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Hydroconversion of Long-Chain n-Alkanes on Pt/HZSM-5 Zeolite

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Zeolite catalysts of medium-pore size are getting increasing acceptance in commercial processes, e.g., in hydrodewaxing of middle distillates. In this process n-paraffins and part of the isomers with one methyl branching are selectively hydrocracked in order to improve the low temperature properties, especially the pour point. Nonetheless, relatively little is known on the shape-selectivity effects occuring during hydroconversion of long-chain alkanes on medium-pore zeolites. Recently, the authors reported (1) on the shape-selective isomerization and hydrocracking of n-decane on Pentasil zeolites. The present paper extends these data to the homologous series of n-alkanes with 9 to 16 carbon atoms.

A Pt/HZSM-5 zeolite catalyst was employed throughout this study. The zeolite with a Si/Al ratio of 60 was prepared according to published methods (2). It was loaded with 0.5 wt.-% of platinum by contact with an aqueous solution of $[Pt(NH_3)_4]Cl_2$. The catalytic experiments were conducted with the pure n-alkanes in a hydrogen atmosphere at a total pressure of 2 MPa and a hydrocarbon partial pressure of 20 kPa except for n-hexadecane where the latter was 10 kPa to avoid condensation at low reaction temperatures. A fixed bed reactor was used. $W/F_{n\text{-}alkane}$ was in the order of 100 g·h/mol. With each feed the reaction temperature was varied between 200 and 300 °C so that a wide range of conversion could be covered. Product analysis was achieved by capillary GLC techniques.

Two types of reaction occur during hydroconversion of n-alkanes on Pt/HZSM-5, viz. isomerization and hydrocracking. In Fig. 1 the yields of branched isomers and of hydrocracked products are plotted versus temperature for the experiments with n-nonane and n-pentadecane.

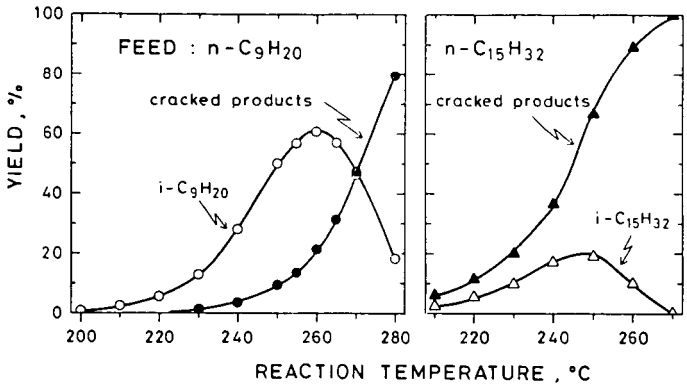

Fig. 1: Hydroconversion of n-Nonane and n-Petadecane on Pt/HZSM-5

While n-nonane can be isomerized under mild conditions without significant hydrocracking the yield of i-pentadecanes from n-pentadecane is low throughout the whole range of temperature and, hence, of conversion. The quantitative evaluation of the influence of reaction temperature on conversion shows that the apparent energy of activation decreases with increasing chain length. This could indicate increasing diffusional resistances.

The distributions of i-alkanes formed by isomerization of the n-alkanes differ substantially from those observed over faujasite zeolites (3). In particular, methyl isomers strongly predominate on Pt/HZSM-5 up to 90 % conversion. Small amounts of dimethyl isomers with one branching in the 2-position are also formed while ethyl isomers are absent. These results are best interpreted in terms of product shape-selectivity.

Distributions of individual methyl isomers formed from three selected n-alkanes at moderate conversions around 10 % are given in Table 1. The main product from n-nonane is 2-methyl-octane. This is in principal agreement with our earlier results (1) of n-decane conversion on Pt/HZSM-5 and might reflect a restricted transition state shape-selectivity. On the other hand, roughly equal amounts of individual methyl isomers are formed from n-tridecane and n-pentadecane (Table 1). These distributions are problably close to equilibrium.

Table 1: Distributions of Methyl Isomers Formed from Various n-Alkanes (Values in mol-% of total methyl isomers)

Feed	n - C_9H_{20}	n - $C_{13}H_{28}$	n - $C_{15}H_{32}$
Temperature, ^oC	230	220	210
Conversion, %	14.6	10.6	9.3
Yield of i-C_mH_{2m+2}, %	13.2	8.2	2.8
	2-M-Oc 42.6	2-M-Do 15.0	2-M-Te 14.6
	3-M-Oc 38.0	3-M-Do 22.3	3-M-Te 18.8
	4-M-Oc 19.4	4-M-Do 18.0	4-M-Te 15.4
		5-M-Do 22.8	5-M-Te 15.5
		6-M-Do 21.9	6-M-Te 18.0
			7-M-Te 17.7

Hydrocracking on Pt/HZSM-5 is purely ionic, i.e., no hydrogenolysis on Pt-sites takes place. This can be concluded from the absence of methane and ethane. Typical carbon number distributions of the cracked products from n-tetradecane and n-pentadecane are depicted in Fig. 2. For comparison the corresponding distributions on a Y-type zeolite with a pure primary cracking selectivity are given.

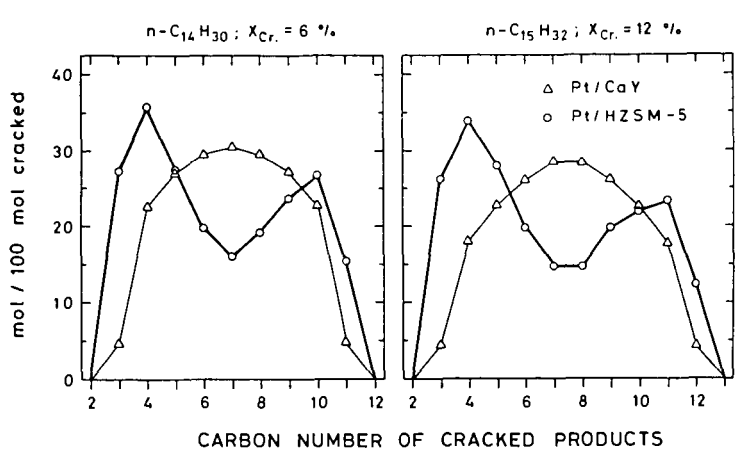

Fig. 2: Carbon Number Distributions in Hydrocracking of n-Tetradecane and n-Pentadecane

The curves for Pt/HZSM-5 are not fully symmetrical which is indicative of some secondary cracking. It is evident that the cracking selectivity on Pt/HZSM-5 deviates considerably from the one on faujasites. In particular, more C_3 and C_4 as well as C_{m-3} and C_{m-4} (m = carbon number of feed) are formed on ZSM-5. Moreover, the distribution curves for the medium-pore zeolite exhibit distinct minima.

The cracked products on Pt/HZSM-5 consist of n-alkanes and methyl isomers. Detailed isomer distributions will be given in the paper. A reaction network for shape-selective rearrangements and β-scissions in the pores of ZSM-5 will be developed.

References

(1) P.A. Jacobs, J.A. Martens, J. Weitkamp, and H.K. Beyer, Farad. Discuss. Chem. Soc. 72, 353 (1982)

(2) R.J. Argauer and G.R. Landolt, US Patent No. 3 702 886 (1972)

(3) J. Weitkamp, Ind. Eng. Chem., Prod. Res. Devel., in press