



Zeolite catalyzed highly selective synthesis of 2-methoxy-6-acetylnaphthalene by Friedel-Crafts acylation of 2-methoxynaphthalene in acetic acid reaction media

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ABSTRACT

Zeolite catalyzed Friedel-Crafts acylation of 2-methoxynaphthalene to produce 2-methoxy-6-acetylnaphthalene with high selectivity and conversion has been a challenging task, because the obtained compound is a key intermediate for an anti-inflammatory agent, Naproxen. However, no satisfactory results have been obtained with zeolite catalysts, and harmful solvents have been used to gain a high selectivity together with a high conversion. Here, we report the synthesis of 2-methoxy-6-acetylnaphthalene from 2-methoxynaphthalene with a high selectivity and a high conversion under an unprecedented simple reaction system; acetic anhydride as an acetylating agent, acetic acid as a solvent, and proton-type zeolite catalysts with low acidity. Among the examined zeolites, a proton-type H-MOR ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$) with a low acid content shows a conversion of 82% and an 86% selectivity for 2-methoxy-6-acetylnaphthalene. Further, detailed control experiments using H-MOR catalyst in acetic acid solvent were carried out to propose a plausible reaction mechanism.

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1. Introduction

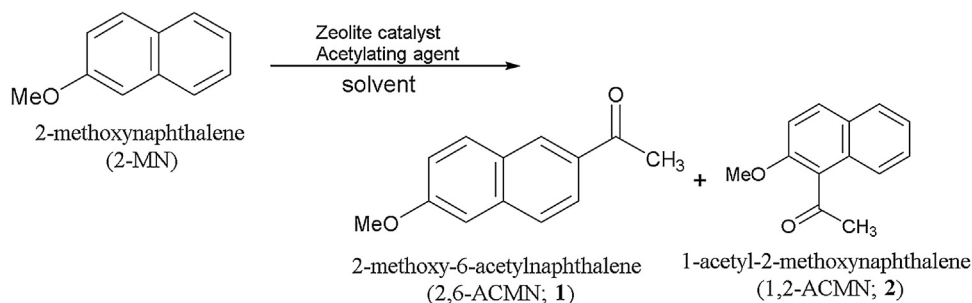
Friedel–Crafts acylation, an efficient method for preparing acetylated aromatics, has been widely used in both laboratory-scale synthesis and practical production of chemicals. The resulting acetylated aromatics are important substances that are widely used for manufacturing products such as pharmaceuticals, agrochemicals, flavors and fragrances. Generally, the acylation reaction can be adequately promoted by a Lewis-acid catalyst such as HF, BF_3 and AlCl_3 . However, because there is a growing demand for the development of environmentally benign chemical processes, the use of alternative catalysts, such as solid-acid catalysts, has attracted attention. In particular, zeolite-catalyzed reactions of anisole to give 4-acetylanisole have been investigated by many researchers, and the highly regioselective synthesis of this isomer has been attributed to the shape-selectivity of the zeolite catalysts [1–3].

2-Methoxy-6-acetylnaphthalene (2,6-ACMN; **1**) shown in Scheme 1 is a key intermediate used in the synthesis of the anti-inflammatory agent, Naproxen, [(2S)-2-(6-methoxy-2-naphthyl)propanoic acid]. In 1999, Heinichen and Höldrich

reported the acetylation of 2-methoxynaphthalene (2-MN) catalyzed by H-BEA zeolite in sulfolane as a solvent to give a 54% conversion of 2-MN with a 49% selectivity for **1** [4]. In 2000, Lee et al. comprehensively explored the acetylation of 2-MN by using acetic anhydride (Ac_2O) in the presence of H-Y, H-MOR, and H-BEA zeolite catalysts in 1,2-dichloroethane solvent. The reaction over H-MOR ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 8.0$) resulted in a 60% conversion of 2-MN with a low selectivity for **1** (8.4%), and it was also claimed that 1-acetyl-2-methoxynaphthalene (1,2-ACMN; **2**) was formed at the external surface of the zeolite [5]. A mechanism for the reaction on H-BEA zeolite in nitrobenzene as a reaction medium has been proposed by Fromentin et al. [6]. Some researchers have claimed that in acylation reactions of 2-MN by zeolite catalysts, the formed 1,2-ACMN (**2**) reverts to the starting substance 2-MN [6–8]. Approaches to the reactions over H-BEA zeolite by using microwave irradiation have been recently reported by Bai et al. [9], whereas Blanco et al. used a modified heteropoly acid catalyst [10]. However, no satisfactory synthesis of the isomer **1** has been accomplished by the acetylation of 2-MN. A kinetic study of the acetylation of 2-MN over dealuminated H-Y zeolite revealed that the reaction proceeds by an Eley–Rideal mechanism, and the formation of 1,8-ACMN and the deacetylated compound have been also discussed [11]. In 2008, Schster and Höldrich introduced a reaction catalyzed by a Nafion/silica hybrid catalyst in sulfolane and toluene solvents that showed a high conversion and a high selectivity for **1** with small

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Scheme 1. Friedel-Crafts acylation of 2-methoxynaphthalene over zeolite catalyst.

amounts of 1,7-ACMN accompanied. However, reactions on ion-exchanged BEA zeolites such Fe³⁺-exchanged BEA in sulfolane gave low conversions and low selectivities [12]. Many investigators have explored zeolite-catalyzed acylation reactions of 2-MN; however, the reactions require harmful solvents such as nitrobenzene, 1,2-dichloroethane, and sulfolane to achieve a high conversion of 2-MN and a high selectivity for **1**.

In another approach, Gunnewegh et al. used the mesoporous silica [Al]MCM-41 to achieve a 42% conversion of 2-MN and a 96% selectivity for **2** in 1,2-dichloroethane or nitrobenzene as solvents [13]. Reactions with mesoporous silica or ion-exchanged clay as catalysts did not give satisfactory results, and the reactions were carried out in nitrobenzene or 1,2-dichloroethane as solvents [14]. An examination of numerous reports on the acetylation of 2-MN over zeolite catalysts strongly suggests that the acetylation of 2-MN generally occurs in a kinetically controlled manner at the 1-position, leading to **2**, whereas the acetylation at the 6-position gives **1** as the thermodynamically more stable product that could be formed in a shape-selective manner [5,15].

Because there was no satisfactory established method for the selective synthesis of **1** from 2-MN by a zeolite-catalyzed Friedel-Crafts acylation, we attempted to overcome this problem on the basis of the following concepts: (i) the use of a zeolite catalyst, (ii) the use of Ac₂O or acetic acid (AcOH) as the acylating agent, and (iii) the use of an appropriate solvent. The last is a critical factor, because the progress of the Friedel-Crafts acylation is severely dependent on the combination of catalyst and solvent that is used. Furthermore, the reaction must be green and environmentally benign, and it must not require harmful or hazardous solvents, such as nitrobenzene, 1,2-dichloroethane, and sulfolane, as used previously. Therefore, the development of an alternative reaction system is a challenging and urgent task in constructing a green chemical process [16].

Here, we report the development of a Friedel-Crafts acylation of 2-MN by Ac₂O in an acetic acid medium over zeolite catalysts that proceeds with a high conversion together with a high selectivity. We present reaction profiles based on the control experiments over an H-MOR (SiO₂/Al₂O₃ = 200) catalyst in acetic acid and propose a plausible mechanism of this catalytic reaction.

2. Experimental

2.1. Characterization

Powder X-ray diffraction (XRD) was measured by a Shimadzu XRD-6000 diffractometer with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). Elemental analyses were performed using a X-ray Fluorescence Spectroscopy (XRF) (Bruker S8 Tiger). Nitrogen adsorption and desorption isotherm measurements were carried out on a Belsorp 28SA apparatus (Bel, Japan). Solid-state ²⁹Si magic angle spinning (MAS) NMR and ²⁷Al NMR spectra were recorded at ambient tempera-

ture by using a 4-mm diameter zirconia rotor at a spinning rate of 6 kHz (ECA-500 NMR spectrometer, JEOL). The ratios of SiO₂/Al₂O₃ in MOR (200) is almost the limit of measurement, and MOR(200) was allowed to adsorb NH₃ using an ammonia water (NH₃ aq.) for enhancement of the intensity. Thermal gravimetric and differential thermal analyses (TG-DTA) were carried out by using a Shimadzu DTG-50 analyser at a ramping rate of 10 °C/min under an air stream. The crystal size and morphology were measured by a field emission scanning electron microscopy (FE-SEM) (S-4800; Hitachi High-Technologies, Japan). The products were analysed by a Shimadzu Gas Chromatograph GC-18 with FID (Column: Ultra-1 capillary column; Agilent Technologies, U.S.A.).

2.2. Materials

2-Methoxynaphthalene and 2-methoxy-6-acetylnaphthalene were purchased from Tokyo Chemical Industry, Co., LTD. Acetic anhydride and acetic acid and other solvents were purchased from Nacalai Chemicals. All of used zeolites are commercially available; BEA(25) was purchased from Zeolyst, other zeolites such as LTL(6) (TSZ-500HOA, Tosoh), FER(17) (TSZ-720KOA), H-Y(5.6), H-Y(300) (USY HSZ-390HUA), H-MOR (TSZ-600HOA, HSZ-630HOA, TSZ-650HOA, HSZ-690HOA) and H-ZSM-5(190), H-ZSM-5(70) (HSZ-860NHA and HSZ-870NHA) were purchased from Tohsoh. NaY(200) was purchased from JGC Catalysts and Chemicals and protonated before use. H-BEA zeolites (SiO₂/Al₂O₃ = 150 and 200) were hydrothermally synthesized by the HF method [17]. MAPO-5 (MgO/Al₂O₃ = 0.1) and ZAPO-36 (ZnO/Al₂O₃ = 0.1) were prepared according to our recent reports [18,19]. Zeolite catalysts were used after calcination at 600 °C for 4 h. The numbers in parentheses are SiO₂/Al₂O₃ ratio.

2.3. Reaction

The typical reaction procedure; the prescribed amount of 2-MN (2.0 mmol), an acetylating agent (acetic anhydride, 20 mmol) and zeolite catalyst (0.50 g) were suspended in AcOH (10 mL), and then the resulting mixture was stirred at 150 °C. After cooling to room temperature, a small portion of the reaction solution was filtrated and an aliquot was analysed by GC to determine the product yield and selectivity for each isomer.

2.4. Analysis of the occluded organic molecules in the zeolite

The catalyst well-dried at 90 °C was put in a Teflon beaker, and suspended in cold water. Then, HF solution (55%) was added dropwise slowly to resolve the zeolite. Resulting mixture was transferred to a separatory funnel, and organic compounds were extracted with CHCl₃ (20 mL \times 2). The organic layer was washed with brine and dried with Na₂SO₄, and then, evaporated to dryness. Obtained solid including the extracted products were resolved in

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