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Sulfided Pt Catalysts

Monitoring Surface Chemical State and Catalytic Properties in n-Hexane Reactions

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The amount and valence state of sulfur in sulfided Pt catalysts was monitored, together with parallel studies of the catalytic properties of these catalysts in order to clarify the catalytic effect of S in different chemical states on reactions of low-temperature n-hexane reforming. Pt black and 6% Pt/SiO$_2$ (EUROPT-1) were sulfided by H$_2$/H$_2$S. X-ray photoelectron spectroscopy (XPS) detected both sulfate and sulfide. The chemical state of Pt corresponded to metallic Pt with low amounts of S containing surface adlayer and/or PtS present. This could be observed with Pt black and also with EUROPT. With S present, both catalysts lost ca 95% of their activity in n-hexane transformation at 603 K, n-hexenes being the predominant products. Prolonged runs with n-hexane as well as regenerations using O$_2$ and H$_2$ removed most sulfidic S from Pt black and about half of the original activity came back. Isomers and methylcyclopentane were produced in this state with high selectivities. Some reactivation of EUROPT (where no sulfate could be detected) occurred within one single run. A uniform scheme is proposed to describe the effects of sulfate and sulfide. Accordingly, sulfate acts as a structural modifier occupying a fraction of the active surface. Sulfide in small amounts, in turn, has a bonding modifier effect and poisons selectively benzene and fragmentation, enhancing (within the reduced activity) the selectivity of C$_5$-cyclization and, possibly, also that of isomerization.

1. INTRODUCTION

Sulfur is one of the oldest known poisons of metal catalysts (1). There is no agreement in the literature for the chemical state, the mechanism of action and stability of sulfur on Pt. Some results pointed to the accumulation of sulfur on the surface in a chemisorbed state or as surface PtS (2–4). Platinum–sulfur interaction could initiate surface faceting (5a, 6) or particle migration (2, 7). In some cases, a separate PtS phase was also detected in supported catalyst of high dispersion by electron microscopy (5b, 6) and extended X-ray absorption fine structure (EXAFS) (7). XPS results pointed to the presence of a sulfur containing adlayer (3).

In any case, sulfur influences activity and selectivity of metal catalysts. For example, it is applied intentionally to suppress excessive fragmentation activity of commercial naphtha reforming catalysts (8). Platinum alone can also catalyze various skeletal alkane reactions including isomerization, C$_5$-cyclization, aromatization, fragmentation, and accompanied by dehydrogenation to hexenes (9, 10). Dees *et al.* (11) added sulfur to supported Pt, Ir, and Pt–Ir and noted that at a 50% surface coverage, hydrogenolysis, and aromatization yields dropped by a factor of 50–100, whereas C$_5$-cyclization showed only a 5–10-fold decrease. Adding a submonolayer sulfur to Pt or Pt–Re (111) single crystal surface suppressed hydrogenolysis and promoted C$_5$-cyclization of n-hexane (12). This latter effect was observed also with Pt black and was attributed to S present as sulfide (13). Menon and Prasad (14) distinguished "reversibly" and "irreversibly" adsorbed sulfur on Pt/Al$_2$O$_3$ and Pt–Re/Al$_2$O$_3$ under naphtha reforming conditions (773 K), without specifying their likely chemical state. Polysulfides and adsorbed sulfur were detected electrochemically on a Pt electrode in aqueous medium (15).

One of the possible classifications of modifiers (such as sulfur) distinguishes "structural" and "bonding" modifiers: the former type influences the structure of active site (or ensemble), whereas the latter alters the bonding (electronic interaction) between the active intermediate and catalyst (16). Kim and Somorjai (12) in their single crystal study underlined the structural effect. The school of Barbier, in turn, stressed the electronic effect of S on metals (1, 15, 17), based, partly on the comparison of electron acceptor sulfur with that of electron donor Cu (17). They regarded sulfur as a stable entity on Pt catalysts. On the other hand, PtS is thermodynamically unstable even at lower temperatures (4, 18); H$_2$ stripped S from Pt catalysts above 673 K as H$_2$S (19). Reaction between surface sulfur and reacting hydrocarbons (20, 21) could also contribute to sulfide removal.

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Our earlier $H_2{}^{35}S$ radiotracer study (22) reported on the possibility of sulfur retention and removal by H_2, as well as by exchange with inactive H_2S/H_2. Most (but not all) sulfur could be hydrogenated off from Pt/Al_2O_3 at 623 K, while exchange dominated on $Pt–Re/Al_2O_3$.

The use of X-ray photoelectron spectroscopy (XPS) for studying supported catalysts is rendered difficult due to binding energy (BE) deviations caused by inhomogeneous surface electrostatic charging. They can be larger than the real chemical shift of the Pt 4f line caused by sulfidation or oxidation (3, 23). Hence, it was difficult to draw conclusions on the chemical state of Pt in such samples. That was one of the reasons why we selected sulfided platinum *black* as a model catalyst for our earlier XPS study (13). A sulfur adlayer and/or a minor PtS was detected in the Pt 4f region, both being surface components rather than a separate phase (13). The S 2p region indicated sulfur present in two chemical states: sulfate and sulfide. They influenced the catalytic properties rather markedly (13). Sulfate could have arisen by oxidation of primary sulfide entities; we tentatively identified it (13) with the "irreversible" sulfur species suggested earlier (14). At the same time, the presence of S decreased the amount of C and O impurities, in agreement with the results of Barbier *et al.* (1).

The present work completed the study of Pt black and extended the investigations to a standard Pt/SiO_2 catalyst, EUROPT-1, too. Our aim was to clarify the correlation between the amount and valence state of sulfur on sulfided Pt catalysts and the activity and selectivity changes caused by S. To this end, the surface was monitored by (XPS) and n-hexane test reactions were carried out in different states of Pt. As a result, we hoped that we shall be able to explain the effect of specific sulfur species on different reactions of low-temperature n-hexane reforming.

2. EXPERIMENTAL

A Pt black catalyst reduced from H_2PtCl_6 by hydrazine (24) was treated at 633 K in hydrogen for 1 h (code: Pt), specific surface: 5.9 m^2/g, corresponding to a dispersion of 2%. Another sample of this Pt was sulfided at 633 K by a mixture of 50 Torr H_2S and 450 Torr H_2 (code: Pt–S). A standard 6% Pt/SiO_2 catalyst, EUROPT-1 (25, 26) was used for comparison as it was and after the same procedure of sulfidation, codes EPT and EPT-S, respectively. n-Hexane was reacted in a closed-circulation loop; for details, see (13, 24). A typical run consisted of reacting a mixture of 10 Torr n-hexane (nH) and 120 Torr hydrogen for 70 min. After sulfidation, two Pt black samples were studied. One sample was used in n-hexane reaction as described above (code: "Pt–S, 1 run nH"). Another Pt black sample (code: "Pt–S, much nH") was used in six runs at $p(nH) = 10$ Torr H_2 pressures varying between 60 and 480 Torr. This was followed by a final 60 min run of $p(nH) = 10$ Torr and $p(H_2) = 120$ Torr. The number of $O_2–H_2$ regenerations between runs was seven. EUROPT was studied without sulfidation and with 1 run n-hexane as described above. The catalysts were transferred to the XPS apparatus (exposing them to surrounding air). XPS of powdered samples placed in a stainless steel sample holder was carried out with a Leybold LHS 12 MCD instrument equipped with a hemispherical analyzer. XP spectra were subjected to satellite subtraction, Shirley background subtraction and integration to calculate surface concentrations on the basis of homogeneous model. As for further experimental details, see earlier papers (13, 23, 24, 27).

3. RESULTS

3.1. *Electron Spectroscopy*

The composition of Pt samples were found earlier to be 53 to 60% Pt, 14 to 20% O and 20 to 23% C (13). The present samples were cleaner, exposing ca 60% Pt (Table 1). After sulfidation (sample "Pt–S") around 5% S was also present. Its concentration decreased during repeated n-hexane reactions. This was accompanied by increasing Pt intensities due, in part, to the removal of carbon and oxygen (Table 1).

The Pt 4f peaks of all catalysts showed similar shapes. Metallic Pt predominated. The maximum BE of Pt 4f 7/2 of sulfided samples showed a minor (0.2–0.3 eV) shift towards lower binding energies as compared with the 71.1 eV found for clean Pt, due, likely to the formation of isolating overlayer containing sulfur which impeded the perfect electric conductivity between the sample and the instrument. The appearance of such a shift and its gradual decrease with less and less S present may serve as an indirect physical evidence that sulfide was spread over the whole surface of the sample consisting of aggregates of small crystallites (24).

Difference spectra can be used to get evidence on the presence of Pt sulfide. The BE maximum of PtS lies at a BE value higher by 1.2 eV than that of pure Pt (28). This component was minor on the difference spectrum "Pt–S" minus "Pt–S 1 run nH" (**1**–**2** in Fig. 1), indicating that these

TABLE 1

Surface Concentration of Pt and Sulfur Components on Pt Black Samples

Sample	Concentration, %[a]				
	Sulfide	Sulfate	Pt	O	C
Pt (reg.)	—	—	69.2	16.1	14.7
Pt–S	1.94	2.86	58.9	18.2	18.1
Pt–S 1 run nH	1.80	2.60	59.9	14.1	21.6
Pt–S much nH	0.30	2.70	60.6	14.2	22.2

[a] Related to Pt (4f) + O (1s) + C (1s) + S (2p) = 100%. The calculations were carried out using the S 2p, Pt 4f, O 1s, and C 1s line intensities.

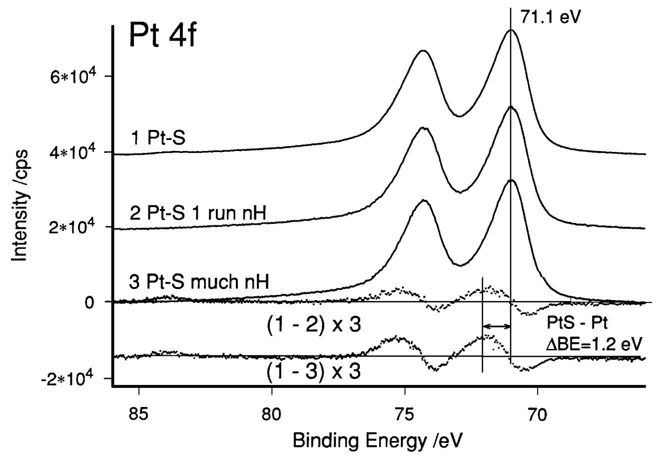

FIG. 1. Pt 4f lines of sulfided Pt black catalysts and their difference spectra. The peak intensities were normalized to each other before calculating difference spectra, taking the Pt 4f 7/2 maxima as the reference value. We corrected the spectra for the small negative BE shift in sulfided samples due to physical reasons (see text). The PtS component is shown by the vertical line corresponding to its BE max (13, 28). The intensities of difference spectra have been enlarged three times for the sake of clarity.

states were close to each other. A marked difference in the spectrum ("Pt–S" minus "Pt–S much nH"), i.e., **1–3** in Fig. 1, pointed to a more marked S removal after a longer use of Pt in hexane reactions (see also Fig. 2).

The Pt 4f lines of EUROPT-1 were broader and less intense (Fig. 2). The BE values shifted due to electrostatic charging were calibrated to the Si peak in SiO_2. This still caused an error of about 0.5 eV (Pt 4f 7/2 at 71.6 eV), indicating an inhomogeneous charging (23) and/or interaction of Pt atoms with support O atoms. The intensity of the PtS signal on the difference spectrum was more marked than with Pt black.

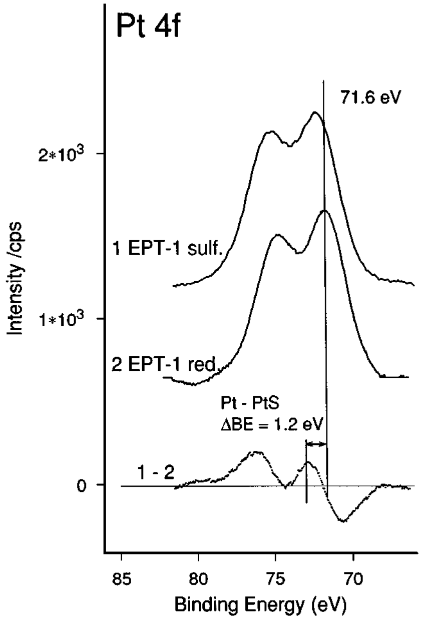

FIG. 2. Pt 4f lines of unsulfided and sulfided EUROPT-1 and their difference spectrum. The intensities of the two Pt peaks were normalized to each other and the BE shift due to imperfect energy scale correction was preserved (Pt 4f 7/2 at 71.6 eV). The difference spectrum is shown on the same scale as the parent spectra.

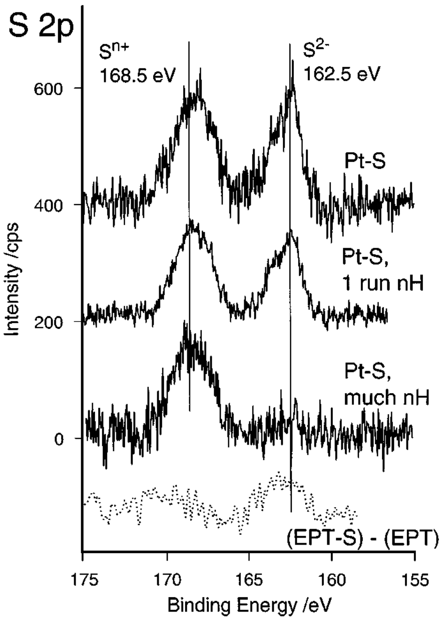

FIG. 3. S 2p lines of unsulfided and sulfided Pt catalysts. "True" spectra are shown for Pt black in various states (upper three lines). A difference spectrum between sulfided and unsulfided Pt/SiO_2 has been added. X-ray satellite subtraction was the only spectrum processing possible in this case of rather noisy parent spectra (superimposed to the inelastic satellite peak of the Si 2s peak); no proper background subtraction was possible. Hence, this spectrum should be regarded as a qualitative indication of the likely presence of sulfide.

Increasing exposure to n-hexane did not remove sulfate and sulfide uniformly (Table 1). The sulfide peaks decreased within the S 2p sulfur region (Fig. 3). This selective sulfide removal agrees with literature results (4, 18, 19). No detectable increase of the sulfate peak could be observed as a consequence of oxygen exposure during repeated regenerations (Fig. 3, Table 1), in agreement with earlier results (13).

No *direct* observation of sulfur was possible in the S 2p region of EUROPT-1. However, a difference spectrum of the corresponding (unfortunately noisy) region of sulfided and unsulfided Pt/SiO_2 showed a small buckle where the sulfide S 2p line should be (Fig. 3) and we believe that is more than coincidence. The region corresponding to sulfate could not be distinguished from the background noise.

3.2. Catalytic Runs

The *conversion* of n-hexane dropped dramatically upon sulfidation of both catalysts by a factor of 10–20 (Fig. 4). The

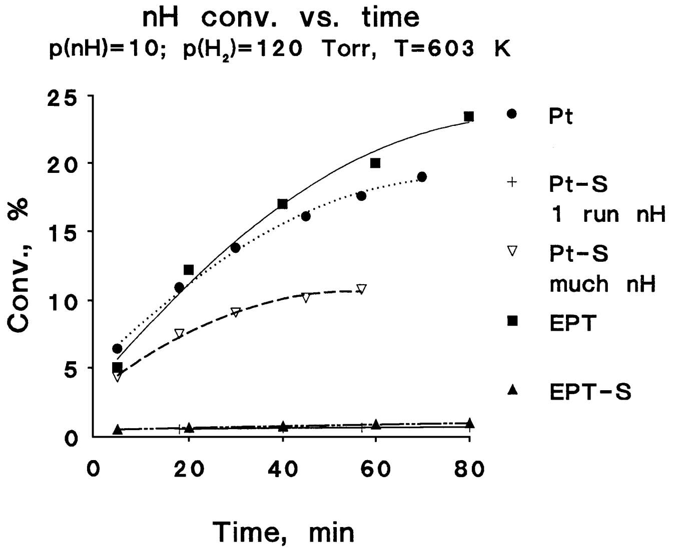

FIG. 4. Conversion of n-hexane on unsupported Pt and Pt/SiO$_2$ (EUROPT-1) catalysts before and after sulfidation as a function of reaction time in a closed-loop circulation reactor.

same was true for EUROPT-1. About 60% of the original activity of Pt black was recovered during repeated catalytic runs and regenerations ("Pt–S, much nH"), parallel with the removal of sulfide component (see Figs. 3 and 4). Since the surface after sulfidation could not be determined without affecting the sulfur coverage, no turnover frequencies were calculated.

The *selectivities* of isomerization, C$_5$-cyclization, aromatization, and hydrogenolysis were similar on unsulfided Pt black during one typical run (Fig. 5a). Dehydrogenation was minor and the amount of hexenes decreased with time. The almost completely deactivated "Pt–S 1 run nH" produced hexenes with more than 90% selectivity (Fig. 5b) and this selectivity pattern did not change with time. Hydrogenolysis selectivity reached 5–6%. MCP and isomers appeared near to detection limit with no benzene at all. "Pt–S, much nH" which recovered about half of its activity produced MCP and isomers with selectivities higher than that observed over clean Pt (Fig. 5c). Benzene and hydrogenolysis selectivities were, in turn, considerably lower, that of hexenes followed roughly the trend found with Pt. The absolute yield of hexenes was nearly the same (around 0.5%) in all three cases.

As reported earlier (25, 29), EUROPT-1 exhibited a lower fragmentation and higher MCP and isomer selectivity than Pt black in the fresh state (Fig. 6a). Sulfided EUROPT ("EPT-S") gave also hexenes as the main products (Fig. 6b). However, it kept some of its higher isomerization selectivity and, although the conversion was low (Fig. 4), a certain shift of selectivities towards isomerization was observed during run.

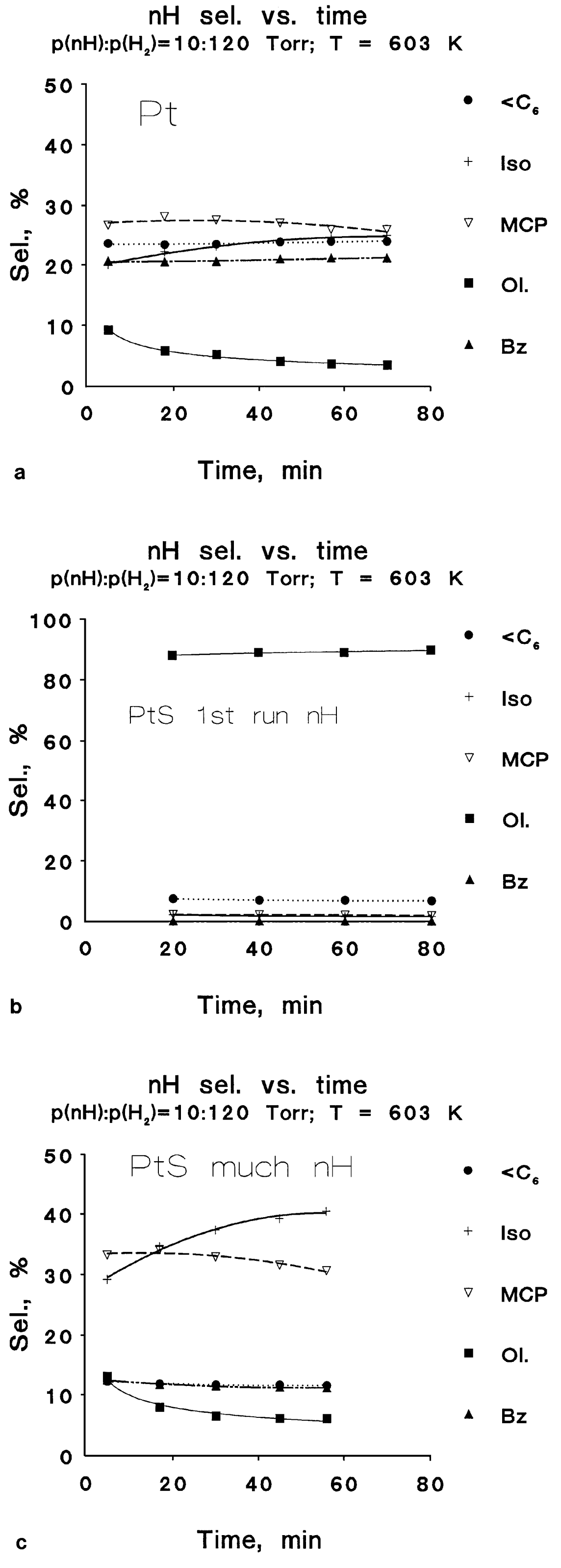

FIG. 5. Product selectivities as a function of reaction time on Pt black catalysts. Selectivities have been calculated for reacted C$_6$ entities; i.e., the mole number increase during fragmentation has been taken into consideration: (a) Pt; (b) Pt–S, 1 run nH; (c) Pt–S, much nH.

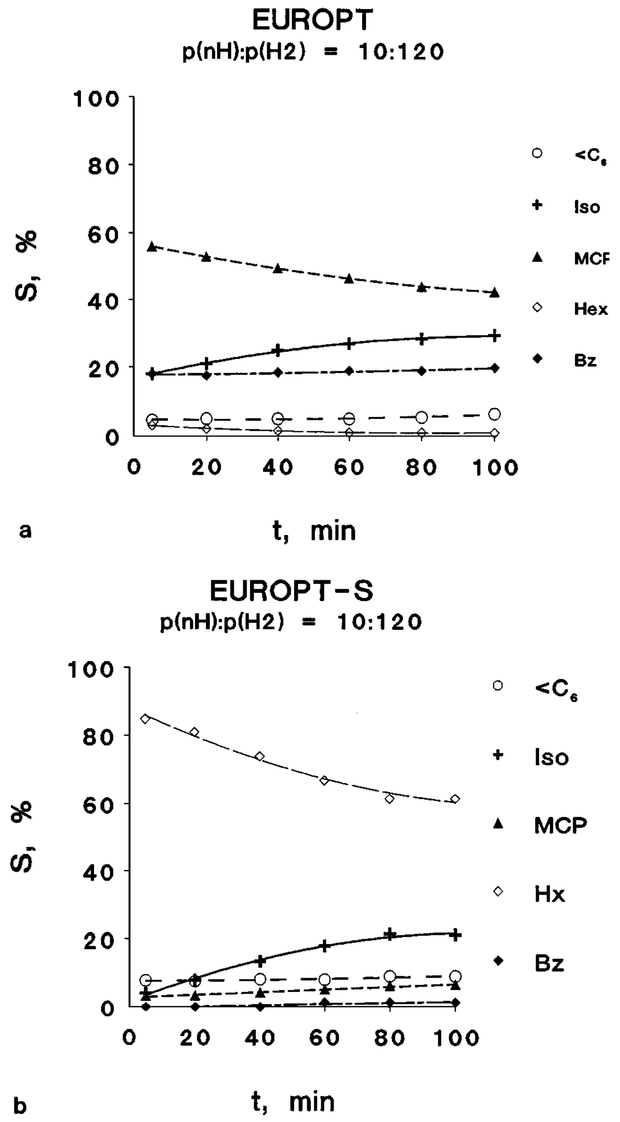

FIG. 6. Selectivities of individual products as a function of reaction time on Pt/SiO_2 (EUROPT-1) catalysts: (a) EUROPT-1; (b) EUROPT-1 sulfided.

4. DISCUSSION

The Pt 4f and the S 2p regions show that sulfur was present in two chemical forms: as sulfide and as sulfate. Exposure of the samples to air as well as repeated regenerations involving oxygen could have caused sulfate formation. Earlier results (13) indicated that this reaction required a long time (weeks rather than days). Air exposure during shelf life of unsulfided Pt black must have resulted in its considerable oxygen coverage (Table 1) present mainly as adsorbed OH/H_2O species, with no bulk Pt oxide (27). The rather marked metallic Pt 4f peaks (Fig. 1) indicate that not only Pt oxide (27) but also the Pt sulfide contribution should be minor. Considering the 2% dispersion of Pt black, the sulfur concentration measured by XPS (Table 1) up to almost 5% would ensure a rather full coverage of the particles, even if we assume some aggregation of sulfate and some surface PtS formation. No bulk PtS phase was likely here.

As opposed to Pt black, the PtS contribution in the difference spectrum of sulfided minus unsulfided EUROPT-1 is rather marked (Fig. 2). Since EUROPT has a dispersion (D) of 60% (25), a remarkable fraction (30–50%) of its Pt atoms can participate in the formation of a monomolecular surface layer. This was found in the oxidation of EUROPT-1 producing a monomolecular surface PtO layer detected by X-ray diffraction (XRD) (30). A similar surface sulfide (even in submonolayer quantities) could comprise a relatively high number of Pt atoms. XPS indicates a marked electronic interaction between Pt and S. This alone, however, does not mean the formation of a bulk PtS phase. PtS was, indeed reported when various supported catalysts were sulfided (7, 31). This was accompanied by a reconstruction of the Pt phase resulting in coalescence of small Pt crystallites into larger PtS rafts as shown by EXAFS (7) and electron microscopy (5, 31). Other EXAFS results, however, pointed to Pt migration and particle growth *without* bulk PtS formation (2). Particle growth was attributed in both cases to H_2S adsorption on alumina (7) and Al containing LTL zeolite. These S entities would then intrude between Pt and its support and, by doing so, loosen the metal–support interaction (2). Electron microscopy, in turn, showed no agglomeration of the metal upon sulfidation of a 1% Pt supported on silica (32). Silica support may not be suitable for the attack of S from the support side. In agreement with Fukunaga and Ponec (32), we regard PtS formation and a major restructuring of sulfided EUROPT-1 unlikely in our case.

Various intermediates have been proposed for different skeletal reactions over Pt, the first step of all being a dissociative adsorption of the alkane on a Pt atom (9). The availability of sites of various geometry may determine further reaction pathways as shown in Fig. 7: C_5-cyclization and related isomerization would require two-atom sites (9, 33–35), aromatization likely three-atom ensembles (36), and hydrogenolysis various multiatom sites, kink and B5 sites preferred (9, 10, 29). Just the absence of the latter type was regarded as the reason for the low hydrogenolysis selectivity on EUROPT-1 (25). There is also the long-disputed problem of single-atom Pt sites (37, 38); these may contribute to hydrogenolysis and isomerization over EUROPT of high dispersion (29, 39). These were active, however, only in the presence of sufficient hydrogen; no signs of single-atom catalyzed isomerization were observed on carbonized catalysts (29). "Pt–C" ensembles were regarded, in turn, as centers suitable for dehydrogenation to hexenes (9, 10) especially with a high coverage of Pt by chemisorbed hydrocarbonaceous entities when all other reaction possibilities ceased (29, 39).

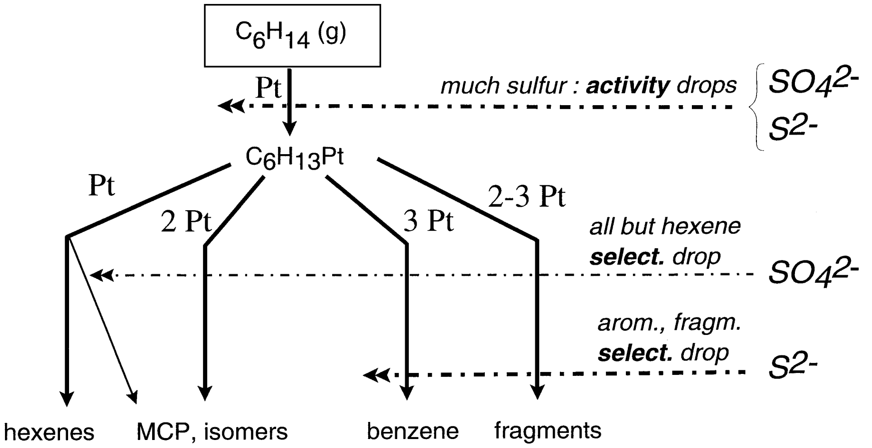

FIG. 7. A scheme of skeletal alkane reactions on Pt and the possible effect of various types of S on their pathways. Thick arrows denote the possible reaction pathways, together with their likely active ensembles (9, 29, 33, 34). Isomerization and C_5-cyclization on single-atom sites (37, 38) has been denoted by a thin arrow. The negative effects of sulfate and sulfide on activity and selectivity have been symbolized by double-headed arrows. Apart from activity drop due to covering the metal surface for which sulfide is just as responsible as sulfate (upper arrow), the effect of sulfide in small amounts on selectivities is more specific (lower thick arrow) than that of sulfate (lower thin arrow) whose presence permits only dehydrogenation on single-atom sites.

Sulfate and sulfide both must have been responsible for deactivation. Sulfate is more stable than carbonaceous deposits; that is why the original activity could not be recovered completely. However, they affected selectivities of different reactions in a different way (11–14, 19, 22). We attributed a "structural modifier" poisoning effect to sulfate and a "bonding modifier" effect to sulfide (13): the former suppressing activity by occupying a fraction of the active surface; the latter affecting various reactions in a nonuniform way, influencing, first, aromatization and also fragmentation. The present results permit us to refine this picture further (Fig. 7). In the case of "Pt–S, 1 run nH" sulfate *and* sulfide together must have covered most of the metal sites. Thus, the overall activity decreased drastically (Fig. 4). Ion scattering spectroscopy (ISS) showed that sulfur was a real surface component (13) as opposed to C and O which could be accumulated in interparticle grains, cracks, etc. (24, 27). The remaining single-atom sites (Pt–S ensembles, like Pt–C ensembles assumed earlier (10, 25, 29, 39)) were still able to produce hexenes. The selectivity pattern remained the same during a run of several minutes (Fig. 5b), indicating no changes in surface composition and state, as confirmed also by the S 2p spectra (Fig. 3, upper two curves). When some sulfide was removed, likely by reacting with hydrogen during regenerative treatments (19, 22), the residual sulfate could still hamper the overall activity (Fig. 4) but the "bonding modifier" effect of the remaining low amount of sulfide on the selectivity became very pronounced, with a preference of C_5-cyclization and related isomerization (Fig. 5c).

The activity drop on sulfided EUROPT-1 was very similar to that of Pt black (Fig. 4) and this indicates that their likely surface state and coverage were also rather alike. Two differences can be seen in the selectivities (Fig. 6b): some isomers appeared along with hexenes and the selectivities changed even during one run showing a sort of "self-healing" after sulfur poisoning. It is possible that the particular ordered structure of Pt in EUROPT-1 (25, 30) rendered some single-atom isomerization (29, 37, 38) still possible, e.g., on corner atoms of its regular cubooctahedra. An interaction between S and chemisorbed hydrocarbons during run to give organic S compounds (20, 21) may have resulted in their migration towards the support, the metal–support boundary favoring accumulation of carbonaceous deposits (39, 40). Thus, a few isomerizing active sites could have been liberated.

These selectivity changes towards isomers and MCP in the presence of small amounts of S^{2-} agree with literature data. Enhancement of C_5-cyclization was observed also with Pt (111) + S (12). The isomer selectivity from n-hexane increased by up to a factor of two on a sulfided Pt/SiO_2 (and so did that of MCP to a lesser extent) with about threefold drop of the conversion (32).

As outlined in Fig. 7, the uniform activity suppression by sulfate must be different from the selective effect of sulfide. Sulfate may belong to the "irreversible" sulfur necessary for tempering hydrogenolysis in industrial naphtha reforming catalysts (14). Sulfide, in turn, impedes fragmentation and aromatization both requiring multiple ensembles, although their active sites are probably different (9, 10, 29, 34, 36). It is still an open question if single-atom sites for isomerization—C_5-cyclization became activated in the presence of sulfide or if sulfide shifts the general pathway from the more dehydrogenated surface intermediates of benzene and fragments towards less dehydrogenated intermediates of the C_5-cyclic reactions, in a way analogous to the effect of hydrogen (9, 41). Both should imply that small amounts of sulfide (as opposed to extensive carbonization) should not prevent hydrogen chemisorption necessary for the sites active in forming saturated C_6 products.

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