THE ROLE OF ION EXCHANGE METHOD OF Na-ZSM-5 ZEOLITE AND INFLUENCE HYDROGENATION COMPONENTS ON PROPERTIES AND ACTIVITY OF DEWAXING CATALYSTS*

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Hydrocracking of n-hexane and diesel oil fraction over presulfided NiMo, Mo and Ni catalysts has been carried out using a high pressure flow reactor system. The ion-exchanged form of ZSM-5 extrudates (50% alumina binder) was loaded with 2—20 wt. % of metals. The results indicate that, using Ni/H-ZSM-5 zeolite obtained by incorporation of nickel by ion exchange treatment of NH_4-ZSM-5 from nickel nitrate solution, it is possible to obtain sufficiently active catalysts for low-temperature hydrocracking process. The catalysts containing Ni-ZSM-5 zeolites (Ni/H-ZSM-5 or Ni/Na-ZSM-5) were superior to catalyst prepared by using P/H-ZSM-5. It was found that nickel was an essential hydrogenation components of low temperature hydrocracking catalysts.

The developments in the application of zeolite catalysts to hydroprocessing technology dates back early to the 1960's when Y zeolite became to be used[1,2]. Over the last few years much interests has been given to the application of high-silica, medium-size zeolites, such as ZSM-5, as main component of the catalysts. Zeolite H-ZSM-5 possesses strong acidic properties which make it a suitable catalyst for hydrocarbon reactions proceeding via carbonium ion intermediates. In addition, the pore system of this type of zeolites hinders the formation of large hydrocarbon molecules[3] thus preventing a rapid deactivation of acid catalysts. The potential advantages include also employment of the zeolite hydrophobicity and thermostability. This has led to the development and commercial use of several novel processes in petrochemical industry. Due to these properties, H-ZSM-5 is appropriate for the conversion of n-paraffin (wax) molecules to a mixture of lighter hydrocarbons[4]. Typically, a pour-point reduction of 40 – 30 K can be achieved for the base oils with 70 – 90% oil yield under relatively mild pressure and temperature conditions. The catalytic de-

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waxing process is not restricted to application in lube base oils but can also be used to improve the cold-flow properties of gas oils[5,6]. Using n-hexane, it has been shown that the activity of the pentasils depends strongly on the SiO/Al_2O_3 ratio[7,8].The amount of coke was higher with a lower Si/Al ratio.

In connection with the bifunctional action of metal loaded zeolite catalysts with defined chemical composition, differences in catalytic properties could be attributed to difference in the method of metal and zeolite incorporation.

To continue our studies of hydrocracking activity of catalysts containing ZSM-5 for high-boiling hydrocarbons conversion[9–11], we have investigated the role of ion exchange method of Na-ZSM-5 zeolite and the influence of hydrogenation components on the properties and activity of dewaxing catalysts.

EXPERIMENTAL

Catalyst Preparation

ZSM-5 zeolite with molar SiO_2/Al_2O_3 ratio 35 : 1 and Na contents 1·75 wt. % was used. It was prepared according to a procedure which has been described elsewhere[12].

The Ni-ZSM-5 zeolite were prepared by:

A) Two-step ion exchange treatment of NH_4-ZSM-5 by a 0·3 mol/l nickel nitrate solution, the ion exchange was allowed to proceed for 1·5 h at 353 K and the product is denoted as zeolite A.

B) One-step ion exchange treatment of Na-ZSM-5 by a 0·1 mol/l nickel nitrate solution in the presence of CH_3COOH—CH_3COONa, the ion exchange was allowed to proceed for 3 h at 373 K, the product is zeolite B.

C) Two-step ion exchange treatment of H-ZSM-5 with the nickel nitrate solution as for the zeolite A; the product is zeolite C.

For the first step of ion exchange of Na-ZSM-5 an ammonium chloride solution (zeolite A) or hydrochloric acid (zeolite C) were used. The materials after exchange were washed and dried at 383 K for 24 h.

The P/H-ZSM-5 was prepared by deposition of phosphorus on H-ZSM-5 from a 1 mol/l H_3PO_4 solution at 353 K during 6 h. The sample was evaporated to dryness and then dried at 383 K for 24 h (zeolite D).

All these samples were then heated by gradually raising the temperature up to 823 K and maintained at this temperature for 3 h. Catalyst formation was performed by placing an aqueous suspension of the zeolite in contact with an aqueous suspension of aluminium hydroxide (wet method) and extrusion.

The ion-exchanged ZSM-5 extrudates (50% alumina binder) were loaded with 2 to 20 wt. % of metals in oxidic forms (NiO, MoO_3). The catalysts containing molybdenum oxide and nickel oxide were prepared by two-step impregnation of alumina-zeolite carriers. Comparison of Ni-Mo and Co-Mo systems indicates that activity rises when Ni-Mo catalysts are used[13].

Procedures

Before catalytic runs, the catalyst samples were calcined at 753 K for 3 h under static conditions in air atmosphere and then reduced and sulfided. Exact description of the experimental method is given elsewhere[14]. According to this procedure, 4 cm^3 of the catalysts of mesh size of 0·75–1·02 mm were reduced for one hour in the reactor at the temperature of 293–593 K and hydrogen pressure of 3·5 MPa. After reduction, the catalysts were sulfided using hydrocarbon feed and CS_2 (ratio 100 : 1) at 593–613 K for 3 h. The feedstock was obtained from Płock Refinery (hydrocarbon mixture boiling in the range of diesel oil fraction). The hydrocracking was studied at 593–613 K, 3·5 MPa, LSHV of 3 h^{-1} and H_2: CH = 500 in a microreactor flow system. Gaseous product was analysed in selected cases by an on-line gas chromatograph using Apiezon L (30%) on Chromosorb W-NAW column.

The characteristics of surface acidity of the samples were obtained by the temperature programmed desorption of ammonia. The sites desorbing NH_3 within the temperature range of 473–573 K were defined as sites of weak acidity (W), within 573–723 K as intermediate (M) and at 723–823 K as strong sites (S).

The zeolites were also characterized by the IR spectra between 1 300 and 3 600 cm^{-1}. Concentrations of acid centers of different kind (Brønsted and Lewis) were estimated by pyridine chemisorption and their strength by pyridine desorption at 573 and 673 K. Porous structure has been investigated by benzene adsorption.

RESULTS AND DISCUSSION

Effect of Ion Exchange Treatment

The zeolite and catalysts used are listed in Tables I and II. The measurements indicate that in the nickel-exchanged zeolites stronger acidic centers (S^+) than in basic Na--ZSM-5 zeolite were created. It has been found that to increase the concentration of Brønsted acid sites (BAS) the method *A* of nickel introducing is preferable. The results obtained show that there was no collapse of the crystalline lattice structure when nickel was incorporated by method *A*. If nickel was introduced by the method

TABLE I

Characteristics of the zeolites and catalysts

Samples	Number of acid sites (10^{19} g^{-1})			Temperature dependence of sites, %				Na wt. %	Ni wt. %	P wt. %
	Brønsted		Lewis	Brønsted		Lewis				
	strong	weak		573 K	673 K	573 K	673 K			
Zeolite A	7·3	2·9	1·5	100	78·6	37·5	12·5	0·01	1·38	—
Zeolite B	3·2	0·7	2·3	59·2	44·5	41·7	25·0	0·83	0·44	—
Zeolite D	1·8		3·6	—	—	—	—	0·01	—	2·3
Catalyst A	7·6	2·1	2·2	85·3	75·0	68·7	48·7	—	—	—
Catalyst A-1	6·4	1·2	5·2	43·8	24·8	33·6	29·4	—	4·5	—

B, the crystalline lattice structure slightly collapsed (about 10%). With the P/H-ZMS-5 zeolite, 50% crystallinity of the lattice was still preserved.

TABLE II

Acidic sites distribution determined by TPD of NH_3

Samples	Acidity, mmol/g[a]				S^+
	W	M	S	total	
Zeolite A	0·17	0·72	0·50	1·34	12[b]
Catalyst A-1	0·11	0·31	0·19	0·61	14·5[c]
Zeolite B	0·22	0·82	0·39	1·43	8[b]
Catalyst B	0·14	0·40	0·10	0·64	14·5[c]
Zeolite D	0·05	0·10	0·00	0·15	0[b]
Catalyst D	0·11	0·27	0·06	0·44	7·5[c]
Zeolite C	0·22	0·71	0·40	1·33	13[b]
Na-ZSM-5	0·16	0·83	0·29	1·28	1
Al_2O_3	0·12	0·25	0·06	0·43	—

[a] The acidity was determined for samples pressed into pellets with 10 wt. % graphite, crushed and sieved to 0·25—0·75 mm. Average pore volume and pore radius of the catalyst were 0·30 $cm^3 . g^{-1}$ and 4 nm, respectively (data for pore 1·5—100 nm). [b] Concentration of ultra strong acid sites (S^+) desorbed ammonia at temperatures above 823 K is expressed by: $[S^+] = 100$ (peak height of NH_3 for Ni/Z-ZSM-5 at 823 K)/(peak height of NH_3 for Na-ZSM-5 at 823 K) in arbitrary units. [c] $[S^+]$ see Table III.

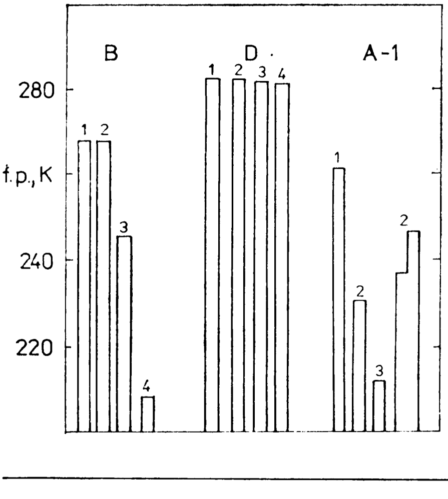

FIG. 1

Effects of the ion exchange method of Na-ZSM-5 zeolite on the catalyst activity (freezing point (f.p.) and yield of liquid product): catalyst B, catalyst D and catalyst A-1. Reaction temperature (K): 1 593, 2 613, 3 633, 4 653. *a*/*a** yield of liquid product before (*a*) and after removing the low boiling fraction below the initial boiling point of the feed (*a**) in %: 1 98/98*, 2 99/95*, 3 97/89*, 4 88/87* f.p. 208 K (B); 1 100, 2 100, 3 99, 4 99 (D); 1 95/93*, 2 93/88*, 3 92/87*, 2 95/89* (A-1)

Hydrocracking activities are compared in Fig. 1 for the three Mo-Ni catalysts (A-1, B, D). The results indicate that by using zeolite A, it is possible to obtain sufficiently active catalysts for low-temperature hydrocracking process. The catalysts containing Ni/ZSM-5 zeolites were superior to the catalysts prepared by using P/H-ZSM-5.

From the data on n-hexane (Fig. 2) it is evident that, in accordance with the literature, the activity drops with decreasing concentration of strong Brønsted sites. Cracking mechanism recently proposed includes the formation of unconventional carbonium ions with penta-coordinated carbon and involves the participation of only strong Brønsted sites. Within the temperature range of 523 – 673 K, the conversion of n-hexane and yield of $C_1 - C_5$ hydrocarbons were much higher for the catalyst containing zeolite A (catalyst A-1) than for the catalyst containing zeolite B (catalyst B). The largest amounts of products above the boiling temperature of normal C_6 fraction (HBF) were formed in the presence of catalyst A-1. In accordance with the results of other research studies, an increase in the concentration of strong acidic sites leads to increaed yield of dehydrocyclization products.

From the data on n-hexane and diesel oil fraction conversion in the presence of catalysts A-1 and B, it is evident that, in accordance with the previous work, the hydrocracking activity increases with increasing acidity of strong acid sites determined by TPD of NH_3 (Table II).

Effect of Hydrogenation Components

The influence of the amount of hydrogenating components on the activity was investigated for catalysts containing Ni/H-ZMS--5 zeolite (zeolite A). The charac-

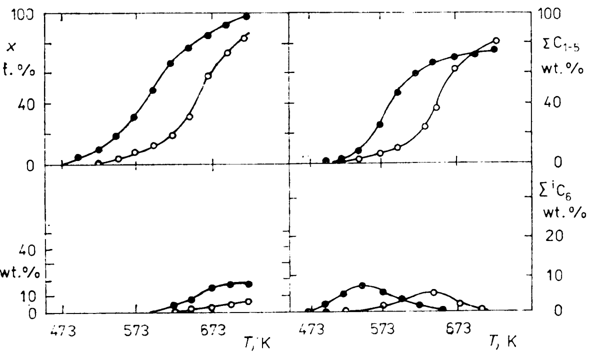

FIG. 2

Conversion of n-hexane (x) and product distribution over catalyst ● A-1 and ○ B teristics of the catalysts given in Table III show that acidity, acid sites distribution and contribution of S^+ acidic centers were strongly influenced by the amount of hydrogenating components. As shown in Fig. 3, hydrocracking activity rapidly increased when nickel as a hydrogenating component was used. The catalyst containing a lower amount of metal (supported Mo catalyst A-4) was less active than the catalyst containing additionally 4 wt. % of nickel (catalyst A-1).

TABLE III

Effects of the incorporated metal on the acidity of the catalysts

Catalyst	Amount of metal oxides, wt. %		Acidity, mmol g^{-1}				S^{+a}
	MoO_3	NiO	W	M	S	total	
A-1	16	4	0·11	0·31	0·19	0·61	14
A-4	16	—	0·16	0·42	0·10	0·69	16
A-2	8	4	0·15	0·38	0·13	0·66	18
A-3	4	4	0·13	0·45	0·23	0·81	55
A-5	—	4	0·14	0·50	0·23	0·88	52
A-6	—	2	0·14	0·49	0·27	0·90	53
C-6	—	2	0·18	0·45	0·21	0·84	53
A	—	—	0·16	0·39	0·25	0·81	64
C	—	—	0·11	0·45	0·23	0·79	75

[a] $[S^+] = 100.$ (peak height NH_3 for the catalyst at 823 K)/(peak height NH_3 for Ni, H-ZSM-5 at 823 K) in arbitrary units.

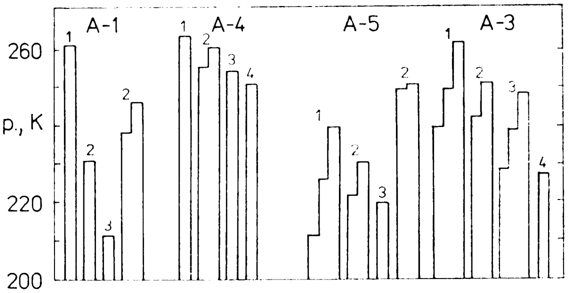

FIG. 3

Effects of the incorporated metal on the activity of catalysts: A-1, A-4, A-5, A-3. Reaction temperature (K): **1** 594, **2** 613, **3** 633, **4** 653.

Further experiments were performed to try to explain how the activity is affected by the presence of molybdenum. The results show a decrease in the activity with molybdenum addition. The distribution of the components (Table IV) in the gaseous product shows significant differences between Mo-Ni (A-3) and Ni (A-5) catalysts. For the catalyst containing nickel, the amount of C_1-C_3 is remarkably higher than for the catalyst containing additional molybdenum. The above described experiments indicate that the effect of nickel on the catalyst activity is very sensitive to the presence of molybdenum. This is, in our opinion, the main result presented in this communication.

The n-hexane conversion on catalyst A increases faster than on catalyst A-5. Nickel introduction into the Al_2O_3-Ni/H-ZSM-5 system exhibited a marked change of catalyst activity. The incorporation of 4 wt. % of nickel (catalyst A-5) results in

TABLE IV

Distribution of the gaseous products (reaction temperature 633 K)

Catalyst	Gas composition, wt. %						
	$C_1 + C_2$	C_3	i-C_4	n-C_4	i-C_5	n-C_5	C_5^+
A-3	5·1	55·0	10·6	21·0	4·0	4·1	0·2
A-5	8·0	64·7	10·5	12·5	2·6	1·6	—

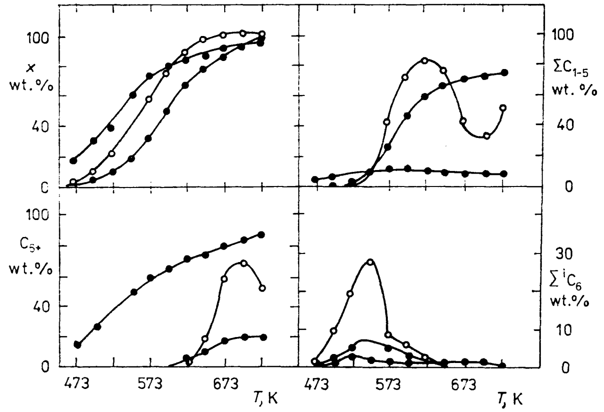

FIG. 4

Conversion of n-hexane (x) and product distribution over catalysts ● A, ○ A-5, ⊗ A-1 a shift of formatio nof C_{6+} (HBF) products to a higher temperature (about 150 degree) and also affects the dependence of C_{6+} yield on the reaction temperature (Fig. 4). The reaction products on the catalyst A were essentially hydrocarbons boiling above normal C_6.

A comparison effect of the ion exchange method *A* and *C* of Na-ZSM-5 in respect of the activity of nickel catalysts indicates that the procedures used for the catalysts A and A-6 provide the highest hydrocracking activity (yield of C_1-C_3, yield of liquid product before and after removing the low boiling fraction below the initial boiling point of the feed see – Fig. 5, Table V). Method *C*, when used for ion exchange treatment, affects the stability of the catalyst. However, the initial activity decreases significantly.

TABLE V

Effects of ion exchange method on the yield of C_1-C_4 hydrocarbons (in wt. %) at different reaction temperature

Catalyst	593 K		613 K	
	C_1-C_3	C_3/C_4	C_1-C_3	C_3/C_4
A	67·3	2·3	71·9	2·8
C	64·9	2·0	64·8	1·9
A-6	65·4	2·2	71·3	2·5
C-6	61·3	1·6	62·5	1·6

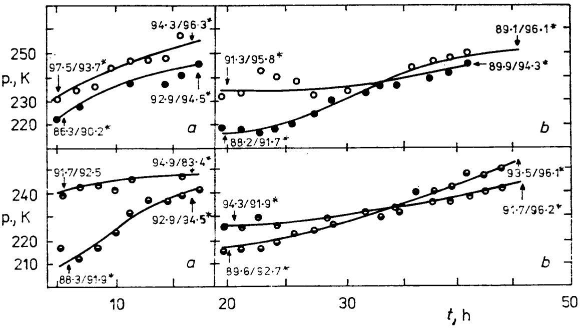

FIG. 5

The role of ion exchange method of Na-ZSM-5 zeolite on activity of catalysts ● A, ○ C, ◒ A-6, ◓ C-6; *a* reaction temperature 593 K, *b* reaction temperature 613 K

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