JOURNAL OF CATALYSIS 66, 463–464 (1980)

NOTES

An Anomaly in the Case of Catalytic Cracking

It had been thought that the addition of liquid water to an amorphous silica–alumina cracking catalyst may enhance its activity and/or its selectivity by increasing the number of Brönsted sites. We have investigated the cracking of *n*-hexadecane with four catalysts at very low temperatures, both in the presence and absence of liquid water.

It was determined that cracking could be observed in all cases at 250°C, a temperature considerably below that at which it is normally expected to occur. While the amounts of cracked product were very small (1–1.5% conversion), they were sufficient for gas chromatographic analysis.

Catalysts used in this work were:

(1) Davison Chemical Company silica–alumina, 35 activity index fluid bed catalyst, SMR 5–1721, 25% Al_2O_3 DR #498 A-D Davison Index 19.
(2) Houdry Process Corporation silica–alumina crushed pellets, 46 activity index #36 D2–54Z (HSA-300).
(3) Davison Chemical Company FCC catalyst (zeolite) SMR 5–1721 CBZ-1.
(4) Mobil Oil Corporation Durabead 9, crushed pellets (zeolite) Reference No. TE-15029.

Experimental work was carried out in a stirred glass flask, containing the *n*-hexadecane, catalyst, and, in some cases, water. Ten grams of catalyst, 15 g of hydrocarbon, and 1 g of water were used. The flask was immersed in an oil bath and heated at 250°C for 1 hr. A condenser was connected to the flask, and at the end of each experiment the overhead product was returned to the flask contents, which were then sampled and analyzed. Prior to use, all catalysts were calcined in dry air at 500°C, and if water was to be added, it was added dropwise while shaking the flask. The contents were then permitted to equilibrate in an inert atmosphere for 24 hr at room temperature before adding the hydrocarbon.

In all cases, the presence of water reduced catalyst activity. In all but one case, product distributions were nearly identical. Liquid products ranged from C_4 to C_{15}, with a paraffin/olefin ratio of 1:2 and a branched/straight chain ratio of 1:2. In the case of one catalyst (catalyst 1 above), the product distribution was radically altered in the presence of water, indicating a change in the cracking mechanism. In this case (which was confirmed in several repeat runs) the liquid products were much more evenly distributed through the C_4–C_{14} range with minimal chain branching and an unusually high paraffin/olefin ratio indicative of hydrogen transfer. Figure 1 shows the liquid product distribution over this catalyst in the absence of water (the same product distribution was obtained with the other three catalysts, both in the presence and absence of water) and the quite different product distribution obtained in the presence of water. This phenomenon was also found to prevail in a run at more severe conditions (300°C and 2000 psi pressure for 45 min), carried out in an autoclave to obtain higher conversion. This latter run exhibited the expected increase in the amount of cracked product without a change in the product distribution previously encountered with this catalyst in the presence of water.

It seems that a carbonium ion mechanism cannot explain the absence of olefins and branched chain hydrocarbons. The product distribution, except for the lack of olefins,

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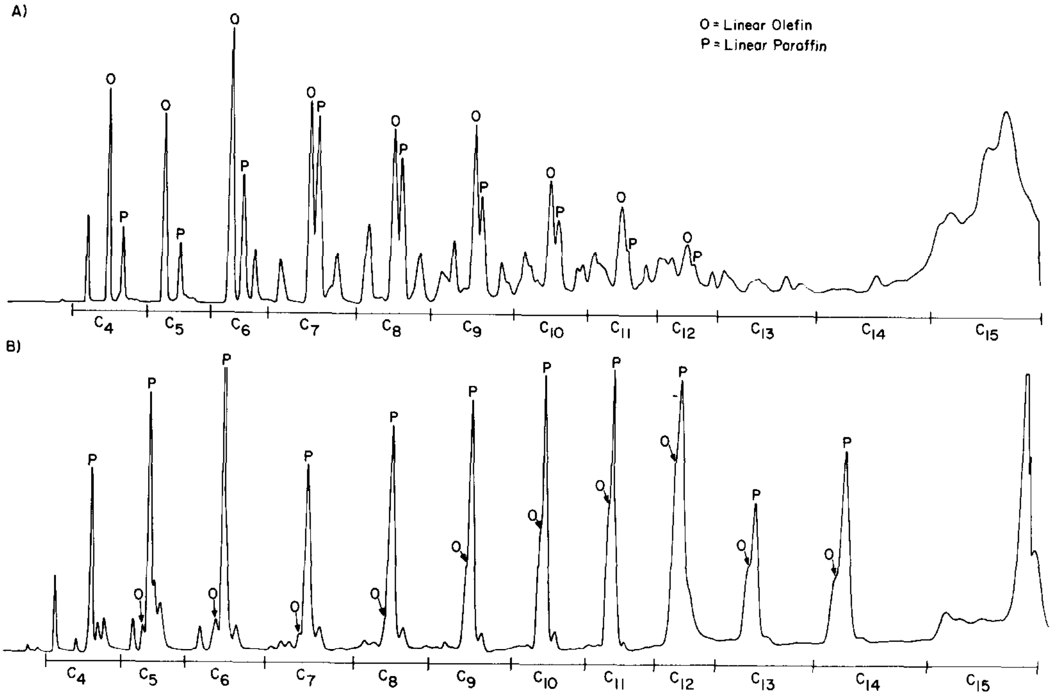

FIG. 1. Gaschromatograms of marked product. A) absence of water; B) presence of water.

more resembles a free-radical reaction. There is also no satisfactory explanation for the source of the hydrogen necessary to form saturated hydrocarbons from the parent hexadecane. Complicating the situation further is the lack of variables which can account for the different behavior of similar silica–alumina catalysts (35 and 46 activity). Variation of reaction time has demonstrated that neither product distribution changes during the course of the reaction, hence there is no sequential change in mechanism. There is a possibility, however, that although the total coke formation is greater in the absence of water, the amount of coke deposited proportional to the weight of cracked products may be higher with liquid water present. Formation of this coke could yield an adequate source of hydrogen, but this does not explain why this should occur only in the presence of the lower activity catalyst.

ACKNOWLEDGMENT

This work was supported by a grant from the Office of University Research, Fossil Fuels, U. S. Department of Energy.

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Received January 4, 1980; revised May 28, 1980