Electronic Supplementary Information (ESI)

Cellulose Monoliths Supported Metal/Organic Framework as Hierarchical Porous Materials for Flow Reaction

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Experimental

Materials. N, N-dimethyl formamide (DMF) and triethylamine (TEA) were obtained from Nacalai Tesque, Inc. (Kyoto, Japan). 1-hexanol, ammonium persulfate (APS) and commercially available cellulose acetate (CA) with molecular weights (Mn= 5.0×10^4 ; 39.7 wt.% acetyl content) were supplied by Sigma-Aldrich Co. Y. Acryloyl chloride (AC), sodium p-styrene sulfonate (SSS), sodium hydroxide, zirconium(IV) chloride anhydrous, zinc nitrate dexahydrate (Zn(NO₃)₂·6H₂O) (\geq 99.0%) and 1,4-benzenedicarboxylic acid were all purchased from Wako Chemicals (Osaka, Japan). 2-methylimidazole (HMIM) (\geq 99.0%) was provided by TCI, Ltd. (Tokyo, Japan). The other organic solvents were offered by graduate school of engineering, Osaka University. Deionized (DI) water was used when water is involved. All chemicals and reagents were of analytical grade and used without further purification.

Synthesis of C-g-PSS monoliths. *C-g-PSS* monolith was obtained via free-radical polymerization by treatment of acryloyl group-introduced cellulose monolith with sodium *p*-styrene sulfonate (SSS) in the presence of APS initiator to acquire suitable anchoring sites for the growth of ZIF-8. Firstly, cellulose monolith (CM) was prepared by deacetylation of cellulose acetate (CA) monolith which was fabricated through the thermally induced phase separation (TIPS) method.¹ Then, obtained dried CMs (anhydrate glucose unit around 0.012 mol) were immersed in appropriate amount of DMF solvent followed by adding distilled TEA (0.18 mol). After thorough mixing and infiltration, excess AC (10:1 molar ratio to the hydroxy groups in cellulose) was added dropwise to the mixture while magnetic stirring in an ice bath. The condensation reaction of hydroxyl group of cellulose monoliths and acryloyl chloride was conducted at room temperature for 24 h and then completely washed with DI water. Finally, 1 mol L⁻¹ of SSS and 1.0 mol% of APS (corresponding to SSS) were added in the mixture of AC modified cellulose monoliths (ACCMs) and DI water.

The mixture was sufficiently deaerated and well homogenized by stirring for 5 h at room temperature. The free-radical polymerization was carried via heating the mixture in an oil bath at 70 °C for 24 h. After the reaction, the resultant PSS functionalized cellulose monoliths (C-g-PSS) were completely washed with DI water before characterizations.²

Preparation of ZIF-8 precursor and ZIF-8 crystals. The ZIF-8 crystals precursor was prepared by mixing methanolic 2-methylimidazole (HmIm) and Zn(NO₃)₂·6H₂O methanolic solutions in plastic vials and stirred for 20 min at room temperature as reported in other literature.³ It has been mentioned earlier that the structure and performance of the ZIF-8 crystals can be greatly influenced by the reactant concentration.⁴ Thus, the nucleation effect of different ZIF-8 reactant concentration on sulfonate-decorated monolith was discussed in this work. When the concentration of ZIF-8 was measured, the obtained samples were referred to as ZIF-8-*nc* (*n*=1, 2, 3 and 4) as shown in Table S1. ZIF-8-2c had a similar concentration to that reported by Rafti M.⁵ The ZIF-8 crystals were obtained by transferring the reaction mixture to a tightly capped vessel and heating it in a programmable oven at a rate of 5 °C to 100 °C, and maintaining this temperature for 5 h before cooling to room temperature. The obtained white crystals were collected by centrifugation, thoroughly washed with methanol, and dried at room temperature.

Synthesis of ZIF-8@PSS monoliths. ZIF-8@PSS monoliths were prepared by coating the PSS functionalized cellulose monolith with a thin layer of ZIF-8 MOF using a pump injection method. Firstly, the sulfonate-decorated monolith was tightly fitted into a heat shrink tubing and connected to a digital quantitative tubing pump (DSP-100SA, As One, Japan) and a ZIF-8 precursor vessel circulatory system by polypropylene tubing. This was done to ensure a constant controllable flow rate. The reaction was left to proceed at room temperature for appropriate time to allow for ZIF-8 growth. Finally, the monolith was copiously washed with methanol. The pump injection time and

flow rate of ZIF-8 precursor were analyzed. When x of reaction time had passed, the obtained samples were referred to as ZIF-8-*x*t (x=10, 20, 30 and 40 min), and when m of ZIF-8 flow rate was performed, the obtained samples were referred to as ZIF-8-*m*f (m=0.2, 0.5, 1 and 1.5 mL min⁻¹).

Synthesis of UiO-66. Standard synthesis of UiO-66 MOF was performed by dissolving ZrCl₄ (0.053 g, 0.227 mmol) Zirconium(IV) chloride anhydrous and 1,4-benzenedicarboxylic acid (0.034g, 0.227 mmol) in DMF (24.9 g, 340 mmol) at room temperature. The thus obtained mixture was sealed and placed in a pre-heated oven at 120 °C for 24 hours. Crystallization was carried out under static conditions. After cooling in air to room temperature the resulting solid was filtered, repeatedly washed with DMF and dried at room temperature.

Characterization. The morphologies of all samples were analyzed by scanning electron microscopy (Hitachi SU3500, Japan) with an accelerating voltage of 10kV. The XRD patterns of C-*g*-PSS, ZIF-8@PSS and UiO-66@PSS monoliths were obtained by using an X-Pert diffractometer, at the wavelength of 1.54 Å. The generator voltage was 45 kV and the generator current was 200 mA. The surface chemical composition of ZIF-8@PSS monolith was determined using X-ray photoelectron spectroscopy (XPS). The XPS spectra was recorded using a Kratos Ultra 2 spectrometer employing a monochromatic Aluminum K α X-ray source. The survey and high-resolution XPS spectra were collected at fixed analyzer pass energies of 160 eV and 10 eV, respectively. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Shimadzu Sequential Plasma Emission Spectrometer ICPS-7510) were used to confirm the successful coating of ZIF-8. Nitrogen adsorption/desorption isotherms were measured at 77K using a NOVA 4200e surface area & pore size analyzer (Quantachrome Instruments). Before measurements, the sample was degassed at room temperature under vacuum for at least 6 h. The specific surface area was

calculated based on the Brunauer-Emmett-Teller (BET) model. The monoliths' mechanical response towards compressive stress were recorded on a table-top material tester (Shimadzu EZ Graph, Japan) at room temperature using a 500 N load cell at 5 mm min⁻¹ compression rate. Samples were measured in triplicates and their elastic modulus was determined from the initial linear slope obtained from the stress–strain plot. The stress at yield was recorded to show monoliths compression strength. High-performance liquid chromatography (HPLC) was used for following the conversion process in the catalytic reaction.

Evaluation of permeability. The fundamental law governing fluid flow through porous media is Darcy's Law, and it holds true for cases where the porous material is already saturated with the fluid. A considerable number of experimental studies have reported the significance of the concept of permeability in the petrochemical industry. Permeability is the capacity of a medium to transmit fluids, and it portrays the resistance to fluid flow through pores. The apparatus used to measure for permeability has been described in our previous study.¹

As a permeable material, tightly fixed monolith was connected to a digital quantitative tubing pump and a digital pressure gauge (KDM30) by polypropylene tubing and rinsed with water before each measurement to ensure stability at a constant flow rate. Permeability is generally regarded as absolute regardless of the working fluid because the permeability coefficient B_0 is only determined by the structure of the porous medium. Darcy's law⁶ describes the equation of permeability using measurable quantities.

$$B_0 = \frac{L \times v \times \mu}{\Delta P} \tag{1}$$

 $v = q/A \tag{2}$

In which *L* is the length of monolith (cm), *v* is the linear velocity of a given fluid in flow system (cm s⁻¹), μ is the viscosity of fluid (Pa·s), *q* is flow rate (mL s⁻¹), *A* is cross sectional area to flow (cm²), *B*₀ is permeability of porous medium, Darcy (1 Darcy=1×10⁻⁸ cm²), ΔP is the pressure drop when influent flowing through the monoliths (Pa).

Catalysis. The flow-through catalytic experiments were carried out following a procedure reported in the literature with some changes.⁷ The monolith was first thoroughly washed with copious amount of ethanol. The mixture of reactant composed of 3.3 mL benzaldehyde, 3.42 mL ethyl cyanoacetate, and 2.28 mL dimethyl sulfoxide was conducted in a glass vial with a rubber plug and pumped through the monolith at a desired flow rate. The eluent was collected back to the glass vial. The monolith microreactor was deployed in a water bath at 60 °C. The mixture in the glass vial was periodically monitored by HPLC. The benzaldehyde conversion and product yield were calculated. The batch reaction using catalyst of ZIF-8 crystals or ZIF-8@PSS monolith was carried out in a round-bottom glass flask with mechanically stirring under similar condition.

To quantitatively evaluate the catalytic activity of microreactor, the turnover frequency (TOF : defined as number of moles of benzaldehyde reduced per mole catalyst per hour) was calculated according to the equation below:

$$TOF = \frac{n_{benzaldehyde}}{t \cdot n_{catalyst}} = \frac{(C_0 - C) \cdot v}{n_{catalyst}}$$

where n is the number of moles. t means reaction time and v represents the flow rate. Here the $n_{catalyst}$ in monolith (moles of 2-methylimidazole) was calculated to be 0.03 mmol according to the ICP results.

References

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Results

Table S1. ZIF-8 reactant concentrations				
ZIF-8	HMIM concentration	Zn(NO3) ₂ •6H ₂ O concentration		
	in methanol (g/L)	in methanol (g/L)		
ZIF-8-1c	2.3	3.7		
ZIF-8-2c	4.6	7.4		
ZIF-8-3c	9.2	14.8		
ZIF-8-4c	23.0	37.0		

Table S2. Porous parameters comparison of C-*g*-PSS and ZIF-8@PSS monolith prepared by pump injection method (pump injection time: 30 min).

	Surface area	Total pore volume	Average pore diameter
Sample	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	(nm)
C-g-PSS	18.5	0.05	10.06
ZIF-8-1f@PSS	261.9	0.16	2.41
ZIF-8-0.2f@PSS	228.4	0.15	2.56

Table S3. The amount of zinc at different flow rate and pump injection time.

Flow rate (Time)	Zn (wt. %)
1 mL min ⁻¹ (10 min)	6.7
1 mL min ⁻¹ (20 min)	7.3
1 mL min ⁻¹ (30 min)	8.1
1 mL min ⁻¹ (40 min)	8.5
0.2 mL min ⁻¹ (30 min)	6.2
0.5 mL min ⁻¹ (30 min)	7.5
1.5 mL min ⁻¹ (30 min)	9.7
1.5 mL min ⁻¹ (20 min)	8.5



Fig. S1. SEM surface images of ZIF-8@PSS prepared by LbL method with different reactant concentrations: (a) ZIF-8-1c@PSS; (b) -2c; (c) -3c; (d) -4c; (e) cross-sectional image of ZIF-8-1c@PSS monolith prepared by LbL method; (f) boundary morphology of ZIF-8-@PSS monolith using pump injection method; (g) cross-sectional image of UiO-66@PSS monolith using pump injection method (flow rate: 1 mL min⁻¹, pump injection time: 20 min).



Fig. S2. FT-IR spectra of CM, ZIF-8@CM washed with methanol and without washing.

For the comparative experiment, pristine cellulose monolith was used for the adsorption of ZIF-8 by the same pump injection method and was analyzed by FT-IR. Bigger size of ZIF-8 particles can be intercepted by the porous structure of CM, and some are stored in the pores present in the monolith. However, it can't be immobilized on the cellulose support, and will be totally washed with methanol from unmodified cellulose monolith.



Fig. S3. Compression stress-strain curves of C-g-PSS and ZIF-8@PSS monoliths.



Fig. S4. Powder X-ray diffraction (XRD) patterns of C-g-PSS, ZIF-8@PSS and UiO-66@PSS monoliths.

Powder XRD patterns of C-*g*-PSS, ZIF-8@PSS and UiO-66@PSS hybrid monolith are collected in Fig. S4. C-*g*-PSS monolith was amorphous with no observable XRD diffraction peaks. All of the prominent peaks, including 011, 002, 112, 022, 013, and 222, correspond to those of pure ZIF-8 crystals were observed for the ZIF-8@PSS monolith.⁷ The well-defined peaks revealed a high degree of crystallinity. In the case of UiO-66@PSS monolith, all diffraction patterns of UiO-66 are preserved; these patterns are in agreement with data published in the literature.⁸ This result indicates that the UiO-66 has been successfully anchored in the pores of cellulose monolith.



Fig. S5. XPS spectra of a ZIF-8@PSS monolith. The binding energies of the Zn 2p3/2 and 2p1/2 peaks are 1021 eV and 1044 eV, respectively.



Fig. S6. H¹NMR spectrum of reaction agents and product of the Knoevenagel condensation reaction.