

Surface Chemical Engineering of a Metal 3D-Printed Flow Reactor Using a Metal–Organic Framework for Liquid-Phase Catalytic H₂ Production from Hydrogen Storage Materials

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Cite This: <https://doi.org/10.1021/acsami.3c10945>



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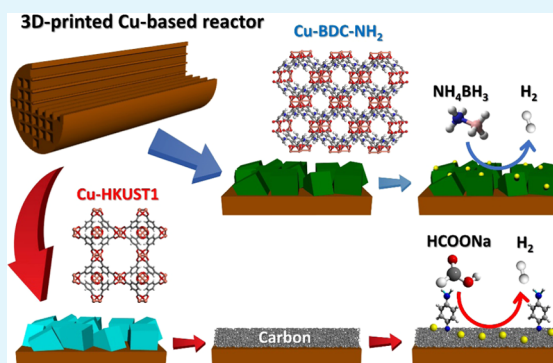
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ABSTRACT: The accurate positioning of metal–organic frameworks (MOFs) on the surface of other materials has opened up new possibilities for the development of multifunctional devices. We propose here a postfunctionalization approach for three-dimensional (3D)-printed metallic catalytic flow reactors based on MOFs. The Cu-based reactors were immersed into an acid solution containing an organic linker for the synthesis of MOFs, where Cu²⁺ ions dissolved in situ were assembled to form MOF crystals on the surface of the reactor. The resultant MOF layer served as a promising interface that enabled the deposition of catalytically active metal nanoparticles (NPs). It also acted as an efficient platform to provide carbonous layers via simple pyrolysis under inert gas conditions, which further enabled functionalization with organic modifiers and metal NPs. Cylindrical-shaped catalytic flow reactors with four different cell densities were used to investigate the effect of the structure of the reactors on the catalytic production of H₂ from a liquid-phase hydrogen storage material. The activity increased with an increasing internal surface area but decreased in the reactor with the smallest cell size despite its high internal surface area. The results of fluid dynamics studies indicated that the effect of pressure loss becomes more pronounced as the pore size decreases.

KEYWORDS: metal 3D printing, flow reactor, metal–organic framework, postfunctionalization, hydrogen



1. INTRODUCTION

Catalysis plays a critical role in numerous industrial processes ranging from chemical transformation to environmental remediation.^{1–3} Catalytic reactors are critical components in a wide variety of chemical processes, providing a controlled environment for the optimal catalytic reactions. However, research on catalysts is mainly focused on improving activity and stability; reactor properties such as fluid dynamics, heat transmission, and mass transfer, which greatly affect catalysts' properties, tend to be neglected from academic viewpoints.^{4,5} Conventionally, these catalytic reactors are manufactured using techniques such as casting, extrusion, or machining.⁶ However, these traditional methods often impose limitations in terms of design complexity, material selection, and cost-effectiveness and further hinder the exploration of novel materials with desirable catalytic properties.⁷

Three-dimensional (3D) printing technology, also known as additive manufacturing (AM) technology, is currently being explored for many different applications, including electrochemical devices,^{8,9} biomaterials,^{10–12} and microfluidic devices.^{13,14} Recently, 3D-printing technologies have opened new possibilities for the fabrication of intricate catalytic reactors with tailored geometries and improved performance.^{15–17} Direct ink writing (DIW),^{18,19} fused deposition modeling

(FDM),^{20,21} and stereolithography (SLA)^{22,23} are conventionally used to print functional catalysts or reactors. One of the most important advantages of these methods is design flexibility; the creation of complex internal and external geometries (e.g., sophisticated flow channels, multiscale structures, and gradient porosities) enables enhanced mass transfer and catalytic efficiency. Another important characteristic is versatility in material selection. A wide range of metal sources, including alloys, composite materials, and even catalyst-functionalized powders, can be used, enabling the catalytic properties and stability to be optimized. In addition, this technology can be easily scaled up for mass production, ensuring cost-effectiveness.

More recently, metal 3D-printing methods, such as selective laser melting (SLM),^{24–27} selective laser sintering (SLS),^{28–30} and direct metal printing,^{31,32} have been extended into the

Received: July 25, 2023

Revised: October 10, 2023

Accepted: October 11, 2023

catalysis field because they can be used to integrate a catalyst and reactor into a single system.³³ We have demonstrated that metal 3D printing is a feasible method to prepare a multifunctional self-catalytic reactor (SCR) using Hastelloy X powder as a starting material.³⁴ Selective electrochemical dissolution of the SCR successfully transformed the original inert surface, which consisted of a Cr- and Fe-based passivation layer, into a Ni-enriched surface that is active as a robust catalyst for CO₂ methanation. Notably, we demonstrated that SCR enabled a continuous increase in catalytic activity through a simple refreshment process driven by a self-dissolution mechanism. We also demonstrated the feasibility of custom control of catalyst performance using microorder crystal orientation and structure control induced by a scan strategy in the laser metal AM process.

In the present study, we propose a postfunctionalization approach for a 3D-printed metallic catalytic flow reactor based on metal–organic frameworks (MOFs), which are an intriguing class of ultraporous materials composed of metal ions coordinated with organic linkers. Because of their large surface area, excellent adsorption capacity, and high electronic conductivity, they have attracted considerable attention as superior materials for catalysis, gas sorption, energy storage, and membranes.^{35–38} To apply these unique characteristics of MOFs to advanced devices, researchers have been focusing on the patterning of metal surfaces by photolithography,^{39,40} imprinting,⁴¹ or spray coating.⁴² Herein, we report that thin layers of MOFs can be successfully fabricated via the controlled dissolution of Cu²⁺ ions on a Cu-based 3D-fabricated catalytic reactor. The obtained MOF layer can function not only as a promising interface that enables the deposition of catalytically active metal nanoparticles (NPs) but also as an efficient precursor for the formation of carbonaceous layers by simple pyrolysis under an inert gas atmosphere. The functionalized metal 3D-printed reactor can be used for catalytic H₂ production from liquid-phase hydrogen carriers. The computational fluid dynamics behavior was also investigated on the basis of geometrical aspects of the reactor structures.

2. EXPERIMENTAL SECTION

2.1. Fabrication of 3D-Printed Catalytic Flow Reactors. Cu-0.8 atom % Zr powder (Sanyo Special Steel) was used as a starting material. The specimen was fabricated by laser powder bed fusion (LPBF) using an EOS M209 printer equipped with a 400-W Yb-fiber laser. The building stage was preheated to 80 °C to avoid an unexpected temperature change as a result of the laser energy input. The building chamber was filled with high-purity Ar to maintain an O₂ concentration less than 100 ppm. The catalytic flow reactors with a cylinder shape (23 mm diameter × 70 mm length) and four different cell densities (Type 1, Type 2, Type 3, and Type 4) were fabricated by scanning strategy X. The process parameters included a fixed layer thickness (*h*), laser power (*P*), hatch spacing (*d*), and scan speed (*v*) of 0.02 mm, 360 W, 0.10 mm, and 250 mm/s, respectively. For detailed characterization of the specimens, a thin substrate with dimensions of 10 × 20 × 0.5 mm³ was also fabricated by using a similar method.

2.2. Fabrication of Pd/Cu-BDC-NH₂ on 3D-Printed Cu-Based Catalytic Flow Reactors. Cu-BDC-NH₂ crystals were deposited by the following procedure. Typically, 280 mL of dimethylformamide (DMF), 4.321 g of BDC-NH₂ (2-amino-1,4-benzenedicarboxylic acid, Tokyo Chemical Industry), and 4.34 mL of HNO₃ aq were mixed and then ultrasonicated for 30 min. The 3D-printed catalytic flow reactor (Type 1) was placed in a glass vessel equipped with a feed pump. The glass vessel was preheated at 80 °C from outside with a ribbon heater.

The preconditioned mother liquor was pumped into the glass vessel at a flow rate of 10 mL·min⁻¹ and kept for 24 h at 80 °C. Details of the system setup are illustrated in Figure S1. The obtained specimen was washed with DMF several times to remove excess BDC-NH₂ and dried under vacuum, giving Cu-BDC-NH₂@Cu. The amount of BDC-NH₂ was adjusted to 10.4, 14.9, and 18.4 g for the Type 2, Type 3, and Type 4 reactors, respectively.

As a Pd precursor, 45.68 mg of palladium(II) acetate (Pd(OAc)₂) was dissolved in 200 mL of methanol. The preconditioned solution was pumped into the glass vessel containing Cu-BDC-NH₂@Cu (Type 1) at a flow rate of 35 mL·min⁻¹ for 3 h at room temperature. The obtained specimen was washed with methanol several times and dried under vacuum, giving Pd/Cu-BDC-NH₂@Cu. The amount of Pd(OAc)₂ was adjusted to 110.33, 157.88, and 194.97 mg for the Type 2, Type 3, and Type 4 reactors, respectively. The fabrication of Pd/Cu-BDC-NH₂ on a flat Cu substrate (10 mm × 20 mm × 0.5 mm) was carried out under similar conditions.

2.3. Fabrication of Cu-HKUST1 on 3D-Printed Cu-Based Catalytic Flow Reactors. Cu-HKUST1 crystals were deposited by the following procedure. Typically, 400 mL of benzyl alcohol, 9.874 g of H₃BTC (1,3,5-benzenetricarboxylic acid, Nacalai Tesque), and 4.34 mL of HNO₃ aq were mixed and then ultrasonicated for 30 min. The 3D-printed catalytic flow reactor (Type 1) was placed in a glass vessel equipped with a feed pump. The glass vessel was preheated at 80 °C from the outside with a ribbon heater. The preconditioned mother liquor was pumped into the glass vessel at a flow rate of 10 mL·min⁻¹, and the vessel was maintained at 80 °C for 24 h. The sample was washed with ethanol several times to remove excess BDC-NH₂ and subsequently dried under vacuum. This treatment was performed twice to attain complete coverage, giving Cu-HKUST1@Cu.

2.4. Fabrication of Pd/Carbon-PhNH₂@Cu. The as-synthesized Cu-HKUST1@Cu sample was heat-treated at 400 °C for 3 h under flowing N₂ (100 mL·min⁻¹), affording carbonized carbon@Cu. Amine functionalization was performed by flowing an aqueous solution that contained acetone (50 mL) and an excess of *p*-phenylenediamine (PDA, 3.244 g) at room temperature for 24 h to give carbon-NH₂@Cu.

As a Pd precursor, 22.48 mg of Pd(OAc)₂ was dissolved in 200 mL of methanol. The preconditioned solution was pumped into a glass vessel containing carbon-NH₂@Cu (Type 1) at a flow rate of 20 mL·min⁻¹ for 3 h at room temperature. The obtained specimen was washed with methanol several times and dried under a vacuum, giving Pd/carbon-NH₂@Cu. The amount of Pd(OAc)₂ was adjusted to 87.13, 134.68, and 175.6 mg for the Type 2, Type 3, and Type 4 reactors, respectively. Pd/carbon-NH₂ was also prepared on a flat Cu substrate (10 × 20 × 0.5 mm³) under similar conditions.

2.5. Characterization. Thermogravimetric analysis (TGA) of the powdered HKUST1 was performed on a Rigaku Thermo Plus EVO2 TG8121 system in the temperature range from 50 to 550 °C at a heating rate of 10 °C·min⁻¹ with the sample under flowing N₂ (10 mL min⁻¹). Powder X-ray diffraction (XRD) patterns were recorded by using a Rigaku Ultima IV diffractometer equipped with a Cu K α radiation source (λ = 1.54056 Å). Surface morphology of the samples was observed by scanning electron microscopy (SEM) using a JEOL JSM-6500 scanning electron microscope. Prior to SEM observations, the sample surfaces were coated with Au/Pd or C using an ion-sputtering device (Sanyu SC-701MK II). Transmission electron microscopy (TEM) images were acquired using a field-emission transmission electron microscope (Hitachi Hf-2000) operated at 200 kV.

2.6. Dehydrogenation from Ammonia Borane. The 3D-printed catalytic flow reactor was placed in a glass vessel equipped with a feed pump. The glass vessel was kept at 30 °C by being heated with a ribbon heater. A 250 mL aqueous solution of ammonia borane (AB, NH₃BH₃, 1.543 g) was pumped into the glass vessel at a flow rate of 20 mL·min⁻¹, and the evolved H₂ gas was trapped in a gas buret.

2.7. Dehydrogenation from Sodium Formate. The 3D-printed catalytic flow reactor was placed in a glass vessel equipped

with a feed pump. The glass vessel was kept at 75 °C by a ribbon heater. An aqueous solution (200 mL) of sodium formate (SF, HCOONa, 13.6 g) was pumped into the glass vessel at a flow rate of 27 mL·min⁻¹, and the evolved H₂ gas was trapped in a gas buret.

2.8. Computational Fluid Dynamics. The computational fluid dynamics (CFD) was simulated using Advance/Flow/Red ver. 5.4 (AdvanceSoft Corp.) for four different cell densities. The 3D geometry of the entire shape was analyzed for the Type 1 reactor, and the 3D geometry of one channel was analyzed for the Type 2, 3, and 4 reactors. The cell dimensions (width and length) corresponded to those of each 3D-fabricated reactor. The minimum calculated grid width on the wall was 0.00625 mm. The inlet flow rate was low and uniform; the velocity in the *x*-direction was 0.002 m·s⁻¹, and those in the *y* and *z* directions were zero. Therefore, the Navier–Stokes flow was used. For a wall surface, an adiabatic no-slip wall was adopted.

3. RESULTS AND DISCUSSION

3.1. Pd/Cu-BDC-NH₂@Cu. Cylindrical-shaped catalytic flow reactors with a diameter of 23 mm, length of 70 mm, and four different cell densities (Type 1, Type 2, Type 3, and Type 4) were fabricated by LPBF using Cu-0.8 atom % Zr powder as a starting material. The LPBF is the most widely used metal AM process using selective laser melting. First, the powdered raw material is evenly applied to the build plate with a recoater in a thin layer of 10–200 μm. The material is selectively melted with a high-intensity laser energy. The build platform is then lowered, and a new layer of powder is spread across the previous layer using the recoater. Finally, the three-dimensional objects can be obtained by repeating the melting and coagulation process for each layer and stacking two-dimensional objects (Figure 1a). The structure and internal surface areas of the four types of reactors are listed in Figure 1b. No lattice was present in the Type 1 reactor. To increase

the internal surface area, the number of channels was increased from 29 for the Type 2 reactor to 113 for the Type 4 reactor; the thickness of the pillars was fixed at 0.2 mm.

The direct growth/deposition from the mother liquor under solvothermal conditions, the stepwise layer-by-layer growth, and the direct deposition of presynthesized MOF crystals by dip coating or spin coating are typical methods used to fabricate MOF layers on metallic substrates.⁴³ Here, we functionalized the surface of the metallic reactors with a Cu-based MOF, Cu-BDC-NH₂, by continuously flowing a DMF solution containing BDC-NH₂ (2-amino-1,4-benzenedicarboxylic acid) as an organic linker and a low-concentration HNO₃ solution at 80 °C for 24 h (Figure 2a). Notably, the Cu-based reactors themselves act as a precursor of the Cu node for MOF synthesis without the addition of external Cu²⁺ sources, where Cu²⁺ ions dissolved in situ under acidic conditions are assembled to form Cu-BDC-NH₂ crystals through coordination with the BDC-NH₂ linker on the surface of the Cu-based reactors (Cu-BDC-NH₂@Cu). The reactor surface changed from brown to dark green, corresponding to Cu-BDC-NH₂ crystals (Figure 2b,c). Finally, Pd nanoparticles (NPs) were formed from a methanol solution of Pd(OAc)₂, in which methanol acts as not only a solvent but also the in situ reducing agent for Pd²⁺, affording Pd/Cu-BDC-NH₂@Cu. In our preliminary experiment, the Pd NPs cannot be loaded on an as-synthesized 3D-printed reactor without modification with MOF.

The characterization was carried out by using a specimen fabricated on a flat Cu substrate under similar flow conditions for 24 h. The X-ray diffraction (XRD) pattern showed several sharp peaks assignable to Cu-BDC-NH₂ crystals, almost consistent with the XRD pattern of the powdered sample (Figure 2d). But the disappearance and shift of peaks can be observed, which is presumably due to the specimen displacement effect caused by the difference between the height of the sample holder surface and the sample surface, X-ray shielding owing to the surface roughness effect, and sample transparency effect caused by the low filling rate of the MOF crystals on Cu substrate compared with powdered sample.⁴⁴ SEM images show densely packed cubic and octahedral crystals with diameters ranging from 20 to 30 μm and without interparticle cavities (Figure 2e). The cross-sectional view demonstrated densely packed Cu-BDC-NH₂ crystals (Figure 2e). The thickness was determined to be 20–30 μm, consistent with the size of the crystals (Figure 2f). This suggests that the Cu-BDC-NH₂ crystals exist in a single layer, and the densely packed crystals suppress the dissolution of Cu²⁺ from the Cu substrate, thereby preventing excessive crystal deposition/accumulation. In a preliminary experiment, the intensity of the diffraction patterns of the specimen treated for a shorter time (only 3 h) was negligible, the surface coverage of the Cu substrate was apparently low, but the primary crystal size remained almost unchanged (Figure S2). If the simultaneous intergrowth mechanism is dominant, the primary crystal size of Cu-BDC-NH₂ should increase with increasing reaction time. These results indicate that layering of Cu-BDC-NH₂ in the initial stage proceeds via continuous nucleation and growth of individual crystals on the Cu substrate rather than via a simultaneous intergrowth mechanism. A TEM image of the specimen on a flat substrate shows the formation of Pd NPs with a mean particle diameter of 8.0 nm (Figure 2g). A peeling-off test using standard Scotch tape confirmed almost no physical damage, suggesting its high mechanical stability

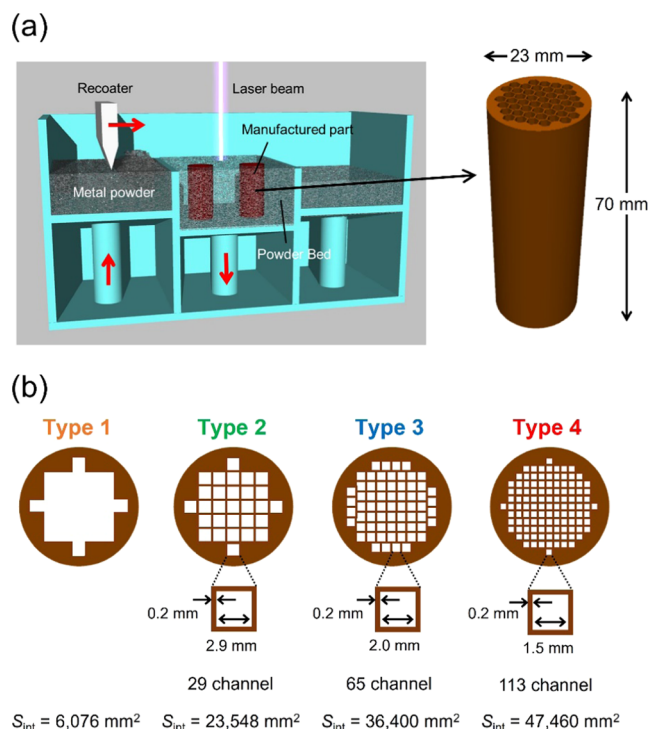


Figure 1. Schematic of (a) the LPBF apparatus for the fabrication of Cu-based flow reactors in a cylinder shape and (b) the cross-sectional structure and the internal surface areas of four different types of reactors.

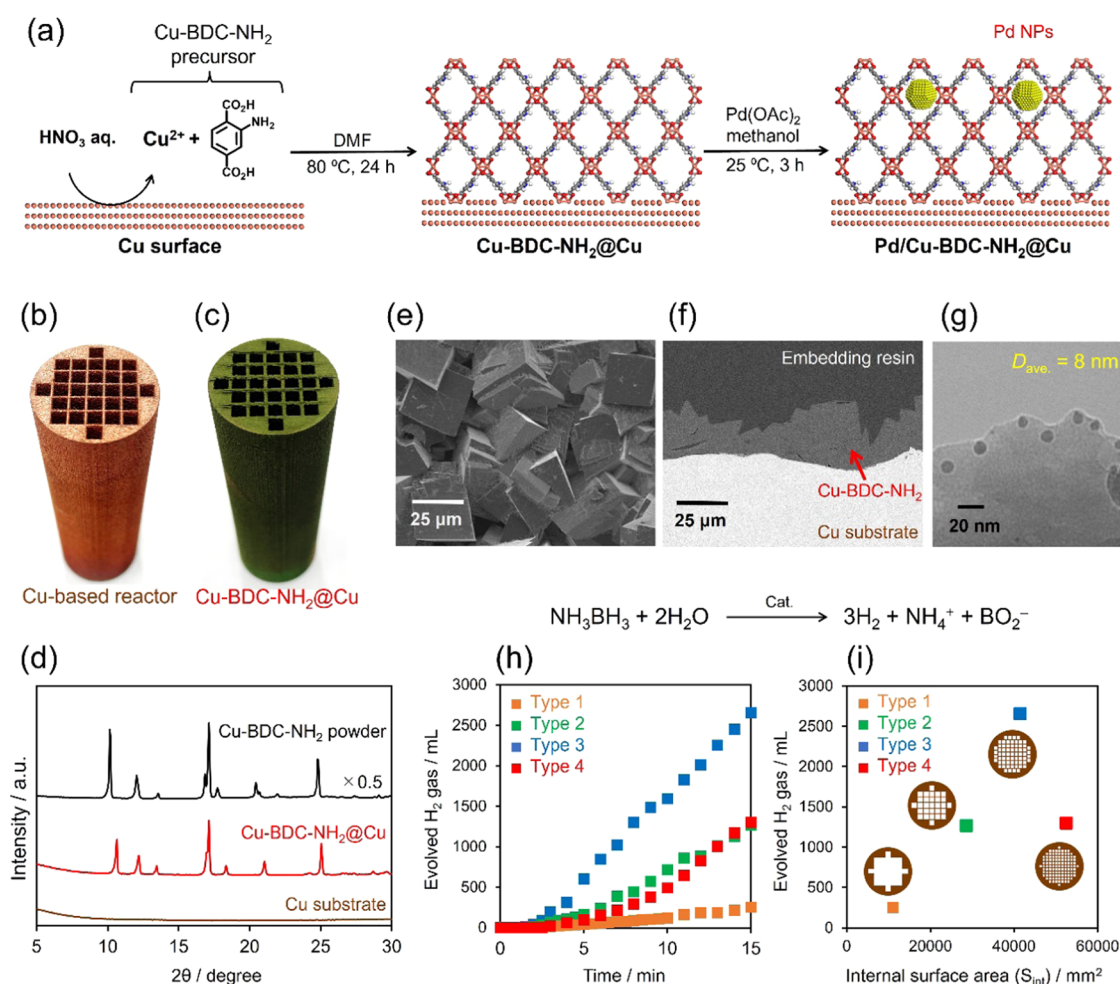


Figure 2. (a) Synthesis procedure for Cu-BDC-NH₂@Cu and Pd/Cu-BDC-NH₂@Cu; (b) photographs of an as-printed Cu-based reactor and (c) Cu-BDC-NH₂@Cu reactor; (d) XRD profiles; (e) SEM image of Cu-BDC-NH₂@Cu; (f) cross-sectional SEM image of Cu-BDC-NH₂@Cu; (g) TEM image of Pd/Cu-BDC-NH₂@Cu; (h) time course of H₂ evolution in the liquid flow reaction system based, where AB is hydrolyzed using different types of catalytic reactors; and (i) the relationship between the internal surface area (S_{int}) of each reactor and the volume of evolved H₂ gas.

originates from the tight contact between the MOF crystal and the Cu substrate. Moreover, the MOF crystals exist in a single layer with the thickness of about 20–30 μm , which allows the only surface modification of the 3D-fabricated reactor without disturbing the internal channel structure.

The Cu K-edge FT-EXAFS spectrum of the original Cu substrate shows a sharp peak due to the contiguous Cu–Cu bonds; the peak is not substantially shifted from that observed in the spectrum of the Cu foil. After functionalization with Cu-BDC-NH₂, a peak derived from Cu–O bonds appeared at 1.65 Å; this peak is assumed to originate from a Cu node moiety in the MOF framework (Figure S3). The N 1s XPS spectrum of Cu-BDC-NH₂@Cu shows a peak at 399.5 eV originating from the C–N–C moiety of the BDC-NH₂ linker (Figure S4a). The Cu 2p XPS spectrum of the Cu substrate indicated that metallic Cu was present. The peaks were broadened and shifted to higher binding energies after functionalization, suggesting that the Cu node was contained in the MOF framework (Figure S4b). All of these results confirm the successful covering of the Cu substrate with Cu-BDC-NH₂ crystals.

The Pd/Cu-BDC-NH₂@Cu was placed in a well-fitted glass tube to investigate its applicability as a fixed-bed catalytic

reactor. H₂ production by the hydrolysis of AB was used as the model reaction. AB has emerged as a promising hydrogen storage material because of its nontoxicity, high theoretical hydrogen gravimetric capacity (19.6 wt %), and high stability in solid form under ambient conditions.⁴⁵ The use of various metal catalysts in this reaction has been widely investigated, where H₂ has been stoichiometrically produced in a 3:1 (H₂/AB) molar ratio.⁴⁶ In the present study, an aqueous AB solution was pumped into the reactor at a flow rate of 20 mL min^{−1}, and the evolved H₂ gas was trapped in a gas buret.

The time course of H₂ production using the four types of reactors with different cell densities is plotted in Figure 2h. The evolved H₂ linearly increased for all of the samples, and the highest activity was attained with the Type 3 reactor consisting of 65 channels. Figure 2i shows the relationship between the internal surface area (S_{int}) of each reactor and the evolved H₂ gas, showing a good correlation for the Type 1, 2, and 3 reactors. These results mean that Pd/Cu-BDC-NH₂ was homogeneously distributed within the internal channel of the reactors. However, the catalytic activity of Type 4, consisting of 113 channels, drastically decreased despite the high internal surface area. We considered that the pressure loss might be related to the decrease in the amount of H₂ produced in the

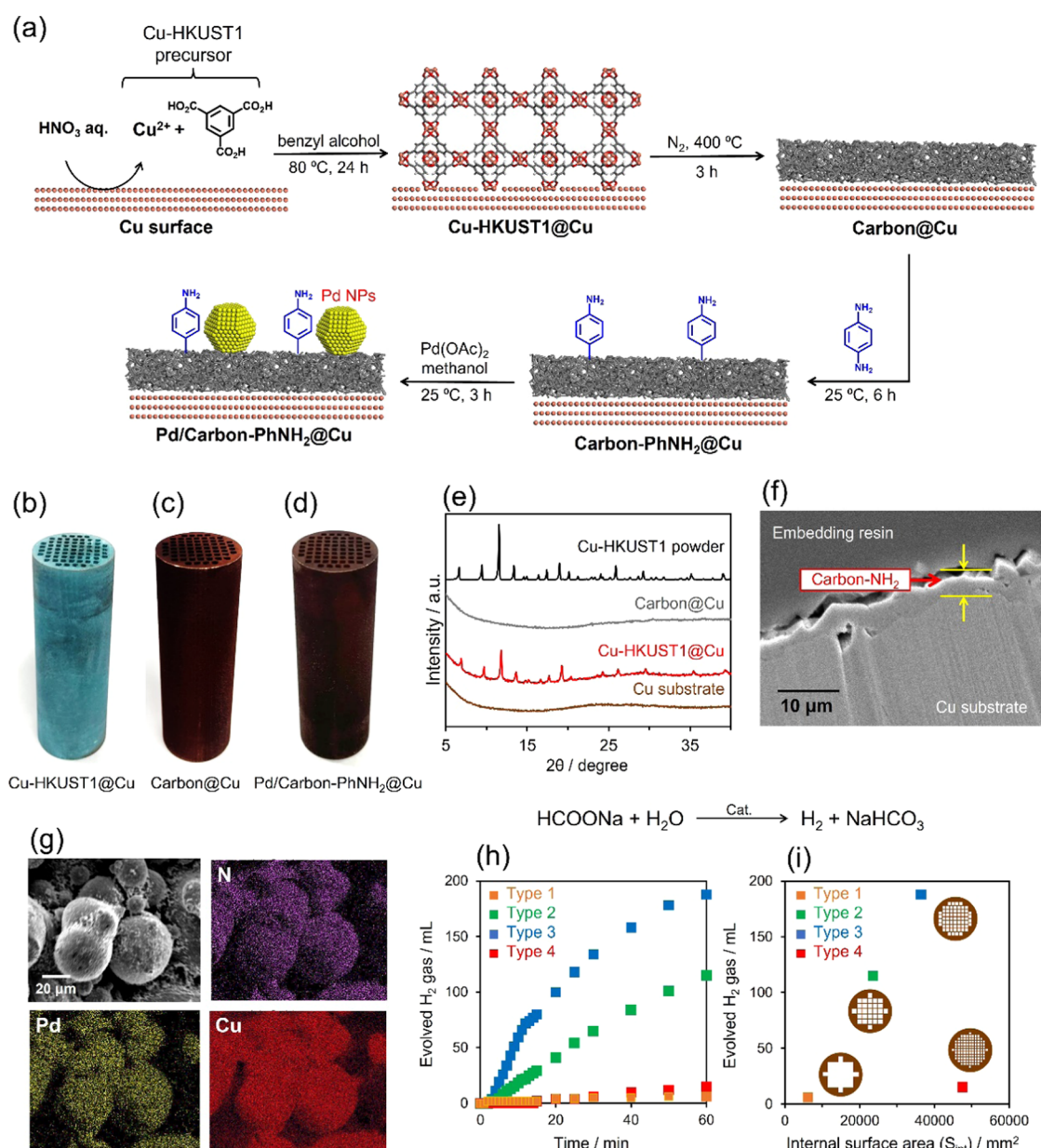


Figure 3. (a) Procedure for the synthesis of Cu-HKUST1@Cu, carbon@Cu, carbon-PhNH₂@Cu, and Pd/carbon-PhNH₂@Cu; (b) photographs of Cu-HKUST1@Cu; (c) carbon@Cu; and (d) Pd/carbon-PhNH₂@Cu. (e) XRD profiles; (f) cross-sectional SEM image of carbon@Cu; (g) SEM image and EDX mapping image of Pd/carbon-PhNH₂@Cu; (h) time course of H_2 evolution in the liquid flow reaction system based on hydrolysis of SF using different types of catalytic reactors; and (i) relationship between the internal surface area (S_{int}) of each reactor and the volume of evolved H_2 gas.

Type 4 reactor. This phenomenon will be discussed further later.

3.2. Pd/Carbon-PhNH₂@Cu. According to the schematic procedure in Figure 3a, the surface of the 3D-printed catalytic flow reactors was functionalized with Cu-HKUST1 by continuously flowing a benzyl alcohol solution containing H_3BTC (1,3,5-benzenetricarboxylic acid) as an organic linker and a trace of low-concentration HNO_3 at 80°C for 24 h. The obtained Cu-HKUST1@Cu sample was carbonized by pyrolysis at 400°C for 3 h under inert conditions. The carbon@Cu was further functionalized with *p*-phenylenediamine (PDA), followed by the deposition of Pd NPs using a methanol solution of $\text{Pd}(\text{OAc})_2$, affording Pd/carbon-PhNH₂@Cu. Here, we employed Cu-HKUST1 instead of Cu-BDC-NH₂ in order to eliminate the contamination of

nitrogen atoms in the carbon layer. This helps confirm the successful modification of the surface carbon layer with PDA for further catalytic applications.

After the functionalization with Cu-HKUST1, the reactor was sky blue; it became dark brown after carbonization (Figure 3b,c). Almost no color change was observed after the deposition of Pd NPs (Figure 3d). The carbonization process of Cu-HKUST1 was monitored by TGA (Figure S5). The first and second mass losses at ~ 150 and $\sim 250^\circ\text{C}$ can be attributed to the evaporation of residual guest molecules, such as water and benzyl alcohol, respectively. The drastic decrease in mass observed at $\sim 350^\circ\text{C}$ in the TGA curve is attributed to the carbonization of Cu-HKUST1, accompanied by the elimination and degradation of organic linkers.

Table 1. Fluid Flow Parameters for Cylindrical-Shaped Catalytic Flow Reactors with Four Different Cell Densities

	hydraulic diameter D_H/mm	Reynolds number Re^b	pipe friction coefficient λ^c	pressure loss (theoretical) $\Delta p/\text{Pa}$	pressure loss (CFD) $\Delta p/\text{Pa}$	total pressure loss/Pa
type 1	12.8	28.7	2.2	0.0243	0.0179	0.0179
type 2	2.9	6.5	9.9	0.473	0.418	12.1
type 3	2.0	4.5	14.3	0.996	0.879	57.2
type 4	1.5	3.4	19.0	1.77	1.57	177

^a $D_H = \frac{4A}{L}$ A: Cross-sectional area, L: wet edge length of the channel. ^b $Re_{D_H} = \frac{\rho u D_H}{\mu}$ μ : 8.91×10^{-4} kg/m·s, density (ρ): 997.1 kg/m³, flow velocity in x-direction (u): 0.002 m/s. ^c $\lambda = \frac{64}{Re_{D_H}}$ Pressure loss (theoretical): $\Delta p = \frac{1}{2} \lambda \frac{L}{D_H} \rho u^2$, tube length (L): 70 mm.

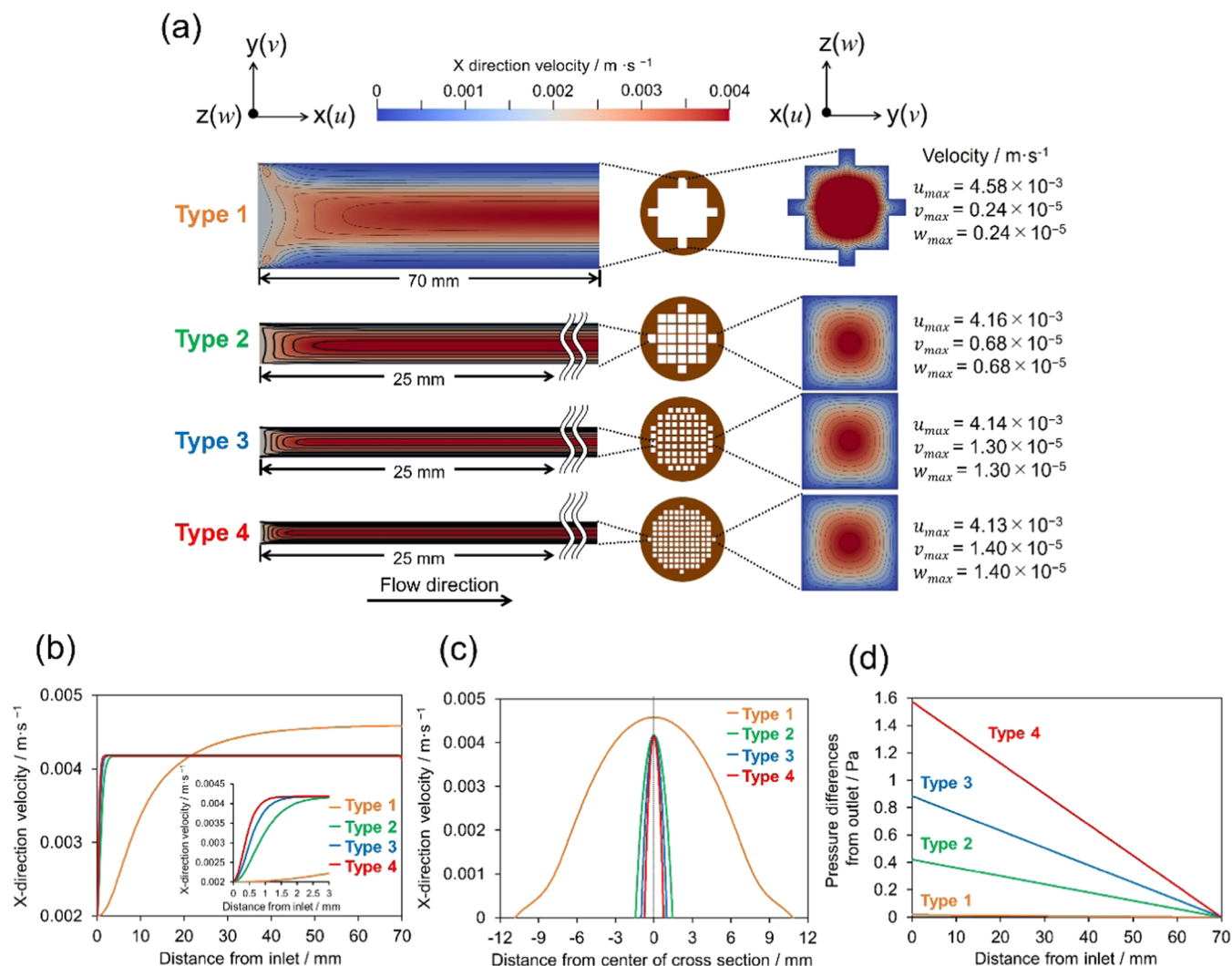


Figure 4. (a) x-Direction velocity distribution in the xy cross section ($z = 0$) and the velocity distributions in the yz cross section ($x = 0$) at the outlet position for the four types of reactors; (b) x-direction velocity profile from the inlet; (c) radial velocity profiles; and (d) pressure differences from the outlet.

The XRD patterns of Cu-HKUST1@Cu show several sharp peaks assignable to Cu-HKUST1 crystals; these peaks completely disappeared after carbonization (Figure 3e). The cross-sectional SEM observation of carbon-PhNH₂@Cu indicates a densely packed carbon phase with a thickness of 2–5 μm (Figure 3f). The EDX mapping of Pd/carbon-PhNH₂@Cu shows that the N and Pd atoms were homogeneously dispersed on the Cu substrate (Figure 3g). SEM image showed the spherical morphology of Cu substrate slightly changed after the calcination at 400 $^{\circ}\text{C}$.

The applicability of Pd/carbon-PhNH₂@Cu as a fixed-bed catalytic reactor was evaluated in H₂ production from hydrolysis of sodium formate (SF, HCOONa). Formic acid (FA) is an especially promising liquid organic hydrogen carrier because of its high gravimetric and volumetric hydrogen content (4.4 wt %, 53.4 kg m⁻³), low toxicity, and low flammability.⁴⁷ The selective dehydrogenation of FA is favored thermodynamically ($\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2$; $\Delta G = -48.4$ kJ mol⁻¹), which ensures that pure H₂ is generated without the formation of CO and H₂O via a competitive dehydrogenation pathway ($\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O}$; $\Delta G = -28.5$ kJ mol⁻¹).

The released CO₂ is problematic from the viewpoint of global warming, although CO₂ can be used to regenerate FA via hydrogenation with H₂. Alternatively, a formate/bicarbonate redox equilibrium ($\text{HCOO}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{HCO}_3^-$) can achieve carbon-neutral H₂ storage without the formation of CO₂ and CO.⁴⁸

As plotted in Figure 3h, the evolved H₂ increased with increasing reaction time for all of the samples, and the highest activity was attained with Type 3 among the four types of reactors with different cell densities. The time course of the H₂ evolution using a type 3 reactor shows the reaction rate decrease after 10 min, which is presumably due to the inhibition of the flow of the liquid reaction medium by the generated H₂ gas. In a separate experiment, Pd/carbon@Cu without the functionalization by phenylenediamine showed a drastic decrease in activity after 10 min despite a similar initial reaction rate (Figure S6). This result is presumably explained by the anchoring effect of the amine-functionalized carbon support, which suppresses the undesired agglomeration of the Pd NPs during the catalytic reaction.^{49,50} The relationship between the S_{int} of each reactor and the evolved H₂ gas showed good correlation for the Type 1, 2, and 3 reactors, whereas a drastic decrease in the catalytic activity was observed for the Type 4 reactor despite its high S_{int} (Figure 3i). This tendency corresponds well with the observed H₂ production from the hydrolysis of AB (Figure 2i). One probable reason is the low loading amount of Pd NPs for Type 4 reactors (0.003 g), which is almost similar to that of Type 1, while lower than those of Type 3 and Type 2 reactors (0.007 g). However, the low activity of Type 4 cannot be explained, even considering its low loading amount. Judging from the above result, we suspected that the modification with MOF may not be uniform for the Type 4 reactor, which prevents the smooth reaction at the inner wall of the reactors.

3.3. Computational Fluid Dynamics Study. The hydraulic diameter ($D_{\text{H}} = 4A/L$) of the Type 1 reactor is 12.8 mm, where A is the cross-sectional area and L is the wet edge length of the channel. Assuming that the working fluid is water at 298 K, the viscosity (μ) is $8.91 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$, the density (ρ) is 997.1 kg m^{-3} , and the flow velocity in the x -direction (u) is fixed at 0.002 m s^{-1} , the Reynolds number ($Re = \rho D_{\text{H}} u / \mu$) can be determined to be 28.7 (Table 1). The Re values of the Type 2, 3, and 4 reactors are 6.5, 4.5, and 3.4, respectively, which means that the flow is laminar; the water was therefore treated as an incompressible fluid because of its low speed.

Figure 4a shows the x -direction velocity distribution in the xy cross section ($z = 0$). For the Type 1 reactor, the uniform flow distribution at the inlet becomes a laminar flow velocity distribution through the entrance region. Similarly, a laminar flow velocity distribution is observed for the Type 2, 3, and 4 reactors. The velocity distributions for all of the reactors in the yz cross section ($x = 0$) at the outlet position are also shown, where the y - and z -direction velocities are ~ 0.1 to $\sim 0.3\%$ of the x -direction velocity (Figures S7 and S8). Thus, the x -direction velocity is dominant, and the influence of the secondary flow on the main flow is not significant. A more detailed x -direction velocity profile is shown in Figure 4b. For Type 1, the velocity gradually increased and became almost constant at 5 cm from the inlet. However, for the Type 2, 3, and 4 reactors, the flow is fully developed near the inlet; thus, the effect of the inlet on the channel is considered negligible. It has been reported that the pressure drop mainly affects the

velocity in the vicinity of the inlet of the reactor, so the velocity recovers within a few millimeters from the inlet and then becomes constant.⁵ Figure 4c shows the radial velocity profiles. The Type 2, 3, and 4 reactors have similar cross-sectional geometries and therefore similar parabolic velocity distributions, in which the pressure drop mainly affects the velocity near the wall surface and has little effect on the velocity at the center of the reactors. However, the Type 1 reactor deviates from the parabolic velocity distribution because of its different cross-sectional shape. The pressure differences from the outlet are also depicted in Figure 4d, which shows that the pressure loss increases with decreasing size of the flow path. This result is consistent with the tendency of the x -direction wall shear stress, which increases with decreasing size of the flow path (Figure S9).

Table 1 summarizes the pipe friction coefficient (λ) and theoretical and CFD pressure loss (Δp). The values of pressure loss obtained from theoretical and CFD simulations are in close agreement. As the cross-sectional area of each channel decreases, the area dominated by viscosity increases, and the Reynolds number decreases. As a result, the pressure loss per channel increases dramatically. Although the whole cross-sectional areas of the four reactors are similar, the pressure loss across the reactor of Type 4 is 10,000 times greater than that of Type 1 and approximately 3 times higher than that of Type 3. The pressure drop mainly affects the velocity near the wall surface and has little effect on the velocity at the center of the reactors. Therefore, the catalytic reaction that occurs on the surface of the channel wall does not easily proceed, and the activity of the Type 4 reactor remains low.

We also conducted a numerical investigation of the pressure loss induced by the sudden contraction of the cross-sectional area at the inlet of the reactor because the fluid flows from wide pools into narrow channels of the catalytic reactor (Figure S10). The values were calculated to be 4.4×10^{-4} , 0.02, 0.03, and 0.059 Pa for the Type 1, 2, 3, and 4 reactors, respectively. The pressure loss across the Type 4 reactor is 1340 times greater than that across the Type 1 reactor and ~ 2 times greater than that across the Type 3 reactor. Such a drastic increase in the pressure drop at the inlet of the Type 4 reactor might also influence the catalytic activity.

4. CONCLUSIONS

Cylindrical-shaped catalytic flow reactors with four different cell densities were fabricated by a metal 3D-printing technique using Cu-0.8 atom % Zr powder. The surface of the metallic reactors could be functionalized with densely packed Cu-BDC-NH₂ thin layers without using external metal precursors by continuously flowing a DMF solution containing an organic linker and dilute HNO₃. Following the deposition of Pd NPs, the functionalized metal 3D-printed reactors can be used for catalytic H₂ production from AB in the liquid phase. Similarly, Cu-HKUST1 thin layers can be fabricated by treatment with a benzyl alcohol solution containing the corresponding organic linker and a trace of dilute HNO₃, which enables carbonization by pyrolysis under inert conditions. After further functionalization with *p*-phenylenediamine, followed by the deposition of Pd NPs, the reactors efficiently catalyzed the production of liquid-phase H₂ from aqueous sodium formate. For both reactions, the relationship between the S_{int} of each reactor and the evolved H₂ gas showed good correlation for the Type 1, 2, and 3 reactors, whereas a drastic decrease in the catalytic activity was observed for the Type 4 reactor. A fluid dynamics

study revealed that the catalytic reaction that occurs on the surface of the channel wall in the Type 4 reactor does not easily proceed because the pressure loss for the Type 4 reactor is 10,000 times greater than that of the Type 1 reactor and approximately 3 times greater than that for the Type 3 reactor. This strategy can be applicable to a variety of MOF-based materials with high versatility. Furthermore, 3D-fabricated reactors allow a uniform thermal distribution over the whole reactor due to the high thermal conductivity through the compactly connected thin channels, which cannot be attained by conventional ceramic reactors. Further investigation to take advantage of the present synthetic method is now under investigation.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.3c10945>.

XRD, SEM, FT-EXAFS, XPS, thermogravimetric analysis, and computational fluid dynamics study (PDF)

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Author Contributions

K.M. supervised the project and wrote the manuscript. T.F. and H.H. performed the catalyst preparation, characterization, and catalytic reactions. H.-J.K. helped with the catalyst

preparation. T.N. helped with the sample preparation and supervised the project. H.Y. helped supervise the project.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by Grants-in-Aid for Scientific Research (A21H050980 and T22K189200) from the Japan Society for the Promotion of Science (JSPS). Part of this work was supported by the Yashima Environment Technology Foundation. This work was also partly supported by CREST-Nanomechanics: Elucidation of macroscale mechanical properties based on understanding nanoscale dynamics for innovative mechanical materials (Grant Number: JPMJCR2194) from the Japan Science and Technology Agency (JST); TEM experiment was carried out by using a facility in the Research Center for Ultra-High Voltage Electron Microscopy, Osaka University. The synchrotron radiation experiments for XAFS measurements were performed at the BL01B1 beamline in SPring-8, with approval from JASRI (2022A1076 and 2022B1807). The computational fluid dynamics study was performed using Advance/FlowFront/Ver. 5.4 with the assistance of AdvanceSoft Corporation.

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