

Acylation of 2-methoxynaphthalene over ion-exchanged β -zeolite

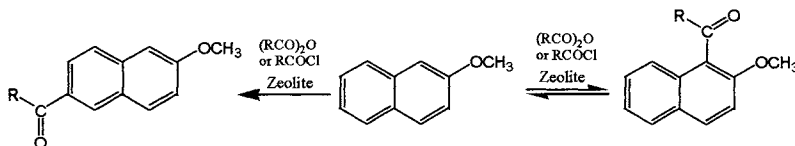
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Friedel-Crafts acylation of 2-Methoxynaphthalene was carried out over various ion-exchanged β zeolites ($M^{n+}\beta$, where M^{n+} : In^{3+} , Zn^{2+} , Al^{3+} , Fe^{3+} , La^{3+}) with various anhydride (acetic, propionic and benzoic anhydrides), or acyl chloride (acetyl, propionyl and benzoyl chlorides) acylating reagents. The results suggested that selectivity towards the 6-substituted products was higher with the larger size anhydrides, propionic and benzoic anhydrides. The metal cation type within the zeolite significantly influenced the extent of conversion and product distribution. That La^{3+} exchanged zeolite displayed higher selectivity for the 6-position acylated product with anhydrides ascribed mainly to narrowing of channels by the presence of $La(OH)^{2+}$ ions that leave no room for the formation of more bulky isomeric forms and to enhanced Bronsted acidity of the zeolite. With acyl chlorides, the recovery of ketone products was found to be remarkably low. 1-Acyl-2-methoxynaphthalenes actively underwent decylation when acyl chlorides were used as the acylation reagent.

1. INTRODUCTION

Friedel-Crafts acylation of aromatics is an important method for synthesis of aromatic ketones, used largely as intermediates in the fine chemical industry [1]. The selective acylation of 2-methoxynaphthalene (2-MN) is of particular interest. For example, 2-acetyl-6-methoxynaphthalene (6-AcMN) is recognised to be an important intermediate for the production of an anti-inflammatory drug, (S)-Naproxen [2]. It was shown a decade ago that zeolites can be used as heterogeneous catalysts for the acylation of 2-MN by acetic anhydride, and in that the selective formation of 6-AcMN was achieved with H β catalyst [3].



Since then, a number of studies reporting the effect of various parameters (e. g., solvent and zeolite types, temperature, substrate-to-catalyst ratio, zeolite modification) on the

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acylation of 2-MN over zeolites have appeared [4]. Yet, to our knowledge, there appears to be no existing report that investigated the catalytic effect of ion-exchanged β -zeolites on the acylation reactions of 2-MN, though it is known that the type and amount of metal cation on zeolite may influence the strength and distribution of acid sites. Gunnewegh et al. [4b] studied the acylation of 2-MN over Zn^{2+} exchanged MCM-41, in which Zn-MCM-41/acetyl chloride combination was found to be less favourable than in the case of H-MCM-41/acetic anhydride combination for both selectivity and regenerability. The leaching of zinc was another problem for the former combination as well.

There are a few studies in which ion exchanged $-Y$, mordenite and ZSM-5 zeolites were used in acylation of various arenes other than 2-MN. Chiche and co-workers showed that rare-earth-exchanged $-Y$ could catalyse the acylation of alkylbenzenes with carboxylic acids [5,6]. Gaare and Akporiaye [7] found that LaY was very active in the acylation of anisole and the yield increased with the level of La. Laidlaw et al. [8] determined that Zn- and Fe-exchanged zeolites ($-Y$, mordenite and ZSM-5) were very active on the benzylation of toluene. The extensive leaching of Zn was observed in the reactions, while Fe mostly remained on the zeolite.

In this study, we report the catalytic activity of the cation-exchanged β -zeolite in acylation of 2-MN, using various anhydride and acyl chloride reagents. The metal cations loaded onto zeolite by ion-exchange method were In^{3+} , Zn^{2+} , Al^{3+} , Fe^{3+} , and La^{3+} . Acylation studies were also carried out over HY and $\text{M}^{n+}Y$. However, since the conversion of 2-MN and selectivity to the 6-acylated isomer was substantially low, 20-30% and <10%, respectively, the results from the $-Y$ type zeolite are not presented here.

2. EXPERIMENTAL

2.1. Catalyst treatment and characterisation

β -Zeolite in protonated form (H β) was obtained by the calcination of $\text{NH}_4\beta$ -zeolite (Zeolyst International, CP-814E, $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio: 25) at 550°C for 10 h in air atmosphere. Metal cations were loaded onto the zeolite by stirring 5 g of $\text{NH}_4\beta$ in a 40 ml solution of 0.3 M of the proper metal chloride or metal nitrate at 80°C for 4 h. Following the ion-exchange process, the zeolite suspension was filtered, washed thoroughly by deionised water and finally dried at 120°C overnight.

BET surface areas of calcined zeolite samples were measured on a Micrometrics ASAP-2010. The cation content of samples was determined using atomic absorption and ICP-emission methods. The characteristics of catalysts are given in Table 1.

Bronsted and Lewis acidities of samples were examined by FTIR analyses of pyridine adsorbed samples following a procedure given previously [9].

2.2. Acylation reactions

Acylation reactions were carried out in a 50 ml three necked round-bottom flask connected to a condenser in an oil bath under nitrogen atmosphere. The freshly activated (550°C, 10 h) 1 g of catalyst was added quickly into the flask while still hot. 10 Mmol 2-MN, 20 mmol

Table 1
Physico-chemical properties of the ion-exchanged β -Zeolites used in the study.

M^{n+}	Metal Cation Content, wt%	BET surface area (m^2/g)	Micropore Volume (cm^3/g)
H^+	-	584	0.192
In^{3+}	2.1	461	0.160
Zn^{2+}	1.9	452	0.148
Al^{3+}	ND ^a	445	0.145
Fe^{3+}	3.4	459	0.145
La^{3+}	0.7	395	0.133

^aND: Not determined

acylating reagent and 4.5 mmol tetradecane as an internal standard were dissolved in 20 ml nitrobenzene which was previously dried over $CaCl_2$ and distilled before use, and then introduced into the reaction flask through a dropping funnel.

The reactions were performed at 130°C unless otherwise stated. Aliquots of samples were taken periodically and analysed by GC and GC/MS techniques.

2.3. Synthesis of authentic compounds

1-Acyl-2-methoxynaphthalenes were synthesised by acylation of 2-MN over a stoichiometric amount of $AlCl_3$ with the corresponding acyl chloride compound. Dry dichloromethane solution of 2-MN was cooled down to -15°C. Acyl chloride was added gradually and stirred for an hour at -15°C. At the end of reaction, to the mixture was added dilute HCl solution and the product was extracted by dichloromethane and purified by recrystallization using petroleum ether and by column chromatography on silica gel using hexane-dichloromethane as eluent.

6-AcMN was commercially available. However other 6-Acyl-2-methoxynaphthalene compounds were recovered from zeolite catalysed acylation of 2-MN through column chromatography using hexane-dichloromethane eluent.

3. RESULTS AND DISCUSSION

3.1. Acylation of 2-methoxynaphthalene with anhydrides

Some general remarks can be drawn on the basis of the results from acylation reactions performed with anhydrides. Regardless of the structure of anhydride and metal type on the zeolite used, 1-acyl and 6-acyl methoxynaphthalene products were the major acylation products, while selectivity of other acylated isomers was <10% overall. Except the reactions with propionic acid, 8-acyl isomer of other ketone products comprised the most (3-5%). Overall ketone selectivity was generally >95%. No indication of protideacylation reaction [3,10] or intermolecular trans-acylation reactions [11], which were reported to be principal reaction types responsible for deacylation of 1-acyl-2-methoxynaphthalene primary product, were observed in the presence of anhydrides.

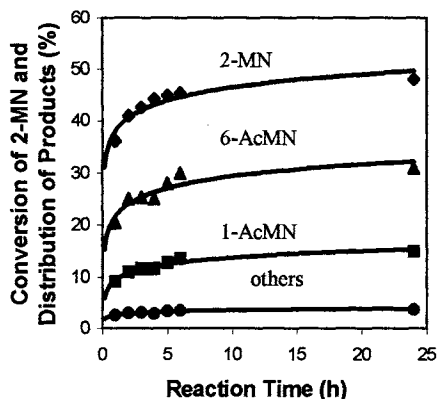


Figure 1. Acylation of 2-MN with acetic anhydride over H β at 130°C

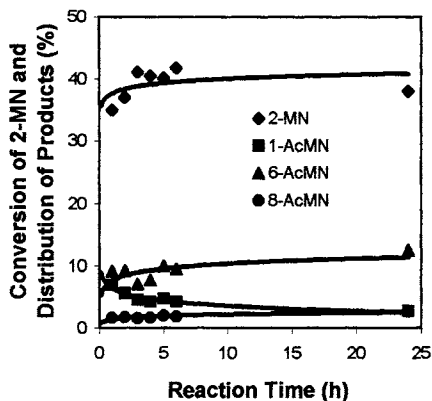


Figure 2. Acylation of 2-MN with acetyl chloride over H β at 130°C

Figure 1 shows the reaction run for the acylation of 2-MN with acetic anhydride over H β at 130°C. Apparently the conversion almost ceased after 6 h of reaction time and that there appears no indication of interconversion between product types.

The results of the acylation reactions of 2-MN with acetic anhydride over ion exchanged β zeolites are presented in Table 2. Longer reaction times slightly lowered the 6-AcMN product selectivity, while the 1-AcMN selectivity increased slightly in general when reactions were performed with acetic anhydride.

Table 2

Acylation of 2-methoxynaphthalene by acetic anhydride over Mⁿ⁺ β zeolite.

M ⁿ⁺	Time (h)	Conversion%	Product Selectivity%	
			1-AcMN	6-AcMN
H ⁺	2	40	28	65
	24	48	30	62
H ⁺ ^a	2	47	27	68
	24	47	30	63
In ³⁺	2	46	37	56
	24	58	41	53
Zn ²⁺	2	20	28	66
	24	36	29	64
Al ³⁺	2	34	27	65
	24	46	30	63
Fe ³⁺	2	32	29	64
	24	43	32	61
La ³⁺	2	34	19	75
	24	41	21	73

^aat 160°C

With the H β zeolite, the elevation of reaction temperature to 160°C increased the conversion rate, though the maximum 2-MN conversion was comparable to that obtained at the lower reaction temperature after 24 h of reaction. The acylation reactions were terminated at this conversion level due to catalyst deactivation. It showed no effect on the product selectivity as well.

Ion exchanging the β zeolite influenced its catalytic activity for acylation reactions. At 130°C, although the conversion rate and maximum conversion of 2-MN were the highest with In β , this catalyst gave rise to the lowest selectivity for 6-AcMN. The conversion of 2-MN with other cation-exchanged zeolites was either comparable to or less than that observed with H β zeolite. The greatest selectivity for 6-AcMN product was obtained with La β -zeolite. However, the conversion of 2-MN was lower with this catalyst than with H β . Zn²⁺ exchanged zeolite displayed the lowest activity to the acetylation reaction.

The regio-selectivity of acylation reactions should be influenced by the geometry of channels within zeolite. The introduction of larger cations reduced the effective size of these channels as can be deduced from the reduced BET surface areas of the ion-exchanged zeolites (Table 1), La loaded zeolite having the lowest BET surface area. However, intrinsic activity of cations can also play direct role in conversion of 2-MN and regio-selectivity of the products. It was reported that different metal halide compounds revealed different regio-selective activity to the acylation of 2-MN when used in catalytic amounts [13].

FTIR analyses of pyridine adsorbed samples revealed that H⁺-, Al³⁺-and La³⁺- β zeolites contained only Bronsted acidity, while In³⁺, Fe³⁺ and Zn²⁺ exchanged zeolites contained both Bronsted and Lewis acid sites. In β and Fe β zeolites comprised similar Lewis-Bronsted ratio while the zinc exchanged zeolite possessed the highest proportion of Lewis sites. It has been reported that La exchange enhances the Bronsted acid strength of zeolites [7,14]. Bronsted acid sites appear to be more important in polarisation of anhydride into a more electrophilic species which then attacks the benzene ring resulting in the formation of ketone.

Table 3

Acylation of 2-methoxynaphthalene by propionic or benzoic anhydride over Mⁿ⁺ β zeolite.

Anhydride	M ⁿ⁺ -	Time (h)	Conversion%	Product Selectivity%	
				1-ACMN	6-ACMN
Propionic	H ⁺	2	36	12	75
		24	50	11	75
	In ³⁺	2	35	13	75
		24	56	13	75
	La ³⁺	2	28	7	81
		24	43	7	79
Benzoic	H ⁺	2	23	20	74
		24	64	22	72
	In ³⁺	2	29	71	29
		24	45	60	38
	La ³⁺	2	2	12	88
		24	3	9	91

Table 3 presents the results from the acylation of 2-MN with propionic anhydride or benzoic anhydride. The comparison of the data given in Tables 2 and 3 indicates that regioselectivity of products is dependent on the anhydride structure used. The higher ether conversion and selectivity to the acylation at 6-position were achieved with propionic and benzoic anhydrides than with acetic anhydride over H β . Yet, benzoic anhydride afforded a slower reaction rate. This may be due to slower diffusion of bulkier benzoic anhydride. Molecular size of 1-acyl products should follow the order benzoyl>propionyl>acetyl. Hence, the formation of more bulky isomers, such as 1-acyl isomer, should be disfavoured owing to sterical constraints placed by the geometry of straight channels within the zeolite, which has 7.6 x 6.4 Å opening.

With propionic anhydride, the overall selectivity to the 1- and 6- position acylation was lower (85-87%), this being due to the formation of a diacylated ether product (3-4%) and increased selectivity to an acylated isomer with unknown structure (6-7%). Analogous to those with acetic anhydride, somewhat higher conversion was achieved over In β , yet product distribution was comparable. The conversion was lower and 6-position acylation was more selective over La β .

The conversion of 2-MN with benzoic anhydride over In β was lower compared to that achieved with H β , and the selectivity trend altered in favour of 1-benzoyl-2-methoxynaphthalene product with the catalyst. In the case of La β , the conversion was only <3%. These results indicate that penetration of bulky anhydride thorough catalyst pores is highly restricted with the presence of cations and eventually blocked with the presence of La.

3.3. Acylation of 2-methoxynaphthalene with acyl halides

Activity of catalysts was distinctly different for acylation reactions with acyl chlorides as compared to the reactions with anhydrides. Some distinct features were observed when the reactions were performed in the presence of acyl halides: the product recovery was substantially low with acyl halides and excluding the reaction performed over Fe β with acetyl

Table 4

Acylation of 2-methoxynaphthalene by acetyl chloride over Mⁿ⁺ β zeolite.

M ⁿ⁺ -	Time (h)	Conversion%	Product Recovery% ^a	Product Selectivity%		
				1-AcMN	8-AcMN	6-AcMN
H ⁺	2	37	50	29	11	61
	24	38	50	19	14	68
In ³⁺	2	44	28	25	15	60
	24	46	25	8	15	73
Zn ²⁺	2	60	37	8	23	69
	24	59	43	2	28	70
Al ³⁺	2	34	59	27	9	62
	24	46	47	16	12	71
Fe ³⁺	2	32	59	29	4	64
	24	43	44	32	11	61
La ³⁺	2	37	75	39	8	53
	24	39	74	26	10	64

^aBased on 2-methoxynaphthalene consumed.

Table 5.

Acylation of 2-methoxynaphthalene by acyl chlorides over $M^{n+}\beta$ zeolite.

Acyl chloride	M^{n+} -	Time (h)	Conversion %	Product Recovery ^a	Product Selectivity%		
					1-ACMN	6-ACMN	8-ACMN
Propionyl	H^+	2	45	74	18	41	6
		24	53	64	12	47	6
	Zn^{2+}	2	69	45	1	56	11
		24	74	45	2	72	13
Benzoyl	H^+	2	66	59	50	38	5
		24	79	50	30	56	6
	Zn^{2+}	2	72	77	38	46	5
		24	81	51	22	61	6

^aBased on 2-methoxynaphthalene consumed.

chloride, 1-acyl substituted product was significantly lowered as the reaction proceeded (Figure 2 and Tables 4 and 5).

The reaction mixture appeared dark brown or black, while it was yellow for the reactions with acid anhydrides. These indicate that catalytic activity was altered by the interaction of some primary or secondary reagents present within the reaction medium that favoured condensation reactions and deacylation of 1-acyl isomer.

Excluding $La\beta$, metal exchanged β zeolites resulted in higher conversion than those attained with $H\beta$ after 24 hour of acylation reaction with acetyl chloride. However product recovery determined by GC was significantly low. The results with $Zn\beta$ appear to be interesting. The higher conversion over $Zn\beta$ which has relatively higher Lewis acidity accompanied lower 1-AcMN and higher 8-AcMn (Table 4). Conversion values with $La\beta$ were comparable to those achieved with $H\beta$. Nevertheless, the product recovery was the highest.

With propionyl chloride a mono acylated product of 2-MN with an unknown isomeric form was determined. Its relative selectivity was 35 and 28% at the second hour of reaction and 27 and 12% after 24 h, with $H\beta$ and $Zn\beta$, respectively. On the other hand, 1-acyl substituted product selectivity was negligible with $Zn\beta$ analogous to the case with acetyl chloride (Table 5).

The 1-acyl selectivity was still high for the reaction with benzoyl chloride. In comparison, $Zn\beta$ is more active in deacetylation and selective formation of 6-benzoyl-2-methoxynaphthalene directly. Probably, most of the 1-benzoyl-2-methoxynaphthalene product forms at the outer surface of the catalyst mainly over $Zn\beta$ and that it is improbable for this isomer to penetrate to active centres within the narrow sized channels to undergo deacylation which accounts for the higher recovery of 1-benzoyl-2-methoxynaphthalene.

4. CONCLUSIONS

On the basis of the results summarised above, it can be stated that cation-exchanging the β -zeolite remarkably alters its activity in acylation of 2-MN and product regio-selectivity as well. $La\beta$ yielded higher 6-acyl-2-methoxynaphthalene selectivity with anhydrides. 2-MN

conversion was lower with ion-exchanged β and even negligible with La β when benzoic anhydride used as acylating reagent probably due to size incompatibility between the cation blocked channels and transition states, and lesser diffusibility of the anhydride. Overall ketone selectivity for the acylation reactions with acyl chloride reagents was found to be significantly low due to facile formation of carbonaceous materials. 1-Acyl-2-methoxynaphthalenes were noticed to undergo deacylation in the presence of acyl chloride, while no such attitude occurred with anhydrides.

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