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NOTE

Role of Dehydrogenation Activity in the Catalytic Isomerization and Dehydrocyclization of Hydrocarbons

Dual function catalysts, consisting of a dehydrogenation component supported on an acidic oxide, are commonly used for the isomerization and dehydrocyclization of hydrocarbons (*1*). A correlation between isomerization activity and dehydrogenation activity of such catalysts has been reported by Ciapetta and co-workers (*1*). In these studies the effect of dehydrogenation activity was determined by varying the nature of the dehydrogenation component, i.e., chromia vs. molybdena vs. platinum, all supported on silica-alumina. These studies showed that isomerization activity increased with increasing dehydrogenation activity and suggested a critical dehydrogenation activity beyond which further increase would have little effect. A relation between dehydrocyclization and dehydrogenation activity was also indicated. In the present study, the effects of dehydrogenation activity on the isomerization and dehydrocyclization activity of a single catalyst system, platinum-alumina, have been determined by varying platinum content and noting the effect on the rates of conversion of *n*-heptane and methylcyclopentane.

EXPERIMENTAL

The *n*-heptane and methylcyclopentane were contacted with catalyst in the presence of hydrogen, using a flow reactor technique described previously (*2*). Catalyst charges of 3.0 to 6.0 g were used. The reaction products were analyzed by a chromatographic procedure described elsewhere (*3*). The hydrocarbons used in this work were Phillips pure grade (>99 mole % purity). The hydrocarbons and hydrogen were dried to less than 5 ppm water using procedures described previously (*2*). The platinum on alumina catalysts used in this study contained 0.10, 0.30, and 0.60% platinum. The alumina was prepared from a sample of beta alumina trihydrate (*4*) supplied by Davison Chemical Co. x-Ray diffraction measurements confirmed that it was beta alumina trihydrate. The trihydrate was calcined in air for 4 hr at 593°C to activate the alumina. The surface area of the resulting alumina was 200 m^2/g. The activated alumina was impregnated with aqueous chloroplatinic acid, which was followed by a second 4 hr calcination in air at 593°C. The finished catalysts were stripped with a mixture of water vapor and nitrogen to remove the chlorine. The catalysts used in the *n*-heptane runs were stripped for 18 hr at 538°C, and were then air-dried for 5 hr at 538°C. This treatment decreased the chlorine to about 0.02 wt % and decreased the alumina surface area from 200 to 130 m^2/g. The catalysts used in the methylcyclopentane runs were stripped for 30 hr at 372°C, and were air-dried for 5 hr at 510°C. This treatment also decreased chlorine to about 0.02 wt % but resulted in a final alumina surface area of 190 m^2/g. The catalysts were pretreated with hydrogen for 3 hr at 527°C prior to introducing hydrocarbon reactant.

RESULTS

Typical product distribution data for *n*-heptane and methylcyclopentane at low conversions (5–10%) over a platinum on alumina catalyst are shown in Table 1. The observed reactions of *n*-heptane include isomerization, dehydrocyclization, and hydrocracking. The isomerization reaction leads predominantly to the formation of 2- and 3-methylhexanes, with little formation of dimethylpentanes. The main prod-

TABLE 1
TYPICAL PRODUCT DISTRIBUTION DATA[a]

Reactant	n-Heptane	Methylcyclopentane
F/W[b]	0.45	1.28
Mole % conversion to:		
C_5-	1.3	—
2-Methylpentane	—	0.6
3-Methylpentane	—	0.4
Dimethylbutanes	—	0.2
n-Hexane	0.1	2.0
2-Methylhexane	2.6	—
3-Methylhexane	5.0	—
Dimethylpentanes	0.2	—
Cyclohexane	—	0.1
Methylcyclohexane	0.1	—
Dimethylcyclopentanes	0.1	—
Benzene	—	1.4
Toluene	0.4	—
Mole % unconverted	90.2	95.3

[a] 471°C, 21 atm, H_2/hydrocarbon = 5, 0.3% Pt catalyst.

[b] Gram moles of hydrocarbon charged per hour per gram of catalyst.

uct of dehydrocyclization is toluene, with some formation of C_7 cycloparaffins. Methylcyclopentane undergoes isomerization–dehydroisomerization to form cyclohexane and benzene, the latter in larger amounts at the conditions used in this work. A ring splitting reaction is also observed, leading to the formation of hexanes.

TABLE 2
EFFECT OF PT CONTENT ON REACTIVITIES OF n-HEPTANE (nC_7) AND METHYLCYCLOPENTANE (MCP) OVER PT-AL_2O_3

Pt content, wt %	0	0.10	0.30	0.60
Reaction rates[a]				
Isomerization of nC_7				
471°C	0	0.035	0.035	0.038
527°C	0	0.12	0.13	0.12
Dehydrocyclization of nC_7				
471°C	0	0.0022	0.0027	0.0045
527°C	0	0.020	0.025	0.035
Isomerization–Dehydroisomerization of MCP				
471°C	0	—	0.019	0.021
499°C	0	—	0.039	0.043

[a] Gram moles per hour per gram of catalyst at 21 atm and H_2/hydrocarbon = 5.

Rate data are shown in Table 2 as a function of catalyst platinum content. The rates were calculated using the relation

$$r = (F/W)\Delta x \qquad (1)$$

where F represents the feed rate of hydrocarbon reactant in gram moles per hour, W is the weight of catalyst in grams, and Δx is the fraction of hydrocarbon converted in a particular reaction. Since the data were obtained at low conversion levels (<10% at 471°C, about 20% at 527°C), the rates obtained in this way represent initial rates. Rates were found to be reproducible within about 10%. The rates are listed as zero for zero per cent platinum, since no isomerization, dehydroisomerization, or dehydrocyclization were observed over a sample of alumina alone. The rate of isomerization of n-heptane is essentially constant over the range from 0.10 to 0.60% platinum. The rate of dehydrocyclization, however, increases by 75 to 100%. When platinum content is increased from 0.30 to 0.60%, the rate of isomerization–dehydroisomerization of methylcyclopentane increases by about 10%. This latter difference could be within experimental error.

Unpublished data obtained in this Laboratory indicate that the dehydrogenation activity of a platinum-alumina catalyst (as measured by the rate of conversion of methylcyclohexane to toluene) is proportional to platinum content over the range from 0.1 to 0.6% platinum.

Considerable evidence is available supporting a mechanism in which isomerization of saturated hydrocarbons proceeds via gas phase olefin intermediates formed on platinum sites of the catalyst (*2,5,6*). The independence of isomerization rate on platinum content (dehydrogenation activity) above a certain level indicates that the formation of olefin intermediate is not a limiting factor in the reaction at the conditions of this work. However, a similar type of interpretation does not appear to be adequate for dehydrocyclization, since the rate increases with platinum content throughout.

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