Robust Bifunctional Core−Shell MOF@POP Catalyst for One-Pot Tandem Reaction

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S *Supporting Information*

ABSTRACT: A new bifunctional acid−base catalyst, core−shell UiO-66@SNW-1, with robust chemical and thermal stability, recyclability, and durable catalytic activity is synthesized by a convenient, universal strategy. Interestingly, this hybrid material can effectively catalyze deacetalization-Knoevenagel condensation reaction in the presence of excellent compartmentalization to spatially isolate opposing acid−base sites.
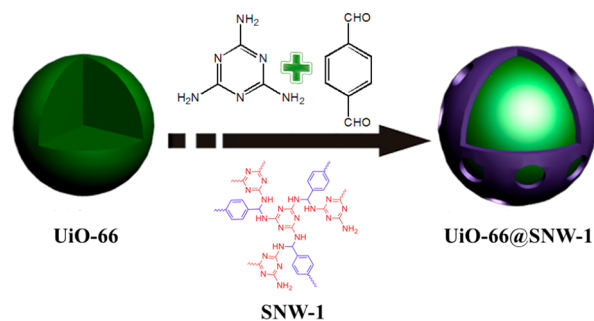
One-pot tandem reactions have attracted great attention owing to their natures of simple synthetic procedures and atom efficiency.[1] The multifunctional solid catalysts possessing different catalytic sites are extremely applicable to catalyze tandem reactions.[2] For example, metal−organic frameworks (MOFs), montmorillonite, porous organic polymers (POPs), mesoporous silicas, etc., which contain coexistent acidic and basic sites, have been applied for tandem reaction.[3]

MOFs, a promising class of porous crystalline materials, assemble with metal centers and various organic linkers.[4] Because of their large surface areas, tunable pore size, recoverability, and chemical diversity, MOFs usually show great potential for versatile applications, such as gas storage and separation, carbon capture, sensing, drug delivery, catalysis,[5] etc.[6] Recently, the catalytic property of MOFs has attracted a great attention by researchers. Most MOFs are appropriate for single-site catalysis, thus preparing multifunctional MOFs catalyst has remained challenging.[7] The main limitation in the catalytic field depended on how to introduce other functional sites and maintaining the natural features.[8] MOF-based hybrid materials are an emerging multifunctional material that combines MOFs with other MOFs, enzymes, magnetic metal oxides, and polymers.[9] These hybrid materials demonstrate admirable properties compared with single species in a catalytic field. Porous organic polymers (POPs), as a new kind of developed porous material, are entirely constructed from organic building blocks with reticular chemistry through covalent bond formation.[10] POPs possess high surface areas, variable functional groups, and adjustable pore sizes that offer unprecedented possibilities for catalysis.[11] However, to prepare acid−base bifunctional catalysts of POPs is not straightforward, especially when Lewis acid and base sites tend to quench each other. Therefore, to develop new types of hybrid MOFs@POPs is of great strategic significance owing to their potentially improved performance over those of individual components and extensive applications in heterogeneous catalysis. Recently, Zhang and co-workers successfully developed a new type of NH₂-MIL-68@TPA-COF core−shell hybrid material and applied it to degradation of rhodamine B.[12] Xie et al. reported a MOF@POP nanocomposite (UNM) that showed great potential in biomedical fields and cancer treatment.[13] The Hu group also developed a series of MIL-101@Pt/FeP-CMP composite materials that possess Lewis acid sites to activate C=O bond.[14] To the best of our knowledge, the performances of these core−shell MOFs@POPs hybrid materials are superior to the individual components.

On the basis of the above-mentioned strategies, the use of MOFs@POPs hybrid materials as a single catalytic system could combine their respective advantages while effectively eliminating their weakness. Therefore, the fabrication of MOFs@POP hybrid materials with multifunctional catalytic sites would be of great promise for extending the application of MOFs and POPs. In this work, a new MOF@POP (UiO-66@SNW-1) was prepared under solvothermal conditions and presented as an original platform for catalyzing the one-pot tandem deacetalization-Knoevenagel condensation reaction (Scheme 1). Delightedly, the core−shell UiO-66@SNW-1,

Scheme 1. Schematic Illustration Showing the Fabrication of UiO-66@SNW-1

consisting of Lewis acid sites (the Zr clusters in UiO-66) and Brønsted base sites (aminal groups in SNW-1), can act as a highly efficient bifunctional catalyst for the one-pot tandem reaction. Impressively, the bifunctional core−shell UiO-66@SNW-1 catalyst exhibited more preeminent catalytic performance than the the the parent UiO-66, SNW-1, and UiO-66-NH₂.

To investigate the crystallinity and structural stability of UiO-66@SNW-1 hybrid material, the comprehensive charac-

terization was performed by powder X-ray diffraction (PXRD). As shown in Figure S1, the identically strong Bragg diffraction peaks of UiO-66 and UiO-66@SNW-1 revealed that SNW-1 is amorphous and the crystalline structure of UiO-66 does not alter in the process of growth of POPs. The FT-IR spectrum of UiO-66@SNW-1 matched well with UiO-66 as well as SNW-1 and further indicated that the UiO-66@SNW-1 was successfully formed. The presence of the distinct stretching band for the triazine ring at ≈1550 and 1480 cm^{-1} indicates the formation of SNW-1 (Figure S2 and S3). In addition, the chemical and thermal stability of core−shell UiO-66@SNW-1 hybrid material were investigated by PXRD. When the hybrid material was soaked in different solvents for 48 h, PXRD patterns remained unchanged, which indicated no framework collapse during chemical stability tests (Figure 1 and S4). FT-
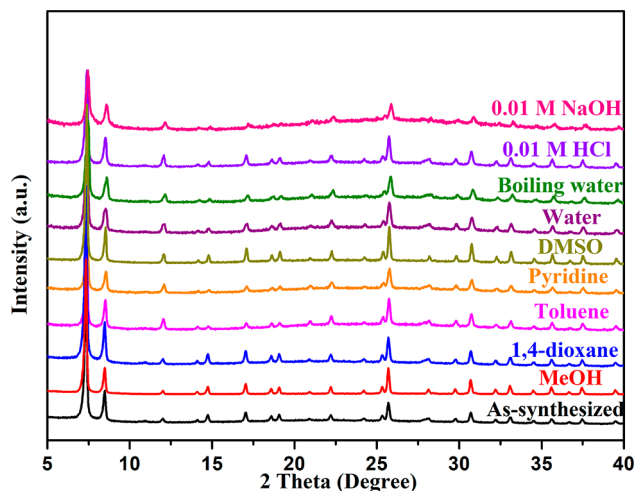

Figure 2. SEM images of (a) UiO-66, (b) SNW-1, (c) UiO-66@SNW-1 hybrid material. (d) TEM image of UiO-66@SNW-1 hybrid material.

Figure 1. Chemical stability tests for UiO-66@SNW-1 monitored by PXRD.

IR spectrum further proved that the structure is intact without damage (Figure S5). The variable-temperature PXRD and thermogravimetric analysis (TGA) were also investigated, and the results revealed that UiO-66@SNW-1 hybrid material could be stable up to 400 °C in air (Figure S6 and S7).

The core−shell UiO-66@SNW-1 hybrid material was investigated by scanning and transmission electron microscopy (SEM and TEM, in Figure 2). As shown in Figure 2a−c, SEM images showed that UiO-66 has an angulated nanocrystal with smooth surfaces and the surfaces of the pristine UiO-66 become rough after growing SNW-1. The SNW-1 coating in the TEM images can be distinguished by a lighter contrast than that of the inner MOF. TEM image analysis of UiO-66@SNW-1 revealed that the surface of the UiO-66 is coated with SNW-1 material (∼25 nm thickness) (Figure 2d). The weight ratio of UiO-66:SNW-1 in UiO-66@SNW-1 is determined to be ≈1:0.56 on the basis of the TGA analyses. The N$_2$ sorption properties of core−shell UiO-66@SNW-1 material were analyzed by the Brunauer−Emmett−Teller (BET) method at 77 K. The results of core−shell UiO-66@SNW-1 hybrid material exhibited type IV isotherms, and the surface area was measured as 354 m^2 g^{-1}. The N$_2$ sorption properties of the UiO-66@SNW-1 revealed that the microporous characteristics of the hybrid material with a very high degree of cross-linking by SNW-1 (Figure S8).

Recently, the development of bifunctional heterogeneous catalysts for promoting one-pot tandem reactions has currently
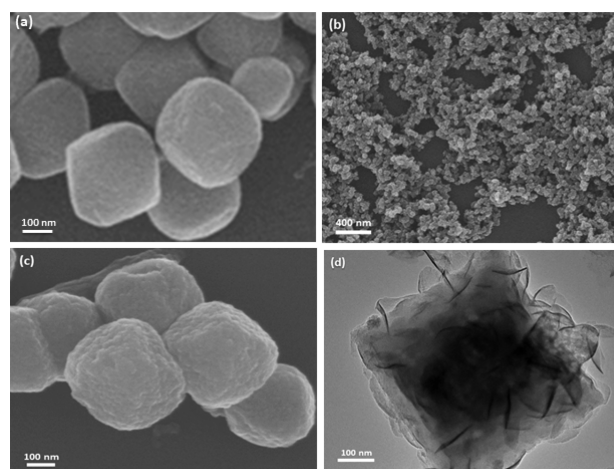
drawn much attention. The UiO-66@SNW-1 hybrid material contained abundant unsaturated Zr centers, which can be used as Lewis acid sites for catalyzing deacetalization reaction and the aminal groups in SNW-1 as a weak Brønsted base sites can be utilized for catalyzing Knoevenagel reaction. Thus, deacetalization-Knoevenagel reaction was selected to explore the catalytic performance of core−shell UiO-66@SNW-1 hybrid material. The catalytic activity of hybrid material was evaluated in the presence of 50 mg of activated UiO-66@SNW-1 as a model reaction, wherein benzaldehydedimethylacetal (a) (2.0 mmol) reacts with malononitrile (2.1 mmol) in DMSO-d_6 (2.0 mL) under a N$_2$ atmosphere at 80 °C for 12 h. The conversion and yield were monitored by ^{1}H NMR spectroscopy. In this case, excellent yield (99.6%) of the desired product 2-benzylidenemalononitrile (c) was observed (Table 1). Compared with other previous catalysts such as Yb-BCD-NH$_2$, MIL-101(Al)-NH$_2$, and PCN-124 (Table S2),[15] UiO-66@SNW-1 hybrid material also exhibited good catalytic

Table 1. One-Pot Tandem Deacetalization-Knoevenagel Condensation Reaction and Monitored by ^{1}H NMR[a]

entry	conv of a (%)	yield of b (%)	yield of c (%)
UiO-66@SNW-1	99.6	trace	99.6
second cycle	99.5	trace	99.5
third cycle	99.4	trace	99.4
fourth cycle	99.6	trace	99.6
fifth cycle	99.5	trace	99.5
UiO-66-NH$_2$	75.2	0.9	74.3
UiO-66	99.5	83.3	16.2
SNW-1	∼0	trace	trace
no catalyst	∼0	trace	trace
UiO-66+SNW-1	99.4	17.5	81.9

[a]Reaction conditions: benzaldehyde dimethylacetal (2.0 mmol), malononitrile (2.1 mmol), DMSO-d_6 (2 mL), and catalyst (50 mg); reaction temperature, 80 °C; reaction time, 12 h.

activity for deacetalization-Knoevenagel reaction. In detail, the kinetic investigation revealed that the reaction completes within 12 h (Figure S9). On the basis of the control experiments, the tandem reaction can be considered as two sequential steps: first, the unsaturated Zr clusters catalyzed benzaldehyde dimethylacetal (a) to generate benzaldehyde (b); second, the aminal groups in SNW-1 catalyzed Knoevenagel condensation reaction to produce 2-benzylidenemalononitrile (c). To better comprehend the necessity of the catalyst for this tandem reaction, the same model reaction was carried out without catalyst. The reaction without UiO-66@SNW-1 can scarcely react to product over 12 h. When UiO-66 used as catalyst to boost this tandem reaction, the first step deacetalization reaction was efficient but the second step Knoevenagel condensation reaction did not take place. When only SNW-1 was used as catalyst, the target product could not be detected. In addition, as contrasted with UiO-66-NH$_2$, the catalytic effect of UiO-66@SNW-1 was better on deacetalization-Knoevenagel condensation reaction. The activity on the physical mixture of UiO-66 and SNW-1 (UiO-66: SNW-1 = 1:0.56) was relatively lower than UiO-66@SNW-1 which confirmed the advantages of the core–shell structural design of the UiO-66@SNW-1 material. The reason was assigned to the two catalytic parts being joined together, making the mass transfer process more efficient.[16] A leaching test indicated that no active species leached into the solution and the heterogeneity of the catalyst is directly proved (Figures S10). After tandem reaction, the catalyst could be removed by centrifuging and reused at least for five cycles without a noticeable change in its activity (Figures S11). The crystallinity and structural integrity of core–shell UiO-66@SNW-1 hybrid material did not change even after five cycles, indicating its great recyclability and excellent stability for the one-pot tandem deacetalization-Knoevenagel condensation reaction (Figures S12, S13, S14).

In conclusion, a bifunctional acid–base catalyst, core–shell UiO-66@SNW-1 hybrid material, has been successfully developed to boost the catalytic performance toward one-pot tandem deacetalization-Knoevenagel condensation reaction. The core–shell UiO-66@SNW-1 hybrid material contained both Lewis acid and Brønsted base sites and showed large surface areas as well as high chemical and thermal stability. In the meantime, high chemical stability and thermal stability, microporous characteristics of core–shell UiO-66@SNW-1 hybrid material is markedly beneficial for heterogeneous catalysis. Finally, this work highlighted the prominent catalytic performance of core–shell UiO-66@SNW-1 hybrid material for one-pot tandem deacetalization-Knoevenagel condensation reaction. This strategy would be extensively employed in the development of functional MOFs hybrid materials and high performance heterogeneous catalyst. Our ongoing work will deal with systematically preparing MOFs@POPs hybrid materials that can be applied in tandem reaction.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b02303.

Materials and general methods, PXRD pattern, FT-IR spectra, TGA curves, adsorption–desorption isotherms, ^{1}H NMR spectra, conversions and yields from hot filtration reactions, recycle capacity tests, SEM and TEM images, and data from condensation reactions (PDF)

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Notes

The authors declare no competing financial interest.

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