

## Direct Evidence for Dual-Functional Cyclization of Paraffins over Platinum Reforming Catalysts

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The reaction of *n*-heptane containing 100 ppm of sulfur using either a platinum on charcoal catalyst or an alumina catalyst produces relatively few ring hydrocarbons. The large increase in ring production observed when both catalysts are intimately mixed is good evidence that the paraffin cyclization reaction can proceed by a dual-functional mechanism.

Paraffin cyclization is one of the important reactions occurring in platinum reforming. There is evidence that reforming catalysts can catalyze paraffin cyclization reactions "monofunctionally" on the platinum surface with no cooperation from the acid sites. For example, Nix and Weisz (1), using fluidized mixed catalyst experiments, have shown that increasing the amount of the platinum component leads to a significant increase in toluene production from *n*-heptane. Sinfelt and coworkers (2) found that the dehydrocyclization rate increases with platinum content for Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, while the paraffin isomerization rate is independent of platinum content above a certain level. Further evidence of paraffin cyclization on platinum surfaces has been provided by Kazanski and Liberman (3), using platinized charcoal, and Barron and coworkers (4, 5), using both supported catalysts and evaporated films. In addition, a unique idea has been advanced by McHenry and coworkers (6), who have shown a correlation between the dehydrocyclization activity of platinum catalysts and the amount of platinum extractable with acetylacetone or HF. They proposed that platinum which forms a special complex with the alumina support has high activity for the dehydrocyclization reaction; however, there is some

question concerning the stability of this complex under reducing conditions (7).

This paper presents evidence that paraffin cyclization reactions can also proceed by a dual-functional mechanism. This concept was suggested as early as 1953 by Mills and coworkers (8). In addition, Fomichev and coworkers (9) have found cyclopentane and cyclohexane hydrocarbons in the products obtained from the reactions of 1-hexene and 1-heptene on an Al<sub>2</sub>O<sub>3</sub> catalyst. However, in contrast to ring isomerization reactions and paraffin isomerization reactions, the dual-functional mechanism does not appear to have been experimentally demonstrated with the paraffin cyclization reaction. This is not surprising because of the problems encountered in studying a reaction that can presumably proceed by either or both of two mechanisms once the platinum is introduced into the catalyst composition.

In the present study, a mixed catalyst experiment with *n*-heptane is described. In this experiment the platinum function is sulfur poisoned to a level such that, while direct cyclization on the platinum surface appears negligible, sufficient dehydrogenation activity is maintained to provide the unsaturated intermediates required for dual-functional reactions.

## EXPERIMENTAL

The experiments described here were carried out in a Vycor pressure reactor. The *n*-heptane used was Phillips pure grade. Reaction conditions were: Temperature, 900°F; hydrogen partial pressure, 12.0 atm; and hydrocarbon partial pressure, 1.13 atm. The hydrocarbon flow rate was 16.0 cc/hr. Reaction products were analyzed by gas chromatography using a capillary column with the three-component substrate mixture described by Schwartz and Brasseaux (10). In three of the four runs reported here, thiophene was added to the *n*-heptane to give 100 ppm by weight of sulfur.

The alumina had been prepared by reaction of aluminum with water in the presence of mercuric acetate and had a surface area of 329 m<sup>2</sup>/g. The platinum on charcoal catalyst (Pt/C) contained 0.5% Pt and was obtained from Englehard Industries. The mixed catalyst composition used here was prepared by the technique of Weisz and Swegler (11). The two components were ground separately to a particle size of about 5 μ after which appropriate parts by weight of the two components were blended.

## RESULTS

The ring hydrocarbons obtained from *n*-heptane using 0.25 g of the Pt/C catalyst with and without 100 ppm S in the paraffin charge are shown in Table 1. These results show that the sulfur almost completely quenches the cyclization reactions. Also given in Table 1 is the conversion of *n*-heptane to the two *n*-heptenes (*cis*-3-heptene and *trans*-3-heptene) which were detected and measured in these experiments. The three remaining *n*-heptene isomers were not measured since they were not separated from other hydrocarbons in the reaction mixture by the particular chromatographic column employed. As shown in Table 1, conversion to the 3-heptenes is essentially the same with or without the sulfur, and unpublished data obtained in this laboratory indicate that the observed 3-heptenes/*n*-heptane ratio is

TABLE 1  
EFFECT OF SULFUR ON RING PRODUCTION  
OBTAINED FROM *n*-HEPTANE WITH  
Pt/C CATALYST

Catalyst weight (g):	0.25	0.25
Sulfur added to <i>n</i> -heptane (ppm):	None	100
Mole percentage <i>n</i> -heptane converted to:		
Ethylcyclopentane	1.99	—
1,1-Dimethylcyclopentane	.01	—
1,2-Dimethylcyclopentanes	1.33	.11
1,3-Dimethylcyclopentanes	.15	—
Methylcyclohexane	—	—
Toluene	1.45	.01
3-Heptenes	.74	.76

very close to the equilibrium ratio for these reaction conditions. Thus, despite the presence of sulfur, the Pt/C catalyst retains significant and for our purposes probably sufficient dehydrogenation activity.

Table 2 summarizes the pertinent results obtained in three experiments with *n*-heptane containing 100 ppm S. In the first two experiments 0.25 g of Pt/C and 0.50 g

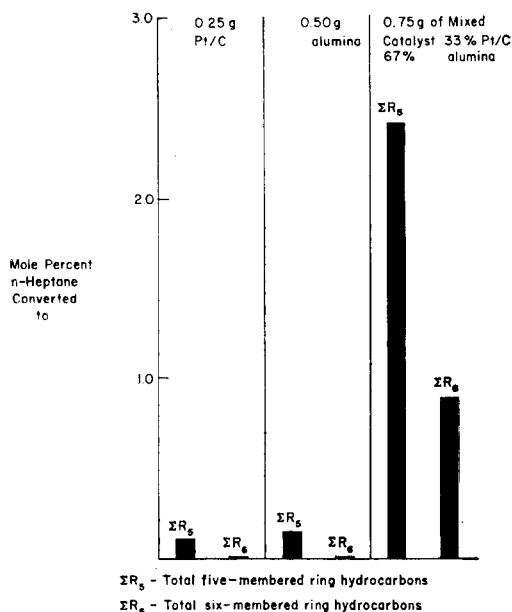


FIG. 1. Comparison of ring production from *n*-heptane with and without mixing of catalyst components.

TABLE 2  
COMPARISON OF RING PRODUCTION FROM HEPTANE WITH AND WITHOUT MIXING  
OF CATALYST COMPONENTS

Catalyst:	0.25 g of Pt/C	0.50 g of Al <sub>2</sub> O <sub>3</sub>	0.75 g of mixed catalyst containing 33% Pt/C and 67% Al <sub>2</sub> O <sub>3</sub>
Sulfur added to <i>n</i> -heptane (ppm):	100	100	100
Mole percentage <i>n</i> -heptane converted to:			
Ethylcyclopentane	—	.02	.28
1,1-Dimethylcyclopentane	—	—	.09
1,2-Dimethylcyclopentanes	.11	.06	1.03
1,3-Dimethylcyclopentanes	—	.07	1.04
Methylcyclohexane	—	—	.12
Toluene	.01	.01	.77
3-Heptenes	.76	—	.65

of alumina were run separately. In the third experiment, 0.75 g of a mixed catalyst containing 33% of the dehydrogenation component (Pt/C) and 67% of the acid component (Al<sub>2</sub>O<sub>3</sub>) was employed. The total amount of both five-membered and six-membered ring hydrocarbons obtained in the three runs of Table 2 are compared graphically in Fig. 1. The large increase in ring production obtained with the mixed catalyst demonstrates that the paraffin cyclization reaction can proceed by a dual-functional mechanism in which olefins are produced by the dehydrogenation function and then cyclized on the acid function.

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