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Removal of Carbonaceous Residues by Deuterium from Pt Catalysts

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Mixtures of hexane (*n*H) and hydrogen (H_2) were reacted over EUROPT-1 (6.3% Pt/SiO_2) and Pt black. In addition to gas-phase products, including isomers, methylcyclopentane, fragments, and benzene, firmly chemisorbed entities were also produced. They may be C_1 units or—highly dehydrogenated—polymeric deposits. Removal of these surface carbonaceous entities was studied upon exposing them to deuterium between 293 and 673 K. Deuterium "hydrogenated off" surface CH_x species and "hydrogenolyzed" polymeric deposits. The amount and the composition in methane isotopomers was monitored as a function of time and removal temperature. The effect of the temperature and the *n*H/H_2 ratio during carbonization was systematically studied over EUROPT-1. The initial mixture removed initially from both catalysts contained mostly CD_3H and CD_2H_2. These methane molecules must have originated from the most reactive surface species (methylidyne and methylene). C_1 removed from Pt black contained, as a rule, more deuterium. The estimated H/C ratio in surface precursors was 0.4–0.9 ($CD_4 \gg CHD_3 > CH_2D_2 > CH_3D$). The H/C ratio in the case of EUROPT-1 was, in turn, 1–1.5 ($CHD_3 > CH_2D_2 \approx CD_4 > CH_3D$). The amount of C_1 removed from EUROPT-1 showed a maximum as a function of the removal temperature between 350 and 450 K and further increased above 573 K. The removed methane contained more D when the catalyst was heated in the absence of hydrogen before removal. The deuterium content of methanes was indicative of the degree of dehydrogenation of their surface precursors. Dehydrogenation was significantly higher on Pt black. These observations are in good agreement with the propensity of EUROPT-1 to produce more saturated gas-phase products.

Key Words: **carbonaceous deposits; deuterative removal; deuteromethanes; platinum black; platinum-on-silica; EUROPT-1; hexane; H/D isotopic exchange.**

1. INTRODUCTION

Carbonaceous deposits are accumulated on the surface of Pt catalysts during hydrocarbon transformations (1–6). The structure as well as the amount of deposited "coke" is still argued. Somorjai and coworkers reported large amounts of carbon on Pt single-crystal surfaces during hydrocarbon transformations, assuming three-dimensional (3D) deposits, two-dimensional—disordered—overlayer, and C atoms ("Pt–C" ensembles) (4, 5). X-ray photoelectron spectroscopy (XPS) corroborated the formation of 3D carbon islands on Pt black catalysts after exposure to hexane (7–9). Three-dimensional deposits contained strongly graphitized fractions as well as C_xH_y polymers. Gallezot *et al.* (10) found that the local structure of the carbonaceous deposit formed on Pt/Al_2O_3 catalyst after reaction with cyclopentane was a disordered arrangement of polyaromatic molecules rather than graphitic or pregraphitic deposits. A large part of the carbon was on the support in this case. Deposits of the latter type could also be observed on Pt by electron microscopy (9). Webb (11) proposed that carbon on Pt catalysts during reaction was present as "hydrocarbonaceous deposits," pointing out that they were not fully dehydrogenated. Barbier visualized the overall structure as "C_xH_y species," containing methylene groups and aromatic and polyaromatic rings as well as pseudographitic phases (3). Various studies reported different values for the C/H ratio in the residual carbon deposit: 0.5–1 (3), 0–1.5 (5), 0–1.8 (12) or 0–2 (6).

Several factors influence the structure and the amount of deposited carbon. The reaction temperature and the hydrogen excess were the most important. The morphology of the residues changed continuously from 2D (<550 K) to 3D (>600 K) (4). More C_1 species were observed in the C 1s XPS peak after low-temperature treatment, turning into more graphitic residues after high-temperature treatments (8). Increasing the amount of hydrogen in the reaction mixture hindered the formation of coke (1, 2, 9, 13). Carbon accumulation from propane + propene was slower on Pt–Sn/Al_2O_3 when excess H_2 was present. Nevertheless the amount of "reversible" carbon was much lower (14).

At least two different coke formation routes have been identified, one involving C_1 units, the other proceeding by polymerization of surface polyenes (15). C_1 fragments can migrate and aggregate rapidly on the surface (16). *trans*-Polyenes polymerized rather than aromatized after

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trans–cis isomerization in the absence of hydrogen (17). This process could occur under conditions of aromatization. Carbon deposition on highly dispersed Pt/SiO_2 catalysts was attributed to the C_1 route whereas the polyene route predominated over low-dispersion catalysts (16).

As opposed to deactivation, "beneficial" effects of surface carbon include an increased catalyst stability or improved selectivity toward the desired product(s) (2, 18). C_xH_y species retained from the intermediates of hydrogenolysis occupy the most active sites where mainly fragmentation occurs. Sárkány (19, 20) described three stages in the catalyst life. Freshly regenerated catalyst ("Pt–H") exhibited high activity in hydrogenolysis. A "Pt–C–H" state developed corresponding to the steady-state activity in nondegradative alkane reactions (18). An inactive Pt–C state was reached after longer runs.

No direct method is available to study surface carbon during the reaction. UHV, necessary for surface spectroscopy, dehydrogenated residual carbon (21). Temperature programmed oxidation (TPO) is quantitative and is able to distinguish between carbon on metallic or support sites (3, 22, 23). However, TPO provides limited information on the structure of carbon deposits. This method revealed that no coke deposition occurred on a silica as opposed to the alumina support (24).

Several results have been published in the literature concerning the removal of carbonaceous residues by hydrogen after exposure to hydrocarbons and/or hydrocarbon–hydrogen mixtures (16, 19, 20, 21, 25–31). Some experiments were carried out in continuous flow reactors. The removal process took place immediately after the reaction by switching from the reaction mixture to hydrogen either directly or after an inert gas treatment (19, 20, 25–27). In these cases mostly methane and other reaction products (such as benzene or methylcyclopentane) could be hydrogenated off from the catalyst surface (25, 27). Matusek *et al.* (28, 29) used a closed-loop reactor, where the hydrogenative removal was carried out after evacuation of the reaction mixture. The relative abundance of methane removed in this procedure was much higher than the amount formed during the reaction.

Others examined the catalyst by using surface spectroscopic techniques after the hydrogenative removal of hydrocarbons (21, 30, 31). In that case UHV conditions were both applied after the exposure to hexane as well as after the hydrogenation; thus the surface species were dehydrogenated.

Whatever the method, most authors agreed that only a fraction of the residual carbonaceous deposits could be removed by hydrogen (21, 25–31). Gravimetric studies by Sárkány found that at least two C atoms per surface Pt atom (C/Pt_s) accumulated during hexane transformation on the surface of Pt black. The C/Pt_s was only 0.3–0.5 C/Pt_s on EUROPT-1. Hydrogen removed up to 50–80% of this amount (19, 20). Similar results were observed by Auger spectroscopy (AES), where the C/Pt ratio was in between 0.21 and 0.34 when the reactant was just evacuated after the run and as low as 0.09 when the run was concluded by a hydrogen flushing (21). C/Pt ratios of ca. ~0.5 and ~3 were found upon ethane and ethene adsorption between 323 and 573 K on a Pt foil and subsequent evacuation (31). Hydrogen flushing removed about the same *amount* of C, independently of the coverage. The work function change indicated hydrogenation of the residual carbon between 323 and 423 K (30, 31).

Isotopic tracer methods can provide important information on the interaction between the reactants and the catalyst, such as the hydrogen spillover (30) or the incorporation of labeled hydrogen (D) into the reaction products (33). In the present work we used deuterium (D_2) in order to determine more precisely the possible origin and reactivity of the retained surface entities.

The majority of the hydrocarbons removed from various Pt catalysts after hexane reaction consisted of methane (28). The question arises as to whether this methane originated from residual C_1 species or whether it was produced by degradation of larger surface hydrocarbon entities. The reality of this latter process is supported by XPS, showing that "regeneration" of Pt black using H_2 treatment increased the fraction of "atomic C" in the C 1s region at the expense of "graphitic" and "polymeric" C (9). Removal of residual hydrocarbonaceous deposits by deuterium can give additional information since the yields of removed deuteromethanes will reflect the structure of residual surface C_1 species. The D uptake (calculated from received H/D ratio) is also informative about the degree of dehydrogenation of larger residues accumulated during catalytic reactions. The present paper concentrates on the isotopic composition of methane removed by D_2 from two catalysts: Pt black and 6% Pt/SiO_2 (EUROPT-1). We carried out the deuterative removal experiments at various temperatures as well as after different carbonizing conditions. These results are studied in conjunction with the product composition obtained from hexane on the two catalysts.

2. METHODS

2.1. Catalytic Tests

Catalytic runs were carried out in a closed-loop reactor (volume $\cong$ 70 ml) described earlier (34). Mixtures of hexane (13 mbar) and hydrogen (160 mbar) were contacted with 2.9 mg of 6.3% Pt/SiO_2—EUROPT-1—(35) or 11.2 mg of Pt black—reduced by HCHO, $D = 1.36\%$—(36) at different temperatures. The catalyst was regenerated between runs at the temperature of the previous reaction as follows: 40 mbar of air for 2 min, evacuation, and 133 mbar of hydrogen for 3 min (28). The products were analyzed gas chromatographically using a 50-m CP-Sil glass capillary column and FID detector (28).

The activity of the carbonized catalysts was also checked. The catalyst was pretreated by the mixture of 13 mbar of hexane and 80 mbar of hydrogen for $t = 20$ min at $T = 603$ K. The loop was then evacuated ($t = 10$ min) and filled up again with the mixture of 13 mbar of hexane and 160 mbar of hydrogen. The activity and the selectivity of the carbonized sample was compared with the regenerated one.

2.2. Deuterative Removal

Both the reaction (pretreatment) and the deuterative removal were carried out in a closed-loop reactor (loop volume = 47 ml + reactor volume ≅ 13 ml), analogously to the catalytic measurements. The same amount of 83.6 mg of EUROPT-1 or 100.6 mg of Pt black was used for all studies. Between experiments the catalyst was regenerated under O_2 and H_2 (28). The "pretreatment" reaction consisted of a 20-min exposure to a mixture of hexane (nH) and hydrogen—$p(H_2) : p(n\text{H}) = 50 : 20$ or $50 : 5$ mbar at different temperatures (T_P). Several MS analyses were carried out after pretreatment. They showed that less that 40% methane was present in the final mixture after hexane reactions, before deuterative removal of the surface residues. The loop was then *evacuated* at 293 K for $t = 10$ min, except for one set of experiments where the evacuation temperature (T_E) was varied from 273 to 573 K. The *removal process* was finally carried out by introducing 50 mbar of D_2 onto the catalyst and increasing the temperature stepwise to $T_R = 293, 373, 473, 573,$ and 673 K. For each step, the catalyst was contacted with circulating deuterium for 30 min at constant temperature before cooling the sample to 293 K and evacuating it at the same temperature. All masses from $m/e = 12$ (C) to 20 (CD_4) were monitored continuously using a quadrupole mass spectrometer, in the multiple ion detection mode. Impurities, such as water and longer hydrocarbons, were removed from the gas circulation using a liquid N_2 trap. Blank measurements were carried out to permit background subtraction. The composition in methane isotopomers was calculated using a system of linear equations derived from the fragmentation pattern of pure methane that was measured separately (see the Appendix).

3. RESULTS

3.1. Hexane Transformation over EUROPT-1 and Pt Black

As discussed earlier, reaction of hexane over EUROPT-1 (37–39) and Pt black catalysts (36) fall in five categories: hydrogenolysis, isomerization, C_5 cyclization, aromatization, and dehydrogenation to hexenes. Figure 1 shows the conversion and selectivity values at a selected temperature, 603 K. The conversion reached ~15% with Pt black and ~35% on EUROPT-1. The initial ($t = 5$ min) TOF values were 50 h^{-1} for EUROPT-1 and 25 h^{-1} for Pt black. Selectivities were rather different on the two catalysts. The selectivity of isomer and methylcyclopentane (MCP) formation was the highest on EUROPT-1, while that of hydrogenolysis was much lower than on Pt black. Benzene selectivity was roughly the same on both catalysts. Hexene selectivity was low, 3–5% on Pt black and ca. 1% on EUROPT-1. It is remarkable that hardly any change was observed in these values during a run of 50 min (conversion ca. 5–35%). Thus, no secondary reactions took place in this range. The fragment distribution offers a good fingerprint of the catalysts (40). Fragment distribution within the hydrogenolysis products ($<C_6$) is reported in Table 1. Platinum promoted the single rupture reaction of alkanes with a slight preference for forming two propane fragments. A minor multiple rupture to methane also took place (36, 39). More C_1 was observed in this fraction over EUROPT-1 compared to Pt black. Again, there was only a little change in the product distribution as a function of reaction time (the abundance of methane increased slightly).

Figure 2 presents the activities and selectivities of different products as a function of the reaction temperature. As expected (34, 36, 39), lower temperatures favored the formation of saturated products (isomers, MCP). The importance of "dehydrogenative" reactions, aromatization and dehydrogenation (together with hydrogenolysis), increased

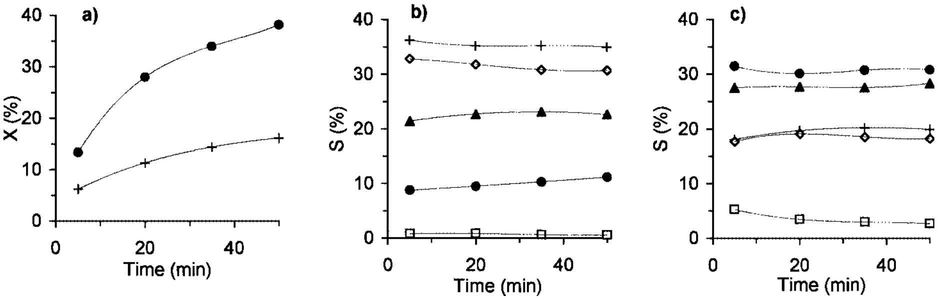


FIG. 1. Transformation of hexane on EUROPT-1 and Pt black at $T = 603$ K, $p(n\text{H}) : p(H_2) = 13 : 160$ mbar. (a) Conversion as a function of reaction time. +, Pt black; ●, EUROPT-1. (b and c) Selectivity of different products on EUROPT-1 (b) and on Pt black (c) as a function of reaction time. Symbols (b and c): ●, fragments ($<C_6$); +, skeletal isomers; ◇, methylcyclopentane (MCP); ▲, benzene; □, hexenes.

TABLE 1

Fragment Distribution (mol%) within the $<C_6$ Fraction (in Fig. 1) as a Function of Reaction Time[a]

	EUROPT-1				Pt black			
Molecule	5 min	20 min	35 min	50 min	5 min	20 min	35 min	50 min
C_1	43	46	50	53	26	27	28	28
C_2	18	15	13	11	19	18	18	18
C_3	14	14	13	12	31	30	29	28
C_4	11	11	10	10	13	14	14	14
C_5	14	14	14	14	10	11	11	11

[a] $T = 603$ K; $p(n\mathrm{H}) : p(\mathrm{H}_2) = 13:160$ mbar.

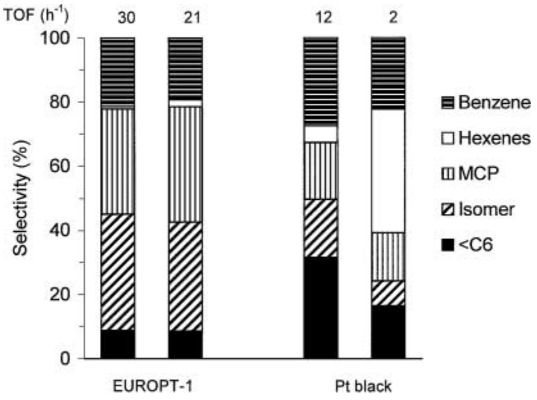


FIG. 3. Comparison of the catalytic patterns of regenerated (left column) and intentionally carbonized (by $p(n\mathrm{H}) : p(\mathrm{H}_2) = 10:80$ mbar, $T = 603$ K, $t = 20$ min) catalysts: EUROPT-1 and Pt black. The TOF values are given above the columns.

with the temperature. The catalytic behavior of Pt black and EUROPT-1 has been recently compared in detail (41).

Catalytic activity was also checked after carbonization and compared with the results obtained on regenerated catalyst (Fig. 3). Some 70% of the original activity of EUROPT-1 remained after the treatment, while only 17% did in the case of Pt black. The selectivity toward the different product classes hardly changed on EUROPT-1; thus deactivation could be called "nonselective deactivation" ($S/S_0 \approx 1$ for all the products). In the case of Pt black the selectivity of hexene formation increased drastically, while isomer and fragment formation was hindered by "coke" on Pt black, according to earlier observations (9, 42, 43). This behavior is called "selective deactivation" ($S/S_0 \neq 1$).

3.2. Analysis of the Deuterium Content of Methane Removed from EUROPT-1

3.2.1. The removal process. Figure 4 represents the amount of C_1 molecules removed from EUROPT-1 after exposure to a hexane and hydrogen mixture, $p(n\mathrm{H})$: $p(\mathrm{H}_2) = 20:50$ mbar, at $T_\mathrm{P} = 603$ K. The amount of methane removed from the surface at $T_\mathrm{R} = 293$ K was negligible and did not increase with time. At 293 K, the most reactive species left the surface rapidly—low-energy barrier for desorption—and no other species could be removed from EUROPT-1. The effective removal procedure started at $T_\mathrm{R} = 373$ K. The amount of C_1 molecules leaving the surface increased linearly as a function of time at 373, 473, and 573 K. This linear behavior indicates that the consumption of surface species had virtually no effect on the rate of removal, i.e., it was "zero order" with respect to the remaining CH_x species. On the other hand, at $T_\mathrm{R} = 673$ K, the evolution of the amount of methane desorbing from the catalyst surface could be described by a saturation curve. Thus, at $T_\mathrm{R} = 673$ K, the progressive consumption of the surface species, reacting with deuterium, decreased the desorption rate. Only a part of all removable species was deuterated off during 30 min at each temperature, except at $T_\mathrm{R} = 673$ K. Thus, methane released at the beginning of each procedure could have come off at lower temperatures, in the case of longer runs at the previous T_R, and/or at any temperatures

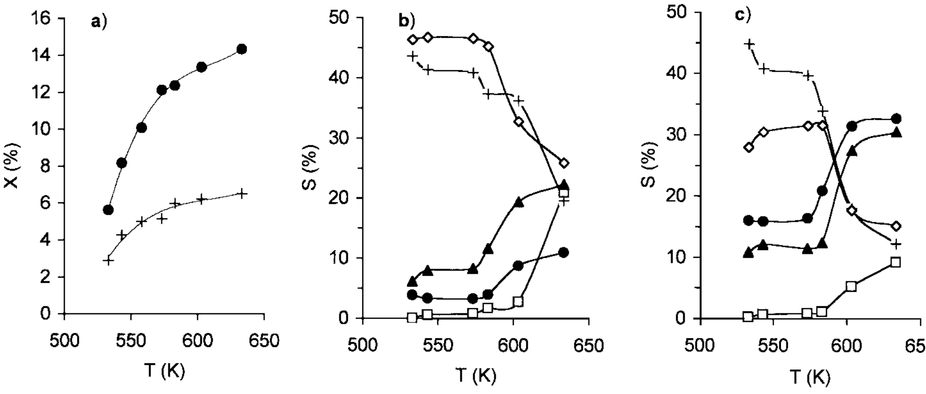


FIG. 2. Temperature dependence of hexane transformation on EUROPT-1 and Pt black. Symbols are the same as in Fig. 1. Reaction conditions: $p(n\mathrm{H}) : p(\mathrm{H}_2) = 13:160$ mbar, $t = 5$ min. (a) Conversion as a function of reaction temperature. +, Pt black; ●, EUROPT-1; (b and c) Selectivity of different products on EUROPT-1 (b) and on Pt black (c) as a function of reaction temperature. Symbols: ●, fragments ($<C_6$); +, skeletal isomers; ◇, methylcyclopentane (MCP); ▲, benzene; □, hexenes.

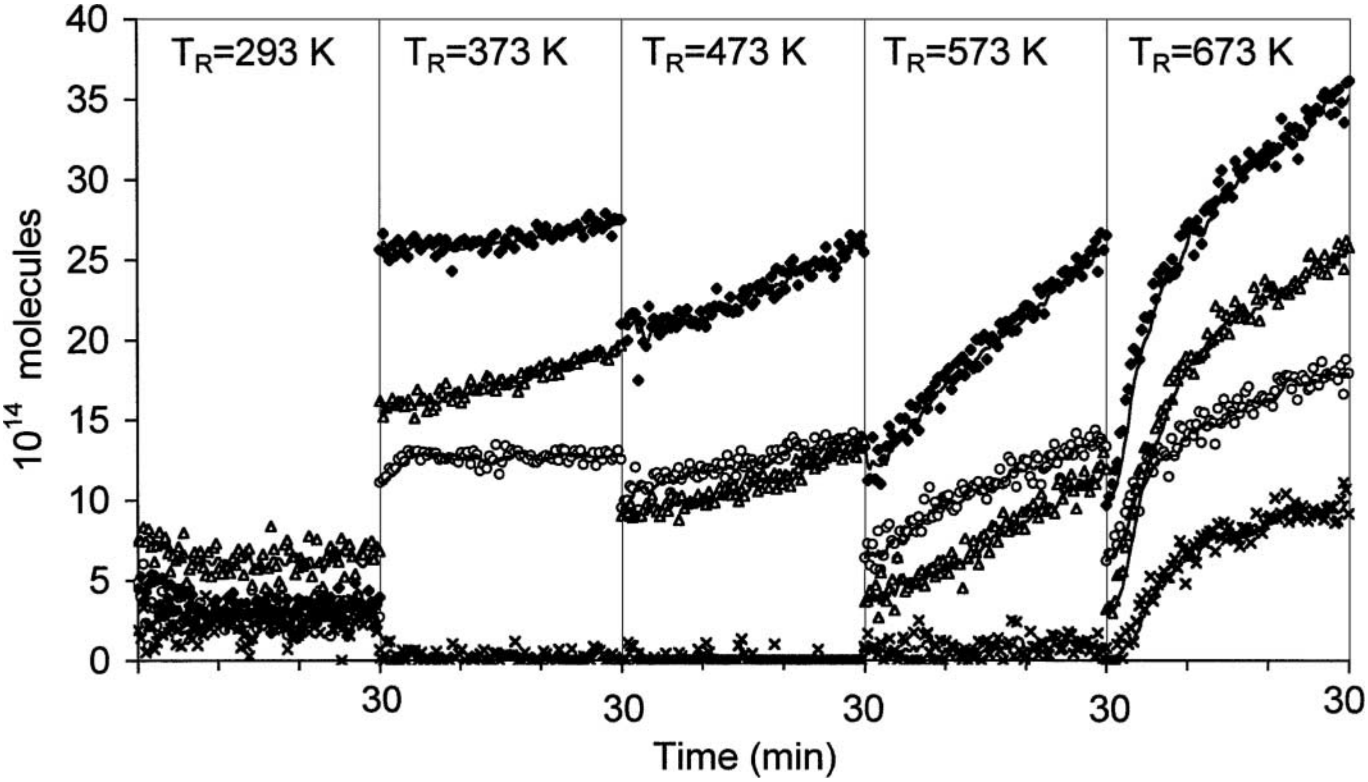


FIG. 4. Amount of C_1 fragments deuterated off from EUROPT-1 by deuterium at different removal temperatures (T_R). Pretreatment was carried out under a hexane/hydrogen mixture—$p(n\mathrm{H}) : p(\mathrm{H}_2) = 20:50$ mbar—at $T_P = 603$ K for 20 min. Evacuation temperature (T_E), after the pretreatment and in-between the removal steps at different T_R, was 293 K. ○, CD_4; ◆, CHD_3; △, CH_2D_2; ×, CH_3D.

in between the two stages. These "longer" runs, however, may have required unpractically long measurement times. The "saturation curves" at $T_R = 673$ K shows that 30 min was sufficient to displace almost all reactive surface species.

At any T_R, the most abundant methane isotopomer removed from EUROPT-1 was CD_3H (Figs. 4 and 5), except at $T_R = 293$ K, where CD_2H_2 was the main product (Fig. 4). CD_2H_2 and CD_4 were present in noticeable amounts at all removal temperatures (Figs. 4 and 5). The increase in CDH_3 concentration at $T_R = 673$ K is surprising, especially if one considers its very low abundance at lower removal temperatures. The quantity of CD_2H_2 also increased at 673 K. Thus, not only the mechanism of removal but also the origin, structure, and/or location of the parent carbonaceous species must have been different at 673 K.

Before discussing all the results, the capabilities of the method, its limitations as well as the ways of avoiding possible misinterpretations should be considered.

(a) One of the most important questions about the removal process is whether the methanes deuterated off represent the surface composition on the catalyst surface or whether there was a possible exchange of D_2 and H–C bonds of surface species or in the gas-phase. Primary H/D exchange might occur on the surface hydrocarbons before and during the removal procedure. In this case the following reaction can take place parallel to the C–C and C–Pt splitting:

$$\mathrm{C{-}H} + \mathrm{D(Pt)} \rightarrow \mathrm{C{-}D} + \mathrm{H(Pt)}.$$

Poly-C_xH_y deposits undergo deuterative splitting into CD_xH_y units before subsequent removal. *This hydrogenolytic* splitting was the main source of their removal as methane (44). If surface species had been only saturated and fragmented by deuterium, the protium (^{1}H) content of the removed C_1 would be the same as the one of the parent surface deposits. An extensive H–D exchange was reported in the aromatic end products from mixtures of C_8H_{18} and C_8D_{18} after reaction at 775 K over Pt-based catalysts. At this temperature, with prevailing aromatization, the mostly unsaturated surface intermediates had a relatively long lifetime (45, 46). In contrast, no exchange was reported in the unreacted feed in the absence of gas-phase hydrogen. In the presence of D_2, they underwent mainly single exchange, corresponding to the primary surface intermediate, $C_nH_{2n-1}Pt$ (47). If a marked H–D exchange occurred in the present study, the amount of highly deuterated species leaving the catalyst surface, for example CD_4, should increase progressively as a function of time. Figure 4, in turn, shows either a linear increase or a "saturation" (Fig. 4, $T = 673$ K) of CD_4. Thus, the amount of CD_4 deuterated off per unit

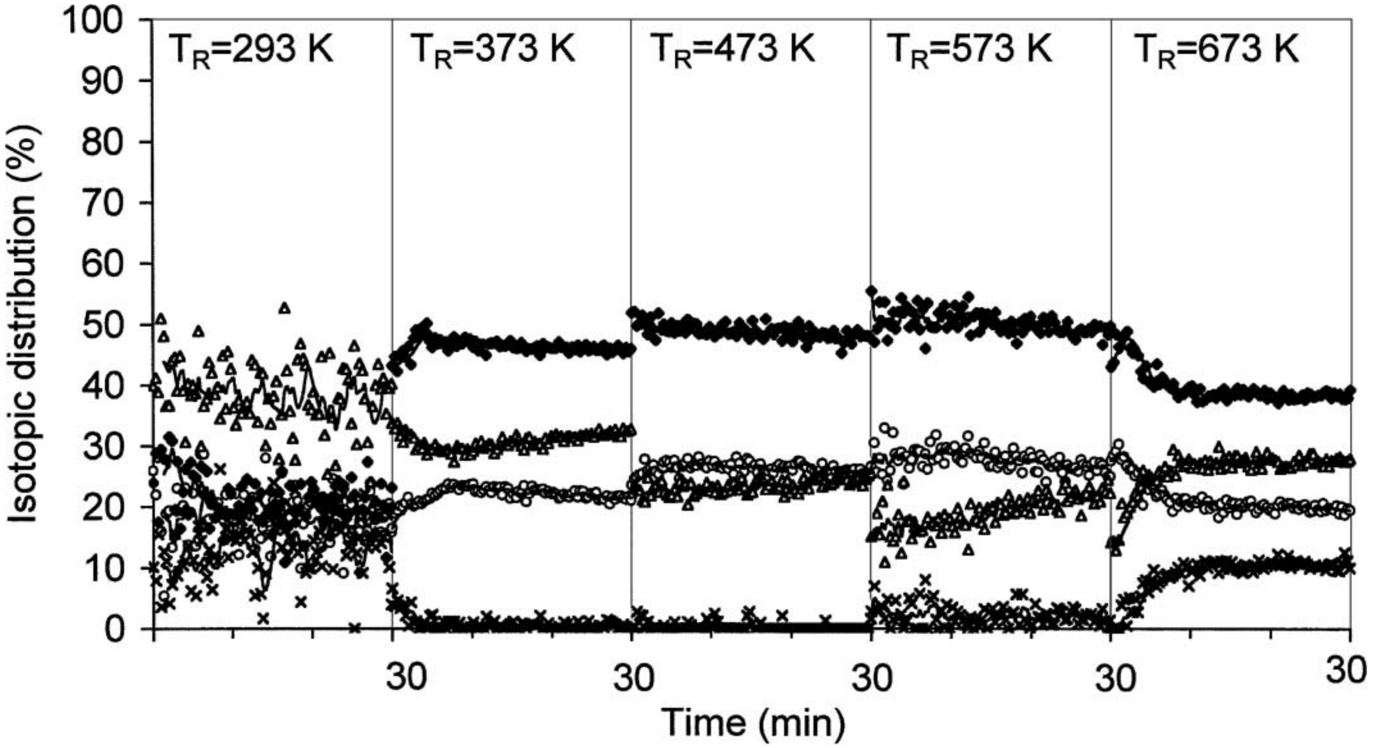


FIG. 5. Isotopic distribution among C_1 molecules deuterated off by deuterium from EUROPT-1 at T_R. Conditions, see Fig. 4. Pretreatment hexane/hydrogen mixture, $p(n\mathrm{H}) : p(\mathrm{H}_2) = 20 : 50$ mbar; $T_P = 603$ K for 20 min. Evacuation temperature, T_E, was 293 K. ○, CD_4; ◆, CHD_3; △, CH_2D_2; ×, CH_3D.

of time is either constant or decreasing: concentration of deuteromethanes was constant as a function of time (Fig. 5). In our case, the relatively low rate of H–D exchange could be explained by the low ^{1}H content in the parent carbonaceous deposits (Table 2). In fact the H/C ratio varied between 1.1 and 1.5.

(b) Secondary H–D exchange could occur between D_2 and the desorbed deuteromethane molecules. In fact, H–D exchange of methane was shown to occur at about 333 K on a "clean" (nonpretreated) Pt surface (48). Nevertheless, in our case, carbonaceous deposits covered a large fraction of the surface (4, 5, 8, 43) and only a few Pt sites remained accessible. The H–D exchange was reported to be very slow on carbon-covered metal (49). In fact in our case, only minor amounts of HD and H_2 where detected during the removal process. Furthermore, the exchange between removed methane molecules was also negligible, as shown by the constant concentration of deuteromethanes as a function of time (Fig. 5).

(c) C_1 molecules detected by MS could be fragments of larger hydrocarbons desorbed during the removal process. Although earlier experiments (see also Fig. 11) showed that mostly methane left Pt black after exposure to various $n\mathrm{H}/\mathrm{H}_2$ mixtures (28), larger hydrocarbons were trapped at liquid nitrogen temperature before MS analysis to eliminate this interference. The trap was removed at the end of each run and the products were analyzed by the mass spectrometer together with the circulating C_1 species. The mixture contained more than 80% C_1 in the case of Pt black and was more than 65% in the case of EUROPT-1, in agreement with earlier removal experiments by H_2 (28). The exact composition of the trapped mixture could not be determined precisely. Nevertheless, benzene and hexane were clearly identified in the mass spectrum, in accordance with earlier observations (28).

TABLE 2

Initial ($t = 5$s at $T_R = 293$ K) and Cumulative[a] Isotopic Composition (in%) in C_1 Molecules Removed from EUROPT-1[b]

	483 K		543 K		573 K		603 K	
Molecule	Initial	Cum.	Initial	Cum.	Initial	Cum.	Initial	Cum.
CD_4	18.5	24.4	16.8	24.2	16.0	25.6	17.8	22.6
CD_3H	43.1	41.7	41.5	41.6	37.5	40.4	28.1	43.9
CD_2H_2	34.7	30.6	39.6	29.2	33.3	28.5	44.1	28.7
CDH_3	3.7	3.3	2.1	5.0	13.2	5.5	10.0	4.8
$H/C_{\mathrm{surf.}}$[c]	1.2	1.1	1.3	1.2	1.4	1.1	1.5	1.2

[a] The cumulative composition corresponds to the average distribution in C_1 molecules after a complete reaction cycle from $T_R = 293$–673 K.

[b] Pretreatment was carried out with $p(n\mathrm{H}) : p(\mathrm{H}_2) = 20 : 50$ mbar at T_P for $t = 20$ min; evacuation was carried out at $T_E = 293$ K.

[c] The $H/C_{\mathrm{surf.}}$ is the approximated H/C surface ratio calculated from the isotopic distribution in methane isotopes (in%): $(3 \times CDH_3 + 2 \times CD_2H_2 + CD_3H)/100$.

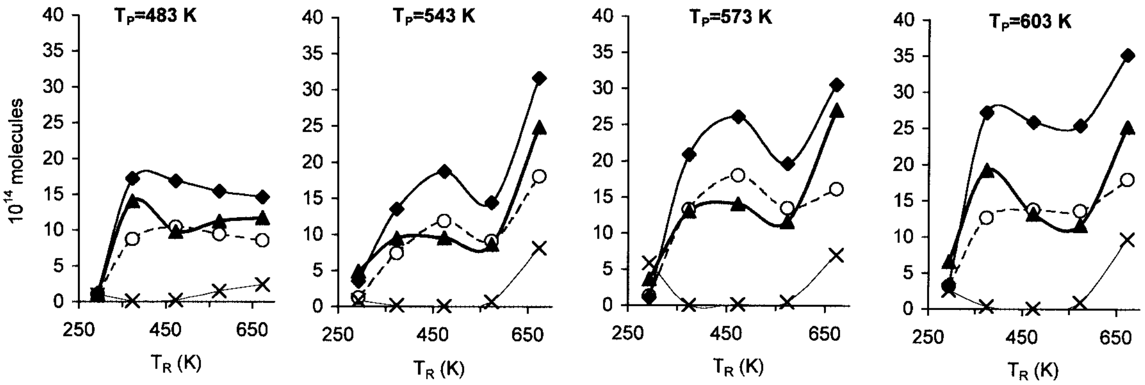


FIG. 6. Evolution of the cumulated amount of C_1 molecules removed from EUROPT-1 after a 30-min reaction as a function of T_R. Pretreatment was carried out for 20 min with $p(n\mathrm{H}) : p(\mathrm{H_2}) = 20:50$ mbar at four different temperatures (T_p): 483, 543, 573, and 603 K. $T_E = 293$ K. ○, CD_4; ◆, CHD_3; ▲, CH_2D_2; ×, CH_3D.

3.2.2. Variation in the pretreatment conditions. Evolution of the total amount of C_1 isotopomers leaving the surface of EUROPT-1 during one removal cycle (five steps, 30 min each) as a function of the removal temperature (T_R) is presented in Fig. 6 for different temperatures of pretreatment (T_p). The amounts of CD_4, CD_3H, and CD_2H_2 exhibited first a maximum for all T_P. The amount of C_1 species originating from the surface also sharply increased above $T_R = 573$ K, when the pretreatment was carried out at a temperature (T_p) higher than 483 K (Fig. 6). The total amount of C_1 species desorbed in the first "maximum" increased with the pretreatment temperature. In contrast, the amplitude of the second maximum seems to be independent of T_P. The two "maxima," observed for $T_P \geq 543$ K, may be characteristic of two different types of carbonaceous deposits and/or two different mechanisms for methane formation. The first "maximum" could be associated to the presence of "weakly adsorbed" species. Among them, "$\equiv$CH" leading to CHD_3 appears to be the most abundant on the surface. This observation is in agreement with previous work (50). The concentration of this species increased with the pretreatment temperature. The second "maximum" only appeared when the hydrocarbonaceous deposit was formed at $T_P \geq 540$ K and could be associated with the presence of "strongly bonded" carbonaceous deposits. They contained a higher proportion of carbenic species (=CH_2) and/or more larger chemisorbed molecules.

The initial isotopic composition in methanes removed from EUROPT-1 at 293 K could be used to estimate the structure of the most reactive C_1 surface species (Table 2). In fact, these species could be important reaction intermediates in the hydrogenolysis process (51). The concentration in CD_2H_2 and CDH_3 was significantly higher in the initially removed mixture and must have originated from the most reactive surface entities (51). Furthermore, the average H content in the carbonaceous deposits could be estimated (Table 2). The initially removed methanes systematically contained more H. These species, as well as other hydrocarbonaceous residues, could retain hydrogen and would act as H buffers during the reactions (5, 6, 52). The average H/C ratio did not change significantly with the pretreatment temperature.

The influence of the H_2/nH ratio during the pretreatment was also studied. Figure 7 presents the results obtained

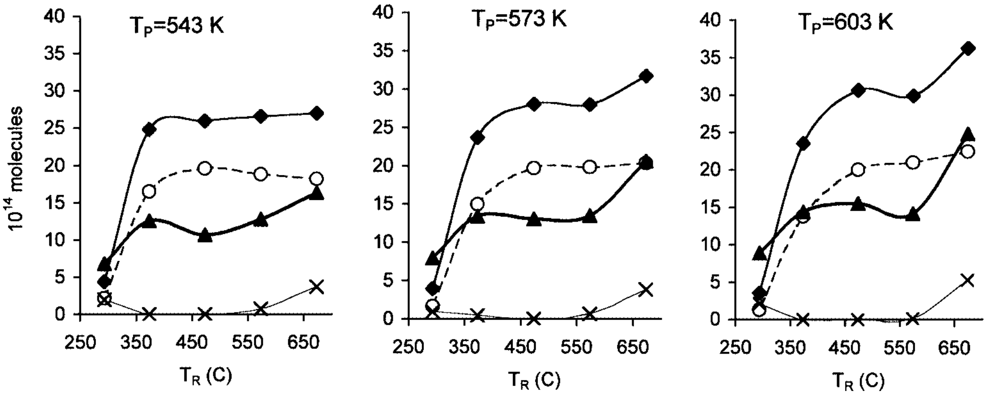


FIG. 7. Evolution of the cumulated amount of C_1 molecules removed from EUROPT-1 after a 30-min reaction as a function of T_R. Pretreatment was carried out for 20 min with a hydrocarbon-lean mixture, i.e., $p(n\mathrm{H}) : p(\mathrm{H_2}) = 5:50$ mbar at different temperatures (T_p): 543, 573, and 603 K. $T_E = 293$ K. ○, CD_4; ◆, CHD_3; ▲, CH_2D_2; ×, CH_3D.

after a pretreatment with a “hydrocarbon-lean” mixture, i.e., $p(H_2):p(n\mathrm{H}) = 50:5$ mbar. These results were compared to those obtained after a pretreatment with a “hydrocarbon-rich” mixture (Fig. 6). The “later increase” discussed earlier did not clearly appear in Fig. 7. In this case the shape of the curves rather resembled those observed after exposure at $T_P = 483$ K in Fig. 6. The two maxima only appeared after a pretreatment at 603 K (Fig. 7). Thus, increasing the excess in hydrogen would have the same effect as a decrease in the reaction temperature (T_p).

Table 3 clearly shows that the initially removed methane molecules after pretreatments with a “hydrocarbon-lean” mixture contained more H. The most abundant product in Table 2 was CD_3H, as opposed to the CD_2H_2 shown in Table 3 (after hydrogen-lean pretreatment). Its relative concentration increased with T_P in the latter case, especially in the initial methane fraction. The higher “cumulative” H/C ratio indicates that the overall amount of carbonaceous deposits must have been less after hydrocarbon-lean pretreatment; thus even the more dehydrogenated residues left the surface during a deuteration of 30 min.

The effect of the evacuation temperature (T_E) was also evaluated after pretreating the EUROPT-1 sample at $T_P = 603$ K with $p(n\mathrm{H}):p(H_2) = 20:50$ mbar. The initial isotopic composition (Fig. 8) showed that evacuation at high temperature led to markedly more dehydrogenated surface methane precursors (53).

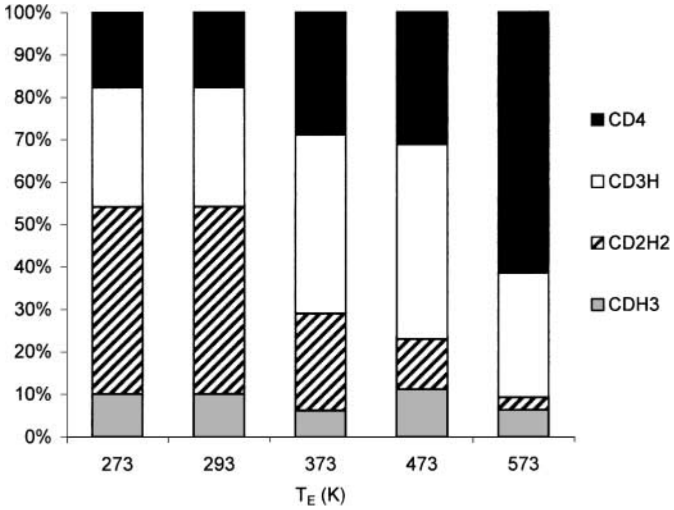


FIG. 8. Evolution of the initial ($t = 5$ min) isotopic distribution in C_1 isotopes removed from EUROPT-1 as a function of the evacuation temperature (T_E). Pretreatment: 20 min under $p(n\mathrm{H}):p(H_2) = 20:50$ mbar at $T_P = 603$ K.

3.3. *Analysis of the Deuterium Content of Methane Removed from Pt Black*

Whatever the removal temperature was, the amount of C_1 species deuterated off from the Pt black surface increased linearly as a function of time under D_2 (Fig. 9). The relatively high rate of deuteration at ambient temperature indicates a considerable amount of weakly bonded carbonaceous surface species. Furthermore, the same linear “removal curve” at all temperatures (cf. Figs. 4 and 9) indicates that the mechanism of the deuteration remained the same at any removal temperature. On the surface of Pt black, carbonaceous species might be present in such high concentrations that their progressive consumption did not affect the reaction rate.

TABLE 3

Initial ($t = 5$ s at $T_R = 293$ K) and Cumulative[a] Isotopic Composition (%) of C_1 Molecules Removed from EUROPT-1[b]

Molecule	543 K Initial	543 K Cum.	573 K Initial	573 K Cum.	603 K Initial	603 K Cum.
CD_4	17.6	30.1	13.0	28.7	9.6	27.3
CD_3H	35.2	43.6	34.6	43.3	33.5	43.0
CD_2H_2	40.3	23.7	46.8	25.7	51.4	27.0
CDH_3	6.9	2.6	5.6	2.3	5.5	2.7
$H/C_{surf.}$[c]	1.4	1.0	1.5	1.0	1.5	1.0

[a] The cumulative composition corresponds to the average distribution in C_1 molecules after a complete reaction cycle from $T_R = 293$–673 K.

[b] Pretreatment was carried out with a hydrocarbon-lean mixture: $p(n\mathrm{H}):p(H_2) = 5:50$ mbar at T_P for $t = 20$ min; evacuation was carried out at $T_E = 293$ K.

[c] The $H/C_{surf.}$ is the approximated H/C surface ratio calculated from the isotopic distribution in methane isotopes (in %): $(3 \times CDH_3 + 2 \times CD_2H_2 + CD_3H)/100$.

The evolution of methane isotopomers as a function of the removal temperature (T_R) on Pt black was markedly different from that observed on EUROPT-1 (cf. Figs. 6 and 10). CD_4 was the major product deuterated off from Pt black. The amounts in CD_3H and CD_2H_2 were much smaller than in the case of EUROPT-1. No maxima appeared in the case of Pt black (Fig. 10). The amount of CD_4 increased continuously as T_R increased, while CD_3H decreased. Other products only appeared in negligible amounts and no significant changes were observed as a function of T_R. The average H/C ratio was lower on Pt black (Table 4) than on EUROPT-1 (Table 2). As 30–70% of methane still contained some H (protium) we concluded that the deposit removable by deuterium was not excessively dehydrogenated (Tables 2–4).

4. DISCUSSION

4.1. *Possible Relations between the Reaction Intermediates and the Removed Products*

The isotopic composition in methanes leaving the intentionally carbonized catalyst surface may supply important, although indirect, information on the possible structure and composition of both reaction intermediates of skeletal reactions of hexane (54) and carbonaceous deposits produced from them. Although the reaction mechanism is not the

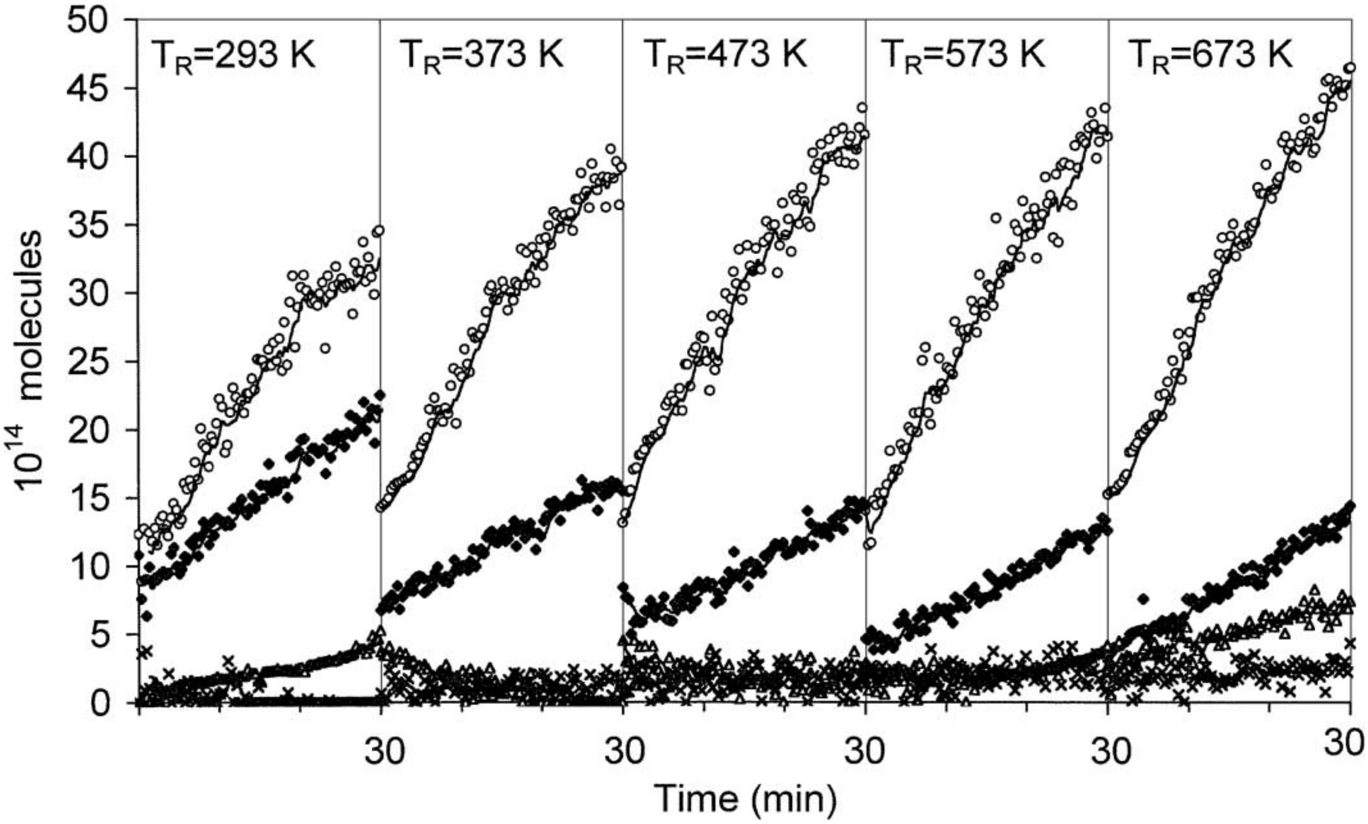


FIG. 9. Amount of C_1 fragments deuterated off from Pt black by deuterium at different removal temperatures (T_R). Pretreatment was carried out for 20 min with $p(n\mathrm{H}) : p(\mathrm{H}_2) = 20:50$ mbar at $T_P = 603$ K. Evacuation temperature (T_E), after the pretreatment and in-between the removal steps at different T_R, was 293 K. ○, CD_4; ◆, CHD_3; △, CH_2D_2; ×, CH_3D.

subject of the present paper, a brief summary of the basic statements is presented. Two neighboring metal atoms were proposed for C_5 cyclization and ring opening, leading to MCP and isomers (55). Single hydrogenolysis might be related to these reactions (56), likely involving 1,3- or even 1,4-interactions between the reactant and one or two Pt atoms (57, 58), attached with single or double bonds preferentially to "ledge structures." Dauscher *et al.* (59) attributed multiple fragmentation to these sites. Several other ideas concerning the hydrogenolysis of hydrocarbons on Pt were also proposed (60–62). Three metal atoms in hexagonal geometry were found to be the active site for aromatization

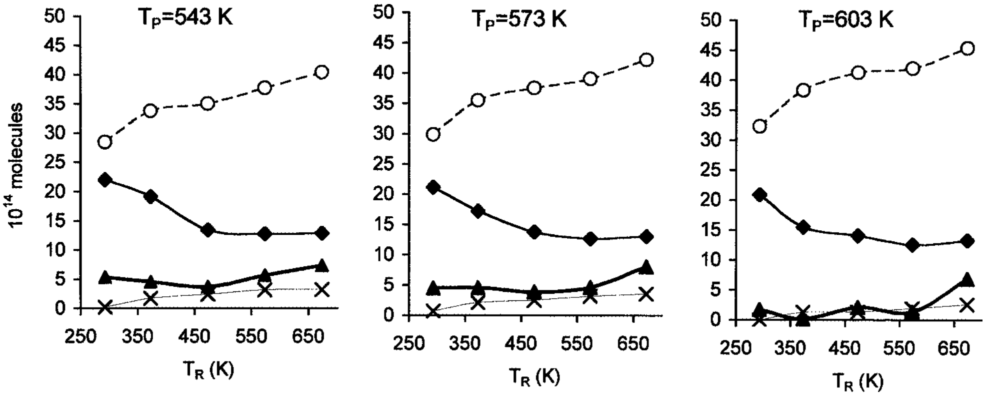


FIG. 10. Evolution of the cumulated amount of C_1 molecules removed from Pt black after a 30-min reaction as a function of T_R. Pretreatment was carried out for 20 min with $p(n\mathrm{H}) : p(\mathrm{H}_2) = 20:50$ mbar at different temperatures (T_p): 543, 573, and 603 K. $T_E = 293$ K. ○, CD_4; ◆, CHD_3; ▲, CH_2D_2; ×, CH_3D.

TABLE 4

Initial ($t = 5$ s at $T_R = 293$ K) and the Cumulative[a] Isotopic Composition (in%) in C_1 Molecules Removed from Pt Black[b]

	543 K		573 K		603 K	
Molecule	Initial	Cum.	Initial	Cum.	Initial	Cum.
CD_4	40.3	59.9	39.9	61.5	46.9	67.5
CD_3H	33.3	27.4	31.9	26.0	35.4	25.9
CD_2H_2	19.1	9.1	19.4	8.5	13.4	4.1
CDH_3	7.3	3.6	8.8	4.0	4.3	2.5
$H/C_{surf.}$[c]	0.9	0.6	1.0	0.6	0.8	0.4

[a] The cumulative composition corresponds to the average distribution in C_1 molecules after a complete reaction cycle from $T_R = 293$–673 K.

[b] Pretreatment was carried out with $p(n\text{H}) : p(\text{H}_2) = 20:50$ mbar at T_P for $t = 20$ min; evacuation was carried out at $T_E = 293$ K.

[c] The $H/C_{surf.}$ is the approximated H/C surface ratio calculated from the isotopic distribution in methane isotopes (in%): $(3 \times CDH_3 + 2 \times CD_2H_2 + CD_3H)/100$.

(63). One Pt atom (or possibly Pt–C ensemble) induced dehydrogenation to hexenes (56).

In the present experiments, reaction of hexane was stopped by evacuation of the reaction mixture. Chemisorbed moieties (that had been reaction intermediates) lost one or two H atoms and become "frozen" on the surface. Hydrogenative desorption would require free metallic sites in the their vicinity, as suggested by Frennet *et al.* in the "multisite adsorption model" (64a–64c). These sites would dissociate deuterium that could react (i) with chemisorbed C_1 forming methanes upon hydrogenative desorption (58) or (ii) with C_n deposits in the vicinity, inducing their hydrogenolytic decomposition to $C_xH_yD_z$. These species could also form methane in further reaction. The results are insufficient to decide whether dissociated D atoms or chemisorbed D_2 according to the "reactive" mechanism (65) were active in this removal. The necessity of "free Pt sites" to dissociate H_2 or D_2 near the surface C is supported by the hindering of methane formation in the hydrogenative removal of residues from Pt–Sn/Al_2O_3 catalysts (29). The deuterium content of methane in the removed fraction would depend on their degree of dehydrogenation. This is markedly different with the two catalysts (Fig. 11), although the amount of methane removed by hydrogen was found to be similar to each other (28).

The removal of surface residues by hydrogen showed small differences between EUROPT-1 and Pt black catalysts. The technique we used here (applying hydrogen after evacuation of a batch reactor) removed mostly methanes from the surface of both catalysts exposed to an alkane/hydrogen mixture (28), even though the fragmentation was only a minor reaction during the previous run (Figs. 1 and 2). The number of C atoms removed by hydrogen corresponded to a C/Pt ratio between 1.2 and 1.3 for both EUROPT-1 and Pt black (28).

The present deuterative removal experiments, however, prove that surface precursors removed as methane by hydrogen, shown in Fig. 11, must be different on the two catalysts, in accordance with catalytic observations (Section 3.1)

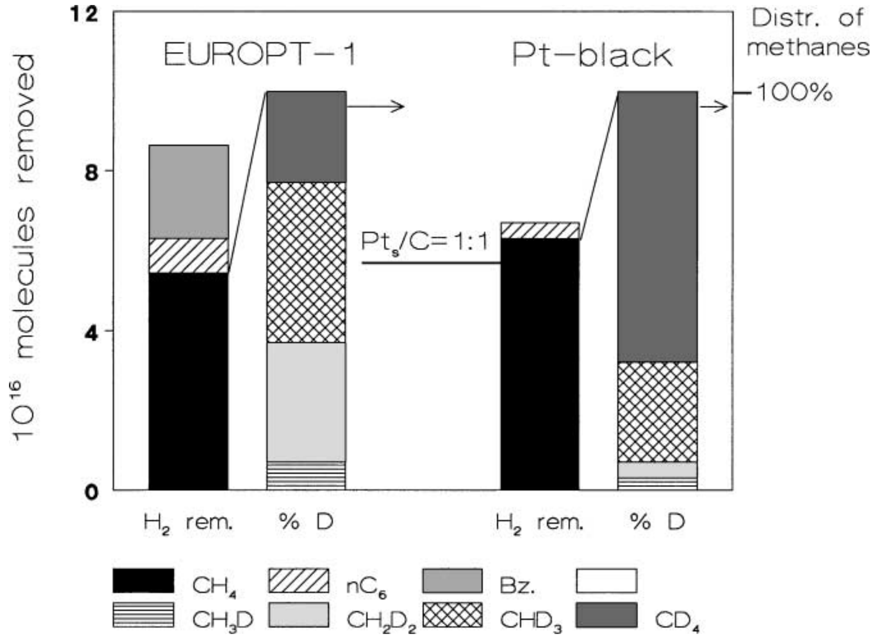
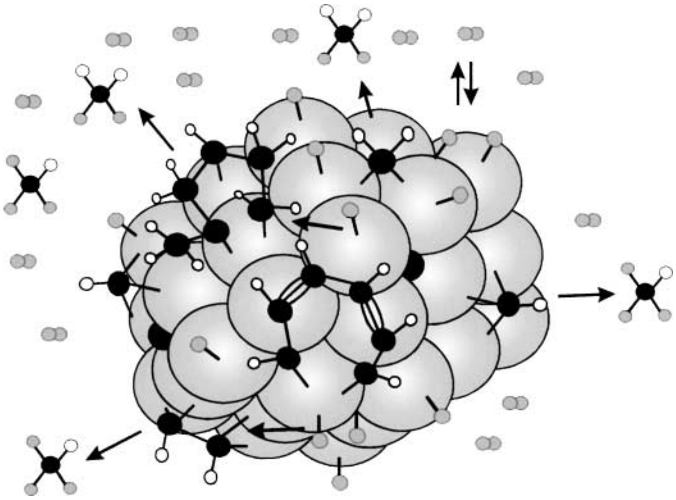


FIG. 11. Number of molecules removed by hydrogen treatment of Pt black and EUROPT-1 after reacting with hexane+H_2 (columns 1 and 3). Actual Pt surface, 35×10^{16} Pt atom; conversion in the preceding reaction, 10% in both cases. After Ref. (28). Pretreatment: $p(n\text{H}) : p(\text{H}_2) = 4:160$ mbar at $T = 603$ K. Deuterium distribution in the methane fraction removed by D_2 treatment (columns 2 and 4)—present work: total distribution after pretreatment, $p(n\text{H}) : p(\text{H}_2) = 20:50$ mbar; $T_P = 603$ K.

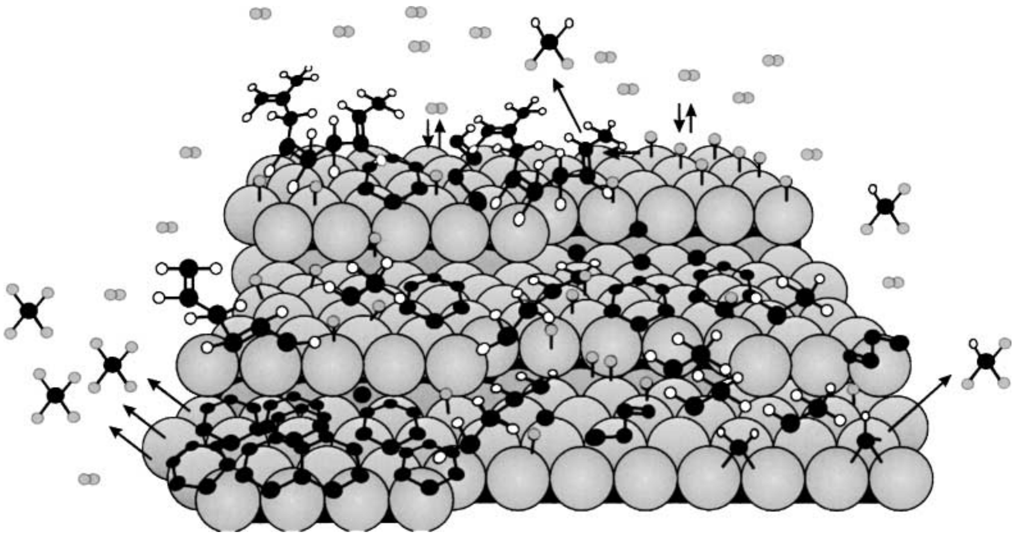


SCHEME 1. Schematic illustration of different carbonaceous species on the surface of EUROPT-1—depicted after Ref. (66)—and their possible removal by deuterium. H atoms are shown as small empty circles, D atoms as small gray circles, and C atoms as larger black circles.

and with earlier results (15, 16). The main difference between the two catalysts is the size of the contiguous Pt islands.

EUROPT-1 contains a nearly perfect 55-atom cubooctahedral structure (38, 66) with (100) faces of nine Pt atoms and (111) faces of six Pt atoms (Scheme 1). Particles of EUROPT-1 are too small to form large chemisorbed hydrocarbonaceous molecules. Edges, corners, or possible imperfections can be active in multiple hydrogenolysis leading to methane (Table 1) (38, 39). Scheme 1 shows an adsorbed benzene precursor that may have occupied the 6-atom (111) planes and a possible C_5 cyclic intermediate on the (100) plane (38, 39). Such intermediates could be removed either without decomposition (Fig. 11) (28) or in the form of methane after their hydrogenolytic rupture. The carbonaceous deposits can be formed on its surface via the "C_1 route" (15, 16): fragmentation of larger adsorbates would produce methylene and methylidyne radicals. Their removal leads to abundant CD_3H and CD_2H_2 in the gas phase (Fig. 11). This procedure is symbolized by individual C_1 units on EUROPT-1 (Scheme 1). A theoretical study also showed the stability of different chemisorbed C_1 units: CH_3, CH_2, CH, or even C atoms and their probable recombination on the surface (50).

Pt black can expose larger free Pt surfaces (43). Scheme 2—based on Wrammerfors' thesis (67)—illustrates the possible presence of monomeric, oligomeric hydrocarbonaceous intermediates and residues on a large stepped Pt surface, resembling, likely, that of Pt black. The C_1 carbonization route cannot be excluded. However, whenever aromatization takes place, *trans*-dienes and trienes are, likely, formed and their polymerization would lead to larger chemisorbed molecules (17, 55). They may be attached to the surface with several C–Pt bonds. This "polymerization route" may be more pronounced on Pt black than on EUROPT-1 (15, 16). Besides the reaction intermediates, the surface would be covered by embedded C atoms (shown in Scheme 2 below the edge of the upper terrace), "graphitic," "polymeric," "disordered" surface deposits with multiple C–Pt bonds. The latter type is the main reason for deactivation (43). All these structures were detected on Pt black by XPS and TEM studies (8, 9, 43) after exposure to mixtures of hydrogen and hexane (or hexadiene). Deuterium chemisorbed from the gas phase would attack C_1 or C_n species, splitting off C_1 units which then would appear as deuteromethanes, mostly CD_4 (Fig. 11) in the gas phase (Scheme 1). XPS measurements showed that hydrogen can



SCHEME 2. Schematic illustration of the surface of a larger Pt particle and possible carbonaceous residues. Adapted after the thesis of Wrammerfors (67). The possible removal occurs by interaction of CH_x units, by C atoms with surface deuterium, and by hydrogenolytic splitting of larger carbon chains.

facilitate the migration of carbon atoms between surface and subsurface positions (8). This procedure is usually accompanied by structural rearrangement of Pt black (8b). Thus, it is possible that "dissolved" deuterium removes carbon atoms from a subsurface position as CD_4. This procedure was definitely more pronounced in the case of Pt black.

4.2. Structure of Carbonaceous Deposits as Indicated from the Deuterative Removal

Unfortunately no sharp boundary appeared between the deuteromethanes originating from the different kinds of surface species during the removal process. On EUROPT-1, however, different sections could be distinguished in the removed C_1 as a function of the removal temperature (Figs. 6 and 7), as opposed to that on Pt black (Fig. 10). Such differences could be explained either by the different nature of the deposits or by the different mechanisms for carbonaceous deposit formation and removal. The residues may be classified as follows depending on the hydrogen removal pathway.

The *(i) most reactive carbonaceous species* must have appeared among the products removed initially at ambient ($T_R = 293$ K) temperature. At the beginning of the removal process, large amounts of CD_3H desorbed from both EUROPT-1 and Pt black. CD_4 was the most abundant in the case of unsupported Pt and CD_2H_2 was the second highest component desorbing from EUROPT-1 (Tables 2–4). The precursor of these molecules might be C_1 entities produced from the multiple rupture of hexane which remained on the catalyst surface when the reaction was stopped. Pt black produced about three times more fragments during hexane transformation (Figs. 1 and 2), and also more methane, than did EUROPT-1. In accordance, considerable amounts of C_1 were removed at ambient temperature from Pt black (Fig. 9) as opposed to that from EUROPT-1 (Fig. 4). Thus they might originate from primary C_1 fragments. The H/C ratio in this initial fraction was between 1.2 and 1.5 with EUROPT-1, and almost independent of the hydrogen partial pressure during the exposure (Tables 2 and 3). The H/C ratio, as a rule, was lower than 1 for Pt black (Table 4). Thus, these single C-atom entities retained on unsupported Pt—including also subsurface C (8, 43)—are more dehydrogenated than their counterparts on the surface of Pt/SiO_2.

Since the number of removed C atoms exceeded the number of surface Pt sites (Fig. 11), it should also be assumed that surface species remaining from *(ii) intermediates of nondegradative reactions* (aromatization, C_5 cyclization, or isomerization) can form methane directly by interacting with hydrogen (both protium and deuterium) (11, 28). Surface hydrogen atoms would attack carbonaceous deposits left over (64) and induce hydrogenolytic C–C bond splitting to be removed as C_1. Self-reactivation reported during the subsequent test run on Pt black pretreated and evacuated under the same conditions (9) also indicates the possibility of their removal during the reaction. These "reversible intermediates," which may be detected as "disordered" carbon by XPS in UHV condition (8, 43), are at the frontier between reaction intermediates and residual carbonaceous deposits (14, 68). The hydrogenolytic splitting of larger surface C units is supported by the appearance of C_2–C_5 fragments in the hydrogenative removal of residues from Pt–Sn/Al_2O_3 catalysts (29), where their breaking up to C_1 units must have been hindered.

Finally, some *(iii) "irreversible" carbon* could not be removed by hydrogen at all (16, 19, 21, 30, 68). Such deposits are accumulation and gradual dehydrogenation of the above precursors leading to the deactivated Pt–C state (19, 20). These deposits are strongly bonded to the surface and/or very deeply dehydrogenated. The present study provides no information about their structure. These may be named "residual" or "spectator" species leaving the surface at only very high temperature.

5. CONCLUSIONS

Carbonaceous residues remained after reactions of hexane on Pt black and Pt/SiO_2 (EUROPT-1). Conversions up to 35% were reached with rather constant selectivities. More fragments ($S \sim 35\%$) were formed on Pt black than on EUROPT-1 ($S \sim 10\%$). However, EUROPT-1 produced more methane within the $<C_6$ fraction. The selectivity toward saturated C_6 products (MCP and isomers) was ca. 70% on EUROPT-1 and ca. 40% on Pt black.

The corresponding deuterative removal of the carbonaceous residues gave mostly methane, in spite of the rather low methane selectivity upon reaction. Deuterium content provided useful information on the possible degree of dehydrogenation of surface methane precursors. CD_4 prevailed on Pt black whereas CHD_3 was the most abundant product removed from EUROPT-1.

The average H/C ratio in the methane precursors, as indicated from the overall D content in the methane, was 1–1.5 with EUROPT-1 and below 1 with Pt black. This value decreased somewhat when the temperature of the previous reaction was higher.

The deuterium content in the methanes leaving the surface at the beginning of the removal procedure, as a rule, was smaller than in the total removed amount. This difference was more pronounced with Pt black. This observation indicates that the most reactive surface entities must have been less dehydrogenated.

More methane left the catalyst surface at higher removal temperature. With EUROPT-1 a maximum appeared between 350 and 450 K. The "amplitude" of this "maximum" increased as the pretreatment temperature or the hydrogen-to-hexane ratio increased (Figs. 6 and 7). This was in a very good agreement with the activity in hexane conversion. A second increase was reached around 650 K, where also the abundance of CH_2D_2 and CHD_3 increased at the expense of CD_4 on EUROPT-1. The relative abundance of the different isotopomers as a function of the removal temperature was different on the two catalysts. No second maximum appeared with Pt black where CD_4 prevailed under any condition.

Precursors of deuteromethanes on EUROPT-1 are mostly chemisorbed C_1 units: CH_3, CH_2, CH, or even C atoms (50) formed in the multiple rupture of hexane. Nevertheless, hydrogenolytic splitting of larger chemisorbed hydrocarbons ("frozen intermediates") is also possible (44). Treatments with hydrocarbon-lean mixtures led to fewer deposits, the most reactive fraction of which was less dehydrogenated. On Pt black with larger contiguous Pt surfaces, in turn, more chemisorbed hydrocarbons were formed and their oligomerization was also more likely. Surface and subsurface C atoms (8) may be also responsible for the large amount of CD_4 here.

APPENDIX: CALCULATION OF THE AMOUNT OF REMOVED MOLECULES FROM MID DATA

Methane fragmentations were measured in an empty reactor. One can write

$$CH_4 \rightarrow i CH_4 + j CH_3 + k CH_2 + l CH + m C.$$

We obtained

$$\begin{aligned} m/z &= 16(CH_4),\ i = 44.4\%,\\ m/z &= 15(CH_3),\ j = 38.5\%,\\ m/z &= 14(CH_2),\ k = 8.4\%\\ m/z &= 13(CH),\ l = 5.2\%\\ m/z &= 12(C),\ m = 3.5\%, \end{aligned}$$

where i, j, k, l, and m are the fragmentation constants for methane.

We assumed that (i) "the probability of ionization of each species to form the corresponding molecule–ion is not affected by the number of hydrogen or deuterium atoms in the molecule" (Ref. (69), p. 224) and the fragmentation of each molecule is approximately the same (69). Further we assumed that the (ii) C–H and C–D cleavage occurs with the same probability. Any possible error caused by these assumptions was not higher than the normal scattering of the measurements (Figs. 4, 5, and 9).

$$\begin{aligned} CDH_3 &\rightarrow i CDH_3 + 1/4\, j CH_3 + 3/4\, j CH_2D + 1/2\, k CH_2\\ &\quad + 3/4\, l CH + 1/4\, l CD + m C\\ CD_2H_2 &\rightarrow i CD_2H_2 + 1/2\, j CH_2D + 1/2\, j CHD_2\\ &\quad + 1/6\, k CH_2 + 2/3\, k CHD + 1/6\, k CD_2\\ &\quad + 1/2\, l CH + 1/2\, l CD + m C\\ CD_3H &\rightarrow i CD_3H + 1/4\, j CD_3 + 3/4\, j CD_2H + 1/2\, k CD_2\\ &\quad + 1/2\, k CHD + 1/4\, l CH + 3/4\, l CD + m C\\ CD_4 &\rightarrow i CD_4 + j CD_3 + k CD_2 + l CD + m C \end{aligned}$$

During MS analysis, masses (m/z) of 12–20 were continuously monitored. The background, measured before every removal process for 10 s, was systematically subtracted. The sensitivity of the mass spectrometer was set to 10^{-11} mbar and the total pressure was regulated to 10^{-6} mbar. Raw data are denoted M12–M20 and expressed in percentage of the total pressure in the MS. Normalization to ΣM resulted in m12–m20. From these data derives the normalized concentrations in C_1 species (a–e), as shown in Table 5.

After Table 5, the following calculations can be made.

$$\begin{aligned} &\text{m}20 = i \cdot e \Rightarrow e = \text{m}20/i,\\ &\text{m}19 = i \cdot d \Rightarrow d = \text{m}19/i,\\ &\text{m}18 = j \cdot e + 1/4 \cdot j \cdot d + i \cdot c \Rightarrow\\ &\quad c = 1/i \cdot (\text{m}18 - j \cdot e - 1/4 \cdot j \cdot d),\\ &\text{m}17 = 3/4 \cdot j \cdot d + 1/2 \cdot j \cdot c + i \cdot b \Rightarrow\\ &\quad c = 1/i \cdot (\text{m}17 - 3/4 \cdot j \cdot d - 1/2 \cdot j \cdot c),\\ &\quad a = 1 - (b + c + d + e), \end{aligned}$$

TABLE 5

Normalized Concentrations in C_1 Species

Mass	Fragment	CH_4(a)	CDH_3(b)	CD_2H_2(c)	CD_3H(d)	CD_4(e)
m12	C	m	m	m	m	m
m13	CH	l	$3/4 l$	$1/2 l$	$1/4 l$	
m14	CH_2, CD	k	$1/2 k + 1/4 l$	$1/2 k + 1/2 l$	$3/4 l$	l
m15	CH_3, CDH	j	$1/4 j + 1/2 k$	$2/3 k$	$1/2 k$	
m16	CH_4, CDH_2, CD_2	i	$3/4 j$	$1/2 j + 1/6 k$	$1/2 k$	k
m17	CDH_3, CD_2H		i	$1/2 j$	$3/4 j$	
m18	CD_2H_2, CD_3			i	$1/4 j$	j
m19	CD_3H				i	
m20	CD_4					i

and

$$A = a \cdot \Sigma M, \quad B = b \cdot \Sigma M, \quad C = c \cdot \Sigma M,$$
$$D = d \cdot \Sigma M, \quad E = e \cdot \Sigma M.$$

where A, B, C, D, and E are respectively the "absolute" concentrations of CH_4, CDH_3, CD_2H_2, CD_3H, and CD_4 in the MS as well as in the reactor. The amount of CH_4 was practically zero and was further ignored ($a \approx 0$, $A \approx 0$).

The deuterium pressure in the reaction loop was set to 50 mbar (5066.25 Pa). Moreover, the loop volume is 59.8 cm^3 (5.98×10^{-5} m^3) and the fill-up temperature was ambient (293 K), so that the total number of the molecules in the loop could be calculated as follows:

$$\begin{aligned} N &= N_A \cdot \frac{p \cdot V}{R \cdot T} \\ &= 6 \times 10^{23} \cdot \frac{5066.25\ \text{Pa} \cdot 5.98 \times 10^{-5}\ \text{m}^3}{8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \cdot 293\ \text{K}} \\ &= 7.5 \times 10^{19}. \end{aligned}$$

From the overall number of deuterium molecules in the loop we could calculate the number of removed molecules using the concentration values (A, B, C, D, E).

ACKNOWLEDGMENTS

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