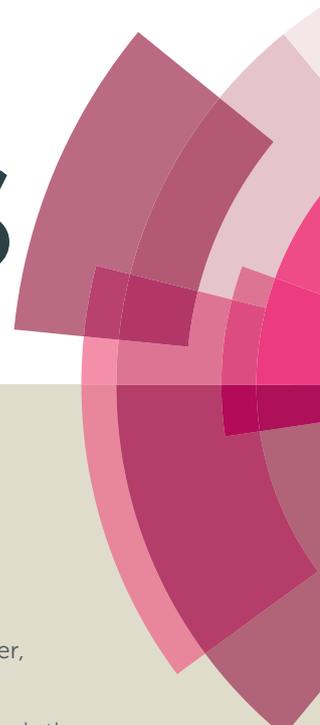


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## COMMUNICATION

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**Synthesis of Zeolite@Metal Organic Framework Core-Shell Particles as Bifunctional Catalysts†**Received 00th January 2012,  
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**Zeolite@metal organic framework (ZSM-5@UiO-66) core-shell composite has been synthesized for the first time by solvothermal growth of UiO-66 on the surface of ZSM-5 particles. The acidity from ZSM-5 and the basicity from the amine groups in UiO-66 obtained by post-synthetic modification of the metal clusters endow ZSM-5@UiO-66 a bifunctionality for cascade reactions.**

Metal-organic frameworks (MOFs) are an emerging class of crystalline microporous materials. The uniform micropores and high surface areas enable them a number of potential applications, including separation, storage, and heterogeneous catalysis<sup>1</sup>. The structure of MOFs is constructed by metal ions or clusters that act as lattice nodes and are held in place by multidentate organic ligands. Since a range of metal clusters and organic ligands can be built into MOFs, a wide structural diversity and highly designable pore sizes and shapes in MOFs are expected, which endow MOFs with tunable cavity architectures and properties<sup>2</sup>. Furthermore, the primary framework of MOFs can be functionalized through pre- or post-synthetic modification of metal clusters and/or organic ligands, and thus offers the possibility for fine-tuning their pore dimensions and local environment inside the micropores<sup>3</sup>. The great tunability in structures and functional properties of MOFs offer a great potential for many practical applications.

In addition to tailoring the structure of MOFs, synthesis of MOF-based composites is another approach to advance their functionalities for practical applications<sup>4</sup>. MOF-based composites are generally formed by physical or chemical mixing of MOFs with inorganic and/or organic substrates. Recently, MOF-based composite membranes and spherical solids have been prepared for direct uses in gas or liquid separations and as catalysts in heterogeneous catalytic reactions. For example, ZIF-8/Matrimid membranes were prepared by a solution blending approach and the as-prepared membranes were found to enhance the transport of CO<sub>2</sub> gas from the CO<sub>2</sub>/CH<sub>4</sub> gas mixtures<sup>5</sup>; Uniform coating of Cr-MIL-101 inside the macropores of a cylindrical cordierite monolith was achieved by the secondary growth technique and the composite was used as stable catalyst in liquid-phase oxidation reactions<sup>6</sup>; Silica@MOF core-shell composite spheres were fabricated by the seeded growth method and they were used as stationary phases for chromatographic separation to overcome the problems such as low column efficiency, high column back pressure, and undesirable peak shapes caused by the direct packing of MOF particles of irregular shapes<sup>7</sup>. These studies

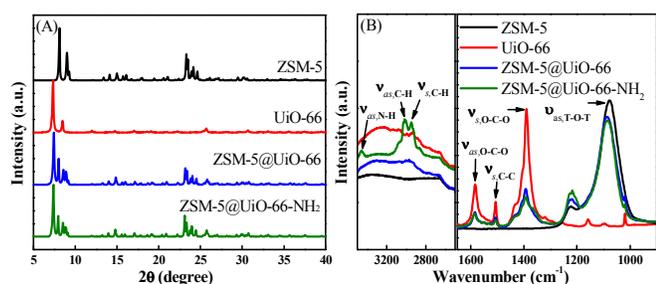
illustrate the research efforts in advancing MOF-based composites into technical materials for practical applications.

In this study, we report the synthesis of zeolite@MOF core-shell composites by solvothermal growth of MOF on the surface of zeolite support and demonstrate an application of this material as a bifunctional acid-base catalyst in two-step cascade reactions. Zeolites are crystalline microporous aluminosilicates, widely used as heterogeneous catalysts, adsorbents, and ion-exchange materials in petrochemical and fine chemical industries<sup>8</sup>. As porous materials, zeolite and MOF share common characteristics of high surface areas and uniform micropores but they differ in thermal/mechanical stability and structural flexibility<sup>9</sup>. In this context, the zeolite@MOF composites are expected to be a novel and useful porous system where inorganic zeolite and organic MOF components impart the advantages of higher thermal, mechanical and structural stability of zeolites and specific functionality and high flexibility of MOFs for a variety of applications. To our knowledge, however, the integration of MOF and zeolite into core-shell structured composites has not been reported in literature.

In our study, Zeolite Socony Mobil-5 (ZSM-5) and Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(O<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>)<sub>6</sub> (UiO-66) were chosen as components in the zeolite@MOF composites. ZSM-5 is a medium pore zeolite with pore system consisting of two types of intersecting straight and zig-zag 10 member ring channels, widely studied as membrane materials in xylene separation and catalysts in petroleum refinery<sup>10</sup>. UiO-66 is Zr-containing MOF composed of hexameric Zr<sub>6</sub>O<sub>32</sub> units linked by 1,4-benzene-dicarboxylate (BDC) ligands and it has excellent stabilities not typically found in common porous MOFs<sup>11</sup>. The ZSM-5@UiO-66 composite is a promising material to be chemically and thermally stable for various applications. In particular, the composite was explored as a bifunctional acid-base catalyst (denoted as ZSM-5@UiO-66-NH<sub>2</sub>) in which the basic site resulted from post-synthetic modification of the composite that allowed the functionalization of the UiO-66 with basic amine groups and the acid sites were generated by the presence of tetrahedrally coordinated framework aluminum in the ZSM-5.

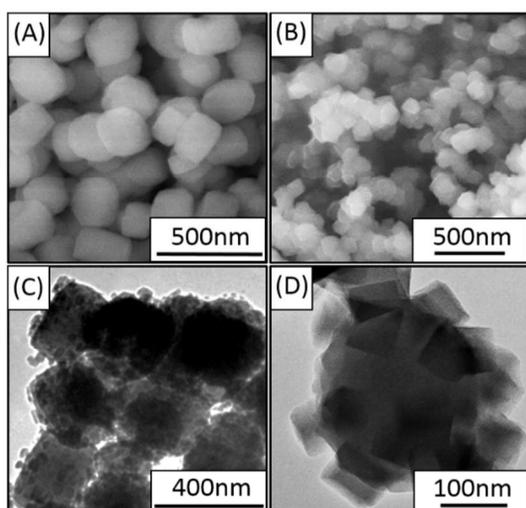
Synthesis of ZSM-5@UiO-66 was carried out by the hydrothermal crystallization of ZSM-5 followed by the solvothermal growth of UiO-66 from its synthetic solution in the presence of dispersed ZSM-5 particles. The incorporation of amino groups into ZSM-5@UiO-66 composite was conducted by post-synthetic modification of the Zr metal clusters with ethylene diamine using a reported method<sup>12</sup>. Details on the synthesis of ZSM-5, UiO-66, ZSM-5@UiO-66, and ZSM-5@UiO-66-NH<sub>2</sub> are described in section S1 of ESI.†

Powder X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy were employed to study the formation of zeolite@MOF composite and the results are shown in Fig. 1.



**Fig. 1** XRD patterns (A) and FTIR spectra (B) of ZSM-5, UiO-66, ZSM-5@UiO-66, and ZSM-5@UiO-66-NH<sub>2</sub>, respectively.

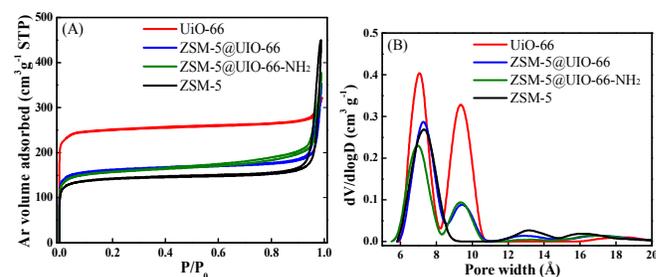
The reflection peaks in XRD patterns of ZSM-5 and UiO-66, respectively, are consistent with those reported for the topologies of bare zeolite and MOF materials<sup>10a, 11</sup>. The appearance of reflection peaks of ZSM-5 and UiO-66 in the XRD pattern of ZSM-5@UiO-66 (Fig. 1(A)) indicates co-existence of zeolite and MOF topological structures in the composite. The incorporation of amine group into ZSM-5@UiO-66 did not deteriorate the crystal phases of ZSM-5 or UiO-66 because XRD pattern of ZSM-5@UiO-66-NH<sub>2</sub> is identical to that of ZSM-5@UiO-66. FTIR spectra further confirm the results of XRD analysis on the formation of ZSM-5@UiO-66 composite. Fig. 1(B) illustrates the absorption bands centered around 1390, 1506, and 1583 cm<sup>-1</sup> that correspond to the O-C-O symmetric stretching ( $\nu_{s,O-C-O}$ ), C-C ring symmetric stretch ( $\nu_{s,C-C}$ ), and O-C-O asymmetric stretching ( $\nu_{as,O-C-O}$ ) vibrations, respectively, of the organic BDC linkers in UiO-66<sup>13</sup>. The absorption band centered at 1087 cm<sup>-1</sup> is attributed to the asymmetric stretching vibration of T-O-T (T: Si or Al) ( $\nu_{as,T-O-T}$ ) in the framework of the ZSM-5 zeolite<sup>14</sup>. The appearance of these absorption bands, for example, 1087 cm<sup>-1</sup> and 1390 cm<sup>-1</sup>, in ZSM-5@UiO-66 and ZSM-5@UiO-66-NH<sub>2</sub> indicates the co-existence of ZSM-5 and UiO-66 in the composite. The presence of amine groups in ZSM-5@UiO-66-NH<sub>2</sub> is revealed by the asymmetric ( $\nu_{as,C-H} = 3016$  cm<sup>-1</sup>) and symmetric ( $\nu_{s,C-H} = 2947$  cm<sup>-1</sup>) stretching vibrations of C-H and asymmetric stretching ( $\nu_{as,N-H} = 3460$  cm<sup>-1</sup>) of bonded -NH<sub>2</sub>, respectively<sup>15</sup>.



**Fig. 2** SEM images of ZSM-5 (A) and UiO-66 (B) particles. (C) and (D) show the TEM images of ZSM-5@UiO-66-NH<sub>2</sub> composite particles.

The morphologies of ZSM-5, UiO-66, and ZSM-5@UiO-66-NH<sub>2</sub> composite samples were observed with scanning electron microscope (SEM) and transmission electron microscope (TEM), and the representative images are shown in Fig. 2. The ZSM-5 zeolite (Fig. 2(A)) consists of short cylindrical particles with an average width of ~ 250 nm and thickness of ~ 180 nm and well crystallized smooth surfaces. The UiO-66 (Fig. 2(B)) that was crystallized in the synthetic conditions for ZSM-5@UiO-66 contains aggregated cubic particles with average size of ~ 100 nm. ZSM-5@UiO-66 composite (Fig. 2(C)-D)) contains bulk ZSM-5 core and sparse UiO-66 particles on the ZSM-5 surface, showing clearly the formation of core-shell zeolite@MOF structure. The similarity between the lattice parameters of ZSM-5 ( $a = 20.090$  Å,  $b = 19.738$  Å,  $c = 13.142$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ) and UiO-66 ( $a = b = c = 20.700$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ) might lead to an epitaxial growth of UiO-66 from ZSM-5 crystal surface<sup>11, 16</sup>. Nanosized zeolite seeds have been reported to promote the fast growth of MOF crystals<sup>17</sup>.

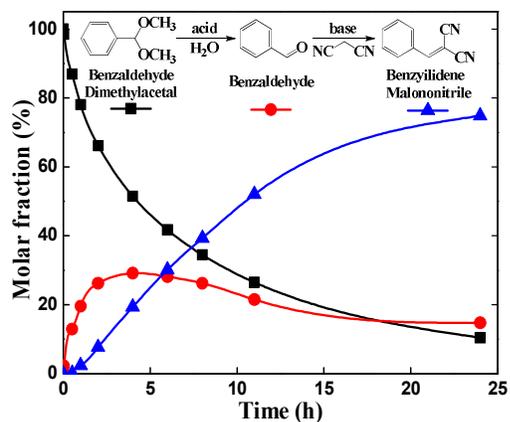
The textural properties of the zeolite@MOF composite was analyzed by the argon (Ar) and nitrogen (N<sub>2</sub>) adsorption-desorption isotherms as shown in Fig. 3 and Table S1 in ESI†. As expected, ZSM-5@UiO-66 composite has less and more Ar uptake compared to the bare UiO-66 and ZSM-5, respectively (Figure 3(A)). Incorporation of amine groups into ZSM-5@UiO-66 by post-synthetic modification of Zr metal clusters with ethylene diamine does not significantly reduce the micropore volume of the composite material. Non-local density functional theory (NLDFT) pore size analysis (Fig. 3(B)) derived from the adsorption branch of Ar isotherms on the basis of spherical/cylindrical pore model indicates that UiO-66 has dual micropore systems with sizes of 7.2 Å and 9.6 Å, corresponding to its tetrahedral and octahedral cages, respectively<sup>18</sup>. The same pore model was applied to the bare ZSM-5 and the resultant micropore size of ZSM-5 is 7.1 Å, slightly larger than the typical size (5.2 Å) of ZSM-5 (Fig. S4, ESI†). The ZSM-5@UiO-66-NH<sub>2</sub> has slightly smaller micropore sizes compared to ZSM-5@UiO-66 due to the incorporation of amine groups into UiO-66. These results demonstrate that the integration of ZSM-5 and UiO-66 into a composite preserves topological features of both microporous materials, which is important for their applications as catalysts in heterogeneous catalysis.



**Fig. 3** Ar adsorption-desorption isotherms (A) and NLDFT pore-size distribution (B) of ZSM-5, UiO-66, ZSM-5@UiO-66, and ZSM-5@UiO-66-NH<sub>2</sub>, respectively.

To illustrate the catalytic activity of the ZSM-5@UiO-66-NH<sub>2</sub> catalyst, one-pot synthesis of benzylidene malonitrile from malonitrile and benzaldehyde dimethyl acetal, a process involving the hydrolysis of the acetal catalyzed by the Brønsted acid sites followed by a Knoevenagel condensation catalyzed by the basic sites was carried out. More specifically, benzaldehyde dimethyl acetal was hydrolyzed to produce benzaldehyde which reacted with malonitrile to give benzylidene malonitrile (the reaction scheme shown in Fig. 4). The first reaction step requires acid sites which can be supplied by the framework Al-O(H)-Si sites in the ZSM-5 core, while the subsequent condensation step involves the basic sites from

the amine groups in the UiO-66 shell of the composite. Fig.4 shows the conversion of benzaldehyde dimethyl acetal and formation of the benzaldehyde intermediate that is reacted through the consecutive Knoevenagel condensation with malononitrile to give the final benzylidene malononitrile product. The mass fractions of the ZSM-5 and UiO-66 in the composite catalyst are 58.6 wt% and 41.4 wt%, respectively, analyzed from thermalgravimetric analysis (Fig.S4, ESI †). A systematic modulation on the fractions of zeolite and MOF components in the composite by tuning the ratios of their precursor materials in the synthesis will optimize the composite catalyst for desired cascade reactions. The integration of MOF and zeolite into a single particle assures uniform mixing of dual functionality of the catalyst for cascade reactions in fixed bed reactors in comparison with physical mixture of both materials.



**Fig. 4** Results of the catalytic activity of ZSM-5@UiO-66-NH<sub>2</sub> composite for acetal hydrolysis-Knoevenagel condensation cascade reaction. Molar fractions of benzaldehyde dimethylacetal, benzaldehyde, and benzylidene malononitrile are shown, respectively.

## Conclusions

In conclusion, ZSM-5@UiO-66 core-shell composite particles were synthesized by solvothermal growth of UiO-66 shell on the surface of ZSM-5 particles that were pre-synthesized via hydrothermal crystallization. Post-synthetic modification of the composite with ethylene diamine in the UiO-66 framework incorporated amine groups into the composite. The acidity in ZSM-5 generated by aluminum in the tetrahedral site of the zeolite framework and the basicity in UiO-66 originated from the amine groups enabled the ZSM-5@UiO-66 composite acid-base bifunctionality for catalytic cascade reactions. The synthesis of benzylidene malononitrile from malononitrile and benzaldehyde dimethyl acetal, a process involving the hydrolysis of the acetal catalyzed by the Brønsted acid sites in zeolite followed by a Knoevenagel condensation reaction catalyzed by the basic sites in MOF confirmed the bifunctional activity of the ZSM-5@UiO-66-NH<sub>2</sub> composite. The present work is the first example of the synthesis of zeolite@MOF composites and the demonstration of its potential as bifunctional catalysts in one-pot cascade reactions. This study is an important platform toward zeolite@MOF nanoporous composite systems that integrate the advantages of thermal, mechanical and structural stability of inorganic zeolites and the specific functionality and high flexibility of MOFs for a variety of applications in the future.

## Acknowledgments

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† Electronic Supplementary Information (ESI) available: Experimental procedures and materials characterization, elemental composition analysis from energy dispersive x-ray spectroscopy, N<sub>2</sub> adsorption-desorption isotherms and textural property of these materials, thermalgravimetric analysis, and catalytic cascade reactions over bare zeolite and MOF catalyst. See DOI: 10.1039/c000000x/

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