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Post-synthetic modification of coordination networks

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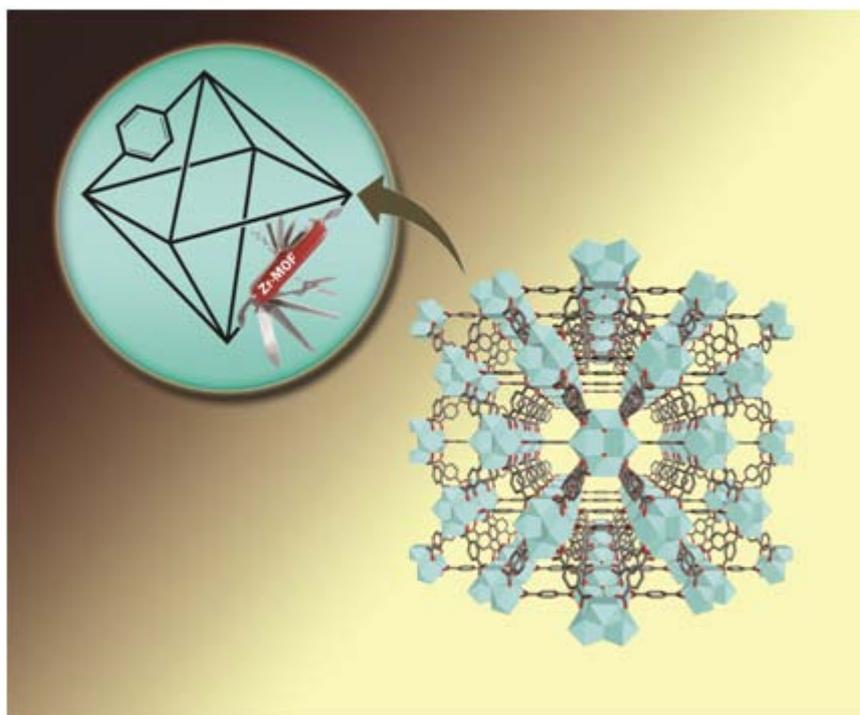


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PAPER

Post-synthesis functionalization of MIL-101 using diethylenetriamine: a study on adsorption and catalysis†

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An effective metal organic framework (MOF) catalyst (DETA-MIL-101) was prepared by grafting an electron-rich triamine functional group to the open metal sites in MIL-101. The samples were characterized *via* XRD, FT-IR, and N₂ adsorption-desorption measurements, and their N content was measured using EA. The CO₂ and H₂O adsorption-desorption properties were measured and compared with those of non-functionalized MIL-101. Their catalytic performances in the Knoevenagel condensation between benzaldehyde and malononitrile were examined, and the catalyst stabilities were confirmed using recycling and hot filtering experiments. Finally, the Pd²⁺ ions (0.5, 1.0, and 3.0 wt%) were immobilized onto the amine species that were grafted to the MIL-101 using PdCl₂ and were tested for Heck reactions of the acrylic acid and iodobenzene in *N,N*-dimethylacetamide as a solvent with triethylamine additives as a function of time. The catalyst stability was re-established *via* recycling and hot filtering experiments.

Introduction

Metal–organic frameworks (MOFs) are crystalline porous solids composed of a one, two, or three dimensional networks of metal ions or clusters held in place *via* multidentate organic molecules.^{1–5} MOFs have attracted great scientific interest due to their high specific surface areas and pore volumes, and they have potential applications in gas storage, separation, and heterogeneous catalysis.^{3,5–13}

Functionalization in MOFs, which can be broadly classified as either direct or post-synthesis modifications, is routinely conducted using diverse functional groups for various applications.^{14–17} The former strategy involves the use of pre-functionalized moieties such as metalloligands or the functionalized organic linker introduced for MOF synthesis.^{18–22} Direct functionalization offers the advantage of a simple single-step synthesis that enables straightforward introduction of the desired functionality during the MOF synthesis.^{23–25} However, self-assembly among the synthesis precursors can be hampered by changes in the metal precursors or ligands, which can result in the failure to form crystals.²⁵ Post-synthesis modification, alternatively, attempts a modification over the pre-formed MOF host using coordination to the organic part with organic reagents or noble/transition metal precursors. The insertion of

new pendant groups on or into the MOF allows the modification of its properties while retaining its crystallinity.^{22,25–28}

Concurrent with the emergence of MOFs with high porosity and structural stability,^{6,7} there has been increasing attempts to assign new chemical functionality or improve the structural stability over the parent MOF using systematic post-synthesis modifications. In this regard, there have been three significant areas of experimentation: (1) enhancing the gas adsorption capacity or selectivity through the introduction of a specific organic functional group or doping agent that interact strongly with the target gas molecules,²⁹ (2) assigning catalytically active sites in the organic moieties in MOFs or introducing noble metals for heterogeneous catalysis in organic reactions, and (3) creating and encapsulating metal nanoparticles.²⁶ Among these areas, the introduction of an amino-group to the MOFs has been particularly effective: promotion of the adsorption of global warming CO₂ gas^{30–32} and the catalytic application of amine-functionalized IRMOF-3 or amino-MIL-53 for Knoevenagel reactions have been reported.³³ These grafted amines can also serve as binding sites for noble metals such as Pd, Pt, and Au; furthermore, subsequent reduction can also produce immobilized metal particles.^{26,34}

Kitagawa and colleagues³⁵ proposed that some MOFs with coordinatively unsaturated metal sites (CUS) can be effectively functionalized post-synthetically by inducing chemical bonding with electron-rich molecules, leading to applications in catalysis and sorption.³⁶ Chang *et al.* subsequently reported the successful grafting of ethylenediamine on CUS in MIL-101 and the formation of Pd nanoparticles after hydrazine reductions of the immobilized Pd-acetate precursor.^{26,37} MIL-101(Cr) was envisaged to be useful as a support material for heterogeneous catalysis with a BET surface area in excess of 3000 m² g^{−1} being

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† Electronic supplementary information (ESI) available: XRD patterns, N₂ adsorption-desorption isotherms and TEM-EDX mapping images of MIL-101, DETA-MIL-101, and Pd_n-DETA-MIL-101 samples prepared in this work. See DOI: 10.1039/c2ce06608d

a robust MOF that exhibits potentially high concentrations of unsaturated chromium sites (up to 3.0 mmol g⁻¹).³⁸

In this study, MIL-101 was also used as a host material for the post-synthesis functionalization of diethylenetriamine, and its adsorptive properties for CO₂ and H₂O were tested. The basic properties of the grafted MIL-101 were evaluated using the Knoevenagel condensation as a probe reaction. Subsequently, Pd(II) ions were introduced to the amine-grafted MIL-101, and its catalytic activity was tested for Heck coupling reactions. Diethylenetriamine (DETA) was expected to be a better amine source than ethylenediamine (ED) due to the increased number of electron-rich N sites in the former, which are more shielded from the electron-deficient Lewis acidic CUS in MIL-101. In order to ensure objective evaluations of the catalyst stability, rigorous tests were conducted using recycling and hot filtering experiments. The experimental results established that the amine-grafting over the Lewis acidic open metal sites in the MIL-101 is an effective method of preparing a highly active and stable heterogeneous catalyst for liquid phase catalytic reactions.

Experimental

Synthesis

Synthesis of MIL-101. MIL-101 was hydrothermally synthesized following the procedure reported by Férey *et al.*³⁸ with a slight modification. Typically, 1.6 g of Cr(NO₃)₃·9H₂O (99%, Aldrich), 0.64 g of benzenedicarboxylic acid (H₂BDC, 98%, Aldrich), 0.16 g of hydrofluoric acid (48 wt%, DC Chemical), and 19.2 g of de-ionized water were mixed *via* stirring. The substrate mixture was transferred to a Teflon-lined autoclave and heated at 493 K for 8 h in a convection oven. After the reaction, the mixture was cooled to and maintained at 423 K for 1 h; then, the mixture was cooled naturally to room temperature. The crystal growth of the residual BDC occurs during the cooling step, which allows easier separation of the product.³⁹ The solid green product obtained after the hydrothermal reaction was filtered through 100 μm sieves to remove the crystalline BDC and then through 25 μm filter paper to separate the dissolved BDC. After drying at 423 K overnight, the powder was soaked in ethanol at 353 K for 24 h. Dried powder was added to *N,N*-dimethylformamide (DMF, 99%, Aldrich) and the mixture was ultrasonicated for 1 h in order to remove the crystallized BDC that remained inside the MIL-101 pores. Finally, the solvent was removed in a vacuum at 423 K for 12 h.

Amine-functionalization of MIL-101. The MIL-101 (500 mg) dehydrated at 423 K for 12 h was suspended in 50 ml of toluene (anhydrous 99.8%, Aldrich). To this suspension, an appropriate amount (1.5 ml) of diethylenetriamine (DETA, 99%, Aldrich) was added and the mixture was stirred under reflux for 8 h. The product was recovered by filtration and washed with toluene, de-ionized water and ethanol, and then dried at 373 K for amine-functionalized MIL-101. In this paper, the MIL-101 grafted with DETA is denoted as DETA-MIL-101. The amine content of the product was examined *via* elemental analysis.

Pd-DETA-MIL-101. Prior to Pd loading, the DETA-MIL-101 was treated at 423 K for 12 h in a vacuum in order to remove the

water residue in the sample. 18 mg of PdCl₂ (99%, Aldrich) was dissolved in 30 ml of ethanol and dispersed *via* ultrasonication for 20 min. Then, 500 mg of DETA-MIL-101 was added to reactor and heated to 323 K for 3 h with continuous stirring. The solid was recovered *via* filtration, washed with ethanol, and then dried at 373 K overnight. As determined using an ICP analysis, the metal loading achieved was 3.06 wt%.

The 0.5 and 1.0% Pd-loaded samples were also prepared using the same procedure. Based on the ICP analysis, the actual Pd loading of the samples was 0.52 and 1.04 wt%, respectively. The samples are denoted as Pd_{*n*}-DETA-MIL-101 in this study, where *n* is the Pd wt% of the catalysts.

Characterization

The X-ray powder diffraction patterns of the DETA-MIL-101 samples were measured using a Rigaku diffractometer with Cu-Kα radiation (λ = 1.54 Å) at 0.5°/min. The BET surface areas were determined using a Micromeritics ASAP 2020 surface analyzer at 77 K. Prior to the adsorption measurements, the samples were activated at 423 K for 12 h in a vacuum. The amount of amine grafted to the MIL-101 samples was measured using an elemental analyzer (Flash EA1112, Thermo). The palladium content in the MIL-101 was measured using ICP-OES (Optima 7300DV) and the TEM-EDX (JEM-2100F, JEOL) analysis was conducted to verify the status of the Pd dispersion.

Adsorption measurements

CO₂ adsorption measurements. CO₂ adsorption isotherms under static conditions were obtained using a BELsorp(II)-mini (BEL, Japan) at 273 and 298 K with activated solid samples. Before the adsorption measurements, the samples were also activated at 423 K for 12 h in a vacuum. The experimental adsorption data were fitted to the Langmuir–Freundlich equation, and the heat of adsorption was calculated by applying the Clausius–Clapeyron equation (1), as follows:

$$\left[\frac{\partial \ln P}{\partial (1/T)} \right]_q = \frac{-\Delta H}{R} \quad (1)$$

where *P* is the pressure, *T* is the temperature, *q* is the amount adsorbed, *R* is the gas constant, and Δ*H* denotes the heat of adsorption.

Water vapor adsorption measurements. The water vapor adsorption measurement was conducted using a BELsorp-Max (BEL, JAPAN) at 298 K (*P*₀ = 3.169 kPa). Water vapor was developed by vaporizing water in an ultra-high vacuum at 313 K; the water was purified using soaking procedures that included repeatedly freezing the water with liquid nitrogen and melting the water and removing the bubbles from other dissolved gases impurities. Prior to the water vapor adsorption test, samples were removed through the same pretreatment as used in the N₂ adsorption.

Catalytic measurements

Knoevenagel condensation. The Knoevenagel reaction between benzaldehyde and malononitrile using the DETA-MIL-101 catalyst was undertaken in a magnetically stirred round flask.

Before commencing the reaction, the DETA-MIL-101 was treated at 383 K for 6 h in a vacuum in order to remove the water residue in the sample. A mixture of DETA-MIL-101 (0.05 g), 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 reaction vessel was stirred for 5 min to disperse the DETA-MIL-101 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. After the reaction, the catalyst was separated *via* filtration. The products were analyzed using a gas chromatograph (Agilent 7890, HP-5 column; 30 m, 0.320 mm, 0.25 μ m) and the conversions were calculated based on the *n*-dodecane as an internal standard.

A hot filtering experiment was performed by separating the catalyst from the reaction mixture after 1 h of reaction time, and the filtrate was then maintained at room temperature for an additional 2 h.

Heck reaction. The Pd-loaded DETA-MIL-101 was treated in a vacuum at 383 K for 6 h prior to the reaction. The reactions were performed in a 200 ml of 2-neck flask fitted with a reflux condenser. Equimolar amounts (15 mmol) of acrylic acid and triethylamine, iodobenzene (10 mmol), and the catalyst (20 mg) were added to the 25 ml *N,N*-dimethylacetamide (DMA, Aldrich) as a solvent; the mixture was stirred at 393 K. Samples of 0.1 ml were withdrawn periodically using a syringe and were analyzed using a gas chromatograph (Acme 6000, Younglin, Korea) equipped with a flame ionization detector and a high performance HP-5 capillary column.

A hot filtering experiment was performed by separating the catalyst quickly from the reaction mixture after 2 h of reaction time, and the filtrate was then maintained at 383 K for an additional 2 h.

Results and discussion

Firstly, the physico-chemical properties of the synthesized MIL-101 were verified before conducting post-modification. The characteristic peaks were in good agreement with the data reported by Férey *et al.* (see ESI†, Fig. S1),³⁸ and the specific BET surface area of the obtained MIL-101 was *ca.* 3020 m² g⁻¹ (see ESI†, Fig. S2); even though somewhat less than the highest value claimed,²⁶ other leading groups also report the surface area in the range of 2200–3200 m² g⁻¹.^{10,39–41} The XRD patterns were not affected by the subsequent DETA grafting but small decreases in the peak intensities due to the guest inclusion were observed.

Compared with the bare MIL-101, the DETA-MIL-101 exhibited a significant decrease in the adsorbed N₂ amount and the corresponding BET surface area was also decreased from 3020 to 1560 m² g⁻¹, which reflects the successful grafting of the bulky triamines to the CUS partially blocking the pores.³⁷ It was further confirmed that the DETA was grafted onto the MIL-101 *via* FT-IR as shown in Fig. 1; the ν (NH) stretching regions (approximately 3100–3600 cm⁻¹) and ν (CH) stretching regions (2890 and 2950 cm⁻¹) indicate the presence of the DETA.²⁶ The grafted amine amount were measured at 9.86 wt% of N content *via* EA, which corresponds to *ca.* 70% of the CUS sites in

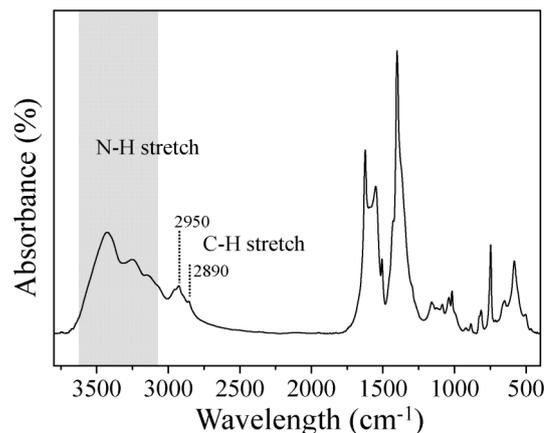


Fig. 1 FT-IR spectrum of DETA-MIL-101.

MIL-101 interacting with the DETA, and *ca.* 30% of free-chromium sites remained. It is believed that those grafted DETA molecules near the external surface of MIL-101 act as a diffusion barrier, which make free amine molecules entering the inner core of MOFs increasingly difficult.⁴²

The water vapor adsorption measurements over the MIL-101 and DETA-MIL-101 are shown in Fig. 2. The water vapor adsorption isotherms provided information on the surface nature (hydrophilicity/hydrophobicity) of the MOFs. The water vapor adsorption isotherm of the MIL-101 demonstrated a 2-step adsorption behavior; the steep adsorption steps at $P/P_0 = 0.41$ and 0.48, respectively, reflecting the pore filling of the mesoporous cages comprised of microporous supertetrahedra. The MIL-101 cages with sizes of 34 Å are accessible to the adsorptive molecules *via* 16 Å window openings, and these two types of pores are expected to be filled consecutively. Both step adsorption pressure values were very close, which implies a similar hydrophilicity.⁴³ After the DETA grafting, however, the adsorbed water amount significantly decreased compared with the bare MIL-101 and the characteristic 2-step water adsorption behavior disappeared. Apparently, the grafted DETA molecules in the MIL-101 decrease the number of free CUS, and the material became hydrophobic despite a large fraction of pore volume remaining after grafting (decreased from 1.8 to 1.1 cm³ g⁻¹). DETA-MIL-101 showed

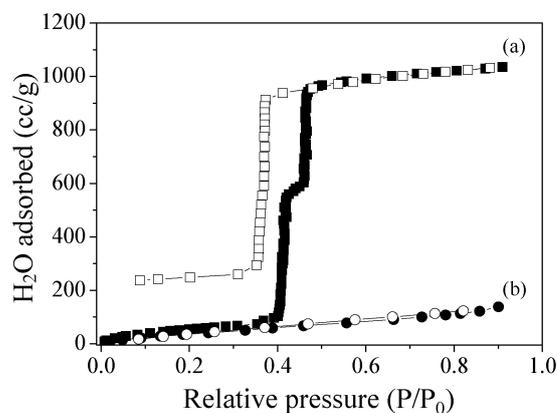


Fig. 2 Water vapor adsorption-desorption isotherms of (a) MIL-101 and (b) DETA-MIL-101 at 298 K (filled mark: adsorption; blank mark: desorption).

small but steady increase in water sorption to *ca.* 140 cm³ g⁻¹ at $P/P_0 = 1.0$; the total amount of water adsorbed is similar to that by very hydrophobic ZIF-8.⁴³ Hydrophobic organic constituents in DETA have eliminated *ca.* 70% of the Lewis acidic sites, so reduction in water sorption capacity is expected. However, weak adsorption may take place over the N sites in DETA-MIL-101. No hysteresis was observed in DETA-MIL-101 in contrast to the large hysteresis in MIL-101, which supports that adsorption sites in each case are different.

Fig. 3 shows the CO₂ adsorption isotherms of the MIL-101 and DETA-MIL-101 to 101.3 kPa at 273 and 298 K, respectively. Both samples demonstrated linearly increasing adsorption isotherms at 273 K and became convex with decreased CO₂ adsorption amounts at 298 K. As shown in Fig. 3(I), MIL-101 exhibits significantly higher CO₂ adsorption capacity than DETA-MIL-101; the maximum CO₂ adsorption capacities were 141 and 43 mg g⁻¹ at 273 K, and 79 and 31 mg g⁻¹ at 298 K for MIL-101 and DETA-MIL-101, respectively. It is very likely that the significantly reduced surface area from 3020 to 1560 m² g⁻¹ after the DETA grafting in DETA-MIL-101 is responsible for this reduction of the CO₂ capture capacity in a high pressure range. The linear relationship between total surface area and gas adsorption capacity has been repeatedly demonstrated for MOFs as well as other microporous materials for many gases including CO₂.^{44,45} However, in a low pressure range ($P < 15$ kPa), DETA-MIL-101 showed higher adsorption

amounts than those of MIL-101, which implies stronger binding of CO₂ to the amine species grafted. Indeed, the heat of the CO₂ adsorption for DETA-MIL-101 decreased sharply with the CO₂ loading amount (from 69 to 28 kJ mol⁻¹), which is somewhat higher than that of MIL-101 (from 45 to 22 kJ mol⁻¹). It is known that the high isosteric adsorption heat for CO₂ at low loading conditions in MIL-101 is due to the CUS in MIL-101 interacting with the CO₂ quadrupole.⁴⁶ However, the DETA grafted on the MIL-101 operates as a Lewis base that can capture the acidic CO₂ gas more strongly than the Lewis acid CUS of the MIL-101 through the promotion of a formation of carbamate-like complex.⁴⁷

Next, the DETA-MIL-101 was tested as a catalyst for the Knoevenagel condensation reaction of benzaldehyde and malononitrile. The effects of the reaction parameters, such as the catalyst amount and reaction time, on the product yield were investigated and the results are summarized in Table 1. The benzaldehyde conversion after 1 h of reaction steadily increased as the catalyst amount was increased from 10 to 50 mg and reached *ca.* 97%. Using 20 mg of catalyst, the conversion also increased from 60 to 98% as the reaction time increased from 1 to 2 h. TOF increased with the reactant concentration (entry 3 and 4), and there is a scope for further improvement by adjusting the catalyst loading. The conversion further increased to 100% after 2 h of reaction using 50 mg of catalyst. In order to evaluate the stability of the DETA-MIL-101 in the liquid phase reaction, a catalyst recycling test was performed. To this end, the catalyst was recovered *via* filtration at the end of reaction, washed with toluene and ethanol, activated at 423 K for 4 h in a vacuum in order to remove the adsorbed species, and then reused for reaction. As shown in Table 1, the benzaldehyde conversions for three repeated runs using 50 mg of catalyst remained almost constant. The powder XRD patterns and N₂ adsorption-desorption measurements of the fresh catalyst and those after the third run were also examined (data not shown); these showed identical diffraction patterns and N₂ adsorbed amounts. The EA analysis also confirmed that there was no significant leaching (the N content of the DETA-MIL-101 catalyst was 9.86 to 9.83 wt% after the fresh and third run). A catalyst filtering experiment in toluene exhibited a truly heterogeneous reaction; the reaction did not occur without DETA-MIL-101 in the filtrate. The experimental data in this study were also compared with the activities of other MOF and ZIF catalysts reported in the literature for the same reaction. As illustrated in Table 1, DETA-MIL-101 is a highly active heterogeneous catalyst for Knoevenagel condensation reaction, which proceeds under relatively mild reaction conditions of lower temperatures compared with other catalysts.

The amines grafted on a MOF can serve as binding sites for noble metals. In this work, three Pd_n-DETA-MIL-101 samples were prepared with *ca.* 0.5, 1, and 3 wt% Pd loadings *via* immobilization of the Pd²⁺ ions using PdCl₂; the TEM-EDX and ICP-OES analyses confirmed the 0.52, 1.04, and 3.06 wt% Pd loadings. Metal ions reduction agents were not used for the catalyst preparation, and nanoparticles by agglomeration of the Pd complex were not detected at $2\theta = 40^\circ$ in the XRD analysis (see ESI†, Fig. S1(c) and S1(d)). The highly dispersed state of the Pd ions was also confirmed by the TEM-EDX mappings (see ESI†, Fig. S3, S4, and S5).

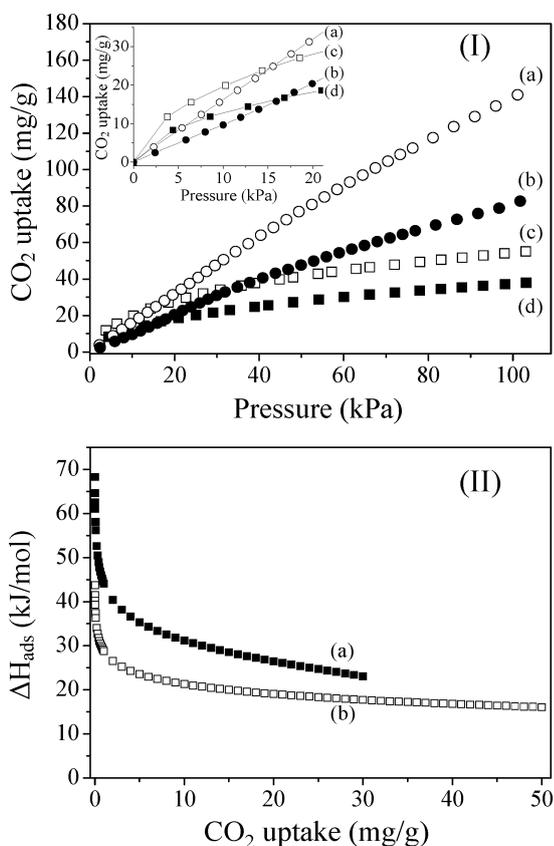


Fig. 3 (I) CO₂ adsorption of MIL-101 and DETA-MIL-101: MIL-101 at (a) 273 K and (b) 298 K, and DETA-MIL-101 at (c) 273 K and (d) 298 K. (II) Related heat of the CO₂ adsorption of (a) DETA-MIL-101 and (b) MIL-101.

Table 1 Summary of the catalytic activity of Koevenagel reaction for DETA-MIL-101 catalysts

Catalysts	Conditions			Conv. (%)	TOF (h ⁻¹)	Ref.
	Catal. amount (mg)	Time (h)	Temp. (K)			
DETA-MIL-101	10 ^a	0.5	RT	18	9	This work
		1		31		
	20 ^a	0.5	RT	48	13	This work
			1			
		2		98		
		2 ^d		60		
	20 ^b	0.5	RT	61	45	This work
			1			
		2		65		
	20 ^c	0.5	RT	98	108	This work
			1			
		2		71		
	50 ^a	0.5	RT	98	8	This work
1				74		
2			97			
3			100			
1 ^e			100			
1 ^f			97			
Blank ^g	—	18	RT	0		This work
IRMOF-3 ^h	50	2	313	99		33
NH ₂ -MIL-53 ^h	50	2	313	—		33
ZIF-8 ⁱ	20	4	RT	100		48
ED-MIL-101 ^j	20	19	353	98		37

^a Reaction conditions: 1.9 mmol of benzaldehyde and 3.8 mmol of malononitrile in 5 ml of toluene. ^b 10 mmol of benzaldehyde and 10 mmol of malononitrile in 25 mL of toluene. ^c 19 mmol of benzaldehyde and 19 mmol of malononitrile in 25 ml of toluene. ^d Catalyst was filtered-off after 1 h and the reaction was continued using the filtrate. ^e 1st recycle. ^f 2nd recycle. ^g without catalyst. ^h 8 mmol of benzaldehyde and 7 mmol of ethyl cyanoacetate in 5 ml of DMSO. ⁱ 1.9 mmol of benzaldehyde and 3.8 mmol of malononitrile in 5 ml of toluene using 20 mg of catalyst. ^j 10 mmol of benzaldehyde and 10 mmol of ethyl cyanoacetate in 25 mL of cyclohexane.

The Pd_n-DETA-MIL-101 catalysts were tested as a catalyst for the Heck coupling reaction of the iodobenzene and acrylic acid in the DMA with TEA used as an additive. As summarized in Table 2, TOF is higher at lower Pd loading due to better dispersion of the active sites. The Pd_{3,1}-DETA-MIL-101 exhibited somewhat higher conversion after 2 h of reaction (83% iodobenzene conversion) than that of the Pd_{1,0}-DETA-MIL-101 (78%) in Fig. 4; however, the conversions reached 96% and leveled off after 4 h of reaction for both Pd_{3,1}-DETA-MIL-101 and Pd_{1,0}-DETA-MIL-101. The conversions were maintained at 96% after the third recycling run. In order to further evaluate the stability of the Pd_n-DETA-MIL-101 in the liquid phase reaction, a hot filtering experiment was performed. As shown also in Fig. 4, there was no reaction in the catalyst-free filtrate, which confirmed its heterogeneous reaction. The ICP-MS analysis also supported the absence of leaching (the Pd content of the Pd_n-DETA-MIL-101 catalyst was 3.06 wt% to 3.05, respectively, for the fresh and third run mixtures).

Conclusions

Post-synthesis grafting of DETA onto the coordinatively unsaturated Cr sites in MIL-101 (DETA-MIL-101) was performed and its adsorptive/catalytic properties were evaluated after careful product characterization. Overall, the significant reduction in the surface area after DETA grafting caused a reduction in the CO₂ capture capacity, but the stronger interaction of the N species in the DETA-MIL-101 with CO₂ resulted in higher adsorption heat compared with that of MIL-101 in low pressure regions (< 15 kPa). The grafted DETA molecules can block the pores in the MIL-101, and the hydrophilic nature of the bare MIL-101 host turns hydrophobic. DETA-MIL-101 proved to be a very active and stable catalyst for Knoevenagel condensation between benzaldehyde and malononitrile in mild reaction conditions. The Pd²⁺ ions (0.5, 1.0 and 3.0 wt%) were immobilized on the amine species grafted to the MIL-101 using PdCl₂; they were also tested for Heck reactions of the acrylic acid and iodobenzene. Again, the high

Table 2 Summary of the catalytic activity of Heck reaction for Pd_n-DETA-MIL-101 catalysts^a

Samples	Pd-contents (mmol g ⁻¹ -catalyst)	Conversion (%)	TOF ^b (h ⁻¹)
Pd _{0,5} -DETA-MIL-101	0.0488	13	2661
Pd _{1,0} -DETA-MIL-101	0.0977	21	2149
Pd _{3,1} -DETA-MIL-101	0.2875	36	1252

^a Reaction conditions: 15 mmol of acrylic acid, 10 mmol of triethylamine, 10 mmol of iodobenzene, and the catalyst (20 mg) were added to the 25 ml *N,N*-dimethylacetamide (DMA, Aldrich) as a solvent. ^b The TOF values were calculated using the initial activity data taken at 30 min.

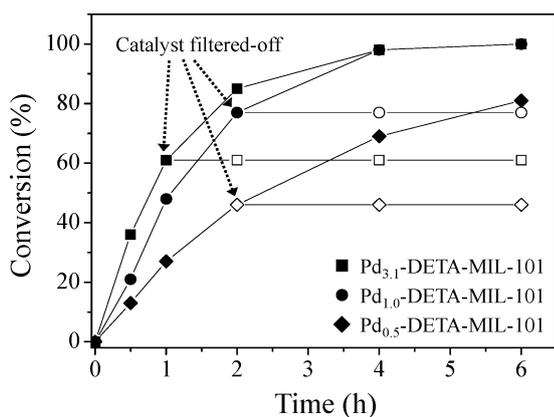


Fig. 4 Catalytic activity in the Heck reaction as a function of the reaction time. The reaction was performed in 10 mmol of iodobenzene, 15 mmol of acrylic acid, 15 mmol of triethylamine, and 20 mg of catalyst in 25 ml of DMA as a solvent at 393 K.

catalyst activity and stability were examined *via* recycling runs and hot filtering experiments accompanied by ICP analyses, which confirmed the heterogeneous nature of the conducted reaction.

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