

DETERMINATION OF THE HYDROCRACKING AND HYDROISOMERIZATION ACTIVITIES OF CATALYSTS CONTAINING ZEOLITES Y AND ZSM-5 FOR HIGH BOILING HYDROCARBONS CONVERSION

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Hydrocracking, hydroisomerization activities and selectivities were investigated using silica-alumina, silica-alumina-Y, and silica-alumina-ZSM-5 catalysts. The results show that white oil cracking activity of H-ZSM-5-containing catalyst is much higher than the cracking activity of H-Y. The work has shown that it is possible to carry out hydrocracking process at temperature 593–613 K and space velocity $2-3 \text{ h}^{-1}$ (pressure 5.1 MPa, H_2 : CH = $500 \text{ Nm}^3 \text{ m}^{-3} \text{ h}^{-1}$) using H-ZSM-5 containing catalysts. In such conditions, 76–84 wt. % of liquid product from white oil was obtained. After removing the low boiling fraction (below the initial boiling point of the feed), the lowering of the freezing point from 252 to 235 K was noticed.

The method of preparation is one of the factors influencing the hydrocracking and hydroisomerization activity. For aluminosilicates as carriers, the effect of this factor on the physico-chemical properties and activity of the catalysts was already described¹.

Molecular sieves are used as components of such catalysts. This work is aimed at comparison of the effect of zeolite H-Y and H-ZSM-5 on the activity and selectivity of the hydrocracking catalysts. The possibility to decrease the operating temperature (or to increase the space velocity) was studied.

Studies of n-paraffins over H-ZSM-5 zeolite have been performed². However, the effect of H-ZSM-5 zeolite on the hydrocracking catalysts has not been reported.

EXPERIMENTAL

Catalysts containing 16% molybdenum oxide and 4% nickel oxide were prepared by impregnation of carriers. Aluminosilicates 70% Al_2O_3 , 30% SiO_2 or mixture of aluminosilicates with 10% zeolite were used as supports.

The experiments were carried out in a continuous flow high pressure microreactor unit. Exact description of the experimental methods is given elsewhere³. According to this procedure, 4 cm^3 of the catalyst of mesh-size 0.75–1.02 mm were reduced for one hour in the reactor at 593 K and hydrogen pressure 5.1 MPa. After reduction, the catalysts were sulphided using white oil and CS_2 (ratio 80 : 1) at 633 K. Catalysts were tested in the temperature range of 553–653 K, space velocity from 1 to 3 h^{-1} , at pressure 5.1 MPa and H_2 : CH = $500 \text{ Nm}^3 \text{ m}^{-3} \text{ h}^{-1}$.

In testing the hydrocracking and hydroisomerization activities of the catalysts, white oil of the following properties was used: $d^{293} = 0.862 \text{ g cm}^{-3}$, init. b.p. 447 K, 40% distilled at 633 K, freezing point 252 K.

The method employed for these studies was IR spectroscopy which has been shown to be useful in studying the conversion of paraffinic and cycloparaffinic hydrocarbons mixture⁴.

The structural parameters, $\text{CH}_2^{\geq 6}$, $\text{CH}_2^{=4-5}$, $\text{CH}_2^{\geq 3}$, $\text{CH}_2^{\geq 2}$, $\text{CH}_2^{\geq 1}$, (n — number of CH_2 groups in paraffinic chains), % C_A for the products and feed were determined according to the methods reported in literature⁵⁻⁸. Hydrocracking activity is determined as a change of number of CH_2 groups in a chain containing six carbon atoms or more $\text{CH}_2^{\geq 6}$ and amounts of the products boiling below the initial boiling point of the white oil (low boiling fraction — LBF). LBF's were calculated from gas chromatographic measurements using 2 m column packed with 3% silicone oil on Chromosorb W-NAW.

The gaseous products were analyzed by gas chromatographic method using 3.6 m column packed with 30% Apiezon L on Chromosorb W-NAW. Porous structure has been investigated from Benzene Adsorption and Mercury Porosimetry Methods. Acidity was determined by temperature-programmed desorption of NH_3 ; the sites desorbing ammonia at temperature 453–573 K were defined as sites of weak acidity, at 573–723 K as intermediate ones, and at 723–823 K as strong sites.

RESULTS AND DISCUSSION

The catalysts used are summarized in Table I. In the case of the catalysts 3 and 4 two different methods for introducing H-ZSM-5 zeolite were used. Zeolite H-Y (catalyst 2) was introduced in the same way as H-ZSM-5 for catalyst 3.

The results indicate the importance of the aging process of the mixture of both components on acidic properties of the catalysts. Catalysts 2 and 3 obtained according to such procedure have higher total acidity. Aging process influences also pore volume distribution (Table II).

TABLE I

Characteristics of the catalysts: 1 $\text{Al}_2\text{O}_3\text{SiO}_2$; 2 $\text{Al}_2\text{O}_3\text{SiO}_2/\text{H-Y}$; 3 $\text{Al}_2\text{O}_3\text{SiO}_2/\text{H-ZSM-5}$; 4 $\text{Al}_2\text{O}_3\text{SiO}_2/\text{H-ZSM-5}$

Catalyst	Bulk density kg m^{-3}	Porosity $V_{\text{H}_2\text{O}}^{298\text{K}}$ $\text{dm}^3 \text{ kg}^{-1}$	BET area $10^3 \text{ m}^2 \text{ kg}^{-1}$	Acidity ^a , mol kg^{-1}			
				<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
1	560	0.68	215	0.553	0.166	0.312	0.075
2	710	0.48	291	0.777	0.225	0.413	0.139
3	650	0.55	256	0.751	0.226	0.400	0.125
4	630	0.66	227	0.639	0.135	0.359	0.099

^a Determined by temperature-programmed desorption of NH_3 . Designation: *a* total acidity;

^b weak acidic sites; *c* intermed. acidic sites; *d* strong acidic sites.

As shown in Fig. 1, the activity of H-ZSM-5 containing catalyst 3 in the hydrocracking of white oil is much higher than that of H-Y containing catalyst 2. At temperatures of 553–633 K no influence of the space velocity on the hydrocracking activity of catalyst 3 was observed. When the process was carried out at temperature

TABLE II

Comparison of pore volume distribution in $\text{dm}^3 \text{kg}^{-1}$ for cat. 1 – cat. 4

Pore diameter ^a , nm	Catalyst			
	1	2	3	4
0–1.5	0.006	0.018	0.000	0.015
1.5–3.0	0.059	0.129	0.138	0.066
3.0–5.0	0.202	0.146	0.111	0.179
5.0–10.0	0.140	0.057	0.116	0.135
10.0–33.3	0.100	0.034	0.095	0.100
33.3–100.0	0.053	0.020	0.034	0.052
PM 100.0–7 500.0	0.122	0.067	0.062	0.072
0–7 500.0	0.682	0.471	0.556	0.619

^a BM Benzene Adsorption Method, PM Porosimetry Method.

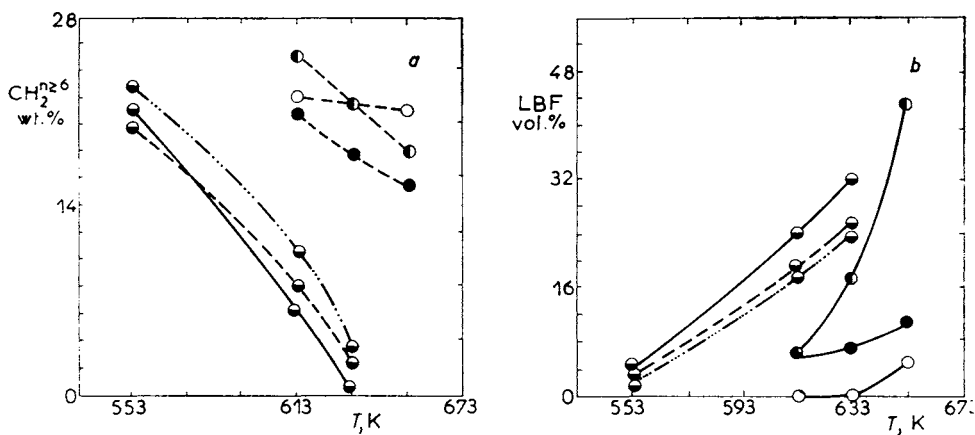


FIG. 1

Effect of temperature on white oil hydrocracking. *a* Change of $\text{CH}_2^{\geq 6}$ groups; white oil — $\text{CH}_2^{\geq 6} = 28$. *b* Change of the amounts of LBF. \circ cat. 1, \bullet cat. 2, \ominus cat. 3, \bullet cat. 4, ——— LHSV = 1, - - - - LHSV = 2, - · - · - LHSV = 3 h^{-1}

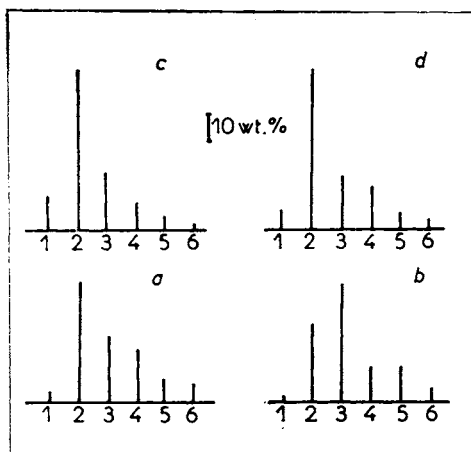


FIG. 2

Distribution of the components of gas (reaction temperature 633 K, LHSV = 2 h^{-1})
 a cat. 1, b cat. 2, c cat. 3, d cat. 4; 1 $\text{C}_1 + \text{C}_2$, 2 C_3 , 3 i- C_4 , 4 n- C_4 , 5 i- C_5 , 6 n- C_5

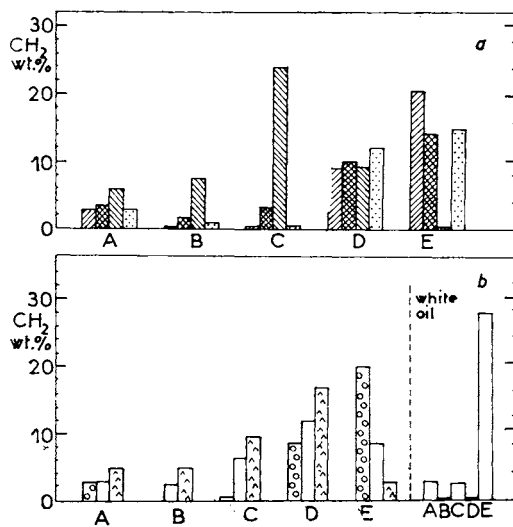


FIG. 3

Dependence of the amount A $\text{CH}_2^{\eta=1}$, B $\text{CH}_2^{\eta=2}$, C $\text{CH}_2^{\eta=3}$, D $\text{CH}_2^{\eta=4-5}$, E $\text{CH}_2^{\eta \geq 6}$ on a catalysts at $T = 633 \text{ K}$, LHSV = 1 h^{-1} , from the left to the right at A cat. 1 - cat. 4 and on b temperature on catalyst 3, LHSV = 2 h^{-1} , from the left to the right at A $T = 553 \text{ K}$, 613 K, 633 K

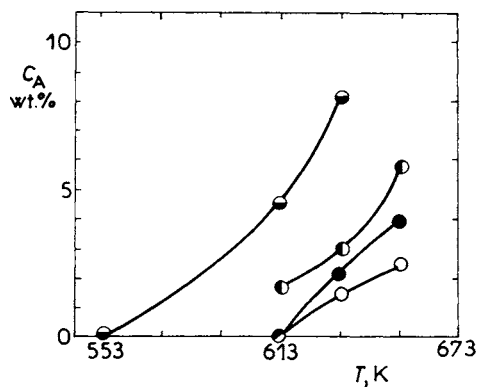


FIG. 4

Effect of temperature on aromatic compounds content in the liquid product, LHSV = 2 h^{-1} . \circ cat. 1, \bullet cat. 2, \ominus cat. 3, \bullet cat. 4

613 K and space velocity $2-3 \text{ h}^{-1}$, 76–84% liquid product from white oil was obtained.

The distribution of the components in the gaseous product of white oil hydrocracking shows significant differences (Fig. 2). For the catalysts containing H-ZSM-5 (cat. 3 and 4), the main component of the gaseous product was propane. The amount of $i\text{-C}_4 + i\text{-C}_5$ is remarkably higher in the case of catalyst 2 in comparison to others. The overcracking observed in presence of catalyst containing H-ZSM-5 is in agreement with the results of *n*-hexane² and decaline⁹ transformation in the presence of pure zeolite. From the comparison of the results of liquid product structure analysis it results that in the case of catalyst 3, low chain length paraffinic structure elements are present (Fig. 3).

Structural analysis of liquid product indicates that the introduction of H-ZSM-5 zeolite is an important factor influencing the catalyst activity. The selectivity of catalyst depends also on the method of preparation (% C_A remarkably increases when the aging process was used – Fig. 4). In the literature, the increase of aromatic hydrocarbons content^{2,9,10} is explained by higher hydrogen transfer activity⁹.

Thus, the results indicate that by using the H-ZSM-5 zeolite one can obtain sufficiently active catalysts for low temperature hydrocracking process.

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