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# Comparison of the catalytic performance of the metal substituted cage type mesoporous silica catalysts in the alkylation of naphthalene

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#### ABSTRACT

Alkylation of naphthalene with propylene to diisopropylnaphthalenes (DIPN) for the use as a highquality solvent was carried out over mesoporous AlSBA-1, GaSBA-1 and FeSBA-1 catalysts. The AlSBA-1 and GaSBA-1 catalysts were very active in alkylation while the FeSBA-1 samples, although initially active, deactivated quickly. Activity of the SBA-1 catalysts increased with the amount of Al, Ga or Fe incorporation into the silica framework. Regardless of the alkylation activity, all SBA-1 catalysts showed rather low isomerization activity and as a result low 2,6-DIPN selectivity was observed. The AlSBA-1 and GaSBA-1 catalysts proved to be promising for DIPN solvent synthesis due to their high alkylation activity and stability together with low 2,6-DIPN selectivity.

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### 1. Introduction

Diisopropylnaphthalene (DIPN) isomeric mixture is used as a high-quality solvent for copying materials and in many other applications [1–3]. In Europe the DIPN solvent is produced by Ruetgers Kureha Solvents GmbH (Duisburg, Germany) and is known under the commercial name "Ruetasolv DI". It consists of DIPN isomeric mixture (more than 98%), however, to guarantee liquid state of the solvent at low temperature, content of DIPN isomers with high solidification point, such as 2,6-DIPN (m.p. 68.5 °C [1]) should be limited.

On the other hand, the 2,6-DIPN isolated from the isomeric mixture can be used as a raw material for the production of advanced polymers. DIPN product is generally prepared by the alkylation of naphthalene or isopropylnaphthalene (IPN) with propylene or other alkylating agents using acidic catalysts. However, depending on DIPN product destination, alkylation process may require the catalysts with completely opposite properties.

Pore size of wide-pore zeolites is in the range between the critical diameter of slim  $\beta$ , $\beta$ -DIPN (2,6- and 2,7-DIPN) isomers and that of bulky  $\alpha$ , $\beta$ -DIPN (1,3-, 1,6- and 1,7-DIPN) and  $\alpha$ , $\alpha$ -isomers (1,4- and 1,5-DIPN). Therefore, DIPN isomers can be differentiated

by the wide-pore zeolites and shape selectivity in the naphthalene alkylation is expected leading to a high  $\beta$ , $\beta$ -selectivity. Among the wide-pore zeolites, high silica mordenite was found to be the best candidate for the synthesis of 2,6-DIPN selectively [4–13]. Owing to its optimal pore size and favourable one-dimensional (1D) pore system, mordenite catalysts promoted a 2,6-DIPN selectivity as high as 70% and the 2,6-DIPN/2,7-DIPN ratio in the range of 2–3 [7–9]. Additional enhancement in shape selectivity of mordenites was achieved by deactivation of the external surface of zeolite crystals [10,11]. A high 2,6-DIPN selectivity and a high ratio of 2,6-DIPN/2,7-DIPN were also reported for disproportionation of IPN over mordenite [14].

It is also possible to obtain DIPN products rich in isomers other than the 2,6-DIPN by selecting the proper catalyst and reaction conditions. For instance, Sugi at al. [13] have recently reported a significantly higher 2,7-DIPN selectivity than that of 2,6-DIPN over CIT-5 catalyst in the alkylation of naphthalene. A high 2,7-DIPN selectivity (up to 67%) was also observed in disproportionation of IPN over HY and H-beta zeolites [14]. It has also been reported that a high yield of DIPN isomers with both alkyl substituents attached to one naphthalene ring, i.e. 1,3-DIPN and 1,4-DIPN can be obtained over zeolite catalysts under the optimized reaction conditions favouring the pore mouth selectivity [15]. For example, alkylation of naphthalene with propylene over the zeolite Y modified with calcium and rare earth metals at 200 °C gave DIPN product containing 44% 1,4-DIPN and 12% 1,3-DIPN.

The synthesis of DIPN mixture for use as a high-quality solvent requires active and stable catalysts but producing a DIPN mixture

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poor in 2,6-isomer, the compound disadvantageous due to its high melting point. Mesoporous materials are the adequate catalysts for this purpose, owing to their ordered structure, wide pores and mild acidity [16]. Even bulky substrates and products can easily diffuse inside the pores. Also bulky precursors of carbonaceous deposits can be easily removed from the pores by a liquid product stream.

A high and durable activity of Al–MCM-41 catalysts in alkylation of 2-IPN and naphthalene with isopropanol has been reported [17– 19]. MCM-41 possesses linear arrays of 1D mesopores which do not have any connectivity between the pores whereas mesoporous MCM-48 exhibits three-dimensional (3D) pore system with much higher surface area that is easily accessible to the bulky reactant molecules. This feature makes the MCM-48 material superior catalyst over the MCM-41. It has been reported earlier that Al–MCM-48 showed much higher catalytic activity than the Al–MCM-41 in the alkylation of naphthalene using isopropanol as the alkylating agent [20,21]. We also confirmed a high catalytic activity of Al– MCM-48 catalysts in the alkylation of naphthalene with propylene which afforded a low 2,6-DIPN selectivity [22].

The mesoporous SBA-1 material has an ordered 3D pore structure with large cages A (ca. 4 nm) and slightly smaller cages B (ca. 3.3 nm) accessible through wide windows (>2 nm) [23–25], thus it is expected to be a promising catalyst for alkylation of naphthalene to DIPN.

The successful incorporation of Al species into SBA-1 framework was confirmed by catalytic activity of AlSBA-1 catalysts in the reaction of n-decane conversion [24]. On the other hand, the catalytic activity of FeSBA-1 and GaSBA-1 samples was observed in the reaction of alkylation of phenol with tert-butanol [25,26]. We also confirmed catalytic activity of GaSBA-1 samples in alkylation of naphthalene with propylene [27].

In this paper we report on the results of the catalytic activity of the SBA-1 catalysts containing various amounts of Al, Ga or Fe in the isopropylation of naphthalene with propylene as an alkylating agent in order to effectively produce DIPN mixture with low 2,6-DIPN isomer content.

#### 2. Experimental

Al, Ga or Fe atoms were incorporated into the silica framework of SBA-1 catalysts by direct synthesis route in a highly acidic medium according to the methods described by Vinu et al. [24–26]. Values in parentheses in the name of catalysts denote the  $n_{\rm Si}/n_{\rm Me}$  ratio, where Me refers to Al, Ga or Fe, respectively. The properties of the catalysts were confirmed by XRD, N<sub>2</sub> sorption, MAS-NMR, IR and EPR (Fe<sup>3+</sup>) spectroscopy. Some properties of mesoporous SBA-1 catalysts are shown in Table 1. The amorphous aluminosilicate ASA(6) ( $n_{\rm Si}/n_{\rm Al}$  ratio = 6) and the mesoporous Al–MCM-48(26) catalyst ( $n_{\rm Si}/n_{\rm Al}$  ratio = 26) were also used for the comparison studies. More details on Al–MCM-48(26) properties can also be found in [21].

Table 1

Properties of SBA-1 samples substituted with various metals.

The properties of SBA-1 were investigated by adsorption of pyridine and NO used as probe molecules followed by FTIR spectroscopy. All samples in the form of self-supporting wafers were activated under vacuum ( $10^{-4}$  mbar) at 400 °C prior to the adsorption of probe molecules. The adsorption temperatures were 170 °C for pyridine (POCh Gliwice, analytical grade, dried over 3A molecular sieve), and ambient temperature for NO (Linde Gas Polska, 99.95% purified by freeze-and-thaw procedure prior to each adsorption). For quantitative measurements pyridine was first adsorbed at the excess at 170 °C then desorbed at the same temperature for 20 min. These conditions were sufficient for the removal of the physisorbed species only, leaving intact pyridine molecules bonded to Brønsted and Lewis acid sites.

IR spectra were recorded with a Bruker Tensor 27 spectrometer equipped with an MCT detector and working with the spectral resolution of 2 cm<sup>-1</sup>. Spectra presented in this work are normalized to the standard 10 mg pellet (density 3.2 mg cm<sup>-2</sup>).

Alkylation experiments were carried out in a down flow reactor in the temperature range 120–300 °C, under a high pressure (3 MPa), a naphthalene/propylene mole ratio of 1.5 and a feed flow 20 g g<sup>-1</sup> h<sup>-1</sup>. Inlet temperature was changed starting from the lowest set point and reaction conditions at each set point were stabilised for 1 h at each temperature. So the higher the test temperature the longer was time on stream (TOS). Nevertheless, preliminary deactivation tests at 150 °C revealed that the most active catalyst samples did not show propylene conversion decrease for TOS longer than 8 h. Because Fe-containing samples were less active and deactivated quicker than Al- and GaSBA-1 catalysts, we started experiments from 150 °C.

More details on alkylation procedure are described in [22]. Alkylation products were analyzed by a GC equipped in FID detector, using a 60-m-long HP-INNOWax capillary column, according to the method described elsewhere [28]. Product samples were also qualitatively confirmed by GC–MS.

#### 3. Results and discussion

Mesoporous SBA-1 with different metal atoms viz. Ga, Al, and Fe in the framework was prepared using cetyltriethylammonium bromide as a structure directing agent. The textural parameters and elemental composition of the all the materials prepared with different  $n_{\rm Si}/n_{\rm Me}$  ratios are listed in Table 1. As can be seen in Table 1, the amount of metal atom in the framework increases with increasing amount of the metal species in the initial gel. However, the  $n_{\rm Si}/n_{\rm Me}$  ratio of the all the metal substituted SBA-1 materials is much higher than the ratio in the respective synthesis gels. This could be mainly due to a high solubility of the metal source in the acidic medium. Fig. 1 shows the powder XRD patterns of the representative metal substituted SBA-1 samples. All the samples displayed several peaks at lower angles, which can be indexed to

Sample	$n_{\rm Si}/n_{\rm Me}$ (in gel)	$n_{\rm Si}/n_{\rm Me}~({\rm AAS})$	$A_{\rm BET} [m^2 g^{-1}]$	$d_{\rm p} [{\rm nm}]$	$V_{\rm p}  [{\rm cm}^3 {\rm g}^{-1}]$	Brønsted centres per g of catalyst	Lewis centres per g of catalyst
AlSBA-1(39)	2	39	1324	1.9	0.64	52	79
AlSBA-1(64)	3.3	64	1350	2.0	0.67	20	59
AlSBA-1(180)	10	180	1341	2.1	0.69	7	17
GaSBA-1(17)	10	16.9	1260	2.49	0.67	65	795
GaSBA-1(40)	20	39.6	1365	2.44	0.70	59	461
GaSBA-1(90)	40	90.3	1410	2.42	0.75	26	249
FeSBA-1(90)	40	90	1350	2.4	0.71	20	74
FeSBA-1(120)	67	120	1390	2.4	0.70	52	113
AIMCM-48(26)	25	26	1245	2.1	0.56	65	147
ASA(6)	-	6	323	-	0.32	-	-

Where  $n_{\rm Si}/n_{\rm Me}$  = molar ratio of Si to Al, Ga or Fe, respectively;  $A_{\rm BET}$  = BET surface area;  $d_{\rm p}$  = pore diameter;  $V_{\rm p}$  = pore volume.



**Fig. 1.** Powder XRD patterns of metal substituted SBA-1: (a) AlSBA-1(39), (b) GaSBA-1(40), and (c) FeSBA-1(36).

the (1 1 1), (2 0 0), and (2 2 0) reflections of the face-centred-cubic *Fm3m* symmetry. These results indicate that the materials possess a 3D well-ordered cage type porous structure and the structural order of the materials is retained even after the metal incorporation. The detailed characterization of the materials with different metal atoms and their contents can be found in our earlier reports [24–26].

Acidity measurement can shed some light on the actual location and status of metallic sites because of two reasons. First, if metal is located at the surface of the SBA-1 walls, i.e. in the tetrahedral environment, it should create Si–O–Me bridge, this way becoming a source of Brønsted acidity. Metal-containing extraframework species can be detected as Lewis sites. The number of acidic sites of both types is usually lower than the metal content measured by chemical analysis because probe molecules cannot react with metallic species buried within the walls and with the part of the oligomeric species [29]. At the same time, such hidden metallic species would be also inaccessible to reactant molecules [30]. For quantification of acid centres pyridine is the best probe for both Brønsted and Lewis acid sites, as absorption coefficients of arising 1545 and 1450 cm<sup>-1</sup> bands are independent of the type of zeolite, its composition or morphology [31].

The results of pyridine adsorption experiments are summarized in Table 1. Generally, the higher was the  $n_{\rm Si}/n_{\rm Me}$  ratio, determined by chemical analysis, the higher was the concentration of both Brønsted and Lewis centres in investigated samples except for the

#### Table 2

Results of alkylation of naphthalene with propylene over AlSBA-1 catalysts.



**Fig. 2.** IR spectra of NO adsorbed on FeSBA-1(90) (a) and FeSBA-1(120) (b). Spectra normalized to the standard 10 mg sample. The background spectra of activated samples were subtracted.

FeSBA-1 series. Alkylation is the reaction proceeding mainly on the Brønsted acid centres via carbocationic transition state, therefore the concentration of Brønsted sites is thought to be the primary factor influencing the conversion in the reaction of naphthalene isopropylation. As it was already mentioned, the concentration of acid sites for the FeSBA-1 samples was not consistent with the  $n_{\rm Si}$ / $n_{\rm Fe}$  ratio determined by the chemical analysis. Iron in zeolites and mesoporous materials is usually easily reduced from Fe<sup>3+</sup> to Fe<sup>2+</sup> species, and also oligomerizes readily. Therefore, the presence of different forms of iron may be the reason of higher acidity of the FeSBA-1 sample with lower iron loading.

To verify this hypothesis, NO was adsorbed in both samples, because the frequency of the NO maxima depend not only on the oxidation states of specific iron species but also on their location in geometrically different environment. In this experiment, NO was adsorbed in the excess and then the gaseous phase together with weakly bonded species were removed by a short evacuation. As it can be seen in Fig. 2, the IR bands arising from the NO adsorption are different for FeSBA-1 samples. The band at  $1820 \text{ cm}^{-1}$ , characteristic of the Fe<sup>2+</sup> trinitrosyls (Fig. 2, spectrum a), is

Temperature [°C]	Conversion [%]	Selectivity to		2-IPN in IPN [%]	DIPN isomers distribution				
		IPN [%]	DIPN [%]		2,6-DIPN	2,7-DIPN	$\alpha$ , $\beta$ -Isomers	α,α-Isomers	
AlSBA-1(39)									
120	83.9	68.4	19.5	27.3	4.5	3.0	41.5	50.4	
150	94.9	70.6	18.0	30.5	5.6	4.4	45.7	44.3	
200	96.8	63.8	18.7	40.6	7.9	6.0	57.5	27.5	
250	96.5	60.0	18.6	75.9	25.8	21.9	45.7	5.0	
300	95.3	67.9	21.7	90.2	37.0	36.3	26.1	0.6	
AlSBA-1(64)									
120	77.4	82.6	12.3	26.1	4.3	2.3	44.6	48.9	
150	78.7	78.5	15.8	28.5	4.5	2.2	45.1	48.3	
200	96.2	77.2	15.1	40.3	7.5	5.5	57.4	29.6	
250	98.9	66.2	19.3	72.9	23.3	18.4	50.3	6.1	
300	97.1	83.0	12.8	90.1	36.7	35.6	26.3	0.0	
AlSBA-1(180)									
120	52.6	81.0	13.0	26.5	5.1	2.2	43.2	49.6	
150	55.9	84.1	11.9	26.4	3.3	1.8	43.0	51.9	
200	97.4	73.8	20.7	33.9	5.4	3.4	49.8	40.6	
250	97.3	67.3	17.7	54.7	12.8	9.9	62.8	14.6	
300	97.5	76.3	16.8	88.6	36.7	32.3	29.6	1.4	

Table	3
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Results of alkylation of naphthalene with propylene over GaSBA-1 catalysts.

Temperature [°C]	Conversion [%]	Selectivity to		2-IPN in IPN [%]	DIPN isomer	DIPN isomers distribution		
		IPN [%]	DIPN [%]		2,6-DIPN	2,7-DIPN	$\alpha,\beta$ -Isomers	α,α-Isomers
GaSBA-1(17)								
120	97.0	74.2	18.2	26.0	4.2	2.9	42.4	49.6
150	98.3	69.9	22.8	31.3	4.7	3.4	51.0	40.0
200	98.0	62.7	24.5	51.7	16.7	15.2	55.7	10.8
250	98.1	62.1	28.7	85.1	33.7	32.2	31.2	2.0
300	97.9	69.8	24.1	89.7	36.1	36.0	26.1	0.9
GaSBA-1(40)								
120	95.6	75.9	17.7	26.5	4.1	2.4	41.7	51.0
150	98.7	80.2	13.6	29.6	4.9	3.2	46.6	43.6
200	97.5	78.8	13.9	42.9	7.8	6.0	59.9	25.2
250	97.6	72.2	14.1	82.2	28.4	24.4	42.9	2.9
300	96.1	74.1	15.6	91.3	38.8	36.9	24.3	0.0
GaSBA-1(90)								
120	70.4	78.9	15.5	25.7	3.8	2.2	42.3	50.5
150	74.7	78.2	14.2	26.7	3.3	2.7	43.9	50.1
200	98.7	75.7	17.4	34.8	5.3	3.4	52.3	38.2
250	97.2	74.5	17.3	73.9	21.8	17.8	52.2	6.6
300	97.6	83.6	12.7	90.6	37.2	35.9	25.9	0.5

dominating the spectrum of FeSBA-1(90). It was suggested by Feretti at al. [32] that the band of  $Fe^{2+}(NO)_3$  at  $1810 \text{ cm}^{-1}$  is a measure of iron dispersion—if three NO molecules can be bonded onto one centre, therefore this particular centre have to be isolated from other iron species and exposed at the surface. Such iron can be at the same time a single Lewis centre. Therefore in FeSBA-1(90), the significant part of iron, introduced during synthesis is present in the extraframework, reduced and isolated form of Fe<sup>2+</sup> cations.

In the spectrum of the FeSBA-1(120), the most intensive is the band of NO bonded onto Fe<sup>3+</sup> oligomeric species [32]. Lower Fe loading prevented the reduction of most of the species. Even though they are present as extraframework centres, they are still trivalent. Other intensive band, present after NO adsorption on this sample is the band at 1585 cm<sup>-1</sup>, arising from negatively charged form of NO, the most probably NO<sub>3</sub><sup>-</sup>, bonded via one of its oxygen atoms [33]. At the same time, the presence of the band at 2224 cm<sup>-1</sup> (not shown in Fig. 2) is pointing at the presence of N<sub>2</sub>O, suggesting that NO underwent disproportionation when contacted with this sample. Summarising, it is evident that iron was differently distributed, being more dispersed and reduced in FeSBA-1(120) sample, which explains its higher acidity.

Results of the isopropylation of naphthalene over AlSBA-1, GaSBA-1 and FeSBA-1 mesoporous catalysts with different amounts of Al, Ga, and Fe incorporated into the silica framework are collected in Tables 2–4, respectively.

AISBA-1 and GaSBA-1 catalysts were more active than FeSBA-1 samples. Both GaSBA-1 and AISBA-1 catalysts were active even at the temperatures as low as 120 °C, whereas the FeSBA-1 samples

required temperatures higher than 150 °C. Lower conversion over FeSBA-1(90), despite higher concentration of the acid centres, may be explained by the lower acid strength of iron-based Brønsted centres [34]. Moreover, FeSBA-1 catalysts visibly deactivated and, therefore, in the tested temperature range, propylene conversion lower than 42% was observed (Table 4). Initially, propylene conversion increased with temperature ramp to 250 °C but further temperature elevation did not cause any increase in the conversion. For both FeSBA-1 samples higher propylene conversion was observed at 250 °C than at 300 °C. This maximum in propylene conversion plot was caused by overlapping two effects: the activity increase with temperature ramp and the rapid catalyst deactivation with time on stream. The experiments were performed starting from the lowest temperature and the reaction temperature was increased step by step, therefore, the higher the test temperature the longer was time on stream. The origin of the rapid deactivation of FeSBA-1 catalysts is not clear at present and would require additional investigation.

Over the most active AlSBA-1 and GaSBA-1 samples, i.e. those with the highest metal content and higher acidity, a high conversion was achieved at 120 °C (Fig. 3). The propylene conversion increased with temperature and at temperature higher than 200 °C, practically total propylene was consumed in the reaction carried out over all GaSBA-1 and AlSBA-1 catalyst samples at our test conditions.

In the tested range of  $n_{\rm Si}/n_{\rm Me}$  ratio, if the higher was the Al, Ga or Fe content in the SBA-1 catalyst and higher Brønsted acidity, the higher activity was observed. For GaSBA-1 and AlSBA-1 catalysts it is discernible at temperature lower than 200 °C, when the increase

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Temperature [°C]	Conversion [%]	Selectivity to		2-IPN in IPN [%]	DIPN isomers distribution				
		IPN [%]	DIPN [%]		2,6-DIPN	2,7-DIPN	$\alpha$ , $\beta$ -Isomers	α,α-Isomers	
FeSBA-1(90)									
150	5.7	99.3	0.7	27.0	-	-	-	-	
200	37.4	89.0	8.7	28.5	4.1	1.8	44.1	50.0	
250	42.0	83.8	11.0	33.3	6.7	2.7	47.4	43.2	
300	18.5	79.9	0.0	36.8	-	-	-	-	
FeSBA-1(120)									
150	4.9	85.2	0.0	29.8	-	-	-	-	
200	13.8	84.0	4.2	29.2	0.0	0.0	47.5	52.5	
250	28.9	84.8	10.7	32.3	6.0	3.6	46.4	44.0	
300	19.0	79.1	6.6	35.8	6.1	7.1	44.9	41.9	



**Fig. 3.** Temperature relationship of propylene conversion for various catalysts. Symbols: (▲) AlSBA-1(39); (▲) AlSBA-1(180); (□) GaSBA-1(40); (◊) GaSBA-1(90); (■) FeSBA-1(90); (×) ASA(6) (dashed line); (○) AlMCM-48(26) (dashed line).

in propylene conversion with Ga or Al content can be observed (see Tables 2 and 3). Fig. 4 illustrates the influence of the  $n_{\rm Si}/n_{\rm Me}$  ratio in Al-, Ga- and Fe-SBA-1 catalysts on the propylene conversion achieved in naphthalene alkylation carried out at 150 °C and confirms the increase in catalyst activity with a larger amount of metal incorporation. Similarly, a propylene conversion of 84% was achieved over the AlSBA-1(39) (52 H<sup>+</sup>/g) catalyst, whereas 77% over AlSBA-1(64) (20 H<sup>+</sup>/g) and only 53% over AlSBA-1(180) (7 H<sup>+</sup>/ g) (Table 2) at the reaction temperature of 120 °C. As shown in Table 3, GaSBA-1(17) and GaSBA-1(40), with similar number of Brønsted acid centres, exhibited similar propylene conversion (96-97%) at 120 °C, but the conversion of only 70% was observed over the GaSBA-1(90) catalyst with significantly lower number Brønsted acid centres. Such a relationship of activity is reasonable, because quantity of active sites on the SBA-1 catalyst surface is expected to increase with a larger amount of trivalent metal species incorporated into the silica framework.

A comparison of propylene conversion achieved on FeSBA-1(90) sample with that of GaSBA-1(90) and even with activity observed on AlSBA-1(180), i.e. the catalyst with a smaller trivalent metal content, demonstrates clearly that the incorporation of Fe was the least effective for the alkylation of naphthalene, the most probably due to lower acid strength of the iron-based acid centres. It is worth to mention that intensity of the 1545 cm<sup>-1</sup> band of protonated pyridine was so small for AlSBA-1 and FeSBA-1 samples that the usual way of measuring the acid strength by pyridine thermodesorption and comparison of the intensities of this band for different desorption temperatures would have been laden with too great error to be trustworthy.

Fig. 3 compares temperature relationship of propylene conversion in the alkylation of naphthalene carried out over selected



**Fig. 4.** Propylene conversion obtained at 150 °C as a function of  $n_{Si}/n_{Me}$  ratio in various SBA-1 catalysts. Symbols: ( $\square$ ) GaSBA-1; ( $\blacktriangle$ ) AlSBA-1; ( $\blacklozenge$ ) FeSBA-1.

samples of mesoporous SBA-1 catalysts with the results obtained over the amorphous aluminosilicate ASA(6) and the AIMCM-48(26).

GaSBA-1 and AlSBA-1 were found to be more active than the ASA(6). Propylene conversion at 150 °C in the case of GaSBA-1(40), AlSBA-1(39) and GaSBA-1(17) mesoporous catalysts was in the range of 95–99%, whereas ASA(6) afforded only 86%.

Regardless of  $n_{\rm Si}/n_{\rm Me}$  ratio, all GaSBA-1 and AlSBA-1 samples were more active than the AlMCM-48(26) catalyst and propylene conversion greater than 56% was observed at 150 °C in the former case, whereas only 15% in the latter catalyst. Under similar conditions other AlMCM-48 samples, i.e. with higher  $n_{\rm Si}/n_{\rm Me}$  ratio, revealed even lower propylene conversion than that of the AlMCM-48(26) [22].

When comparing acidity of the catalysts (Table 1), the lower alkylation activity of the AlMCM-48(26) is surprising. The AlMCM-48(26) sample possessed more Brønsted and Lewis acid sites than AlSBA-1 catalysts what is in accordance with quantities of the incorporated Al atoms. Moreover, the concentration of Brønsted sites in the AlMCM-48(26) was not lower than those of GaSBA-1 samples. Therefore, pore structure of SBA-1 type seems to be superior in alkylation of naphthalene to that of MCM-48.

It is a well-known fact that naphthalene nucleus is initially alkylated at  $\alpha$ -positions, that are kinetically preferred, and next the  $\alpha$ -alkylnaphthalenes isomerize to more thermodynamically stable  $\beta$ -alkylnaphthalenes. Therefore, products of naphthalene monoisopropylation obtained at mild conditions and a short contact time are rich in 1-IPN but those achieved under severe reaction conditions and prolonged time became abundant in 2-IPN. Similarly, DIPN product obtained at kinetic conditions is rich in  $\alpha,\alpha$ - and  $\alpha,\beta$ -isomers, whereas that with composition close to thermodynamic equilibrium is rich in 2,6-DIPN and 2,7-DIPN isomers [35,36]. Since 2,6-DIPN is undesirable isomer in DIPN mixture applied as a high-quality solvent, a selective alkylation catalyst with a low isomerization activity is profitable.

Fig. 5 shows a temperature relationship of 2-IPN content in IPN products obtained by naphthalene isopropylation over various catalysts. As expected, the 2-IPN content increased in IPN isomeric mixture with increasing the reaction temperature for each tested catalyst. Regardless of the alkylation activity, all SBA-1 catalysts showed a relatively low isomerization activity. As compared with amorphous aluminosilicate, SBA-1 catalysts gave a lower 2-IPN selectivity in alkylation. This is also true even for the samples with the highest alkylation activity (AISBA-1(39), GaSBA-1(40) and GaSBA-1(17)). For example, more than 80% of 2-IPN in IPN was detected if alkylation was carried out over ASA(6) catalyst at 200 °C, whereas the products obtained on SBA-1 catalysts contained only 29–52% of 2-IPN (Fig. 5 and Tables 2–4).



**Fig. 5.** Temperature relationship of 2-IPN distribution in IPN obtained on various catalysts. Symbols: ( $\blacktriangle$ ) AlSBA-1(39); ( $\diamondsuit$ ) AlSBA-1(180); ( $\bigtriangleup$ ) GaSBA-1(17); ( $\Box$ ) GaSBA-1(40); ( $\times$ ) ASA(6) (dashed line); ( $\bigcirc$ ) AlMCM-48(26) (dashed line).



**Fig. 6.** Temperature relationship of 2,6-DIPN content in DIPN products obtained on various catalysts. Symbols: ( $\blacktriangle$ ) AlSBA-1(39); ( $\diamondsuit$ ) AlSBA-1(180); ( $\bigtriangleup$ ) GaSBA-1(17); ( $\Box$ ) GaSBA-1(40); ( $\diamondsuit$ ) GaSBA-1(90); ( $\times$ ) ASA(6) (dashed line); ( $\bigcirc$ ) AlMCM-48(26) (dashed line).

Similarly as in alkylation, the GaSBA-1 catalysts were slightly more active in isomerization of IPN than the AISBA-1 catalysts. For instance, IPN obtained at 200 °C on GaSBA-1(40) and AISBA-1(39) catalysts contained 43% and 41% of 2-IPN, respectively. The 2-IPN content amounted to 82 and 76% for GaSBA-1(40) and AISBA-1(39), respectively, at the reaction temperature of 250 °C. Isomerization requires stronger acid centres than alkylation, the presence of the Lewis acid sites, much more numerous for GaSBA-1 may have inductive effect on the acid strength of the Brønsted centres [37].

The mesoporous AIMCM-48(26) sample revealed a lower isomerization activity than GaSBA-1 and AISBA-1 catalysts, especially at a high temperature, but its alkylation activity was also lower than that of SBA-1 catalysts. Mesoporous FeSBA-1 catalysts were the least active samples both in alkylation and isomerization. In the same way as in alkylation, the isomerization activity increased with increasing the metal content in AISBA-1 or GaSBA-1 catalysts.

For isomerization of diisopropylnaphthalenes a relationship similar as in the case of IPN was observed and a relatively small quantities of 2,6-DIPN were formed. Content of 2,6-DIPN and 2,7-DIPN in DIPN mixture increases with the increase of alkylation temperature for all tested catalysts (Tables 2–4). The relationship of 2,6-DIPN content in DIPN shown in Fig. 6 clearly indicates a higher isomerization activity of the ASA(6) than those of mesoporous SBA-1 and MCM-48 catalysts. The 2,6-DIPN isomer comprised 34% of DIPN mixture obtained in alkylation of naphthalene with propylene at 200 °C over the ASA(6) but only 5–8% over SBA-1 samples, except for the most active GaSBA-1(17) catalyst over which 2,6-DIPN content approached 17%.

Analogously to monoalkylation, the higher was the Al, Ga or Fe content in the SBA-1 catalysts the higher 2,6-DIPN content in DIPN mixture was observed (Fig. 6 and Tables 2-4). This result indicates that, although lower than that of alkylation, the isomerization activity of catalysts also rose with amount of the incorporated metal. Nevertheless, the active centres containing Ga seem to slightly be more effective in isomerization of DIPN isomers to 2,6-DIPN and 2,7-DIPN than the Al centres (compare results obtained at temperatures higher than 200 °C), possibly due to inductive effect of Lewis sites on the strength of Brønsted centres. Isomeric composition of DIPN products obtained in alkylation at the reaction temperatures on or lower than 200 °C over GaSBA-1(40) and AlSBA-1(39) was practically the same (Tables 2 and 3). At a higher temperature DIPN mixture achieved over GaSBA-1(40) contained slightly more  $\beta$ , $\beta$ -isomers than that obtained on AlSBA-1(39). For instance, the DIPN product obtained at 250 °C over GaSBA-1(40) exhibited the isomers of 2,6-DIPN, and 2,7-DIPN to be 28 and 24%, respectively, whereas those obtained over AlSBA-1(39) were 26 and 22%, respectively.

The unique properties of AlSBA-1 and GaSBA-1 catalysts of a relatively high alkylation activity along with low isomerization activity make them very useful in the synthesis of DIPN highquality solvent. They give not only a product poor in 2,6-DIPN but also a relatively low 2,6-DIPN content be obtained in a wide range of operating temperature that is important if a catalyst deactivation is compensated by the process temperature increase. For instance, if a DIPN product with 2,6-DIPN content lower than 15% is required, then alkylation over the ASA(6) catalyst can be carried out at temperature not higher than 170 °C (cf. Fig. 6), whereas over the GaSBA-1(90), AlMCM-48(26) and AlSBA-1(180) in the temperature ranges up to 230, 250 and even 270 °C, respectively.

#### 4. Conclusions

Alkylation of naphthalene with propylene to diisopropylnaphthalenes (DIPN) over mesoporous AlSBA-1, GaSBA-1 and FeSBA-1 catalysts was investigated. GaSBA-1 catalysts were slightly more active than AISBA-1 and FeSBA-1 revealed the lowest activity mainly due to rapid deactivation. Moreover, AISBA-1 and GaSBA-1 proved to be more active alkylation catalysts than amorphous aluminosilicate and mesoporous AlMCM-48 catalyst. On the other hand, SBA-1 catalysts revealed a relatively low isomerization activity, therefore, selectivities of both 2-IPN in monoalkylation and 2,6-DIPN and 2,7-DIPN in dialkylation were lower than those observed over other alkylation catalysts. Consequently, DIPN isomeric mixture was poor in 2,6-isomer. In the tested range of  $n_{\rm Si}/n_{\rm Me}$  ratio, if the higher was the Al, Ga or Fe content in the SBA-1 catalyst the higher activity both in alkylation and isomerization was observed. The high alkylation activity and a low 2,6-DIPN selectivity could make the GaSBA-1 and AlSBA-1 mesoporous materials promising catalysts for the synthesis of DIPN solvent.

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