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Reactions of n-hexane on Pt–Sn/Al_2O_3 and removal of retained hydrocarbons by hydrogenation

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n-hexane was reacted on two Pt–Sn/Al_2O_3 catalysts, one prepared by coimpregnation (**T**) the other by using a bimetallic PtSn complex precursor (**N**). Both catalysts produced isomers, methylcyclopentane fragments and benzene, the aromatic selectivity being higher on catalyst **N**. The hydrocarbon entities remaining after reaction were removed by hydrogen treatment. They contained methane, C_2–C_5 fragments (not observed on Pt, thus unique for PtSn) and benzene. The possible state and composition of chemisorbed carbonaceous entities during reactions are discussed. More hydrocarbons, including slightly more methane could be hydrogenated off from catalyst **N** of lower dispersion. The higher overall activity of catalyst **N** in the presence of more than one C per surface Pt points to its higher coke tolerance.

Keywords: Pt–Sn/Al_2O_3 catalysts, platinum–tin catalysts, complex bimetallic precursor for Pt–Sn, catalyst carbonization, hydrocarbonaceous deposits, hydrogenation of coke precursors

1. Introduction

Skeletal reactions of alkanes (with six or more C atoms) include dehydrocyclization of alkanes into aromatics, along with their skeletal isomerization and C_5-cyclization [1,2]. Apart from supported Pt, its bimetallic combinations, such as Pt–Sn, are also of practical importance [3,4]. Earlier works of us compared n-hexane reactions on Pt–Sn/Al_2O_3 catalysts prepared by traditional coimpregnation (**T**) or using a new, bimetallic complex precursor, $[Pt(NH_3)_4][SnCl_6]$ (**N**) [5–7]. Catalytically inactive Sn has been claimed to dilute contiguous Pt surface to create smaller ensembles favorable for nondegradative reactions. To this respect, metallic additives, such as Sn, may occupy similar sites as single C atoms [8] claimed to be present during catalysis. The electronic and geometric effects of Sn are very likely interdependent [9,10].

“Hydrocarbonaceous entities” may play an important role – and may be even essential – in creating active sites for nondegradative hydrocarbon reactions [4,11–13]. Determination of their amount and position during or after reaction is rather difficult, considering also the possible spillover of various coke precursors between metal and support sites [14,15]. (a) Gravimetry is a direct method: Sárkány reported this way 0.5–2 C atoms per surface Pt on various supported catalysts. However, this method gives no information on the actual state and position of C during catalytic reactions. (b) Applying optical or electronic spectroscopy [15] was excellent for homogeneous acidic catalysts [16] but their application may be more difficult when metallic and also active support sites are present. Each of the following indirect methods have also their own drawbacks: (1) Surface analysis requiring ultrahigh vacuum after reaction may induce the dehydrogenation of “coke precursors” into coke [17]. (2) Oxidation of surface carbon [14] could distinguish between metal and support sites by destroying all carbon present. (3) Hydrogen treatment after terminating the catalytic reaction [13,18] would give hints on the amount of *removable* carbon accumulated during reaction and on their possible state. However, the amount of *removable* C is not necessarily equal to that of the residual C: H_2 flow removed reportedly not more than a few per cent of the total deposit [13]. In addition, coke or their precursors would interact with hydrogen in secondary hydrogenolytic processes.

Of those methods, none of them perfect, we applied the technique of hydrogenating off the hydrocarbons from various unsupported and supported Pt catalysts [19]. The fraction leaving unsupported Pt consisted of almost 100% methane, while benzene and unreacted hexane were abundant in the case of various supported Pt catalysts [19a]. The amount of C removed per surface Pt atoms varied considerably: its amount was about 1 for EUROPT-1 (6% Pt/SiO_2) and could reach ∼1.2 C/Pt_s for Pt black. A 0.6% Pt/Al_2O_3 retained just above 1–1.2 C/Pt_s [19a]. Increasing the hydrogen pressure from 120 to 400 Torr decreased the amount of retained C/Pt_s by a factor of ∼2. That CH_4 predominated in the hydrocarbons removed from Pt black and not with supported catalysts, pointed to the minor role of migration of C_1 units [15] in producing removed entities.

The present study reports analogous measurements with Pt–Sn/Al_2O_3 catalysts. The behaviour of the two prepa-

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rations **T** and **N** (*vide supra*) will be compared, to check how the obviously finer distribution of Pt with respect to Sn in sample **N** influences the amount and chemical state of removed hydrocarbons.

2. Experimental

The preparation and characterization of alumina-supported Pt–Sn catalysts **T** and **N** have been described [5–7]. The same γ-alumina was used as the support. Pt: 0.48 wt%, Sn: 0.31 wt%, dispersion, D: 18% for **N**; Pt: 0.52 wt%, Sn: 0.24 wt%, D: 61% for **T** [6]. The catalysts (new samples, 50 mg each) were placed into a closed-loop circulation reactor [5,6] after drying and were pretreated with circulating hydrogen at 623 K for 1 h. n-hexane (nH) was of Merck gas chromatography grade (>99.9% purity). 3 Torr (0.4 kPa) hydrocarbon was admixed to 120 Torr (16 kPa) hydrogen and reacted at 603 or 663 K. The reaction was terminated after 90 s at 603 K and 70 s at 663 K. This was sufficient to reach ~10% conversion on catalyst **T** and ~14% with catalyst **N**. After completing the run, the reactor was evacuated for 15 min, then 100 Torr (13.3 kPa) hydrogen was introduced at 603 K and the mixture analyzed. A 50 m capillary column coated with CP-Sil 5 was used for gas chromatographic analysis after reaction and hydrocarbon removal [5–7]. The amount of n-hexane retained by the glass apparatus was 3×10^{15} molecules; this was taken into account when evaluating the number of n-hexane molecules hydrogenated off. Results of three parallel experiments are reported.

3. Results and discussion

Table 1 includes the amount of transformed n-hexane molecules as well as the amount of molecules removed by hydrogen treatment. The actual activities reported earlier for catalyst **N** were dependent on its process of reduction. It usually exhibited higher turnover frequency and lower specific activity (per mass Pt) than catalyst **T** [6,7]. The results in table 1 show more transformed n-hexane molecules on sample **N** with lower overall surface. The differences for the specific activities [5–7] may be due to our newly reduced sample as opposed to stabilized ones (subjected to several regeneration cycles) in earlier reports. Our partly published results [5–7,20] show that the parameters of the reduction process influenced largely the specific surface and the number of Pt atoms determined by H_2–O_2 titrations may not be necessarily equal to the number of active sites. That catalyst **N** showed a higher activity than catalyst **T** in the presence of obviously more than one C atom per Pt may indicate its superiority in “coke tolerance”.

Table 1
Characteristic values of n-hexane conversion and removal by H_2 treatment.[a]

	Catalyst **T**		Catalyst **N**	
	603 K	663 K	603 K	663 K
Pt atoms	80	80	78	78
Surface Pt atoms[b]	49	49	14	14
Transformed n-hexane[c]	237	235	320	343
Removed hydrocarbon[c]	5.15	6.16	6.40	6.71
Ratio C/Pt_s[d]	0.64	0.76	2.72	2.85
$CH_4/(C_2–C_5)$[e]	1.2	2.1	1.6	2.6

[a] Runs of 90 s at 603 K, 70 s at 663 K to obtain identical conversions at both temperatures (~10% for catalyst **T** and ~14% for catalyst **N**). Values are related to one charge of each catalyst.

[b] Expressed as $\times 10^{16}$ Pt atoms.

[c] Calculated as $\times 10^{16}$ C_6 molecules reacted and removed, respectively, even if not all of the removed hydrocarbons consisted of C_6 molecules.

[d] Ratio of removed C atoms (6 × “C_6 molecules”) per surface Pt atom.

[e] Within the hydrocarbons removed.

The number of molecules removed by hydrogenation was about 40–50 times less than the amount converted. It was slightly higher with catalyst **N** and at 663 vs. 603 K on both catalysts. There was no direct proportionality between the reacted and removed molecules.

Figure 1 shows the selectivities of the products formed, expressed as C_6 units reacted (corresponding to the overall reaction rates of table 1). *Under the conditions studied*, there were no dramatic differences between the two catalysts, although the higher aromatization and lower C_5 cyclizing propensities of catalyst **N** can be observed. The larger amount of benzene and hexenes at 663 K meets expectations [5–7].

Figure 2 shows the amounts of hydrocarbons hydrogenated off, expressed as C_6 molecules. The composition of the removed hydrocarbons was rather similar in all cases but quite different from that observed in the reaction. The precursors of isomers, cyclopentanes, did not appear in the fraction removed by hydrogen. (Methylcyclopentane was observed only in one case: with 6% Pt/SiO_2 in a high hydrogen excess [19b].) Fragments were its main components, consisting of mainly methane and, to a lesser extent, C_2–C_5 alkanes. Their abundance was lower at 663 K and with catalyst **N**. Benzene was the main component in the C_6 fraction, apart from a minor amount of n-hexane. About a half of the originally measured hexane molecules ought to be subtracted due to the “wall effect”. Considering the relatively low carbonization temperature (~600 K), it seemed likely that adsorption on support sites could contribute to production of unreacted feed molecules. The amount of benzene was obviously larger in the case of catalyst **N** and this is also true if selectivities rather than absolute amounts were considered.

The samples contained the same mass of Pt ($\sim 80 \times 10^{16}$ Pt atom) but the number of surface Pt (measured by hydrogen titration) was different in the two samples: 49×10^{16} Pt atom in catalyst **T** and 14×10^{16} Pt atom in catalyst **N** [6]. Comparing these values with the number of removed entities, one can roughly estimate slightly less than one C atom retained per surface Pt on catalyst **T**, but this number was much higher than unity with catalyst **N**. These

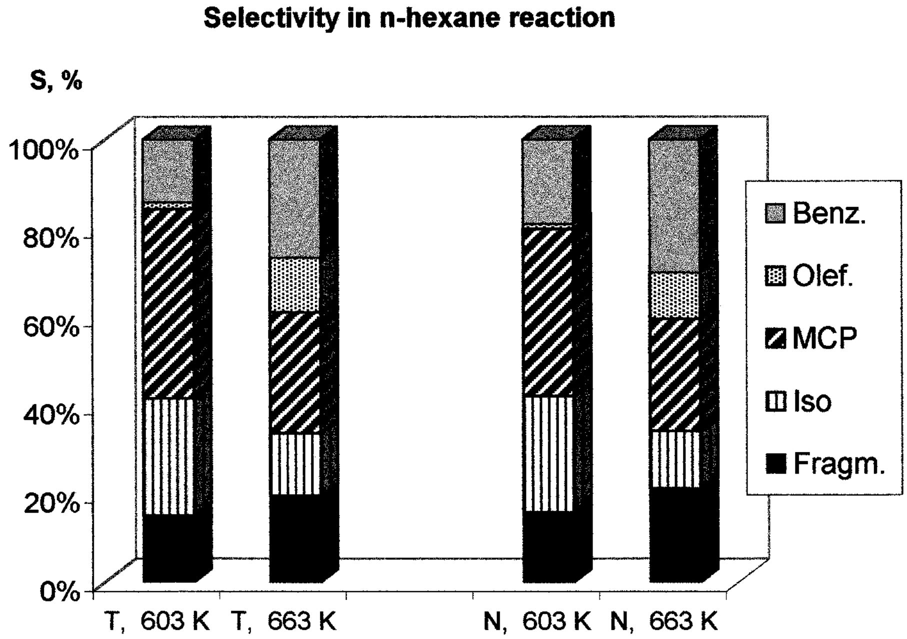

Figure 1. Selectivity of n-hexane reactions at $T = 603$ and 663 K. Conversion: 10% with catalyst **T** and ~14% with catalyst **N**.

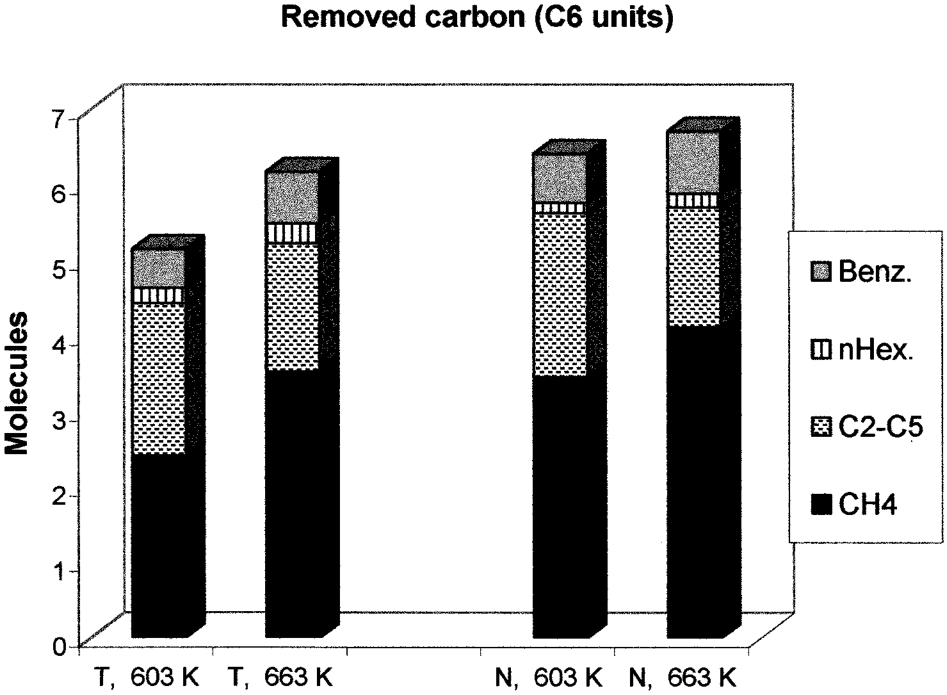

Figure 2. The amount and distribution of products (expressed as $\times 10^{16}$ C_6 molecules) removed from catalysts **T** and **N** by hydrogen treatment after the runs shown in figure 1.

values confirm the view of the necessity of migration of coke precursors from metallic sites to support sites [15]. One has to recall that the "coke" on Pt/Al_2O_3 corresponding to 3–6 C/Pt_s [14b] – as measured by TPO – was deposited at higher temperatures activating also support acid sites.

Sárkány [15] distinguished three types of carbonaceous deposit on Pt/Al_2O_3: one on metal particles, one on metal–support perimeter and one entirely on the support. They all may originate from highly dissociated entities adsorbed on Pt and migrating afterwards to alumina. Two routes of coking have been proposed, one involving polyenes and the other highly dissociated CH_x entities. This latter, "C_1 route" was inhibited but the polyene route was promoted by adding Sn to Pt/Al_2O_3 where most coke was situated on the support [15]. Tin removed accordingly some of the site blocking effect of carbonaceous deposits and altered also the coverage of metal sites by highly dehydrogenated carbonaceous deposits [21].

The question arises whether and to what extent the composition of the products removed by hydrogenation correspond to the true structure(s) of adsorbed "hydrocarbonaceous layer" [11,13] during catalysis. Evacuation of the present closed-loop setup after run may promote dehydrogenation of residual C [17].

The surface may also contain CH_x species ($x = 1$ or 2) [15] which give CH_4. This is supported by the isotopic exchange between ^{12}C and ^{14}C in chemisorbed n-heptane and its various products formed from larger coke precursor molecules during reaction with hydrogen [22]. Alternatively or in addition, CH_4 can be formed by hydrogenolyzing larger hydrocarbon chain(s) or three-dimensional C deposits by H_2 [11]. Their hydrogenolytic splitting may contribute to methane production. The appearance of "Pt–C" entities in the XP spectrum of a Pt black [23] replacing graphitic C upon hydrogen treatment points to the reality of the latter assumption. It is probably also true in the case of our catalysts.

Dehydrogenated C_2–C_5 may also be present. The supported *Pt–Sn catalysts are unique* to this respect: hydrocarbons removed from monometallic Pt catalysts contained no C_2–C_5 fragments after reaction of n-hexane [19]. This is in agreement with Sn suppressing the "C_1 route" of coking [15]. Thus, the diluting effect of Sn should prevent a complete breakup of the residual molecules, either during accumulation or during removal by hydrogenation. This confirms the importance of larger contiguous Pt islands in deep hydrogenolysis. That the relative abundance of the larger fragments was somewhat lower on catalyst **N** may mean that more CH_x units could remain on its Pt atoms present in finer distribution between Sn atoms.

The third component remaining on the surface may comprise presumably deeply dissociated C_6H_{6-x} aromatic rings. It may be recalled that aromatization in a temperature-programmed reaction system (involving adsorption of the reactant at low temperature and a programmed heating in vacuum monitoring the desorbed products by mass spectrometry) pointed to such species being the precursors of benzene formation [24]. The aromatic ring would accordingly be formed by reaction of these surface species with hydrogen.

According to the particular nature of the removed hydrocarbons coming from the hydrogenation of the hydrocarbonaceous entities remaining after reaction we can assume as a conclusion that the hydrogenation concerns mainly coke (or coke precursors) and also highly dissociated adsorbed species.

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