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RESEARCH NOTE

Pt/Graphite Nanofiber Catalyst in *n*-Hexane Test Reaction

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Five percent Pt on a "platelet-type" graphite nanofiber was active in skeletal reactions of *n*-hexane at lower temperature than Pt/SiO$_2$. The turnover frequencies showed maxima in both cases as a function of hydrogen pressure, *p*(H$_2$). Pt/graphite nanofiber produced significantly more isomers than EUROPT-1 at lower temperature and higher *p*(H$_2$). The selectivity of fragments was small, and their distribution showed almost perfectly random rupture. The propensities for both features can be explained by there being more surface H available with the nanofiber support. It is indicated that this combination may be a promising metal catalyst for low-temperature alkane isomerization reactions.

Key Words: **platinum/graphite nanofiber; Pt/GNF catalyst; EUROPT-1; graphite nanofiber catalyst support; *n*-hexane transformations.**

INTRODUCTION

Graphite nanofibers (GNF) appear to be novel and unique catalyst supports (1). Previous studies have demonstrated that nickel on GNF tended to acquire a much larger particle size than those found for the same metal loading on oxide supports, but the exceptional activity of the former system for hydrogenation was attributed to morphology and metal–support electronic interaction phenomena rather than to the effect of dispersion (2). Graphite nanofibers of different structure showed higher activity than Ni/Al$_2$O$_3$ in the hydrogenation of 1-butene or 1,3-butadiene (3).

Hydrogenation of C=C double bonds is a "structure-insensitive" reaction (4) taking place at around 350–400 K. "Structure-sensitive" reactions of alkanes—including isomerization, C$_5$-cyclization, aromatization, and hydrogenolysis—require higher temperatures, 500–700 K (4–6). Pt in various forms, unsupported (7) and dispersed on oxide supports (8), is an active and well-known catalyst for these reactions. The product distribution shows a distinctive response to the availability of surface hydrogen: ample hydrogen favors the formation of saturated C$_6$ products, in particular, skeletal isomers, while aromatization and dehydrogenation selectivities are higher at lower hydrogen pressures (5, 9).

Up to this point in time there have been no reports of the catalytic properties of platinum supported on graphite nanofibers. The performance of other metals dispersed on this type of carrier were examined in hydrogenation reactions (3). In the current investigation we have attempted to extend the understanding of the unusual properties afforded by the graphite nanofiber support from an examination of the behavior of this system concerning skeletal alkane reactions.

METHODS

The graphite nanofibers selected for this study were of the "platelet" variety and were prepared according to the procedures described in a previous paper (10). In this type of material the graphite platelets constituting the structure are aligned in a direction perpendicular to the fiber axis in such a manner that the exposed surface consists entirely of edge carbon atoms. The platinum precursor salt, $[Pt(NH_3)_2](NO_3)_2$, was dissolved in *n*-butanol and added in small increments to a "platelet"-type of graphite nanofiber to form a slurry. The impregnate was dried overnight at 323 K, calcined in air at 523 K (4 h), reduced at 573 K (20 h), and passivated in 2% O$_2$ for 1 h at 300 K. It was stored in surrounding air. The sample contained 5% Pt with a dispersion $(D) = 20\%$, as determined by O$_2$–H$_2$ titration.

Catalytic runs were performed in a closed-loop circulation reactor (7). A capillary OV 101 GC column was used for product analysis. The catalyst was prereduced at 573 K for 1 h in 200 Torr H$_2$. Gas mixtures of 10 Torr *n*-hexane (Merck GC grade) and H$_2$ (60 to 480 Torr) were allowed to react with the Pt/GNF catalyst between 483 and 603 K. A well-characterized "standard" 6% Pt/SiO$_2$ (EUROPT-1) $(D = 60\%)$ was used as the reference catalyst (8, 11, 12).

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TABLE 1

Overall Turnover Frequencies (TOF, in Units of h^{-1}) of n-Hexane over Various Pt Catalysts[a]

		$p(H_2)$ (Torr)				
Catalyst	T (K)	60	120	240	360	480
Pt/graphite nanofiber	483	2	2	1.5	0.5	0.5
	513	11	9	6	4	4
	543	19	22	21	15	12
	573	28	37	48	43	38
	603	17	66	90	102	98
EUROPT-1	483			no activity observed		
	513	10	5	—	—	2
	543	19	30	27	—	11
	573	24	45	62	67	52
	603	25	49	85	124	127

[a] Here, $p(nC_6) = 10$ Torr, $p(H_2) = 120$ Torr; sampling, 5 min. Results for EUROPT-1 have been taken from Ref. (12).

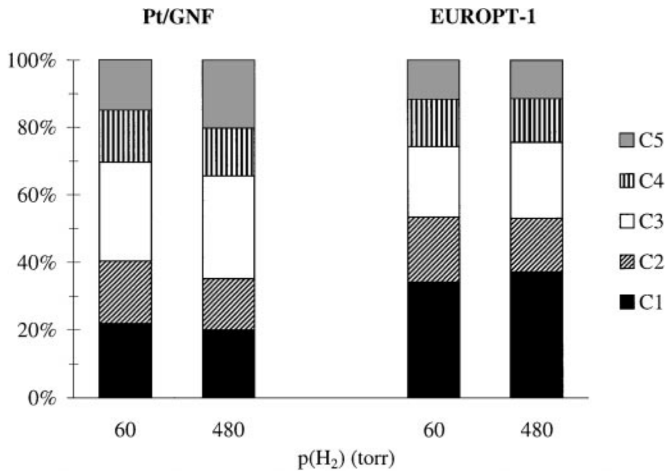

FIG. 2. Fragment distribution on Pt/GNF and EUROPT-1 (normalized to $\Sigma < C_6 = 100\%$) at two hydrogen pressures and $T = 543$ K.

RESULTS AND DISCUSSION

Onset of the n-hexane reaction occurred at lower temperature over the Pt/GNF catalyst than over EUROPT-1. The turnover frequencies (TOF) on the two catalyst systems approached each other as the temperature was progressively increased, EUROPT-1 becoming superior only above ∼573 K (Table 1), although its dispersion was about three times as high as that of the Pt/GNF sample. Maxima appeared in the TOF values as a function of the hydrogen pressure (8, 12). The TOF values at $T = 603$ K and $p(H_2) = 120$ Torr were comparable to those reported for Pt/KL, of 50–70 (13), and exceeded those reported for Pt/NaY, of 20–40 (14).

Figure 1 illustrates typical selectivity values for the two catalysts at 543 K. Both catalysts gave saturated C_6 hydrocarbons, isomers and methylcyclopentane (MCP), as the main products. The abundance of skeletal isomers was, however, more pronounced on Pt/graphite nanofiber. The fragment selectivities of EUROPT-1 were reported to be much lower than those of other supported Pt catalysts. This was also true for the carbon-supported Pt. In addition, the aromatization selectivities were close to each other. These values for the two catalysts approached each other at increasing temperatures, Pt/GNF producing less hexenes even at 603 K. The isomer selectivity of Pt on the nanofiber support was still higher, ∼65% vs 60% on EUROPT-1, along with 11–12% benzene on both catalysts.

Although hydrogenolysis is a side reaction in this system, the fragment distribution offers a good fingerprint testing protocol for the catalysts. Platinum promotes single rupture of alkanes (forming two fragments) with a minor multiple rupture to methane superimposed at lower $p(H_2)$ even with EUROPT-1 (8, 9). Figure 2 shows the existence of a slight hydrogen dependence of fragment distribution with EUROPT-1 and Pt/graphite nanofiber catalysts. The

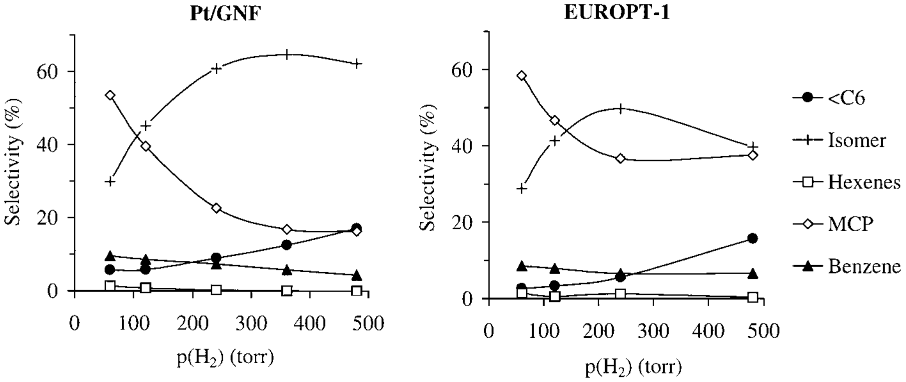

FIG. 1. Selectivities on n-hexane reactions as a function of hydrogen pressure at $T = 543$ K: (left) Pt/GNF; (right) EUROPT-1 (12). The corresponding conversion values were between 2 and 6%, somewhat higher on Pt/GNF.

latter produced almost random fragment distribution with no multiple splitting. The minor preference for splitting the C_6 chain to give two propane fragments was found to be characteristic of the Pt component, this tendency increasing at higher hydrogen excess (8, 14).

In summary, these preliminary experiments have shown that a Pt catalyst on a graphite nanofiber support can activate *n*-hexane at lower temperatures than oxide-supported catalysts, with an outstanding isomerization selectivity. It exhibited also an exceptionally low fragmentation selectivity, similar to Pt/SiO_2, which has a much higher dispersion. The thermodynamics of benzene formation is unfavorable at low temperature, and this aspect may be one of the reasons for the low benzene selectivity. The high selectivity of isomers and the lack of multiple fragmentation, as well as the enhanced propane formation, point to a higher abundance of surface H at the active sites. This may be due to the high hydrogen storage capacity of the nanofiber support (15).

Considering that fragments are useless in naphtha upgrading and that aromatics are less and less desirable products, Pt on a graphite nanofiber support may be a promising high-selectivity isomerization catalyst active at relatively low temperatures. Further studies are in progress to compare the performance of Pt dispersed on graphite nanofibers possessing different structures. A small and reproducible (∼8%) hydrogen spillover was observed in O_2–H_2 titration. Its appearance and extent under various conditions will also be studied separately.

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