



Towards applications of metal–organic frameworks in catalysis: Friedel–Crafts acylation reaction over IRMOF-8 as an efficient heterogeneous catalyst

Lien T.L. Nguyen^a, Chi V. Nguyen^b, Giao H. Dang^a, Ky K.A. Le^a, Nam T.S. Phan^{a,*}

^a Department of Chemical Engineering, HCMC University of Technology, VNU-HCM, 268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Viet Nam

^b Department of Chemical and Food Engineering, Lac Hong University 10 Huynh Van Nghe, Buu Long Ward, Bien Hoa, Viet Nam

ARTICLE INFO

Article history:

Received 5 July 2011

Received in revised form 10 August 2011

Accepted 14 August 2011

Available online 22 August 2011

Keywords:

Metal–organic framework

Friedel–Crafts acylation

Heterogeneous catalyst

IRMOF-8

Leaching

Reuse

ABSTRACT

A highly porous metal–organic framework (IRMOF-8) was synthesized by a solvothermal method, and used as an efficient heterogeneous catalyst for the Friedel–Crafts acylation reaction. The solid catalyst was characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), atomic absorption spectrophotometry (AAS), and nitrogen physisorption measurements. High conversions were achieved in the presence of a catalytic amount of the IRMOF-8 (1–5 mol%) without the need for an inert atmosphere. The solid catalyst could be facily separated from the reaction mixture by simple centrifugation, and could be reused without a significant degradation in catalytic activity. No contribution from homogeneous catalysis of active acid species leaching into the reaction solution was detected.

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1. Introduction

Metal–organic frameworks (MOFs) have been considered as promising materials for their potential applications in gas separation and storage, sensors, drug delivery, and catalysis [1–5]. These materials consist of metal ions or clusters acting as nodes and polyfunctional organic ligands as linkers [6]. Compared to conventionally used microporous and mesoporous inorganic materials, these metal–organic structures exhibit advantages such as high surface areas, tunable pore sizes, and the ease of processability, flexibility, structural diversity, and geometrical control [7–9]. In the field of catalysis, several MOFs have been used as solid catalysts or catalyst supports for a variety of organic transformations such as Knoevenagel condensation [10,11], aldol condensation [12], oxidation [13–17], epoxidation [18,19], hydrogenation [20], Suzuki cross-coupling [21], transesterification reaction [22–24], Friedel–Crafts alkylation [25,26], epoxide ring-opening reaction [27–29], methylation of aromatic amines [30], activation of alkynes [31], domino coupling and cyclization reactions [6], and alkene cyclopropanation [32]. As in the case of zeolites, the application of MOFs in catalysis is undoubtedly an area that will attract further research in the near future [28,33,34].

Friedel–Crafts acylation reactions of aromatic compounds with acid chlorides are considered as fundamental and important

processes in organic synthesis as well as in industrial chemistry [35]. Traditionally, these reactions require the presence of more than stoichiometric amounts of anhydrous strong Lewis acids such as AlCl₃, TiCl₃, FeCl₃, or SnCl₄ [36]. These methods suffer from high amounts, toxicity and corrosion of the catalysts, generation of a large amount of waste, and difficult purification of products [37]. Moreover, these catalysts are highly moisture sensitive and hence moisture-free reaction conditions are required to achieve the optimal yields of the desired aromatic ketones [36,38]. With the increasing emphasis on green chemistry, environmentally benign processes should be developed to improve the green credentials of the reaction [39,40]. For the development of greener processes, moisture-insensitive and easy handling solid acid catalysts are desired [41]. Furthermore, the use of solid acid catalysts offers easy catalyst recovery and recycling, as well as product separation. At the same time, the catalyst recovery also decreases contamination of the desired products with hazardous or harmful metals [38,42]. Indeed, several solid acid catalysts have been investigated for the Friedel–Crafts acylation reactions, such as metal triflate loaded SBA-15 [43], mesoporous superacid catalyst [40], zeolite [44–46], hybrid zeolitic-mesostructured materials [47], modified clay [48,49], nafion/silica composite materials [50], mesoporous sulphated zirconia [51], and mesoporous sieve AIKIT-5 [52]. Although interesting results have been achieved for the Friedel–Crafts acylation reaction, they have not led to any very important industrial application [53]. In this work, we wish to report the utilization of a highly porous metal–organic framework (IRMOF-8) as an efficient heterogeneous catalyst for liquid phase

* Corresponding author. Tel.: +84 838222447.

E-mail address: ptsnam@hcmut.edu.vn (N.T.S. Phan).

Friedel–Crafts acylation reactions. High activity was observed without the need for an anhydrous condition, and the IRMOF-8 catalyst was easily isolated from the reaction mixture and reused without significant degradation in activity.

2. Experimental

2.1. Materials and instrumentation

All reagents and starting materials were obtained commercially from Sigma–Aldrich and Merck, and were used as received without any further purification unless otherwise noted. Nitrogen physisorption measurements were conducted using a Quantachrome 2200e system. Samples were pretreated by heating under vacuum at 150 °C for 3 h. A Netzsch Thermoanalyzer STA 409 was used for thermogravimetric analysis (TGA) with a heating rate of 10 °C/min in air. X-ray powder diffraction (XRD) patterns were recorded using a Cu K α radiation source on a D8 Advance Bruker powder diffractometer. Scanning electron microscopy studies were conducted on a JSM 740 Scanning Electron Microscope (SEM). Transmission electron microscopy studies were performed using a JEOL JEM 1400 Transmission Electron Microscope (TEM) at 100 kV. The IRMOF-8 samples were dispersed on holey carbon grids for TEM observation. Elemental analysis with atomic absorption spectrophotometry (AAS) was performed on an AA-6800 Shimadzu. Fourier transform infrared (FT-IR) spectra were obtained on a Bruker TENSOR37 instrument, with samples being dispersed on potassium bromide pallets.

Gas chromatographic (GC) analyses were performed using a Shimadzu GC 17-A equipped with a flame ionization detector (FID) and a DB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μ m). The temperature program for GC analysis heated samples from 100 to 130 °C at 15 °C/min; then heated them from 130 to 200 °C at 50 °C/min; then heated them from 200 to 215 °C at 1.5 °C/min; then heated them from 215 to 300 °C at 50 °C/min and held them at 300 °C for 3 min. Inlet and detector temperatures were set constant at 300 °C. *n*-Hexadecane was used as an internal standard to calculate reaction conversions. GC–MS analyses were performed using a Hewlett Packard GC–MS 5972 with a RTX-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.5 μ m). The temperature program for GC–MS analysis heated samples from 60 to 280 °C at 10 °C/min and held them at 280 °C for 2 min. Inlet temperature was set constant at 280 °C. MS spectra were compared with the spectra gathered in the NIST library.

2.2. Synthesis of IRMOF-8

In a typical preparation [54,55], a solid mixture of zinc nitrate tetrahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) (0.37 g, 1.40 mmol) and 2,6-naphthalenedicarboxylic acid (0.06 g, 0.27 mmol) (NDCH) was dissolved in 15 mL of *N,N'*-dimethylformamide (DMF) in a 20 mL vial. The vial was tightly capped and heated at 100 °C in an isothermal oven, and held at this temperature for 24 h. After unassisted cooling of the vial to room temperature, crystals formed in the vial were removed by decanting with mother liquor. The solid product was washed with DMF (3 \times 10 mL) by immersing the sample in the solvent without stirring for 3 days. After that, the DMF was exchanged by dichloromethane (DCM) (2 \times 10 mL) for 2 days. The residual solvents were removed under vacuum at 140 °C for 5 h, yielding 0.061 g pale-yellow cubic-shaped crystals (71% based on 2,6-naphthalenedicarboxylic acid). Found C: 46.00, H: 2.47, Zn: 28.43%, $\text{Zn}_4\text{O}(\text{NDC})_3$ requires C: 46.99, H: 1.97, Zn: 28.32%.

2.3. Catalytic studies

The Friedel–Crafts acylation of toluene with benzoyl chloride using the IRMOF-8 catalyst was carried out in a magnetically stirred round bottom flask fitted with a reflux condenser. In a typical reaction, a mixture of toluene (0.60 mL, 5.60 mmol), benzoyl chloride (0.98 mL, 8.40 mmol) and *n*-hexadecane (0.15 mL) as an internal standard was added into a 50 mL flask containing the IRMOF-8 (64 mg, 5 mol%). The catalyst concentration was calculated with respect to the zinc/toluene molar ratio. The resulting mixture was stirred at 100 °C for 6 h. Reaction conversion was monitored by withdrawing aliquots from the reaction mixture at different time intervals, quenching with an aqueous NaOH solution (1%, 0.1 mL). The organic components were extracted into diethyl ether (3 \times 1 mL) which was then dried over anhydrous Na_2SO_4 , and analyzed by GC with reference to *n*-hexadecane. The product identity was further confirmed by GC–MS. The IRMOF-8 catalyst was separated from the reaction mixture by simple centrifugation, washed with copious amounts of anhydrous toluene and DCM, dried under vacuum at 100 °C for 5 h, and reused if necessary. For the leaching test, a catalytic reaction heated to 100 °C was stopped after 1 h, analyzed by GC, and centrifuged to remove the solid catalyst. The reaction solution was then stirred with heating to 100 °C for a further 5 h. Reaction progress, if any, was monitored by GC as previously described.

3. Results and discussion

3.1. Catalyst synthesis and characterization

In this work, the IRMOF-8 was synthesized using zinc nitrate tetrahydrate and 2,6-naphthalenedicarboxylic acid by a solvothermal method in DMF, according to a literature procedure developed by Yaghi and co-workers [54–58]. As a member of isorecticular metal–organic framework family, IRMOF-8 is constructed by 2,6-naphthalenedicarboxylate (NDC) linkers joining Zn_4O clusters to produce an extended three-dimensional cubic porous network, which has the formula unit $\text{Zn}_4\text{O}(\text{NDC})_3$ [55,57,59,60]. In the synthesis procedure of porous MOF-based materials using formamide solvents, the solvent exchange should be carried out as this step will facilitate the evacuation of the material frameworks [1,2,61]. It was therefore decided to immerse the IRMOF-8 samples in excess DCM at room temperature without stirring for 2 days. During this solvent exchange step, strongly interacting DMF molecules were replaced by more weakly interacting DCM molecules that would be facilely removed under vacuum at high temperature in the subsequent activation step [61]. This activation step was also crucial to obtain a fully porous structure [62]. It was found that the IRMOF-8 was achieved as pale-yellow cubic-shaped crystals in a yield of 71% (based on 2,6-naphthalenedicarboxylic acid). From experimental point of view, it should be noted that decreasing the zinc:NDC molar ratio resulted in a significant drop in the yield of the IRMOF-8.

The IRMOF-8 was then characterized using a variety of different techniques. Elemental analysis with AAS indicated a zinc loading of 4.38 mmol/g. The crystalline phase purity of the IRMOF-8 after the activation step was confirmed by powder XRD analysis [62]. The overall XRD patterns of the IRMOF-8 were in good agreement with the theoretical patterns from the single crystal data, and with those previously reported in the literature [54,62–64]. A very sharp peak below 10° (with 2θ of 6.0) was observed on the XRD diffractogram of the IRMOF-8, indicating that a highly crystalline material was achieved (Fig. 1). As with other MOF-based materials, the XRD patterns of the IRMOF-8 exhibited a better crystallinity as compared to those of other crystalline materials such as SBA-15, SBA-16, MCM-41, and MCM-48 where broader peaks were normally observed on

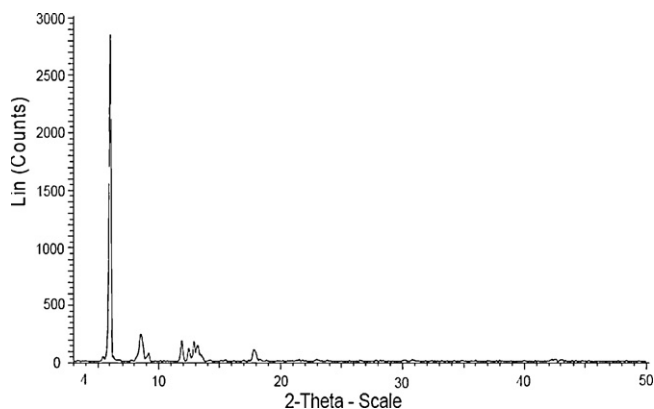


Fig. 1. X-ray powder diffractogram of the IRMOF-8.

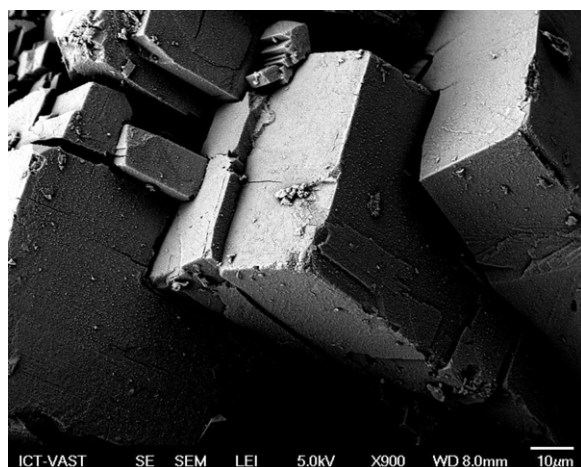


Fig. 2. SEM micrograph of the IRMOF-8.

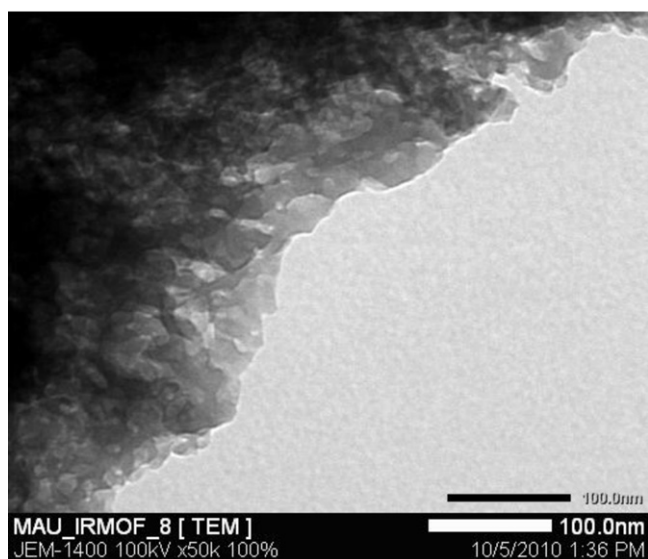


Fig. 3. TEM micrograph of the IRMOF-8.

their diffractograms [65]. The SEM micrograph showed that well-shaped, high quality cubic crystals were obtained for the IRMOF-8 (Fig. 2). The XRD patterns, together with the SEM image, indicated that the IRMOF-8 sample was highly crystalline. Images from TEM analysis showed that the IRMOF-8 possessed a highly porous structure (Fig. 3). Indeed, the TEM image of the IRMOF-8 was different

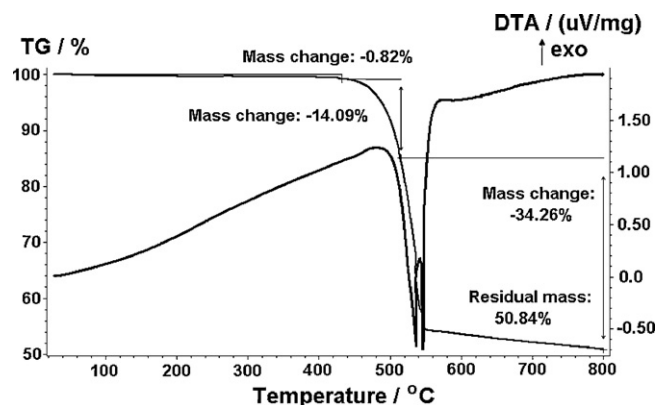


Fig. 4. TGA analysis of the IRMOF-8.

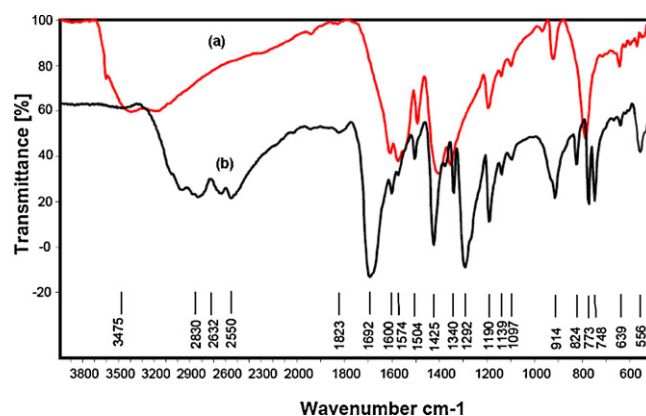
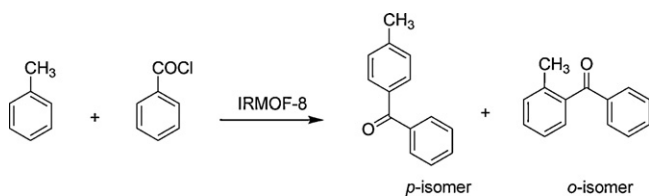


Fig. 5. FT-IR spectra of the IRMOF-8 (a), and 2,6-naphthalenedicarboxylic acid (b).

from that of conventionally used microporous and mesoporous inorganic materials.

BET surface areas of up to $2110\text{ m}^2/\text{g}$ were observed for the IRMOF-8, which is significantly higher than those of conventionally used microporous and mesoporous inorganic materials [1]. As with other solid materials, it is necessary to investigate the thermal degradation of the IRMOF-8 since many applications would depend on its thermal stability [66]. The most significant feature in the TGA result for the IRMOF-8 was that little weight loss was observed between the temperature range of $200\text{--}450\text{ }^\circ\text{C}$, indicating that the IRMOF-8 was stable up to over $450\text{ }^\circ\text{C}$ (Fig. 4). The thermal stability of the IRMOF-8 ensured that it could be used across a wide temperature range. FT-IR spectra of the IRMOF-8 exhibited a significant difference as compared to that of 2,6-naphthalenedicarboxylic acid (Fig. 5). There were strong peaks at $1574\text{--}1600\text{ cm}^{-1}$ in the spectra of the IRMOF-8, which was lower than the $\text{C}=\text{O}$ stretching vibration observed in free 2,6-naphthalenedicarboxylic acid (1692 cm^{-1}). These strong peaks were due to the stretching vibration of carboxylate anions, which were formed from the reaction of the linkers with the metal ions [67,68]. Furthermore, broad bands near 3400 cm^{-1} were assigned to the $\text{O}\text{--}\text{H}$ stretching vibration of the physisorbed water. This could be rationalized based on the fact that the moisture was absorbed into the sample when it was being dispersed on potassium bromide pallets in air for FT-IR analysis. Indeed, TGA analyses were carried out for a series of IRMOF-8 samples, indicating that the material was highly hygroscopic, and it absorbed moisture readily during the handling or the storage of the sample. If the analysis was performed right after the activation step, no moisture was found in the material (Fig. 4). However, the presence of water was clearly observed for samples stored or handled in air.



Scheme 1. Friedel–Crafts acylation of toluene with benzoyl chloride using IRMOF-8 catalyst.

3.2. Catalytic studies

The IRMOF-8 was assessed for its activity as a solid acid catalyst in the Friedel–Crafts acylation of toluene with benzoyl chloride to form *p*-benzoyltoluene as the major product and *o*-benzoyltoluene as the minor one (Scheme 1). The initial reaction was carried out using 5 mol% IRMOF-8 catalyst relative to toluene at 80 °C for 6 h. It was observed that the reaction could afford over 50% conversion under this condition without the need for an inert atmosphere, with a selectivity to *p*-benzoyltoluene of 80% being obtained. No trace amount of *m*-benzoyltoluene was detected from the product mixture. Initial studies addressed the effect of temperature on the reaction conversion, having carried out the reaction using 5 mol% IRMOF-8 catalyst and benzoyl chloride:toluene molar ratio of 5:1 at 80 °C, 90 °C, and 100 °C, respectively. Aliquots were withdrawn from the reaction mixture at different time intervals and analyzed by GC, giving kinetic data during the course of the reaction. It was found that increasing the reaction temperature from 80 °C to 90 °C led to a significant enhancement in reaction rate. A conversion of 72% was achieved after 6 h at 90 °C, while the reaction selectivity remained almost unchanged with 80% of *p*-benzoyltoluene being observed. As expected, a higher reaction conversion was obtained for the reaction carried out at 100 °C (Fig. 6). It was previously reported that the liquid-phase Friedel–Crafts acylation of toluene could be carried out in the temperature range of 60–120 °C, depending on the nature of the catalyst as well as the nature of the substrates [36,37,69–72]. Longer reaction time and/or higher catalyst concentration were needed to achieve reasonable conversion values at lower reaction temperature. Indeed, several Friedel–Crafts acylation processes have been effectively operated at 100 °C [36,72].

The reagent ratio is also an important factor that should be taken into consideration. Friedel–Crafts acylation reactions are normally carried out under solvent-free condition, and a large excess of one reagent is required to act as the reaction medium [36,37,70–72]. However, organic solvents were previously employed for the reaction in several cases, including both homogeneous and heterogeneous processes [37,69,73–75]. In this research, it was found that the Friedel–Crafts acylation reaction of toluene with benzoyl chloride using the IRMOF-8 catalyst could occur under solventless condition, and that the reagent molar ratio had a profound effect on the reaction conversion. Interestingly, decreasing the benzoyl chloride:toluene molar ratio from 5:1 to 4:1 resulted in a significant enhancement in reaction rate, with 82% conversion being obtained after 6 h at 100 °C for the latter case. Moreover, the reaction using 5 mol% IRMOF-8 catalyst at 100 °C afforded a conversion of up to 95% after 6 h at the benzoyl chloride:toluene molar ratio of 1.5:1. It should be noted that the reaction was carried out under solvent-free condition, and the excess benzoyl chloride could also act as the solvent for the reaction. In a heterogeneous reaction, mass transfer limitation in the system might have a significant effect on the reaction rate. Therefore, increasing the amount of the solvent could lead to a drop in reaction rate. From experimental points of view, it should be noted that using a benzoyl chloride:toluene molar ratio of less than 1.5:1 could cause difficulty in stirring the

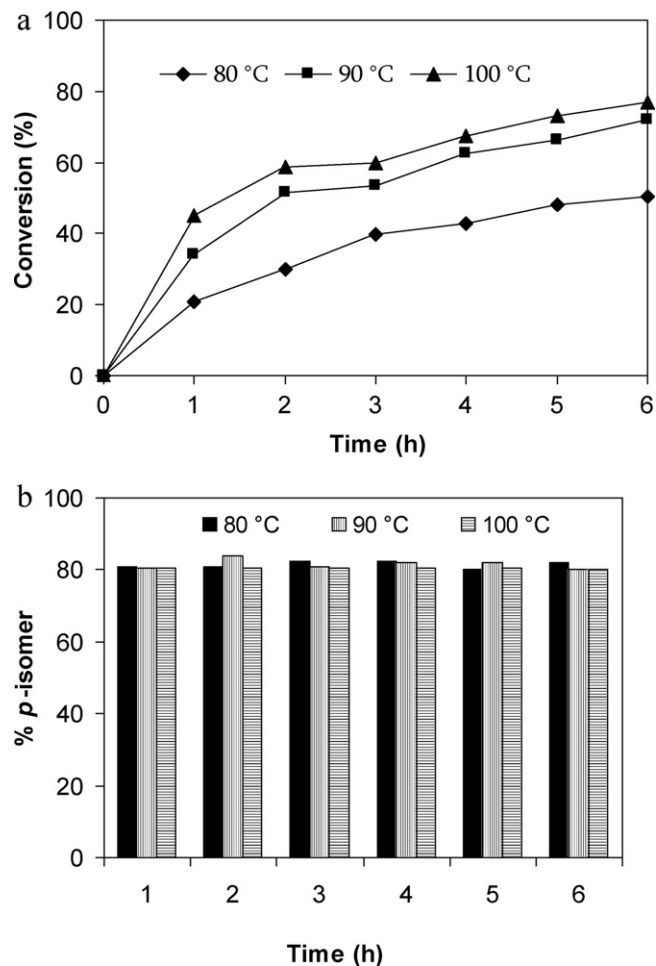


Fig. 6. Effect of temperature on reaction conversion (a) and reaction selectivity (b).

reaction mixture containing the solid catalyst. It was also observed that the selectivity to the *p*-isomer remained almost unchanged, being approximately 80% upon changing the reagent molar ratio from 5:1 to 1.5:1 (Fig. 7). The reaction selectivity observed for the acylation reaction using the IRMOF-8 catalyst was comparable to that previously reported in the literature, where the *p*-isomer ratio in the product mixture could range from 66% to 99%, depending on the nature of the catalyst as well as the reaction condition [36,69,70,72,76].

With such results in hand, we then decided to investigate the effect of catalyst concentration on reaction conversion. It was previously reported that in many cases, more than stoichiometric amounts of the Lewis acid such as anhydrous AlCl_3 , TiCl_4 , and FeCl_3 were needed for the Friedel–Crafts acylation reaction due to complex formation with the oxygen atom of the aroyl products [37,76]. Replacement of environmentally unacceptable anhydrous Lewis acids with solid acids has been a desired approach to effectively reduce the amount of catalyst for Friedel–Crafts acylation reactions. Indeed, by using solid acid catalysts such as mesoporous superacid catalyst [40], beta zeolite [44,45], hybrid zeolitic-mesostructured materials [47], and modified clay [48,49], the catalyst concentrations could vary from less than 1 mol% to more than 10 mol%, depending on the nature of the catalyst as well as that of the substrate. The catalyst concentration, with respect to the zinc content in the IRMOF-8, was studied in the range of 1–5 mol% relative to toluene. The reaction was carried out using a benzoyl chloride:toluene molar ratio of 1.5:1 at a reaction temperature of 100 °C for 6 h. It was found that the Friedel–Crafts acylation of toluene and

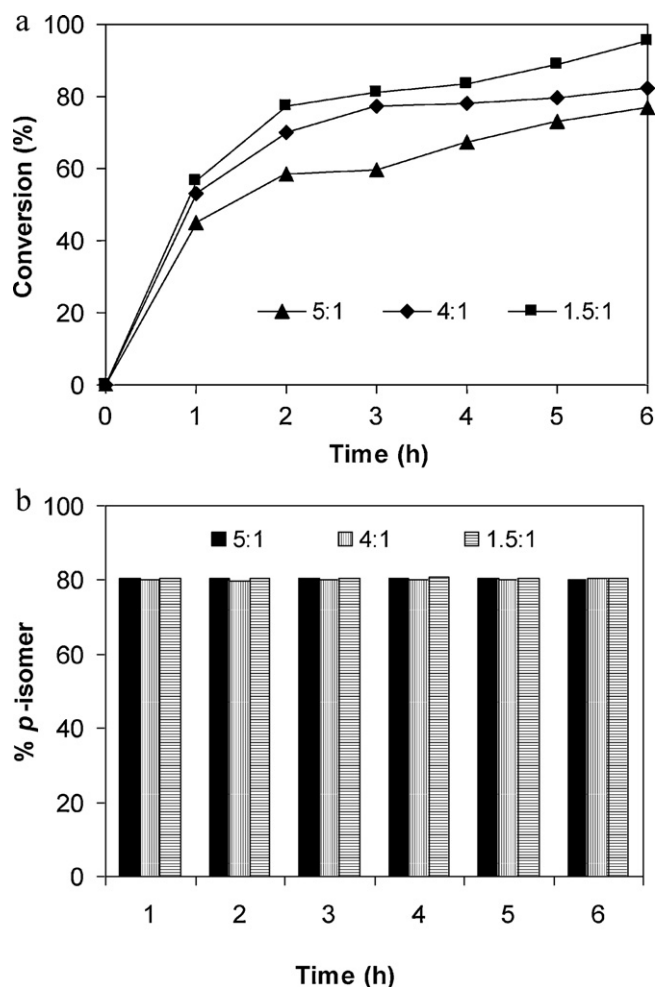


Fig. 7. Effect of benzoyl chloride:toluene molar ratio on reaction conversion (a) and reaction selectivity (b).

benzoyl chloride proceeded readily in the presence of a catalytic amount of the IRMOF-8. Conversions of 95%, 90%, and 88% were achieved after 6 h at the catalyst concentration of 5 mol%, 3 mol%, and 1 mol%, respectively. The catalyst concentrations used for the Friedel–Crafts acylation reaction in this study were therefore comparable to those in the literature. As expected, it was found that the selectivity to the *p*-isomer remained almost unchanged, being approximately 80% in the catalyst concentration range of 1–5 mol% (Fig. 8).

The activity of the IRMOF-8 in the Friedel–Crafts acylation of toluene was also compared to that of MOF-5 (also called IRMOF-1), a well-known member of isorecticular metal–organic frameworks. The MOF-5 was synthesized and characterized as previously reported [25]. The reaction using the MOF-5 catalyst was carried out using a benzoyl chloride:toluene molar ratio of 1.5:1 at a reaction temperature of 100 °C for 6 h. Kinetic studies indicated that the IRMOF-8 exhibited slightly higher activity than the MOF-5. Reaction conversions of 90%, 88%, and 82% were observed after 6 h at the MOF-5 concentration of 5 mol%, 3 mol%, and 1 mol%, respectively. Furthermore, the selectivity to the *p*-isomer of the reaction using the IRMOF-8 (approximately 80%) was also slightly higher than that for the case of the MOF-5 (approximately 77%). However, it was apparent that the MOF-5 could be used as an alternative catalyst for the Friedel–Crafts acylation reaction. Indeed, Farriseng and co-workers previously reported that the IRMOF-8 and MOF-5 exhibited almost similar activity in the Friedel–Crafts alkylation reaction of toluene and *tert*-butyl chloride, though slightly

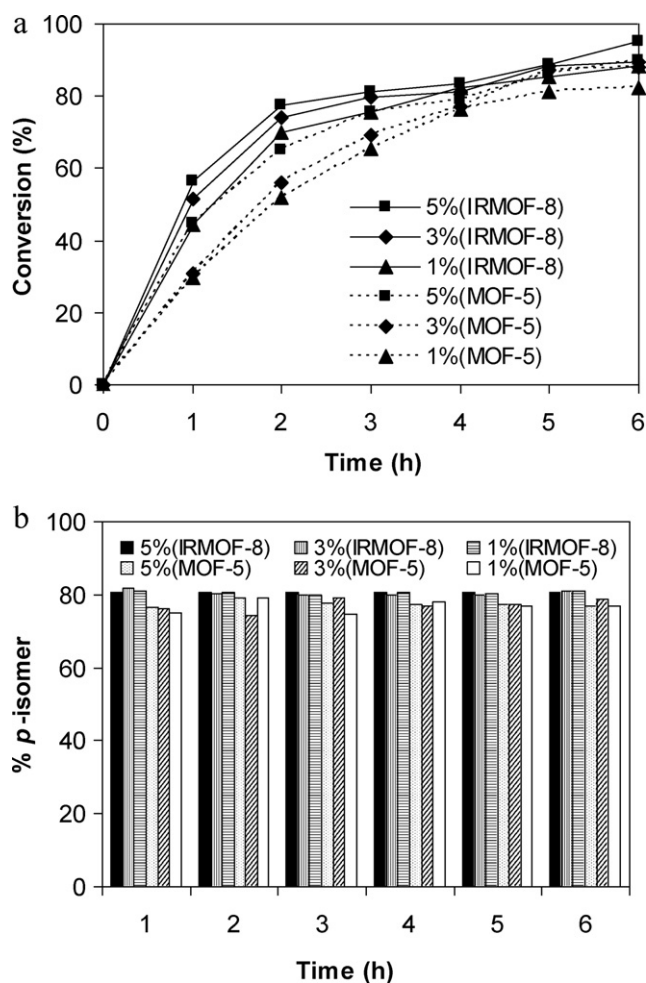


Fig. 8. Effect of catalyst concentration on reaction conversion (a) and reaction selectivity (b).

higher conversions and selectivity were observed for the case of the IRMOF-8 [77]. It should be noted that MOF-5 (composition of $Zn_4O(BDC)_3$ in which BDC = 1,4-benzenedicarboxylate) is topologically similar to IRMOF-8 (composition of $Zn_4O(NDC)_3$ in which NDC is 2,6-naphthalenedicarboxylate), and the MOF-5 possessed significantly higher surface areas than those of the IRMOF-8. However, the median pore diameter of the IRMOF-8 was larger than that of the MOF-5 [56], thus indicating that the pore size of the IRMOFs might have a more pronounced effect on the reaction than the surface areas.

For a liquid-phase reaction using solid catalysts, an important problem that should be taken into account is the possibility that some of active sites could migrate from the solid phase to the solution and that these leached species could become responsible for a significant part of the catalytic activity [78]. In order to determine if leaching was a problem for the Friedel–Crafts acylation reaction using the IRMOF-8 catalyst, an experiment was performed to estimate the contribution of leached active species to the total reaction conversion by performing a simple centrifugation during the course of the reaction to remove the solid catalyst. If the reaction conversion continued increasing after the solid catalyst was removed, this would indicate that the real active species was leached acid rather than the solid IRMOF-8 catalyst. The organic phase was separated from the solid catalyst after 1 h reaction time by simple centrifugation, having used 5 mol% of fresh IRMOF-8 catalyst at 100 °C. The reaction solution was then transferred to a new reactor vessel, and stirred for an additional 5 h at 100 °C with aliquots being sampled

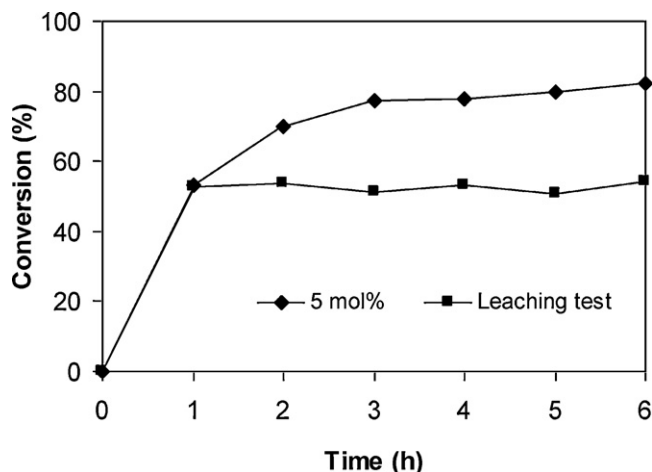


Fig. 9. Leaching test indicated no contribution from homogeneous catalysis of active acid species leaching into reaction solution.

at different time intervals, and analyzed by GC. The data from GC analysis results gave quantitative information about residual, catalytically active acid in the reaction solution. Within experimental error, no further reaction was observed after the solid IRMOF-8 was removed, proving that there was no contribution from leached active species and that conversion was only being possible in the presence of the solid IRMOF-8 catalyst (Fig. 9).

As mentioned earlier, the replacement of environmentally unacceptable homogeneous Lewis acids with solid acids offers several advantages including easy catalyst recovery and recycling. Indeed, solid acid catalysts were previously investigated for the Friedel–Crafts acylation reactions, and it was reported that several of them could be recycled and reused [44,45,48,79]. The IRMOF-8 catalyst was therefore investigated for recoverability and reusability in the Friedel–Crafts acylation reaction over five successive runs. The reaction was carried out at 100 °C using the benzoyl chloride:toluene molar ratio of 1.5:1 at 5 mol% catalyst for 6 h. After each run, the catalyst was separated from the reaction mixture by simple centrifugation, then washed with copious amounts of toluene to remove any physisorbed reagents. The recovered IRMOF-8 was dried under vacuum at 100 °C overnight, and then reused in further reactions under identical conditions to those of the first run. Aliquots were withdrawn from the reaction mixture at different time intervals and analyzed by GC, giving kinetic data during the course of the reaction using the fresh and recycled catalyst, respectively. It was found that the IRMOF-8 catalyst could be recovered and reused in further reactions without a significant degradation in activity. Conversions of 95%, 95%, 96%, 90%, and 82% were achieved after 6 h for the 1st, 2nd, 3rd, 4th, and 5th run, respectively. The selectivity to the *p*-isomer remained almost unchanged over five successive runs, being approximately 80% for all cases (Fig. 10). Although it was previously reported that no loss of activity was observed for reused solid catalysts in the Friedel–Crafts acylation reaction, no kinetic data was provided [35,40]. Indeed, only conversions at the end of the experiment were mentioned. Unfortunately, stable activity cannot be proven by reporting only similar reaction yields at long times. Kinetic studies are the true test of catalyst deactivation [78]. Further investigations would be needed to clarify the reason of the catalyst deactivation in the Friedel–Crafts acylation reaction using the IRMOF-8. However, it was found that the IRMOF-8 crystals were broken into smaller particles after three catalytic runs. Particle agglomeration was then observed in the 4th and 5th runs, which should be one of the reasons of the catalyst deactivation.

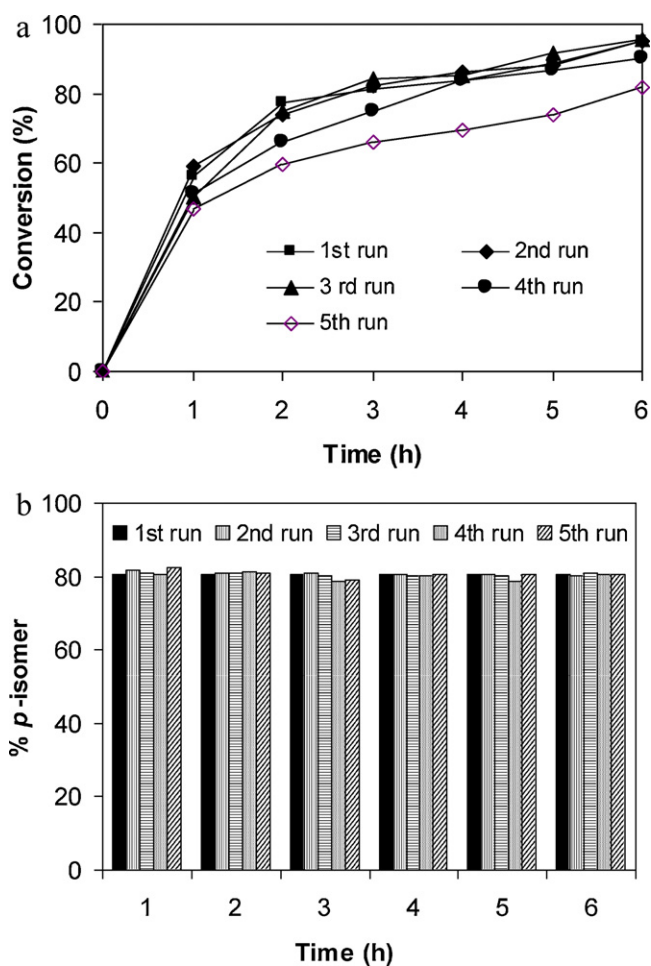


Fig. 10. Catalyst recycling studies: conversion (a) and selectivity (b).

The study was then extended to the Friedel–Crafts acylation reaction of benzoyl chloride with several aromatic hydrocarbon having different substituents, including anisole, toluene, *p*-xylene, and ethylbenzene, respectively. Reactions were carried out at 100 °C with 5 mol% catalyst loading and at the benzoyl chloride:aromatic hydrocarbon molar ratio of 1.5:1. However, it was difficult to observe the difference of the reaction rate as the benzoylation proceeded with high conversions in all cases. It was therefore decided to decrease the catalyst concentration to 3 mol% when investigating the effect of different substituents on the reaction conversion and selectivity. As expected, the anisole benzoylation using the IRMOF-8 catalyst proceeded with a higher reaction rate than that of toluene. This result is consistent with the classical Friedel–Crafts acylation mechanism, in which the reaction is favored by the presence of more electron-donating groups in the aromatic substrate. Indeed, Choudhary, Jang and co-workers employed several solid acid catalysts for the Friedel–Crafts benzoylation and found that the reactivity of the aromatic nucleus increased with the number of electron-donating groups [36,80]. Interestingly, the rate of the toluene benzoylation using the IRMOF-8 catalyst was found to be significantly higher than that of *p*-xylene, which is different from the classical Friedel–Crafts acylation mechanism. Experimental results also indicated that the reaction of ethylbenzene proceeded slower than the case of toluene, with 70% conversion being observed after 6 h (Fig. 11). It was also found that the selectivity to the *p*-isomer in the reaction of anisole was slightly higher than the case of toluene and ethylbenzene. The fact that *p*-xylene and ethylbenzene were less reactive than toluene in

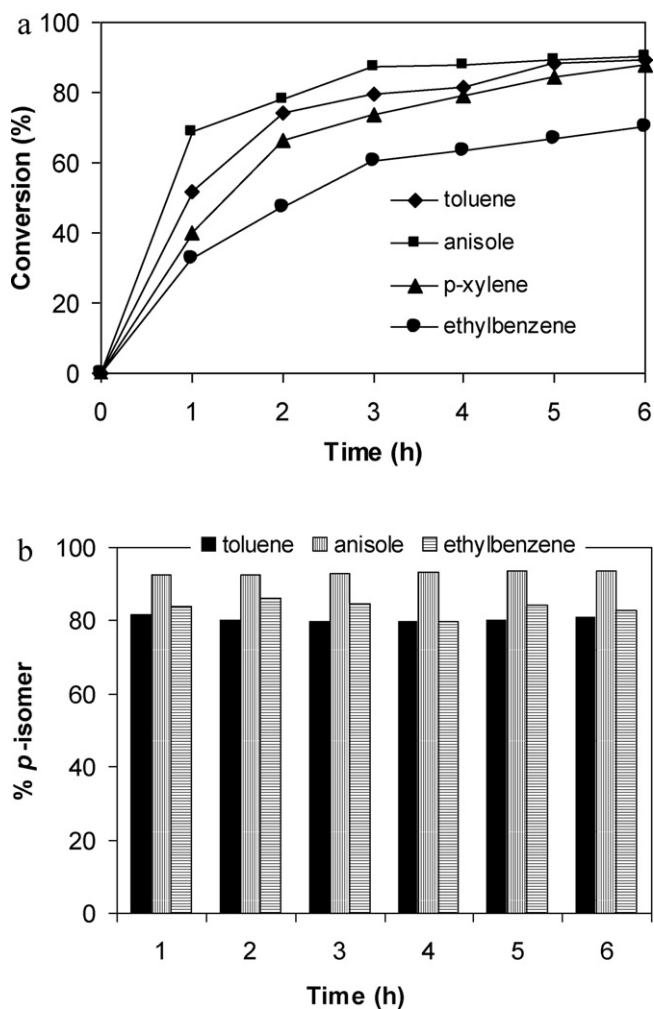


Fig. 11. Effect of substituents on reaction conversion (a) and reaction selectivity (b).

the benzoylation reaction still remains to be explained in further investigation.

The effect of different acylation reagents on the Friedel–Crafts acylation reaction of toluene was also studied, having carried out the reaction using benzoyl chloride, 4-methoxybenzoyl chloride, and 4-chlorobenzoyl chloride, respectively, at 100 °C with 3 mol% catalyst loading and at the reagent molar ratio of 1.5:1. It was found that the reaction of 4-methoxybenzoyl chloride afforded 93% conversion after 6 h, while a conversion of 83% was observed for the case of 4-chlorobenzoyl chloride (Fig. 12). Indeed, Fernandes and co-workers previously reported that the presence of electron-withdrawing groups in the acyl chloride significantly reduced the yield of the Friedel–Crafts acylation reaction [37]. In contrast, Posternak and co-workers reported a positive effect of electron-withdrawing groups in the acyl chloride for the Friedel–Crafts acylation reaction [76]. Although the zinc center is of medium acidity, the acylation reaction could proceed to high conversions in the presence of a catalytic amount (1–5 mol%) of the IRMOF-8 without the need for an inert atmosphere. Farrusseng and co-workers previously employed IRMOFs as catalysts for Friedel–Crafts alkylation, and proposed that Zn–OH species, which were formed as structural defects in the synthesis step or upon water adsorption, could contribute to the catalytic activity of the IRMOFs [26,77]. Choudhary and co-workers previously carried out the Friedel–Crafts acylation using zeolite-based catalysts in the presence of moisture, and pointed out that new Bronsted acid sites created by the interac-

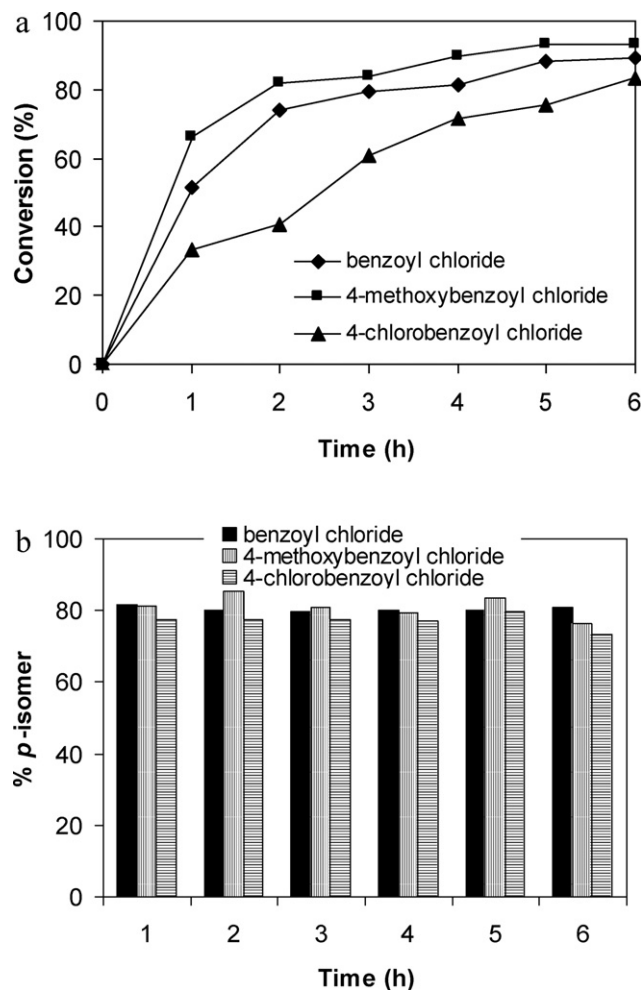


Fig. 12. Effect of different acylation reagents on reaction conversion (a) and reaction selectivity (b).

tion of the moisture with the Lewis acid sites of the catalyst could enhance the reaction rate appreciably [80]. The exact catalytic centers still remain to be clarified, though it could be proposed that both Lewis acid and Bronsted acid sites might be responsible for the catalytic activity of the IRMOF-8. However, further studies would be necessary to elucidate the acid centers present in the catalyst, as well as the mechanism of the Friedel–Crafts acylation reaction using the IRMOF-8.

4. Conclusions

In conclusion, highly crystalline porous IRMOF-8 was achieved by a solvothermal method using zinc nitrate tetrahydrate and 2,6-naphthalenedicarboxylic acid. The IRMOF-8 was characterized using a variety of different techniques, including FT-IR, TEM, SEM, XRD, TGA, AAS, and nitrogen physisorption measurements. The Friedel–Crafts acylation of toluene and benzoyl chloride proceeded readily in the presence of a catalytic amount of the IRMOF-8 (1–5 mol%), without the need for an inert atmosphere. The solid catalyst could be easily separated from the reaction mixture by simple centrifugation or filtration, and could be reused without a significant degradation in catalytic activity. No contribution from homogeneous catalysis of active acid species leaching into the reaction solution during the course of the reaction was detected. The IRMOF-8 catalyst clearly exhibited advantages over conventional Lewis acid catalysts such as anhydrous AlCl_3 , TiCl_4 , and FeCl_3 , and could be used as an alternative to other solid acid catalysts for the

Friedel–Crafts acylation reaction. The fact that the IRMOF-8 was readily synthesized using a simple procedure would be interesting to the chemical industry. Current research in our laboratory has been directed to the design and synthesis of several MOF-based catalysts for a wide range of organic transformations.

Acknowledgements

The Vietnam Department of Science and Technology is acknowledged for financial support through contract No. 40/2010/HD-NDT.

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