Cyclohexylation of naphthalene over unmodified HY zeolites

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Cyclohexylation of naphthalene was studied over four commercial unmodified HY zeolites. Approximately equal results were obtained on HY (ZF 515, ZF 520, CBV 720) zeolites. The best results were obtained with cyclohexylbromide as alkylating agent in *n*-nonane and in *n*-decane as solvents at boiling point. Conversion of naphthalene was max. 97%, 2,6-selectivity 43% and β,β'-selectivity 77%.

Keywords: alkylation; cyclohexylation; naphthalene; cyclohexylnaphthalenes; zeolites

1. Introduction

2,6-dialkylnaphthalenes are starting materials for 2,6-naphthalene dicarboxylic acid, which is an intermediate product for polyesters with special qualities (plastics, fibres) and for preparation of thermotropic liquid crystal polymers. Because of thermodynamic constraints [1], the selective production of 2,6-dialkylnaphthalene is not possible on classical acid catalysts.

Zeolites with high para-selective properties have been recently studied for the alkylation of polynuclear aromatics, especially naphthalene [2–9]. The alkylation of naphthalene with methanol over various zeolites has been first reported [2,3]; a high β-selectivity is observed with ZSM-5 zeolites, but not with large-pore mordenites and faujasite type zeolites. Such a β-selectivity is found over the latter catalysts in the case of the isopropylation of naphthalene with propene [4–6], isopropyl bromide [7] and, more recently, isopropanol [8,9]. A good selectivity for the formation of 2-isopropylnaphthalene and 2,6- and 2,7-diisopropylnaphthalenes is obtained, but the selective formation of the 2,6-isomer is not possible in any case. Moreover, the isolation of this compound from the reaction mixture and mainly its separation from its 2,7-isomer are very difficult. In a previous work [10,11], we found that 2,6-dicyclohexylnaphthalene could be easily separated from the alkylation mixture by crystallization, in the liquid phase cyclohexylation reaction of naphthalene over HY zeolites.

This paper deals with extended studies of such a cyclohexylation reaction over various dealuminated HY zeolites; in particular, we report on the influence of different reaction parameters, like solvent, temperature as well as type and mode of addition of the cyclohexylating agent.

2. Experimental

Materials. Naphthalene, cyclohexylbromide and cyclohexene were analytical grade purity (Aldrich Chemicals), *n*-alkanes C_8–C_{11} were dried and then purified by distillation. The catalysts, HY zeolites ZF 515 and ZF 520 were from Zeocat, Montoir de Bretagne (France), CBV 720 and CBV 760 from PQ Zeolites (The Netherlands). Zeolites were calcined in air 6 h at 400°C with linear temperature programme 50°C h^{-1}. Typical data of the zeolite catalysts are listed in table 1.

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 cooler, dropping funnel, thermometer and sampler. In a typical run, 1.3 g (10.1 mmol) of naphthalene and 25 cm^3 of solvent (*n*-alkane C_8–C_{11}) were placed into the reactor. The freshly calcined catalyst (0.25 g) was added at the desired temperature and then 3.3 g (20.2 mmol) of cyclohexylbromide or 1.65 g (20.1 mmol) of cyclohexene was added at once or drop by drop during different times. The reaction mixture was stirred at the reaction temperature and the alkylation was controlled by gas-chromatography.

Analysis. Samples of the reaction mixture were withdrawn from the reactor at various times (from 0.5 to 6 h) and after cooling and filtration of the catalyst they were analyzed by gas-chromatography using a 15 m OV-1 capillary column. The oven temperature was pro-

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Table 1
Characteristics of zeolite catalysts

Zeolite HY	Si / Al overall	Si / Al framework	Na_2O (wt%)	a_0 (nm)	Porosity ($cm^3\ g^{-1}$) micro- (t-plot)	Porosity ($cm^3\ g^{-1}$) meso- (BJH)	S_{BET} ($m^2\ g^{-1}$)
ZF 515	15	15	0.1	2.431	0.269	0.243	762
ZF 520	20	20	0.1	2.428	0.277	0.263	780
CBV 720	13	19	0.04	2.431	0.249	0.230	736
CBV 760	30	48	0.01	2.424	0.217	0.234	675

grammed from 60 to 275°C with a slope of 12°C/min and then 20 min isothermal conditions were applied.

3. Results and discussion

Cyclohexylation of naphthalene described in this paper is a continuation of our previous work [7], but under different experimental conditions. Originally, cyclohexylation was performed in an autoclave under autogenous pressure at the temperature of 200°C and in cyclohexane as solvent.

In this work, cyclohexylation was studied in an open reactor, n-alkanes (C_8–C_{11}) were used as solvents and reaction was carried out under reflux of the reaction mixture. The influence of the nature of zeolites, solvents, reaction temperature and the mode of addition of alkylating agent has been investigated.

3.1. The nature of zeolites

The catalytic activity of four dealuminated zeolites was studied in the alkylation reaction of naphthalene with cyclohexylbromide. The alkylation proceeded under reflux in n-decane as the solvent (175°C). The results obtained are summarized in table 2.

Similar conversions of naphthalene were obtained over the HY zeolites ZF 515, ZF 520 and CBV 720, with which the reaction is nearly quantitative after 2 h. The ratio of 1-CN (CN = cyclohexylnaphthalene) against the 2-CN was 8 over ZF 515, and 4 over the two other zeolites. In all cases, all ten DCN (dicyclohexylnaphthalene) isomers were detected, but 2,6- and 2,7-DCN are the main dicyclohexyl derivates to be formed. The zeolite ZF 515 leads to the highest β,β'-selectivities (43% in 2,6- and 77% in 2,6- + 2,7-), but the highest yield of 2,6-DCN is reached over CBV 720 and ZF 520 (23 and 22% respectively).

In the previous paper [11], the alkylation of naphthalene was carried out over ZF 520, but in an autoclave, at 200°C under autogenous pressure; under these conditions, using cyclohexyl bromide as alkylating agent, conversion of naphthalene was 94% after 10 min reaction only, and the selectivities were respectively 43% in 2,6- and 79% in 2,6- + 2,7- (β,β'-selectivity) (table 2, run 5). The ratio of 1-CN against 2-CN was 12 at this reaction time, which is a relatively high value compared to 4, obtained with the same zeolite in the present work. This result can be explained by the gradual isomerization of the kinetic product, 1-CN, with time.

Dealuminated HY zeolite CBV 760 with the highest Si / Al ratio (table 1) was less active. After 2 h of reaction, the conversion of naphthalene was only 50% and the main alkylation product was MCN (monocyclohexylnaphthalene) with the ratio of 1-CN/2-CN = 1.2. The 2,6-selectivity was only 18% and β,β'-selectivity 35%. These low shape-selectivities depend probably on the lower microporosity of this zeolite in comparison with the previous types. This can be connected also with a higher content of nonframework Al in CBV 760 zeolite

Table 2
The comparison of catalytical activity of zeolite catalysts [a]

Catalyst	Time (min)	Conv. N (%)	Distribution of products (%) 1-CN	2-CN	2,6-DCN	2,7-DCN	XY-DCN	Selectivity (%) 1-CN/ 2CN	2-CN/ MCN	2,6-DCN/ DCN	2,6+2,7-DCN/ DCN
HY (ZF 515)	120	97	62	8	13	10	7	8	12	43	77
HY (ZF 520)	120	97	34	9	22	18	17	4	21	39	70
HY (ZF 520) [7] run 5 [b]	10	94	49	4	20	16	10	12	8	43	79
HY (CBV 720)	120	93	33	8	23	20	16	4	20	39	73
HY (CBV 760)	120	50	49	40	2	1.8	7	1.2	45	18	35

[a] CN – cyclohexylnaphthalene, MCN – monocyclohexylnaphthalenes, DCN – dicyclohexylnaphthalenes, N – naphthalene, T = 175°C, mol. ratio cyclohexylbromide/naphthalene = 2 : 1, solvent n-decane, addition of cyclohexylbromide was drop by drop 1 h into the reaction mixture.
[b] Cyclohexylation of naphthalene with cyclohexylbromide in an autoclave at the temperature of 200°C and cyclohexane as a solvent was used. (1% TCN in the product).

Table 3
The influence of reaction temperature on alkylation of naphthalene by cyclohexylbromide [a]

T (°C)	Solvent	Time (min)	Conv. N (%)	Distribution of products (%)					Selectivity (%)			
				1-CN	2-CN	2,6-DCN	2,7-DCN	XY-DCN	1-CN/ 2-CN	2-CN/ MCN	2,6-DCN/ DCN	2,6+2,7-DCN/ DCN
125	*n*-C_8	120	67	57	32	4	3	4	2	36	36	64
150	*n*-C_9	120	97	59	9	13	11	8	7	13	41	75
150	*n*-C_{10}	120	40	69	26	2	1	2	3	27	40	60
175	*n*-C_{10}	120	93	33	8	23	20	16	4	20	39	73
196	*n*-C_{11}	120	94	32	8	22	17	21	4	20	37	65

[a] Zeolite HY CBV 720, mol. ratio cyclohexylbromide/naphthalene = 2 : 1, addition of cyclohexylbromide was drop by drop during 1 h.

(table 1). The lower catalytic activity of this zeolite (table 2) in comparison with the previous types might be caused by lower acidity and by rapid deactivation of this catalyst.

3.2. *The influence of solvent and temperature*

The influence of the reaction temperature on the alkylation process was studied in the temperature range 125–196 °C (table 3). The preliminary experiments in different solvents, e.g. chlorobenzene, decaline and *n*-alkanes, have shown that *n*-alkanes C_9–C_{11} have suitable characteristics for the studied reaction in the open system and cyclohexane was suitable under autoclave conditions. The best results of alkylation were obtained at the boiling points of these solvents. This effect is evident from the results at 150°C in *n*-nonane (under reflux) and in *n*-decane. Thus, the conversion of naphthalene under reflux in *n*-nonane was 97% after 2 h; however, in *n*-decane at the same temperature only 40%. This is valid also at the other temperatures. This effect is probably connected with the influence of external diffusion.

The best results were obtained at the temperatures 150 and 175°C under the reflux. At the temperature 196°C 2,6- and β,β'-selectivities were lower (higher production of XY-DCN).

3.3. *The influence of the mode of addition of alkylating agent*

The cyclohexylation of naphthalene depends also on the manner of adding the alkylating agent into the reaction mixture. From the results summarized in table 4 it is evident that better results were obtained when cyclohexylbromide was added continuously (drop by drop). The great excess of the alkylating agent in the reaction mixture at the beginning of the reaction (addition at once) leads to a rapid deactivation of the catalysts. The conversion of naphthalene after 1 h was 57% and after 2 h 60% and then it remained constant. For this reaction the system is optimal for a continuous addition of cyclohexylbromide (drop by drop) during 0.5–1 h. This rate of addition of cyclohexylbromide to the reaction mixture is convenient for its immediate alkylation reaction.

3.4. *The influence of the alkylating agent*

Alkylation of naphthalene with cheaper and noncorrosive cyclohexene under the studied reaction conditions produces 2,6-DCN isomer in a very low yield (table 5). It is connected with dimerization of cyclohexene and deactivation of the zeolite catalysts. It indicates the lower naphthalene conversion, lower formation of 2,6- and 2,7-DCN isomers and selectivity of reaction.

4. Conclusions

The dealuminated HY zeolites ZF 515, 520 and CBV 720 are very active catalysts for cyclohexylation of naphthalene. Conversion of naphthalene and β,β'-

Table 4
The influence of addition of alkylating agent to the reaction mixture [a]

Addition of alkyl. agent	Time (min)	Conv. N (%)	Distribution of products (%)					Selectivity (%)			
			1-CN	2-CN	2,6-DCN	2,7-DCN	XY-DCN	1-CN/ 2-CN	2-CN/ MCN	2,6-DCN/ DCN	2,6+2,7-DCN/ DCN
at once	120	60	57	28	6	5	4	2	33	40	73
drop by drop											
0.5 h	120	97	49	7	18	14	12	7	13	41	73
1 h	120	93	33	8	23	20	16	4	20	39	73
2 h	120	79	70	10	8	6	6	7	13	40	70

[a] Catalyst HY CBV 720, mol. ratio cyclohexylbromide/naphthalene = 2 : 1, *T* = 175°C (*n*-decane).

Table 5
The influence of alkylating agent on cyclohexylation of naphthalene [a]

Alkyl. agent	Time (min)	Conv. N (%)	Distribution of products (%)					Selectivity (%)			
			1-CN	2-CN	2,6-DCN	2,7-DCN	XY-DCN	1-CN/ 2-CN	2-CN/ MCN	2,6-DCN/ DCN	2,6+2,7-DCN/ DCN
CHBr	30	80	50	11	15	14	10	5	17	38	74
	60	89	32	10	22	20	16	3	24	38	73
	120	93	33	8	23	20	16	4	20	39	73
CH	30	80	48	22	10	9	11	2	32	33	63
	60	83	41	24	10	9	16	2	37	28	54
	240	84	42	23	10	8	17	2	35	29	51

[a] CHBr – cyclohexylbromide, CH – cyclohexene, catalyst HY CBV 720, mol. ratio CHBr/N = 2 : 1, T = 175°C (*n*-decane), addition of alkylating agent was drop by drop during 1 h.

selectivity reach 97% and max. 77% respectively. The 2,6-selectivity is max. 43%. Such catalytic properties are connected with the high acidity of these zeolites and with the relative spacious channel system for the studied reaction.

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