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Communication

Continuous synthesis for zirconium metal-organic frameworks with high quality and productivity *via* microdroplet flow reaction

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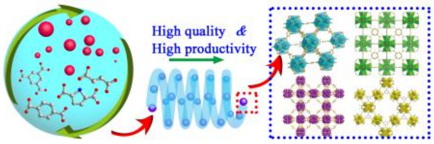
Graphical abstract



A series of Zr-based metal-organic frameworks were continuously synthesized with high quality and high productivity through microdroplet flow reaction.

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ABSTRACT

Zirconium metal-organic frameworks (Zr-MOFs) represent the most promising candidates among MOFs for industrial utilizations owing to their high porosity and excellent stability. However, the efficient synthesis of Zr-MOFs combining with continuous production, high productivity and good product quality still remains a critical issue for practical applications. Herein, we report an efficient method of synthesizing a series of Zr-MOFs through a microdroplet flow reaction, which is more accommodate the requirements of industrial production. Four types of Zr-based MOFs with different ligands and topologies (MOF-801, MOF-804, DUT-67 and MOF-808) were produced as a pure phase of high quality crystalline with uniform morphologies. Furthermore, this series of Zr-MOFs were obtained in a continuous way and at a space-time yield (STY) highly up to 367.2 $kg{\cdot}m^{-3}{\cdot}d^{-1}$. These MOFs exhibit the similar pore structure and thermal stability with that prepared from conventional solvothermal synthesis. CO_2 sorption studies on these MOFs demonstrate that the hydroxyl groups on ligand can render MOFs with high CO_2/N_2 selectivity.

Metal-organic frameworks (MOFs), an emerging class of multifunctional porous materials, have attracted extensive attentions due to their unprecedented surface areas, variable structures and tunable functionalities [1-4]. Thanks to these characteristics, they have found plenty of applications including gas storage [5,6] and separation [7,8], catalysis [9-11], drug delivery [12], photoelectronics [13] and sensing [14] *et al*. Furthermore, the derivatives of MOFs also have displayed promising potentials in energy storage and energy conversion technologies [15-19]. The prerequisite for realizing real-world applications is the ability to produce MOFs at large scale, and at the same time ensuring high quality and low cost of the product. However, the efficient synthetic technique combining with continuous production, high productivity and good product quality remains a critical issue for practical applications [20]. In order to diminish the gaps between laboratory synthesis and industrial production, some synthetic techniques, such as sonchemical [21,22], microwave [23,24], spray drying [25], electrochemical [26], aerosol [27], mechanochemical [28,29], and flow chemistry synthesis [30-32], have been explored. Despite of significant advances, few MOFs appear to be commercially available at large quantities (kilogram scale) [33,34]. Therefore, the development of facial and efficient synthetic methods for MOFs is essential.

Zr-based MOFs, typically contain multi-topic Zr-O clusters connected by organic ligands, exhibit high porosity, excellent thermal/hydro stability, rich topologies and tunable functionalities [35,36]. Owing to these merits, they have been considered as one of the most promising candidates among MOFs for practical applications [37]. Although several Zr-based MOFs have been reported in recent years [38-40], the investigation of synthetic methodologies for Zr-based MOFs is still rare. Recently, some groups have