

Catalytic Reactions of *n*-Hexane on K-Free and K-Doped Pt Black

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A Pt black produced by reduction of H_2PtCl_6 by hydrazine hydrate contains no potassium impurity. Electron microscopy shows more regular polyhedral particles in this catalyst, as opposed to the rounded ones seen after reduction with HCHO in the presence of KOH [Z. Paál, H. Zimmer, J. R. Günter, R. Schlögl, M. Muhler, *J. Catal.* 119, 146 (1989)]. The surface purity after reduction and deliberate addition of KOH was studied by X-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy and the respective catalytic propensities were tested in reactions of hexane isomers. Different compositions were obtained after line-fitting the O 1s and C 1s regions in these cases, ethylene treatment producing more graphite and C_2H_4 polymer. Carbon removal was easier in the presence of KOH either after catalytic runs or after an artificial carbonizing with ethylene. The role of KOH can be (i) to facilitate aggregation of surface carbon and (ii) to promote its catalytic oxidation. Adding little KOH increased catalytic activity; much KOH, in turn, caused deactivation. No maxima were observed in the product yields from *n*-hexane as a function of the hydrogen pressure with the present Pt catalysts. The effects of the different morphology or higher surface purity of the present samples can be more important reasons for this than the presence or absence of potassium. © 1995 Academic Press, Inc.

INTRODUCTION

Previous studies reported on the model reactions of heptane isomers (1) and *n*-hexane (2) on Pt black catalysts. Electron microscopy (1), X-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron spectroscopy (UPS) (2) were added as physical catalyst characterization methods. The Pt blacks were prepared by reduction of H_2PtCl_6 with HCHO in the presence of concentrated KOH; hence, they contained up to 2% K impurities. These preparations are called hereafter "Pt/HCHO." Catalyst morphology as well as the amount and chemical state of C and O impurities (3) could have contributed to the differ-

ences in the catalytic propensities of Pt blacks sintered at two temperatures.

A comparison of the K-containing and K-free Pt blacks can elucidate if and to what extent the presence of potassium affects the catalytic properties of Pt and if so, whether it is a direct effect or an indirect one by influencing the morphology and surface purity of Pt. Alkali metals represent a particular additive for Group 8–10 metal catalysts (4, 5). The changes in adsorptive properties of Pt under the action of alkali metal additives were studied by electron spectroscopy (6–9). A catalytically oriented study described the effect of K on the reactions of *n*-hexane on a Pt(111) single crystal surface (10). The overall activity decreased drastically with as little as 2% K on the surface in the range between 550 and 625 K. Adding K influenced not only the activation energy and selectivity of *n*-hexane reactions but also the hydrogen content of carbonaceous residues left behind by the reactant (10).

A practically potassium-free Pt can be prepared by using hydrazine as the reducing agent, resulting in a somewhat cleaner catalyst (3). The present study reports the (i) morphology (studied by electron microscopy and X-ray diffraction), (ii) surface state and composition (studied by XPS and UPS), and (iii) catalytic properties of this Pt black catalyst. The possible effect of K has been studied by deliberate addition of KOH to the samples. The present results are compared with those observed with Pt/HCHO samples (1–3). Keeping in mind that the amount, position, and chemical state of surface carbon can markedly influence catalytic properties in hydrocarbon transformations (1, 2, 11–13), in addition to carbon accumulation during catalytic runs with *n*-hexane–hydrocarbon mixtures, a more severe procedure, namely, ethylene treatment, was applied to produce carbonized Pt. The effects of K on the carbon content, its state, and possible removal were also studied.

EXPERIMENTAL

Catalysts: Preparation and Sample Identification

A diluted (1 : 10) aqueous solution of hydrazine hydrate was added dropwise for 40 min to 20 ml of 35% H_2PtCl_6

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under stirring. A dark gray precipitate was formed. After 48 h, the liquid was boiled to remove residual ammonia, washed with bidistilled water for several days, and then filtered. The specific surface (BET, N₂) was 7.1 m² g⁻¹ in the fresh state and 5.9 m² g⁻¹ after hydrogen treatment at 600 K.

Sample **0** (also called **Pt-0**) denotes the reduced Pt black with no other treatment.

Sample **I** was obtained by sintering sample **0** in hydrogen at 473 K in a way described earlier (1, 2).

Sample **II** was obtained by dripping 0.25 ml 0.085 g liter⁻¹ aqueous KOH onto sample **I** in a way analogous to that used for preparing a Pt/K⁺ foil (9).

Sample **III** was obtained from sample **I** by dripping 0.1 ml of 0.042 g liter⁻¹ KOH solution (five times less K than that used for sample **II**).

Sample **IV** was obtained after pretreatment in H₂ at 600 K and having run test reactions with mixtures of *n*-hexane (*n*H) and hydrogen (H₂) over 0.1 g of sample **I**. This catalyst was used in catalytic tests only.

Sample **IV/K** was obtained by adding a drop of 0.042 g liter⁻¹ KOH solution to the used sample **IV** without taking it out of the catalytic tube.

Samples **I/eth** and **II/eth** were obtained by treating samples **I** and **II** with an ethylene flow of 1 bar at 600 K (no diluting gas added) after their first XPS measurements.

Electron Spectroscopy

The detailed procedure was reported earlier (2, 3, 14, 15). Briefly, Pt 4f, C 1s, K 2p, and O 1s XPS lines were monitored with MgK α anode excitation (1253.6 eV, pass energy, 50 eV). The energy scale was calibrated to Au 4f 7/2 binding energy (BE) = 84.0 eV. No electrostatic charging was observed except for some inhomogeneous charging in one of the components of the C 1s region (3, 14). With a sample under analysis, the pressure was ca. 10⁻⁹ mbar. He I (21.2 eV) and He II (40.8 eV) spectra were recorded in UPS, with pass energies of 4 and 20 eV, respectively (3, 14). All spectra were measured at 300 K.

Electron spectra of all samples (**0**, **I**, **I/eth**, **II**, **II/eth**, **III**, and **IV/K**) have been measured in two states:

—“as received” means no treatment after they are introduced into the UHV system;

—“regenerated” means an *in situ* treatment with O₂ and H₂ at 600 K in the preparation chamber of the UHV apparatus (2).

Transmission Electron Microscopy

For transmission electron microscopy (TEM), the material was placed on a specially produced structureless carbon film with a thickness of 4 nm. To this end, the Pt powder was suspended in ethanol and a drop of this suspension was deposited on the carbon film. The remaining solvent

was removed after 1 min. A Siemens Elmiskop 102 operated at 100 kV was used for TEM. An electron optical magnification of 360,000:1 and a diffraction length of 660 nm were sufficient to extract all significant structural and morphological details. The diffraction length was calibrated with thallium chloride.

Catalytic Tests

Samples **I**, **II**, and **III** were tested in a pulse system between 573 and 633 K with 3-methylpentane and *n*-hexane (6 hydrocarbon pulses of 1 ml each into 30 ml min⁻¹ H₂ carrier gas). The products were analyzed in a packed squalane GLC column (1). Mixtures of *n*-hexane (*n*H) ($p = 1.33$ kPa) and hydrogen (H₂) at $p = 16$ or 64 kPa were reacted over 0.1 g of sample **IV** in a glass closed-loop circulation reactor (1, 2). Similar test runs were carried out after the catalyst was transformed into the state **IV/K**. The cumulative length of runs was 120 min with sample **IV** followed by 70 min in the state of **IV/K**. The catalyst was regenerated 46 times with O₂ and H₂ between runs (2).

RESULTS

Catalyst Morphology and Structure

Figure 1 shows electron micrographs of the Pt black in three states: **Pt-0**, **I**, and **II**. **Pt-0** (Fig. 1a) exhibits polyhedral crystallites with some needle-like characteristics. This is in marked contrast with the smaller, rounded crystallites obtained after reduction with HCHO/KOH, hereafter referred to as Pt/HCHO (1). Introducing 15 pulses of hydrocarbons between 573 and 633 K (the period of heating in hydrogen carrier gas was 5–6 h) resulted in some sintering of sample **I**. However, as opposed to Pt/HCHO (1), this involved rounding of larger particles with some sharp edges remaining (Fig. 1b). The same case history (heat cycle and hydrocarbons introduced) for sample **II** (with much KOH added) resulted in complete disappearance of small edges (Fig. 1c). The assignment of the diffraction rings indicated that Pt black in all three states possessed the same crystalline fine structure with different crystallite sizes and shapes, as the electron micrographs have already shown.

The crystallite size of **Pt-0** according to X-ray diffraction was 23 nm (giving an X-ray dispersion of 4.7%), with almost zero stacking fault probability. Its internal lattice stress was rather high, 590 N/mm², compared to 940 N/mm² for a fresh Pt reduced by HCHO (2). Sintering at 473 K (sample **I**) decreased the internal lattice stress to 150 N/mm², the root mean square strains in the (111) and (100) directions being 0.28 and 0.48%, respectively, showing a pronounced anisotropy. These results are in agreement with the elongated particles seen on the electron micrographs

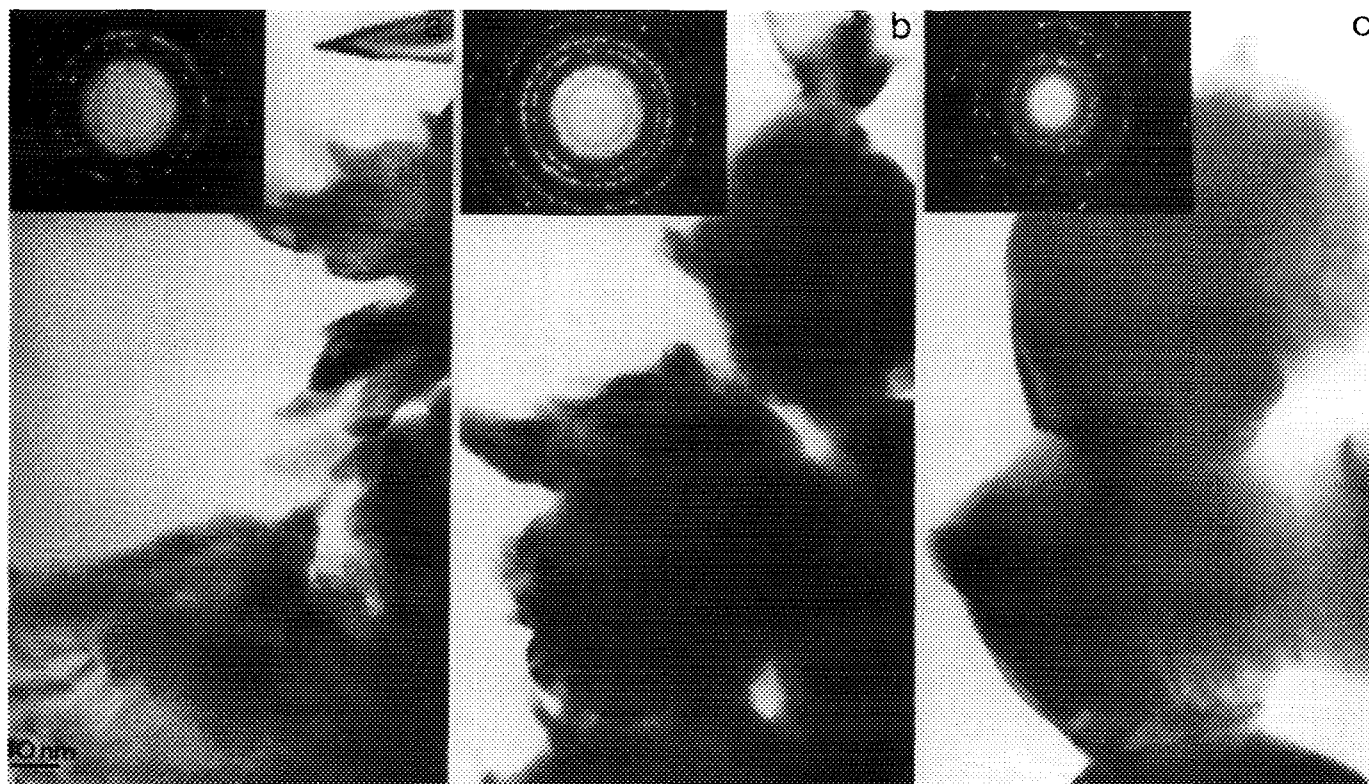


FIG. 1. Electron micrographs and selected area diffraction rings of Pt black catalysts in different states: (a) Pt after reduction (**Pt-0**); (b) Pt after hydrocarbon reactions in the pulse system (**I**); (c) Pt plus much KOH after hydrocarbon reactions in the pulse system (**II**).

(Fig. 1). The X-ray dispersion of the present Pt black (4.7%) was close to the values of Pt/HCHO samples after sintering [3.8 and 5.5%, respectively (2)].

Electron Spectroscopy

XPS. Table 1 shows the composition of all Pt blacks as calculated from the XPS line intensities. They contain, as a rule, less C and more O impurities than Pt/HCHO, but the differences are not very pronounced.

All samples contain oxygen in nonnegligible amounts; thus, the oxidation state of Pt may be of interest. The Pt 4*f* lines for **Pt-0** (Fig. 2) indicate the predominance of pure metallic Pt in both as received and regenerated states. The BE maximum at 71.15 eV agrees well with literature values (3, 15). The slight shift in the intensity ratio of Pt 4*f* 7/2 to Pt 4*f* 5/2 in the as-received spectrum corresponds to that observed in electrochemically oxidized Pt foil (16). Negative peaks appearing in the difference spectrum (regenerated - as received) on the left-hand side of Pt 4*f* 5/2 and 7/2 lines confirm also the presence of chemically bonded Pt: for Pt 4*f* 7/2, the shoulder at ca. BE = 72.4 eV had been attributed to PtO_{ads} and that at ca. BE = 73.5 eV to Pt²⁺ (17, 18). The Pt 4*f* line of the regenerated sample **IV/K** is similar to that of **Pt-0** in the same state (3).

The surface purity can be characterized by the C/Pt ratio

(10). This was pronouncedly lower after addition of KOH, especially with sample **III**. Samples **I** and **II** showed more surface carbon after ethylene treatment than after catalytic runs (Table 2). However, regeneration could restore low C/Pt ratios in both cases. The composition and C/Pt ratios of Pt/HCHO samples (with ca. 1.5–2% K content (2, 19)) were similar (Table 1).

The highest value of the C/Pt ratio appears with sample **IV/K** and points to much carbonaceous residue accumulated during catalytic runs (as received state), which perhaps could not be removed entirely in a single *in situ* regeneration. The lowest C/Pt ratio observed with regenerated **Pt-0** indicates, in turn, that carbon species picked up at room temperature from polluted air (including also possible CO impurity) are more easily removed than those accumulated during high-temperature catalytic runs.

We attempted (2, 3, 14, 15) to decompose the broad C 1s and O 1s envelopes to provide at least semiquantitative information on the abundance of carbon and oxygen species in different chemical states. Table 3 indicates that there are much more graphite and polymeric C_xH_y and less oxidized carbon species on ethylene-treated catalysts than on Pt blacks after *n*-hexane reactions. This difference is most pronounced with sample **I**. Regeneration removed much carbon (graphite and C_xH_y) after ethylene treat-

TABLE 1
Composition of Various Pt Black Samples

Sample ^a	Treatment	Composition, atom (%) ^a				
		O	K	C	Pt	C/Pt
A. Present study						
Pt-0 as received		27	0	28	45	0.62
	Regenerated	20	0	16	64	0.25
I	After reaction	17	0	31	52	0.60
	Regenerated	12	0	32	56	0.57
II	After reaction	19	0.3	23	58	0.40
	Regenerated	15	0.6	23	61.5	0.38
III	After reaction	20	0.6	26	54	0.48
	Regenerated	17	0.4	18	64.5	0.30
IV/K after reaction		23	0.3	38	39	0.97
	Regenerated	24	0.3	33.5	42	0.80
B. Related studies						
Pt/HCHO^b	After reaction	19	0.5	47	33.5	1.40
	Regenerated	19	1.5	27	52.5	0.51
Pt/HCHO^c	After reaction	13	1.3	44	42	1.05
	Regenerated	14	2	22	62	0.35

^a Calculated from XPS line intensities (background subtraction and integration) and normalized to O + K + C + Pt = 100%.

^b Pt reduced with HCHO, presintered at 633 K, after reactions with alkane/hydrogen mixtures for several hundreds of hours (2).

^c Pt reduced with HCHO, presintered at 473 K, after a controlled number of runs with *n*-hexane/hydrogen mixture for ca. 1000 min total reaction time (19).

ment, as opposed to the catalysts after *n*-hexane runs, where *in situ* O₂-H₂ treatment did not decrease markedly the total amount of carbon, although its aggregation is probable as judged from the line distribution.

No particular differences are seen between the O 1s line fitting results for samples **I**, **II**, and **III** in the as received state and those after regeneration. The lower abundance of the O 1s components after ethylene treatment (Table 3) offers circumstantial evidence that the initial displacement of oxygenated surface species by sorbed hydrocarbonaceous entities during a catalytic run, assumed earlier (2, 19), is indeed a reality. The distribution of components is different when regeneration is carried out after *n*-hexane runs or after ethylene treatment. The rather high abundance of PtO (surface PtO or adsorbed O atoms on Pt surface) on ethylene-treated Pt, regenerated state, is worth mentioning. Hardly any H₂O component is observed in those samples (Table 3): it is certain that the amount of water is low but the *total absence* of that peak may be due to an artifact of the fitting procedure. Oxygenated species can also be present as water "clusters" attached to K ions, first of all, in Pt **IV/K** (3).

UPS. The He I spectra of regenerated samples **O**, **I**, **II**, and **III** were rather similar. A He I spectrum of **Pt-0** representing a rather clean state of Pt black was published (see Pt-N in Fig. 4a, Ref. 3). Sample **III** showed a Fermi-edge intensity very close to that **Pt-0** spectrum indicating a similar Pt content in the metallic state, in agreement with Table 1. The main impurity of **Pt-0** (3) appeared as a broad diffuse band at 6–9 eV, corresponding to a mixture of surface PtO, BE maxima 5–7 eV, and/or an OH adlayer, BE maxima 7.8 and 11.1 eV (20). The impurities of a K-containing Pt/HCHO appeared, in turn, as bands with BE maxima ~5.5 and 7–8 eV and were attributed to OH attached to K⁺/Pt sites (BE 5.2 and 8.7 eV, Ref. 6), and to H₂O on K⁺/Pt (BE 8.7 and 11.3 eV, Ref. 21). Similar, lower intensity features appear also with the UP spectra of samples **II** and **III**, mainly around 8–9 and 11–12 eV, while mostly water can be assumed to be on the surface of sample **I** (BE maxima at 5.5, 7.7, and 9.2 eV, Ref. 16). The UPS results show a fair parallelism with the line fitting for the O 1s region in XPS (Table 4).

The shape of UP spectra in the as received samples shows the predominance of a carbonaceous overlayer (3).

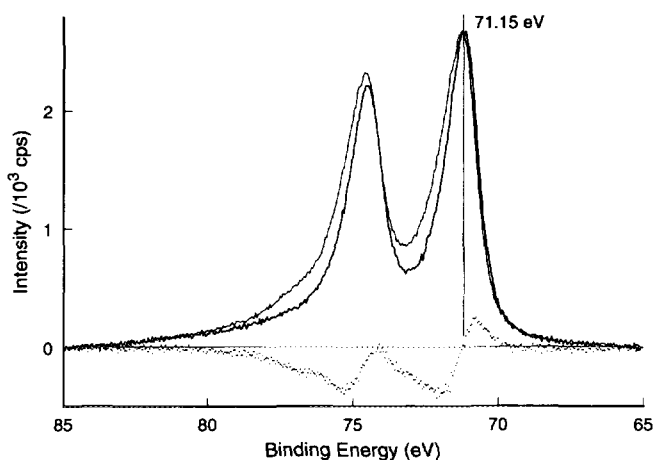


FIG. 2. Pt 4f lines for Pt-0 "as received" (thicker line) and Pt-0 "regenerated" (thinner line). The two intensities were normalized to each other by multiplying the values of the as received spectrum by a factor of 1.4 at BE = 71.15 eV. The difference spectrum (regenerated - as received) is shown by a dotted line. Raw (unsmoothed) spectra are shown.

Carbon accumulated during the ethylene treatment of samples **I** and **II** exhibited one broad band at BE 5–10 eV, as opposed to the "double buckle" spectrum recorded with the same catalysts after catalytic runs (cf. Fig. 7 in Ref. 3). The former bandshape indicates a predominant graphite plus C_xH_y species, whereas the latter points to more oxidized carbon species (3, 22). These conclusions agree well with XPS results (Table 3).

Catalytic Tests

Conversion and selectivity data of 3-methylpentane reactions at three temperatures in a pulse system have been collected in Table 5. The overall activity of sample **II** is lower by a factor of 20 than that of sample **I**. The relatively large amount of K compounds probably covers most of the previously active surface, forming a mechanical obstacle for the reactants to reach the active sites. An enhanced olefin and methylcyclopentane selectivity was characteristic of a catalyst covered by much deactivating carbonaceous overlayer (23). A KOH overlayer may apparently exert the same effect. Adding little KOH, on the other hand, sample **III** increased the overall activity with a selectivity pattern characteristic of a fresh and highly active catalyst that can produce high amounts of isomers and fragments (including secondary products at the high conversion at 633 K). The same activity differences appear with *n*-hexane at 633 K. The very high hydrogenolysis selectivity may be characteristic of the initial stage of a regenerated Pt black catalyst (2, 23, 24).

Samples **IV** and **IV/K** have been tested with *n*-hexane in a closed circulation loop. The overall activity as a func-

tion of contact time is shown in Fig. 3. Conversions rather than turnover frequencies are used here since it is uncertain what fraction of the surface is covered by KOH in **IV/K**. The activity of the KOH-free sample **IV** is generally higher at $p(NH):p(H_2) = 1.33:64$, but it is so at higher conversions only with $p(NH):p(H_2) = 1.33:16$. Sample **IV/K** is more active at the very beginning of the run in both cases.

The typical maxima in the yields of individual products as a function of the hydrogen pressure (1, 25) are not observed with this catalyst in the presence or absence of KOH (Figs. 4a and 4b). Methylcyclopentane, which can be the primary product of isomers (1, 2), is an exception. KOH slightly suppresses hydrogenolysis and promotes isomerization, while the selectivities of other products are similar. In contrast, yields over a fresh Pt/HCHO presintered at 473 K (19) show maxima (Fig. 4c) like those reported earlier (1, 25). The activity values at $p(NH):p(H_2) = 1.33:16$ compare well with those observed with Pt/HCHO. Owing to the different hydrogen pressure response, at a pressure ratio $p(NH):p(H_2) = 1.33:64$, a much lower activity is observed with Pt/HCHO.

The selectivities of the two catalysts have been plotted as a function of the overall conversion. These so-called *S-X* curves (26) indicate an inherent isomerization and aromatization ability at $p(NH):p(H_2) = 1.33:16$ with both catalysts, together with initial high hydrogenolysis and low C_5 -cyclization selectivities (Fig. 5). Secondary splitting of primary products may lead to the increase in hydrogenolysis selectivity over 10% conversion. The initial very high hydrogenolysis selectivity at $p(NH):p(H_2) = 1.33:64$ is more marked without KOH additive. Adding KOH promotes, first of all, isomerization. Both C_5 and C_6 cyclization are unfavorable at higher hydrogen pressures. Olefin formation is negligible under all conditions. The high isomerization selectivity is in agreement with the values obtained in the pulse system at 573 or 603 K (Table 5).

The character of the selectivity curves at the higher hydrogen excess is similar to that reported for Pt/HCHO

TABLE 2

Composition of Pt Black Samples after Ethylene Treatment

Sample	Treatment	Composition (at.%) ^a			
		O	C	Pt	C/Pt
Pt I	C_2H_4	12	42	46	0.91
	Regenerated	27	19	54	0.35
Pt II	C_2H_4	14	45	41	1.10
	Regenerated	33	16	51	0.31

^a Calculated from XPS line intensities (background subtraction and integration) and normalized to O + C + Pt = 100%.

TABLE 3
C 1s Line Components in Various Samples

Sample	Carbon species (%) ^a					
	BE (eV): 283.3 PtC ^b	284.5 Graph. ^b	285.5 C _x H _y ^b	286.3 C-O ^b	287 C=O ^b	> 288 others ^c
I "as rec."	1	9	11	8	2	—
I "reg."	2	4	5	1	—	—
I/eth./"as rec."	—	22	13.5	5	1.5	—
I/eth./"reg."	—	4	8	4	1.5	1
II "as rec."	1.5	8.5	8	3.5	—	2
II "reg."	4	5	4.5	1	—	—
II/eth./"as rec."	—	17	18	6.5	2.5	1.5
II/eth./"reg."	—	5	6.5	3	0.5	1
III "as rec."	6	5.5	4	1.5	1	1
III "reg."	5	5.5	6.5	—	0.5	—
IV/K "as rec."	6	13	10.5	4	2.5	2
IV/K "reg."	—	8	15	7	2.5	1

^a In percentages of the total surface (O + K + C + Pt = 100%).

^b Line identification with approximate BE maxima indicated (2, 3, 15).

^c Probably charged species or carboxylic groups [BE ~288 eV (3)].

(2) and so are hydrogenolysis selectivities at $p(nH)$: $p(H_2) = 1.33:16$.

The distribution of fragments resembled that reported for Pt/HCHO (14): more methane was formed at the beginning of the run, whereas single rupture, mainly in the middle of the molecule, prevailed in the steady state, together with some superimposed multiple splitting (23, 27).

DISCUSSION

Morphology

There is a conspicuous difference between Pt-0 and Pt/HCHO (1). Wang *et al.* (28) postulate that rounded

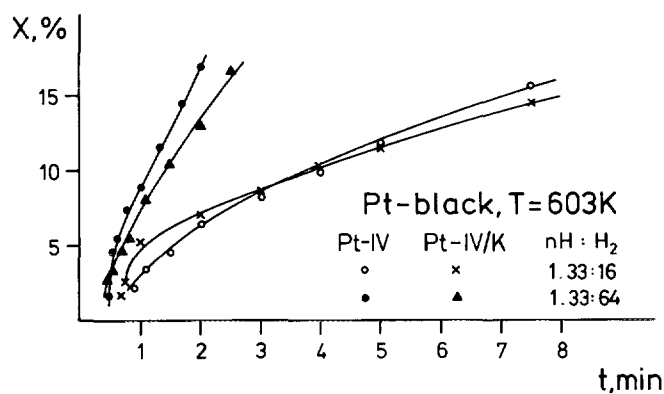


FIG. 3. Overall conversion (X) of n -hexane as a function of reaction time over Pt black with and without KOH (Pt-IV and Pt-IV/K) at two different H_2 pressures.

TABLE 4
O 1s Line Components in Various Samples

Sample	Oxygenated species (%) ^a				
	BE (eV): 530.5 PtO ^b	531.4 OH ^b	532.5 H ₂ O ^b	534 ox. C ^b	> 535 others ^c
I "as rec."	4	5.5	4.5	2	1
I "reg."	2	4	5	—	1
I/eth./"as rec."	6	4	^d	2	0.5
I/eth./"reg."	14	8	^d	4.5	0.5
II "as rec."	7	6	4	1	0.5
II "reg."	4	5.5	4.5	1	—
II/eth./"as rec."	6	4	2.5	—	1
II/eth./"reg."	19	10	4.5	—	—
III "as rec."	6	5.5	4	1.5	1 ^e
III "reg."	5	5.5	6.5	0.5	—
IV/K "as rec."	7	8	4	1.5	3
IV/K "reg."	7	7	4	3.5	3

^a In percentages of the total surface (O + K + C + Pt = 100%).

^b Line identification with approximate BE maxima indicated (2, 3, 15).

^c The peak at BE > 535 eV can be identified tentatively as H₂O attached to K sites (21).

^d No separate peak assigned to water was obtained during fitting.

^e Plus 1.5% at BE ~537 eV.

crystallites can be expected with crystallites containing much sorbed species, whereas clean surfaces should exhibit polyhedral morphology. Reduction with HCHO offers an opportunity for CO/CO₂ adsorption by the Pt crystallites *in statu nascendi*. Reduction of H₂PtCl₆ by the electron beam of an electron microscope (a chemically very clean reducing agent, indeed) produced rather regular polyhedral crystallites (29). The sintering of this catalyst is also different from that observed with Pt/HCHO (1): rounding of crystallites prevailed rather than agglomeration and crystallite size growth, owing, probably, to surface accumulation impurities (carbonaceous residues during catalytic runs, oxygen, and products of coke oxidation, CO and/or CO₂, during regeneration).

Comparison with Pt/HCHO: Are the Differences Due to Morphology, Surface Purity, or K Addition?

Marked differences due to crystallite size and crystallite geometry cannot be expected between the present Pt and Pt/HCHO (2). The most pronounced difference is seen in Fig. 4. Yields exhibiting maxima as a function of the hydrogen pressure (1, 25) were interpreted by assuming a "reactive adsorption" of the alkane as an introductory step, with hydrogen being a part of the active sites (30, 31). Competition between too much hydrogen and the reactant (25, 32) caused the rates to drop at higher $p(H_2)$ values.

TABLE 5
Reactions of Hydrocarbons over Different Pt Catalysts

Sample	<i>T</i> (K)	Conv. (%)	Selectivity (%)				
			< C ₆	Isomer	MCP ^a	Hex ^a	Bz ^a
A. 3-Methylpentane							
I	573	0.8	25	53 ^b	15	7	0
	603	2.3	28	54 ^b	13	5	0
	633	8	29	58 ^b	10	3	0
II	573	0.02	Cannot be evaluated				
	603	0.1	22	31 ^b	12	35	—
	633	0.4	16	44 ^b	19	21	—
III	573	5	22	65 ^b	11	1	1
	603	22	33	58 ^b	6	3	—
	633	63	73	19 ^b	2	3	3
B. <i>n</i> -Hexane							
I	633	2.5	66	26 ^c	7	—	1
II	633	0.2	58	25 ^c	17	—	—
III	633	18	66	29 ^c	3	tr.	2

^a Isomers, saturated C₆ alkanes; MCP, methylcyclopentane; Hex, hexene isomers; Bz, benzene.

^b Mainly *n*-hexane, less 2-methylpentane, and even less 2,2-dimethylbutane.

^c 2-Methylpentane and 3-methylpentane.

This effect was missing with the present catalyst, as opposed to Pt/HCHO (Fig. 4), owing to one or more of the following reasons:

(a) A *direct* effect of K can be the *stabilization* of surface hydrogen by its electronic interaction with the metal, as reported for Pt(111) (8). Pt/HCHO catalysts contain more K than any of the present catalysts. The more pronounced maxima of alkane reactions can be attributed to the higher amount of available surface hydrogen, due to the above effect of potassium.

(b) One source of hydrogen supply may have been hydrogen retained in crystallographically imperfect subsurface areas (33, 34). All the present Pt blacks exhibit more regular polyhedral particles than Pt/HCHO, apparently with less imperfect regions (compare Fig. 1 with the electron micrographs in Ref. 1). X-ray diffraction confirms this statement (2). These less indented particles could retain less H and the hindering effect of higher $p(\text{H}_2)$ would be less manifest. An additional, *indirect* K effect could be facilitating the "hydrogen traffic" between surface and subsurface regions, as reported also for Pd (35).

(c) Quinonic C=O groups as "hydrogen traps" (36) can also consume hydrogen at higher $p(\text{H}_2)$ values, thus decreasing the amount of surface H necessary for reactions of alkanes on Pt-H ensembles. This also can contribute to the appearance of the descending branch of the maximum

curves at higher $p(\text{H}_2)$. The C=O concentration is lower in the present catalyst [max. 2.5%, Table 3, as opposed to values up to 5–6% in Pt/HCHO (2)]. If this turns out to be the case, then this effect would be independent of the K content of the Pt black.

Intrinsic K Effects?

The differences between the present K-free or K-containing Pt catalysts and Pt/HCHO can be attributed to the

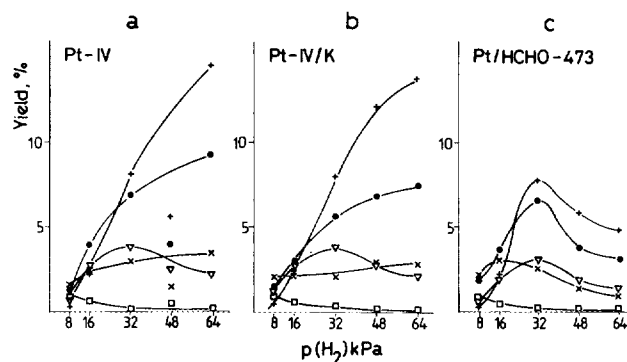


FIG. 4. Yields of individual products (*Y*) as a function of the hydrogen pressure, $p(\text{H}_2)$: (a) Pt-IV; (b) Pt-IV/K; (c) Pt/HCHO containing 2% K, presintered at 473 K (19). ●, fragments; +, isohexanes; ∇, methylcyclopentane; □, olefins; ×, benzene.

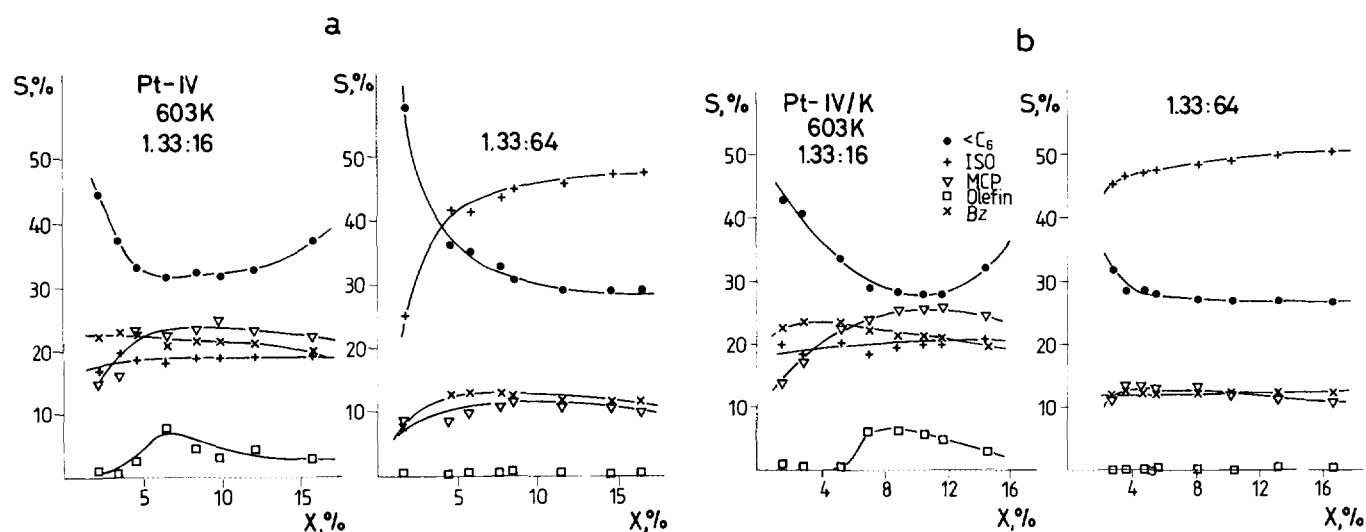


FIG. 5. Selectivities of individual product classes as a function of the overall conversion at two different hydrogen pressures: (a) Pt-IV; (b) Pt-IV/K. Symbols as in Fig. 4.

higher purity of the present sample rather than to more K in Pt/HCHO. Yet adding K to this cleaner Pt somewhat changes its properties. Possible K effects can be discussed in comparison with Pt single crystal results. As for Pt(111), it was stated (10) to have: (i) the the highest overall activity at an optimum K concentration ($\sim 25\%$ of a monolayer as measured by Auger electron spectroscopy, AES); (ii) an enhanced aggregation of carbonaceous deposits in the presence of K; and (iii) a hindrance of the dehydrogenation step by K (fewer hexenes were present). The presence of oxygen and water was not excluded in that study (p. 376 in Ref. 10); hence, the results obtained in Ref. (10) at 573 K with $p(nH):p(H_2) = 2.66:80$ kPa (20:600 Torr) may bear some relevance to ours.

(i) This statement seems to be in good agreement with the results obtained over samples I, II, and III (Table 5), showing the highest conversion at a low K concentration. Further, the accumulation of carbon on this catalyst is also lowest (Table 1) and the removal of carbon is facilitated in the presence of added K (Tables 1 and 2).

(ii) The values of the C/Pt XPS signal in Tables 1 and 2 as well as the increase in the polymer component of C 1s after regeneration (Table 3) confirm qualitatively the second conclusion of Ref. 10. Much higher actual values up to C/Pt ~ 3 were reported on a Pt single crystal with a Pt surface apparently still possessing some catalytic activity. The increased amount of C_xH_y and oxidized carbon after regeneration of IV/K (Table 3) in spite of a decrease in the total amount of carbon also confirms this assumption. Also, Pt/HCHO samples with a higher K content (2) may contain up to 35% graphitic and/or polymeric C_xH_y carbon with respect to the total surface (2, 3) com-

pared with the present catalysts for which this value is below 25%.

Oxidation of graphite is promoted by the presence of potassium ions [Ref. (37) and references therein]. A catalytic effect of K^+ was also reported in the gasification of carbonaceous materials in the reactions of C with H_2O to give CO (38). This effect of K^+ ions can manifest itself as the easier removal of C after a catalytic run and also after ethylene treatment (Tables 1 and 2). This was also valid for the individual C 1s components in samples I, II, and III. In the case of sample IV/K, however, the aggregation of hydrocarbonaceous deposits to polymeric carbon and their oxidation to species containing C-O and C=O groups were more pronounced (Table 3).

(iii) Hexene concentration is determined by surface dehydrogenation as well as by the relative rate of desorption and further reactions of surface unsaturated entities (2). Therefore, the curves of olefin accumulation showing a maximum as a function of reaction time (10) confirm their intermediate character (1, 2, 23). K may then decrease the rate of their formation relative to their further reaction. The low hexene selectivities (Fig. 5) are in agreement with this assumption.

Suppressing hydrogenolysis and enhancing isomerization at higher hydrogen excess are indisputable catalytic effects of added KOH (Figs. 4 and 5). This does not seem to affect aromatization selectivity (Fig. 5). Bearing in mind that C_5 -cyclic isomerization and internal hydrogenolysis are related reactions (39, 40) and also that hydrogenolysis may require more dehydrogenated intermediates, we can conclude, paraphrasing statement (iii) in Ref. (10), that an optimum K concentration can suppress extensive surface dehydrogenation of the reacting alkane.

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REFERENCES

- Paál, Z., Zimmer, H., Günter, J. R., Schlögl, R., and Muhler, M., *J. Catal.* **119**, 146 (1989).
- Paál, Z., Xu, X. L., Paál-Lukács, J., Vogel, W., Muhler, M., and Schlögl, R., *J. Catal.* **152**, 252 (1995).
- Paál, Z., Schlögl, R., and Ertl, G., *J. Chem. Soc. Faraday Trans.* **88**, 1179 (1992).
- Mross, W. D., *Catal. Rev. Sci. Eng.* **25**, 591 (1983).
- Ertl, G., *Catal. Rev. Sci. Eng.* **21**, 207 (1980).
- Kiskinova, M., Pirug, G., and Bonzel, H. P., *Surg. Sci.* **150**, 319 (1985).
- Hugenschmidt, M. B., Dolle, P., Jupille, J., and Cassuto, A., *J. Vac. Sci. Technol. A* **7**, 3312 (1989).
- Zhou, X. L., and White, J. M., *Surf. Sci.* **185**, 450 (1987).
- Bonzel, H. P., and Krebs, H. J., in "Physics and Chemistry of Alkali Metal Adsorption" (H. P. Bonzel, A. M. Bradshaw, and G. Ertl, Eds.), p. 331. Elsevier, Amsterdam, 1989.
- Zaera, F., and Somorjai, G. A., *J. Catal.* **84**, 375 (1983).
- Garin, F., Maire, G., Zyade, S., Zauwen, M., Frennet, A., and Zielinski, P., *J. Mol. Catal.* **58**, 185 (1990).
- Menon, P. G., *J. Mol. Catal.* **59**, 207 (1990).
- Somorjai, G. A., and Zaera, F., *J. Phys. Chem.* **86**, 3070 (1982).
- Paál, Z., Schlögl, R., and Ertl, G., *Catal. Lett.* **12**, 331 (1992).
- Paál, Z., and Schlögl, R., *Surf. Interface Anal.* **19**, 524 (1992).
- Slavin, A., Fusy, J., Jupille, J., Alnot, M., Ehrhardt, J. J., and Cassuto, A., in "Proc. 4 ICSS and 3 ECOSS, Suppl. Le Vide, les Couches Minces," Vol. 201, p. 510.
- Kim, K. S., Winograd, N., and Davis, R. E., *J. Am. Chem. Soc.* **93**, 6296 (1971).
- Peuckert, M., and Bonzel, H. P., *Surf. Sci.* **145**, 239 (1984).
- Paál, Z., and Zhan, Zh., to appear.
- Fisher, G. B., and Sexton, B. A., *Phys. Rev. Lett.* **44**, 683 (1980).
- Bonzel, H. P., Pirug, G., and Winkler, A., *Surf. Sci.* **175**, 287 (1986).
- Evans, S., and Thomas, J. M., *Proc. R. Soc. London A* **353**, 103 (1977).
- Paál, Z., Groeneweg, H., and Paál-Lukács, J., *J. Chem. Soc. Faraday Trans.* **86**, 3159 (1990).
- Paál, Z., Manninger, I., Zhan, Zh., and Muhler, M., *Appl. Catal.* **66**, 305 (1990).
- Paál, Z., *Catal. Today* **12**, 297 (1992).
- Margitfalvi, J., Szedlacsek, P., Hegedüs, M., and Nagy, F., *Appl. Catal.* **15**, 69 (1985).
- Paál, Z., Zhan, Zh., Manninger, I., and Barthomeuf, D., *J. Catal.* **147**, 333 (1994).
- Wang, T., Lee, C., and Schmidt, L. D., *Surf. Sci.* **163**, 181 (1985).
- Barna, A., Barna, B. P., Tóth, L., Paál, Z., and Tétényi, P., *Appl. Surf. Sci.* **14**, 85 (1982–83).
- Parayre, P., Amir-Ebrahimi, V., Gault, F. G., and Frennet, A., *J. Chem. Soc. Faraday Trans. 1* **76**, 1704 (1980).
- Frennet, A., in "Hydrogen Effects in Catalysis" (Z. Paál and P. G. Menon, Eds.), p. 339. Dekker, New York, 1988.
- Paál, Z., in "Hydrogen Effects in Catalysis" (Z. Paál and P. G. Menon, Eds.), p. 449. Dekker, New York, 1988.
- Paál, Z., and Thomson, S. J., *J. Catal.* **30**, 96 (1973).
- Wells, P. B., *J. Catal.* **52**, 498 (1978).
- Solymosi, F., and Kovács, I., *Surf. Sci.* **260**, 139 (1990).
- Schraut, A., Emig, G., and Sockel, H.-G., *Appl. Catal.* **29**, 311 (1987).
- Janiak, C., Hoffmann, R., Sjövall, P., and Kasemo, B., *Langmuir* **9**, 3427 (1993).
- Fujikawa, K., Hayashi, A., Tanaka, H., Kanazuka, T., Kanno, T., and Kodera, T., *Appl. Catal.* **50**, 199 (1989).
- Gault, F. G., in "Advances in Catalysis" (H. Pines, D. D. Eley, and P. B. Weisz, Eds.), Vol. 30, p. 1. Academic Press, New York, 1981.
- Ponec, V., in "Advances in Catalysis" (H. Pines, D. D. Eley, and P. B. Weisz, Eds.), Vol. 32, p. 149. Academic Press, New York, 1983.