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Heterometallic metal-organic framework-templated synthesis of porous Co_3O_4/ZnO nanocage catalysts for the carbonylation of glycerol

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ABSTRACT

The efficient synthesis of glycerol carbonate (GLC) has recently received great attention due to its significance in reducing excess glycerol in biodiesel production as well as its promising applications in several industrial fields. However, the achievement of high conversion and high selectivity of GLC from glycerol in heterogeneous catalytic processes remains a challenge due to the absence of high-performance solid catalysts. Herein, highly porous nanocage catalysts composed of well-mixed Co_3O_4 and ZnO nanocrystals were successfully fabricated via a facile heterometallic metal-organic framework (MOF)-templated synthetic route. Benefiting from a high porosity and the synergistic effect between Co_3O_4 and ZnO, the as-prepared composite catalysts exhibited a significantly enhanced production efficiency of GLC in the carbonylation reaction of glycerol with urea compared to the single-component counterparts. The yield of GLC over the $Co_{50}Zn_{50}$-350 catalyst reached 85.2%, with 93.3% conversion and near 91% GLC selectivity, and this catalytic performance was superior to that over most heterogeneous catalysts. More importantly, the proposed templated synthetic strategy of heterometallic MOFs facilitates the regulation of catalyst composition and surface structure and can therefore be potentially extended in the tailoring of other metal oxide composite catalysts.

1. Introduction

The controlled synthesis of inorganic functional composites is always a hot issue in the field of nanomaterials because of their wide application in rechargeable battery, supercapacitor, catalysis, photocatalysis, etc [1–4]. Despite the great progress made recently, it remains a great challenge to facilely control the composition and structure of composite structure. In recent years, metal-organic frameworks (MOFs) have been frequently used as sacrificial templates in the fabrication of various porous nanostructures [5–8]. As is well known, many MOFs are isomorphic (for example, ZIF-8 and ZIF-67), and therefore the metal ions constituting a given MOF can be readily substituted by a wide variety of heterogeneous metal ions [9,10]. In addition to their optimized properties [11–13], such heterometallic MOFs can be potentially exploited as a universal platform for the designed fabrication of porous composite nanomaterials of controlled composition [14–16]. The biggest advantage of this synthetic strategy is that the heterogeneous nanoparticles produced via the decomposition of heterometallic MOFs are homogeneously mixed together, and thus a large number of heterojunctions are formed between them, which potentially improve the performance of the as-formed composite materials in many important applications including heterogeneous catalysis. However, the research on the application of this synthetic strategy is still insufficient to date.

Among various catalysis reactions, with the development of large-scale biodiesel as a renewable energy source, effective utilization of the by-product glycerol is increasingly becoming an urgent economic and environmental issue. As such, considerable research has been focused on the exploration of green processes for the efficient conversion of glycerol to high value-added chemicals [17–21]. Glycerol carbonate (GLC) is one of the most valuable reaction intermediates among the various glycerol derivatives given its further conversion to important chemical products [22–26]. To date, a variety of catalysis routes of converting glycerol into GLC have been developed, including transesterification with acyclic organic carbonates [27,28], carbodeoxygenation with CO or CO_2 [29–31], and glycerolysis with urea [32–36]. However, despite some progress, the conversion and selectivity of glycerol into GLC remains unsatisfactory largely due to the lack of high

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Table 1
The feeding amounts of $Co(NO_3)_2·6H_2O$ (X) and $Zn(NO_3)_2·6H_2O$ (Y) in the preparation of MOF precursors[a].

No.	MOF precursors	feeding amounts of metal salts		
		Co:Zn	X	Y
1	ZIF-Co	100:0	0.450 g (1.55 mmol)	0
2	ZIF-$Co_{75}Zn_{25}$	75:25	0.338 g (1.17 mmol)	0.116 g (0.39 mmol)
3	ZIF-$Co_{50}Zn_{50}$	50:50	0.225 g (0.78 mmol)	0.232 g (0.78 mmol)
4	ZIF-$Co_{25}Zn_{75}$	25:75	0.112 g (0.39 mmol)	0.348 g (1.17 mmol)
5	ZIF-Zn	0:100	0	0.464 g (1.56 mmol)

[a] 2-methylimidazole was used as ligand for the synthesis of these Co/Zn-MOFs.

performance catalysts. In the above heterogeneous catalysis processes, the production efficiency of GLC has proven to be closely associated with the acid-base property of solid catalysts and their surface area [28,31]. Therefore, the catalytic performance of catalysts would be remarkably enhanced by the rational regulation of their composition and surface structure. As a result, various strategies based on pore formation [37] or on the combination of metal oxides with different Lewis acid/base properties [33,38,39] have been recently developed, proving success in the carbonylation of glycerol. Therefore, it is anticipated that the joint application of pore formation and metal oxide combinations would potentially enable a more significant improvement to the performance of catalysts. Unfortunately, the con-

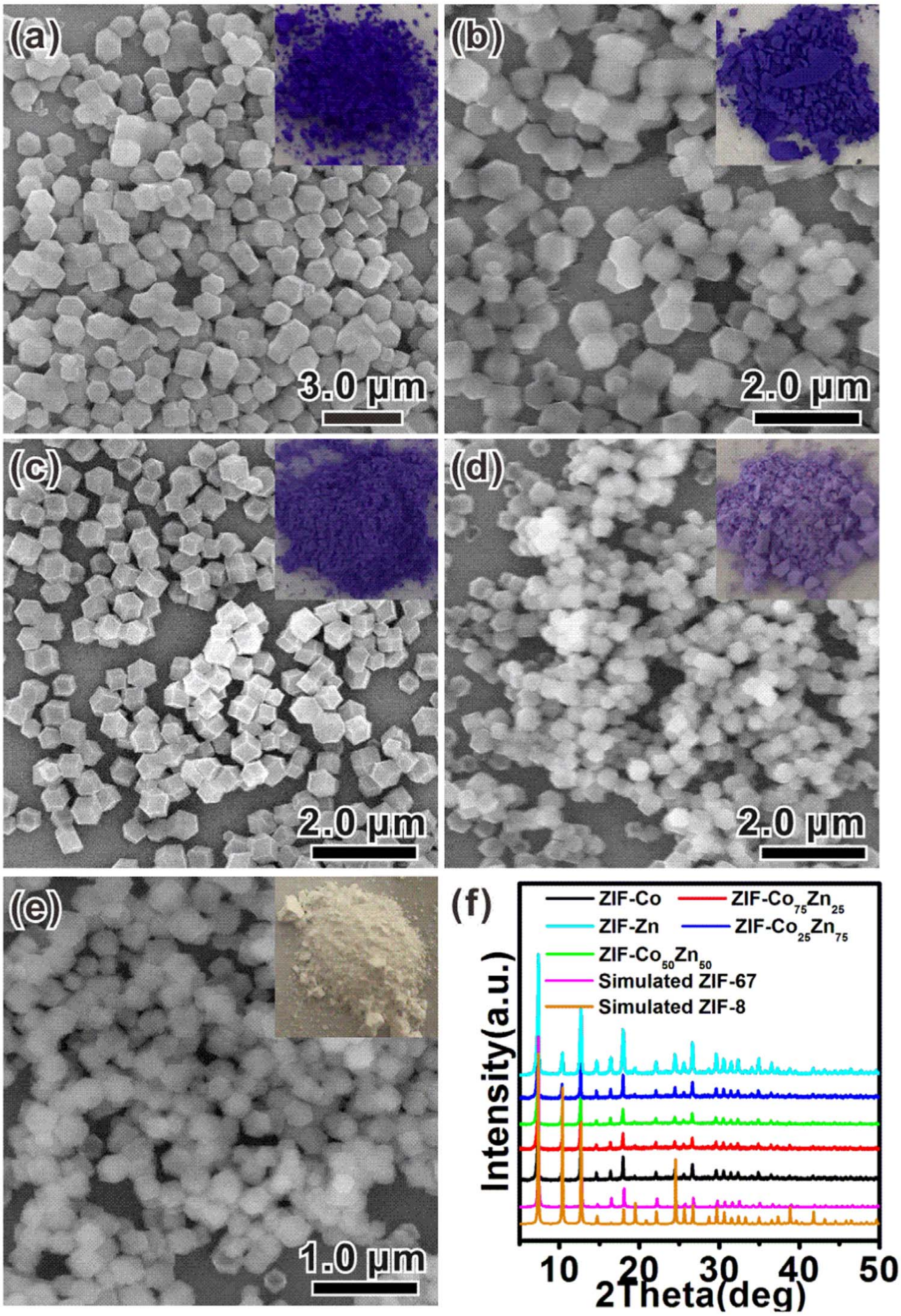

Fig. 1. Low-magnification SEM images of rhombic dodecahedral Co/Zn MOFs: (a) ZIF-Co, (b) ZIF-$Co_{75}Zn_{25}$, (c) ZIF-$Co_{50}Zn_{50}$, (d) ZIF-$Co_{25}Zn_{75}$, and (e) ZIF-Zn; (f) XRD patterns of rhombic dodecahedral Co/Zn-MOFs.