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Crystal Facet Engineering of Copper-Based Metal–Organic Frameworks with Inorganic Modulators

Zhanke Wang, Lei Ge,* Desheng Feng, Zongrui Jiang, Hao Wang, Mengran Li, Rijia Lin, and Zhonghua Zhu*



ABSTRACT: Manipulating the exposed facets of metal-organic frameworks (MOFs) is of importance toward understanding their facet-dependent property in a variety of applications. Herein, we apply a novel inorganic competitive coordination strategy to control the growth orientation of copper-based MOFs (HKUST-1, MOF-14, and Cu-MOF-74) without sacrificing the pore accessibility and crystallinity. Through monitoring the reactant composition, we find that the competitive coordination induced by the added aluminium nitrate mainly affects the crystal growth stage rather than the nucleation stage. The kinetic study further reveals that AI^{3+} competes with Cu^{2+} to coordinate with ligands, restraining the growth rate of certain facets and resulting in the orientated growth of copper-based MOFs. Compared to the reduced pore accessibility of HKUST-1 crystals modulated by the organic modulation method, AI^{3+} -modulated HKUST-1 displays a much larger surface area (>2200 m²/g) and more accessible Cu active sites. Hydroxylation of toluene was utilized as a model reaction to investigate the facet-catalytic activity for as-synthesized HKUST-1. The selectivity of the preferred product cresol increases with the morphology transformation of HKUST-1 from octahedron to cube.

INTRODUCTION

Constructed with inorganic metal-based centers and bridging organic linkers, metal–organic frameworks (MOFs) have attracted tremendous attention over the past two decades.^{1,2} Their unique characteristics such as unsaturated metal sites, high surface areas, and well-defined single active sites provide platforms for the scientific research in catalytic applications.^{3–6} Similar to other nanomaterials, the precise fabrication of crystal facets of MOFs is crucial for the catalytic performance due to the difference of the atomic arrangement among their crystal facets.^{7–10} Therefore, facet engineering on MOFs with specific catalytic activity and selectivity has attracted considerable attention in heterogeneous catalysis.^{11–15}

To date, the well-defined morphologies of MOFs have been successfully synthesized via controlling physical parameters (temperature,¹⁴ heating rate,¹⁶ solvent,^{17,18} etc) and using organic additives.^{19–24} Among those methods, organic additives have been widely introduced into the shape- and size-control of MOFs due to high efficiency and repeatability.²⁵

Generally, the additives can be classified into surfactants,^{19,20} capping agents,²¹ and modulators.^{22,23} Surfactants such as polyvinylpyrrolidone (PVP), cetyltrimethylammonium bromide (CTAB), and sodium dodecyl sulphate could enhance the solubility of organic linkers and inorganic salts to make the size of MOFs uniform,²⁶ while capping agents that contain a single binding moiety such as pyridine have served as the stopper of the crystal growth to form nano-MOFs. Modulators usually contain the same moiety as the organic linkers, which could be competitively coordinated with metal centers to control the crystal growth rate of the specific facet. However, in most cases, organic additives tend to be difficult to remove

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Figure 1. (a) Schematic illustration of the crystal facet engineering strategy with Al^{3+} . SEM images of (b) octahedral (HKUST-1-O), (c) tetrakaidecahedral (HKUST-1-T), and (d) cubic (HKUST-1-C) HKUST-1. (e) Powder XRD patterns (the bottom column is the simulated HKUST-1) and (f) N₂ sorption isotherms (inset: BET surface areas) of the synthesized HKUST-1.

from MOF crystals as they could be incorporated into the crystal structure, which would negatively impact the properties of MOFs in terms of pore accessibility and crystallinity.^{27,28} For example, the BET surface areas of HKUST-1 samples synthesized by PVP,²⁹ pTA,³⁰ and CTAB¹⁹ are only 1155, 554, and 953 m²/g, respectively, much lower than the reported value (above 2000 cm²/g)^{31,32} due to the block of the pore and the defects created on the metal clusters and the organic linkers. Therefore, it is still a challenge in developing a facile strategy to fashion MOFs into the desired shape without influencing the pore structure and crystallinity.

Herein, we reported an inorganic competitive coordination strategy to use aluminium nitrate (Al^{3+}) as the competitive modulator to control the reaction-crystallization rate of specific facets of MOFs. By changing the concentration of Al^{3+} , the morphology of copper-based MOFs could be precisely controlled. At the same time, the surface chemistry of the MOFs, such as the coordination state of the Cu site and accessible open metal sites, could also be adjusted by the competitive modulator, resulting in the increase of catalytic active sites.³³ In addition, due to the difficult coordination of Al^{3+} with selected ligands, the formation of impurities can be minimized under controllable solvothermal conditions. As a result, the pore accessibility and crystallinity will be maintained well after morphology transformation. Due to the high BET surface area and increased active sites on the exposed facets, the modulated MOFs present high selectivity toward cresol in the hydroxylation of toluene.

MATERIALS AND METHODS

Materials. All chemicals including copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, 99%), 1,3,5-benzene tricarboxylic acid (H₃BTC, 95%), 2,5-dihydroxyterephthalic acid (H₂DHTP, 98%), 1,3,5-tris(4-carboxyphenyl)benzene (H₃BTB, 98%), pyrazine (99%), CTAB triethylamine (99.5%), aluminium nitrate nonahydrate (Al(NO₃)₃·9H₂O, 99%), *N*,*N*-dimethylformamide (DMF, 99.5%), toluene

(99.8%), hydrogen peroxide (30%), nonane (99%), p-cresol (99%), o-cresol (99%), benzoic acid (99.5%), benzyl alcohol (99.8%), and acetonitrile (99.8%) were purchased from Sigma-Aldrich without further purification. AR grade methanol, ethanol, and 2-propanol were purchased from Merck.

Synthetic Method. Modulating the HKUST-1 with Aluminium Nitrate. HKUST-1 was synthesized by the solvothermal process, which is similar to previous work with some modifications.³⁴ About 0.252 g of (1.2 mmol) H₃BTC was dissolved in 8 mL of a 1:1 mixture of DMF and ethanol (solution A). In addition, 0.435 g of Cu $(NO_3)_2$: $3H_2O$ (1.8 mmol) and 0, 0.12 and 0.24 mmol of Al $(NO_3)_3$ ·9H₂O were dissolved in 4 mL of water (solution B). Then, solution A was added dropwise into solution B in 5 min, and the as-obtained mixtures were stirred for 15 min before transferring into Teflon-lined stainless-steel autoclaves. After the hydrothermal reaction at 100 °C for 90 min, the autoclaves were washed with methanol 6 times. Ultrasonic was utilized for 2 h during each washing procedure. Finally, the supernatant became clear, and the blue products were dried in a vacuum oven at 60 °C for 8 h.

Modulating HKUST-1 with CTAB. To compare the organic additive effect on the formation of MOF, CTAB was used as a modulator to change the morphology of HKUST-1 according to the literature.¹⁹ CTAB (0, 0.364, and 1.82 g) was dissolved in 50 mL of the 1:1(v/v) mixture of deionized water and ethanol to get solution A. H₃BTC (2.1 g, 0.01 mol) was dissolved in triethylamine (10 mL, 30 wt % in water) to get solution B. Then, 6 mL of 0.1 M Cu (NO₃)₂ and 4 mL of solution B were added into solution A successively under vigorous stirring for 5 min. The resulting blue powder was isolated by centrifugation, washed with ethanol 6 times, and dried in a vacuum oven at 60 °C for 8 h.

Modulating MOF-14 with Aluminium Nitrate. The synthesis procedure of MOF-14 was slightly modified from the literature.^{35,36} $Cu(NO_3)_2$ ·3H₂O (67.6 mg) and different amounts of Al(NO₃)₃·9H₂O (0 and 2 mg) were dissolved in a solvent mixture of ethanol (3 mL) and water (2 mL) in a glass vial. Subsequently, 3 mL of DMF solution of 22.8 mg of H₃BTB and 6.2 mg of pyrazine were added into the vial. The mixture was stirred for 30 min at room temperature and then heated in stainless steel autoclaves at 65 °C for 24 h. After washing with methanol 3 times, the products were dried at 60 °C for 8 h in a vacuum oven.

Modulating Cu-MOF-74 with Aluminium Nitrate. For Cu-MOF-74, typically, a solid mixture of H₂dhtp (0.1486 g), Cu (NO₃)₂·3H₂O (0.3624 g), and Al (NO₃)₃·9H₂O (0 and 56.3 mg) was dissolved in a mixture of DMF (14 mL) and 2-propanol (1 mL). The resulting slurries were then transferred to stainless steel autoclaves. After being heated at 85 °C for 18 h, brown crystals were collected and then washed with methanol 3 times. The as-obtained crystals were dried under vacuum at 60 °C for 8 h.

Time-dependent experiments were conducted under the same synthesis condition of HKUST-1. After heating for a certain time, the autoclave was cooled down with flowing water for 5 min, and then, ultra-high-speed centrifuge was utilized to separate the crystal products and solution. The supernatant was collected for the ICP test. The solid products were washed with methanol 3 times and collected by centrifugation.

Characterization. The X-ray diffraction (XRD) spectra were recorded on a Bruker Advanced X-ray diffractometer (40 kV, 30 mA) under Cu K α radiation (λ = 0.15406 nm) with a scanning rate of 1 °/min. Scanning electron microscope images were obtained using a JEOL JSM-7001F scanning electron microscope with X-ray energy-dispersive analysis spectroscopy. Thermogravimetric (TGA) analysis was conducted using a Perkin Elmer Instruments STA 6000 Thermo Gravimetric Analyser with a heating rate of 5 °C from 30 to 800 °C under N₂. The FTIR spectra were collected using the PerkinElmer STA 6000 equipment. ICP-OES analysis was carried out using a Perkin Elmer Optima 8300 DV. Gas sorption isotherms were carried out using a Micromeritics TriStar II 3020. Raman spectra were recorded on a Renishaw Raman microscope and spectrometer (514 nm laser and 1% output power). The N₂ sorption measurement was

maintained at 77 K after degassing at 150 °C for 12 h. Total specific surface areas were calculated by the BET method. X-ray photoelectron spectra (XPS) were obtained using a Kratos Axis Ultra X-ray Photoelectron spectrometer with monochromatic Al K α (1486.6 eV) radiation at 150 W (15 kV, 10 mA). The binding energies were calibrated by the C 1 s peak of adventitious carbon at 284.8 eV as a reference. Ammonia-temperature programmed desorption (NH₃-TPD) data were collected using Belcat (Microtrac MRB) combined with Belmass (Microtrac MRB). The samples were pretreated with Ar for 30 min at 150 °C and then absorbed anhydrous NH₃ at 100 °C for 30 min. After being flushed with Ar for 60 min in order to remove physisorbed NH₃, saturated samples were heated at 5 °C/min from 100 to 500 °C.

Catalytic Test. The catalyst performance of HKUST-1 on the oxidation of toluene was studied in acetonitrile solution. In a typical reaction, toluene (1.32 g), 30% hydrogen peroxide (3.18 g), and 13.5 mL of acetonitrile together with 60 mg of catalyst were placed in a three-necked flask equipped with a thermometer and an S-shaped condenser tube. The reaction mixture was purged with nitrogen and heated at 60 °C for 4 h. The products were analyzed using GCMS-6890 N (Agilent) equipped with an HP-5MS column (30 m × 250 μ m × 0.25 μ m).

RESULTS AND DISCUSSION

Controlled Synthesis of HKUST-1 with Al³⁺ as the Inorganic Modulator. The inorganic modulation strategy is illustrated in Figure 1a using HKUST-1 as a representative. The copper precursors and BTC ligands were mixed for the nucleation of heterogeneous octahedral particles. After crystal growth, uniform octahedral HKUST-1 (named as HKUST-1-O) is obtained in the absence of Al³⁺ because $\nu_{(111)}$ is much slower than $\nu_{(100)}$. When the Al³⁺ is involved in the solvothermal process, the growth rate along the {100} facet of HKUST-1 is restrained ($\nu_{(111)} \approx \nu_{(100)}$), leading to the formation of tetrakaidecahedral HKUST-1 (HKUST-1-T). With further increasing the Al³⁺, the growth rate along the {100} facet was limited profoundly ($\nu_{(111)} > \nu_{(100)}$). Thereby, the cubic HKSUT-1 (HKUST-1-C) was obtained.

As shown in Figure 1b-d, by increasing the aluminium nitrate amount, the shape of the resultant HKUST-1 changes from octahedron (no aluminium nitrate) with eight exposed {111} facets to tetrakaidecahedron ($Al^{3+}/Cu^{2+} = 1/15$) with both $\{111\}$ facets and $\{100\}$ facets and then to the cube $(Al^{3+}/$ $Cu^{2+} = 2/15$) with six fully exposed {100} facets. Figure 1e shows the comparison of the XRD patterns of all HKUST-1 samples. The sharp and strong identical diffraction peaks of the three morphologies of HKUST-1 are well-indexed compared with the pattern of simulated HKUST-1, indicating the high crystallinity of the produced HKUST-1. In addition, the relative intensity of the (200) lattice to that of the (222) lattice increases significantly with the addition of Al³⁺, which indicates the exposure of $\{100\}$ facets with the addition of Al³⁺. Figure S1 shows a localized scan of as-obtained HKUST-1. There is no Al signal observed at 1.486 keV, indicating that no aluminium was incorporated into the HKUST-1 crystals. ICP-OES was also conducted to investigate the elemental composition of the as-prepared MOFs. As shown in Table S1, only a trace amount of Al was residual in final products. Consequently, high crystallinity and purity of HKUST-1 samples with different exposed facets were synthesized successfully by simply varying the Al³⁺ concentration under controlled solvothermal duration.

Thermal stability and BET surface area were investigated to study the impact of Al^{3+} on the HKUST-1. As shown in Figure 1f, the BET surface areas of the HKUST-1-O, HKUST-1-T,



Figure 2. SEM images of HKUST-1-C collected at different reaction times: (a) 30 min, (b) 45 min, (c) 60 min, and (d) 90 min. (e) Powder XRD patterns of HKUST-1-C at different reaction times. (f) Percentages of Cu^{2+} and Al^{3+} remaining in the reaction solutions (derived from ICP-OES measurements, and error bars represent the standard deviation of triplicates) as a function of reaction time.

and HKUST-1-C are similar, which are 2270, 2295, and 2286 m^2/g respectively. This indicates that the pore accessibility of HKUST-1 was not impacted by the inorganic modulation (Figure S2). While compared to HKUST-1 modulated by organic additives, as shown in Figure S3, the BET surface areas $(<1400 \text{ m}^2/\text{g})$ decrease dramatically after the morphology transformation due to the pore blocking of organic additives, which is matched well with Q. Liu's reports.¹⁹ The thermal behaviors of as-prepared HKUST-1 show similar stages of weight loss (Figure S4). The weight loss of around 3% in the first stage (below 200 °C) is due to the loss of physically adsorbed water, and the major stage of weight loss at 340 °C is due to the decomposition of the frameworks.^{37,38} Therefore, the Al³⁺ has negligible effects on the properties of HKUST-1, which offers a platform to investigate their morphologydependent catalysis performance.

Mechanism of Al³⁺ on the Orientated Growth of HKUST-1. To reveal the growth mechanism of HKUST-1 with Al³⁺ additives, time-dependent experiments were conducted to observe the crystal morphology evolution and the residual concentrations of Al^{3+} and Cu^{2+} in the solution were also monitored. Solid and solution samples were collected at different reaction times, the phase structures of the solid products were characterized by XRD, and the concentration of the reactant was monitored through ICP-OES. As shown in Figure 2a, octahedral HKUST-1 crystals with eight {111} facets are already formed at an early stage (t = 30 min), and the size of crystals ranges from 500 nm to 4 μ m. With prolonging of reaction time, the size of HKUST-1 octahedrons becomes uniform due to Ostwald ripening (Figure 2b). After reaction for 60 min, the octahedrons transfer to the truncated cubes with six $\{100\}$ facets and eight small $\{111\}$ facets (Figure 2c). Obviously, the $\{111\}$ facets decrease with the growth of pubs.acs.org/crystal



Figure 3. (a) Remaining percentages of Cu^{2+} and error bars represent the standard deviation of triplicates, (b) fitting of reaction kinetics, and (c) reaction rate calculated by Cu^{2+} in the reaction solutions with (HKUST-1-C) and without (HKUST-1-O) Al³⁺. (d) Illustration of competitive coordination effects of Al³⁺ with HKUST-1 growth units: 1 and 1' deposition on {100} and {111} facets, respectively; 2 and 2' surface diffusion on {100} and {111} facets, respectively; 3, competitive reaction with Al to coordinate with growth units.

HKUST-1. The {111} facets disappear after 90 min, and meanwhile, the cubes are obtained (Figure 2d). These XRD patterns of HKUST-1 collected at different stages (Figure 2e) also match well with the SEM images. The relative intensity of the (100) peak increases gradually with reaction time, indicating the enlargement of {100} facets. The evolution of HKUST-1 crystals suggests that Al³⁺ manipulates the shape of HKUST-1 at the stage of crystal growth rather than the nucleation stage, which is also confirmed by the change of Al³⁺ concentration. As shown in Figure 2f, the Al concentration decreases modestly at the beginning (within the first 45 min), indicating that Al³⁺ ions were not involved in the nucleation of HKUST-1. Al concentration drops remarkably from 45 to 90 min when the HKUST-1 crystal transfers from octahedrons to cube, indicating that the Al³⁺ has a direct impact on the crystal growth process of HKUST-1. The sharp decrease after 90 min is caused by the coordination of Al³⁺ and BTC ligands to form Al impurities. Therefore, it is of important to control the reaction time to minimize Al impurities. Also the small quantities of impurities produced before 90 min could be washed out by ultrasonic cleaning, which was further confirmed by the mass balance calculation from the ICP test (Table S2).

To further investigate the role of Al^{3+} in the crystal growth of HKUST-1, the kinetics of the crystal growth process of HKUST-1 are fitted by using the precipitation reaction model. We measured the concentration of Cu^{2+} in the solution at different reaction times during the synthesis of HKUST-1-O and HKUST-1-C. As indicated in Figure 3a, the concentration of Cu^{2+} decreases by 75.7% during the crystal growth stage (30–150 min) in the absence of Al^{3+} , while the concentration of Cu^{2+} decreases by only 68.2% during the crystal growth stage in the presence of Al^{3+} . This indicates that the Al^{3+} can

slow down the reaction rate of Cu²⁺ with BTC linkers during the crystal growth stage. In order to further investigate the reaction rate of Cu²⁺, the kinetic curve was fitted by simplifying the reaction-crystallization process as the precipitation reaction (Figure 3b). It is found that the reaction order (γ) of HKUST-1-C (0.9332) is larger than that of HKSUT-1-O (0.5015), indicating that Al³⁺ could change the reaction path of HKUST-1. Because the reaction rate of HKUST-1- C is slower than that of HKUST-1-O, shown in Figure 3c, Al³⁺ may serve as a competitor to slow down the reaction of Cu²⁺ with BTC linkers. Based on the BFDH (Bravais, Friedel, Donnay, and Harker) law,³² the morphology of the crystal is determined by the facets with the slowest growth rate. Cubic HKUST-1 could only be formed when the growth rate of $\{100\}$ facets is slower than that of $\{111\}$ facets. Therefore, Al^{3+} mainly competes with Cu^{2+} to link with BTC ligands on {100} facets, constraining the growth rate of $\{100\}$ facets profoundly.

The mechanism of controlled synthesis of HKUST-1 could be illustrated in Figure 3d. We use a cuboctahedron growth nucleus to represent the crystal seeds containing six square {100} facets and eight triangle {111} facets. Because the d-space of {100} facets is larger than that of {111} facets,³² the growth unit tends to deposit on the {100} facets rather than {111} facets in the absence of Al³⁺ ($r_1 \gg r_1$), resulting in the shrink of {100} facets and the formation of octahedron HKUST-1 with fully exposed {111} facets, while in the presence of high concentration of Al³⁺, these Al³⁺ ions are first deposited on the {100} facets and then replaced by Cu²⁺ due to the weak binding capacity between Al³⁺ and BTC ligands. The competitive coordination between Al³⁺ and Cu²⁺ on {100} facets slows down the surface diffusion of Cu²⁺ on {100} facets ($r_2 \ll r_2$), resulting in a much slower growth rate of {100}

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Figure 4. (a) Reaction scheme for the oxidation of toluene. (b) Selectivity of HKUST-1-O, HKUST-1-T, and HKUST-1-C on the oxidation of toluene. (c) Recycling tests of HKUST-1-C on the oxidation of toluene. (d) XPS spectra of Cu and (e) NH₃-TPD curves of HKUST-1-O, HKUST-1-T, and HKUST-1-C. Error bars represent the standard deviation of triplicates.

facets than that of $\{111\}$ facets. Therefore, cube HKUST-1 with fully exposed $\{100\}$ facets is formed.

To explore the universality of this strategy, aluminium nitrate was utilized to control the morphology of MOF-14 (CuBTB) and Cu-MOF-74 MOFs. As shown in Figure S6, MOF-14 and Cu-MOF-74 with different morphologies were successfully synthesized via adjusting the amount of Al modulator. Their structures were confirmed by XRD patterns (Figure S7). For the MOF-14, the rhombic dodecahedral crystals with fully exposed {110} facets were obtained without Al^{3+} . When Al^{3+} was involved, cubic MOF-14 with six {100} facets was synthesized. The morphology evolution of MOF-14 was similar to that of HKUST-1 due to their similar coordination environment.^{27,35} For the Cu-MOF-74, its morphology could be manipulated from microrods to selfassembly nanorods. It is concluded that the Al³⁺ could be used as a universal modulator to manipulate the copper-based MOFs.

Catalytic Performance of as-Prepared HKUST-1 in Toluene Selective Oxidation. The experiments of toluene hydroxylation were performed to investigate the catalytic performance of HKUST-1 with different morphologies (Figure 4a). The chosen reaction is of importance because the cresol and benzoic acid are widely used to synthesize a diversity of useful chemicals, such as preservatives, perfume, and rubber auxiliary agents.³⁹ Among the products, the cresol isomers are the preferred products since they are more valuable than others.

Reactions were carried out at 60 °C using as-prepared HKUST-1 as the catalyst and hydrogen peroxide as the oxidation agent.⁴⁰ As shown in Figure 4b, HKUST-1-O shows similar selectivity of benzaldehyde and o-cresol, 31 and 30.4%, respectively. The selectivity of p-cresol is only 12.2%. However, HKUST-1-C tends to selectively catalyze toluene to cresol. The selectivity of o-cresol and p-cresol of HKUST-1-C increased to 46.4 and 16.2%, while the selectivity of benzaldehyde and benzoic acid decreased to 16.8 and 13.2%,

respectively. A similar trend is also observed on the HKUST-1 modulated by CTAB. As shown in Figure S8, the selectivity of o-cresol increases from 29.6 to 31.4% and the selectivity of benzaldehyde decreases from 38.6 to 31.4% when the morphology of HKUST-1 transfers from octahedron to cube. The phenomenon confirms that the cubic HKUST-1 with six {100} facets prefers to catalyze toluene to cresol, while the octahedral HKUST-1 with eight {111} facets prefers benzaldehyde products. However, the change on the selectivity of HKUST-1 modulated by CTAB is not as obvious as that by Al³⁺; the reason is that the unsaturated Cu sites were blocked by CTAB and the BET surface area of HKUST-1 modulated by CTAB is much lower than that of their counterparts. The stability of as-prepared HKUST-1 is investigated by XRD and recycle tests. As shown in Figure S9, all HKUST-1 samples maintain their structure well after the catalytic reaction. HKUST-1-C demonstrates almost no loss of its activity after recycling 5 times (Figure 4c). This indicates that the HKUST-1-C could be a potential industrial catalyst for the selectively catalytic conversion of toluene to cresol.

To reveal the relationship between the facet transformation and catalytic selectivity, the catalytic activity sites were investigated by NH₃-TPD. As shown in Figure 4e, the amount of desorbed NH₃ from HKUST-1-C is larger than that from HKUST-1-O and HKUST-1-T. This indicates that the HKUST-1-C possesses more catalytic active sites than others. This is probably due to the easy pore accessibility of HKUST-1-C. As shown in Figure S10, the unsaturated Cu centers of HKUST-1-C are located in large pores (1.08 nm) with a big window (0.9 nm), while the Cu centers of HKUST-1-O are located in small pores (0.53 nm) with a small window (0.46 nm).^{25,31} Therefore, the HKUST-1-C could be fully activated by removing the DMF guests (0.56 nm) coordinated during the synthesis from big pore windows to produce more accessible unsaturated Cu sites. On the contrary, the activation of HKUST-1-O would be difficult due to the smaller pore window size than the diameter of DMF guests. In addition, the HKUST-1-O requires higher temperature (280 °C) to desorb large amounts of chemisorption state NH₃, while HKUST-1-C releases most of NH₃ below 200 °C. This phenomenon indicates that HKUST-1-O possesses more Lewis acid sites with medium acidic strength, while the HKUST-1-C has more Lewis acid sites with low acidic strength. The Lewis acid sites of HKUST-1 are derived from the unsaturated Cu centers, and the Lewis acidity varies with the valence state of Cu and the accessibility of Lewis acid sites. XPS was used to investigate the valence of Cu on the surface of HKUST-1. As shown in Figure 4d, the fitted peak at 934.9 eV and related satellite peaks at 940.1 and 944.3 eV should be ascribed to Cu(II). The small peak at 932.8 eV can be ascribed to Cu(I). It could be found that the ratio of Cu(I) to Cu(II) increases from 17 to 26% with the morphology transformation from octahedron to cube (Figure S11). The Cu(I) species is further confirmed by the Raman test. As shown in Figure S12, the peak at 600 cm⁻¹ could be attributed to Cu(I)-O stretching.^{41,42} Those results also match well with the NH3-TPD results. The Cu(I) metal sites have softer Lewis acidity compared to the Cu(II) metal sites;⁴³ therefore, HKUST-1-C with a large amount of Cu(I) has more low-strength acid sites than HKUST-1-T. In addition, the NH₃ molecules attracted on the unsaturated Cu sites of cubic HKUST-1 can be desorbed much more easily than those within the small pores of HKUST-1-O due to the large diffusion path and low kinetic barrier. This will also

contribute to the increase of low-strength acid sites of HKUST-1-C. Because the hydroxylation of toluene is a nonradical reaction, hydrogen peroxide molecules need to be first activated at copper sites.⁴¹ The activation of hydrogen peroxide by the coordination to a strong Lewis acid could increase the acidity of benzylic C-H bonds,44 which would promote the formation of benzaldehyde. In such a case, HKUST-1-O with medium-strength Lewis acidity prefers to catalyze toluene to benzaldehyde and benzoic acid due to the interaction between hard copper sites and benzylic carbon. In addition, consideration of Pearson's hard and soft acid and base (HSAB) principle,⁴⁵ the hard acids tend to coordinate with hard bases, while soft acids prefer to coordinate with soft bases. The cresol has softer basicity than benzaldehyde. Therefore, the HKUST-1-C with a large amount of soft Lewis acid sites would prefer to catalyze toluene to cresol rather than benzaldehyde, and the cresol product could be diffused to liquid easily from the large pore window size.

CONCLUSIONS

An inorganic modulator competitive strategy was first proposed to manipulate the facets of MOFs, and Al³⁺ showed the universal effect on modulating the crystal morphology of copper-based MOFs (HKUST-1, MOF-14, and Cu-MOF-74). The mechanism study verifies the controllable competitive coordination of Al ions and Cu precursors with ligands restraining the growth rate of HKUST-1 {100} facets, resulting in the orientated growth along the (100) direction. The orientated cubic HKUST-1 shows much higher selectivity toward o-cresol than original octahedral HKUST-1 in the hydroxylation of toluene due to the exposed large pore window on the $\{100\}$ facet and the Cu(I) open metal site created by the competitive strategy. Compared to the commonly used organic modulation method, the inorganic modulation strategy shows its superiority in maintaining the crystallinity and pore accessibility. This work can extend the facet engineering strategy and methodical versatility for precise control of the morphology of MOFs, shedding light on the facet-dependent catalytic research.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.0c01274.

Reaction kinetic fitting method and additional figures of SEM, EDS, TGA, FTIR, TPD, Raman, and N_2 adsorption isotherms (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Lei Ge Centre for Future Material, University of Southern Queensland, Springfield Central, Queensland 4300, Australia; orcid.org/0000-0003-2989-0329; Phone: +61 733653528; Email: l.ge@usq.edu.au; Fax: +61 733654199
- Zhonghua Zhu School of Chemical Engineering, The University of Queensland, Brisbane 4072, Australia; orcid.org/0000-0003-2144-8093; Email: z.zhu@ uq.edu.au

Authors

Zhanke Wang – School of Chemical Engineering, The University of Queensland, Brisbane 4072, Australia

- **Desheng Feng** School of Chemical Engineering, The University of Queensland, Brisbane 4072, Australia
- Zongrui Jiang School of Chemical Engineering, The University of Queensland, Brisbane 4072, Australia
- Hao Wang Centre for Future Material, University of Southern Queensland, Springfield Central, Queensland 4300, Australia
- Mengran Li School of Chemical Engineering, The University of Queensland, Brisbane 4072, Australia; orcid.org/0000-0001-7858-0533
- Rijia Lin School of Chemical Engineering, The University of Queensland, Brisbane 4072, Australia

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.cgd.0c01274

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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