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Dialkylation of Naphthalene with Isopropanol Over H_3PO_4/MCM-41 Catalysts for the Environmentally Friendly Synthesis of 2,6-Dialkylnaphthalene

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Abstract AlMCM-41 materials with SiO_2/Al_2O_3 molar ratios 20, 70, 110, 150, 200, and Si-MCM-41 were synthesized following standard procedures, and loaded with different amounts of H_3PO_4. The catalysts were well characterized by powder X-ray diffraction (XRD), nitrogen adsorption studies, and solid state ^{29}Si, ^{27}Al, ^{31}P, ^{23}Na and ^{1}H MAS NMR spectroscopy. Acidity measurement by FT-IR spectroscopy monitoring of pyridine adsorption reveals that the incorporation of Al in the framework generates Brønsted and Lewis acidity, which increases with the increase in metal content. By loading H_3PO_4 on the AlMCM-41, Brønsted sites increases substantially, but the Lewis sites decrease to a large extent. Liquid phase isopropylation of naphthalene with isopropanol in n-hexane under autogeneous pressure was performed in the temperature range 473–623 K. The optimum feed molar ratio was found to be 1:2:10 (naphthalene:isopropanol:*n*-hexane), where the naphthalene conversion reaches to 85.5%. The β-and β,β-selectivities over 30 wt% H_3PO_4/AlMCM-41(200) were 97.0 and 84.8, respectively, at 85.5% conversion. The main products of the reaction, mono and diisopropylnaphthalenes, were analyzed and identified by gas chromatography and confirmed by GC–MS. The conversion and selectivity of the products are discussed from the point of view of catalyst characteristics and reaction conditions.

Keywords Naphthalene · Isopropanol · 2-Isopropylnaphthalene · 2,6-Di-isopropylnaphthlene · H_3PO_4 · AlMCM-41

1 Introduction

Zeolites are used in alkylation reactions due to their activity, selectivity, thermal stability, reusability and eco-friendly nature. Naphthalene and its derivatives are rich in some refinery streams and in liquids derived from coals via carbonization, pyrolysis and liquefaction. Among the Friedel–Crafts reactions, selective alkylation of naphthalene to β mono- and β,β-dialkylated products is of practical relevance. 2-Naphthol, key intermediate for dyes, pharmaceuticals, and perfumes, can be obtained from 2-alkylnaphthalenes [1]. A diisopropylnaphthalene (DIPN) mixture is used as a high-quality solvent for copying materials [2]. Especially advantageous is the presence of a high content of 2,7-diisopropylnaphthalene in the solvent [3]. The 2,6-diisopropylnaphthalene, isolated from the isomeric mixture, can be used as a raw material for the production of advanced polyester fibers, films that have high heat resistance and strength, and plastics, such as thermo tropic liquid crystalline polymers [1, 4].

Alkyl naphthalenes (AN) are commercially produced by alkylation of naphthalene with an alcohol or alkene using solid acid catalysts [5]. For a large-scale application, it is important to improve the selectivity of this alkylation,

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desirably towards 2- and 2,6-dialkyl products. There are as many as ten possible dialkylnaphthalenes (DAN) including α,α-, α,β-, and β,β-disubstituted isomers. Shape-selective alkylation over molecular sieve catalysts can produce 2-AN, 2,6- and 2,7-DAN. It is difficult to selectively produce 2,6-DAN, because 2,7-DAN is also a major product of β-selective reaction (Scheme 1) [6].

Traditionally, the catalyst used in this process is the strongly Lewis acid $AlCl_3$. It has been reported that, among the two monoalkylated (2-AN and 1-AN) isomers from $AlCl_3$-catalyzed alkylation at 298 K, the equilibrium yield of 2-alkylnaphthalene increases in the order methyl (75.5%) < ethyl (90.5%) < isopropyl (98.5%) < tert-butyl (100%) [5]. It may be considered that this study did not include dialkylation. While $AlCl_3$ is catalytically efficient and readily available commercially, its use as a catalyst is environmentally problematic, as it cannot be regenerated and must be hydrolyzed and disposed of, resulting in a large volume of solid waste [7].

In general, Friedel–Crafts reaction of naphthalene gives initially α and β monoalkylated products, which then undergo further alkylation to a mixture of dialkylated isomers and eventually polyalkylated products. There are several reports on the alkylation of naphthalene using various acid catalysts, such as $BF_3 \cdot H_3PO_4$ [8], $AlCl_3$ [5], zeolites, etc. [1, 4, 6, 9–20]. Among the zeolites H-mordenite, H-beta, HY, HZSM-5 and MCM-22, mordenite has been found to be the preferred catalyst for the synthesis of 2,6-dialkylnaphthalene [6] because of its unique pore structure, offering a suitable confined space for the establishment of shape selective effects [9].

Sugi et al. [10] have investigated the role of the zeolite structure and alkylating agent on the shape-selective catalysis, isopropylation, *sec*-butylation, and *tert*-butylation, of naphthalene over three-dimensional twelve-member (12-MR) zeolites, namely, Y (FAU), beta (BEA), and CIT-1 (CON), and compared to that of H-mordenite (MOR). They have reported that β,β-selectivity and the 2,6-selectivity among DAN isomers, varied with the type of zeolite and alkylating agent. Their results suggest that FAU, BEA, and CON are not shape-selective in isopropylation, and that the isopropylation is mainly controlled kinetically at lower temperatures, and thermodynamically at higher temperatures.

Narayanan and co-workers [11] have reported the liquid phase isopropylation of naphthalene over AlMCM-41. They prepared AlMCM-41 with different Si/Al ratios, and studied the catalytic activity of these catalysts for isopropylation of naphthalene under batch reaction conditions on protonated AlMCM-41, aiming to establish a correlation between the acidity and alkylation activity of various catalysts.

In the present investigation, we report the results of the isopropylation of naphthalene over AlMCM-41 with different SiO_2/Al_2O_3 molar ratios and SiMCM-41, loaded with different amounts of H_3PO_4. We have found that these new compounds are promising catalysts for isopropylation of naphthalene. Further the physico-chemical characteristics and acidity of the catalysts are correlated with catalytic activity and selectivity. The challenging goal was to obtain 2,6-diisopropylnaphthalene (2,6-DIPN) with high selectivity and high 2,6/2,7-DIPN ratio.

2 Experimental

2.1 Materials

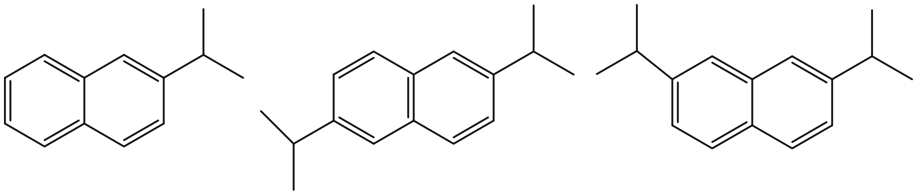
Phosphoric acid, naphthalene, 2-propanol and solvents were obtained from Merck with the maximum purity, and used as received.

2.2 Preparation of the Catalysts

AlMCM-41 molecular sieves were synthesized by a previously described method [21], varying the SiO_2/Al_2O_3 molar ratios, Al source, temperature and reaction time.

2.3 Preparation of H_3PO_4/AlMCM-41 Catalysts

The catalysts were prepared by impregnation of the AlMCM-41 calcined solid with different amounts of H_3PO_4 dissolved in distilled water. The impregnated catalysts were dried at 383 K for 12 h and then calcined in air at 823 K for a period of 4 h before using them in the catalytic reactions. All the impregnated catalysts were pressed into wafers, crushed, and sieved to 20–40 mesh before use in the catalytic runs. Despite some conditions were varied in every synthesis, all samples had the AlMCM-41 structure. The



Scheme 1 Some of the possible products from isopropylation of naphthalene

final catalysts are designated as xH$_3$PO$_4$/AlMCM-41(20), x being the weight percentage of H$_3$PO$_4$ used for impregnation, and AlMCM-41(20) indicating that the sample with SiO$_2$/Al$_2$O$_3$ = 20 was used as support.

2.4 Instrumental

FT-IR spectra of the catalyst were recorded on a Brucker IFS-66 single channel Fourier transform spectrometer with the KBr pellet method. Textural analyses were determined from nitrogen adsorption–desorption isotherms, obtained at 77 K using a Micromeritics Gemini apparatus. The samples were degassed for 2 h at 283 K. Specific surface area was obtained by the BET method, microporous surface area by means of the *t* method, and total pore volume from the adsorption at P/P° 0.95. X-ray diffraction (XRD) patterns were recorded over non-oriented powder samples between 1 and 70° (2θ) at a scanning speed of 2°/min by using a Siemens D-500 diffractometer, at 40 kV and 30 mA, and employing filtered Cu Kα radiation. The equipment was connected to a DACO-MP microprocessor and used Diffract-AT software. The acidity of the samples was evaluated from the Fourier transform IR spectra of adsorbed pyridine, measured using a JASCO FT/IR (680 plus) spectrometer. Approximately 40–50 mg of material that had been previously calcined in air for 4 h at 773 K were pressed (for 3 min at 15 tonnes/cm^2 pressure under approximately 10^{-2} Torr vacuum) into a self supporting wafer of 15 mm diameter. The pretreated wafer was equilibrated with 26 mmHg of pyridine at 473 K for 1 h and evacuated at 473 and 573 K for 1 h in dynamic vacuum. After each treatment, an IR spectrum was recorded at room temperature.

High resolution MAS-NMR experiments were performed at room temperature in a Bruker AVANCE-400 spectrometer, operating at 79.49 MHz (^{29}Si signal), 104.26 MHz (^{27}Al signal), 161.98 MHz (^{31}P signal), 105.84 MHz (^{23}Na signal) and 400.13 MHz (^{1}H signal). ^{29}Si, ^{31}P, ^{1}H (I = 1/2) MAS-NMR spectra were recorded after $\pi/2$ pulse irradiation (4 µs), using a 500 kHz filter.

2.5 Reaction Procedure

Isopropylation reactions were carried out under batch reaction conditions using an autoclave in the temperature region of 473–623 K, at autogenous pressure conditions. The feed was naphthalene:2-propanol:*n*-hexane molar ratio 1:2:10, and to this mixture 0.5 g of a freshly activated catalyst was added. Activation of the catalyst was usually done by calcining it at 573 K in N$_2$ for 2 h. The autoclave temperature was then slowly raised to the required temperature and maintained at the desired temperature during the reaction period of 2.5 h. After the reaction, the autoclave was cooled to room temperature. The reaction mixture was isolated from the catalyst by centrifugation. Product analysis was done on a Shimadzu model 14A gas chromatograph, equipped with a wide bone OV-17 (60 m) capillary column and a FID detector. The product analysis by GC and GC–MS revealed the formation of monoalkylated products 1-isopropylnapthalene (1-IPN) and 2-isopropylnaphthalene (2-IPN), dialkylated products 2,6-diisoproplynapthalene (2,6-DIPN) and 2,7-diisopropylnaphthalene (2,7-DIPN); other DIPN isomers and other products were tri- and tetraisopropylnaphthalenes, alkylnaphthalenes with at least one substituent other than the isopropyl group, propylene oligomers, etc.

3 Results and Discussion

3.1 Characterization of the Catalysts

Detailed physicochemical characterization of the catalysts is found in our earlier reports [21, 22]. However, salient inferences obtained from the characterization results are precisely outlined here. The XRD data indicate that AlMCM-41 samples exhibit the ordered hexagonal structure characterized by an intense reflection peak at a *d* spacing of 3.8 nm [22]. The intensity of this low angle reflection peak did not change as the H$_3$PO$_4$ loading increased. The specific surface area of AlMCM41 samples as calculated by the BET method ranges between 1038 and 668 m^2/g. H$_3$PO$_4$ loading induces a drastic decrease in the specific surface area, to values ranging between 40 and 90 m^2/g, mostly due to external surface area, as micropore surface areas were in the range 4–6 m^2/g. However, this change did not produce any structural distortions of the AlMCM-41. Consequently, it seemed reasonable to propose that loading of H$_3$PO$_4$ on AlMCM-41 did not change the regular arrangement of uniform channels of the support [23]. It might be interesting to mention that by loading of approximately 30 wt% of phosphotungstic acid on AlMCM-41, the specific surface area of the support decreased by less than 20% [24], but loading the same support by approximately the same weight percent of H$_3$PO$_4$, the surface area decreased to a large extent. Probably the crystalline structure of the phosphotungstic acid (Keggin units) and the amorphous structure of the phosphoric acid could explain this difference. The ^{31}P MAS NMR spectra of 30 wt% H$_3$PO$_4$/AlMCM-41(200) exhibited two peaks at −10 and 0 ppm which may correspond to P atom in pyrophosphoric acid or terminal groups and monomeric PO$_4$$^{3-}$ groups, respectively. From analysis of Si, Al and P NMR signals, the formation of Si–O–Al–O–P bridges seemed to be favoured at the surface of AlMCM-41 catalysts [22]. The FT-IR spectrum for the 30 wt% H$_3$PO$_4$/AlMCM-41(70) sample after adsorption of pyridine shows bands of pyridine adducts in the region 1650–1450 cm^{-1}.

The bands at 1545 and 1490 cm^{-1} are characteristic of Brønsted and Lewis acid sites, respectively. Comparison of spectra revealed that 30 wt% H_3PO_4/AlMCM-41(70) possesses a greater amount of acid sites than other catalysts [21]. The concentration of Brønsted and Lewis acid sites was calculated after evacuation at 473 K using the extinction coefficient of bands due to pyridine adsorbed on Brønsted and Lewis acid sites [25, 26].

3.2 Catalytic Studies

Isopropylation of naphthalene with isopropanol was carried out over H_3PO_4–AlMCM-41 catalysts under batch conditions using an autoclave in the temperature range 473–623 K in steps of 25 K using n-hexane as the solvent, under autogenous pressure conditions. The optimized molar ratio of 1:2:10 (naphthalene:isopropanol:*n*-hexane) was maintained for all the catalytic reactions. A typical reaction mixture in the reactor contains naphthalene (2.56 g or 20 mmol), and isopropanol (2.4 g or 40 mmol). *n*-Hexane (10 mL), and 0.5 g of freshly activated catalyst were added to this mixture. As can be seen in Table 1, the temperature chosen for activation of the catalyst could exert a critical impact upon both conversion and selectivity. When the activation temperature increased from 298 to 573 K, the conversion increased, probably due to an increase of the acid strength and loss of the physisorbed water in the catalysts, and at the same time the β-IPN and β,β-DIPN selectivity were also improved. Brønsted acidity should be associated to the presence of tetrahedral Al and Lewis acidity is associated with octahedral Al, thus by increasing the calcination temperature the catalyst loses more Brønsted acidic sites and in this regard one would expect a decrease in conversion and selectivity to diisopropylnaphthalene, which severely occurs at temperatures higher than 573 K.

3.2.1 *Effect of Temperature on the Catalytic Activity*

Isopropylation of naphthalene was carried out over the 5 wt% H_3PO_4/AlMCM-41(20), 10 wt% H_3PO_4/AlMCM-41(70) and 20 wt% H_3PO_4/AlMCM-41(150) in the temperature range 473–623 K in steps of 25 K. The conversion of naphthalene and the selectivity over all the above catalysts towards various alkylated naphthalene are given in Table 2. The conversion of naphthalene was found to increase steadily with increasing the temperature from 473 to 573 K over all the H_3PO_4/AlMCM-41 catalysts, irrespective of the SiO_2/Al_2O_3 ratio and weight percentage of H_3PO_4. A further increase in temperature resulted in a decrease in conversion over all the catalytic systems. This could be related to the loss of Brønsted acid sites and to deactivation of the catalyst due to coking. Usually, the isopropylation of naphthalene gives initially 1-, and 2-IPN, which then undergo further alkylation to a mixture of dialkylated isomers and eventually polyalkylated products. Regarding the selectivity to monoalkylated naphthalene, that for 2-IPN was always higher than that for 1-IPN, and by increasing the temperature this selectivity increased. As the first step in electrophilic aromatic substitution is rate determining and the energy level of its transition state corresponds to the relative stability of the resulting carbocation, attack at C-1 is faster than at C-2. The 2-IPN content in monoalkylated naphthalenes rises very quickly with a temperature increase as a result of more intensive isomerization, and probably at 573 K it approached nearly equilibrium value. As we expected, the selectivity to 2-IPN increased with increasing the temperature, and at the same time the percentage of DIPNs increased in the reaction mixture. Since this reaction is a consecutive reaction [12], more multialkylated products could be formed at high conversions. On the other hand, both 2,6-DIPN and 2,7-DIPN are formed from β substitution. The mono-substitution at position 1 or 2 of naphthalene changes the frontier

Table 1 Effect of activation temperature for the 10 wt% H_3PO_4/Al-MCM-41(70) catalyst on its catalytic activity in isopropylation of naphthalene with isopropanol

Temperature (K)	Time (h)	Naphthalene conversion (%)	Product selectivity (%)			Isomer selectivity (%)				
						IPN	DIPN			
			IPN	DIPN	Others	S_β	2,6	2,7	$S_{\beta\beta}$	2,6/2,7
298	–	37.6	71.4	21.4	7.2	74.1	29.2	26.9	56.1	1.08
473	1	52.8	62.2	29.1	8.7	83.5	35.3	30.6	65.9	1.15
573	1	60.2	58.6	35.3	6.1	91.2	38.6	30.2	68.8	1.27
673	1	50.0	63.5	28.0	8.5	84.8	34.5	29.6	64.1	1.16
673	4	42.7	68.0	24.4	7.6	77.5	31.1	28.7	59.8	1.08
823	1	46.9	65.8	26.2	8.0	80.7	32.8	29.4	62.2	1.11

Reaction conditions: reaction temperature = 548 K, IPA/NAP molar ratio = 2, solvent = *n*-hexane, reaction time = 2.5 h, catalyst weight = 0.5 g electron density in positions 6 and 7. In 1-IPN, position 7 has slightly higher partial rate factor, fr(E), value than position 6. However, position 6 in 2-IPN has higher fr(E) value than position 7. This suggests that during the isopropylation of 2-IPN, the formation of 2,6-DIPN is favored electronically against that of 2,7-DIPN. Moreover, DIPN isomers are divided into β,β-isomers (2,6-DIPN + 2,7-DIPN), α,β-isomers (1,6-DIPN + 1,7-DIPN and 1,3-DIPN) and α,α-isomers (1,5-DIPN and 1,4-DIPN). Intramolecular isomerization, which always accompanies the alkylation reaction, can change the proportions of DIPN isomers, which increases the population of isomers with isopropyl substituents at β-positions at the expense of isomers with substituents at α-positions. Therefore, both the electronic factors and the characteristics of catalyst structure and surface [13] should be taken into account when considering the shape selectivity of naphthalene alkylation.

As mentioned before, the internal surface area of all the catalysts remains almost constant, with values between 4 and 6 $m^2 g^{-1}$, so the differences in the total surface area are due to the external one. This also indicates that microporosity is not important for the catalytic results that are being discussed so far; the influence of the catalysts may be due exclusively to their external surface. The reaction is presumably occurring on the external surface of the catalysts which probably do not induce any shape selectivity. If this is true, we should not be able to observe the benefit of shape selectivity of these new catalysts; however, the system gets close to the thermodynamic conditions. The thermodynamic mixture should contain mainly 2,6- and 2,7-DIPN, and their ratio would be close or even slightly lower than 1. Regarding the shape selectivity, both high 2,6-DIPN and 2,7- DIPN content as well as high 2,6-DIPN/2,7-DIPN ratio can be expected; however, correspondingly also 2-IPN should be the only product of monoalkylation [14]. Based on the conversion of naphthalene and β,β-selectivity, 573 K was considered to be the optimum reaction temperature [15].

3.2.2 *Effect of H_3PO_4*

Improvement of the H_3PO_4/AlMCM-41 catalysts was made by optimizing the H_3PO_4 loading. Variation of H_3PO_4

Table 2 Effect of reaction temperature on the isopropylation of naphthalene over 5 wt% H_3PO_4/AlMCM-41(20), 10 wt% H_3PO_4/AlMCM-41(70) and 20 wt% H_3PO_4/AlMCM-41(150)

Catalyst	Temp (K)	Naphthalene conversion (%)	Product selectivity (%)			Isomer selectivity (%)				
						IPN	DIPN			
			IPN	DIPN	Other	S_β	2,6	2,7	$S_{\beta\beta}$	2,6/2,7
5 wt% H_3PO_4/Al-MCM-41(20)	473	28.3	88.3	11.7	–	74.0	21.4	16.0	37.4	1.33
	498	40.8	75.5	22.1	2.4	80.5	28.6	21.2	49.8	1.34
	523	51.6	67.6	27.3	5.1	87.3	35.7	27.6	63.3	1.29
	548	59.5	61.2	32.1	6.7	89.6	38.3	29.5	67.8	1.29
	573	61.1	57.4	33.5	9.1	93.4	39.0	31.8	70.8	1.22
	598	56.2	51.2	35.0	13.8	92.8	37.1	31.7	68.8	1.17
	623	51.1	55.7	32.2	12.1	92.9	35.5	29.1	64.6	1.22
10 wt% H_3PO_4/Al-MCM-41(70)	473	35.9	83.9	16.1	–	76.4	22.9	17.4	40.3	1.31
	498	46.7	73.0	24.4	2.6	80.5	30.8	23.2	54	1.32
	523	55.3	62.3	35.2	2.5	88.3	36.4	29.3	65.7	1.24
	548	60.2	58.6	35.3	6.1	91.2	38.6	30.2	68.8	1.27
	573	66.6	54.0	36.1	9.9	94.6.	39.9	31.7	71.6	1.25
	598	62.8	53.4	36.4	10.2	93.9	38.6	32.0	70.6	1.2
	623	54.0	54.1	33.2	12.7	93.2	35.3	32.1	67.4	1.09
20 wt% H_3PO_4/Al-MCM-41(150)	473	37.7	74.8	25.2	–	77.0	26.2	18.5	44.7	1.41
	498	51.4	62.1	34.5	3.4	83.1	32.0	23.1	55.1	1.38
	523	64.1	56.5	39.3	4.2	91.5	39.1	28.6	67.7	1.36
	548	72.5	52.3	42.6	5.1	93.7	42.8	31.9	74.7	1.34
	573	75.3	50.0	41.9	8.1	96.2	43.5	32.1	75.6	1.35
	598	69.4	49.1	40.1	10.8	97.3	42.3	32.3	74.6	1.30
	623	60.6	51.5	37.5	11.0	94.9	39.0	31.4	70.4	1.24

Reaction conditions: activation temperature = 573 K, IPA/NAP molar ratio = 2, solvent = *n*-hexane; reaction time = 2.5 h, catalyst weight = 0.5 g loading between 0 and 35 wt% had different effects on the activity and selectivity for the isopropylation of naphthalene. The activity of the catalysts with different H_3PO_4 loadings is compared in Table 3. The first important result was that H_3PO_4-containing catalysts were more reactive than the support alone (without H_3PO_4). The results obtained also showed that the maximum naphthalene conversion and best selectivity was recorded for the catalyst with 30 wt% H_3PO_4, and the further increase of H_3PO_4 loadings resulted in a slow decrease of conversion. It is assumed [16–18] that by treating the aluminosilicate molecular sieves with phosphoric acid, the bridged OH^- groups between Si and Al atoms were replaced by $H_2PO_4^-$ ones. The substitution of the Brønsted acidic hydroxyl groups by the H_2PO_4 groups implies different consequences on the strength and density of the Brønsted acid sites. Strong Brønsted acid sites are converted into weak and moderate Brønsted acid sites, and clearly the resulting terminal hydroxyl groups have a lower acid strength than the bridged hydroxyl groups. The usefulness of moderate and weak Brønsted acid sites for the chosen reaction will be discussed in the following sections. Naphthalene is a nonpolar reagent, and it is thus suggested that only the carbocations formed on the catalyst surface are able to react with naphthalene. Therefore, the high dispersion of H_3PO_4 on AlMCM-41 surface was supposed to favor this reaction. When the H_3PO_4 loading was increased from 5% to 30%, the catalyst acid sites increase largely with H_3PO_4 being highly dispersed on the catalyst surface [19]. 1-Alkylation is a primary step for the naphthalene alkylation reaction, which is facilitated by weak and moderate Brønsted acid sites and dialkylation is a natural follow-up step with the preferred formation of 2,6-DIPN. High temperature and moderate acidity as well as a long reaction period help to improve the naphthalene conversion as well as 2,6-DIPN selectivity at the expense of 2-IPN [11].

3.2.3 *Effect of SiO_2/Al_2O_3 ratio*

The naphthalene conversion and the corresponding selectivity towards various alkylated products over 30 wt% H_3PO_4/SiMCM-41 and 30 wt% H_3PO_4/AlMCM-41 with SiO_2/Al_2O_3 ratios, 20, 70, 110, 150, 200 at 573 K at given naphthalene to isopropanol molar ratio of 1:2 are given in Table 4. The solid with a SiO_2:Al_2O_3 ratio of 200 exhibited high catalytic activity and high β,β-selectivity. For a given reaction temperature, an increasing naphthalene conversion was observed with the increase in Brønsted acidity. Although the reaction occurs mostly on the external surface, it is still possible to have some of the Brønsted acidic sites inside the pores. Therefore, we cannot relate the total Brønsted acidic sites to the conversion of naphthalene. As shown previously [21], the amount of Lewis acid sites increases with a decrease of SiO_2/Al_2O_3 ratio. On the other hand, by loading H_3PO_4 on AlMCM-41, the support loses its strong Brønsted acid sites, which are substituted by weak and medium Brønsted acid sites. Probably these acidic sites were responsible for the initiation of monoalkylation reaction, because of the higher activation energy of this step, and dialkylation can be facilitated by the higher activity of IPN and high reaction temperature. In all conversion levels, selectivity to 2-IPN is almost the same, and the 2,6/2,7-DIPN ratio was around 1.4.

3.2.4 *Effect of Molar Ratio of the Reactants*

Figure 1 summarizes the results of naphthalene isopropylation over 30 wt% H_3PO_4/AlMCM-41(200) using different naphthalene:isopropanol (IPA:NAP) molar ratios 1:1 to 4:1. The reaction was carried out at 573 K for a period of 2.5 h. On increasing the naphthalene to isopropanol molar ratio, from 1:1 to 2:1, the naphthalene conversion increased from 74 to 85.5%. In the molar ratio ranges studied, 2-IPN

Table 3 Effect of H_3PO_4 wt% on the isopropylation of naphthalene over AlMCM-41(150)

Catalyst	Naphthalene conversion (%)	Product selectivity (%)			Isomer selectivity (%)				
					IPN	DIPN			
		IPN	DIPN	Other	S_β	2,6	2,7	$S_{\beta\beta}$	2,6/2,7
Al-MCM-41(150)	60.4	58.6	33.2	8.2	79.4	38.6	35.4	74	1.09
5 wt% H_3PO_4/Al-MCM-41(150)	62.6	55.3	36.1	8.6	91.3	39.9	32.6	72.5	1.22
10 wt% H_3PO_4/Al-MCM-41(150)	69.2	51.7	38.0	10.3	91.5	40.2	32.4	72.6	1.24
15 wt% H_3PO_4/Al-MCM-41(150)	71.0	50.0	39.1	10.9	92.7	44.4	31.2	75.6	1.42
20 wt% H_3PO_4/Al-MCM-41(150)	75.3	50.0	41.9	8.1	96.2	43.5	32.1	75.6	1.35
25 wt% H_3PO_4/Al-MCM-41(150)	76.9	45.3	43.2	11.5	94.4	45.0	33.8	78.8	1.33
30 wt% H_3PO_4/Al-MCM-41(150)	80.3	42.8	44.1	13.1	96.1	47.9	34.6	82.5	1.38
35 wt% H_3PO_4/Al-MCM-41(150)	74.5	43.2	40.4	16.4	96.2	44.5	33.7	78.2	1.32

Reaction conditions: activation temperature = 573 K, reaction temperature = 573 K, IPA/NAP molar ratio = 2, solvent = *n*-hexane, reaction time = 2.5 h, catalyst weight = 0.5 g

Table 4 Effect of SiO_2/Al_2O_3 ratio on the isopropylation of naphthalene

SiO_2/Al_2O_3	Naphthalene conversion (%)	Product selectivity (%)			Isomer selectivity (%)				
					IPN	DIPN			
		IPN	DIPN	Other	S_{β}	2,6	2,7	$S_{\beta\beta}$	2,6/2,7
20	75.9	48.7	41.0	10.3	94.3	43.2	33.0	76.2	1.3
70	78.0	45.4	43.2	11.4	96.8	45.6	33.3	78.9	1.37
110	66.3	51.8	37.1	11.1	90.5	41.5	31.8	73.3	1.3
150	80.3	42.8	44.1	13.1	96.1	47.9	34.6	82.5	1.38
200	85.5	40.6	46.2	13.2	97.0	49.8	35.0	84.8	1.42
Si-MCM-41	78.1	44.1	40.4	15.5	96.2	47.3	34.1	81.4	1.38

Reaction conditions: catalyst = 30 wt% H_3PO_4/AlMCM-41, activation temperature = 573 K, reaction temperature = 573 K, IPA/NAP molar ratio = 2, solvent = *n*-hexane, reaction time = 2.5 h, catalyst weight = 0.5 g

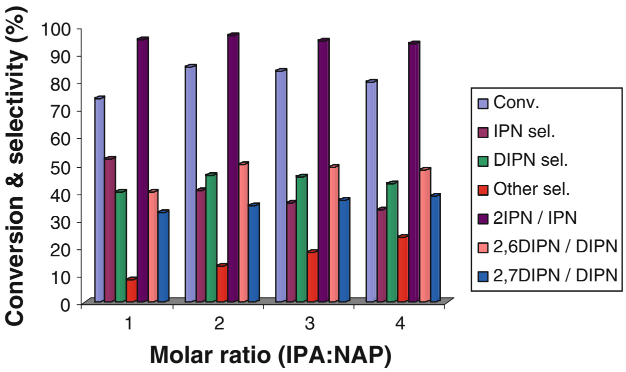


Fig. 1 Effect of (IPA/NAP) molar ratio on the isopropylation of naphthalene. Reaction conditions: catalyst = 30 wt% H_3PO_4/Al-MCM-41(200), activation temperature = 573 K, reaction temperature = 573 K, solvent = *n*-hexane, reaction time = 2.5 h, catalyst weight = 0.5 g

was formed as a major monoalkylated product with a selectivity of 91–97%. This was followed by the β,β selectivity which was about 73–86%. The increase of molar ratio slightly favors the transformation of monoalkylated products to their corresponding dialkylated products. It seems that at low naphthalene:isopropanol molar ratios, the facile monoalkylation takes place. Further availability of alcohol at higher molar ratios facilitates the conversion of monoalkylated products to dialkylated products, especially β,β-selectivity.

3.2.5 Effect of Reaction Time

The effect of reaction time on the isopropylation of naphthalene using 30 wt% H_3PO_4/AlMCM-41(200) was studied at 573 K using a IPA:NAP molar ratio of 2:1. The conversion increased from 49% for a reaction time of 1 h to a maximum of about 89% for a reaction period of 4 h and beyond this period the conversion started to decrease. On the other hand, 2-IPN selectivity decreased from 97% at 2.5 h to about 95% at 6 h, and increased further with the reaction time. β,β selectivity follows the same trend as the conversion, starting from 49.5% at 1 h and increasing to 84.7% at 4 h and then decreases to 71% at 8 h. As the β,β selectivity increased, that for 2-IPN decreased and vice versa. It can also be concluded that improving conversion always goes with higher β,β-selectivity at the expense of 2-IPN (Table 5).

3.2.6 Stability of the 30 wt% H_3PO_4/AlMCM-41(200) Catalyst

The catalytic stability of the 30 wt% H_3PO_4/AlMCM-41(200) catalyst in the isopropylation of naphthalene with isopropanol is shown in Fig. 2. After simply separating the used catalyst from the reaction medium by centrifugation, it was charged into the reaction medium for a new reaction cycle without regeneration. It was revealed that the catalyst deactivates drastically, and at the fourth reaction cycle, the conversion drops to a very low level of less than 30%. Several previous reports [1, 19, 20] claimed that HY, H-mordenite, and PW/SBA-15 catalysts went through severe deactivation due to coking. Therefore, the poor catalytic stability of 30 wt% H_3PO_4/AlMCM-41(200) may be due to formation of coke on the surface of the catalyst during the reaction. In our case, coke formation was evident from the change in the color of the catalysts, which turned black after the reaction, although we have not determined quantitatively the amount of coke. Dealumination may also be expected considering the experimental conditions used, although we have not experimental evidence of dealumination. It is verified that the amount of phosphorus leached is about 5% of the content of the catalysts, this leaching being similar in each run, in every case, about 5 of the content of P present in the catalyst before the run is leached.

Table 5 Effect of reaction time on the isopropylation of naphthalene

Time (h)	Naphthalene conversion (%)	Product selectivity (%)			Isomer selectivity (%)				
					IPN	DIPN			
		IPN	DIPN	Other	S_{β}	2,6	2,7	$S_{\beta\beta}$	2,6/2,7
1	48.7	74	13	13	90.3	27.2	22.3	49.5	1.22
2.5	85.5	40.6	46.2	13.2	97.0	49.8	35.0	84.8	1.42
3	87.0	37.6	50.4	12.0	96.4	50.5	33.8	84.3	1.49
4	88.5	34.8	48.1	17.1	95.1	49.9	34.8	84.7	1.43
6	86.2	32.1	45.9	22.0	94.5	45.1	31.5	76.6	1.43
8	80.1	34.4	40.5	25.1	96.0	40.6	30.4	71	1.33

Reaction conditions: catalyst = 30 wt% H_3PO_4/AlMCM-41(200), activation temperature = 573 K, reaction temperature = 573 K, IPA/NAP molar ratio = 2, solvent = *n*-hexane, catalyst weight = 0.5 g

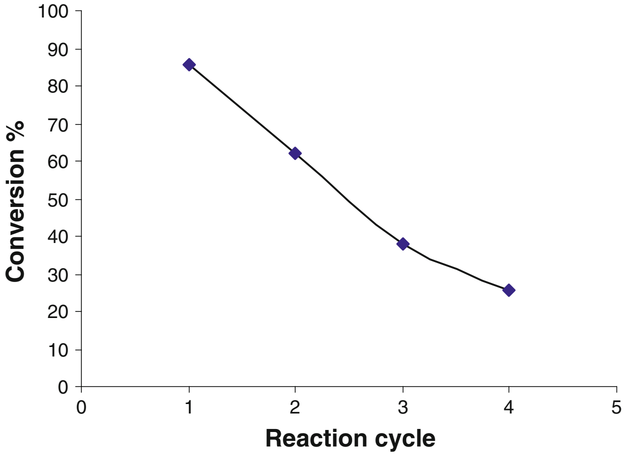


Fig. 2 Activity of 30 wt% H_3PO_4/Al-MCM-41(200) catalyst under successive catalytic tests. Reaction conditions: activation temperature = 573 K, reaction temperature = 573 K, IPA/NAP molar ratio = 2, solvent = *n*-hexane, catalyst weight = 0.5 g, reaction time for one cycle = 3 h

4 Conclusion

In the present study, AlMCM-41 with various SiO_2/Al_2O_3 ratios was synthesized and modified by impregnation with phosphoric acid. Their catalytic performance was examined in the alkylation of naphthalene in the temperature range 473–623 K. The liquid phase isopropylation of naphthalene over H_3PO_4/AlMCM-41 revealed that the reaction parameters such as temperature, SiO_2/Al_2O_3 ratio, weight percentage of H_3PO_4 loading and feed ratio changed both NAP conversion and selectivity. Moderate acidity, high temperature, and longer reaction time improved the NAP conversion and the 2,6/2,7 DIPN ratio. The medium Brønsted acid sites of the catalysts increased with the increase of H_3PO_4 loading and the SiO_2/Al_2O_3 ratio. The investigation showed that the 30 wt% H_3PO_4/Al-MCM-41(200) sample was more active than the other catalysts and optimum reaction conditions were as follows: catalyst activation temperature = 573 K, reaction temperature = 573 K, IPA/NAP molar ratio = 2, reaction time = 3 h. Under the best conditions, values of 50.5% and 87.0% for selectivity of 2,6-DIPN between DIPN products and naphthalene conversion, respectively, were obtained. It is concluded that H_3PO_4/AlMCM-41 is an environmentally friendly catalyst in the liquid-phase for the isopropylation of naphthalene and other reactions that require moderate acid sites.

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