

A Novel Friedel-Crafts Acylation Reaction of Anisole for Production of 4-Methoxyacetophenone with High Selectivity and Sufficient Reusability of Mordenite Zeolite Catalyst

Makoto Makihara, Kenichi Komura*

Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Gifu, Japan

Email: *kkomura@gifu-u.ac.jp

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Abstract

Zeolite catalyzed Friedel-Crafts reactions were examined using acetic anhydride as an acetylating agent and an acetic acid as a solvent. It revealed that the reaction of anisole smoothly occurred quantitatively for 3 h using mordenite zeolite with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$, and with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 110$, the increasing of Brønsted acidity allowed to completely react within 2 h. Furthermore the selectivity of 4-methoxyacetophenone (4-MA) among the isomers was found to be quantitative, no by-products and/or isomers were not detectable. With the excellent recyclability and reusability, the mordenite zeolite exhibited at least 30 times quantitatively both conversion of anisole and selectivity of 4-MA. The mordenite catalysts of fresh and the used after 30 times were characterized. This opportunity obviously indicates the sufficient shape selective catalyst of mordenite zeolite and gives a green synthetic tool for heterogeneous acylation reaction.

Keywords

Zeolite, Friedel-Crafts, Acylation, Mordenite, Shape Selectivity

1. Introduction

Friedel-Crafts acylation reaction is one of the most useful synthetic tools in organic synthesis, because it allows it to be possible for introducing of important moieties such as acetyl and alkyl groups into aromatic compounds. In general textbook of organic chemistry, this reaction can be promoted by Lewis acid catalysts such as AlCl_3 , HF and BF_3 using acid chlorides and alkylhalides for pro-

ducing corresponding substituted aromatics. Unfortunately these conventional reactions produce large amounts of waste after the reaction by work-up, neutralization of catalyst and/or used reagent. Thus necessity of alternating to conventional catalytic reaction and a wide spreading concern for environmental benignity have triggered the development of economic and green chemical processes for Friedel-Crafts reaction. In researches of eco-friendly Friedel-Crafts acylations of anisole, usage of zeolite has been widely developed as promising catalysts as well as the index of shape selectivity of the zeolite due to their validities of three dimensional pore structure, so far [1] [2] [3]. Among the examined zeolite catalysts, reports on using BEA zeolites have been paid much attention, for example, using toluene as solvent [4] [5], neat conditions [6] [7] [8] and fixed-bed vapor phase reaction [9]. Other approaches have been also examined by using mesoporous catalysts [2], MWW zeolitic material using nitrobenzene [10], ZSM-5 zeolite [11], ion-exchanged Y zeolite [12] [13], clays [14] and resin composite silica catalysts [15] [16] [17].

Recently we have successfully developed the highly selective Friedel-Crafts acylation of 2-methoxynaphthalene (2-MN) to obtain 2-methoxy-6-acetyl-naphthalene (2,6-ACMN) by MOR-type zeolite catalyst using acetic anhydride (Ac_2O) as an acylating agent in acetic acid (AcOH) as a solvent, and this reaction system is to be the highest conversion of 2-MN and the selectivity of 2,6-ACMN comparing with ever reported researches [18]. However the reusability of mordenite catalyst was found to be poor due to leaching of Al or heavy coke formation onto the acid site during the reaction, and it is marked that the reaction smoothly occurred using low acid amount of mordenite zeolite with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$ (designated as MOR(200)), whereas usage higher acid amount of mordenite catalyst caused low conversion of 2-MN, offering quite unique specific character of this reaction system. Friedel-Crafts reactions of anisole and some substrates which can be producing key intermediates by mordenite catalyst under our developed system are not clarified yet, therefore, in this report, we wish to disclose the excellent catalytic performance and the shape selectivity of mordenite zeolite, especially using anisole, as illustrated in **Figure 1**.

2. Experiment

2.1. Characterization and Materials

Powder X-ray diffraction (XRD) was measured by a Shimadzu XRD-6000 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Elemental analyses were per-

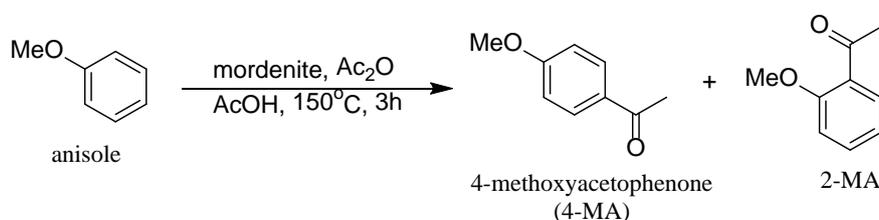


Figure 1. Friedel-Crafts acylation of anisole by mordenite catalyst.

formed using an X-ray Fluorescence Spectroscopy (XRF) (BRUKER S8 TIGER). Nitrogen adsorption and desorption isotherm measurements were carried out on a Belsorp 28SA apparatus (Bel, Japan). Ammonia temperature programmed desorption (NH₃-TPD) experiments were conducted on a TPD-66 apparatus (Bel Japan): the sample was evacuated at 400 °C for 1 h, and ammonia was adsorbed at 100 °C followed by further evacuation for 1 h. Then, the sample was heated from 100 °C to 710 °C at the rate of 10 °C/min in a helium stream. Solid-state ²⁹Si magic angle spinning (MAS) NMR spectra, and ²⁷Al MAS NMR spectra were recorded at ambient temperature by using 4 mm diameter zirconia rotor with a spinning rate of 6 kHz (ECA-500 NMR spectrometer, JEOL Ltd.). Due to ratios of SiO₂/Al₂O₃ in MOR(200) is almost the limit of measurement, thus MOR(200) was adsorbed by NH₃ using aqueous ammonium for enhancement of the intensity. Thermal gravimetric (TGA) and differential thermal (DTA) analyses 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 field emission scanning electron microscopy (FE-SEM) (S-4800; Hitachi High-Technologies Co., Japan). The products were analyzed by a Shimadzu Gas Chromatograph GC-18 with FID (Column: Ultra-1 capillary column; Agilent Technologies, CA, USA).

MOR-type zeolites were gifted from Tohsoh and used after calcination at 500 °C for 5 h under air flow. Whereas organic reagents such as anisole, acetic anhydride and acetic acid were purchased from Tokyo Chemical Industry, Co., LTD. and used without any purification.

2.2. Reaction

The typical reaction procedure; the prescribed amount of anisole (2.0 mmol), an acetylating agent (acetic anhydride, 20 mmol) and zeolite catalyst (0.50 g) were dissolved in AcOH (5 mL), then the resulting mixture was stirred at 150 °C. The product yield and selectivity of the isomers were estimated by GC compared with authentic samples. It is note that, in the conditions, there is no formation of Ac₂O from AcOH.

2.3. Reaction

After the reaction, the mordenite catalyst was recovered by filtration and washed with EtOAc (ca. 20 mL). Resulting zeolite was calcined at 500 °C for 5 h under air flow, and then re-used as the catalyst for next reaction described above.

3. Results and Discussion

Figure 2 shows the reaction profiles of Friedel-Crafts acylation of anisole by MOR(200) and MOR(110) catalysts, respectively. The reactions were carried out using Ac₂O in AcOH at 150 °C. Amazingly, although the acylation of 2-MN by MOR(200) catalyst takes for 48 h to accomplish the reaction, the acetylation of anisole rapidly occurred within 3 h in >99% conversion and the selectivity of 4-MA was detected in >99% in the presence of low acid amount of zeolite cata-

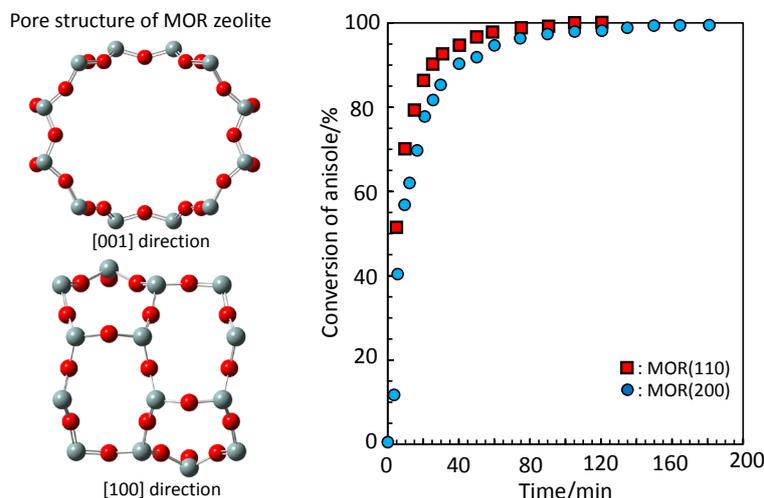


Figure 2. Pore structure of mordenite zeolite [001] and [100] directions (left). Reaction profiles of Friedel-Crafts acylation of anisole over MOR(200) (blue circle) and MOR(110) (red square) (right).

lyst MOR(200). Further, in this reaction system, MOR(110) zeolite also showed the excellent catalytic performance; >99% conversion of anisole and >99% selectivity of 4-MA only for 2 h, respectively. These results obviously indicate that the reaction proceeds by high shape selective manner of mordenite zeolite catalysts, because mordenite has a straight pore channel composed by 12-membered ring along with [001] direction in **Figure 2(left)** [19], thus it allows not only facile formation of the slimmest isomer (4-MA) but also to diffuse out smoothly rather than those of 2,6-ACMN. However the usage of higher acidity MOR(30) catalyst gave moderate conversion in 63%, albeit 4-MA in >99% selectivity. These results suggest that this reaction system does not need a high Brønsted acidity, but the reaction never occurs in the absence of mordenite catalyst.

Other substrates for producing key intermediates were also examined in this reaction system. For examples, utilizing isobutylbenzene affording an ibuprofen intermediate gave low yield in 9%, albeit quantitative *para*-selectivity. The reaction of 4-methoxybiphenyl gave unsatisfactory low yield in 27% with quantitative selectivity of 4'-acetyl-4-methoxybiphenyl in **Figure 3**. Davis *et al.* also claimed the low conversion of isobutylbenzene over BEA zeolite and the effect of external surface contributed significantly, not by shape selective manner of zeolite pore [20].

The experiment of reusability and recyclability of MOR(200) zeolite using anisole and Ac₂O in AcOH (**Figure 4(left)**) gave the amazing result, showing the quantitative conversions of anisole and the selectivities of 4-MA in >99% in 30 times reactions. Obviously this result must be intriguing catalytic performance of MOR(200) zeolite for acylation of anisole leading to 4-MA. **Figure 4(right)** gives the powder-XRD charts of fresh (a) and after 30 times used MOR(200) zeolites (b), respectively. Even many times used, there was no observable for significant different peak patterns in both samples, suggesting that three-dimensional structure of MOR(200) zeolite (the topology of MOR and its framework

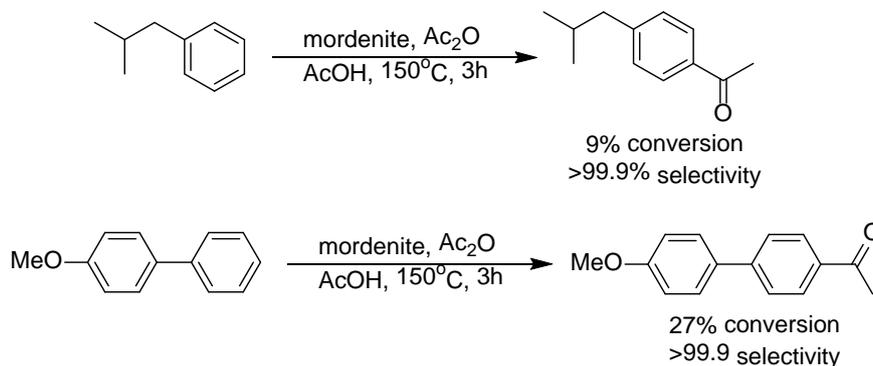


Figure 3. Mordenite zeolite catalyzed Friedel-Crafts acylation of isobutylbenzene (up) and 4-methoxybiphenyl (down).

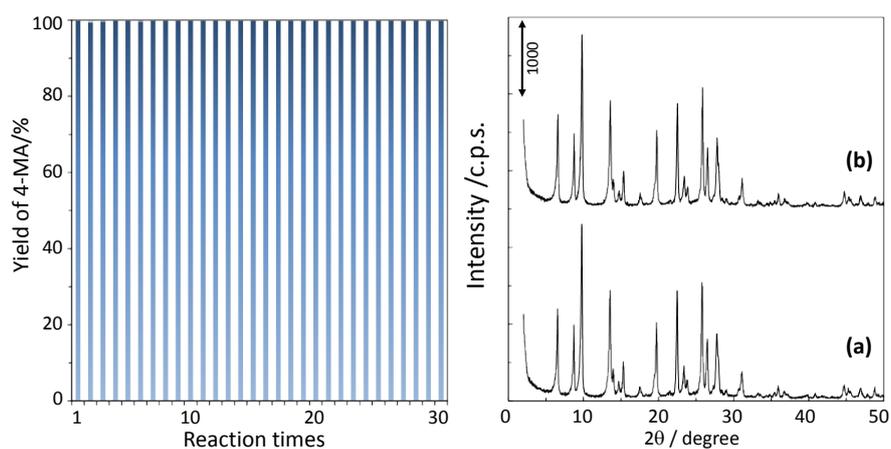


Figure 4. The results of reusability by MOR(200) in Friedel-Crafts acylation of anisole (left) and powder-XRD charts of fresh (a) and after 30 times used MOR(200) (b) zeolite catalysts (right).

structure) was found to be robust enough. **Table 1** gives the textural parameters of the MOR zeolite catalysts. Regardless of decreasing surface area of the used mordenite, the considerable changes of the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$, pore volume and acidity could not be detectable; suggesting that, in practical mind, the mordenite zeolite must be the excellent catalyst in this reaction system for producing 4-MA due to its quantitative conversion, the selectivity, the reusability and the recyclability.

Figure 5 gives the FE-SEM images (left), ^{29}Si MAS NMR spectra (middle) and ^{27}Al MAS NMR spectra of NH_3 -adsorbed mordenite catalysts (right). FE-SEM measurements of fresh (a) and the used zeolite catalysts (b) revealed that the crystal of the used mordenite became rugged surface and smaller particle size. However the amorphous phase and significant collapse of its morphology was negligible in the measurement, reflecting no considerable difference of XRD peaks in **Figure 4**.

^{29}Si MAS NMR spectra of both samples; fresh (a) and the used zeolite (b), were not determined a considerable difference. This result indicates that there is no amorphous silica formation from leaching Si atom during the reaction. How-

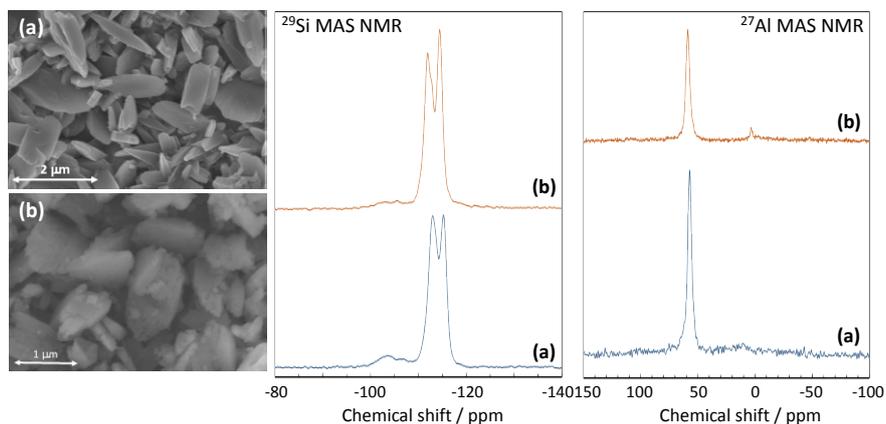


Figure 5. FE-SEM images, ²⁹Si magic-angle-spinning (MAS) NMR spectra and ²⁷Al MAS NMR spectra of fresh MOR(200) (a) and after used mordenite catalyst (b).

Table 1. Textural parameters of mordenite catalysts.

Entry	SiO ₂ /Al ₂ O ₃ ^a	Surface area ^b /m ² ·g ⁻¹	Pore volume ^c /mL·g ⁻¹	Acid amount ^d /mmol·g ⁻¹
1 ^e	200	520	0.27	0.041
2 ^e	106	579	0.35	0.051
3 ^f	195	470	0.28	0.036

^aEstimated by XRF, ^bBET surface area, ^cEstimated from nitrogen adsorption isotherm, ^dMeasured by NH₃-TPD, ^eFresh mordenite, ^fAfter 30 times used mordenite.

ever, in ²⁷Al MAS NMR spectra of NH₃-adsorbed mordenite catalysts (right), it can be observed the octahedral Al atom at 0 ppm which is mainly attributed to existence of Al₂O₃ after the used zeolite (b) in **Figure 5(right)**. This indicates the leaching of Al atom locating at the acid site by the repetitive reactions, because the spectrum of the fresh MOR(200) (a) is not observable at 0 ppm and only tetrahedral framework of Al atom is detected at 57 ppm. In order to enhance the intensity of Al atom using NH₃ as a probe molecule, although the quantitative assign cannot be possible, it can be implied that the peak intensity of octahedral Al atom was very small comparing with that of tetrahedral Al atom. According to the results of XRD, NMR and textural parameters given in **Table 1**, it can be presumed that almost Al atom should be retained at mordenite framework after 30 times reactions having enough acidity for catalysis.

4. Conclusion

Friedel-Crafts acylation of anisole was studied using Ac₂O and mordenite catalyst in AcOH. Interestingly, the low acid amount of mordenite zeolite with SiO₂/Al₂O₃ = 200 (MOR(200)) showed quantitative conversion in >99% for 3 h and the selectivity of 4-MA in >99%. Further it was also found that the MOR (100) catalyst showed quantitative conversion within 2 h with >99% selectivity of 4-MA. Unexpectedly, the higher acid amount of MOR(30) gave moderate conversion in 63% with >99% selectivity. Amazingly, the experiment of reusability and recyclability of MOR(200) zeolite catalyst gave the excellent results; there is

no decline of the catalytic activity and the quantitative selectivity in 30 times reactions of anisole in our reaction system. Based upon characterizations of fresh and the used mordenite zeolites, it presumptively revealed that almost Al atom at Brønsted acid site of mordenite catalyst is hard to leach out from its robust framework structure, therefore the catalytic performances (conversion and shape selectivity) do retain in the repetitive reactions. This distinctive opportunity must be intriguing and offers a novel green synthetic tool by heterogeneous Friedel-Crafts acylation of anisole. The further researches are ongoing in our laboratory.

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