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Hydrocarbon Reaction Path Studies with Fluidized Dual Function Catalyst Component Mixtures*

P. S. NIX AND P. B. WEISZ

From the Socony Mobil Oil Company, Inc., Research Department, Paulsboro, New Jersey

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In a fluidized bed, dual-functional catalytic conversion is obtained by the simple expedient of introducing particles of acid catalyst and particles of dehydrogenation catalyst in desired proportions. This mode of operation makes it possible to rapidly alter the relative effective rate constants of the two catalyst functions. This technique is used to identify rate-controlling components and to localize deactivation phenomena. The studies indicate direct cyclization of paraffins on platinum.

INTRODUCTION

Important hydrocarbon reactions are carried out with dual-functional catalysts, i.e., catalysts having two distinct kinds of activity. Examples are the hydroisomerization and hydrocracking of paraffins and naphthenes. The over-all reaction results from a sequence of successive reaction steps on the different catalytic centers (*1*). Often, or perhaps always, each functional activity is associated with centers of different chemical composition. Consequently, much can be learned about the role of each function in the reaction-path sequence, by varying the number of sites of each kind of activity.

Dual-functional catalysts usually carry both functional components on the same catalyst particle. Whenever chemical means are used to add or to alter one function of such a catalyst, the other function is likely to be affected. For example, when using alumina-base catalyst impregnated with platinum, as a dehydrogenation function, and chloride, as an isomerization function, it is difficult to vary chloride concentration without affecting the platinum activity, and vice versa.

It has been shown (*2–5*) that the two kinds of functional activity need not be present at the same site on the surface of the catalysts. The chemical species formed by one function is able to migrate, by classical diffusion, through the vapor phase to the site of the other function, where the next step of the reaction sequence occurs. It is therefore possible to prepare a dual-functional catalyst by mechanically mixing particles of the two different catalytic materials. Here, the relative reaction-rate constants of each function, per unit volume of reaction space, can be varied independently over a wide range by adjusting the relative amounts of each component in the mixture. However, the full cooperation of the individual catalytic components in the over-all kinetics can be achieved only if the size of the component particles is small enough to permit adequate diffusional flow of gas-phase intermediate from one kind of cite to the other (*2, 4, 5*). Hence, it is usually necessary to work with *component* particle sizes smaller than 100 microns.

If a static bed is filled with a mixture of very small particles, the pressure drop is intolerably high. In previous studies (*2, 3*), mixtures of powdered catalytic

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components were therefore pressed into pellets of appropriate size. The use of such pelleted mixtures has its limitations: Care must be taken to insure uniform mixing of the powders before pelleting. Once a pelletized catalyst is made, its composition cannot be altered, so that a separate preparation of pellets must be made for each desired dual composition. Occasionally, powders are encountered that cannot be made into pellets without the use of a binding agent. These binders introduce foreign materials, that can interact with the catalyst; their removal by combustion has been found by us to alter such catalytic properties as the platinum activity.

New Technique

A technique that overcomes these limitations is the use of a fluidized bed of powdered catalysts of chemically and physically independent "free" component particles. In a fluidized bed, particles are small enough to avoid diffusion limitations, and the turbulence of fluidization provides continuous mixing of the components. Catalyst composition can be altered easily and rapidly. Activity of either component can be increased between runs, simply by pouring additional amounts of either component into the reactor. The role of each function in the over-all reaction path can thus be rapidly explored. Similarly the relative rates of deactivation of each function can be studied.

The fluidized-bed reactor shown in Fig. 1 is made from a Vycor fritted tube; the frit serves both to support the catalyst bed, and to distribute the reactant vapors uniformly to the base of the bed. The tube is about 10 mm in diameter, and 0.3 g to 1 g of catalyst gives a fluidized bed height of between 10 and 30 mm. Heat is supplied through a Nichrome heating ribbon wound about the reactor with adjacent turns spaced 3 to 4 mm apart. The rapid circulation of catalyst within the fluidized bed provides a sufficiently uniform temperature in spite of the spacing between turns of the heating ribbon. A larger concentric glass tube around the reactor provides an annular insulating air space, the ends of which were plugged with glass wool. This design allows visual observation of the catalyst throughout the experiments.

A thermowell projecting into the catalyst bed contains a thermocouple connected to a temperature regulator, which controls the voltage applied to the Nichrome ribbon. Hydrogen is bubbled through liquid hydrocarbon; the resulting mixture of hydrogen and hydrocarbon vapors passes upward through a preheating section, then through the catalyst bed. A fritted-glass cylinder above the reactor removes the small amount of catalyst dust carried out of the reactor. Effluent vapors are sampled and analyzed by chromatography.

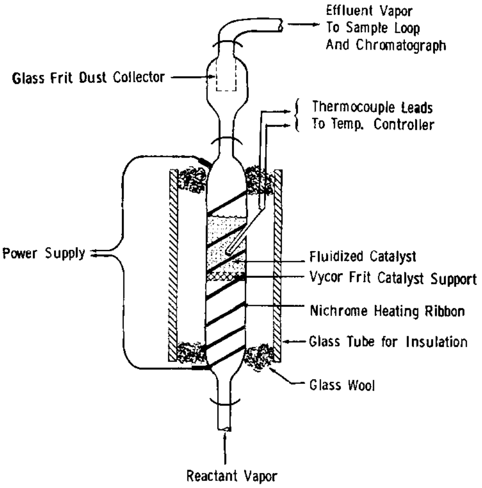


FIG. 1. Fluidized-bed microreactor.

This technique was used to demonstrate mechanistic questions concerning the dual-functional catalyzed reactions of *n*-heptane. The catalyst components used were: Davison silica-alumina fluid cracking catalyst as acidic component; and, as the dehydrogenation component, F-10 alumina, impregnated with chloroplatinic acid to 0.8% platinum, then washed with ammonia to remove its acid activity.

Demonstration of Dual-Functional Cooperation of Loose Mixture of Two Catalyst Components

The cooperative action of the chemically as well as physically distinct catalyst component particles was demonstrated in the dual-functional isomerization of heptane. Experimental conditions and results are given in Table 1.

TABLE 1

Dual-Functional Isomerization of *n*-Heptane in a Fluidized Bed of Mixed Catalyst Components[a]

Catalyst	0.5 g Si/Al	0.05 g Pt/Al	0.5 g Si/Al + 0.05 g Pt/Al
Isoheptanes (%)	Nil	Nil	24

[a] Conditions: Temperature = 700°F; *n*-heptane feed rate = 0.77 g/hr; H_2/nC_7 mole ratio = 19; catalyst: 0.5 g silica-alumina, and 0.05 g Al_2O_3/Pt.

The ability of wholly independent functions to cooperate with each other is thus confirmed more decisively than by earlier experiments (*4*, *5*) with pelleted mixtures. There appears to be no plausible way of coupling the functional components other than by vapor-phase diffusion of olefin intermediates. Any question of migration of catalytic components, specifically, migration of acid component to the platinum-containing particles (*6*), was further avoided by using silica-alumina as the acidic component instead of halide, which some regard as capable of slight volatilization.

Demonstration of Reaction Paths in Paraffin Cyclization vs. Isomerization

The role of each function in the parallel reactions of dehydrocyclization and isomerization of *n*-heptane was demonstrated: In the experiment just described, the platinum-alumina component constituted 9% of the catalyst mixture, and the reaction products also contained 4% toluene. Table 2 shows the result of increasing the amount of platinum component and decreasing the acidic component.

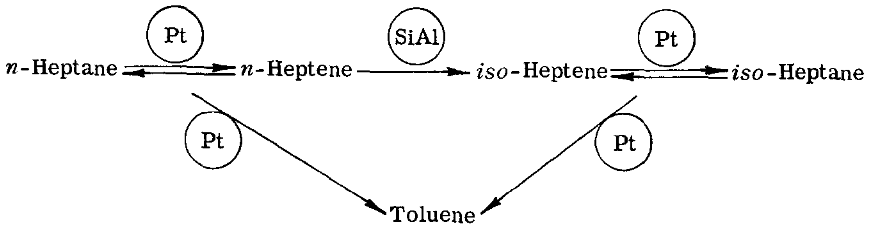
TABLE 2

Effect of Varying Ratio of Pt/Al to Si/Al on the Relative Rates of Dehydrocyclization vs. Isomerization of n-Heptane[a]

Catalyst	0.5 g Si/Al + 0.05 g Pt/Al	0.1 g Si/Al + 0.3 g Pt/Al
Isoheptanes (%)	24	19
Toluene (%)	4	27

[a] Conditions: temperature = 700°F; *n*-heptane feed rate = 0.77 g/hr; H_2/nC_7 mole ratio = 19.

The increased yield of toluene suggests that the rate of cyclization was controlled by the platinum component, whereas the rate of isomerization diminished with the decrease in the amount of silica-alumina. These observations are consistent with the following diagram of reaction paths:



Localization of Activity Decline

A continuation of the same series of experiments served to localize the role of each function in catalyst activity decline as seen in Table 3.

TABLE 3

Selective Aging of the Platinum Component during *n*-Heptane Conversion with a Fluidized Mixture of Pt/Al and Si/Al[a]

Time on stream (min)	Isoheptanes (%)	Toluene (%)
Initial catalyst charge: 0.1 g Si/Al + 0.3 g Pt/Al		
12	19	27
100	19	13
Add another 0.1 g Pt/Al:		
109	19	22

[a] Conditions: temperature = 700°F; *n*-heptane feed rate = 0.77 g/hr; H_2/nC_7 mole ratio = 19.

Toluene yield decreased with time on stream. If the rate of toluene formation was controlled by the platinum activity, as indicated by the previous experiment, then the decline would be due to progressive deactivation of the platinum component.

The yield of isoheptanes, on the other hand, remained constant during the same period. Since previous work had indicated that the rate of isomerization is controlled by the silica-alumina (*4*), we concluded that the silica-alumina had *not* lost activity during this period. The postulated decline in platinum activity would not affect the rate of dual-functional isomerization, so long as the platinum activity remained adequate to maintain near-equilibrium concentration of olefin intermediate. See the above reaction path diagram.

Addition of another 0.1 g of the platinum-alumina component after 100 min provided the final test of the hypothesis. Toluene yield jumped immediately from 13% to 22%, while isoheptanes yield remained unchanged.

CONCLUSIONS

The fluidized mixed-catalyst technique provides a convenient means of studying reaction paths, and the roles of each catalyst function, in dual-functional reaction systems. The most important feature of this technique is the flexibility for rapidly altering catalyst composition.

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