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Activity and stability of alumina zeolite nickel catalysts

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Abstract

The catalytic properties of nickel catalysts (50 wt.% of alumina and 50 wt.% of Ni,H-ZSM-5) were investigated and related to the amount of NiO (0–8 wt.%) and the method of nickel incorporation (8 wt.% NiO). Consideration was also given to the method by which zeolite and alumina were combined. The cracking properties of the catalysts increased when the amount of NiO was raised up to 4 wt.%. To decrease the content of aromatic hydrocarbons in the products it is necessary to raise the amount of NiO to a higher level than 4 wt.%. The catalyst prepared by peptisation of the mixture of zeolite and aluminium hydrogel (with ageing process) displayed reduced activity and stability because of the low susceptibility of NiO to reduction.

Keywords: Nickel catalyst; ZSM-5 zeolite; Activity; Stability

1. Introduction

To improve the cold flow properties of diesel and lubricating oil base stocks, catalytic dewaxing is carried out by *n*-paraffins cracking and/or *n*-paraffins isomerisation. The catalysts based on medium-size pore zeolites like ZSM-5 and SAPO-11 are widely used in industrial dewaxing processes. Owing to their structure, only normal or slightly branched paraffins can react over these zeolites [1–7]. Activity, selectivity and stability of the catalysts for those shape selective reactions depend not only on the porous structure of the zeolite but also on the density of acid sites and their strength distribution, as well as on metal sites distribution and metal–support interaction [8,9]. In the case of alumina zeolite nickel catalysts the interaction between the support and the metal can cause fixation of some active ingredient portions in the form of inactive compounds or favours formation of nickel oxides that are difficult to reduce. The metal–support interaction and consequently the catalytic properties of the catalyst strongly depends on the method of preparation [10–13].

The activity and selectivity of zeolite/Al_2O_3 catalysts can be modified by the method of incorporation of the active ingredient into this system. For example when the ion exchange technique is used to incorporate the nickel (about 1 wt.% Ni) into Na-ZSM-5/montmorillonite (35/65 weight) the metal dispersion achieved is high and there is also a strong metal–support interaction. In such case, the metal sites themselves can be strongly modified by the support and, on the other hand, they can modify the acid sites of the zeolite. Ion exchanged catalysts exhibit a higher catalytic activity in the hydroisomerisation of *n*-decane than do the impregnated ones [14]. When use is made of the recently reported metal vapour method, nickel supported (H-ZSM-5 + Al_2O_3, Al_2O_3 and MgO) catalysts are characterised by extremely active metal particles in a highly dispersed state. These catalysts showed high activity, selectivity and stability toward hydrocracking and isomerisation of hydrocarbons [15]. The most common method for the

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preparation of supported metal catalysts (zeolite/Al_2O_3) is the one involving incorporation of the metal precursor by impregnation.

The objective of this study was to investigate how the method of active compound incorporation (impregnation, forming, impregnation/forming) and the amount of nickel oxide influence the catalytic properties of the bifunctional Ni/ZSM-5/Al_2O_3. Consideration was also given to the method by which zeolite and alumina were combined. The activity and selectivity experiments described here involved white oil and *n*-hexane conversion. Catalyst stability was investigated in the dewaxing of the light vacuum distillate (LVGO) hydroraffinate.

2. Experimental

2.1. Preparation of catalysts

ZSM-5 zeolite with a molar SiO_2/Al_2O_3 ratio of 35:1 and Na content of 1.75 wt.% was prepared according to a procedure described elsewhere [16]. Ni,H-ZSM-5 zeolite (1.4 wt.% of Ni and 0.01 wt.% of Na) was obtained by a two-step ion exchange method using 1 N NH_4Cl and 1 N $Ni(NO_3)_2$ solutions, $T = 90°C$ and $\tau = 2$ h.

Aluminium hydrogel was obtained by coprecipitation; sodium aluminate and nitric acid were added gradually in the presence of ammonium nitrate solution, at pH 9 and 70°C; an additional amount of nitric acid was used for pH adjustment to 7. Samples were dried in air at 110°C for 12 h.

The catalytic systems contained Ni,H-ZSM-5 zeolite and aluminium oxide (50:50). The catalysts differed in the amount of NiO, the method of nickel incorporation, and the method by which zeolite and alumina were combined. The catalysts were prepared by mixing separately obtained peptisates of zeolite and aluminium hydroxide (method E), and by the peptisation of the mixture of zeolite and aluminium hydrogel (method A) in which before peptisation, the mixture of zeolite and aluminium hydrogel were aged in aqueous solution for 4 h and then dried.

The active compound, NiO (2–8 wt.%), was incorporated by impregnation of extrudates (method I) or at the stage of support forming (method F). The method F + I, in which one-half of the active component was deposited at the stage of support forming, and the other half by impregnation was also used. When nickel oxide, partly or completely, was incorporated at the stage of support forming, the acid solution (1% HNO_3) of nickel nitrate was used for peptisation of aluminium hydroxide. Catalyst extrudates were dried at 110°C for 18 h and calcined at 480°C for 3 h. The catalysts under study are listed in Table 1.

Table 1
Methods of catalyst preparation

Catalyst	Method of zeolite and alumina combining	Method of NiO deposition	NiO content (wt.%)
0/E	E	–	–
2/E/I	E	I	2
4/E/I	E	I	4
8/E/F + I	E	F + I	8
8/E/I	E	I	8
8/E/F	E	F	8
8/A/F	A	F	8

2.2. Catalyst characterisation

Nickel and sodium contents were determined with atomic absorption spectrometry, AAS (Perkin Elmer 1100, flame method). Acidity and acid strength distribution were evaluated by temperature-programmed desorption of ammonia (TPD_{NH_3}) in a flow system equipped with a thermal conductivity detector with argon as a carrier. The sample was pre-treated in the stream of argon at 450°C for 2 h and afterwards cooled to the temperature of 180°C. After desorption of physically adsorbed ammonia the sample was heated at a rate of 10°C/min. Acid sites were classified as weak (W), $T_{des} < 300°C$; medium (M), $300°C < T_{des} < 450°C$, and strong (S), $450°C < T_{des} < 550°C$. The amount of ammonia fixed in the catalyst surface at temperatures higher than 550°C was estimated, using the height of the peak at that temperature (mm).

Porous structure was investigated by benzene sorption at 25°C. Adsorption was measured by static techniques, using conventional Mc Bain silica spring balance of sensitivity (300 mm/g). Parameters characterising the porosity of the catalyst were calculated as described elsewhere [17].

Temperature programmed reduction (TPR) measurements were carried out in the AMI-1 catalyst characterisation system (Altamira Instruments). In

TPR measurements, mixtures of 90 vol.% Ar and 10 vol.% H_2 were used at a gas flow rate of 50 cm^3/min and a linear temperature ramp of 20°C/min. After reaching the maximum temperature, the process of reduction was continued isothermally for 1 h, and finally the catalyst was cooled in the stream of argon.

2.3. Catalyst activity

Activity tests in a through-flow high-pressure microreactor system (catalyst bed volume, 4 cm^3; grain size, 1.02–0.75 mm) were carried out with a mixture of alkanes and naphthenes (white oil, $d_{20} = 0.868\,g/cm^3$; IBP = 174°C) and hydroraffinate of light vacuum distillate LVGO ($d_{20} = 0.8657\,g/cm^3$; f.p. = +2°C; S = 0.13 wt.%; IBP = 216°C) as feedstock.

When white oil was used, the catalysts were activated with hydrogen at 320 and 340°C for 2 h. Determinations were performed at LHSV = 2 h^{-1}; H_2:CH = 500 N m^3/m^3; p = 7.0 MPa. The experiments were run in a comparable time regime, 1.5 h at 340, 360 and 380°C. The structural parameters of the products and the feed were determined by IR spectroscopy, according to the method reported in literature [18]. Carbon content in the aromatic structure (%C_A) was established at 1610 cm^{-1}, whereas that in the paraffin structure (%C_P) at 720 cm^{-1}. Making use of the determined content of the carbons fixed in the aromatic structure (%C_A), conclusions were drawn on the dehydrogenation activity of the catalyst. The yield of fractions with final boiling point below the initial boiling point of the feed (low boiling fraction — LBF), measured by the chromatographic method, and variations of the $–(CH_2)_n–$ group content in the paraffin structure of $R–(CH_2)_n–CH_3$ (650–850 cm^{-1}) type were adopted for the assessment of cracking activity.

Catalysts with activities determined by LVGO conversion were activated with hydrogen at 320°C and 5 MPa for 1 h; then they were sulphured at 300 and 320°C (the volume ratio of CS_2 to the feed being 1:80). The process was carried out under the following conditions: 300°C; LHSV = 3 h^{-1}; H_2:CH = 500 N m^3/m^3; p = 3.5 MPa. Catalyst activity assessments were based on the freezing point of the products and yield of the fraction with boiling points below the boiling point of the feed (after stabilisation).

Selectivity of the catalysts to HBH (high boiling hydrocarbons — hydrocarbons with initial boiling point above that of n-hexane) was determined under atmospheric pressure conditions, using n-hexane, in the temperature range of 300–400°C, at a molar ratio H_2:CH = 7:1 and a space velocity of 1 h^{-1}; the amount of the catalyst being 3 cm^3. Prior to determination, each catalyst was activated with hydrogen at 200 and 400°C for 2 h.

3. Results and discussion

3.1. Amount of active component

The porous structure of the catalysts with different amounts of NiO (0–8 wt.%) was characterised by a comparable pore size distribution (Table 2). The volume of micropores ranged from 0.02 to 0.04 cm^3/g and that of mesopores from 0.32 to 0.38 cm^3/g. The mean mesopore radii of the catalysts containing 4 and 8 wt.% of NiO were slightly higher than those of Catalysts 0/E and 2/E/F, amounting to 4.3 and 4 nm, respectively.

Acidity determinations showed that the amount of the hydrogenation component had little effect on acidity. Total acidity of the catalysts ranged within 0.82 mmol NH_3/g (Catalyst 2/E/I) and 0.92 mmol NH_3/g (Catalyst 4/E/I). Medium-strength acid sites were predominant in all of the catalysts tested (Fig. 1). The proportion of acid sites defined as ultra strong (S^+) was also slightly higher for Catalyst 4/E/I. Catalyst 8/E/I + F containing 8 wt.% of NiO (4 wt.% additionally incorporated at the stage of forming) displayed a lower acidity of medium (M),

Table 2
Influence of the amount of NiO on pore volume distribution

Catalyst	0/E	2/E/I	4/E/I	8/E/F + I
V_{MIK} (>1.5 nm)	0.026	0.036	0.016	0.037
V_{MEZ} (1.5–100 nm)	0.351	0.375	0.344	0.318
1.5–3 nm	0.142	0.111	0.086	0.070
3–5 nm	0.130	0.160	0.166	0.123
5–10 nm	0.042	0.042	0.057	0.079
10–33 nm	0.028	0.050	0.022	0.038
33–100 nm	0.009	0.011	0.013	0.009
r_{MEZ}	3.5	3.7	4.3	4.0

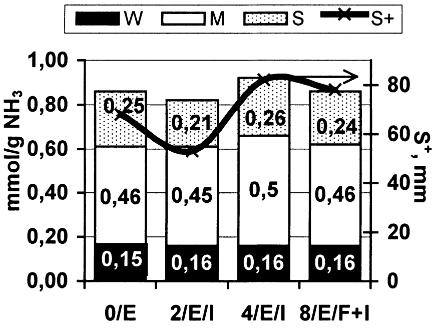

Fig. 1. Acid site strength distribution (TPD$_{NH_3}$).

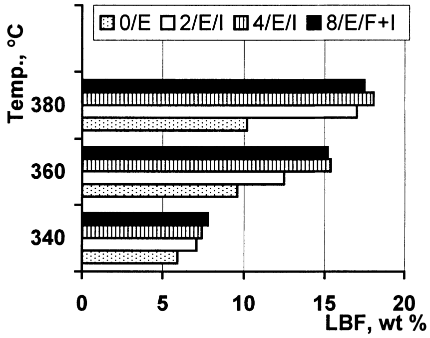

Fig. 2. LBF yields versus temperature (white oil).

strong (S) and ultra strong acid sites (S$^+$) than did Catalyst 4/E/I.

As shown in Fig. 2, over Catalyst 0/E, the LBF yield was the lowest in the entire range of temperatures, approaching 6–10 wt.%. The LBF increased when the amount of nickel oxide incorporated by impregnation was increased up to 4 wt.%. Under experimental conditions, Catalyst 8/E/F + I (loaded additionally with 4 wt.% of NiO at the stage of forming) displayed comparable or even poorer cracking properties (LBF yields) than did Catalyst 4/E/I. This finding was confirmed by the methylene group content in the paraffin chains $(CH_2)^{n\geq 6}$. The products obtained over Catalysts 8/E/F + I and 4/E/I were characterised by a comparable decrease in the $(CH_2)^{n\geq 6}$ content (about 19–23 wt.% as compared to the feed — Table 3).

When Catalyst 0/E was used, the carbon content in the paraffin structure (%C$_P$) decreased by about 25 wt.% as compared to the feed (Table 3, Fig. 3), whereas in the aromatic structure (%C$_A$) it was as high as 8.1 and 12.4% at 340–360 and 380°C, respectively.

The products obtained in the presence of Catalyst 2/E/I containing 2 wt.% of NiO were characterised by a higher %C$_P$ yield (which amounted to 5–10%) than in the presence of Catalyst 0/E. The increase of the active agent amount from 2 to 8 wt.% NiO had only a slight effect on the carbon content in the paraffin structure (Fig. 3).

The carbon content fixed in the aromatic structure strongly depended on the temperature of the reaction. When the process was carried out at 340 and 360°C, %C$_A$ in the products ranged from 8.1% for Catalyst 0/E to about 5% for Catalyst 8/E/F + I. At 380°C, %C$_A$ in the presence of Catalyst 2/E/I was higher by about 10% (as compared to Catalyst 0/E), amounting to 21.6%. To decrease the content of carbons fixed in the aromatic structure, it is necessary to increase the amount of NiO to a level higher than 4 wt.%.

Table 3
Structural parameters of an average hypothetical particle of the product

Catalyst	Temperature (°C)	%C$_A$	%C$_P$	Methylene group content in the chains (wt.%)				
				$(CH_2)_2^{n\geq 6}$	$CH_2^{n=4/5}$	$CH_2^{n=3}$	$CH_2^{n=2}$	$CH_2^{n=1}$
8/E/F + I	340	3.5	55.7	16.7	4.8	4.5	2.8	3.3
	360	5.1	54.8	13.2	6.1	5.1	3.4	4.6
	380	10.3	52.3	12.2	1.5	10.7	5.7	6.0
4/E/I	340	2.8	55.3	15.7	4.9	4.1	2.6	3.0
	360	7.2	50.3	12.2	4.1	5.8	3.3	3.6
	380	22.7	51.7	12.1	1.4	9.7	7.7	4.0
White oil	–	0.1	70.3	35.3	2.0	1.4	0.0	2.7

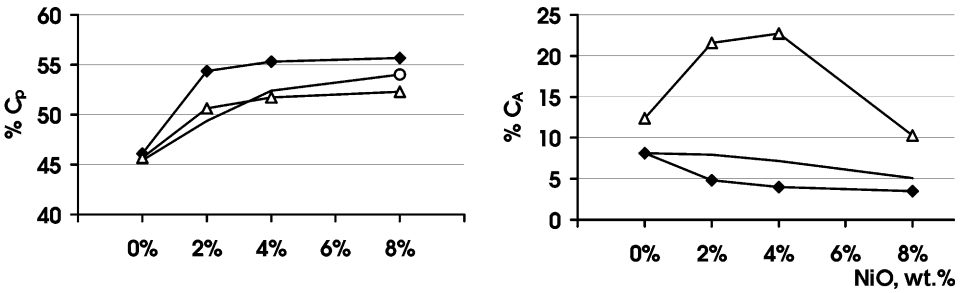

Fig. 3. Carbon content in paraffin ($\%C_P$) and aromatic structures ($\%C_A$) at (◆) 340°C, (○) 360°C and (△) 380°C.

3.2. Method of active component deposition

The method of nickel incorporation had little effect on the pore structure of the catalysts, which were characterised by a comparable pore size of up to 100 nm (about 0.29–0.30 $cm^3\,g^{-1}$) and by a comparable pore size distribution in the range of up to 1.5 nm (about 0.04–0.05 $cm^3\,g^{-1}$), 1.5–3.0 nm (about 0.1 $cm^3\,g^{-1}$), 3–5 nm (about 0.1–0.12 $cm^3\,g^{-1}$), and 5–10 nm (about 0.05–0.08 $cm^3\,g^{-1}$). The mean mesopore radius of the investigated catalysts amounted to approximately 4 nm.

As it may be inferred from TPD_{NH_3} data, the method of nickel incorporation did not affect acidity or acid site distribution. Total acidity varied from 0.86 mmol NH_3/g for Catalysts 8/E/I and 8/E/F + I to 0.90 mmol NH_3/g for Catalyst 8/E/F. Medium-strength acid sites were predominant (50% of total acidity). The proportion of acid sites defined as ultra strong (S^+), i.e., >550°C, was slightly higher for Catalyst 8/E/I.

The results of catalytic activity measurements showed that the method of nickel incorporation exerted a noticeable influence on the catalytic properties (Fig. 4). There was a rapid deactivation of Catalysts 8/E/I and 8/E/F + I compared to the rate of deactivation of Catalyst 8/E/F after 30 h of run. The freezing point of the products obtained over Catalyst 8/E/F approached −20°C even after 40 h. Over this catalyst, the mean freezing point of the samples after stabilisation was the lowest; at the same time, the mean liquid product efficiency was comparatively high (Table 4). The higher stability of the catalyst prepared by the method in which the whole amount of NiO was incorporated at the stage of forming should be attributed to the homogeneous metal dispersion in the whole bulk of the catalyst particle. But it can also

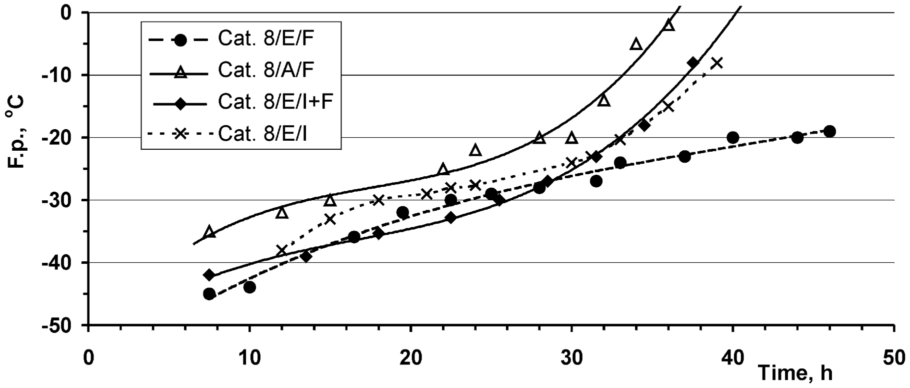

Fig. 4. Stability of catalysts (T = 300°C, LVGO).

Table 4
Characterisation of samples after stabilisation

Catalysts	Mean liquid product efficiency (wt.%)	Mean freezing point (°C)
8/E/F + I	85.5	−24
8/E/I	95.0	−23
8/E/F	95.3	−33
8/A/F	92.7	−22

be attributed to the fact that a smaller amount of the metal has deposited on the active sites of the zeolite and at the pore mouth.

3.3. *Method of zeolite and alumina combining*

In the presence of the Catalyst 8/A/F (which had been prepared by mixing zeolite and aluminium hydrogel in aqueous solution), the freezing points of the products were higher than in the presence of Catalyst 8/E/F (Table 4, Fig. 4). The methods by which zeolite and alumina were combined had only a slight effect on the acidity and porous structure of the catalyst, so this difference in activity could be attributed to another interaction between aluminium oxide and nickel.

The TPR patterns of Catalysts 8/E/F and 8/A/F showed that the method of combining zeolite and alumina influenced the susceptibility of nickel to reduction. Reduction of Catalyst 8/E/F occurred in two stages, with peak maxima at 430–450 and 790–810°C (Fig. 5). The first peak is associated with the reduction of highly dispersed NiO, and the other one with the reduction of Ni ions that reacted with the support to form non-stoichiometric Ni–Al oxides and/or Ni^{2+} located in the zeolite. Hydrogen consumption in the investigated temperature range for Catalyst 8/A/F was indicative of a much lower susceptibility to reduction, which had an influence on the catalytic properties of the metal sites.

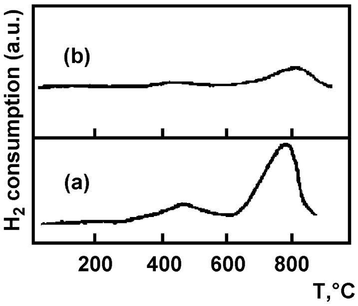

Fig. 5. TPR patterns of (a) Catalyst 8/E/F and (b) Catalyst 8/A/F.

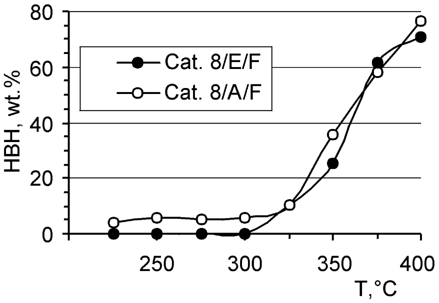

Fig. 6. Conversion of *n*-hexane and HBH yield.

The conversion of *n*-hexane over these catalysts in the temperature range 200–400°C evidences that the metal sites of Catalyst 8/E/F differ from those of Catalyst 8/A/F. Thus, in the presence of the latter, products with boiling points above that of *n*-hexane (HBH) were formed at lower temperatures than in the presence of Catalyst 8/E/F (Fig. 6).

4. Conclusions

The cracking properties of the Ni,H-ZSM-5/Al_2O_3 catalyst increased when the amount of nickel oxide incorporated by impregnation was increased up to 4 wt.% (Catalyst 4/E/I). The catalyst loaded additionally with 4 wt.% of NiO at the stage of forming (Catalyst 8/E/F + I) displayed comparable or in some instances even poorer cracking properties (LBF yields and $CH_2^{n\geq 2}$) than did Catalyst 4/E/I. The increase of the active agent amount from 2 to 8 wt.% of NiO slightly affected the carbon content in the paraffin structure. To decrease the content of carbons fixed in the aromatic structure, it is necessary to increase the amount of NiO to a value higher than 4 wt.%.

The results obtained using hydroraffinate of light vacuum distillate evidenced that the method of nickel incorporation (8 wt.% of NiO) slightly influenced the initial activity on one hand, and strongly affected the stability of the catalysts on the other hand. It was found that when the active compound was incorporated at the stage of forming, the catalyst displayed high stability

(Catalyst 8/E/F). To evaluate the stability of these catalysts under experimental conditions it is necessary to extend the duration of the process over a longer time than 30 h.

The catalyst which had been prepared by the peptisation of the mixture of zeolite and aluminium hydrogel followed by ageing in aqueous solution (Catalyst 8/A/F) displayed lower activity and stability than did the catalyst prepared via mixing peptisates of zeolite and aluminium hydroxide. The active compound, NiO, in Catalyst 8/A/F evidences a low susceptibility to reduction, which should be attributed to a different metal–support interaction.

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