Electronic Supplementary Material (ESI) for Materials Advances.

SUPPLEMENTARY INFORMATION

Highly porous melamine-formaldehyde monoliths with controlled hierarchical porosity toward application as metal scavenger

*Yuki Nakanishi,[a] Yosuke Hara,[a] Riichi Miyamoto,[a] Kazuki Nakanishi,[b,c] Kazuyoshi Kanamori[a]**

[a]Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto 606-8502, Japan
[b]Institute of Materials and Systems for Sustainability, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8601, Japan
[c]Institute for Integrated Cell-Material Sciences, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

Email: kanamori@kuchem.kyoto-u.ac.jp

Experimental

Preparation of the monoliths.

First, w_{PEO} mg of poly(ethylene oxide) (PEO, M_v ~ 100,000 or 200,000, Sigma-Aldrich Inc., USA) was dissolved in *N*,*N*-dimethylformamide (DMF, Kishida Chemical Co., Ltd., Japan) under gentle heating, and then 0.70 g of methylolmelamine (Nikaresin S-260, average molecular weight 260, kindly donated by Nippon Carbide Industries Co. Inc., Japan) was dissolved in the solution. To the solution was added 0.10 mL of 60 wt% nitric acid (Kishida Chemical Co., Ltd., Japan) under stirring, and the solution was allowed to gel at 40 °C. After aging at 40 °C for 24 h and 60 °C for 3 h, the solvent was exchanged with distilled water (Kishida Chemical Co., Ltd., Japan), and hydrothermal treatment was performed at T_{hydro} °C for 24 h. The obtained gel was washed with 2-propanol and *n*-hexane (both from Kishida Chemical Co., Ltd., Japan), and finally dried at 40 °C. The preparation process of a typical sample (MF3-120) is schematically shown in **Figure S1**.

Characterizations of the monoliths.

The pore morphology was observed with a scanning electron microscope (SEM, JSM-IT500HR, JEOL Ltd., Japan) and a transmission electron microscope (TEM, HT7700, Hitachi Hi-Tech Corp., Japan). The nitrogen adsorption-desorption isotherm was obtained by BELSORP-mini (MicrotracBEL Corp., Japan. The sample was degassed at 120 °C under vacuum (< 1 Pa) for 4 h prior to the measurement. The BET surface area and BJH pore size distribution from adsorption branch were obtained using the analysis software of the apparatus. Micropore surface area was calculated by the *t*-plot method. All the analysis was performed using a software BELMaster, which accompanies the apparatus.

Surface modification of conventional silica particles for adsorption experiment.

Silica gel particles (1.0 g, YMC*GEL SIL, particle diameter: 63−210 μm, pore size: ~6.5 nm, BET surface area: ~450 $m^2\ g^{-1}$, YMC Co., Ltd., Japan) were refluxed in 10 % of 3-aminopropyltriethoxysilane solution in toluene (10 mL) for 3 h. Resultant particles (denoted as NH2-silica) were collected on a filter paper and washed with 2-propanol (100 mL) and then acetone (10 mL), and finally dried *in vacuo* to obtain the aminopropyl-modified silica. The ligand content on the silica beads was measured by thermogravimetry-differential thermal analysis (TG-DT, Rigaku co., Ltd, Themo Plus EVO 8120) and calculated on a weight loss corresponding to the combustion of an aminopropyl group. The weight decrease was 7.36 % below 500 °C, and the loading capacity was calculated as 1.27 mmol g^{-1}.

Palladium adsorption test.

A dried monolith MF3-100 was crashed in a mortar and the obtained powder was sieved in the range of 63−212 μm. The granulated MF3-100 (10 mg) was immersed in 10 mL of 0.1 mol L^{-1} HCl containing 100 mg L^{-1} $PdCl_2$, and the mixture was shaken at around 200 rpm. After 1 and 24 h, the supernatant was filtered through a PTFE membrane (0.45 μm), and the Pd concentration of each sample was measured on a UV-Vis spectroscope (V-670, JASCO co. Ltd, Japan) at a wavelength of 474 nm. The aminopropyl-modified silica was treated in the same manner for comparison. Low concentration less than 5 mg L^{-1} was determined with an adsorption spectrum at 489 nm for PdI_2 which was prepared by the addition of potassium iodide (5 mg) into the supernatant (1 mL) before the measurement.

The granulated MF3-100 was packed into a polypropylene syringe (bed size: 5.5 mm in diameter and 10 mm in length, bed volume: 0.24 mL, the particles were fixed with a polyethylene frit without leakage). The $PdCl_2$ solution was continuously flowed into the column at 1.0 mL min^{-1} using a syringe pump. The flowed solution was collected in every 5 mL as the fraction, in which Pd^{2+} concentration was measured by the UV-Vis spectroscopy as above.

Results and discussion

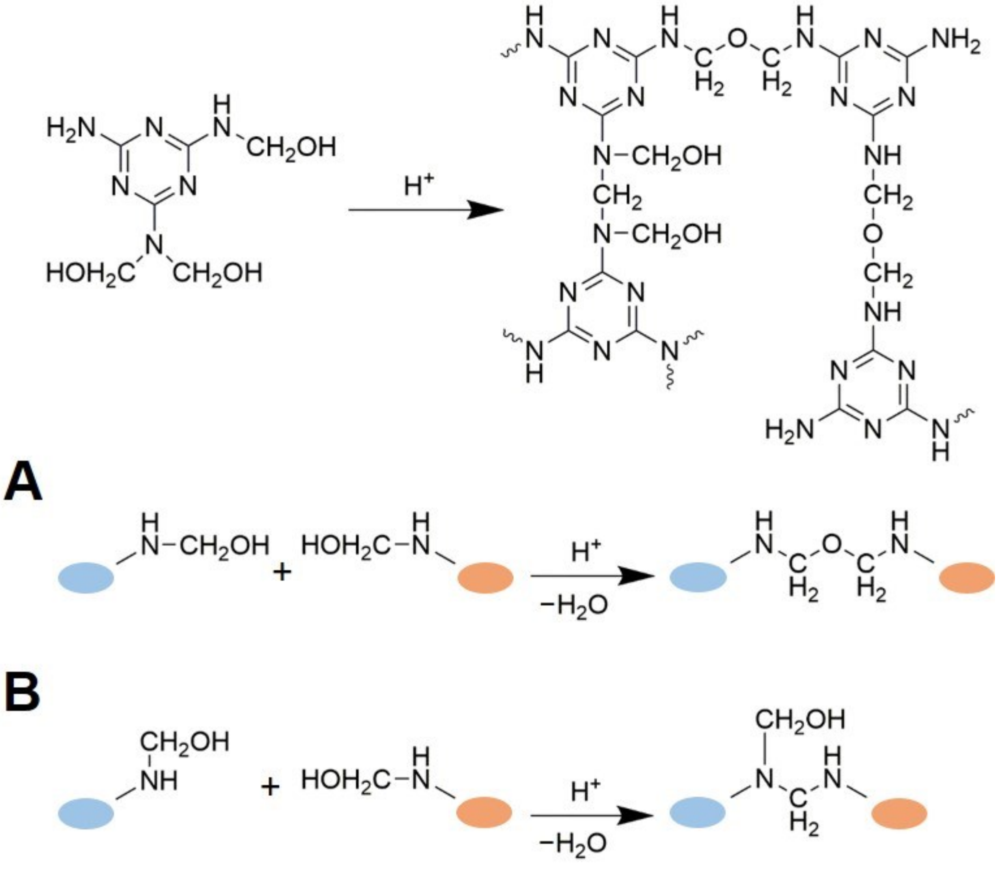

Figure S1. Reaction mechanisms of methylol melamine; dehydrogenative condensation between (A) two methylol groups and (B) methylol and secondary amino groups.

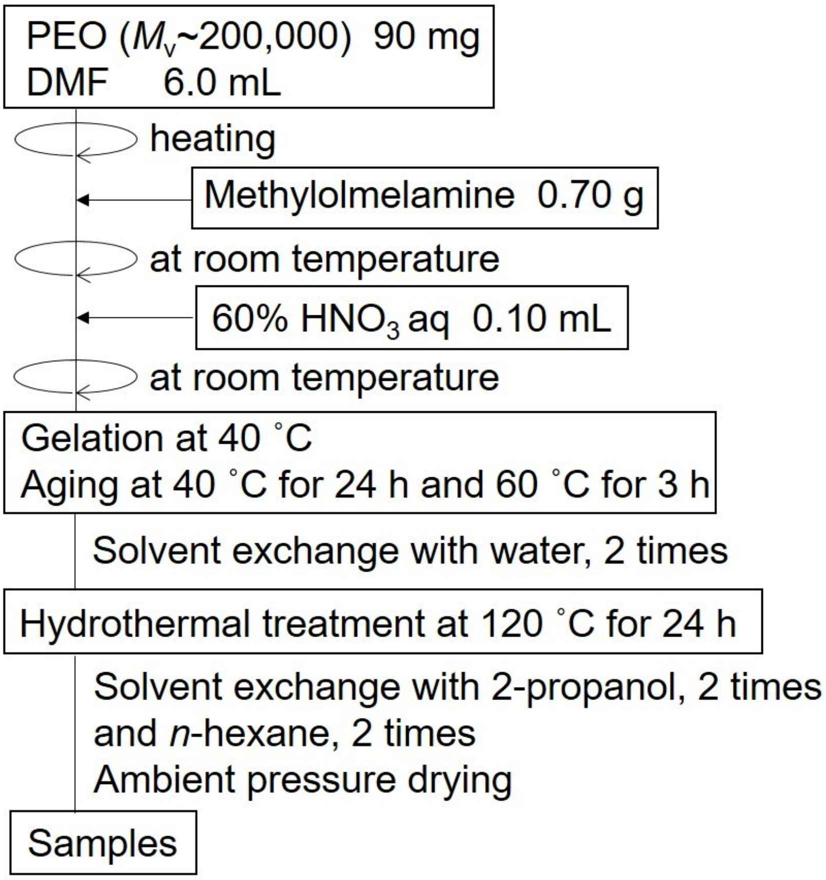

Figure S2. Flow diagram for a typical sample MF3-120.

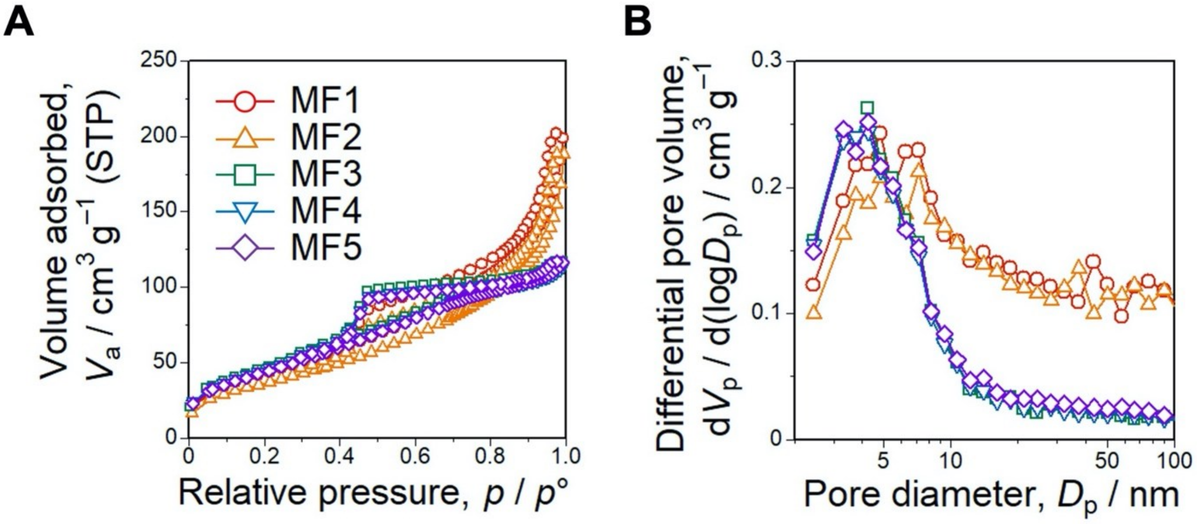

Figure S3. (A) Nitrogen adsorption-desorption isotherms and (B) pore size distribution on the MF polymer monoliths MF1-MF5.

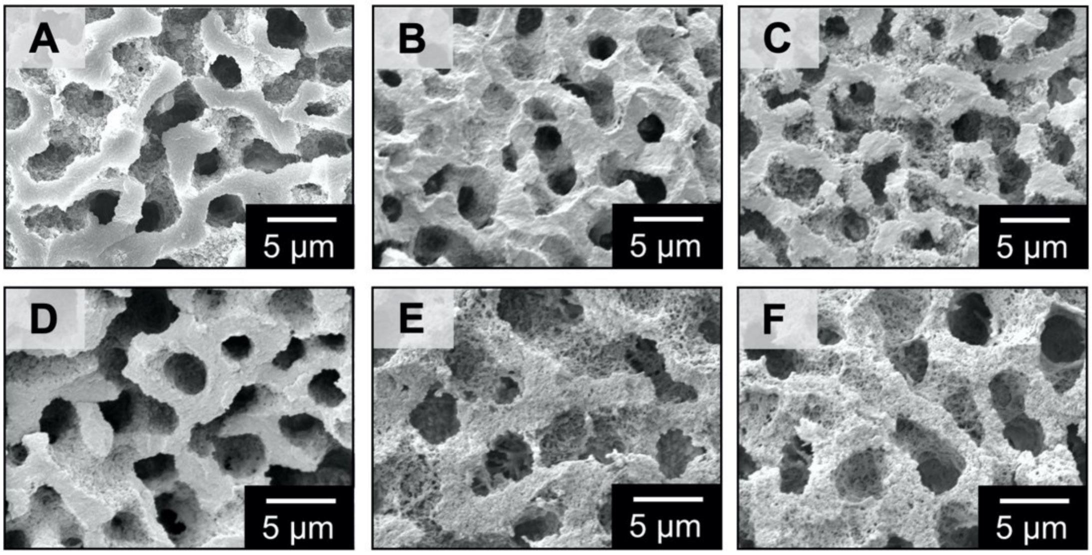

Figure S4. The macroporous morphologies of the samples hydrothermally treated at different temperatures: (A) MF3 (reference), (B) MF3-60, (C) MF3-80, (D) MF3-100, (E) MF3-120 and (F) MF3-140.

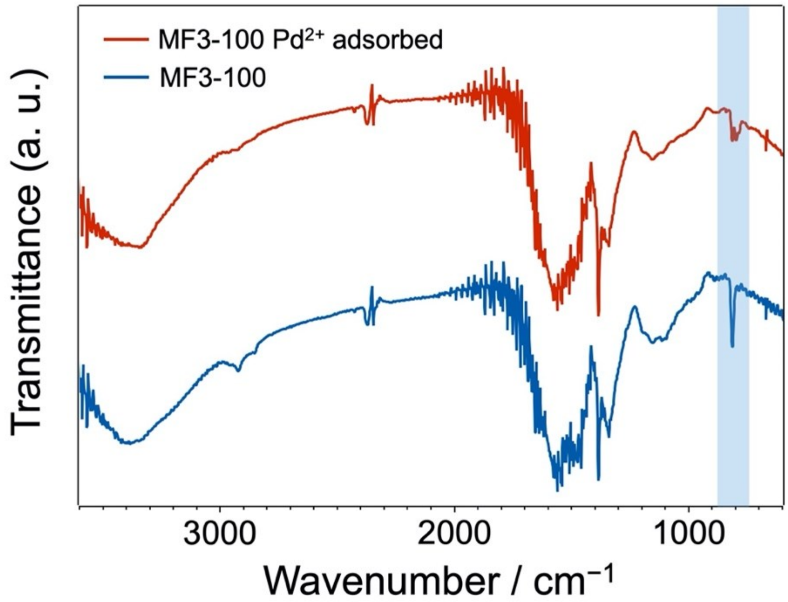

Figure S5. FTIR spectra of the MF3-100 samples before and after adsorption of Pd^{2+}. The absorption band around 800 cm^{-1} due to the triazine ring splits into two bands with a slight shift to a lower wavenumber, suggesting a complex formation with palladium species.

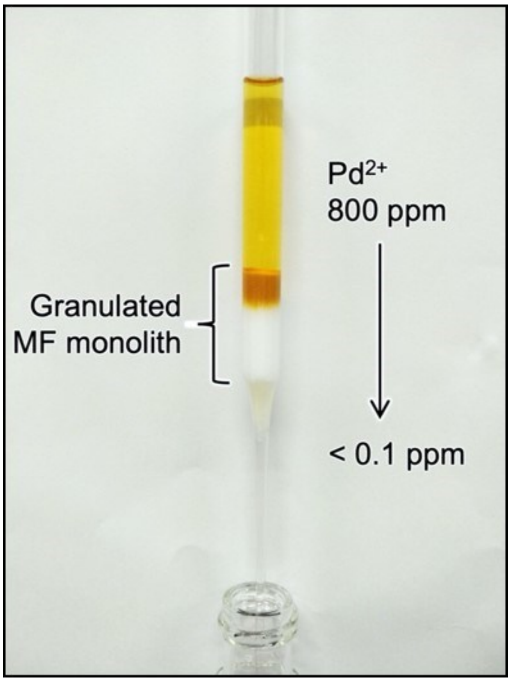

Figure S6. The setup for the adsorption test in a flow system. In this specific case, 800 ppm of Pd^{2+} at inlet was decreased to < 0.1 ppm at outlet.

Table S1. Starting compositions for the MF monoliths.

Sample	Molecular weight (M_v) of PEO	w_{PEO} / mg
MF1	100,000	150
MF2	100,000	170
MF3	200,000	90
MF4	200,000	100
MF5	200,000	110

Table S2. Mesopore properties of MF3-60 treated in different solutions.

Sample	$d_{meso}{}^{a}$ / nm	$V_p{}^{b}$ / cm^3 g^{-1}	$S_{BET}{}^{c}$ / m^2 g^{-1}
MF3-100	8.2	0.75	421
10 % HCl	3.4	0.28	304
6 M KOH	5.5	0.49	400
Xylene	6.6	0.55	447

[a] BJH modal mesopore diameter. [b] Total pore volume.