INFLUENCE OF OLEFINs ON THE CATALYTIC TRANSFORMATION OF PARAFFINS ON ACIDIC ZEOLITES

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Received January 4, 1978
Accepted April 14, 1978

The activity and selectivity of zeolites in n-octane cracking in a gradientless flow reactor and in a flow-circulation setup with intermediate hydrogenation have been studied. At concentrations lower or equal to $10^{-3}$ mmol/l, olefins are not involved in the cleavage of paraffin molecules. At concentrations higher than $10^{-3}$ mmol/l, olefins act as promoters of the cracking reactions.

The cracking of paraffins on acidic catalysts is known to be a cascade of consecutive and parallel (secondary) reactions /1/. The addition of olefins to the reaction mixture accelerates the cleavage /2/ and isomerization /3/ of paraffins.

These two factors, i.e. secondary reactions and the promoting action of olefins, significantly hinder studies of the relation between the catalyst surface properties and the character of paraffin transformations. Probably, owing to this, different opinions exist on the nature of active sites of the solid cracking catalysts. In general, models of protonic /1/ and aprotic /4/ surface active centers as well as of the catalytic effect of hydrocarbon residues are in use to explain the mechanism of cracking.

To elucidate the role of the active centers of cracking catalysts and the mechanism of paraffin transformations, the process should be studied in the absence of secondary reactions and the promoting effect of olefins. In the present study an in-
Intermediate hydrogenation reactor was employed \( /5/ \) to investigate the activity and selectivity of zeolites under cracking conditions with and without secondary transformations of the products.

**EXPERIMENTAL**

HNaY (0.9\% Na) and ScHNaY zeolites were prepared by the ion exchange method. Two setups were employed to measure the activity and selectivity of zeolites in n-octane cracking. A microcatalytic short-cycle pulse reactor \( /6/ \) was used as a gradientless flow installation as well. A hydrogenation reactor for lowering the olefin concentrations, with a commercial platinum-alumina catalyst AP-56 (0.5\% Pt on \( \text{Al}_2\text{O}_3 \)) was applied. The cracking (Cr) and hydrogenation (H) reactors were consecutively introduced into the circulation loop and then placed into a furnace. Their temperature was regulated independently. Olefins formed during a single passage of the reaction mixture through Cr (the conversion degree of the initial material per one passage did not exceed 0.5\% after 150–200 cycles) entered into H, wherein they were hydrogenated. The concentration of olefins in the reaction mixture after leaving H was less or equal to \( 10^{-6} \) mmol/l, while at the outlet of Cr it was appreciably higher and varied from \( 10^{-5} \) to \( 10^{-3} \) mmol/l. This value is, however, by 2–3 orders of magnitude lower than that observed in the pulse installation.

Prior to the experiments, the catalysts were activated in hydrogen flow at 550 °C for 2 hrs. The experiments were carried out at 350 °C in hydrogen at 1.8 atm. As shown by the preliminary results, the catalyst activities and selectivities under hydrogen and He are identical.

**RESULTS AND DISCUSSION**

Figure 1 represents the activity of HNaY and ScHNaY zeolites in n-octane cracking as a function of the contact time. These curves are extremal in their character for both catalysts without intermediate hydrogenation. The catalyst activity falls