An attempt to bridge the pressure and material gap with a disperse model catalyst for low-temperature alkane reforming

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Received 29 September 1999; accepted 18 January 2000

Pt black was exposed to n-hexane/H_2 mixtures between 483 and 663 K followed by O_2 and H_2 treatments at 603 K. XP and UP spectra were measured without exposing the samples to air. 20–30% carbon accumulated after hydrocarbon exposures. O_2 removed most carbon. The surface C content *increased* after a subsequent contact with H_2, C 1s showing more “atomic carbon” as opposed to graphite after n-hexane exposure. Anisotropic recrystallization of Pt black favoring (220) and (311) lattice planes occurred under hydrogen-rich conditions. Both findings were attributed to a H_2-induced solid-state rearrangement; H atoms penetrating into the crystal lattice, force subsurface carbon and oxygen atoms to the surface and a concomitant restructuring would occur. Thus another “hydrogen effect” has been recognized, leading to structures favorable for skeletal reactions of alkanes.

Keywords: Pt black, n-hexane, XPS, UPS, XRD, surface carbon, surface oxygen, catalyst restructuring, crystal anisotropy

1. Introduction

The advent of the methods of surface science opened a new chapter in the study of heterogeneous catalysts but had also a side effect: the problem of the “pressure gap” appeared [1,2]. Surface studies carried out in ultrahigh vacuum (UHV) represented one side of the gap, “real” catalytic studies applying macroscopic pressures being the other side. Single crystal studies using an isolation chamber offered a kind of solution to bridge this gap [3,4], as shown by Somorjai and associates in alkane reactions on various single crystal planes, followed by surface analysis. However, the applicability of results obtained with single crystals to disperse systems is necessarily limited. The use of unsupported metals of high dispersion such as platinum black may be a good compromise [5]: they expose polycrystalline crystal faces but no support effects would hamper its spectroscopic study [6,7].

Results obtained with Pt black exposed to n-hexane at several mbar pressures in a preparation chamber of a photoemission spectrometer will be reported. Surface composition and valence states were analyzed by X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) in various stages: before treatment, after exposure to n-hexane and after an O_2–H_2 regeneration process which could fully restore Pt activity in catalytic runs [7]. The catalyst samples treated were investigated further by X-ray diffraction (XRD), to identify structural changes associated with photoelectron spectra as well as with simulated catalytic batch reactor operation.

2. Experimental

The Pt black catalyst was reduced from a solution of H_2PtCl_6 by boiling it with 10% aqueous hydrazine solution [7]. The freshly reduced catalyst was presintered at 473 K in hydrogen flow for 3 h at 473 K. Heating the freshly reduced catalysts caused a severe sintering [8], but the surface and particle size after this pretreatment was stable [7]. Its specific surface was 2.64 $m^2\,g^{-1}$ after sintering. XRD showed its crystallite size to be $\sim$24 nm. The relative lattice strain of the unsintered sample was 0.08% and the a lattice constant 3.920 Å. The strain of the presintered sample dropped to 0.05% and the a lattice constant reached the literature value of 3.923 Å [9].

For surface analysis, the powdered samples (stored in air) were placed in the cavity of a stainless-steel sample holder [10]; the good electrical contact between a metal powder and the spectrophotometer excluded any electrostatic charging. Other experimental details were reported earlier [8,10]. The samples were heated up to the desired temperature. Then H_2 gas was introduced and, having reached the desired pressure, vapors of a Merck gas chromatography grade n-hexane (>99.9%) were added. The exposure lasted for 20 min, after which the gas was removed by evacuation and the sample was left to cool. UHV conditions were reached at about 520 K.

One lot of Pt black was measured without any treatment (**1/1**). It was contacted with 270 mbar H_2 (XPS: **1/2**; in XRD, sample **1**). A second lot (sample **2**) was treated subsequently with 13 mbar n-hexane (nH) plus 80 mbar H_2 at 483 (**2/1**), 543 (**2/2**), 603 (**2/5**) and 663 K (**2/6**). Between these exposures, the sample was “regenerated” *in all cases* with 27 mbar O_2 (5 min) and 270 mbar H_2 (20 min). However, spectra in the regenerated states were only recorded after treatment **2/2** and noted as **2/3** (O_2 treatment) and **2/4** (H_2 treatment). Sample **3** was exposed to 160 mbar H_2, afterwards to 13 mbar $n\text{H} + 160$ mbar H_2 at 603 K.

The sample was transferred after each treatment to the measuring chamber to perform UPS and XPS measurements. He II UPS spectra were measured with a pass energy of 12 eV. XPS monitored O 1s, C 1s and Pt 4f regions in the pass energy mode (48 eV) by a Leybold LHS 12 MCD ESCA apparatus [6,11]. We assumed a homogeneous model (justified with a powdered sample where the outer surface was far from being flat [10]) and used literature sensitivity factors [12] for quantitative analysis.

XRD measurements were carried out with samples taken out from the ESCA. 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 K_α radiation, $\lambda = 154.06$ pm, at ambient temperature.

3. Results

The surface composition of the sample after different treatments is reported in table 1. Oxygen and carbon impurities were identified in all cases [6,7,14], their amount changing, however, very markedly after different treatments. H_2 removed only part of the low amount of oxygen adsorbed during storage in surrounding atmosphere for a few weeks. At the same time, H_2 treatment increased the amount of surface carbon (**1/2**).

Exposure to n-hexane at higher and higher temperature increased carbon accumulation up to 603 K. This stopped between 603 and 663 K. Using a higher hydrogen pressure (160 mbar) at 603 K (sample **3**) gave still about as much carbon as the exposure at 543 K with $n\text{H} : \text{H}_2 = 13 : 80$ (sample **2/2**). Oxygen "regeneration" produced the cleanest surface (in terms of Pt reaching nearly 90%, the rest mostly C). Hardly any change occurred in the oxygen percentage after contact with H_2. In spite of general belief, hydrogen did *not* remove *all* surface oxygen. It induced again an *increase* in the amount of the surface carbon (table 1). This could not have arisen from impurities of H_2 since the same treatment *removed* most carbon from a Rh black sample [15].

The Pt 4f peaks were rather similar to each other, and agreed well to those of clean metallic Pt [6,10]. Figure 1 compares the O 1s spectra of the untreated sample (**1/1**) as well as after selected treatments (**1/2**, **2/2**, **2/3** and **2/4**). Adsorbed OH and/or H_2O represented the majority of surface oxygen in the untreated sample **1/1** [14], surface PtO at ~529.5–530 eV as well as oxidized carbon components above 534 eV [16] were negligible (figure 1). H_2 at 603 K caused no dramatic changes. Exposure to n-hexane (**2/2**) removed almost all surface O rather uniformly. A subsequent oxygen treatment (**2/3**) increased the chemisorbed H_2O and OH components (the chemisorbed O at BE $\approx$ 529.5–530 eV was practically nil). Some OH transformed into adsorbed H_2O after H_2 treatment (**2/4**).

Figure 2 compares C 1s spectra after the same treatments. Graphite-like carbon prevailed in all cases. Least C was present after O_2 at 603 K (**2/3**). The C 1s peaks after nH and H_2 treatments (**2/2** and **2/4**) were rather close

Table 1

Surface composition of the samples after different treatments.

Sample[a]	Composition[b] (at%)		
	Oxygen	Carbon	Pt
1/1 as is	4.5	11.5	84
1/2 as is + H_2, 603 K	3	15	82
2/1 nH/H_2, 483 K	1	21	78
2/2 nH/H_2, 543 K	1.5	25.5	73
2/3 O_2, 603 K, after **2/2**	2	8.5	89.5
2/4 H_2, 603 K, after **2/3**	2.5	20	77.5
2/5 nH/H_2, 603 K	0.5	32.5	67
2/6 nH/H_2, 663 K	~0	31	69
3 nH/H_2, 603 K[c]	7	26	67

[a] The first number represents the number of the sample (placed in the preparation chamber), the second the number of its treatment while shifting it between the preparation and measuring chambers of the photoemission instrument. Regeneration by 27 mbar O_2 before **2/2** and **2/6**, resulted in compositions nearly identical to **2/3** at both temperatures.

[b] As determined from the areas of the O 1s, C 1s and Pt 4f lines, using sensitivity factors taken from [12].

[c] $p(H_2) = 160$ mbar.

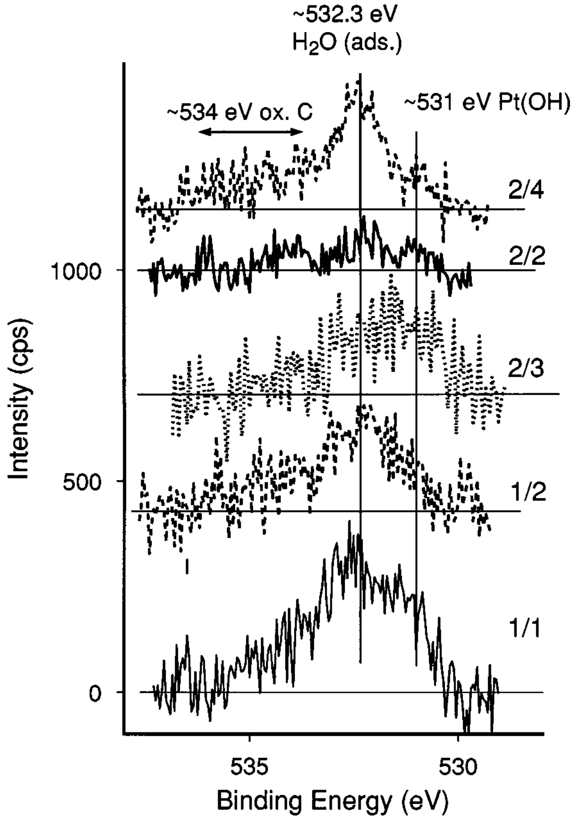

Figure 1. O 1s region of samples **1/1**, **1/2**, **2/2**, **2/3** and **2/4**. Sample designations are as in table 1 (in a sequence corresponding to figure 2). Spectrum intensities are shown as measured and shifted along the ordinate for clarity. The positions of likely peak components are shown.

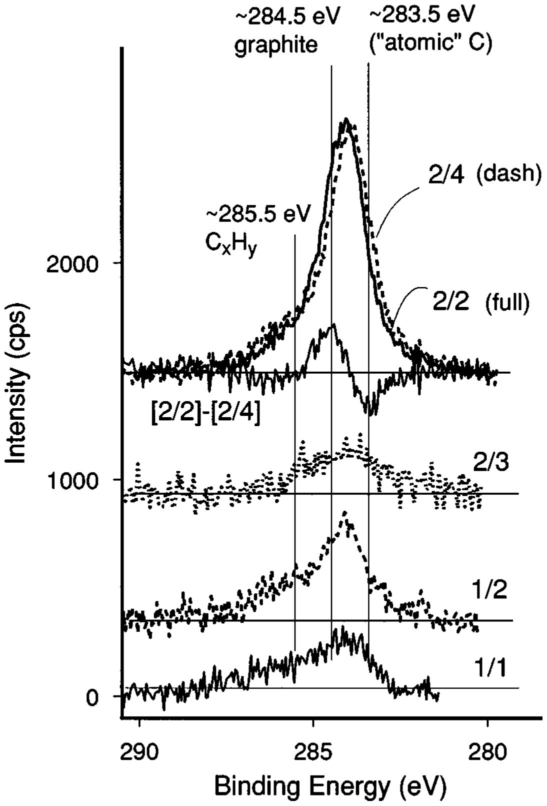

Figure 2. C 1s region of samples **1/1**, **1/2**, **2/2**, **2/3** and **2/4**. The difference spectrum [**2/2**] – [**2/4**] is also shown. Spectrum intensities are shown as measured. The positions of likely peak components are shown.

to each other. Using the technique of spectrum subtraction [17] could supply additional information. Note that *no intensity normalization was needed* to calculate the difference spectrum [**2/2**] – [**2/4**]! A considerable amount of "graphitic" carbon was present after n-hexane treatment [18] and a similar abundance of "atomic" carbon appeared upon H_2 exposure. The latter may be identified with individual carbon atoms or surface CH_x species [19] and/or carbon atoms on the surface or intercalated into the Pt lattice, these latter entities being reportedly more stable [20].

Figure 3(a) shows He II UP spectra of samples **1/1** and **3** together with the spectrum of a clean Pt black sample (**C**). Spectrum **C** with a very high Fermi-edge intensity is practically identical to the He II spectrum of a clean Pt single crystal [21] and is close to that reported earlier for a polycrystalline Pt foil of similar purity [6a]. The untreated sample (**1/1**) showed a high Fermi-edge intensity; however, a difference spectrum [**1/1**] – [**C**] showed its pronounced coverage by overlayer-type oxygenated and carbonaceous impurities [6]. The intensity loss between 0 and ~4 eV BE range is rather pronounced with sample **3**.

Figure 3(b) shows three typical spectra of series **2**. The Fermi-edge intensities after different treatments are in qualitative agreement with the Pt percentages detected by XPS (table 1): it was highest after O_2 treatment (**2/3**). Difference spectra reveal more clearly the surface species present. The difference between the spectra after nH and H_2 treatments ([**2/2**] – [**2/4**]) was rather small. The subtraction of the spectrum after O_2 exposure from those of the nH and H_2 treated samples ([**2/2**] – [**2/3**] and [**2/4**] – [**2/3**]), in turn, indicated the accumulation of (hydro)carbonaceous species with their

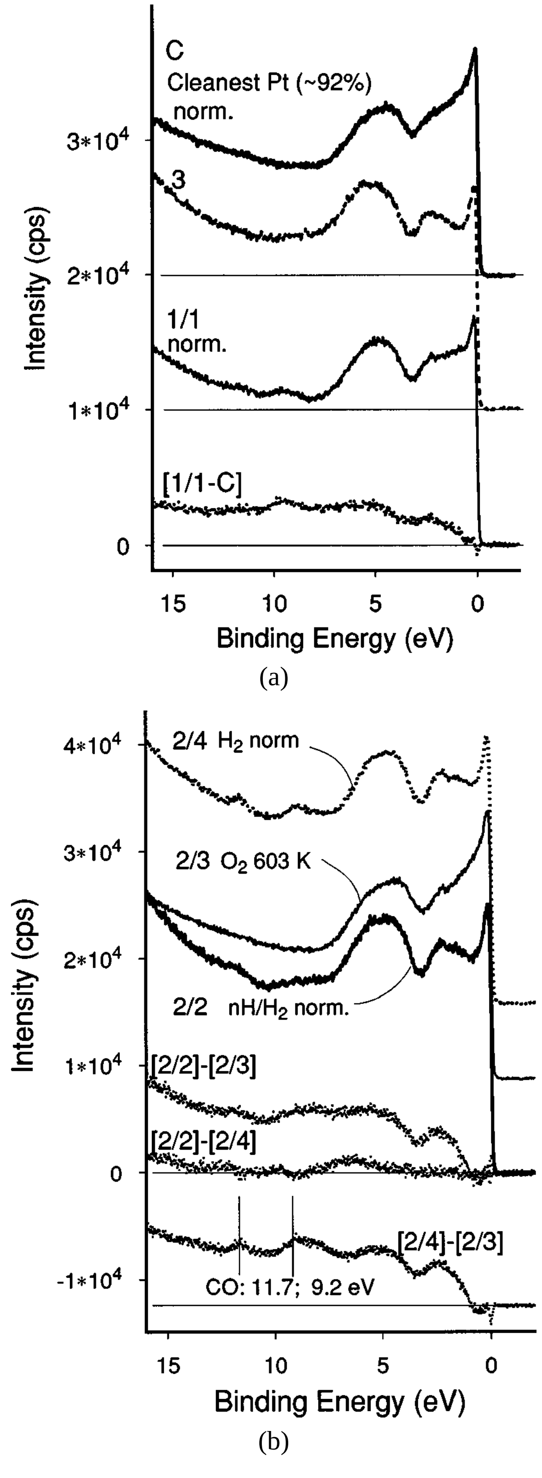

Figure 3. (a) He II UP spectra of sample **1/1** and **3** together with a spectrum of the cleanest Pt black (**C**), measured under similar conditions. Spectrum intensities have been normalized to that of sample **3**; the difference spectrum [**1/1**] – [**C**] was calculated from normalized spectra. (b) He II UP spectra of sample **2** after different treatments as shown in table 1: **2/2** (nH/H_2, 543 K), **2/3** (O_2, 603 K), **2/4** (H_2, 603 K) and the respective difference spectra after intensity normalization at the Fermi-edge (BE = 0 eV).

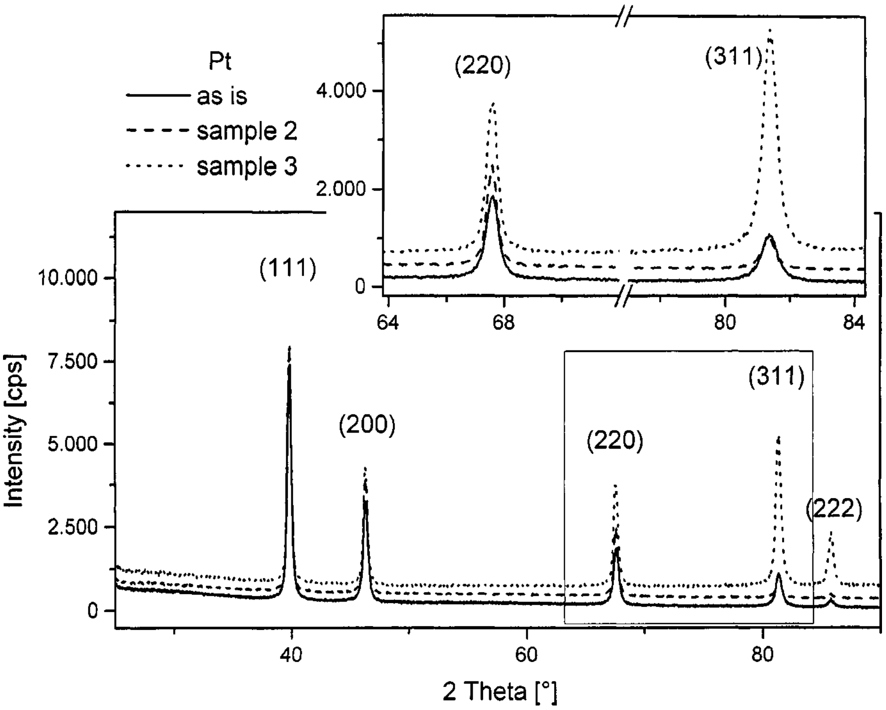

Figure 4. The high diffraction angle section of the X-ray diffractograms measured after treatments **2/6** (dashed line) and **3** (dotted line) together with the diffractogram of untreated, sintered Pt black (**1/1**, full line). The inserted plot reveals the (220) and (311) lines in more detail. The relative intensities of the full-line spectrum were close to those expected with an ideal Pt crystal [9].

σ-bonds giving rise to a broad maximum between $\sim$5 and 11.5 eV *both* after nH and H_2 exposures. This agrees well with the changes in the C 1s region (figure 2). UPS after implantation of C atoms to a Pt foil [23] exhibited maxima at lower BE values: 5.5–6.5 eV indicating their minor Pt–C electronic interactions. Note the small CO peaks [1] appearing when the untreated catalyst contacted with H_2 (**1/2**) and also when H_2 followed high-temperature oxygen regeneration (**2/4**). The spectra after **2/5** and **3** (not shown) were rather similar to **2/2**, without any traces of CO peaks.

Three X-ray diffractograms in figure 4 indicate that the positions and relative intensities of higher-order reflections in the "as prepared" sample correspond to literature values [9]. The same intensity ratio was found for sample **2** which underwent repeated heating–cooling cycles (up to 663 K) and exposures to various gases. However, a marked increase in the (220) and (311) lines appeared in sample **3** heated only once up to 603 K and exposed to n-hexane in the presence of a higher hydrogen pressure (see inset focusing on reflections at higher angles).

4. Discussion

Exposure of Pt black to various gases resulted in the presence of various amounts of several adsorbed species. Rather marked carbon coverages were noted on Pt single crystals during their active period in alkane reactions [4,24]. Hydrogen flushing prior to evacuation removed some of this surface carbon [25]. "Hydrocarbonaceous" adsorbates were assumed during n-hexane reaction on Pt in excess H_2 [26] with up to two C atoms per Pt_{surf}, depending on the H_2 pressure.

Large amount of carbon was present after exposure of Pt to n-hexane [6,14]. Exposure *without any hydrogen* resulted in the presence of a well-defined three-dimensional carbon overlayer with a broad maximum in UPS centered at $\sim$7.5 eV [13]. Higher temperatures decreased the amount of "retained" hydrogen [22], thus exposures to n-hexane at 483, 543, 603 and 663 K could leave behind more and more carbon (table 1). The C 1s spectra were similar and this was true also for sample **3**. The C 1s difference spectrum in figure 2 reveals a mainly graphitic carbon and much less C_xH_y polymer after exposure to n-hexane. One of the main points to be stressed is that H_2 treatment after O_2 resulted in the appearance of *additional surface carbon* (table 1, figure 2). This surface contained more "atomic" carbon than the carbon layer created by n-hexane (figure 2) indicating disruption of surface C–C bonds during regenerations. These "atomic C" entities must have migrated more easily from subsurface to surface positions, facilitated by penetration of (small) adsorbed H atoms to subsurface layers. The probability of this process is supported by a similar abundance of "atomic" carbon in a spectrum recorded at 603 K as compared with that measured after cooling the sample [14]. C and O atoms forced to the surface by penetrating H atoms may also react to form CO appearing in minor amounts in the untreated Pt and also after H_2 exposure (figure 3(b)). Surface C and O atoms reacted to give CO on Rh [27]; CO on Ag surface must have involved the reaction of subsurface O atoms with surface carbon [28].

Hydrogen penetration was reported to be responsible for the profound solid-state rearrangement of small Pt crystallites [8]. XRD indicated that a solid-state rearrangement process also occurred here: a very pronounced bulk recrystallization of Pt appeared after treatment "**3**", resulting in a preferential appearance of the (220) and (311) lattice planes. The doubling of step heights of a single crystal upon heating it in hydrogen [29] – exposing preferentially (311) structures – may have been the commencement of this process, reversible with single crystals. Major restructuring took place when much hydrogen was present along with n-hexane (sample **3**). Demuth [30] attributed the intensity variation in the UP spectrum of a Pt single crystal between $\sim$2 and 4 eV (figure 3(a)) to structural changes. Repeated exposures to n-hexane up to 663 K removed any structural anisotropy (diffractogram **2** in figure 4, measured after treatment **2**/**6**). XR diffractograms were simulated (not shown here in detail) using a model crystal of Pt. All tetrahedral and octahedral sites were occupied with carbon atoms in the first model. A significant increase in the intensity of the lines mentioned above was not observed. Thus, we can exclude an interpretation that an intercalation of carbon into the bulk of Pt would cause restructuring. A definite increase was observed, however, using a texture model of the Pt crystallites to simulate the pattern – this may explain the hydrogen-induced restructuring.

We stress the enhanced "flexibility" [31] of our unsupported, disperse catalyst, as opposed to single crystal surfaces. Its rearrangement can be highly anisotropic and can occur at much lower temperatures than reported for heating Pt black in UHV [32] or upon alternating exposures to O_2 and H_2 for supported Ru, Rh, Ir [33]. We thus present an example for the importance of studying catalytic properties at pressures sufficient to induce gas–solid state interactions [31], transforming an "as prepared" catalyst into its active form (restructured Pt with a modified electronic and crystal structure due to the presence of subsurface atoms from the reactants). The catalytic consequences can be rather pronounced: more open (220) and (311) structures formed preferentially in hydrogen-induced restructuring were favorable for skeletal alkane reactions [4,24,34]. We believe that *hydrogen* (rather than just heat treatment [32]) was mainly responsible for the solid-state rearrangement. Further studies are in progress to clarify its possible reactions with other surface species.

Acknowledgement

ZP thanks the Department of Inorganic Chemistry of the Fritz-Haber-Institut for inviting him for an extended stay rendering these measurements possible.

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