Facet-dependent catalytic activity of ZIF-8 nanocubes and rhombic dodecahedra based on tracing substrate diffusion in pores by SERS: a case study for surface catalysis of MOFs†

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We employed ZIF-8 rhombic dodecahedra and nanocubes as catalysts to obtain insights into the surface catalysis of MOFs based on facet-dependent catalytic activity for Knoevenagel condensation. The location of catalytic reactions was identified by using spiky Au@ZIF-8 single-core structures as surface-enhanced Raman scattering active substrates for aldehyde detection.

The use of metal–organic frameworks (MOFs) as heterogeneous catalysts for a wide range of chemical reactions has attracted intriguing attention due to their tunable compositions and structures for easy introduction of catalytic sites into pores.1 Exploiting their internal structures has been a conventional way to upgrade the catalytic performance of MOFs, but the effect of their external surface structures has been seldom discussed. Unsaturated coordination metal ions on external surfaces can serve as Lewis acid catalytic sites with higher activity compared to saturated coordination metal ions of internal pores.2 Therefore, understanding external surface catalysis well provides the possibility to design MOF catalysts with extremely high catalytic activity for some specific reactions. On this basis, well-defined MOF polyhedral shapes enclosed by different facets could be engineered for study of external surface catalysis. To achieve this purpose, MOFs should possess high chemical and thermal stability, as well as high symmetry crystal structures. To meet these needs, zeolitic imidazolate framework-8 (ZIF-8) with cubic sodalite-related structures can be employed as a candidate for elaborating facet-dependent catalytic activity.3 In this research, we chose ZIF-8 in shapes of rhombic dodecahedron (named as RD) with {110} facets and nanocube (named as NC) with {100} facets with different densities of Zn²⁺ ions as Lewis acid catalysts for Knoevenagel condensation.

To the best of our knowledge, in many cases, identifying the location of catalytic sites was dependent on the size between substrates and MOF pores. However, albeit some guest molecules were larger than the framework aperture in size, they could diffuse into the internal pores.4 It was desirable to develop an effective strategy for probing the location of substrates while studying MOFs’ surface catalysis. Surface-enhanced Raman scattering (SERS) has emerged as a powerful optical analytical tool for trace detection of molecules near the surface of plasmonic metal nanoparticles (NPs).5 Herein, we design SERS-active structures, single-core spiky Au@MOF composites, for exploration of substrate molecule diffusion behavior in MOF pores.

ZIF-8 rhombic dodecahedra (RDs) were prepared by mixing Zn(NO₃)₂ and 2-methylimidazole (Hmim) in methanol and heating at 50 °C without perturbation for 2 h.6 Transmission electron microscopy (TEM) images (Fig. 1a and b) clearly reveal that the uniform ZIF-8 NPs are rhombic dodecahedral in shape with a narrow size distribution of about 135 nm (Fig. S1, ESI†). The polyhedral shapes are closely associated...
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with the facets in the single crystal structure, and a complete RD is enclosed by twelve {110} planes. On the other hand, utilization of structure directing agents (SDAs) is a conventional method to control the growth of NP crystal planes. High-yield ZIF-8 NCs enclosed by six {100} facets with a narrow size distribution were obtained by hydrothermal synthesis, while cetyltrimethylammonium bromide (CTAB) as a SDA was introduced into an aqueous solution of Zn(NO₃)₂ and Hmim. The preferred attachment of CTAB molecules on {100} facets, which resists the growth of the facets, causes ZIF-8 NCs to be formed. TEM images (Fig. 1d and e) reveal that uniform ZIF-8 NCs of about 115 nm size are synthesized (Fig. S1, ESI†). The crystal structures of both ZIF-8 nanocrystals are attributed to the cubic sodalite-related structure crystallites that are determined by X-ray diffraction (XRD), and no impurity is observed from both XRD patterns (Fig. S2, ESI†). To elucidate the density of Zn²⁺ ions on both facets, the corresponding crystal structures observed from <110> and <100> directions are shown in Fig. 1c and f, respectively.

The terminated surface plane of ZIF-8 is the layer of Zn²⁺ ions that are bound into the bulk crystal structure by three mim (deprotonated Hmim) linkers. The density of unsaturated Zn²⁺ ions at the apexes of the polyhedra on {110} facets is 2.8, calculated from the unit cell; the density of Zn²⁺ ions increases to 4 for the {100} facets (Fig. S3, ESI†). The population of Lewis acid sites is equal to the product of the surface density of Zn²⁺ ions and the total external surface area. Owing to the porous structures, the external surface area cannot be determined by the 

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trace Zn element (∼0.06 wt% with respect to ZIF-8 RDs; ∼0.05% with respect to ZIF-8 NCs) was measured in solution after 1 h of catalytic reaction.

To further affirm whether the catalytic species were leached, ZIF-8 was removed from the catalytic system after reacting for 10 min. The rest of the mixture was shaken for an additional 1 h. The conversion of benzaldehyde is not obviously changed, suggesting that the leaching of ZIF-8 hardly occurs and the contribution of the catalytic reaction from mim and Zn2+ leached in solution can be ignored. Accordingly, ZIF-8 was removed from the reaction mixture after 1 h; the following leaching experiment was also carried out by introducing extra benzaldehyde (100 μL) due to substrate deple- tion during the catalytic process. A very small amount of the newly-added substrate was converted when the reaction was extended to another 1 hour, indicating that a few catalytic species were leached from ZIF-8. Hence, to investigate the facet-dependent catalytic activity of ZIF-8, the reaction needs to be limited over a short period of time. As such, if the reaction time is reduced to 2 and 5 min, the conversion of benzaldehyde decreases to 54% and 67% in the presence of ZIF-8 NCs and 44% and 56% in the presence of ZIF-8 RDs (Table 1).

Knoevenagel condensation is very sensitive to aldehyde substrates. To understand the effect of substrates on the reaction, aldehyde substrates were extended to p-substituted benzaldehyde, including the electron-withdrawing group (−NO2) and the electron-donating group (−CH3). In contrast to other aromatic aldehydes, 4-nitrobenzaldehyde generally exhibited enhanced reactivity, and was almost completely consumed after reaction for only 10 min when ZIF-8 NCs or RDs were used as catalysts (Table 1). Correspondingly, both ZIF-8 nanocrystals exhibited lower catalytic activity for Knoevenagel condensation of malononitrile and 4-methylbenzaldehyde as compared to other aromatic aldehydes under identical conditions. More interestingly, the time-dependent conversions of aldehydes, including 4-methylbenzaldehyde, benzaldehyde and 4-nitro-benzaldehyde, in a ZIF-8 NC suspension are much higher than those in a ZIF-8 RD suspension. They are about 1.65, 1.23, and 1.05 times larger than ZIF-8 RDs at the initial reaction of 2 min for the respective aldehydes (Table 1). On the basis of these results, ZIF-8 NCs possess higher catalytic performance for different aldehydes.

Identical amounts of ZIF-8 NCs and RDs should possess the same number of catalytic sites theoretically and exhibit similar catalytic performances for the same substrates. Therefore, we speculate that the internal pores of ZIF-8 could not be involved in catalyzing Knoevenagel condensation due to the size of the aldehyde being larger than that of the pore apertures (0.34 nm) of ZIF-8 (Fig. S9, ESI†). To confirm this speculation, we engineer a single-core spiky Au@ZIF-8 heterostructure by a seed-mediated growth process to investigate the diffusion behavior of aromatic aldehydes, monitored by SERS (Fig. 3a and b). Owing to the strain energy induced by the lattice mismatch between the core and the shell, only multifaceted crystallites of ZIF-8 shells can be obtained. Spiky Au NPs were allowed to generate many hotspots at sharp corners to localize the electric field and 4-nitrobenzaldehyde was chosen as the SERS tag due to the weak interaction of the nitro group with Au NPs. If 4-nitrobenzaldehyde diffused into the ZIF-8 pores and approached the Au NPs within several nanometers, the Raman intensity was enhanced by the localized electric field although the spiky Au NPs were modified by a small amount of polyvinylpyrrolidone molecules (Fig. 3c). Au@ZIF-8 nanocomposites were incubated in a 4-nitrobenzaldehyde ethanolic solution during different periods of time. The characteristic Raman peaks of 4-nitrobenzaldehyde cannot be found after incubating for 1 h. When the incubation time was increased to 12 h, the NO2 stretching band (1344 cm−1), phenyl ring breathing band (1596 cm−1), as well as the C=O stretching band (1704 cm−1), appeared. The intensity gradually enhanced while prolonging the incubation time to 18 and 24 h. If an excitation

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a Reaction conditions: 4.4 mol% ZIF-8 nanocrystals in ethanol/toluene as solvent (3.5 mL) related to aldehyde (0.95 mmol), shaking for different durations at room temperature.

b Conversion was determined by GC using n-dodecane as internal standard.
frequency of 785 nm of a laser instead of 633 nm is used, according to a previous report, the Raman signals of 4-nitrobenzaldehyde were not observed. In contrast to spiky Au@ZIF-8, with pure ZIF-8 nanocrystals it is not possible to visualize the diffusion behavior of aldehyde molecules based on the change of Raman signals (Fig 3d). In light of the SERS results, 4-nitrobenzaldehyde is retarded to enter the cavity by apertures of ZIF-8.

Therefore, the Knoevenagel condensation of aldehyde with malononitrile catalyzed by activated sites in the cavity is restricted. Unsaturated coordination Zn\(^{2+}\) ions located at the external surfaces of ZIF-8 are considered as catalytic sites after heat treatment. The coordination of Zn\(^{2+}\) ions with malononitrile is an important step towards Knoevenagel reaction, and is confirmed by the cyano group stretching band in the Raman spectra (Fig. S10. ESI\(^+\)) The intermediates are immobilized on the active sites in favor of the deprotonation of \(-\text{CH}_2\text{-}\) for the subsequent condensation reaction. The adjacent Zn\(^{2+}\) ions separated by 6 Å can interact with two N atoms of malononitrile. In toluene/acetonitrile, the weak catalytic performance of ZIF-8 NCs for Knoevenagel reaction (conversion of benzaldehyde 47% after 10 min) could be attributed to the competition of acetonitrile with malononitrile for adsorption on the Lewis acid sites. Therefore, the different catalytic performance between ZIF-8 NCs and RDs could be attributed to the difference in population of Zn\(^{2+}\) ions on their external surfaces. Albeit both ZIF-8 nanocrystals have similar external surface areas, ZIF-8 NCs possess a higher density of unsaturated coordination Zn\(^{2+}\) ions, leading to enhanced catalytic activity for Knoevenagel condensation.

The proposed catalytic mechanism should be attributed to the Zn\(^{2+}\) ion-induced deprotonation behavior of active \(-\text{CH}_2\text{-}\). First, two negatively charged N atoms of malononitrile are allowed to interact with two corresponding Zn\(^{2+}\) ions, leading to the formation of much more positively charged \(\alpha\)-H of the \(-\text{CH}_2\text{-}\) group with stronger acidity. Second, the activated \(\alpha\)-H is lost from malononitrile, resulting in the formation of a hydridon and a carbaniion stabilized by Zn\(^{2+}\) ions. Third, the active carbonyl carbon atom attacks the carbaniion to form a carbon–carbon bond and the hydridon polarizes the carbonyl group of the aldehyde to produce a hydroxyl group. Finally, dehydration occurs on the intermediate by combination of the hydroxyl group with another \(\alpha\)-H of malononitrile, accounting for the formation of a carbon–carbon double bond, and then adducts are obtained by desorption of N atoms from Zn\(^{2+}\) ions and catalytic sites of ZIF-8 are recovered (Fig. 4).

In summary, the facet-dependent catalytic properties of MOFs have been systematically investigated through design and synthesis of well-defined ZIF-8 NCs and RDs. In combination with the SERS spectra of bulky aromatic aldehydes, the external surface Zn\(^{2+}\) ions that coordinated with three N atoms of mim ligands were used as acidic sites for Knoevenagel condensation. Although identical amounts of ZIF-8 RDs and NCs possessed similar external surface areas in our study, ZIF-8 NCs exhibit an enhanced catalytic performance in both samples due to the much higher density of unsaturated coordination Zn\(^{2+}\) ions on \{100\} facets. The novel catalytic model gives insights into the catalysis of external surfaces in porous materials, which is greatly desirable for the construction of MOF catalysts with fascinating performance for some specific organic reactions.

Acknowledgements

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Notes and references