Isopropylation of Naphthalene over Dealuminated H-Mordenites

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The effect of dealumination on catalytic properties of H-mordenites and modification of dealuminated H-mordenites by impregnation with 10 mass % of cerium was studied for isopropylation of naphthalene with propylene in a tubular reactor at a temperature of 220 °C and at atmospheric pressure. Dealumination of mordenites ($n(SiO_2)/n(Al_2O_3) = 14$—67) increases the 2,6-selectivity and β,β'-selectivity from 45 % to 69 % and from 92 % to 100 %, respectively. The deactivation of external acid sites of dealuminated H-mordenites by cerium impregnation (10 mass % of cerium) led to an increase in the 2,6-selectivity to 75.5 %. The β,β'-selectivity was 100 % for all cerium-modified zeolites tested.

2,6-Dialkylnaphthalenes are raw materials for the production of 2,6-naphthalenedicarboxylic acid, which is an intermediate product for polyesters with special properties (plastics, fibres) and for the preparation of thermotropic liquid crystal polymers [1—4].

In the last years a great attention has been devoted to the alkylation of naphthalene to 2,6-dialkylnaphthalene. Over classical acid catalysts, however, only equilibrium composition can be obtained [2].

Because of requirement of highly selective 2,6-dialkylnaphthalene formation the alkylation of naphthalene could be effective over shape-selective zeolite catalysts only. Such zeolites have been intensively investigated for alkylation of polyaromatic hydrocarbons, mainly for naphthalene and biphenyl [5].

The highest β,β'-selectivity (76 %) for methylation of naphthalene was reached over H-ZSM-5 zeolite [2]. Wide-porous zeolites are not suitable for this reaction. For isopropylation of naphthalene to 2,6-diisopropylnaphthalene dealuminated mordenites have been used [3]. As alkylation agent of naphthalene, propylene [3, 4], isopropyl bromide [5] or isopropyl alcohol [6, 7] can be used.

The alkylation of naphthalene with propylene in an autoclave reactor was mainly studied in the liquid phase. In this connection, the influence of the type and modification of zeolite and of reaction conditions was investigated. The best results were obtained over dealuminated H-mordenites where the conversion of naphthalene was 80 % and the 2,6-selectivity 65—70 % [4]. Over dealuminated H-mordenites modified by cerium the conversion was 60 % and the 2,6-selectivity

70 % [8], but under a higher propylene pressure in the autoclave.

Japanese authors [8] studied the selectivity of isopropylation of naphthalene over H-mordenite ($n(SiO_2)/n(Al_2O_3)$ ratio = 128) modified with max. 50 mass % of cerium. The alkylation proceeded in the liquid phase at a temperature of 250 °C and at a pressure of 0.8 MPa (autoclave-reactor). The highest 2,6-selectivity (70 %) was obtained over mordenite catalyst modified with $\geq$ 30 mass % of cerium. A further increase in cerium concentration on mordenite had no influence on the 2,6-selectivity of the alkylation reaction.

The addition of a small amount of water to the reaction mixture has a positive effect on both 2,6- and β,β'-selectivities, but is negative for the conversion of naphthalene [9]. The effect of water is linked with the conversion of a part of Lewis centres to Brönstedt centres and with partial deactivation of acid sites on the surface of zeolite. The hindrance of external surface for nonselective alkylation can be reached by silanization [5] or by impregnation with suitable metal cations.

Zeolite catalysts were also used for cyclohexylation of naphthalene by cyclohexyl bromide and cyclohexene [10, 11]. Cyclohexylation of naphthalene has advantage of easier separation of the desired 2,6-isomer from the reaction mixture [11].

A very high 2,6-selectivity (84 %) was obtained in *tert*-butylation of naphthalene over HY zeolites in the liquid phase at 160 °C. At a 52 % conversion of naphthalene, the β,β'-selectivity was 98 % and the $n(2,6\text{-DTBN})/n(2,7\text{-DTBN})$ ratio was 5.9. The next increase in the reaction temperature causes a dramatic

Table 1. Characteristics of Zeolite Catalysts

| Zeolite | $n(SiO_2)/n(Al_2O_3)$ | S_{BET} | | Acidity (acid sites) | |
| | | $m^2\ g^{-1}$ | | $mmol\ g^{-1}$ | |
		HM	HM + 10 % Ce	HM	HM + 10 % Ce
HM(0)	14	478	455	1.214	0.672
HM(1)	16	485	461	0.961	0.738
HM(2)	27	503	479	0.625	0.897
HM(3)	32	514	489	0.515	0.438
HM(4)	43	530	505	0.460	0.275
HM(5)	67	557	518	0.308	0.171

HM(0) = Zeolon 100H (Norton, USA). The relative error for determination of S_{BET} is equal to ± 3 %. The relative error for determination of acidity is equal to ± 5 %.

decrease in the 2,6-selectivity [12].

In this work, the influence of dealumination of H-mordenite and modification of dealuminated mordenites with cerium was investigated for isopropylation of naphthalene in the gas phase at atmospheric pressure in a laboratory tubular reactor.

EXPERIMENTAL

Materials

Naphthalene and cyclohexane were of anal. grade purity. Propylene with purity of 99.9 % was purchased from Slovnaft, Bratislava. The basic mordenite Zeolon 100 H was from Norton, USA. A series of dealuminated zeolites (Table 1) was prepared by dealumination of the basic zeolite gradually with 0.2 M-, 0.5 M-, 1 M-, 2 M- and 5 M-HCl under reflux for 6 h.

After drying at 110 °C in vacuum, the zeolites were calcined at 500 °C for 6 h. Samples of these zeolites were impregnated with an ethanolic solution of cerium nitrate to obtain 10 mass % of cerium in zeolites after drying and calcination at 500 °C. The surface area of catalysts was determined by the BET method, and the acidity of catalysts by the Temperature Programme Desorption of Ammonia (TPDA) method.

Apparatus and Procedure

Alkylation of naphthalene with propylene was carried out in a tubular reactor. The alkylation reactions were carried out at 220 °C, atmospheric pressure, and Weight Hour Space Velocity (WHSV) equal to 0.468 h^{-1} The catalysts were prepared by crashing zeolite tablets and by sieving to particles diameter 0.6—1 mm. Before using, the catalysts were activated in the reactor in a flow of nitrogen at a temperature of 400 °C for 15 h. The isopropylation reactions at given temperature and WHSV of propylene were carried out with propylene in the ratio n(naphthalene) n(cyclohexane) n(propylene) = 1 10 2. Samples of the reaction mixture were analyzed by gas chromatography.

Analysis

The composition of the reaction mixture was determined by GC using a 25 m capillary column OV-1. The oven temperature was programmed from 60 to 275 °C with a temperature increase of 7.5 °C min^{-1} and then 22 min isothermally. The relative error of the analysis was ± 3 %.

RESULTS AND DISCUSSION

Results of testing of dealuminated mordenites HM(0)—HM(5) after 1 and 5 h of alkylation are summarized in Table 2. The highest conversion of naphthalene was always obtained after 1 h of reaction and then it gradually decreased as a consequence of catalyst deactivation. The 2,6-selectivity (n(2,6-DIPN)/Σn(DIPN)) increased with time on stream (not for the basic zeolite catalyst HM(0)) and also with dealumination of the basic zeolite catalyst. At given reaction conditions, the 2,6-selectivity and the β,β'-selectivity increased from 45 to 69 % and from 92 to 100 %, respectively. Dealumination of basic mordenite zeolite influenced also the ratio n(2,6-DIPN)/n(2,7-DIPN) which changed from 1.0 to 2.4 for the basic zeolite, which is in good agreement with the published results for the liquid phase [3, 4].

The selectivity of this reaction increases with dealumination of mordenite zeolites as a consequence of the acidity decrease. The formation of coke with time of reaction probably influences the openings and free diameter of pores and blocks the outer surface of zeolites. This phenomenon has the main influence on the selectivity of the mentioned alkylation reaction. Formation of other isomers of DIPN (XY-DIPN) is suppressed and gradually decreases with dealumination of zeolite as a consequence of the above given changes, mainly on the zeolite surface.

The modification of dealuminated mordenite zeolites by cerium impregnation had a positive effect on 2,6- and β,β'-selectivities. From the results given in Table 3 it is evident that modification of dealuminated

Table 2. Isopropylation of Naphthalene over Dealuminated H-Mordenites

Zeolite	Time/h	C_N	Distribution of product/%			Distribution of DIPN/%			Selectivity/%		n(2,6-DIPN)
		%	ΣMIPN	ΣDIPN	ΣPIPN	2,7-DIPN	2,6-DIPN	XY-DIPN	$S_{2,6\text{-DIPN}}$	β,β'-sel	n(2,7-DIPN)
HM(0)	1	69.8	38	27.6	4.1	12.5	12.9	2.2	46.7	92	1.0
	5	19.1	10.9	6.0	2.2	2.4	2.7	0.9	45	85	1.1
HM(1)	1	59.2	32.2	21.7	5.3	9.1	10.5	2.1	48.4	90.3	1.2
	5	24.1	11.8	10.3	2.0	3.7	5.9	0.7	57.3	93.2	1.6
HM(2)	1	54.1	24.5	24.9	4.7	9.2	13.7	2.0	55	91.9	1.5
	5	33.2	17.1	14.8	1.3	5.4	8.6	0.7	58.5	95.2	1.6
HM(3)	1	53.3	22.5	27.5	3.3	9.2	16.6	1.7	60.3	93.8	1.8
	5	35.5	17.9	15.7	1.9	5.4	9.6	0.7	61.1	95.5	1.8
HM(4)	1	51.8	30.3	18.8	2.7	5.9	11.9	1.0	63.3	94.7	2.0
	5	20.1	12.1	8.0	–	2.5	5.5	–	69	100	2.2
HM(5)	1	14.1	10.8	2.6	0.6	0.7	1.7	0.2	65.4	92.3	2.4
	5	2.0	1.4	0.3	0.3	0.1	0.2		67	100	2.0

C_N – conversion of naphthalene, $S_{2,6\text{-DIPN}} = n(2,6\text{-DIPN})/\Sigma n(\text{DIPN})$, β,β'-selectivity $= (n(2,6\text{-DIPN}) + n(2,7\text{-DIPN}))/\Sigma n(\text{DIPN})$, MIPN – monoisopropylnaphthalenes, DIPN – diisopropylnaphthalenes, PIPN – polyisopropylnaphthalenes. The relative error is equal to $\pm$ 3 %.

Table 3. Isopropylation of Naphthalene over Dealuminated H-Mordenites Modified with 10 mass % of Cerium

Zeolite + 10 % Ce	Time/h	C_N	Distribution of product/%			Distribution of DIPN/%		$S_{2,6\text{-DIPN}}$	n(2,6-DIPN)
		%	ΣMIPN	ΣDIPN	ΣPIPN	2,7-DIPN	2,6-DIPN	%	n(2,7-DIPN)
HM(0)	1	15.8	8.6	5	2.2	1.8	3.2	64	1.8
	5	9.7	5.6	4.1	–	1.5	2.6	63.4	1.7
HM(1)	1	19.4	9.3	8	2.1	2.7	5.3	66.2	2.0
	5	7.3	4.2	3	–	1.0	2.0	66.7	2.0
HM(2)	1	27.9	12.1	15.8	–	5.3	10.5	66.5	2.0
	5	12.3	6.2	6.1	–	1.9	4.2	68.9	2.2
HM(3)	1	37.1	17.9	19.2	–	6.1	13.1	68.2	2.1
	5	12.9	6.8	6.1	–	1.8	4.3	70.5	2.4
HM(4)	1	34.7	15.7	18.9	–	6.0	12.9	68.2	2.2
	5	14.1	8.8	5.3		1.3	4.0	75.5	3.1
HM(5)	1	3.3	2.7	0.4		0.1	0.3	75	3.0
	5	4.8	3.7	0.8	0.2	0.2	0.6	75	3.0

β,β'-selectivity $= 100$ % for all experiments. The relative error is equal to $\pm$ 3 %.

mordenites with 10 mass % of cerium enhances the 2,6-selectivity max. to 75.5 % and β,β'-selectivity to 100 % for all tested cerium-doped mordenite zeolites.

The practical absence of other DIPN isomers over cerium-modified mordenites is not surprising since these isomers are formed probably on the outer surface of zeolite and in the case of modified zeolites its surface is very probably covered by cerium. However, cerium partly covers also the entrance openings of windows of zeolite pores, which has a positive influence on both 2,6- and β,β'-selectivities, because of different diffusivities of 2,6-DIPN and of other isomers out through the openings of zeolites.

The dependence of 2,6-selectivity and β,β'-selectivity on the degree of dealumination of zeolites and modification of these zeolites with cerium is presented in Fig. 1. The selectivity of both unmodified and modified zeolites increases significantly with the $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ ratio to the value 45, and then only moderately.
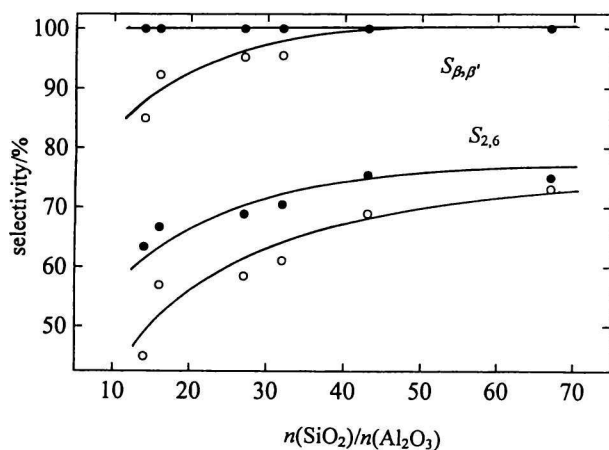

Fig. 1. Dependence of selectivities of 2,6-DIPN and β,β'-isomers on $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ ratio after 5 h of reaction. ○ HM, ● HM(Ce).

The 2,6-selectivity for cerium-modified mordenites increased to 75 % for the most dealuminated zeolites HM(4) and HM(5). The dependence of the β,β'-selectivity on $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ ratio for unmodified H-mordenites reached 100 % for the most dealuminated zeolites.

The impregnation of dealuminated H-mordenites with cerium probably leads to the covering of outer surface of zeolites and partial covering of openings of the zeolite pores. This is a very effective method how to increase the desired 2,6-selectivity of naphthalene isopropylation.

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