Mechanochemical Dry Conversion of Zinc Oxide to Zeolitic Imidazolate Framework

Shunsuke Tanaka,^{*a,b} Koji Kida,^a Takuya Nagaoka,^a Takehiro Ota^a and Yoshikazu Miyake^{a,b}

^a Department of Chemical, Energy and Environmental Engineering, Kansai University, 3-3-35 Yamatecho, Suita-shi, Osaka 564-8680 Japan.

^b Organization for Research and Development of Innovative Science and Technology (ORDIST), Kansai University, 3-3-35 Yamate-cho, Suita-shi, Osaka 564-8680 Japan.

^{*} Tel: +81-6-6368-0851; Fax: +81-6-6388-8869; E-mail: shun_tnk@kansai-u.ac.jp (S. Tanaka)

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Experimental Procedures

Chemicals

All the commercially available chemicals were used without any further purification. Zinc oxide (ZnO) powders (nano-size; product ID 265-01261 and large size; product ID 267-00975) were purchased from Wako Pure Chemical Industries and used after drying at 120 °C. Rhodamine B (RhB), and methanol were purchased from Wako Pure Chemical Industries. 2-methylimidazole (Hmim) and zinc nitrate hexahydrate were purchased from Sigma-Aldrich Japan.

Mechanochemical Dry Conversion

All reactions were performed at 0.1 mole scale. In a typical reaction, a mixture of 8.1 g ZnO and 16.4 g Hmim was placed in a 300 ml ceramic pot (93.4% $Al_2O_3/5\%$ SiO₂) containing 100 YTZ[®] balls (94.9 % ZrO₂+HfO₂/4.8% Y₂O₃, 10 mm diameter each) and then milling at a rotation rate of 100 rpm (UBM-2, Masuda Co. Ltd., Japan). The products were rinsed with deionized water for removal of unreacted Hmim and then dried for 24 h under reduced pressure at 40 °C.

Preparation of ZIF-8 Monocrystals According to the Literatures for Comparison Test

ZIF-8 (500 nm): 0.744 g of zinc nitrate hexahydrate was dissolved in 10 ml of deionized water and added to a solution consisting of 12.3 g of Hmim in 90 ml of deionized water. The mixture was stirred at room temperature. The solution quickly became cloudy and a suspension was obtained. 24 h later, the suspension was centrifuged and washed with methanol three times. The products were then dried for 24 h under reduced pressure at 40 °C. (Ref. K. Kida et al., *CrystEngComm* **15**, 1794, 2013)

ZIF-8 (30 nm): 0.372 g of zinc nitrate hexahydrate was dissolved in 10 ml of methanol and added to a solution consisting of 0.513 g of Hmim in 70 ml of methanol. The mixture was stirred at room temperature. The solution quickly became cloudy and a suspension was obtained. 24 h later, the suspension was centrifuged and washed with methanol three times. The products were then dried for 24 h under reduced pressure at 40 °C. (Ref. J. Cravillon et al., *Chem. Mater.* **21**, 1410, 2009)

Characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a MiniFlex 600 (Rigaku) by using Cu Ka radiation with λ = 1.5418 Å; the copper anode was operated at 30 kV and 15 mA. The crystallite diameter, D, of ZnO and ZIF-8 crystals was determined from the measured (101) and (011) diffraction peaks, respectively, using the Scherrer formula;

$$D = \frac{K\lambda}{\beta\cos\vartheta}$$

where K is the Scherrer constant, 0.94, λ is the X-ray wavelength, β is the full width at half maximum of the diffraction curve, and ϑ is the Bragg diffraction angle.

Thermogravimetric analysis (TGA) was carried out with a DTG-60H (Shimadzu) under air flow at a heating rate of 5 $^{\circ}$ C min⁻¹.

Nitrogen adsorption/desorption isotherms were measured at 77 K using a BELSORP-max (Bel Japan). The samples were degassed at 200 °C under vacuum. Brunauer–Emmett–Teller (BET) model surface area, S_{BET} , and Langmuir model surface area, S_{L} , were calculated from the nitrogen adsorption branches. A part of the nitrogen adsorption isotherm in the P/P_0 range 0.01–0.1 was fitted to the BET equation to estimate the S_{BET} and the S_{L} calculation was performed using all data points. The total pore volume, V_{total} , was calculated from the amount of nitrogen adsorbed at $P/P_0 = 0.95$. The micropore volume, V_{micro} , was calculated from the α_{s} -plot method.

Field emission scanning electron microscope (FESEM) images were recorded on an S-4800 (Hitachi High-Tech) at an acceleration voltage of 1–5 kV. Transmission electron microscopy (TEM) images were recorded on a JEM-2010 (JEOL) at an acceleration voltage of 200 kV. The diameters of more than 200 particles in the FESEM or TEM images were measured to determine the average particle size, d_n , and coefficient of variation, C_v , defined by the following equations:

$$d_{n} = \sum n_{i}d_{i}/\sum n_{i}$$
$$C_{v} = \sqrt{\sum (d_{i}-d_{n})^{2}/\sum n_{i}}/d_{n}$$

The batch mode adsorption studies for an organic dye, RhB, were carried out by agitating 40 mg of sample in 20 mL of dye solution (initial concentration 0.01 mM). For comparison, pure ZIF-8 monocrystals were also tested as an adsorbent. The mixture was continuously shaken in a shaking bath until the equilibrium was reached. After adsorption, the dye concentration was determined using an UV-visible spectrophotometer UV-2450 (Shimadzu). The wavenumber for the detection is 554 nm. The adsorption capacities of RhB, *q* (mmol/g), were calculated using the following mass balance equation;

$$q = \frac{(C_0 - C_{eq})V}{W}$$

where C_0 and C_{eq} (mM) are initial and equilibrium concentration, respectively, and V (ml) and W (g) are the volume of the liquid phase and the mass of the adsorbent, respectively.



Fig. S1 TEM images and size distribution of raw ZnO nanoparticles (scale bar; 20 nm).



Fig. S2 Time course of PXRD pattern of ZnO–Hmim mixture in the mechanochemical dry conversion (left) and crystallite diameters of ZnO and ZIF-8 crystals in the product (right). The product was prepared using nano-sized ZnO powders ($d_n = 24$ nm). Pure ZIF-8 monocrystals, average particle size of 500 nm, were prepared according to the literature (Ref. K. Kida et al., *CrystEngComm* **15**, 1794, 2013).



Fig. S3 PXRD patterns of the products after removal of unreacted Hmim. The product was prepared using nano-sized ZnO powders ($d_n = 24$ nm).



Fig. S4 TGA curves of the products (left) and time course of the ZnO conversion (right).



Fig. S5 Nitrogen adsorption/desorption isotherms of the products.



Fig. S6 PXRD patterns of ZnO, Hmim, and product. The product was prepared using large ZnO particles ($d_n = 373$ nm). The reflection peaks attributed to ZIF-8 were rarely observed even after 240 h.



Fig. S7 Particle size distribution of large ZnO particles and FESEM images of the raw ZnO and product (scale bar; 1 μ m). ZnO poorly reacted with Hmim, of which the ZnO conversion was 15%. The conversion correlates with the external surface area of ZnO.



Fig. S8 TEM images of the products prepared using large ZnO particles (d_n = 373 nm) (scale bar; 200 nm (a,b), 50 nm (c,d), 20 nm (e), 10 nm (f)). The parts showing light and dark contrasts correspond to ZIF-8 and ZnO, respectively. The ZIF-8 layers about 20 nm thick were grown from the ZnO crystal.



Fig. S9 TEM images of the mechanochemically dry converted ZIF-8 (scale bar; 100 nm (d), 50 nm (a,e,f), 10 nm (b,g), 5 nm (c,h,i)). The products were prepared using ZnO nanoparticles (d_n = 24 nm). (a–g) The parts showing light and dark contrasts correspond to ZIF-8 and ZnO, respectively. Whereas the resultant nanoparticles of larger size included the untransformed ZnO, the smaller particles did not include ZnO. (h,i) ZIF-8 channels can be observed.



Fig. S10 Particle size distributions of mechanochemically dry converted ZIF-8 (240 h).



Fig. S11 Optical photographs for dye solution (a) before and (b–d) after adsorption by (b) nano-sized ZnO powders (d_n = 373 nm), (c) ZIF-8 monocrystals of 500 nm in size, and (d) mechano-chemically dry converted ZIF-8 (240 h).



Fig. S12 UV-visible spectra for dye water (a) before and (b–e) after adsorption by (b) nano-sized ZnO powders, (c) ZIF-8 monocrystals of 500 nm in size, (d) mechanochemically dry converted ZIF-8 (240 h), and (e) ZIF-8 monocrystals of 30 nm in size.

Table S1 Ads	sorption Ca	apacities for	RhB on ZnO), ZIF-8 monoc	rystals, and ZIF	polycrystals (2	.40 h).

Sample	S _{BET}	SL	V _{micro}	V _T	q
	$/ m^2 g^{-1}$	$/ m^2 g^{-1}$	/ cc g ⁻¹	$/ cc g^{-1}$	/µmol g ⁻¹
ZnO (<i>d_n</i> = 24 nm)	30	35	< 0.01	0.37	0.3
ZIF-8 monocrystal (500 nm)	1550	1870	0.65	0.68	3.0
ZIF-8 monocrystal (30 nm)	1650	1840	0.64	1.06	9.0
ZIF-8 polycrystal	1180	1290	0.45	0.76	8.8

Note that the apertures of 6-membered ring of ZIF-8 are as narrow as 3.4 Å, although the diameter of pore cavities is 11.6 Å. The bulky RhB molecules hardly enter the pore cavities. Therefore, adsorption should occur mainly on the external surfaces and grain boundaries. Despite containing nonadsorptive ZnO, ZIF-8 polycrystals (30–150 nm) prepared by mechanochemical dry conversion has high adsorption capacity.