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Expanding Applications of Metal−Organic Frameworks: Zeolite Imidazolate Framework ZIF-8 as an Efficient Heterogeneous Catalyst for the Knoevenagel Reaction

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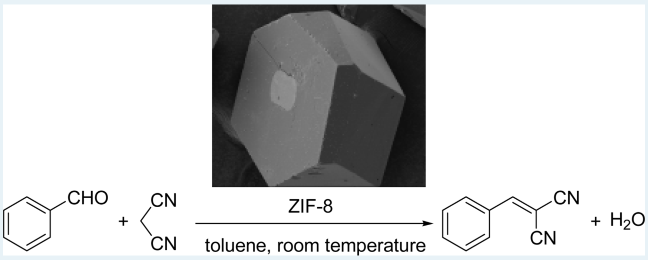

ABSTRACT: A highly porous zeolite imidazolate framework (ZIF-8) was synthesized by a solvothermal method, and used as an efficient heterogeneous catalyst for the Knoevenagel reaction. The solid catalyst was characterized using a variety of different techniques, including X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), dynamic laser light scattering (DLS), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), atomic absorption spectrophotometry (AAS), and nitrogen physisorption measurements. Quantitative conversion was achieved under mild conditions. The ZIF-8 catalyst could be facilely separated from the reaction mixture, and could be reused without significant degradation in catalytic activity. Furthermore, no contribution from homogeneous catalysis of active species leaching into reaction solution was detected.

KEYWORDS: metal−organic framework, zeolite imidazolate framework, Knoevenagel reaction

1. INTRODUCTION

Metal−organic frameworks (MOFs) are currently receiving significant attention for their potential applications in gas separation and storage, sensors, and catalysis.[1−4] Compared to conventionally used microporous and mesoporous inorganic materials, these metal−organic structures exhibit the potential for more flexible rational design, by controlling the size and the functionalization of the organic linkers.[5,6] Zeolite imidazolate frameworks (ZIFs), being classified as a new subclass of MOFs, have emerged as a novel type of highly porous materials, combining advantages from both zeolites and conventional MOFs.[7,8] Several reactions have been carried out using conventional MOFs as solid acid catalysts or catalyst supports such as Knoevenagel condensation,[9,10] aldol condensation,[11] oxidation,[12,13] hydrogenation,[14] Suzuki cross-coupling,[15] transesterification reaction,[16] Friedel−Crafts alkylation,[17,18] and epoxide ring-opening reaction.[19,20] However, since the discovery of the first ZIF sample, research works have been mostly focused on synthesizing new ZIFs and investigating their applications in gas storage, and indeed reports of catalytic studies on ZIFs for organic transformations have been very limited in the literature.[13,21,22]

The Knoevenagel condensation of aldehydes with compounds containing activated methylene groups is one of the most useful and widely employed methods for carbon−carbon bond formation with numerous applications in the synthesis of fine chemicals[23] as well as heterocyclic compounds of biological significance.[24] Conventionally, this reaction is catalyzed by weak bases like primary, secondary, and tertiary amines under homogeneous conditions, which could require upward of 40 mol % catalyst with the attendant difficulties in catalyst recovery and recycling.[25] Over the past few years, various solid-supported catalysts have been applied to this reaction such as amine-functionalized mesoporous zirconia,[26] mesoporous titanosilicate,[27] basic MCM-41 silica,[28−30] nanocrytalline ceria−zirconia,[31] zeolites exchanged with alkylammonium cations,[32] amine-functionalized superparamagnetic nanoparticles,[33] chitosan hydrogel,[34] and MOFs.[9,10] However, to the best of our knowledge, the Knoevenagel condensation catalyzed by ZIFs was not previously mentioned in the literature. In this work, we wish to report the utilization of ZIF-8 as an efficient heterogeneous catalyst for the low temperature liquid phase Knoevenagel reaction. High activity was observed and the ZIF-8 catalyst was easily isolated from the reaction mixture by simple filtration and reused without significant degradation in activity.

2. EXPERIMENTAL SECTION

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.

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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 Kα 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 ZIF-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. The particle size distribution of the ZIF-8 was determined by dynamic laser light scattering (DLS) method using a LA 920. 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 an DB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC analysis heated samples from 60 to 200 at 20 °C/min and held them at 150 °C for 1 min; then heated them from 150 to 160 at 1 °C/min and held them at 200 °C for 2 min; then heated them from 200 to 300 at 50 °C/min and held them at 300 °C for 4 min. Inlet and detector temperatures were set constant at 300 °C. *n*-Dodecane 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 μm). The temperature program for GC-MS analysis heated samples from 60 to 280 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 ZIF-8. In a typical preparation,[35] a solid mixture of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) (1.88 g, 6.33 mmol) and 2-methylimidazole (H-MeIM) (0.43 g, 5.82 mmol) was dissolved in 130 mL of *N*,*N*′-dimethylformamide (DMF), then distributed in 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 mother liquor from the mixture, chloroform (20 mL) was added to the vial. Colorless polyhedral crystals were collected from the upper chloroform layer, washed with DMF (3 × 15 mL) for 3 days. After that, the DMF was exchanged by dichloromethane (DCM) (3 × 15 mL) for 3 days. The residual solvents were removed under vacuum at 200 °C for 6 h, yielding 0.26 g of white polyhedral crystals (23% based on 2-methylimidazole).

2.3. Catalytic Studies. The Knoevenagel reaction between benzaldehyde and malononitrile using the ZIF-8 catalyst was carried out in a magnetically stirred round-bottom flask. Unless otherwise stated, a mixture of ZIF-8 (0.02 g, 5 mol %), benzaldehyde (0.2 mL, 1.9 mmol), and *n*-dodecane (0.2 mL, 0.88 mmol) as an internal standard was placed into a 25 mL flask containing 4 mL of toluene. The catalyst concentration was calculated with respect to the zinc/benzaldehyde molar ratio. The reaction vessel was stirred for 5 min to disperse the ZIF-8 in the liquid phase. A solution of malononitrile (0.25 g, 3.8 mmol) in toluene (1 mL) was then added, and the resulting mixture was stirred at room temperature for 6 h. Reaction conversion was monitored by withdrawing aliquots from the reaction mixture at different time intervals, quenching with acetone, filtering through a short silica gel pad, analyzing by GC with reference to *n*-dodecane, and further confirming product identity by GC-MS. The ZIF-8 catalyst was separated from the reaction mixture by simple centrifugation, washed with copious amounts of anhydrous toluene and DCM, dried under vacuum at 200 °C for 6 h, and reused if necessary. For the leaching test, a catalytic reaction was stopped after 1 h, analyzed by GC, and centrifuged to remove the solid catalyst. The reaction solution was then stirred for a further 5 h. Reaction progress, if any, was monitored by GC as previously described.

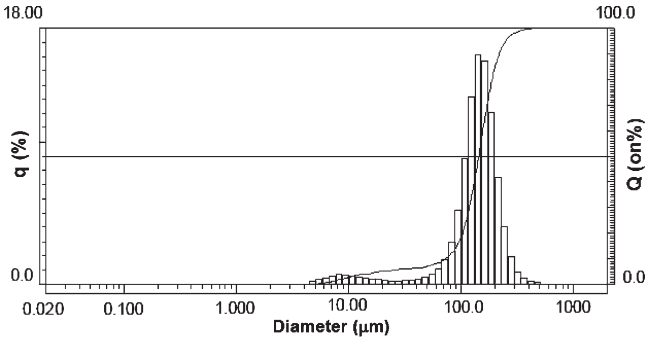


Figure 1. Particle size distribution of the ZIF-8.

3. RESULTS AND DISCUSSION

3.1. Catalyst Synthesis and Characterization. In this work, the ZIF-8 was synthesized using zinc nitrate hexahydrate and 2-methylimidazole by a solvothermal method in DMF, according to a literature procedure.[35] It was previously reported that in the ZIF-8 structure, zinc atoms were connected through nitrogen atoms by 2-methylimidazolate (MeIM) linkers to form corresponding MOFs, producing nanosized pores formed by four, six, eight, and twelve membered ring ZnN_4 tetrahedral clusters.[8,36] When synthesizing porous MOF-based materials, it is necessary to carry out the solvent exchange because this step will facilitate the evacuation of the material frameworks.[1−4,37] The as-synthesized ZIF-8 samples were therefore immersed in excess DCM at room temperature for 3 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 in the subsequent activation step.[37] It was observed that the ZIF-8 was achieved as white polyhedral crystals in a yield of 23%, which is comparable to that of previously reported procedures (normally around 20−25% yield).[3]

The ZIF-8 was then characterized using a variety of different techniques. Elemental analysis with AAS indicated a zinc loading of 4.2 mmol/g. The particle size distribution of the ZIF-8 was obtained from the DLS analysis, showing an average size of 143 μm (Figure 1). The SEM micrograph showed that well-shaped, high quality cubic crystals with crystal sizes ranging between approximately 100 and 200 μm were obtained (Figure 2). A very sharp peak below 10° (with 2θ of 7.2) was observed on the XRD diffractogram of the ZIF-8, indicating that a highly crystalline material was achieved (Figure 3). Furthermore, the XRD patterns of the ZIF-8 exhibited a better crystallinity as compared to that of silica-based materials such as SBA-15, SBA-16, and MCM-41 where broader peaks were normally observed on their diffractograms.[38] Indeed, high crystallinity is always expected when synthesizing MOF-based materials. The overall XRD patterns

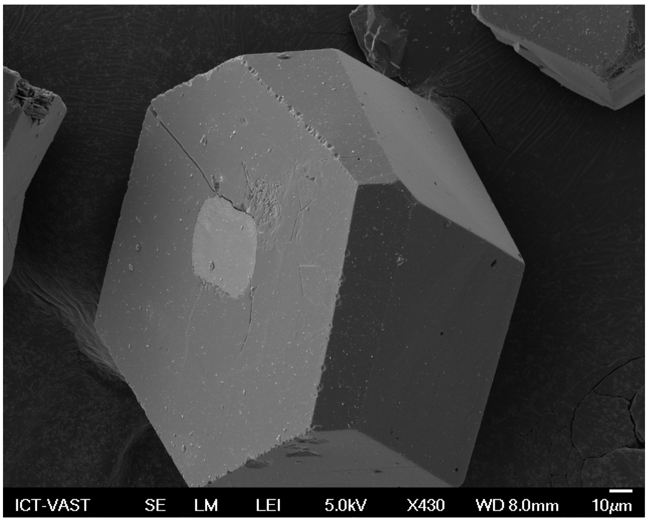


Figure 2. SEM micrograph of the ZIF-8.

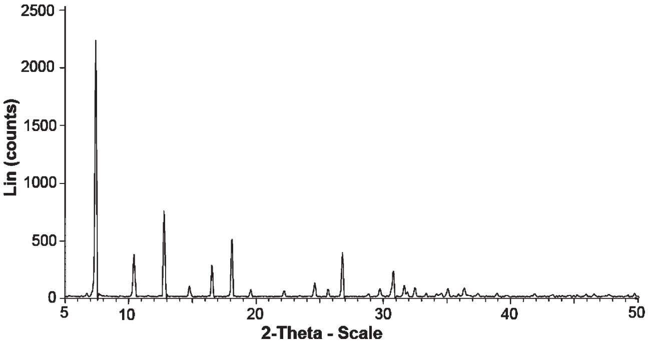


Figure 3. X-ray powder diffractogram of the ZIF-8.

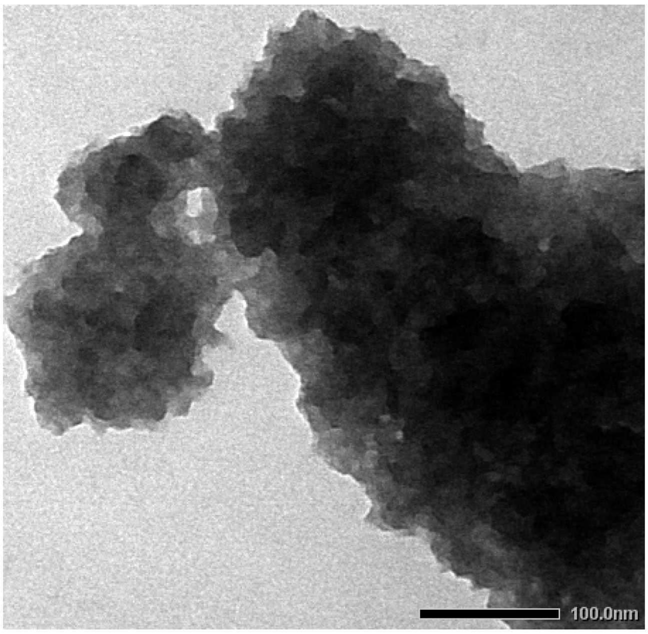


Figure 4. TEM micrograph of the ZIF-8.

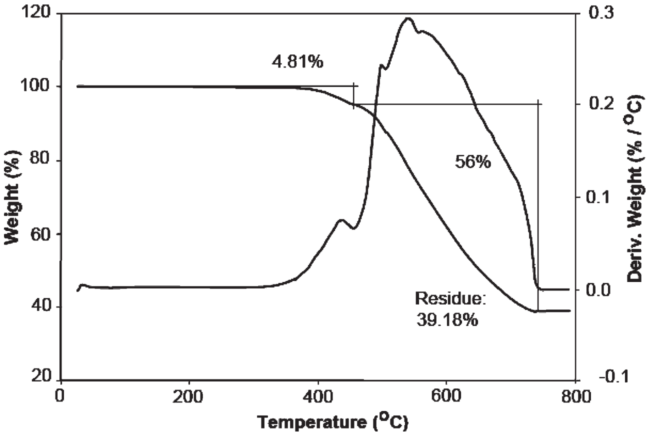


Figure 5. TGA analysis of the ZIF-8.

of the ZIF-8 were in good agreement with the theoretical patterns from the single crystal data.[21,35,39,40] The SEM images, together with the XRD patterns showed that the ZIF-8 was highly crystalline. As expected, the TEM observation revealed that the as-synthesized ZIF-8 possessed a highly porous structure (Figure 4), which was different from that of conventionally used microporous and mesoporous inorganic materials.

Thermal degradation investigations of solid materials are necessary as many applications depend on their thermal stability.[41] The most significant feature in the TGA result for the ZIF-8 was that little weight loss was found between the temperature range of 200−400 °C, indicating that the ZIF-8 was stable up to 400 °C (Figure 5). The thermal stability of the ZIF-8 was therefore comparable to that of the literature.[35] It was also found that a sharp weight-loss step of over 55% was observed as the temperature increased from 400 to 700 °C, indicating the thermal decomposition of the ZIF-8 in that temperature range. After the decomposition, approximately 39% of the starting weight remained, corresponding to the formation of zinc oxide. This TGA result ensured the applicability of the ZIF-8 across a wide temperature range.

FT-IR spectra of the ZIF-8 exhibited a significant difference as compared to that of 2-methylimidazole (Figure 6). In the FT-IR spectra of 2-methylimidazole, a strong and broad band, ranging from 3400 cm^{-1} to 2200 cm^{-1} with the maximum at approximately 2600 cm^{-1} was observed, showing the presence of the N−H···N hydrogen bond.[42] Furthermore, the resonance between the N−H···N bending "out of plane" and the N−H stretching vibrations was also found at 1843 cm^{-1} (Figure 6a).[42] The significant features observed for the FT-IR spectra of the ZIF-8 (Figure 6b) as compared to those of 2-methylimidazole were the disappearance of these absorption bands, indicating that the 2-methylimidazole linkers were fully deprotonated during the formation of the ZIF structure. Moreover, absorption peaks at 3138 cm^{-1} and 2933 cm^{-1} due to the stretching vibrations of C−H bonds in the methyl group and the imidazole ring were observed in the spectra of the ZIF-8. It should be noted that these peaks were overlapped by absorption bands of the N−H stretching vibration in the spectra of 2-methylimidazole.

MOF-based materials have received significant attention as promising materials for applications in catalysis, separation, and gas storage because of their exceptionally high adsorption surface areas.[1−3] The largest surface areas of ordered structures such as zeolites or silicas were observed at around 1000 m^2/g [1]. With the invention of MOFs, the surface areas of crystalline porous materials could be significantly improved. In this work, it was found that the ZIF-8 could afford Langmuir surface areas of up to

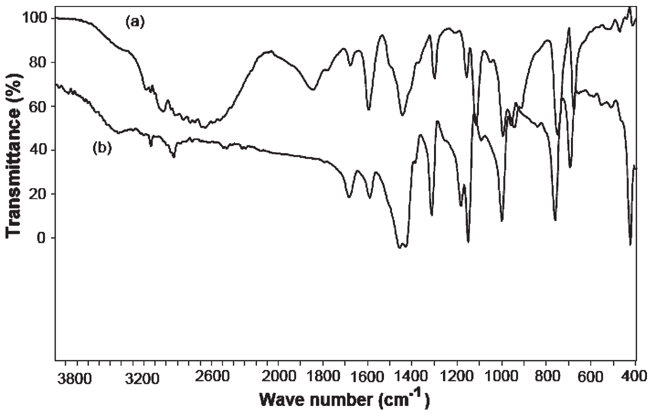
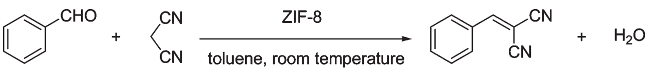


Figure 6. FT-IR spectra of 2-methylimidazole (a) and the ZIF-8 (b).

Scheme 1. Knoevenagel Reaction of Benzaldehyde with Malononitrile Using the ZIF-8 Catalyst



1705 m^2/g, which was in good agreement with the literature. Indeed, several ZIF-8 samples with surface areas ranging from 1300 m^2/g to 1810 m^2/g were previously synthesized using the solvothermal method.[7,35,43] This property would make ZIF-8 an attractive candidate for applications in catalysis. The pore size distribution of porous materials is also one of the important parameters that should be taken into consideration. It was observed that the as-synthesized ZIF-8 exhibited an average pore diameter of 10.1 Å, a value that was still in the microporous regime (<20 Å diameter pore size). However, it should be noted that the six-membered-ring pore windows of the ZIF-8 are as narrow as 3.4 Å,[44] thus inhibiting the accessibility of bulky molecules into the pore cavities.

3.2. Catalytic Studies. The ZIF-8 catalyst was assessed for its activity in the Knoevenagel reaction by studying the condensation of benzaldehyde with malononitrile to form benzylidene malononitrile as the principal product (Scheme 1). The initial reaction was carried out using 5 mol % ZIF-8 catalyst relative to benzaldehyde in toluene. As inspired by green chemistry principles, it was decided to carry out the reaction under room temperature conditions. Aliquots were withdrawn from the reaction mixture at different time intervals and analyzed by GC, giving kinetic data during the course of the reaction. Initial studies addressed the effect of the malononitrile/benzaldehyde molar ratio on reaction conversions, having carried out the reaction at molar ratios of 1:1, 2:1, 3:1, and 4:1, respectively. Using the reagent molar ratio of 3:1, the reaction could give a conversion of 90% after 2 h, and then it could go to completion after 3 h with no trace amount of benzaldehyde being detected by GC. The reaction at the reagent molar ratio of 4:1 occurred readily to give 93% conversion after 1 h, and a complete conversion was achieved after 2 h. As expected, decreasing the malononitrile/benzaldehyde molar ratio resulted in a significant drop in the reaction rate. It was observed that the reaction at the reagent molar ratio of 2:1 still afforded 97% conversion after 6 h, while only 51% conversion was achieved for the reaction using 1 equiv of malononitrile under this condition (Figure 7).

With such results in hand, we then decided to investigate the effect of catalyst concentration on reaction conversion. The catalyst concentration, with respect to the zinc content in the ZIF-8, was studied in the range of 1−5 mol % relative to benzaldehyde. It was observed that quantitative conversion of benzaldehyde was achieved after 3 h at 5 mol % catalyst. As expected, a lower reaction rate was observed for the reaction using 3 mol % catalyst. However, the reaction could afford a conversion of 93% after 3 h, and complete conversion of benzaldehyde was still obtained after 4 h. Decreasing the catalyst concentration to 1 mol % led to a significant drop in the reaction rate, with 85% conversion being achieved after 6 h (Figure 8). The results indicated that the ZIF-8 catalyst was quite active in the Knoevenagel reaction. Furthermore, the reaction rate observed for the ZIF-8 catalyst was higher than some previously reported Lewis acid catalysts, where longer reaction time or/and higher catalyst loading were required for the same reaction.[45] However, the ZIF-8 exhibited less activity in the Knoevenagel reaction as compared to some base catalysts such as amine-functionalized superparamagnetic nanoparticles[33] and amine-functionalized mesoporous zirconia.[26] Indeed, it was previously reported that the catalyst concentration used for the Knoevenagel reaction could vary from less than 1 mol % to more than 10 mol %, depending on the nature of the catalyst.[26,27,46]

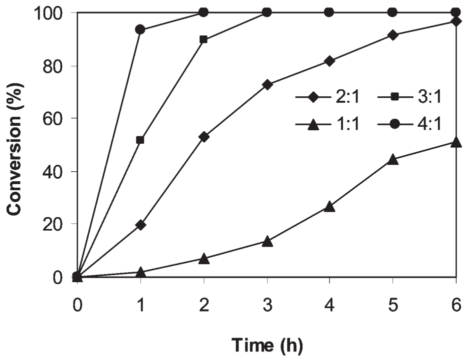


Figure 7. Effect of malononitrile/benzaldehyde molar ratio on reaction conversion.

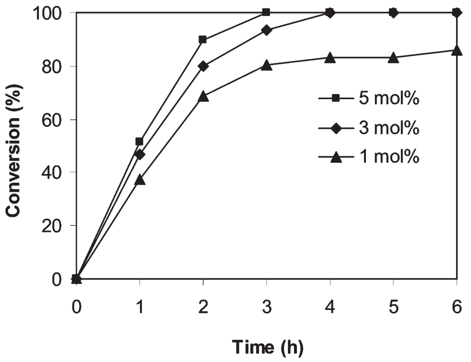


Figure 8. Effect of catalyst concentration on reaction conversion.

When one uses a solid catalyst, a crucial issue is the possibility that some of active sites could migrate from the solid support to the liquid phase and that these leached species could become responsible for a significant part of the catalytic activity.[33] It should be noted that imidazole, 1-methylimidazole, and 2-methylimidazole were previously used as homogeneous base catalysts for the Knoevenagel condensation.[47] However, they could not be recycled and reused, and therefore they are practically

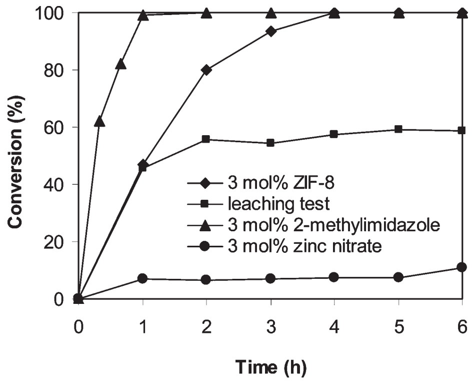


Figure 9. Leaching test indicated no contribution from homogeneous catalysis of active species leaching into reaction solution.

undesirable. Indeed, it was found that the Knoevenagel reaction using 3 mol % of 2-methylimidazole as catalyst instead of the ZIF-8 could afford quantitative conversion after 1 h. As expected, zinc nitrate hexahydrate exhibited very low activity in the Knoevenagel condensation under similar reaction condition, with only 10% conversion being observed after 6 h (Figure 9). To determine if leaching of the 2-methylimidazole linker was a problem for the Knoevenagel reaction using the ZIF-8 catalyst, an experiment was performed to estimate the contribution of leached active species to the catalytic activity by performing a simple centrifugation during the course of the reaction to remove the solid catalyst. If the catalytic reaction continued this would indicate that the active species was leached acid rather than the solid ZIF-8 catalyst. The organic phase was separated from the solid catalyst after 1 h reaction time by simple centrifugation, having used 3 mol % of fresh ZIF-8 catalyst. The reaction solution was then transferred to a new reactor vessel, and stirred for an additional 5 h at room temperature with aliquots being sampled at different time intervals, and analyzed by GC. The data from GC determinations gave quantitative information about residual, catalytically active acid in solution. Within experimental error, no further reaction was observed, proving that there was no contribution from leached active species and that conversion was only being possible in the presence of the solid ZIF-8 catalyst (Figure 9).

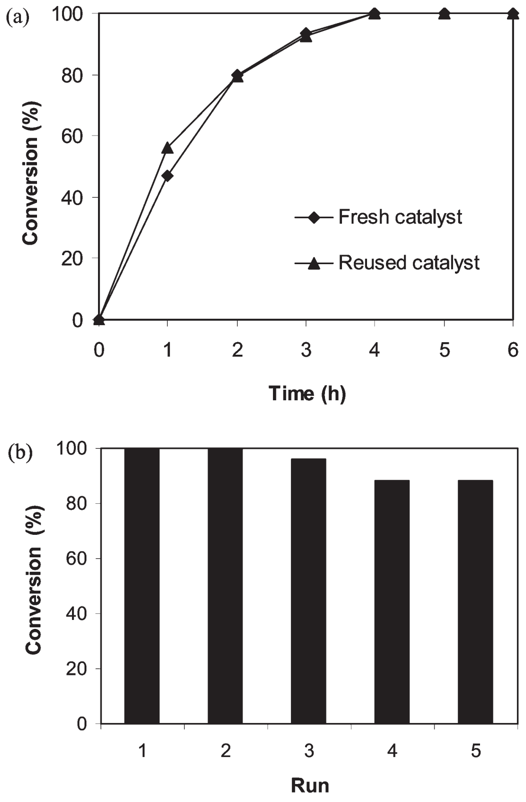


Figure 10. Catalyst recycling studies.

Another point of great concern for most of solid catalysts 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 in the Knoevenagel reaction. The reaction was carried out in toluene at room temperature using 3 mol % of ZIF-8 catalyst for 6 h. After the reaction, the catalyst was separated by simple centrifugation, then washed with copious amounts of anhydrous toluene and DCM to remove any physisorbed reagents, and dried under vacuum at 200 °C overnight. The recovered ZIF-8 catalyst was reused in further reaction under identical conditions to those of the first run with aliquots being sampled at different time intervals, and analyzed by GC. It was found that the ZIF-8 catalyst could be recovered and reused without a significant degradation in activity (Figure 10 a). The ZIF-8 catalyst was also investigated for recoverability and reusability over five successive runs. It was observed that more than 88% conversion was still achieved at the fifth run (Figure 10b). Although it was previously reported that no loss of activity was observed for reused solid catalysts in the Knoevenagel reaction using modified silica,[46] MOF-based material,[9] and modified calcium oxide[48] catalysts, no kinetic data was provided. Indeed, only conversions at the end of the experiment were mentioned. Unfortunately, stable activity can not be proven by reporting only similar reaction yields at long times. Kinetic studies are the true test of catalyst deactivation.[33]

As the six-membered-ring pore windows of the ZIF-8 are as narrow as 3.4 Å,[8,44] it is apparent that larger molecules can not enter the pore cavities. Therefore, reactions using bulky molecules should occur on the external surface of the ZIF-8 particles. Indeed, Chizallet and co-workers recently investigated the transesterification reaction using ZIF-8 as a catalyst, and demonstrated that all active sites are located at the external surface, but not in the microporosity of the material.[22] Smaller size crystals normally exhibit higher catalytic activity because of the increased external surface of smaller crystals.[49] It was therefore decided to investigate the effect of the particle size of the ZIF-8 catalyst on the reaction conversion. The Knoevenagel condensation using the ZIF-8 catalyst with average particle size of 143 μm, 184 μm, and 282 μm (DLS), respectively, was carried out at 3 mol % catalyst concentration in toluene at room temperature. It was found that increasing the particle size of the ZIF-8 catalyst from 143 to 184 μm resulted in a significant drop in reaction rate. A conversion of 76% was observed after 6 h for the reaction using the catalyst with larger particle size, while the reaction could go to completion after 4 h for case of the smaller size catalyst. As expected, smallest reaction rate was observed for the reaction using the largest size catalyst, with 61% conversion being obtained after 6 h (Figure 11).

The study was then extended to the Knoevenagel condensation of several benzaldehyde derivatives having different substituents with malononitrile using the ZIF-8 catalyst. Reactions were carried out in toluene at room temperature with 3 mol % catalyst loading. As with other condensation reactions in which a nucleophilic

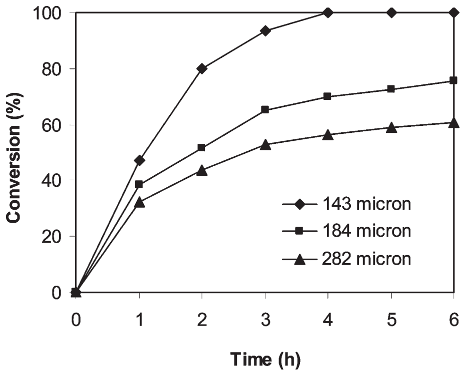


Figure 11. Effect of catalyst particle size on reaction conversion.

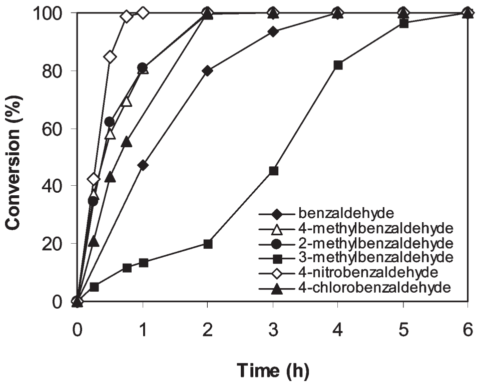


Figure 12. Effect of different substituents on reaction conversion.

addition is the rate-determining step, benzaldehyde derivatives containing electron-withdrawing ("activating") groups are normally more reactive than those with electron-donating ("deactivating") groups in the Knoevenagel condensation.[50] Interestingly, it was observed that the ZIF-8 catalyst exhibited high activity for both benzaldehyde derivatives bearing electron-withdrawing and those containing electron-donating substituents. The reaction of 4-methylbenzaldehyde and 2-methylbenzaldehyde, respectively, with malononitrile proceeded readily to give quantitative conversions after 2 h, though methyl is an electron-donating group. However, it was observed that 3-methylbenzaldehyde was significantly less reactive than the case of benzaldehyde, though the reaction could afford 99% conversion after 6 h. As expected, electron-withdrawing substituents accelerated the reaction rate of benzaldehyde derivatives with malononitrile. Quantitative conversions were achieved after 1 h for the case of 4-nitrobenzaldehyde and after 2 h for the case 4-chlorobenzaldehyde, respectively (Figure 12). Indeed, Liu and co-workers recently reported that both benzaldehyde derivatives containing electron-withdrawing and those having electron-donating substituents afforded high conversions in the Knoevenagel condensation with malononitrile.[51]

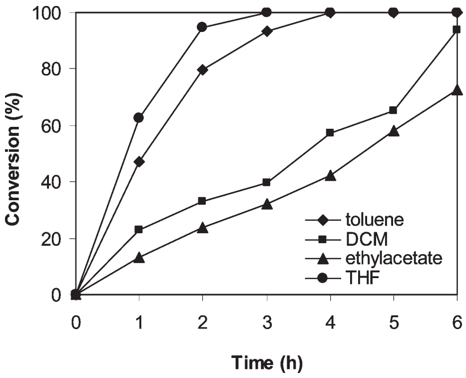


Figure 13. Effect of solvent on reaction conversion.

The sensitivity of a heterogeneously catalyzed reaction to different solvents can usually be of extreme importance, depending on the nature of the catalyst material.[33,52] Macquarrie and co-workers previously reported that the Knoevenagel condensation using silica-supported catalysts had a very limited range of effective solvents, and gave the best reaction rate in nonpolar solvents.[53] In contrast, Gascon and co-workers reported a negative effect of nonpolar solvents on the activity of MOF-based catalyst in the Knoevenagel condensation, while the reaction rate was significantly enhanced in polar solvents.[10,54] Corma and co-workers observed similar results, where the reaction rate decreased dramatically in nonpolar solvents and higher conversions were observed for more polar solvents.[55−57] Moreover, it was also reported that the higher the hydrophobicity of the catalyst, the less the effect of the solvent on the reaction rate.[10] We therefore decided to investigate the solvent effect in the Knoevenagel reaction, using 3 mol % of the ZIF-8 catalyst at room temperature. In this work, it was found that a combination of toluene and the ZIF-8 catalyst afforded excellent conversions for the reaction at room temperature (Figure 13). It was previously proposed that the rate of the Knoevenagel reaction using hydrophilic silica-based catalysts was influenced by the partitioning of the reactants (polar) between the catalyst pores and/or surface (hydrophilic) and the bulk reaction media (i.e., partitioning away from the hydrophilic catalyst pores/surface was decreased with less polar solvents). Nonpolar solvents were advantageous for these hydrophilic silica-based catalysts.[53,58] Although ZIF-8 was highly hydrophobic,[59,60] it was found that the Knoevenagel reaction using this catalyst proceeded readily in toluene. The reaction carried out in ethyl acetate, a relatively polar solvent, afforded a conversion of only 75% after 6 h. Although a slight enhancement in reaction rate was observed for the reaction carried out in DCM as compared to the case of ethyl acetate, the reaction could not go to completion after 6 h. Interestingly, tetrahydrofuran, a relatively polar solvent, was found to be more effective for the reaction as compared to the case of toluene (Figure 13). It should be noted that methanol was completely ineffective for the Knoevenagel reaction using ZIF-8 catalyst with no trace amount of product being detected by GC. Indeed, it was previously reported that polar solvents like methanol and ethanol could be effectively used for several Knoevenagel reactions.[10,54,57,61,62] The result observed for the case of methanol could be rationalized based on the hydrophobility of the ZIF-8 catalyst. However, further studies would be needed to elucidate the effect of solvents on the reaction using the ZIF-8 catalyst.

4. CONCLUSIONS

In conclusion, highly crystalline porous ZIF-8 was achieved by a solvothermal method with the reaction of zinc nitrate hexahydrate and 2-methylimidazole. The ZIF-8 was characterized using a variety of different techniques, including FT-IR, TEM, SEM, XRD, TGA, AAS, DLS, and nitrogen physisorption measurements. The ZIF-8 was used as an efficient heterogeneous acid catalyst for the Knoevenagel reaction. Quantitative conversion was achieved under mild conditions without the need for an inert atmosphere, and the ZIF-8 catalyst 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. It is apparent that the ZIF-8 catalyst can be an alternative to other solid catalysts for the Knoevenagel reaction. Our results here demonstrate the feasibility of applying the ZIF-8 as a catalyst, expanding applications of this porous material from the gas separation and storage to the catalysis field. Current research in our laboratory has directed to the design and synthesis of several ZIF-based catalysts for a wide range of organic transformations.

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