

A Zeolite Imidazolate Framework ZIF-8 Catalyst for Friedel-Crafts Acylation

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Abstract: A zeolite imidazolate framework, ZIF-8, was synthesized and characterized by dynamic laser light scattering, X-ray powder diffraction, scanning electron microscopy, transmission electron microscopy, thermogravimetric analysis, Fourier transform infrared, atomic absorption spectrophotometry, and nitrogen adsorption measurements. The ZIF-8 was highly crystalline and porous with a surface area of over 1600 m²/g. Friedel-Crafts acylation of anisole and benzoyl chloride proceeded well in the presence of ZIF-8 (2–6 mol%) without the need for an inert atmosphere. The reaction afforded a selectivity of 93%–95% to the *p*-isomer. The solid catalyst can be separated from the reaction mixture by simple centrifugation and reused without significant degradation in catalytic activity. There was no leaching of active acid species into the reaction solution.

Key words: imidazolate framework; zeolite imidazolate framework ZIF-8; Friedel-Crafts acylation; porous material; catalysis

Metal-organic frameworks (MOFs) have emerged as a new class of porous crystalline materials with numerous potential applications in gas separation and storage, ion exchange, sensors, drug delivery, catalysis, luminescent and fluorescent materials, and optoelectronics materials [1–5]. By controlling the size and functionalization of the organic linkers, well-defined MOF structures with high surface areas and tunable pore sizes can be achieved, thus offering advantages over traditional microporous and mesoporous inorganic materials [6–8]. In the field of catalysis, several MOFs have already been used as solid catalysts for a variety of organic transformations [9–18]. Zeolite imidazolate frameworks (ZIFs), a new subclass of MOFs, have attracted significant attention as they combine the advantages from both zeolites and conventional MOFs [19,20]. During the past decade, research works have focused on synthesizing new ZIFs for their applications in gas capture and storage. As compared with conventional MOFs, there are few applications of ZIFs as catalysts or catalyst supports for organic transformations in the literature [15, 21–23].

Friedel-Crafts acylation of aromatic compounds with acid chlorides to form arylketones are fundamental and important processes in the production of pharmaceuticals, agrochemicals,

and fragrances [24]. Traditionally, an excess over stoichiometric amounts of anhydrous strong Lewis acids such as AlCl₃, TiCl₃, FeCl₃, or SnCl₄ are required for these reactions [25]. These catalysts are highly moisture sensitive, and therefore moisture-free conditions have to be employed to maximize the atom economy of the reactions [25,26]. Moreover, these catalysts are highly toxic and corrosive, generate a large amount of waste, and cause difficult purification of the products [27]. For green chemistry, moisture-insensitive and easily handled solid acid catalysts should be developed [28]. A variety of solid catalysts have been employed for the Friedel-Crafts acylation reactions, including zeolites [29–31], hybrid zeolitic-mesostructured materials [32], mesoporous superacid catalyst [33], modified clay [34, 35], fly ash-supported cerium triflate [36], metal triflate loaded SBA-15 [37], Ga/SBA-15 supported on carbon nanofibers composite [38], mesoporous sulphated zirconia [39], mesoporous sieve AlKIT-5 [40], nanostructural zinc oxide hollow spheres [41], and silica gel supported aluminium trichloride [42]. In this work, we report the utilization of ZIF-8 as a heterogeneous catalyst for Friedel-Crafts acylation. High conversions were achieved with a catalytic amount of ZIF-8 (2%–6%) without the need for an

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inert atmosphere.

1 Experimental

1.1 Materials and instrumentation

All reagents and starting materials were obtained commercially from Sigma-Aldrich and Merck, and were used as received without further purification unless otherwise noted. X-ray powder diffraction (XRD) patterns were recorded using a Cu K_α radiation source in a D8 Advance Bruker powder diffractometer. Scanning electron microscopy (SEM) studies were conducted on a JSM 740 scanning electron microscope. Transmission electron microscopy (TEM) studies were performed using a JEOL JEM 1400 transmission electron microscope operated at 100 kV. The ZIF-8 samples were dispersed on holey carbon grids for TEM observation. Elemental analysis by atomic absorption spectrophotometry (AAS) was performed on a Shimadzu AA-6800. The particle size distribution of the ZIF-8 was determined by the dynamic laser light scattering (DLS) method using a LA 920. Fourier transform infrared (FT-IR) spectra were obtained on a Bruker TENSOR37 instrument with the sample dispersed on a potassium bromide pellet. Nitrogen adsorption 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 under a nitrogen atmosphere. 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 was from 100 to 130 °C at 15 °C/min, from 130 to 200 °C at 50 °C/min, from 200 to 215 °C at 1.5 °C/min, from 215 to 300 °C at 50 °C/min and then held at 300 °C for 3 min. Inlet and detector temperatures were set at 300 °C. *n*-Dodecane was used as an internal standard to calculate 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 was from 60 to 280 °C at 10 °C/min and then held at 280 °C for 2 min. The inlet temperature was set at 280 °C. MS spectra were compared with the spectra in the NIST library.

1.2 Synthesis of ZIF-8

In a typical preparation [43], a solid mixture of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 3.76 g, 14.7 mmol) and 2-methylimidazole (H-MeIM, 0.43 g, 11.6 mmol) was dissolved in 240 ml of *N,N*-dimethylformamide (DMF) that was then distributed into 20 ml vials. The vial was tightly capped

and heated at a rate of 5 °C/min to 140 °C in a programmable oven and held at this temperature for 24 h, then cooled at a rate of 0.4 °C/min to room temperature. After removal of the mother liquor from the mixture, chloroform (20 ml) was added to the vials. Colorless polyhedral crystals were collected from the upper chloroform layer and soaked in DMF (3×15 ml) for 3 d. After that, the DMF was exchanged for dichloromethane (DCM) (3×15 ml) for 3 d. The residual solvent was removed by vacuum at 200 °C for 6 h, which yielded 0.30 g of white polyhedral crystals (25% yield based on 2-methylimidazole).

1.3 Catalytic test

The Friedel-Crafts acylation of anisole with benzoyl chloride using the ZIF-8 catalyst was carried out in a magnetically stirred round bottom flask fitted with a reflux condenser. In a typical reaction, a mixture of anisole (0.65 ml, 6 mmol), benzoyl chloride (1.4 ml, 12 mmol), and *n*-dodecane (0.2 ml) as an internal standard was added into a 50 ml flask containing the ZIF-8 (69 mg, 6 mol%). The catalyst concentration was calculated with respect to the zinc/anisole molar ratio. The resulting mixture was stirred at 120 °C for 6 h. The reaction conversion was monitored by withdrawing aliquots from the reaction mixture at fixed time intervals and quenching with an aqueous NaOH solution (1%, 0.1 ml). The organic components were extracted using diethyl ether (3×1 ml), dried over anhydrous Na_2SO_4 , and analyzed by GC. The reaction conversion was calculated based on anisole. The product identity was further confirmed by GC-MS. The ZIF-8 catalyst was separated from the reaction mixture by simple centrifugation, washed with copious amounts of anhydrous DCM, dried under vacuum at 100 °C for 5 h, and reused. For the leaching test, a catalytic reaction at 120 °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 120 °C for a further 5 h, and monitored by GC as previously described to determine if there was any further reaction.

2 Results and discussion

2.1 Catalyst synthesis and characterization

The ZIF-8 was synthesized from the reaction between zinc nitrate hexahydrate and 2-methylimidazole in DMF at 140 °C according to a literature procedure [43]. In the zeolite imidazolate framework, zinc atoms in the ZIF-8 structure were connected to nitrogen atoms by 2-methylimidazolate (MeIM) linkers, which created nanosized pores formed by four, six, eight, and twelve membered ring ZnN_4 tetrahedral clusters [20,44]. It was previously reported that the structure of ZIFs was similar to that of conventional zeolites in which the T–O–T bridges (T = Si, Al, P) in zeolites were replaced by M–IM–M bridges (M = Zn, Co, Cu). More interestingly, the bond angles

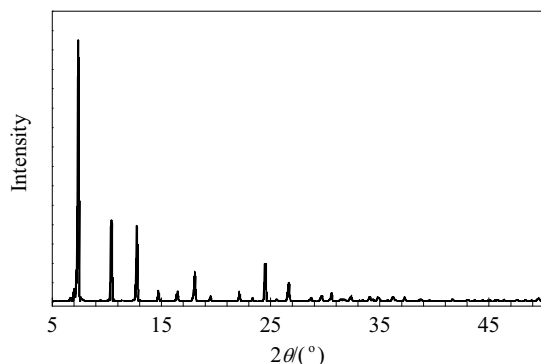


Fig. 1. XRD pattern of the ZIF-8.

in both frameworks are 145° [20]. In the synthesis of porous MOF-based materials using DMF as solvent, a solvent exchange with DCM should be carried out after the solid crystals were formed to facilitate the evacuation of the material framework [1,2,45]. Subsequently, weakly interacting DCM molecules can be easily removed when the ZIF-8 sample is activated under vacuum [45]. The ZIF-8 was obtained as white polyhedral crystals with a yield of 25%, which was comparable with that of previously reported procedures (normally around 20%–25% yields) [3].

The ZIF-8 was then characterized by a variety of different techniques. A zinc loading of 4.17 mmol/g was found from the elemental analysis with AAS. The particle size distribution of the ZIF-8 observed by DLS analysis showed an average size of 159 μm . A very sharp peak below 10° (2θ of 7.20) was observed in the XRD pattern of the ZIF-8, indicating that a highly crystalline material was achieved (Fig. 1). The overall XRD pattern of the ZIF-8 in this work were in good agreement with the patterns from single crystal data [21,43,46,47]. It was apparent that the ZIF-8 had better crystallinity as compared with silica-based materials such as SBA-15, SBA-16, and MCM-41 where broader peaks were observed on their diffractograms [48]. The SEM image showed well-shaped and high quality cubic crystals for the ZIF-8 (Fig. 2). As expected, the TEM analysis revealed that the ZIF-8 possessed a porous structure (Fig. 3) which was different from that of conventionally used

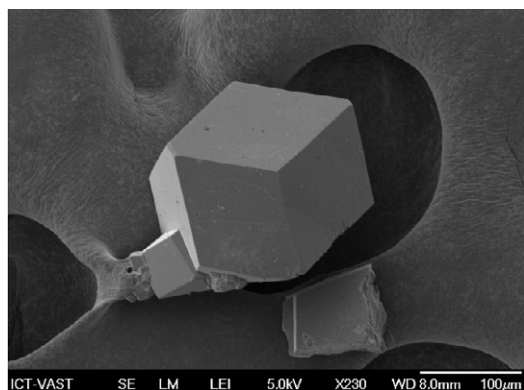


Fig. 2. SEM image of the ZIF-8.

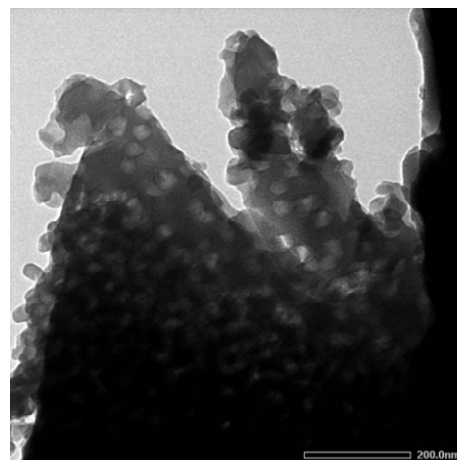


Fig. 3. TEM image of the ZIF-8.

microporous and mesoporous inorganic materials. Nitrogen adsorption measurements (Fig. 4) indicated that the pore structure of the ZIF-8 was complex and contained both mesoporous and microporous pores.

FT-IR spectra of the ZIF-8 showed a significant difference from that of the 2-methylimidazole linker (Fig. 5). In the FT-IR spectra of 2-methylimidazole, a strong and broad band from 3400 to 2200 cm^{-1} with the maximum at 2650 cm^{-1} was assigned to the N–H $\cdots$ N hydrogen bond [49]. The resonance

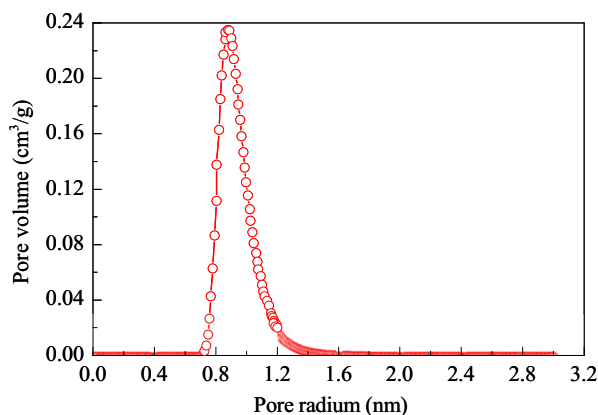


Fig. 4. Pore size distribution of the ZIF-8.

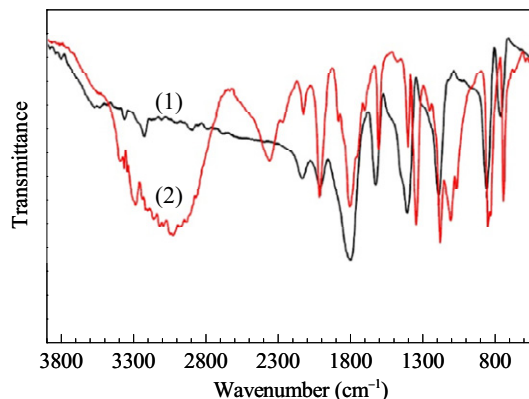


Fig. 5. FT-IR spectra of the ZIF-8 (1) and 2-methylimidazole (2).

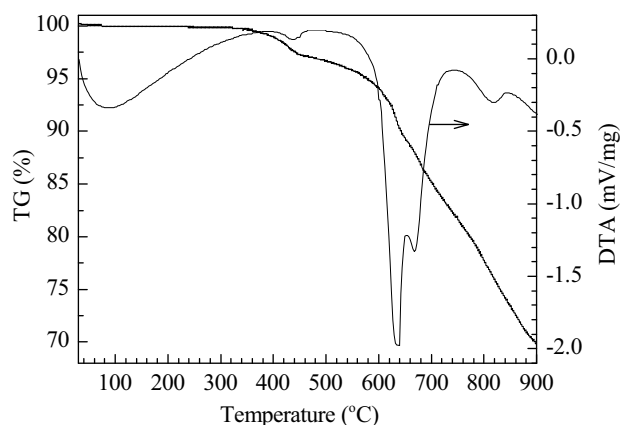
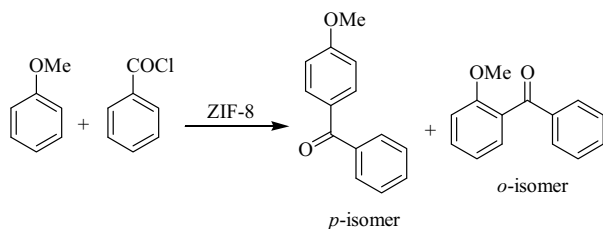


Fig. 6. TGA analysis of the ZIF-8.

between the N–H···N out-of-plane bending and the N–H stretching vibrations was found at 1846 cm^{-1} [49]. These absorption bands were not seen in the spectra of the ZIF-8, confirming that the 2-methylimidazole linkers were fully deprotonated during the formation of the ZIF structure. In the TGA result for the ZIF-8, there was little weight loss in the temperature range of 200–400 °C, indicating that the ZIF-8 was stable up to 400 °C (Fig. 6). The thermal stability of the ZIF-8 was therefore comparable with that reported in the literature [43]. The specific surface area was up to $1632\text{ m}^2/\text{g}$ for the ZIF-8, which was in good agreement with that in the literature. Several ZIF-8 samples with surface areas ranging from 1300 to $1810\text{ m}^2/\text{g}$ were previously reported [19,43,50–8].

2.2 Catalytic test

The ZIF-8 was assessed for its activity as a solid catalyst in the Friedel-Crafts acylation of anisole with benzoyl chloride to form *p*-benzoylanisole as the major product and *o*-benzoylanisole as the minor product (Scheme 1). In the ZIF-8 structure, the six-membered ring pore windows are as narrow as 0.34 nm [20,51], and large molecules cannot enter the pores. Chizallet and coworkers [22] recently investigated the transesterification reaction using ZIF-8 as catalyst, and pointed out that all active sites are located on the external surface, and not in the micropores. It can be inferred that the Friedel-Crafts acylation of anisole with benzoyl chloride would also occur on the external surface of the ZIF-8 particles. Initial studies addressed the effect of temperature on the reaction



Scheme 1. Friedel-Crafts acylation of anisole with benzoyl chloride using ZIF-8 catalyst.

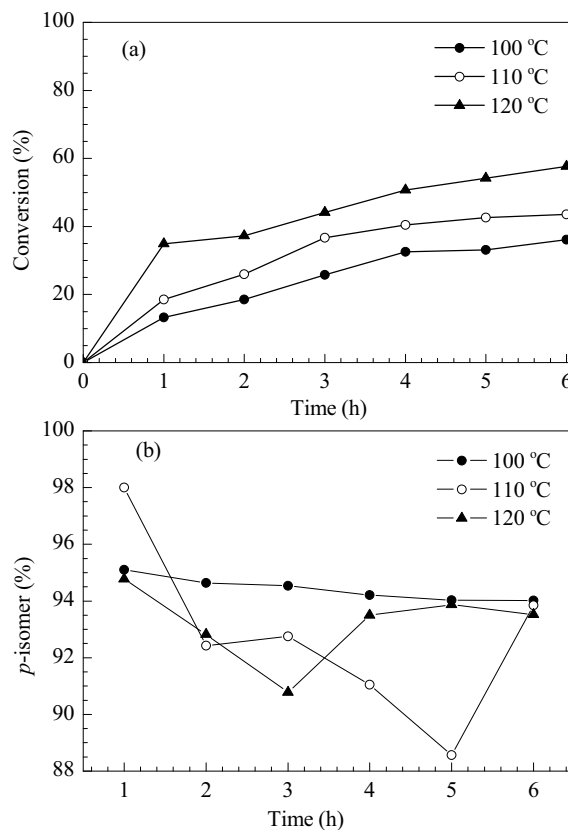


Fig. 7. Effect of temperature on reaction conversion (a) and selectivity (b).

conversion using 4 mol% ZIF-8 catalyst and an anisole:benzoyl chloride molar ratio of 1:4 and 100, 110, and 120 °C. Aliquots were withdrawn from the reaction mixture at different times and analyzed by GC to give kinetic data for the course of the reaction. A conversion of 58% was obtained after 6 h reaction at 120 °C. Decreasing the temperature resulted in a significant drop in the reaction rate, with 44% and 36% conversions after 6 h at 110 and 100 °C, respectively (Fig. 7(a)). The reaction selectivity remained almost unchanged at 93%–95% *p*-benzoylanisole (Fig. 7(b)).

For an organic transformation using a solid catalyst, the reagent ratio is an important factor. In this work, it was found that the reagent molar ratio had a profound effect on the reaction conversion. The data were from the reaction at 120 °C for 6 h, using 4 mol% ZIF-8 catalyst with anisole:benzoyl chloride molar ratios of 1:2, 1:3, and 1:4. The reaction carried out with the reagent ratio of 1:4 afforded 58% conversion after 6 h. Interestingly, decreasing the reagent ratio to 1:4 to 1:3 resulted in an enhancement in reaction rate, with 66% conversion after 6 h. The value improved to 76% for the reaction using the anisole:benzoyl chloride molar ratio of 1:2 (Fig. 8(a)). From the experimental point of view, using a molar ratio of less than 1:2 would cause difficulty in stirring the reaction mixture containing the solid catalyst. In several cases, Friedel-Crafts acylation reactions are carried out under solvent-free condition

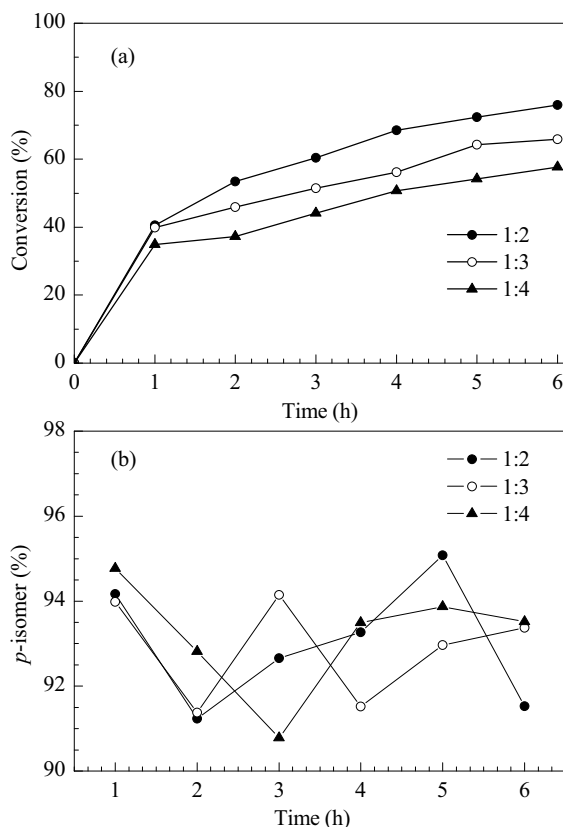


Fig. 8. Effect of anisole:benzoyl chloride molar ratio on reaction conversion (a) and selectivity (b).

with a large excess of one reagent as the reaction medium [25,27,52–54]. In this work, the Friedel-Crafts acylation reaction using the ZIF-8 catalyst was carried out under solvent-free condition with excess benzoyl chloride also acting as the solvent. In a heterogeneous reaction, mass transfer limitation in the system can have a significant effect on the reaction rate. Therefore, increasing the amount of solvent can lead to a drop in reaction rate. The reaction selectivity remained almost unchanged, with 93%–95% *p*-benzoylanisole being observed (Fig. 8(b)).

For a liquid phase organic transformation using a solid catalyst, there is the possibility that some active sites are dissolved into the liquid phase, and these leached species can contribute significantly to the reaction conversion [55]. In order to determine if leaching occurred in the Friedel-Crafts acylation reaction using the ZIF-8 catalyst, an experiment was carried out to estimate the contribution, if any, of leached active species. A simple centrifugation was performed during the course of the reaction to remove the solid ZIF-8. If the catalytic reaction continued, this would indicate that active species had been leached. The solid ZIF-8 catalyst was removed from the reaction mixture after 1 h reaction time by simple centrifugation (the reaction was started with 4 mol% of fresh ZIF-8 catalyst at 120 °C). The liquid phase was then transferred to a new reactor vessel and stirred for an additional 5 h at 120 °C

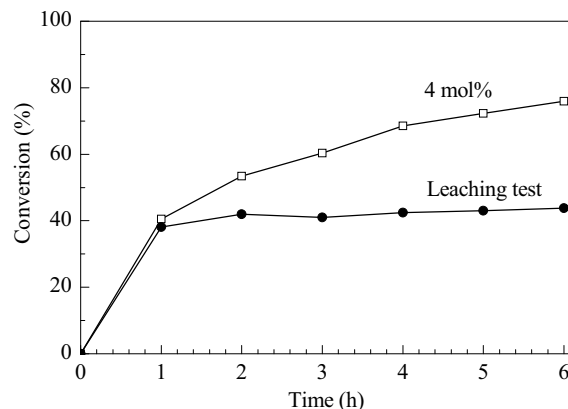


Fig. 9. Leaching test to indicate no active acid species leaching into the reaction solution.

with aliquots being sampled at different times and analyzed by GC. Within experimental error, no further reaction was observed after the solid catalyst was removed from the reaction mixture. Therefore, it can be inferred that there was no leached active species in the liquid phase, and that the reaction could only proceed in the presence of the solid ZIF-8 catalyst (Fig. 9). It should also be noted that no conversion was observed for the reaction in the absence of the ZIF-8 catalyst.

We also investigated the effect of the catalyst concentration on the reaction conversion. It was previously reported that for the Friedel-Crafts acylation using traditional catalysts, an excess over stoichiometric amounts of the Lewis acid can be required, as a complex between the metal and the oxygen atom of the aryl products can be formed in significant amounts [27,56]. The catalyst concentration can be reduced dramatically with several solid catalysts for this reaction, such as mesoporous superacid catalyst [33,36], metal triflate loaded SBA-15 [37], beta zeolite [29,30], and hybrid zeolitic-mesoporous materials [32]. Indeed, the Friedel-Crafts acylation reaction can require from less than 1 mol% to more than 10 mol% catalyst, depending on the nature of the catalyst as well as the substrate. In this work, it was found that the benzoylation reaction of anisole can proceed in the presence of a catalytic amount of the ZIF-8. The reaction has been carried out at 120 °C for 6 h with a reagent molar ratio of 1:2 in the presence of 2 mol%, 4 mol%, and 6 mol% ZIF-8 catalyst. On increasing the catalyst concentration from 4 mol% to 6 mol%, a conversion of 82% was achieved after 6 h. As expected, the reaction proceeded more slowly for the case of 2 mol% catalyst, although 67% conversion was still obtained after 6 h (Fig. 10(a)). The selectivity for the *p*-isomer was almost the same for all cases, with 93%–95% of *p*-benzoylanisole being obtained (Fig. 10(b)). Firouzbadi and co-workers previously used aluminum dodecatungstophosphate as a heterogeneous catalyst for the Friedel-Crafts acylation reaction between anisole and benzoyl chloride, and obtained a selectivity of 80% to the *p*-isomer [57]. In the same reaction using a zeolite-based

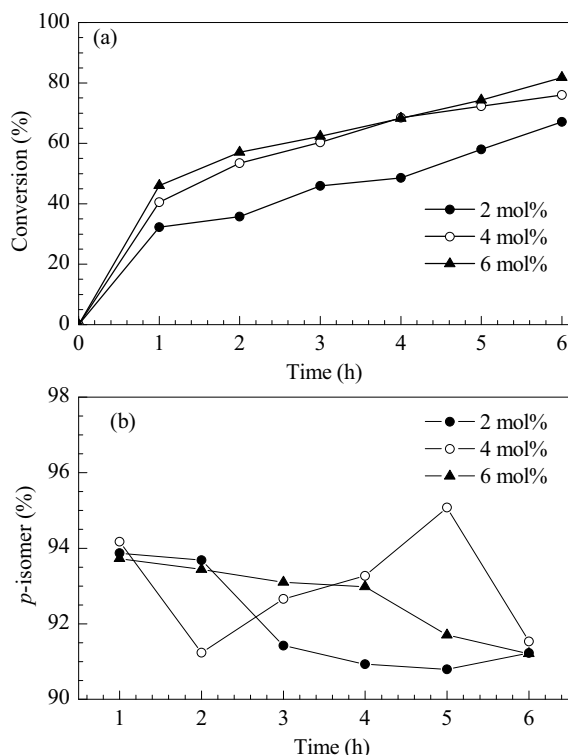


Fig. 10. Effect of catalyst concentration on reaction conversion (a) and selectivity (b).

catalyst, Choudhary and coworkers improved the *p*-isomer selectivity to 90% [58]. Singh and coworkers [59] also achieved a selectivity of 90% for the same reaction using $\text{Cu}(\text{OTf})_2$ as a catalyst. Kemnitz and coworkers [60] improved the selectivity to 93%–95% by using a borate zirconia solid acid catalyst. However, the reaction required the presence of nitrobenzene as solvent [60]. The selectivity of ZIF-8 in the Friedel-Crafts benzoylation of anisole was therefore comparable with those previously reported in the literature. Moreover, it was found that increasing the particle size of the ZIF-8 catalyst resulted in a significant drop in reaction rate. Conversions of 92%, 76%, and 69% were obtained after 6 h reaction using 4 mol% ZIF-8 with particle sizes of 92, 159, and 210 μm , respectively (Fig. 11). Since the reaction occurred on the external surface of the ZIF-8 particles, smaller size crystals should exhibit higher catalytic activity due to the increased external surface of the smaller crystals [61].

The study was then extended to the Friedel-Crafts acylation of anisole with different acylating reagents, including benzoyl chloride, 4-methoxybenzoyl chloride, and 4-chlorobenzoyl chloride. The reaction was carried out for 6 h at 120 °C using 6 mol% ZIF-8 catalyst with the reagent molar ratio of 1:2. Posternak and coworkers [56] previously reported a positive effect of electron-withdrawing groups present in the acyl chloride for Friedel-Crafts acylation. However, Fernandes and coworkers [27] found that the yield of Friedel-Crafts acylation was dramatically decreased in the presence of electron-withdrawing

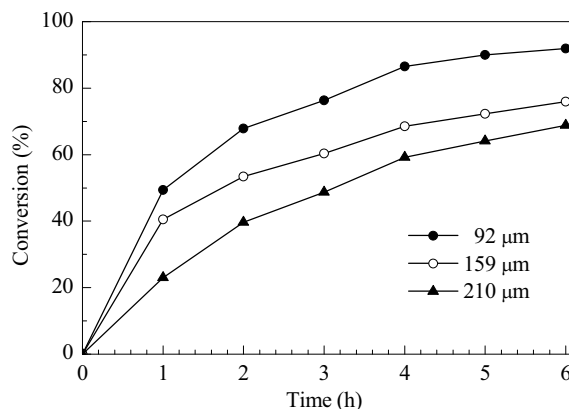


Fig. 11. Effect of catalyst particle size on reaction conversion.

groups in the acyl chloride. In this work, it was observed that the presence of the methoxy group (electron-donating) in the benzoyl chloride structure accelerated the reaction. The acylation reaction of anisole with 4-methoxybenzoyl chloride afforded 87% conversion after 6 h, while 82% conversion was obtained for the case of benzoyl chloride under identical conditions. The experimental result showed that the Friedel-Crafts acylation of anisole with 4-chlorobenzoyl chloride proceeded with more difficulty than in the case of benzoyl chloride, although 73% conversion was still observed after 6 h (Fig. 12(a)). Although the reaction using 4-methoxybenzoyl chloride

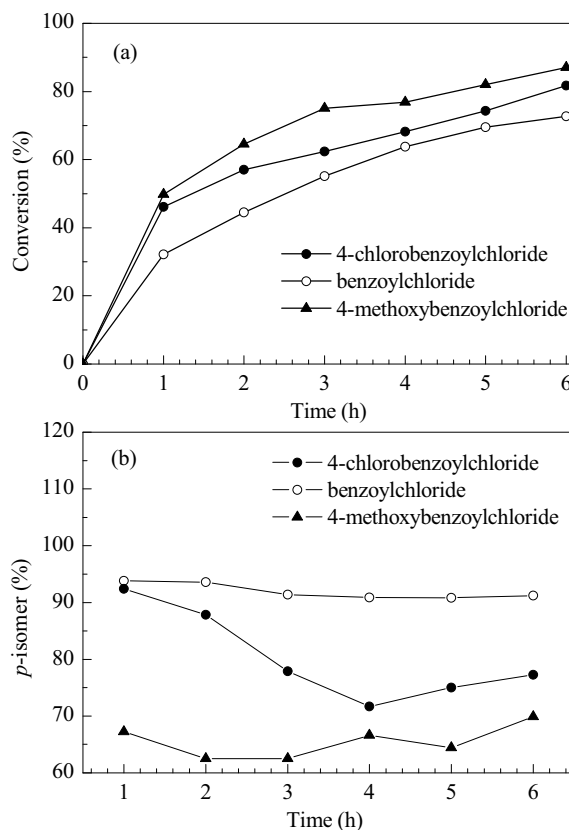


Fig. 12. Effect of different acylation reagents on reaction conversion (a) and reaction selectivity (b).

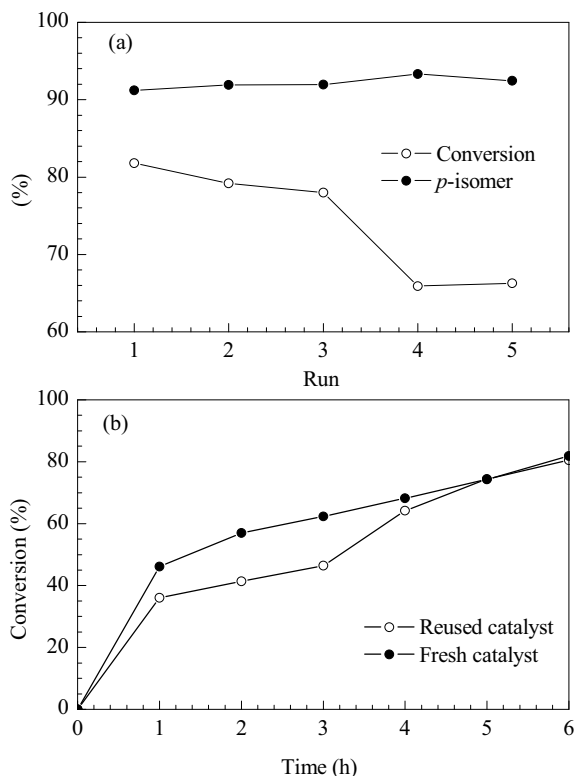


Fig. 13. Catalyst recycling studies.

gave a higher conversion than benzoyl chloride or 4-chlorobenzoyl chloride, a lower selectivity for the *p*-isomer was obtained with this acylating reagent (Fig. 12(b)). Chizallet and coworkers [22] previously investigated the presence of acid-basic sites in the ZIF-8 by combining CO adsorption monitored by FT-IR and DFT calculations, and confirmed that some strong Lewis acid sites (in particular ZnII species) and strong Brönsted acid sites (NH groups), together with basic sites, existed on the surface of the catalyst [22]. Choudhary and coworkers [58] reported that the rate of the Friedel-Crafts acylation using a zeolite-based catalyst was significantly improved in the presence of new Brönsted acid sites formed by the interaction of moisture with the Lewis acid sites of the

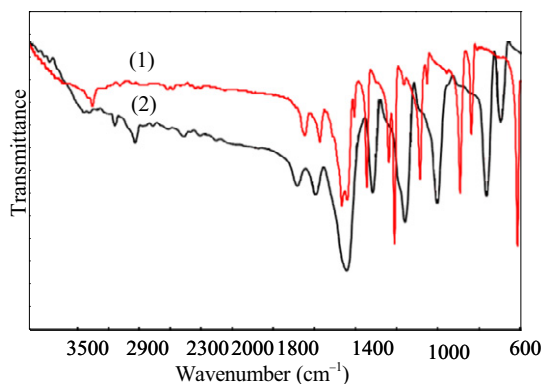


Fig. 14. FT-IR spectra of the reused (1) and fresh (2) ZIF-8.

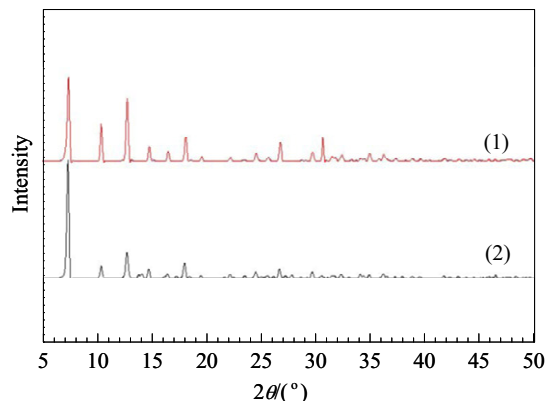


Fig. 15. XRD patterns of the fresh (1) and reused (2) ZIF-8.

catalyst. The combination of Lewis acid and Brönsted acid sites could contribute to the catalytic activity of the ZIF-8 in the Friedel-Crafts acylation reaction, but further studies are necessary to elucidate the acid centers present in the catalyst, and the mechanism of the Friedel-Crafts acylation using the ZIF-8 catalyst.

When one uses a solid catalyst, a crucial issue that should be taken into consideration is the ease of separation as well as the deactivation and reusability of the catalyst. The ZIF-8 catalyst was therefore investigated for recoverability and reusability over five successive runs. The reaction was carried out at 120 °C using the reagent molar ratio of 1:2 and 6 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 and DCM to remove any physisorbed reagents. The recovered ZIF-8 was dried under vacuum at 100 °C overnight, and then reused under identical conditions to those of the first run. It was found that the activity of the ZIF-8 catalyst decreased gradually after each run. However, the catalyst could be reused with conversions of 82%, 80%, 78%, 66%, and 66% after 6 h for the 1st, 2nd, 3rd, 4th, and 5th run, respectively (Fig. 13(a)). Kinetic studies also indicated that the catalytic activity of the ZIF-8 decreased slightly after each use (Fig. 13(b)). The reaction selectivity remained almost unchanged with 93%–95% of *p*-benzoylanisole being observed in all cases. As compared with the FT-IR spectra of the fresh catalyst, a slight difference was observed with the ZIF-8 after the first run (Fig. 14). XRD result of the reused catalyst revealed that the ZIF-8 maintained its crystallinity during the course of the reaction. However, a slight difference in the overall structure was observed for the reused ZIF-8 (Fig. 15). Further investigations are needed to clarify the reason of catalyst deactivation in the Friedel-Crafts acylation reaction using the ZIF-8 catalyst.

3 Conclusions

Highly crystalline and porous ZIF-8 was synthesized from

the reaction of zinc nitrate hexahydrate and 2-methylimidazole by a solvothermal method. The ZIF-8 was characterized by FT-IR, TEM, SEM, XRD, TGA, AAS, DLS and nitrogen adsorption, and used as catalyst for Friedel-Crafts acylation between anisole and benzoyl chloride. The catalyst afforded high conversions with a catalytic amount (4%–6%) without the need for an inert atmosphere. The solid catalyst can be easily separated from the reaction mixture by simple centrifugation or filtration, and can be reused without significant degradation in catalytic activity. There was no active acid leaching into the reaction solution.

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