

# Reaction Profiles of High Silica MOR Zeolite Catalyzed Friedel–Crafts Acylation of Anisole Using Acetic Anhydride in Acetic Acid

Makoto Makihara<sup>1</sup> · Hisakazu Aoki<sup>2</sup> · Kenichi Komura<sup>1,2</sup>

Received: 21 May 2018 / Accepted: 20 August 2018 © Springer Science+Business Media, LLC, part of Springer Nature 2018

## Abstract

Friedel–Crafts reaction of anisole over high silica mordenite zeolite was investigated. Detailed reaction profiles were obtained using various reaction conditions. In particular, the behavior of acetic anhydride during the reaction and the effect on the hydrophilicity of the mordenite zeolite catalyst were investigated.

## **Graphical Abstract**



Keywords Friedel-Crafts acylation · Anisole · Mordenite zeolite

# 1 Introduction

Friedel–Crafts acylation is one of the pivotal synthetic tools to introduce acetyl moieties into aromatic compounds, and almost all such products are widely used as key intermediates such as medicines, cosmetics, flavors and perfumes,

**Electronic supplementary material** The online version of this article (https://doi.org/10.1007/s10562-018-2530-1) contains supplementary material, which is available to authorized users.

Kenichi Komura kkomura@gifu-u.ac.jp

<sup>1</sup> Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Yanagido 1-1, Gifu 501-1193, Japan

<sup>2</sup> Graduated School of Materials Science and Possessing Division, Faculty of Engineering, Gifu University, Yanagido 1-1, Gifu 501-1193, Japan pigments, and engineering plastics [1]. Friedel–Crafts acetylation is generally performed using activated acid or acetic anhydride as acetylating agents in the presence of a stoichiometric amount of Lewis acid catalysts, such as AlCl<sub>3</sub> and BF<sub>3</sub>, in toxic solvents such as dichloroethane and nitrobenzene. Therefore, this reaction has critical drawbacks, in that large amounts of waste are produced during the work-up steps, especially in the neutralization of the activated acid and the catalyst.

Since understanding the essential functions of zeolite such as the solid acid properties over 30 years ago, many developments over the zeolite catalyzed Friedel–Crafts acylation of anisole (AN) to selectively produce 4-methoxyacetophenone (4-MA) have been reported (Scheme 1), and these are well summarized in reviews and books [1–4]. In particular, the use of BEA zeolites (\*BEA-type) and modified ZSM-5 zeolites (MFI-type) has attracted much attention because of their three-dimensional pore systems [5]. For recent



examples within the last decade, attempts have been made to use modified BEA zeolites for fixed-bed continuous flow reactions [6, 7], microwave irradiation [8] and for metal doping of the zeolite [9]. Wu et al. recently reported a reaction using hierarchical nanosized BEA zeolite, which resulted in 66% conversion of AN and >99% selectivity of 4-MA [10]. In 2008, Selvin et al. pointed out that nano-scale range ZSM-5 zeolite exhibited excellent catalytic activity due to enhancement of its surface area [11]. Serrano et al. reported a ZSM-5 zeolitic mesostructured hybrid catalyst [12] and a hierarchical ZSM-5 zeolite in nitrobenzene solvent [13]. Selvin and co-workers also reported efficient acylation using the hierarchical ZSM-5 zeolite with 65% conversion of AN and 99.5% selectivity of 4-MA [14]. Ryoo and co-workers recently reported the same reaction using a ZSM-5 zeolitic nanosponge catalyst, where ca. 80% conversion of AN and 98% selectivity of 4-MA was achieved for 20 h in nitrobenzene solvent [15]. The interest in this reaction has triggered the use of unique zeolite catalysts such as MWW zeolite or its precursors, MCM-22 and MCM-49. Tatsumi and coworkers [16] reported the reaction using Al-MWW (MWWtype) zeolite, and Tatsumi and co-workers also applied an interlayer-expanded zeolite Al-MWW (IEZ-MWW) [17]. Further Xu and co-workers recently attempted fixed-bed continuous flow systems using modified MCM-49 zeolites and claimed that the reaction proceeds at external pockets [18, 19], and Nunes and co-workers reported a kinetic study of this reaction over hierarchical MWW zeolite [20]. As other approaches, Wu and co-workers reported the aluminosilicate IEZ-PLS-3, designated as ECNU-8, where PLS-3 is a layered zeolitic material possessing FER sheets [21], which resulted in the moderate conversion of AN [22, 23]. The use of an aluminophosphate molecular sieve containing Sn(II) with AIF-type topology, denoted as Sn(II)AlPO<sub>4</sub>-5, reported by Sànchez et al. [24]. The Friedel-Crafts acylation of AN has been used as an index for the elucidation of zeolite properties, particularly of their Brønsted acidity; therefore, almost all recent reports have been focused on new materials, their preparation strategies and modification. The use of mordenite (MOR) zeolite has been reported by Tomar and co-workers however, the reaction was performed using propionic anhydride as an acylating agent [25]. The straight one-dimensional 12-ring pore channels of MOR zeolite mean that the diffusion of participating molecules into the

zeolite is more restricted than that of BEA and ZSM-5 zeolites, which are three-dimensional pore systems. Therefore, investigations on Friedel-Crafts acylation over MOR-type zeolites have been limited. Recently, our group has reported on high-silica MOR zeolite catalyzed Friedel-Crafts acylation of 2-methoxynaphthalene using acetic anhydride in acetic acid to afford 2-methoxy-6-acetylnaphthalene with excellent conversion and shape-selectivity [26]. This reaction system can also be successfully applied to anisole (AN), which revealed that high silica MOR zeolite with SiO<sub>2</sub>/  $Al_2O_3 = 110$ , designated as MOR(110), showed the highest conversion of AN and perfect selectivity of 4-MA (>99.9%) within 2 h. The MOR zeolite catalyst was also reusable at least 30 times without loss of conversion of AN and selectivity of 4-MA, and no leaching of Al after reuse of zeolite was observed, even in the acidic reaction medium [27].

Here we report the reaction profiles of the Friedel–Crafts acylation of anisole over a high silica MOR zeolite catalyst using acetic anhydride in an acetic acid medium. In particular, the effects of the  $Ac_2O/AN$  ratio on the catalysis and hydrophilicity of the MOR zeolite catalyst were investigated to understand the detailed reaction system and catalysis.

# 2 Experimental

## 2.1 Characterization and Materials

Powder X-ray diffraction (XRD; Shimadzu XRD-6000) was measured using Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). Elemental analyses were performed using X-ray fluorescence spectroscopy (XRF; Bruker S8 TIGER). Nitrogen adsorption and desorption isotherm measurements were performed using an absorption analyzer (Bel Japan Belsorp 28SA). Acid properties were determined using ammonia temperatureprogrammed desorption (NH<sub>3</sub>-TPD; Bel Japan TPD-66). Solid-state <sup>29</sup>Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) and <sup>27</sup>Al MAS NMR spectra were recorded at ambient temperature using a 4 mm diameter zirconia rotor with a spinning rate of 6 kHz (JEOL ECA-500 NMR spectrometer). The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 110, designated as MOR(110), is almost the limit of measurement; therefore, NH<sub>3</sub> was adsorbed on MOR(110) using aqueous ammonia to enhance the intensity. Thermogravimetric (TGA) and differential thermal analysis (DTA) were conducted using an apparatus (Shimadzu DTG-50) with the ramp rate at 10 °C/min under an air stream. The crystallite size and morphology were measured using field emission scanning electron microscopy (FE-SEM; Hitachi High-Technologies Co. S-4800). Products were analyzed using gas chromatography (GC; Shimadzu GC-18) with a flame ionization detector (FID) and an Agilent Technologies Ultra-1 capillary column. MOR-type zeolites were received from Tosoh Corp. and used after calcination at 500 °C for 5 h under air flow. Organic reagents such as anisole, acetic anhydride and acetic acid were purchased from Tokyo Chemical Industry, Co., Ltd. and were used as-received without further purification.

## 2.2 Preparation of Dealuminated Mordenite

Dealuminated MOR-type zeolite with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=110 was prepared according to a previously reported procedure [28]. Commercially available MOR(25) was added to 8 M HCl solution and stirred for 3 h at 80 °C. The resulting product was washed with distilled water thoroughly and dried at 90 °C for 12 h. The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio was estimated from XRF measurements.

## 2.3 Reaction

A typical reaction procedure involved dissolving a prescribed amount of anisole (1.0 mmol), an acetylating agent (acetic anhydride, 10 mmol) and the zeolite catalyst (0.50 g) in AcOH (5 mL), and then stirring the mixture at 150 °C. The product yield and selectivity of the isomers were estimated by GC and compared with authentic samples. It should be noted that under these conditions, no formation of Ac<sub>2</sub>O from the AcOH solvent occurred.

## 3 Results and Discussion

To understand the zeolite-catalyzed Friedel–Crafts acylation of AN in AcOH, the fundamental reactions and conditions were investigated. The reaction rate is dependent on the amount of MOR zeolite catalyst, which indicates that an increased amount of catalyst increases the reaction rate (see Supporting Information).

## 3.1 Effect of Reaction Temperature

In the most of the reported Friedel–Crafts acylation reactions over zeolite catalysts, the reactions are typically performed at around 80 °C. However, the reaction system we have developed requires higher temperature and is typically promoted at 150 °C over the MOR(110) zeolite because a high silica zeolite does not have sufficient Brønsted acid sites than in often used conventional zeolite catalysts [4]. Figure 1 shows the reaction profiles over the commercial MOR(110) zeolite at different reaction temperatures. Decreasing the reaction temperature caused a decline in the catalytic activity. At 170 °C, a slight decrease in catalytic activity was observed, and the best catalytic performance was at 150 °C. This is because the boiling point of Ac<sub>2</sub>O is 140 °C, and thus vigorous reflux conditions would inhibit interaction between the MOR zeolite and Ac<sub>2</sub>O. The quantities of Al in the MOR catalysts before and after the reaction did not change, which indicates that the reaction system does not damage the MOR zeolite catalyst, and the selectivity of 4-MA was > 99.5% in every case, which is attributed to the shape-selective characteristics of the MOR zeolite catalyst with its straight pore channels. Further the reaction never occur in the absence of zeolite catalyst at 150 °C [27]. The activation energy  $(E_2)$ was estimated from the initial slopes of Fig. 1, except for the value at 170 °C, and it was 1.5 kcal/mol, which is very low when compared with the 11 kcal/mol reported by Derouane et al. under neat conditions over the BEA zeolite catalyst [29]. These results infer that the role of the solvent (AcOH) is also critical to decrease the activation energy in this reaction system.

## 3.2 Effect of Ac<sub>2</sub>O/AN Ratio

Reaction profiles were obtained by varying the  $Ac_2O/AN$  ratios over commercially available MOR(110), and the results are given in Fig. 2. As the  $Ac_2O/AN$  ratio increased,



Fig. 1 Reaction profiles at different reaction temperature. Reaction conditions: MOR(110) (0.5 g), anisole (1.0 mmol),  $Ac_2O$  (7.0 mmol) and AcOH (5 mL)



**Fig. 2** Reaction profiles with different  $Ac_2O/AN$  ratios (open circles: 10, filled circles: 7, filled squares: 4, filled triangles: 1). Reaction conditions: MOR(110) (0.5 g), anisole (1.0 mmol) and AcOH (5 mL)



**Fig. 3** Reaction profiles and  $Ac_2O/AN$  ratio during reactions. Conversion of AN ( $Ac_2O/AN$ ; open circles: 10, open squares: 4).  $Ac_2O/AN$  ratios (filled circles; 10, filled squares; 4)

the conversion of AN was increased, and a satisfactory ratio was determined to be over 7.0. However, the reaction did not proceed at a ratio of  $Ac_2O/AN = 1.0$ , which implies that not only the consumption and/or activation of  $Ac_2O$  into the zeolite should be significantly fast, but also the reaction is severely affected by the amount of  $Ac_2O$ . Therefore, the reaction was conducted with respect to the behavior of  $Ac_2O$  during the reaction. Figure 3 shows the profiles of AN conversion and  $Ac_2O/AN$  ratios for  $Ac_2O/AN$  ratios at 10 and 4.0. The excess amount of  $Ac_2O$  was almost instantly consumed by the zeolite catalyst ( $Ac_2O/AN$  ratio from 10 to around 1.0, Fig. 3, filled circles). When there was a sufficient amount of  $Ac_2O$  in the reaction medium, the conversion of AN was increased and 4-MA was produced with >99.5% selectivity due to the shape-selective manner of the zeolite catalyst (Fig. 3, open circles), whereas  $Ac_2O$  was fully consumed (Fig. 3, filled squares), no increase of conversion was observed from 2 h with a ratio of  $Ac_2O/AN = 4.0$  (Fig. 3, open squares). These results indicate that the conversion of AN is compatible with the amount of  $Ac_2O$  in the reaction solution, and it is also considerable that non-polar  $Ac_2O$ can be rapidly adsorbed into the high silica zeolite catalyst for activation.

#### 3.3 Effect of Hydrophilicity of MOR Catalyst

One of the factors for the success of this system is the hydrophobicity of the MOR zeolite catalyst. The developed Friedel-Crafts acylation system is sufficiently promoted by high silica MOR zeolite catalyst; however, the catalytic activity and shape-selectivity in the Friedel-Crafts acylation of 2-methoxynaphthalene were severely affected by the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, where the use of a low silica MOR zeolite with hydrophilic property declined the catalytic performance [26]. The purpose here is to elucidate the effect of the hydrophilicity of the MOR zeolite; therefore, dealuminated MOR zeolite with  $SiO_2/Al_2O_3 = 110$  [deMOR(110)] was prepared from a commercially available MOR (SiO<sub>2</sub>/  $Al_2O_3 = 25$ ) zeolite by intentionally introducing nest silanol into the zeolite framework, which has more hydrophilic property due to formation of Si-OH moieties. The characterization results are given in the Supporting Information. FE-SEM revealed that deMOR(110) had a slightly aggregated morphology with small rugby-ball-like grains, and <sup>29</sup>Si MAS NMR spectra showed an ca. 10% increase in the amount of  $Q^3$  silicon (SiOH) in deMOR(110) compared with commercially available MOR(110), which indicates the formation of nest silanol in the zeolite. NH<sub>3</sub>-TPD profiles of the MOR(110) and deMOR(110) zeolites are shown in Fig. 4. In the profile for the commercial MOR(110) zeolite, a *l*-peak corresponding to physically adsorbed NH<sub>3</sub> was detected at around 150 °C, and a h-peak was detected at around 400 °C, which corresponds to chemisorbed NH<sub>3</sub> (Fig. 4a). The  $NH_3$ -TPD profile for deMOR(110) showed the two distinct *l*- and *h*-peaks at 180 °C and 400 °C, respectively (Fig. 4b). The desorption peak of NH<sub>3</sub> in the middle range temperature was observed for deMOR(110) zeolite, which is attributed to weak acid-base interaction of NH<sub>3</sub> molecules at nest silanol groups, and also reflects the amount of acid, as given in Table 1. Other estimated parameters such as the Brunauer-Emmett-Teller (BET) surface area and pore volume were similar for these samples. In the



Fig. 4 NH<sub>3</sub>-TPD profiles of MOR(110) (a) and deMOR(110) (b)

Table 1 Textural parameters of MOR(110) and deMOR(110)

Zeolite	BET surface area <sup>a</sup> $(m^2 g^{-1})$	Pore volume <sup>a</sup> $(mL g^{-1})$	Acid amount <sup>b</sup> (mmol g <sup>-1</sup> )
MOR(110)	579	0.35	0.233
deMOR(110)	566	0.32	0.302

<sup>a</sup>Estimated by nitrogen isotherm

<sup>b</sup>Estimated by NH<sub>3</sub>-TPD analysis

deMOR(110) zeolite,  $N_2$  isotherms using Horvath–Kawazoe (HK) and Barrett–Joyner–Halenda (BJH) analyses indicated no meso- and macroporous pores (data not shown), which is reasonable for MOR-type zeolite with 12-ring straight pore channels.

Figure 5 shows reaction profiles for the Friedel–Crafts acylation of AN over commercially available MOR(110) and deMOR(110) catalysts. The commercially available MOR(110) exhibited excellent catalytic performance, i.e. the reaction was completely finished within 2 h. In contrast, the deMOR(110) zeolite with nest silanol groups showed only moderate catalytic activity. This result indicates that the hydrophilic zeolite catalyst is not preferable for the developed reaction system. The reason for this can be considered to be that the participating molecules such as  $Ac_2O$  and AN are hydrophobic and could not easily enter into the MOR zeolite in a highly polar solvent AcOH. Therefore, the catalytic activity declined over the deMOR zeolite. These results suggest that even



**Fig. 5** Reaction profiles over MOR(110) (open circles) and deMOR(110) (open squares) zeolites. Reaction conditions: zeolite (0.5 g), anisole (1.0 mmol),  $Ac_2O$  (7.0 mmol) and AcOH (5 mL)

with a 10% enhanced quantity of  $Q^3$  silicon, the reaction was severely affected by the hydrophilic environment of the zeolite catalyst.

# 4 Conclusion

The high silica MOR zeolite catalyzed Friedel–Crafts acylation of anisole was investigated under various conditions. This reaction system required an appropriate temperature and amount of acetic anhydride. In particular, during the reaction, acetic anhydride was almost instantly consumed over the hydrophobic MOR zeolite, in which the adsorption of participating molecules would compete in a polar solvent. Reaction over a hydrophilic zeolite, dealuminated MOR zeolite, decreased the reaction rate. High silica MOR zeolite is known to have hydrophobic property, i.e. the amount of catalytic active sites (Brønsted acid sites) is insufficient. Therefore, this reaction requires high temperature for sufficient promotion; however, the reason why a large amount of acetic anhydride is required has yet to be clarified. Further research with this reaction system is ongoing in our laboratory.

Acknowledgements This work was partially supported JSPS KAK-ENHI Grant Number 15K05586, 18K05200 and the OGAWA Science and Technology Foundation.

### **Compliance with Ethical Standards**

**Conflict of interest** The authors declare no competing financial interest.

# References

- Čejka J, Morris RE (2017) Theoretical chemistry of zeolite reactivity. In: Opanasenko M (eds) Zeolites in catalysis. Royal Society of Chemistry, Cambridge
- 2. Spagnol M, Gilbert L, Alby D (1996) Ind Chem Libr 8:29
- Čejka J, Coram A, Zones S (2010) Zeolites as catalysts for the synthesis of fine chemicals. In: Climent MJ, Corma A, Ibrorra S (eds) Zeolites and catalysis, vol 3, Wiley, Weinheim
- 4. Bejnlová M, Procházková D, Čejka J (2009) ChemSusChem 2:486
- 5. Sreedhar I, Kantamneni H, Reddy KSK, Raghavan KV (2014) Kinet Catal 55:229
- 6. Zhao D, Wang J, Zhang J (2008) Catal Lett 126:188
- 7. Wei H, Liu K, Xie S, Xin W, Li X, Liu S, Xu L (2013) J Catal 307:103
- Winé G, Vanhaecke E, Ivanova S, Ziessel R, Huu CP (2009) Catal Commun 10:477
- 9. Bai GY, Dou HY, Qiu MD, He F, Fan XX, Ma Z (2010) Res Chem Intermed 36:483
- 10. Huang G, Ji P, Xu H, Jiang JG, Chen L, Wu P (2017) Microporous Mesoporous Mater 248:30
- 11. Selvin R, Hsu HL, Her TM (2008) Catal Commun 10:169
- 12. Serrano DP, García RA, Otero D (2009) Appl Catal A 359:69
- Serrano DP, García RA, Vicente G, Linares M, Procházková D, Čejka J (2011) J Catal 279:366
- 14. Padmanabhan A, Selvin R, Hsu HL, Xiao LW (2010) Chem Eng Technol 33:998

- 15. Kim JC, Cho K, Lee S, Ryoo R (2015) Catal Today 243:103
- Fan W, Wei S, Yokoi T, Inagaki S, Li J, Wang J, Kondo JN, Tatsumi T (2009) J Catal 266:268
- Inagaki S, Imai H, Tsujiuchi S, Yakushiji H, Yokoi T, Tatsumi T (2011) Microporous Mesoporous Mater 142:354
- Wei H, Xie S, Gao N, Liu K, Liu X, Xin W, Li X, Liu S, Xu L (2015) Appl Catal A 495:152
- Wei H, Xie S, Liu K, Xin W, Li X, Liu S, Gu S, Liu S, Xu L (2015) Chin J Catal 36:1766
- 20. Aleixo R, Leitao RE, Martins F, Carvalho AP, Brigas A, Martins A, Nunes N (2017) Mol Catal 434:175
- 21. Ikeda T, Kayamori S, Mizukami F (2009) J Mater Chem 19:5518
- 22. Yang B, Wu H, Wu P (2014) J Phy Chem C 118:24662
- 23. Yang B, Jiang JG, Xu H, Ji P, Wu P (2015) Microporous Mesoporous Mater 203:54
- 24. Sànchez MS, Grieken R, Serrano DP, Melero JA (2009) J Mater Chem 19:6833
- 25. Bhadauria J, Singh BK, Tomar A, Tomar R (2011) J Chem Pharm Res 3:245
- 26. Yamazaki T, Makihara M, Komura K (2017) J Mol Catal A 426:170
- 27. Makihara M, Komura K (2017) Green Sus Chem 7:185
- Oumi Y, Nemoto S, Nawata S, Fukushima T, Teranishi T, Sano T (2002) Mater Chem Phys 78:551
- 29. Derouane EG, Dillon CJ, Hamid SBD (1999) J Catal 187:209