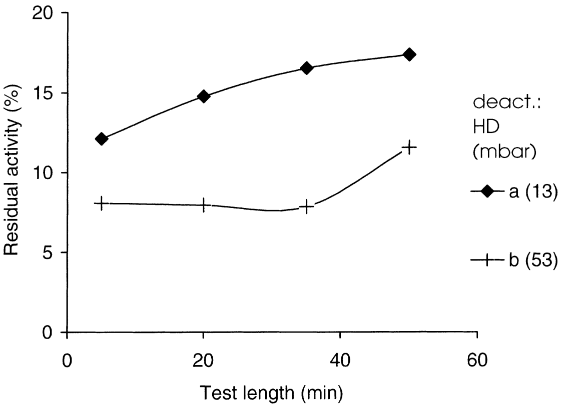

Fig. 5. Residual activity and self-reactivation during a 50 min standard test run ($n\text{H}:\text{H}_2 = 13:160$ mbar, 603 K) after exposure to 2,4HD at two different pressures (**a** and **b**).

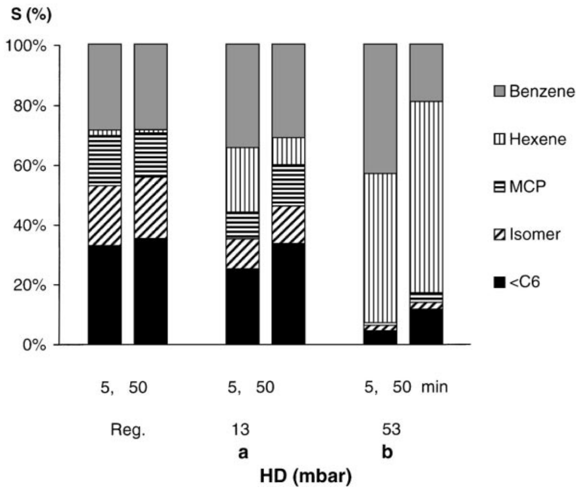

Fig. 6. Selectivities of *n*-hexane transformation in test runs (*n*H:H_2 = 13:160 mbar, 603 K) on a regenerated catalyst and on samples exposed to 2,4HD at two different pressures (**a** and **b**). Selectivity values after 5 and 50 min sampling times are shown.

a similar change after exposure **a**. Exposure **b** resulted in a very efficient inhibition of fragmentation and saturated C_6 formation. The abundance of these products was still low after 50 min (Fig. 6). Benzene selectivity was subject to the least change.

4. Discussion

Garin et al. [18] distinguished (i) “residual carbon” (up to 4%), (ii) “reversible carbon” formed instantaneously during working conditions and (iii) “irreversibly adsorbed carbon” accumulating during reaction and ultimately forming coke on a Pt single crystal or polycrystalline foil. Type (i) may correspond to Menon’s “invisible” carbon [19] and types (ii) and (iii) might be analogous with the “Pt–C–H” and “Pt–C” deposits on Pt as proposed by Sárkány [3,8]. With our dispersed sample, the amount of “residual carbon” was initially ∼18%, increasing to a rather constant ∼28% after repeated carbonization and regeneration cycles. As the test runs showed, its presence influenced neither the activity nor the selectivities and as such may be regarded as a “harmless” carbon [19]. The amount of this “harmless” fraction may, accordingly, change within rather wide limits.

The amount of type (ii) carbon accumulated during reaction [18] would appear mainly as polymeric and graphitic carbon after evacuation, together with type (iii) carbon. Mixtures of n-hexane + H_2 produced less residual carbon [20] than 2,4HD, in agreement with Sárkány’s findings on supported Pt [8]. Carbon may be present as three-dimensional (3-D) deposits [1]. The present carbonized catalysts (**a** and **b**) must have reached (or approached) the “Pt–C” state during hydrocarbon exposure. When the pressure of exposition was increased from 13–53 mbar, the total amount of carbon increased only *slightly* (Table 1). Condensed carbon entities (both graphite and polymer) were more abundant after contacting the catalyst with 2,4HD of 53 mbar pressure (Fig. 3a). However, overall deactivation, the hindering of deactivation and the selectivity changes under the effect of 53 mbar 2,4HD were *considerably* more pronounced. Two types of “harmful” [19] carbon can be present: one that merely blocks a fraction of the surface, rather than interacts electronically with the metal, as confirmed also by the shape of the Pt 4f peak being the same, independently of its carbon coverage. The other, a 3-D carbon deposits acted as a “structural modifier” [21]. This latter material is probably, responsible for decreasing the overall activity. The lower residual activity after treatment **b** is more or less commensurate with the more contiguous carbon present (cf. Figs. 3a and 5) but, upon reaching a critical level, this layer-type coke (or its precursors) must have changed the residual selectivities rather dramatically (Fig. 6). As with Pt/SiO_2, the reactions promoted by the presence of hydrogen: (isomerization and C_5-cyclization, [6]) suffered most, giving way to dehydrogenation on single Pt atoms, even in the presence of carbon atoms in their vicinity. One may visualize this selectivity shift as being caused by the onset of polymerization/graphitization or alternatively, these species were the poisons that transformed into those contiguous entities upon evacuation. The nearly constant aromatization selectivity pointed to deactivation of its three-fold active sites in proportion with overall activity loss.

Adsorbed surface intermediates may be dehydrogenated and desorb as hexenes while their hydrogen can migrate to more carbon-rich (may be graphitic, protographitic or polymeric) carbonaceous deposits in their vicinity. By doing so, it may hydrogenate the latter. Alternatively, hydrogen can initiate their partial hydrogenolysis giving rise eventually to single surface carbon atoms (“atomic C” entities). The idea is supported by the fact that hydrogenolysis increased parallel with the decrease of hexene formation during test-reactions (Fig. 6). The hydrogenolysis of carbonaceous deposits “cleans up” the surface and gives rise to gradual increase of the overall activity (Fig. 5). This process is likely, related to carbon removal from used Pt black mainly in the form of methane [22].

Further experiments are in progress that are designed to investigate the effect of various experimental parameters (temperature, the nature of deactivating hydrocarbon, the presence of H_2) on the amount, chemical state of carbon and on its deactivating action [23]. These will also report electron microscopic investigations.

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