

## Chain Lengthening Reaction on Supported Platinum Catalysts. A Novel Aspect of the Mechanism of Homologation Reactions and Catalyst Deactivation

József Margitfalvi, Mihály Hegedüs, and Ferenc Nagy

Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17, Hungary

Formation of toluene from n-hexane was observed on supported platinum catalysts and is discussed in terms of a surface depolymerization reaction connected with catalyst deactivation rather than the olefin-carbene interaction suggested earlier.

We have recently observed formation of toluene from n-hexane on Pt-Al<sub>2</sub>O<sub>3</sub> catalysts under conditions of selective aromatization.<sup>1</sup> Based on our results, *i.e.* lack of formation of C<sub>6</sub> alkenes and C<sub>7</sub> alkanes, low yields of methane formation, and a correlation between the catalyst deactivation and toluene formation, we suggested that on Pt-Al<sub>2</sub>O<sub>3</sub> catalysts the carbene-alkene insertion mechanism<sup>2,3</sup> was less important and that other surface reactions might be involved in toluene formation. In this communication we present new experimental evidence supporting our suggestion<sup>1</sup> and a novel reaction route is proposed.

Experiments were performed in a slug impulse reactor, described elsewhere.<sup>1</sup> Constant hydrogen flow was maintained between each two consecutive pulses. The impulse was a square-like function for the reaction input (I) as shown in Figure 1. The reactor output (R) had a response function, which consisted of three definite parts: pre-stationary (A), quasi-stationary (B), and post-stationary (C) periods. The criterion for the period (B) was a stabilization in the reactor effluent and in the product distribution within 3 and 6%, respectively. The product distributions measured on different catalysts in the period (B) are summarised in Table 1. For-

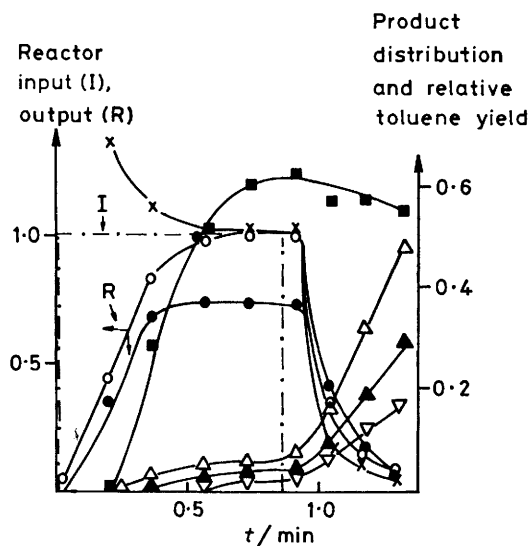
**Table 1.** Conversion and selectivity data for n-hexane dehydrocyclization.<sup>a</sup>

Catalyst sample no.	Conversion (x) and selectivity (S) % <sup>b,c</sup>							Deactivation rate, x <sup>d</sup> /x <sup>e</sup>
	x <sup>e</sup>	S <sub>M</sub>	S <sub>H</sub>	S <sub>B</sub>	S <sub>T</sub>	S <sub>I</sub>	S <sub>C</sub>	
1	76.0	0.5	6.9	74.0	4.0	8.8	2.3	1.26
2	62.0	1.6	9.2	61.5	9.4	13.6	3.9	1.49
3	68.0	0.3	4.3	68.0	2.6	17.3	3.6	1.16

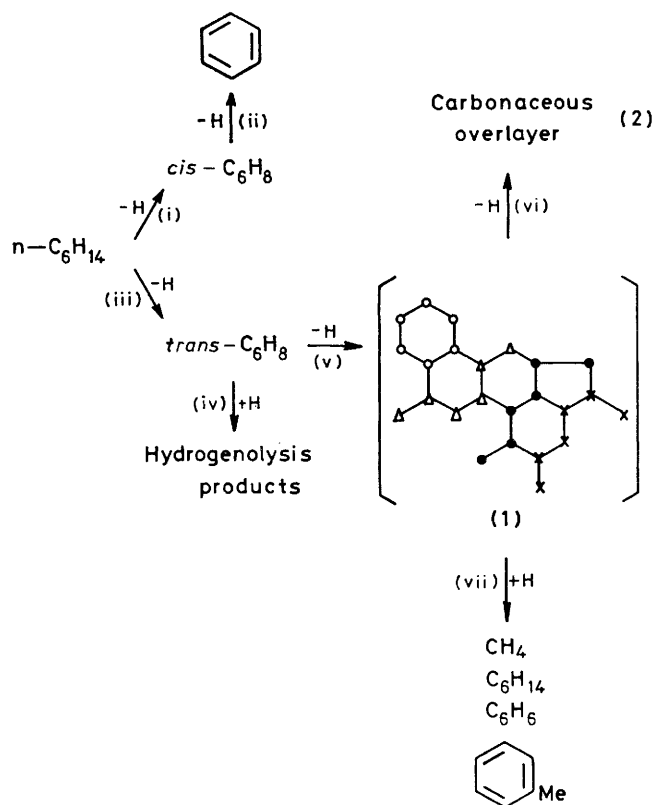
<sup>a</sup> Reaction temperature 753 K; H<sub>2</sub>:C<sub>6</sub>H<sub>14</sub> = 5:1; catalyst mass 0.22 g; catalysts: no. 1 and no. 2, 0.5% Pt-Al<sub>2</sub>O<sub>3</sub>; no. 3, Re and Pt (each 0.35%) on Al<sub>2</sub>O<sub>3</sub>. Before the reaction the samples were calcined (no. 2 and no. 3 at 873 K, no. 1 at 973 K) and reduced (all samples at 973 K). Based on n-hexane which had reacted. M = methane, H = cracking products, B = benzene, T = toluene, I = iso-hexanes, and C = methylcyclopentane. <sup>c</sup> Data obtained after 15–20 impulses. <sup>d</sup> Measured after the first impulse.

mation of toluene was observed under the conditions of selective aromatization without 'deep' fragmentation of the parent hydrocarbon.

Further information was furnished by the product distributions measured in the periods (A) and (C) shown in Figure 1. In the period (A) formation of benzene and other products precedes formation of toluene and the steady state for the formation of toluene needs a longer time to be achieved. From the sequence of the appearance of the reaction products the strength of adsorption of the products' surface intermediates can be evaluated; thus in the formation of toluene a strongly retained surface species may be involved.



**Figure 1.** Impulse reactor input (I) and output (R), product distribution, and relative toluene yields as a function of time of run-on. ○, total reactor outlet; product distribution: ●, benzene; ■, toluene (× 10); X, methane (× 50); relative toluene yield: ▲, catalyst no. 1; △, no. 2; ▽, no. 3.



Scheme 1

In the period (C) the amount of toluene in the reactor output decreases only slightly, while the total reactor output as well as the amount of benzene and methane show a sharp decrease. On catalyst sample no. 2, formation of higher alkyl-aromatic hydrocarbons ( $\text{C}_8$ – $\text{C}_{10}$ ) was also observed in trace amounts. Additional information was obtained by comparing the relative yield of toluene also shown in Figure 1. The relative yields were calculated as the ratio of toluene formed

to the reactor output. On our catalyst samples the relative yield of toluene was high and increased in the same order, no. 3 < no. 1 < no. 2, as the rate of catalyst deactivation (see Table 1).

In the period (C) after a certain time the only reaction products are methane, hexane, benzene, toluene, and traces of higher alkyl-aromatic compounds. We assume one surface precursor, a polymeric cyclic surface overlayer, for the formation of these products and propose the reactions in Scheme 1.

Accepting a consecutive dehydrogenation for *n*-hexane,<sup>4</sup> route (i) leads to benzene formation [via (ii)], while (iii) is an undesired reaction step. The 'transoid' hexadienes will give only hydrogenolysis products or, in a further dehydrogenation step (v), a polymeric cyclic surface overlayer (1) is formed.<sup>5</sup> The fate of (1) depends on the hydrogen available on the catalyst surface. If the hydrogen coverage is low (1) can be further dehydrogenated (vi) to the carbonaceous overlayer (2). Formation of (1) and (2) takes place in every pulse resulting in a decrease in catalytic activity between consecutive pulses. After 15–20 pulses a quasi-steady-state concentration of (1) and (2) is achieved.

If there is enough surface hydrogen route (vii) will be important; *i.e.* hydrodepolymerization of the cyclic surface polymer takes place to yield benzene and toluene as well as traces of methane, hexane, and alkyl-aromatic compounds.

This suggested mechanism for toluene formation on Pt-supported catalysts seems to be more realistic than the olefin-carbene insertion mechanism proposed earlier,<sup>2,3</sup> however, the latter should be of importance on metals with 'metathesis activity'.

Received, 28th August 1981; Com. 1044

## References

- 1 J. Margitfalvi, M. Hegedüs, S. Göbölös, and F. Nagy, *React. Kinet. Catal. Lett.*, in the press.
- 2 C. O'Donohoe, J. K. A. Clarke, and J. J. Rooney, *J. Chem. Soc., Chem. Commun.*, 1979, 648.
- 3 A. Sárkány and P. Tétényi, *J. Chem. Soc., Chem. Commun.*, 1980, 525.
- 4 Z. Paál and P. Tétényi, *Magy. Kém. Foly.*, 1968, **74**, 354.
- 5 Z. Paál, *Adv. Catal.*, 1980, **29**, 319.