THE SHAPE-SELECTIVE ACYLATION OF 2-METHOXYNAPHTHALENE, CATALYZED BY ZEOLITES Y, BETA AND ZSM-12*

Gillian HARVEY and Georg MÄDER
Technisch-Chemisches Laboratorium,
ETH-Zentrum, Universitätsstr. 6, 8092 Zürich, Switzerland

Received September 13, 1991
Accepted October 22, 1991

The Friedel–Crafts acylation of 2-methoxynaphthalene (2MN) was investigated using zeolites USY, Beta and ZSM-12 as catalysts under batch conditions at 100 and 180°C. Two ketone isomers, 1-acetyl-2-methoxynaphthalene (1AC) and 2-acetyl-6-methoxynaphthalene (2AC) were produced; the selectivity of the reaction could be influenced by the zeolite used. USY produced only the 1AC isomer whereas Beta and ZSM-12 produced both. Selective synthesis of 2AC was achieved by optimization of the reaction conditions using zeolite Beta as the catalyst. It was also observed that the 1AC ketone is unstable in contact with acid zeolite catalysts and undergoes protiodeacylation, a reaction previously only observed in the presence of strong mineral acids.

Friedel–Crafts acylation is a versatile method for synthesizing aromatic ketones but is associated with various problems when the reactions are carried out with conventional catalysts. More than stoichiometric amounts of the catalyst (Lewis acids such as $AlCl_3$) are required due to complexation with the ketone which has to be hydrolysed in order to win the product, leading to destruction of the catalyst and problems of waste disposal.

The use of zeolites as catalysts for Friedel–Crafts acylation could solve many of these problems. Reports on zeolite-catalyzed acylation of aromatics have shown that zeolites are a viable alternative to conventional catalysts such as $AlCl_3$. Corma et al.[1] investigated the acylation of anisole by phenylacetyl and phenylpropanyl chlorides catalyzed by HY and HBeta. Chiche et al.[2] acylated toluene with a series of straight-chain carboxylic acids. The reactions were catalyzed by CeY; the highest yield was achieved with octanoic acid but acetic acid failed to acylate at all. In both investigations, the *para* isomer was the predominant isomer produced, which is also observed in classically-catalyzed Friedel–Crafts reactions.

We have investigated the acylation of 2-methoxynaphthalene (2MN) by acetic anhydride catalysed by 12-ring zeolites. Of the possible positions for electrophilic attack, two are most likely: the 1 position yielding 1-acetyl-2-methoxynaphthalene

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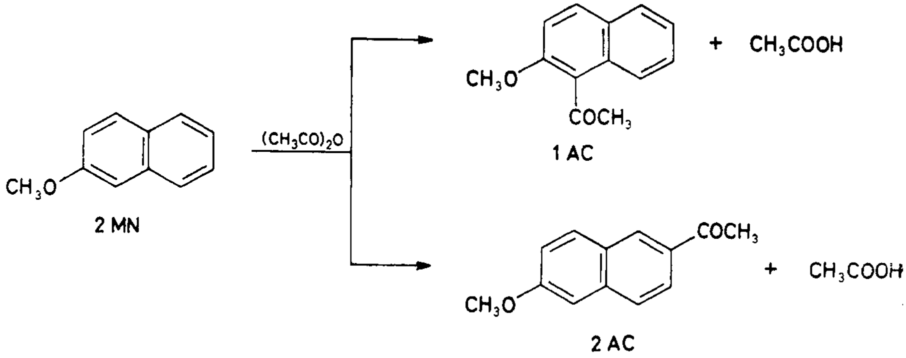
* Presented as a poster at the *International Symposium "Zeolite Chemistry and Catalysis", Prague, September 8—13, 1991.*

(1AC) and the 6 position yielding 2-acetyl-6-methoxynaphthalene (2AC) (see Scheme 1). The aim of the work was to selectively synthesize the ketones by exploiting the shape-selective potential of zeolite catalysis.



SCHEME 1

Under classical catalytic conditions, using $AlCl_3$ as the catalyst, it was possible to obtain one isomer or other by suitable choice of solvent and addition procedure[3]. We have used three 12-ring zeolites, USY, Beta and ZSM-12, as catalysts in this reaction and have found that the choice of the zeolite becomes the most important factor in determining the selectivity of the reaction.

EXPERIMENTAL

Acylation procedure: Acylation of 2MN was performed under batch conditions, at 100 or 180°C, atmospheric pressure, with acetic anhydride as the acyl component and sulfolane as the solvent. 2MN (50 mmol) and acetic anhydride (25 mmol) were dissolved in 25 ml solvent before 1 g of freshly activated (500°C, 1 h) catalyst was added. Each molecule of acetic anhydride acylates one 2MN and gives one molecule of acetic acid. Therefore the 2MN is present in two-fold excess; the values for conversion of 2MN in the tables and figures take this into account. The reaction was run for 24 h and samples were taken periodically and analysed by GC (HP 5890II, cross-linked methyl silicone column, on-column injection).

Zeolite catalyst preparation and characterization: Zeolites Y and Beta were provided by CU Chemische Fabrik Uetikon, ZSM-12 was synthesized according to ref.[4]. Zeolite Y was converted to USY by ion exchange with NH_4NO_3 and calcination at 750°C, the procedure being repeated three times. Zeolite Beta was exchanged with 0·1M-HCl for one hour at room temperature and then calcined at 550°C and ZSM-12 was treated three times with 1M-HCl at 90°C, before being calcined at 550°C. The integrity of the crystal structure after treatment was checked by X-ray diffraction. Elemental analysis was determined by atomic absorption spectroscopy (Varian SpectrAA-10), BET surface areas were measured on a Micromeritics ASAP-2000 and the crystallite sizes were measured by SEM (Hitachi S-900). The results are given in Table I.

RESULTS

When the acylation reactions are carried at 100°C, both USY and Beta catalyse the reaction so efficiently that conversion reaches 63–71% after 3 h (Table II). Then the conversion levels off slowly to a final value of 70–73% after 24 h. ZSM-12 is less active and only reaches a conversion of 23%. The differences between the zeolites become apparent when the products are considered.

When USY catalyses the reaction only one ketone, 1AC, is produced with hig hselectivity. In general, all the reactions performed were very selective for one or both ketones. It seems that the very open internal structure of USY (structure type FAU, ref.[5]) favours electrophillic attack at the most activated 1-position to the extent that no other product is formed.

In contrast to USY, zeolites Beta and ZSM-12 influence the reaction so that both ketones are produced. Beta, in particular, is very active but produces more 1AC

TABLE I

Characteristics of zeolite catalysts

Zeolite	Si : Al	Crystallite size, μm	Surface area (BET), m^2/g
USY	4·7 : 1	1	572
HBeta	25 : 1	<1	665
HZSM-12	65 : 1	2	313

TABLE II

Acylation of 2-methoxynaphthalene at 100°C

Zeolite	Time h	Conversion of 2 MN, %	Yield of 1 AC, %	Yield of 2 AC, %	1AC/2AC ratio
USY	0·25	50·9	47·3	0	–
	3·0	63·3	58·8	0	–
	25·0	70·0	65·9	0	–
HBeta	0·17	44·1	38·0	4·6	8·3
	3·0	71·2	59·8	11·2	5·3
	21·0	73·4	60·8	13·8	4·4
ZSM-12	0·25	9·2	6·0	0·7	8·6
	4·0	16·8	12·3	1·4	8·8
	22·5	23·2	17·2	1·9	9·1

than 2AC throughout. The 1AC : 2AC ratio decreases with reaction time, i.e. the amount of 2AC produced relative to 1AC increases as the reaction proceeds. ZSM-12 is not only less active under the same conditions but yields less 2AC relative to 1AC, and the 1AC : 2AC ratio even increases slightly during the reaction.

The acylation reaction was repeated at higher temperatures with the zeolites Beta (Fig. 1*a*) and ZSM-12 (Fig. 1*b*) to try to improve the 2AC selectivity. At 180°C, the conversion reaches a maximum very quickly for both zeolites but then declines. Parallel to this, the yield of 1AC climbes rapidly and then falls off, indicating that the ketone is unstable in the presence of the catalyst and breaks down. The most

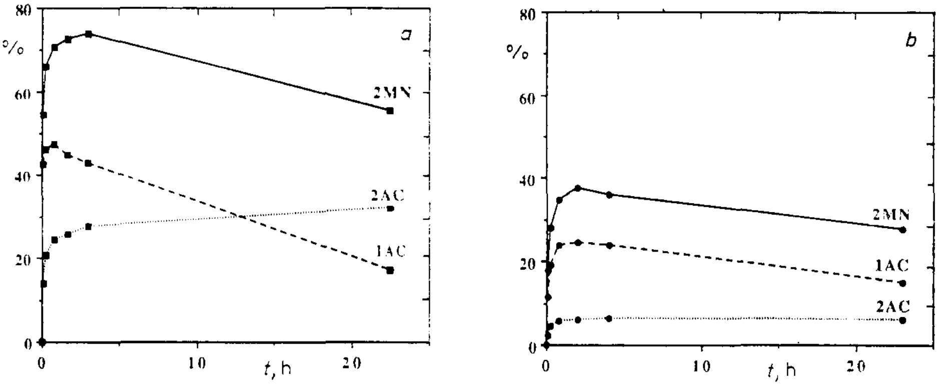


FIG. 1

Acylation of 2-methoxynaphthalene at 180°C catalyzed by zeolites Beta (*a*) and ZSM-12 (*b*). Conversion of 2 MN (———), defined as mole % 2 MN reacted × 0·5; yield of 1 AC (— — —); yield of 2 AC (· · · · · ·)

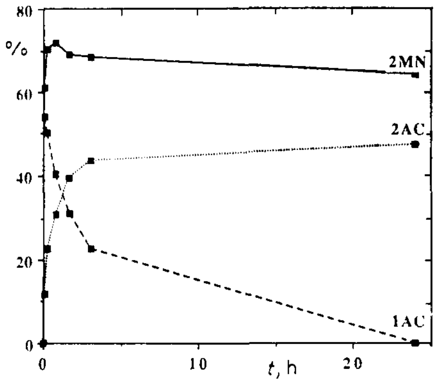


FIG. 2

Acylation of 2-methoxynaphthalene at 100°C catalyzed by a double amount of zeolite Beta. Conversion of 2 MN (———); yield of 1 AC (— — —; yield of 2 AC (· · · · · ·)

probable cause is deacylation, yielding 2MN, which would account for ther eversal in conversion. 2AC, in contrast, continues to form steadily throughout the reaction, with no sign of deacylation occurring. The final 1AC : 2AC ratio attained after 24 h was 0·53 for Beta and 1·85 for ZSM-12, i.e. a large improvement in 2AC selectivity in both cases.

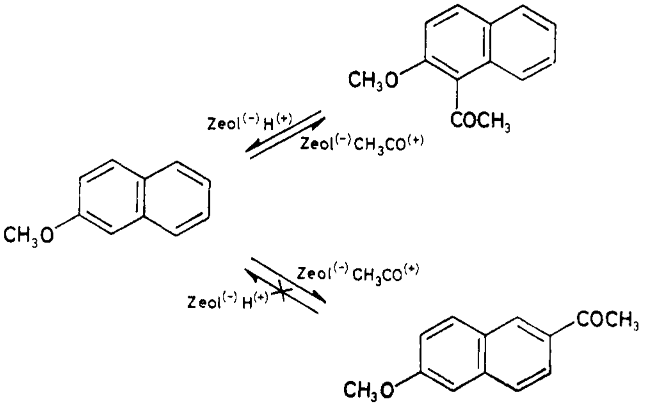
The difference in product selectivities observed for Beta and ZSM-12 compared to USY can be explained by consideration of the framework structures. Zeolite Beta consists of a 3-dimensional, 12-ring channel system, but with a high degree of stacking disorder[6]. The 12-rings making up the channels (2 straight and 1 tortuous, all interconnecting) are non-planar and are smaller in diameter than the 12-rings in USY; approximately 7·3 × 6·0 Å for the straight channels and 5·6 × 5·6 Å for tortuous channel. The more confined internal environment of Beta restricts access to the 1-position of 2MN and increases the chances of attack at the somewhat less favourable 6 position to form the more linear 2AC molecule.

ZSM-12 (MTW) is built up of distorted 12-rings forming a one-dimensional channel system[7]. The diameter of the 12-rings is 5·5 × 6·2 Å compared to 7·4 Å for FAU. The available internal space is therefore considerably restricted. The one-dimensional channel system and the rather large crystals (2 μm) are probably the cause of the low rate of reaction observed.

Increasing the temperature of reaction leads to an increase in the rate of acylation of 2MN but also in the rate of deacylation of the preferentially formed 1AC product. This results in an improvement in the 2AC selectivity as the reaction progresses. In order to optimise the synthesis of 2AC further reaction parameters such as solvent, acyl component and amount of catalyst were varied. Other solvents such as nitromethane and carbon tetrachloride made little difference to the 1AC : 2AC ratio. Acetyl chloride inplace of acetic anhydride led to a reduction in conversion and acetic acid did not acylate at all, as was expected. The most successful experiment is shown in Fig. 2 where the amount of Beta zeolite was doubled (2 g). The reaction temperature was 100°C. The rate of deacylation of 1AC was accelerated to such an extent that after 24 h, 2AC was the only ketone present in the reaction mixture, The selectivity of the reaction fell to 74%, however, possibly due to demethylation to yield acetylnaphthol.

DISCUSSION

Zeolite catalysts can be used successfully for the acylation of 2-methoxynaphthalene. The acid strength of the zeolites, particularly USY and Beta, is sufficient to produce high conversions in reasonable reaction times. The internal pore structures of the 12-ring zeolites also enable the acylation to be performed selectively. The super-cages of USY favour attack at the most activated position, to form 1AC exclusively at temperatures low enough to prevent the deacylation reaction occurring to any great extent. Zeolite Beta, with narrower 12-ring channels and no cages, also allows the acylation at the less favoured 6 position. Selective synthesis of the 2AC isomer is achieved by breaking down the kinetically-controlled product, 1AC, by protiodeacylation. Friedel–Crafts acylation is usually irreversible, but protiodeacylation, electrophillic attack by H^+ at the acyl position, can occur with sterically hindered ketones (generally *ortho*) such as 1AC in the presence of concentrated mineral acids[8]. This has now also been demonstrated in the presence of zeolite catalysts, and can be exploited to allow a thermodynamically stable product such as 2AC to form exclusively (see Scheme 2). The synthesis of 2AC probably occurs through a combination of direct acylation of 2MN and rearrangement of 1AC. A more detailed description of the deacylation of 1AC will be presented elsewhere.



SCHEME 2

This work was supported by KWF project No. 1814.1 "Zeolites as Catalysts", in collaboration with CU Chemische Fabrik Uetikon.

REFERENCES

1. Corma A., Climent M. J., Garcia H., Primo J.: Appl. Catal. *49*, 109 (1989).
2. Chiche B., Finiels A., Gautheir C., Geneste P.: J. Org. Chem. *51*, 2128 (1986).
3. Girdler R. B., Gore P. H., Hoskins J. A.: J. Chem. Soc., C *1966*, 181.
4. Ernst S., Jacobs P. A., Martens J. A., Weitkamp J.: Zeolites *7*, 458 (1987).
5. Meier W. M., Olson D. H.: *Atlas of Zeolite Structure Types*, 2nd ed. Butterworths, London 1987.

6. Newsam J. M., Treacy M. M. J., Koetsier W. T., DeGruyter C. B.: Proc. R. Soc. London, A *420*, 375 (1988).
7. La Pierre R. B., Bohrman A. C. jr., Schlenker J. L., Wood J. D., Rubin M. K., Rohrbaugh W. J.: Zeolites *5*, 346 (1985).
8. Al-Ka'bi J., Farooqi J. A., Gore P. H., Nassar A. M. G., Saad E. F., Short E. L., Waters D. N.: J. Chem. Soc., Perkin Trans. 2 *1988*, 943.