



ISOMERIZATION OF N-ALKANE OVER ZEOLITE CATALYSTS AT SUPERCRITICAL CONDITIONS

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Isomerization of *n*-alkanes is one of most important process in petrochemical refining nowadays. Isoalkanes are perspective compounds in environmentally friendly gasoline: unlike benzene and aromatic they haven't carcinogenic property. Last decade supercritical fluids have been studied mainly as extraction media. But their unique properties used in catalytic reactions insufficiently wide. Supercritical fluids can behave as a liquid exhibiting high solubility and as gas exhibiting high diffusion and low viscosity. It has been shown that coke formation on the surface of catalysts was reduced and that deactivation could be reduced in acid-catalyzed reactions under supercritical conditions [1].

Isomerization of *n*-butane, *n*-pentane and *n*-hexane was carried out in fixed-bed continuous flow reactor. H-forms of zeolites (H-mordenite with Si/Al = 11, H-beta with Si/Al = 37.5 and H-ZSM-5 with Si/Al = 50) were used as catalysts for isomerization. The liquid hourly space velocity was 6 or 30 h⁻¹. The catalytic experiments under supercritical conditions were carried out in the range of temperature 240–360 °C and pressure 60–150 atm. Comparative experiments in gas phase were performed with a mixture of *n*-pentane and helium in a volumetric ratio 1:3 at atmospheric pressure, and at pressure of 25 atm (*n*-pentane is in gas phase). The reaction products were analyzed on-line by using GLC equipped with a capillary column.

The isomerization of *n*-butane, *n*-pentane and *n*-hexane has been studied in a wide range of temperature and pressure. It has been shown that activity and selectivity of catalysts strongly depend on type of zeolite. Received results of C4 and C5 isomerization show that catalytic activity of zeolites increases in following order: H-mordenite > H-ZSM-5 > H-beta. The less selective catalyst is H-ZSM-5 due to prevail the side reactions of cracking and disproportionation. Comparison of supercritical and gas-phase isomerization was carried out by the example of *n*-pentane conversion (at 260 °C and 6 h⁻¹). In gas phase the catalyst completely deactivates during



several hours. Very low activity of the catalyst and fast deactivation in gas phase is connected with oligomerization of byproducts to formation of coke deposits. In contrast under supercritical conditions (at 130 atm) initial value of pentane conversion is more than 2 times higher and decrease of conversion is very slow. Most likely increase in catalyst lifetime is connected with extraction of coke precursors from catalyst surface with supercritical fluids. It has been observed that catalysts after pentane isomerization in gas phase contain more coke deposits, than after reaction under supercritical conditions. The analysis has shown presence of coke deposits of two types. The first type relates to the products of oligomerization, the second - aromatization. A part of heavier products on catalysts after the gas phase was in 2 times more than after the supercritical conditions.

As well as for C₄/C₅ isomerization *n*-hexane conversion and selectivity are defined by structural type of zeolite. But the row of increasing catalytic activity is different: H-ZSM-5 > H-mordenite > H-beta. At the same time H-ZSM-5 remains the least selective catalyst.

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References

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