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## Temperature-responsive dissolution/recrystallization of Zn MOF enables the maximum efficiency and recyclability of catalysts

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A novel strategy through temperature-responsive dissolution and recrystallization process has successfully achieved the 100% atomic utilization and easy recyclability of heterogeneous metal organic framework dimethylammonium zinc formate (DMZnF) catalysts for high-efficiently dehydrogenation of DMF-H<sub>2</sub>O for hydrogen generation. DMZnF dissolves as a homogeneous catalyst at high reaction temperature, and then is recrystallized and recycled as a heterogeneous catalyst at low temperature.

Heterogeneous catalysts with the features of the recovery, reutilization and easy separation of product from catalytic system exhibit higher capability in practical applications than homogeneous ones.<sup>1</sup> However, these particle-like active components only allow the availability of surface atoms for catalysis, leading to their much lower atomic utilization efficiency compared to the homogeneous counterparts.<sup>2</sup> Thus, maximizing the atomic utilization efficiency of heterogeneous catalysts is an ideal but challenging topic. Many efforts have been attempted to achieve this goal via designing the catalysts with the multilevel structures.<sup>3-5</sup> Recently, the single atom catalysts with specific coordination environments have been developed to expose each metal atom for catalysis through complex synthetic method.<sup>6, 7</sup> However, the natural catalytic activity of each single active site is greatly determined by their chemical coordination environments.<sup>8, 9</sup> Also, it is difficult to modulate the chemical states of single active centers, limiting their potentials for a variety of catalytic reactions. Metal organic frameworks (MOFs) with the same active sites as another typical heterogeneous catalyst exhibit the theoretical maximum atom utilization efficiency, which is considered to bridge the gap between homogeneous and heterogeneous catalysis.<sup>10-13</sup> However, the narrow pore of MOFs generally leads to the

limited chemical diffusion of reactants/products and thereby poor chemical kinetics during reactions, making them impossible to reach 100% atom utilization of all active centers.<sup>14</sup> Therefore, it is still significant to explore new strategies to maximize atomic utilization.

As for the homogeneous catalysts, their main feature is that each active site can catalyze the reaction with the same catalytic performance, leading to the 100% atomic utilization efficiency during the reaction.<sup>15</sup> Nevertheless, they are hard to be separated and reused from reaction system compared with heterogeneous ones.<sup>16-18</sup> Therefore, the strategy to combine the advantages of homogeneous and heterogeneous catalysis may realize the maximum efficiency and recyclability of catalysts.

Herein, a metal organic framework dimethylammonium zinc formate ([(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]Zn(HCOO)<sub>3</sub>, DMZnF) with perovskite structure has been successfully demonstrated as a temperature-responsive dissolution/recrystallization catalyst with 100% atomic utilization efficiency for hydrogen production through the dehydrogenation of N,N-dimethylformamide (DMF) and H<sub>2</sub>O. The use of DMF and H<sub>2</sub>O is a promising hydrogen generation system,19 because of their involatile, inflammable, inexplosive and incorrosive properties compared with other carbon hydrides such as formic acid,<sup>20, 21</sup> formaldehyde<sup>22, 23</sup> and methanol.<sup>24, 25</sup> However, there is lack of efficient and reusable non-noble metal catalysts for this desired and prospective hydrogen generation system. Thus, the DMF-H<sub>2</sub>O hydrogen generation system is selected as a model reaction to explore the unique catalytic performance of DMZnF catalysts. The "smart" properties are that DMZnF catalysts can catalyze the hydrogen generation reaction from DMF-H<sub>2</sub>O system as homogeneous catalysts at 120 °C and could be spontaneously separated from the reaction system at room temperature and reused for the next cycle without any treatment.

Initially, the DMZnF catalysts were easily synthesized via adding zinc nitrate to DMF-H<sub>2</sub>O mixed solution at 120 °C under Ar atmosphere. During the preparation process, white solids of ZnO (Figure S1) were generated in the solution, possibly owing to the precipitation between zinc salts and OH<sup>-</sup> in DMF and H<sub>2</sub>O

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Figure 1. (a) The crystal structure of DMZnF metal organic framework. The inset is the optical image of a DMZnF micro-crystal. (b) The XRD patterns of the simulated DMZnF and as-synthesized DMZnF. (c) The hydrogen production from DMF-H<sub>2</sub>O vs. time. **Reaction conditions:** DMZnF/ZnO (40.0 mg) or none catalysts, DMF (4.0 mL), H<sub>2</sub>O (0.2 mL), 120 °C and Ar atmosphere.

solution.<sup>26, 27</sup> On account of easy removal of undesired ZnO solids through hot filtration, the DMZnF catalysts with hundreds of microns were slowly appeared and separated out from the remained supernatant solution (Figure 1a). Single-crystal X-ray diffraction analysis reveals that the solids of DMZnF possess a perovskite-type architecture (Figure 1a, Table S1-S2),<sup>28</sup> in which Zn<sup>2+</sup> ions are octahedrally coordinated by six oxygen atoms from formate groups (HCOO<sup>-</sup>). Meanwhile, the trigonal disordered dimethylammonium ((CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup>, DMA<sup>+</sup>) cations are located in the channel of [Zn(HCOO)<sub>3</sub>-]. Besides, XRD pattern of synthetic DMZnF was highly consistent with simulative one (Figure 1b). As-synthesized DMZnF with R<sup>3</sup>c space group is accordant with the previously reported structure of DMZnF (CCDC number is 266350).<sup>29</sup> Furthermore, the Fourier-transform infrared spectroscopy (FT-IR) and Raman spectra (Figure S2, and Table S3-S4) could further identify the successful formation of DMZnF crystals.<sup>30, 31</sup> In addition, TGA (Thermogravimetric Analysis) and DSC (Differential Scanning Calorimeter) graphs could also reveal the structure of DMZnF catalysts (Figure S3, the detailed description could be found in the supporting information). <sup>32</sup> The specific surface area of DMZnF was 22.8 cm<sup>-3</sup> g<sup>-1</sup> measured by the nitrogen adsorption-desorption isotherms at 77 K (Figure S4a). The relatively small surface area might be attributed to the presence of DMA<sup>+</sup> in the pores of MOF (Figure S4b).

Then, as-synthesized DMZnF crystals were used to catalyze the base-free hydrogen generation from DMF-H<sub>2</sub>O system without treatments. Under the optimized reaction condition, hydrogen was linearly increased with a rate of 0.158 mol<sub>H2</sub> mol<sub>Zn</sub><sup>-1</sup> h<sup>-1</sup> (turnover frequency, TOF, was 0.158 h<sup>-1</sup>) at 120 °C under Ar atmosphere, as shown in Figure 1c. In contrast, no hydrogen could be released from the DMF-H<sub>2</sub>O system in the absence of DMZnF under the same reaction condition. As a referred catalyst, the ZnO powder, which was generated during the synthesis of DMZnF as shown in Figure S1, exhibited bare catalytic activity for the hydrogen generation (Figure 1c). Therefore, the natural catalytic capability of DMZnF could be confirmed by the hydrogen generation from DMF-H<sub>2</sub>O system.

Generally, the metal organic frameworks catalysts are considered as heterogeneous catalysis without any phase transformation. Herein, the different phenomenon was observed from DMZnF catalysed hydrogen generation reaction. At initial state, the heterogeneous DMZnF catalysts were



Figure 2. Catalytic performance of DMZnF for hydrogen production from DMF and water. (a) Optical images of the reaction solution before and after catalytic reactions for 4 cycles. (b) The recycling stability of DMZnF for the hydrogen production from DMF and H<sub>2</sub>O system. **Reaction condition:** DMZnF catalysts (40.0 mg), DMF (4.0 mL), H<sub>2</sub>O (0.2 mL), 120 °C and Ar atmosphere.

dispersed in the reaction system at room temperature (25 °C), forming a turbid solution (Figure 2a). Then, the heterogeneous catalytic reaction was transferred to a homogeneous one during the hydrogen generation process at 120 °C, along with the dissolution of DMZnF, giving a clear solution (Figure 2a). After 6 h reaction, when the reaction system was cooled to room temperature again to terminate the hydrogen generation, the DMZnF catalysts could be spontaneously recrystallized and separated from the DMF-H<sub>2</sub>O system, becoming a turbid solution again. After this process, the Zn<sup>2+</sup> concentration with 6.82×10<sup>-4</sup> mmol mL<sup>-1</sup> could be detected by the ICP-MS analysis, indicating almost complete separation (98.3%) of the catalyst from the liquid solution. Meanwhile, the XRD analysis, FT-IR spectra and Raman spectra revealed that the structure of the recrystalized solids were maintained as DMZnF MOFs through this dissolution and recrystallization process (Figure S5-S6). More importantly, the catalytic performance of DMZnF MOFs could be repeated at least for 4 times with the preserved hydrogen generation rates (Figure 2b), which could be maintained at the range from 0.151 mol<sub>H2</sub> mol<sub>Zn<sup>-1</sup></sub> h<sup>-1</sup> to 0.159  $mol_{H2} mol_{Zn}^{-1} h^{-1}$ .

To further highlight the critical function of this transformation process from heterogeneous catalysis to homogeneous one, the hydrogen generation from DMF and H<sub>2</sub>O system was performed in the typical nonpolar solvent n-heptane, in which the DMZnF catalysts could not be dissolved under the reaction condition. In other words, the hydrogen generation in nheptane represents a typically heterogeneous one. As shown in Figure S6, the hydrogen production rate was only  $0.002 \text{ mol}_{H2}$ mol<sub>Zn<sup>-1</sup></sub> h<sup>-1</sup> in n-heptane solutions via a heterogeneous catalysis, which was 79 times lower than the rate via a homogeneous catalysis (0.158 mol<sub>H2</sub> mol<sub>Zn<sup>-1</sup></sub>  $h^{-1}$ ). The phase of used solid DMZnF catalysts were maintained according to the XRD patterns (Figure S7), revealing the undestroyed catalytic structure. Therefore, this dissolution/recrystallization process benefits not only for the separation of catalysts, but also for the 100% atomic utilization of metal catalysts.

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Then, the operating temperature range was also explored for this unique hydrogen generation system. As shown in Figure S8, the DMZnF catalysts could not be dissolved in the reaction system and show no hydrogen generation at 60 °C, indicating the unsuitable reaction temperature. When the reaction temperature was raised to 80 °C, this dissolution and recrystallization process could be successfully initiated, giving a hydrogen generation rate of 0.003 mol<sub>H2</sub> mol<sub>Zn<sup>-1</sup></sub>  $h^{-1}$ . Also, the rate could be further increased to 0.041 and 0.158  $mol_{H2}$   $mol_{Zn}$ <sup>1</sup> h<sup>-1</sup> at the reaction temperature of 100 °C and 120 °C, respectively. Meanwhile, the phase of DMZnF catalysts were well preserved during the dissolution and recrystallization process (Figure S9). Therefore, the successful operating temperature should be higher than 80 °C to ensure the transformation from heterogeneous catalyst to homogeneous one.

From the above analysis, the DMZnF catalysts exhibited unique catalytic characteristic for the base-free DMF-H<sub>2</sub>O hydrogen generation system. Specially, the catalysts could promote the hydrogen generation through a homogeneous catalytic process, meanwhile, it could be recycled as a heterogeneous catalyst owing to the recrystallization of homogeneous catalysts. Therefore, the DMZnF catalysts realized an efficient and recyclable catalytic performance for the hydrogen generation from DMF-H<sub>2</sub>O system through combining the advantages of both homogeneous and heterogeneous catalysts.

To further explore the catalytic process of DMZnF for the hydrogen production from DMF and H<sub>2</sub>O, various techniques were employed. Previous reports have proved that DMF could react with H<sub>2</sub>O to produce formic acid and dimethylamine with the assistance of metal complexes, as shown in Equation  $1.^{33-35}$  Afterwards, the existence of formic acid in the reaction solution was confirmed by the chromogenic reaction between formic acid and bromocresol green, as shown in Figure S10. Then, hydrogen could be released from the decomposition of formic acid along with the generation of CO<sub>2</sub> (Equation 2).

$$HCON(CH_3)_2 + H_2O \longrightarrow (CH_3)_2NH + HCOOH$$
(1)

$$HCOOH \longrightarrow H-H + CO_2$$
(2)

$$CO_2 + 2 (CH_3)_2 NH \longrightarrow [(CH_3)_2 NH_2]^+ [(CH_3)_2 NCOO]^-$$
 (3)

Obviously, water should play a critical role in this hydrogen generation system. One hydrogen atom in the generated hydrogen gas molecule should be originated from water. When 5.0  $\mu$ L of water was added in the DMZnF catalyzed reaction system, the hydrogen generation rate was 0.09 mol<sub>H2</sub> mol<sub>Zn</sub><sup>-1</sup> h<sup>-1</sup> at the initial reaction stage and trended to be halted at 100 – 126 h (0.002 mol<sub>H2</sub> mol<sub>Zn</sub><sup>-1</sup> h<sup>-1</sup>). At this stage, the yield of hydrogen was 0.27 mmol, which was consistent with the theoretical value based on the amount of the added water (0.28 mmol, Figure 3a). Then, the hydrogen generation rate could immediately increase to 0.05 mol<sub>H2</sub> mol<sub>Zn</sub><sup>-1</sup> h<sup>-1</sup> after adding another 5.0  $\mu$ L of H<sub>2</sub>O in the system. Due to the lack of water in the reaction system, the formate group in the DMZnF catalysts at the stage of platform during the 100-126h was consumed,



Figure 3. Catalytic mechanism (a) The hydrogen production profile with addition of various amount of H<sub>2</sub>O at intervals. **Reaction condition**: DMZnF (10.0 mg), DMF (2.0 mL), H<sub>2</sub>O (5.0  $\mu$ L), 120 °Cand Ar atmosphere. MS analysis of the gaseous products of (b) DMF-H<sub>2</sub>O and (c) DMF-D<sub>2</sub>O systems. **Reaction conditions**: DMZnF (40.0 mg), DMF (4.0 mL), D<sub>2</sub>O/H<sub>2</sub>O (0.2 mL), 120 °Cand Ar atmosphere. (d) The hydrogen generation from HCOOH. **Reaction conditions**: Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O/Zn(HCOO)<sub>2</sub>·2H<sub>2</sub>O (0.3/0 mmol), HCOOH (3.0 mmol), Et<sub>3</sub>N (1.0/0 mmol), toluene (4.0 mL), 120 °C and Ar atmosphere (details in supporting information).

which consequently lead to the reduced hydrogen generation rate. This phenomenon confirmed that one of the hydrogen atoms should be contributed from the water.

To further confirm the origin of  $H_2$  molecule, isotope experiments were also performed, in which  $H_2O$  and  $D_2O$  was used for hydrogen production. The gaseous products were monitored by gas chromatography (GC) and mass spectrometry (MS). When  $H_2O$  was used as reactant, the MS signals of the produced gas at 2 m/z and 1 m/z were assigned to  $H_2$  and  $H^+$ , respectively (Figure 3b). In contrast, the strong MS signal at 3 m/z was observed and assigned to HD, when  $H_2O$  was replaced by  $D_2O$  under the identical reaction condition (Figure 3c). Therefore, the presence of HD strongly revealed  $H_2$  generation with one H atom from water and another H atom from DMF. Both of the formic acid generation and  $H_2$  origination can prove the possible reaction processes as shown in Equation 1 and 2.

In addition,  $CO_2$  was also detected in the gaseous products (Figure 3b-3c and Figure S11a). As shown in Figure S12, the amount of  $CO_2$  increased with the hydrogen generation process. Theoretically, the molar ratio of  $H_2$ : $CO_2$  could be maintained with 1:1 due to the decomposition of formic acid. However, the final molar ratio reached 1.8:1, which could be attributed to the consumption of the generated  $CO_2$  by the dimethylamine with an acid-base reaction, as shown in Equation 3.<sup>34, 36, 37</sup>

From the above analysis, hydrogen could be successfully generated from the DMF-H<sub>2</sub>O system with DMZnF as catalysts. The structure unit of DMZnF contains one  $Zn^{2+}$  ion, one dimethylammonium (DMA<sup>+</sup>, (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup>) and three formate (HCOO<sup>-</sup>). Zn<sup>2+</sup> species can catalyze the DMF and H<sub>2</sub>O to produce formic acid and dimethylamine. However, the formic acid could not be decomposed to release hydrogen only with Zn<sup>2+</sup> as

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catalysts, as shown in Figure 3d. It should be noted that the weak basic of DMA<sup>+</sup> might promote the hydrogen generation from formic acid decomposition. Hence, we employed a similar trimethylamine (Et<sub>3</sub>N) as a substitution to replace gaseous dimethylamine to verify the role of weak basic property in the HCOOH system. As expected, no hydrogen could be generated from formic acid in Et<sub>3</sub>N. While hydrogen could successfully generate from the formic acid in the presence of Zn<sup>2+</sup> and Et<sub>3</sub>N (Figure 3d). To further identify the role of formate in the reaction system, the zinc formate (Zn(HCOO)<sub>2</sub>) was selected as catalyst for the hydrogen generation from HCOOH system. However, the bare amount of hydrogen could be generated with Zn(HCOO)<sub>2</sub> as catalysts, indicating the lack of promotion of formate for the hydrogen generation (Figure 3d). Herein, these results exhibited that Et<sub>3</sub>N rather than formate was closelyrelated and indispensable for the Zn2+ catalyzed hydrogen production from HCOOH system. Analogously, the synergistic effect of DMA<sup>+</sup> and Zn<sup>2+</sup> was identified in the reaction of DMF-H<sub>2</sub>O system.

In summary, a safe, green and cost-effective hydrogen generation method from DMF-H<sub>2</sub>O is realized by the economical DMZnF catalysts without any additives. The temperature of reaction system can work as a "smart" switch to control the DMZnF catalysts as a homogeneous catalyst during the hydrogen generation at high reaction temperature and recycle as a heterogeneous catalyst through spontaneous recrystallization process at room temperature. This strategy shows potentials as the high-effective catalysts for various reaction systems.

## **Conflicts of interest**

There are no conflicts to declare.

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