CYCLOHEXYLATION OF NAPHTHALENE OVER USY ZEOLITES

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The influence of thermal stabilization of NH_4-Y zeolite and modification of USY zeolites with solutions of hydrochloric acid on the cyclohexylation of naphthalene in the liquid phase was studied. Removal of the part of extra-framework aluminium from zeolite structure has a positive effect on both conversion of naphthalene and amount of dicyclohexylnaphthalenes formed. Modification of zeolites leads to an increase in conversion and selectivity of β-substitution in the naphthalene cyclohexylation.

Key words: Alkylation; Cyclohexylation; Naphthalene; 2,6-Dialkylnaphthalenes; Zeolites; Heterogeneous catalysis.

In the recent years much attention has been devoted to the regioselective alkylation of naphthalene with the aim to prepare 2,6-dialkylnaphthalene. 2,6-Dialkylnaphthalenes are precursors for the preparation of naphthalene-2,6-dicarboxylic acid. Polyesters of this acid, such as poly(ethene naphthalene-2,6-dicarboxylate), poly(buthene-1,4-diyl-naphthalene-2,6-dicarboxylate), are raw materials for the production of polyester fibers, resins, engineering plastics and thermotropic liquid crystalline polymers[1].

The selective synthesis of 2,6-dialkylnaphthalene is not feasible using classical Friedel–Crafts catalysts, because only thermodynamic equilibrium composition of the alkyl-, dialkyl- and higher alkylated naphthalenes can be obtained[2]. It was found that zeolites are efficient catalysts for the regioselective alkylations of naphthalene to 2-alkylnaphthalene and 2,6-dialkylnaphthalene[1,3–7].

The highest β,β′-selectivity (2,6- + 2,7-isomers/Σ dialkylnaphthalenes) in the methylation of naphthalene with methanol in gaseous phase were reached over H-ZSM-5 zeolites[3] (β,β′-selectivity was 76%). The large-pore zeolites (H-mordenites and H-Y zeolites) are not suitable for regioselective methylation of naphthalene because all isomers, mono-, di- and polymethylnaphthalenes, are able to form and desorb from the zeolite channels.

For isopropylation of naphthalene to 2,6-diisopropylnaphthalene, dealuminated mordenites[8] are suitable catalysts. As alkylation agents propene[8], isopropyl bromide[7] and isopropyl alcohol[1] can be used. The best results were obtained over dealuminated H-mordenites modified by cerium (conversion of naphthalene 60% and 2,6-selectivity 70% (2,6-isomer/Σ dialkylnaphthalenes))(ref.[8]).

A crucial problem in the preparation of 2,6-dialkylnaphthalene is its separation from the reaction mixture, mainly from the 2,7-isomer. It was found, that 2,6-dicyclohexylnaphthalene can be easily separated from the reaction mixture by crystallization[9,10], which is an advantage of cyclohexylation. The critical diameters of 2,6- and 2,7-dicyclohexylnaphthalene molecules calculated by the molecular mechanics method are 0.71 nm (ref.[11]). H-Y zeolites with pore openings of 0.74 nm (ref.[14]) could be used as catalysts for the regioselective cyclohexylation of naphthalene to β-isomers. Cyclohexylation of naphthalene with cyclohexyl bromide was carried out in the liquid phase over commercial zeolite catalysts. Conversion of naphthalene, β,β′-selectivity and 2,6-selectivity were 97, 77 and 43% (refs[10,13]), respectively.

This paper is a continuation of our previous work[13], where cyclohexylation of naphthalene over commercial unmodified H-Y zeolites was studied. In this contribution, we investigated the modification of parent NH_4-Y zeolite prepared from commercial non-selective Na-Y zeolite with the main aim to increase the catalytic activity and 2,6-selectivity. The influence of thermal stabilization and extraction of extra-framework aluminium with hydrochloric acid from zeolite on catalytic properties of USY zeolites for cyclohexylation of naphthalene was also examined. The aim and results of this work are important for development and preparation of catalysts with higher regioselectivity for cyclohexylation of naphthalene from the parent commercial Na-Y zeolite. This paper tries to find relations between the structure modification of USY zeolites and their catalytic properties in cyclohexylation of naphthalene.

EXPERIMENTAL

Materials

Naphthalene (Lachema), cyclohexyl bromide (Aldrich) and decane (Fluka) were of analytical grade purity.

Catalysts

Zeolite NH_4-Y was prepared by thirteen ion-exchange treatments of the parent Na-Y zeolite (Slovnaft, Bratislava) with 2 м solution of NH_4NO_3 at 80–90 °C for five hours. Zeolite NH_4-Y (Si/Al molar ratio = 2.4, Na_2O = 0.5 wt.%) was thermally stabilized in a deep bed at a temperature of 780 (USY780), 670 (USY670) and 560 °C (USY560) for three hours, whereby the temperature increased with a gradient 4 °C/min. Ultrastable zeolites USY780 and USY670 were subsequently treated with solutions of 2 м NH_4NO_3 at 80 °C to remove residual sodium ions and mainly the cation forms of extra-framework aluminium formed by thermal stabilization (NH_4-USY780, NH_4-USY670). Zeolites, denoted as E_{1-3}, were prepared from NH_4-USY780 and NH_4-USY670 zeolites by extraction of extra-framework aluminium (EFAl) *via* acid leaching with aqueous solutions of hydrochloric acid using the method described in ref.[12]. Zeolites were calcined in the air for six hours at 500 °C before catalytic run.

Apparatus and procedure

The alkylation of naphthalene was carried out at atmospheric pressure in a 100 cm^3 thermostated glass reactor, magnetically stirred and equipped with a condenser, dropping funnel, thermometer and sampler. In a typical run, 1.3 g (10.1 mmol) of naphthalene and 20 cm^3 of solvent (decane) was added into the reactor. The freshly calcined catalyst (0.25 g) was added at the reaction temperature and then 3.3 g (20.2 mmol) of cyclohexyl bromide was dropped during one hour. The reaction was carried out at the boiling point of solvent (175 °C for decane).

Analysis

The reaction mixture after filtration of the catalyst was analyzed by gas chromatography (CHROMPACK CP 9002, FID detector, CSW) using a 15 m OV-1 capillary column (0.32 mm). The oven temperature was programmed from 60 to 275 °C with a slope of 10 °C/min and then 25 min isothermally. The relative error of determination was ±3%.

The bulk Si/Al molar ratio of samples was determined after their decomposition. The silicon and aluminium contents were determined by gravimetric and complexometric methods. The framework Si/Al ratio was determined by the XRD method described in ref.[14].

The acidity of zeolites was determined by TPD (Temperature Programmed Desorption) of ammonia. The samples were calcined in a stream of helium at 500 °C for one hour. Ammonia desorbed between 220 and 550 °C was absorbed in 0.01 м solution of sulfuric acid. The amount of desorbed ammonia was determined by titration of excess acid with 0.01 м NaOH.

The surface of zeolites was characterized by adsorption of nitrogen at the temperature of liquid nitrogen using a SORPTOMATIC 1 800 Carlo Erba instrument. The volume of micropores and surface area of mesopores were determined by the t-plot method[15].

RESULTS AND DISCUSSION

USY zeolites and H-Y zeolite prepared from the parent NH_4-Y zeolite by calcination were used as catalysts for the alkylation of naphthalene with cyclohexyl bromide. The characteristics of catalysts are given in Table I.

The specific surface area of zeolites (without H-Y zeolite) indicated, that zeolites kept their structure after extraction of EFAl by leaching with HCl solution (Table I). This fact was confirmed by the XRD method. All zeolite samples showed a good crystallinity without essential change.

The results of alkylation of naphthalene with cyclohexyl bromide over USY zeolites are given in Table II. The lowest activity for the reaction was obtained with H-Y zeolite – conversion of naphthalene (C_N) was only 21%, the reaction mixture containing mainly monocyclohexylnaphthalenes (20%) and a small amount of dicyclohexylnaphthalenes (less than 2%).

TABLE I
Characteristics of zeolites

Zeolite	Si/Al bulk	Si/Al framework	S_{BET} $m^2\ g^{-1}$	V_{micro} $cm^3\ g^{-1}$	S_{meso} $m^2\ g^{-1}$	Acid sites mmol g^{-1}	EFA1 removal %
H-Y	2.4	2.6	50	–	–	1.04	0
USY760	2.4	10.4	521	0.214	114	0.29	0
NH_4-USY760	3.0	10.4	521	0.227	114	0.43	26
USY670	2.4	9.4	557	0.227	115	0.42	0
NH_4-USY670	3.1	9.4	557	0.227	115	0.60	30.4
NH_4-USY670/E_1	5.2	11.5	643	0.286	102	0.55	66
NH_4-USY670/E_2	5.5	9.3	653	0.287	83	0.61	76.2
NH_4-USY670/E_3	4.4	10.9	627	0.284	75	0.61	61.5
USY560	2.4	7.7	583	0.241	111	0.63	0
USY560/E_1	4.5	14.1	652			0.55	47.3
USY560/E_2	3.7	8.1	677			0.78	48.8
USY560/E_3	3.7	7.6	662			0.73	54.2

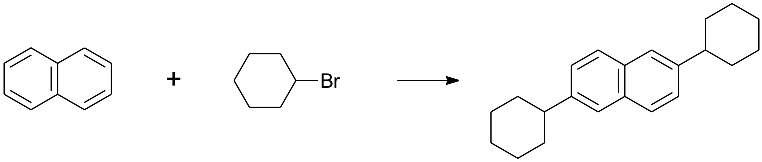
EFA1 removal, amount of extra-framework aluminium removal from total amount of extra-framework aluminium of parent USY zeolite; V_{micro}, volume of micropores; S_{meso}, surface of mesopores.

TABLE II
Cyclohexylation of naphthalene over USY zeolites

Catalysts	C_N %	Distribution of products, %							Selectivity, %		Y
		1-CN	2-CN	ΣCN	2,6-DCN	2,7-DCN	XY-DCN	ΣDCN	$S_{2,6\text{-DCN}}$	$S_{\beta,\beta'}$	
H-Y	21.3	11.2	8.7	19.9	0.4	0.3	0.7	1.4	28.6	50.0	0.07
USY760	46.1	23.9	16.3	40.2	1.7	1.5	2.7	5.9	28.8	54.2	0.15
NH_4-USY760	50.0	27.2	21.2	48.4	0.7	0.5	0.4	1.6	43.8	75.0	0.03
USY670	46.9	26.2	16.4	42.6	1.8	1.7	0.8	4.3	41.9	81.4	0.10
NH_4-USY670	88.0	44.2	8.8	53	15.1	11.7	8.2	35	43.1	76.6	0.66
NH_4-USY670/E_1	91.8	53.2	10.7	63.9	9.7	8.7	9.5	27.9	34.8	65.9	0.44
NH_4-USY670/E_2	91.4	47.9	10.3	58.2	12.0	11.5	9.7	33.2	36.1	70.8	0.57
NH_4-USY670/E_3	95.2	40.3	6.9	47.2	17.6	15.2	15.2	48	36.7	68.3	1.01
USY560	85.9	48.1	9.1	57.2	11.7	11.2	5.8	28.7	40.8	79.8	0.50
USY560/E_1	95.6	39.3	6.9	46.2	16.6	14.0	18.8	49.4	33.6	61.9	1.07
USY560/E_2	65.7	47.2	6.1	53.3	4.7	4.5	3.2	12.4	37.9	74.2	0.23
USY560/E_3	69.3	45.0	12.4	57.4	3.4	2.7	5.8	11.9	28.6	51.5	0.21

CN, conversion of naphthalene; $S_{2,6\text{-DCN}}$ = 2,6-DCN/SDCN, $S_{\beta,\beta'}$ = 2,6- + 2,7-DCN/ΣDCN; Y = ΣDCN/ΣCN; CN, cyclohexylnaphthalene; DCN, dicyclohexylnaphthalene; reaction temperature 175 °C; reaction time 120 min; molar ratio cyclohexyl bromide/naphthalene 2 : 1.

NH_4-Y zeolite is very little stable and its lattice is decomposed during activation. As a consequence, an amorphous aluminosilicate is formed, which is not active catalyst for this reaction. These results confirm the current knowledge that unstable Y zeolites are not suitable catalysts for alkylation reactions (Scheme 1).



SCHEME 1

With an increase in the temperature of NH_4-Y zeolite thermal stabilization, the activity of USY zeolites in cyclohexylation of naphthalene decreases (Table II). This fact is associated with the decrease in specific surface area, acidity of zeolites and consequently with the decrease in the number of active acid sites. The surface area of mesopores formed by thermal stabilization of NH_4-Y zeolite was practically without change. It was found that thermal stabilization of NH_4-Y zeolite leads to a removal of tetrahedral framework aluminium and formation of extra-framework aluminium[16]. A further reason for a decrease in the activity can be the formation of catalytically inactive forms of EFAl at higher temperatures of thermal stabilization. The highest conversion of naphthalene (85.9%) was obtained over USY560 zeolite compared to USY760 and USY670 zeolites (C_N was 46.1 and 46.9%, respectively).The selectivity to dicyclohexylnaphthalenes (DCN) was 28.7% for USY560 zeolite, but less than 6% for USY760 and USY670. The 2,6-selectivity was similar for USY670 and USY560 zeolites (about 41%) and was higher than for USY760 zeolite (28.8%).

Table I indicates that leaching with HCl solutions leads to the removal of aluminium. Extra-framework aluminium was preferentially removed as the framework Si/Al molar ratio changed only slightly for both samples of the catalyst (NH_4-USY670/E_{1-3} and USY560/E_{1-3}).

The activity of zeolites increases after removal of sodium cations and EFAl with a solution of NH_4NO_3. The conversion of naphthalene increases from 46 to 50% for NH_4-USY760 and from 46.9 to 88% for NH_4-USY670 zeolite. For NH_4-USY760 zeolite, the 2,6-selectivity increases from 28.8 to 43.8%, but the selectivity to dicyclohexylnaphthalenes and the desired

2,6-DCN were very low (Σ DCN was less than 2%). For NH_4-USY670 zeolite, the 2,6-selectivity changed only slightly (from 41.6 to 43.1%), but in this case the concentration of DCN and 2,6-DCN markedly increase (from 4.3 to 35% and 0.8 to 8.2%, respectively). From Table I it is evident that the surface area of mesopores does not change by the ion-exchange treatment of zeolite. The increase in the activity is associated with an increase in the number of acid sites (Table I) of these zeolites. The increase in the amount of DCN (for NH_4-USY670 zeolite) can be explained by removal of cations of EFAl, which block acid sites in USY zeolite pores for molecules of naphthalene and alkylnaphthalenes. A further cause can be an easy diffusion of alkylation products away from zeolite pores.

The dependences of naphthalene conversion (C_N) and 2,6-selectivity ($S_{2,6}$) on the conversion of naphthalene to DCN (X) for a series of zeolites NH_4-USY670/E_{1-3} and USY560/E_{1-3} are presented in Figs 1 and 2.

Table II and Figs 1 and 2 show that the 2,6-selectivity was moderately changed by the treatment of zeolites with hydrochloric acid. The dependences of overall conversion of naphthalene and conversion of naphthalene to dicyclohexylnaphthalene on the degree of removal of extra-framework aluminium are plotted in Figs 3 and 4. The overall conversion of naphthalene and conversion of naphthalene to DCN increases with the degree of removal of EFAl until a maximum is reached, and then they decrease for both

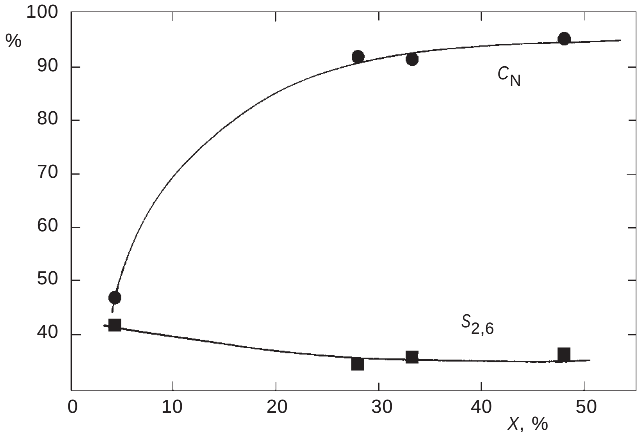


FIG. 1

Dependence of conversion of naphthalene (C_N) and 2,6-selectivity ($S_{2,6}$) on the conversion of naphthalene to DCN (X) in cyclohexylation of naphthalene with cyclohexyl bromide over a series of zeolites USY670 series of zeolites (NH_4-USY670/E_{1-3}, USY560/E_{1-3}). The maximum of conversion was reached at 60% removal of EFAl for NH_4-USY670/E_{1-3} zeolites and at 40% removal of EFAl for USY560/E_{1-3} zeolites. Similar results are shown

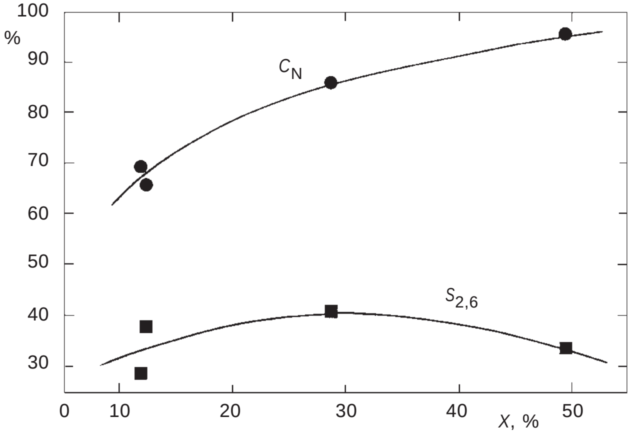


FIG. 2

Dependence of conversion of naphthalene (C_N) and 2,6-selectivity ($S_{2,6}$) on the conversion of naphthalene to DCN (X) in cyclohexylation of naphthalene with cyclohexyl bromide over a series of zeolites USY560

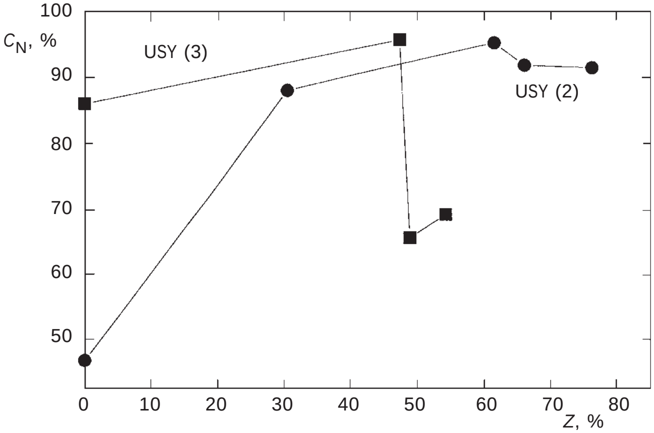


FIG. 3

Dependence of conversion of naphthalene (C_N) on the degree of removal of extra-framework aluminium (Z) from zeolite in Fig. 5. The maximum ratio Y = Σ DCN/Σ CN) was attained at 60% removal of EFAl (NH_4-USY670/E_{1-3}) and 40% removal of EFAl (USY560/E_{1-3}).

The increase in the activity of these zeolites is probably associated with a free access of reactant molecules to acid sites in zeolite structure and easy

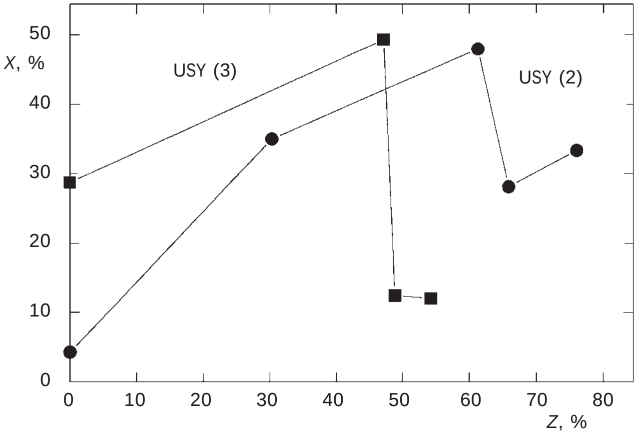


FIG. 4
Dependence of conversion of naphthalene to DCN (*X*) on the degree of removal of extra-framework aluminium (*Z*) from zeolite

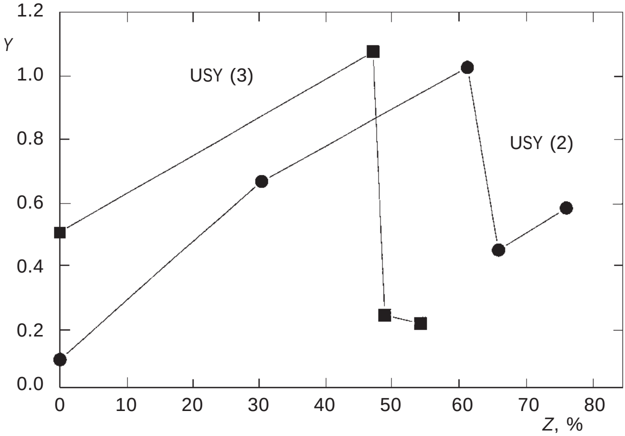


FIG. 5
Dependence of the DCN/CN (*Y*) ratio in the reaction mixture on the degree of removal of extra-framework aluminium from zeolite

desorption of products, in particular of bulky dicyclohexylnaphthalenes, from zeolite pores after removal of EFAl. This fact is confirmed by an increase in the specific surface area for both series of zeolites and by an increase in the micropore volume (NH_4-USY670/E_{1-3}) with the increase in the degree of removal of EFAl (Table I). From Figs 3–5, a decrease in the activity of zeolites at higher degrees of removal of EFAl is evident. However, XRD measurements showed a good crystallinity for all modified zeolites and confirmed the fact that a rapid decrease in activity is not a result of destroying the zeolite structure. The decrease in activity of zeolites could be explained by removal of catalytically active EFAl from zeolite. However, it is difficult to determine catalytically active and inactive forms of EFAl formed in thermal stabilization of NH_4-Y zeolites.

CONCLUSIONS

Ultrastable Y zeolites are suitable catalysts for selective cyclohexylation of naphthalene to 2,6-dicyclohexylnaphthalene. For this reaction, thermal stabilization of zeolite at a temperature lower 700 °C was found to be suitable. An increase in the activity and partly in the 2,6-selectivity can be reached by the removal of residues of sodium ions and cation forms of extra-framework aluminium. This extra-framework aluminium was preferentially removed from zeolite by treatment with hydrochloric acid. The removal of a portion of EFAl leads to a higher formation of dicyclohexylnaphthalene and the required 2,6-DCN. This fact is probably associated with a better access of molecules to acid sites in zeolite pores and easy desorption of products. The removal of a higher amount of EFAl decreases the activity of zeolites in this reaction. This fact is probably caused by the removal of catalytically active EFAl. At that, the 2,6-selectivity practically does not change.

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