大阪工業大学 OSAKA INSTITUTE OF TECHNOLOGY
みらいを つくる つたえる まもる。

工学部　応用化学科　教授　下村　修

ZIF-8 (Zeolitic Imidazolate Framework-8)

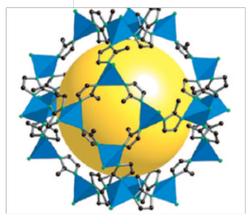


Figure 1. The single crystal x-ray structures of ZIF-8.

- 2価の金属カチオン(Zn^{2+})と2-メチルイミダゾールアニオンから形成される
- サイズを20 nm～1.8 μmに調節可能
- 細孔より大きな分子を吸着することができる
- 強塩基中でも1日構造が安定
- ガスの貯蔵や分離、触媒、ドラッグデリバリー、センサーなどの利用が期待されている

Table 1. Composition of ZIF series of compounds

ZIF-n	Composition	Net[a]	Zeolite[b]	d[c] (Å)
ZIF-1	$Zn(Im)_2$	crb	BCT	6.94
ZIF-2	$Zn(Im)_2$	crb	BCT	6.00
ZIF-3	$Zn(Im)_2$	dft	DFT	8.02
ZIF-4	$Zn(Im)_2$	cag	-	2.04
ZIF-5	$In_2Zn_3(Im)_{12}$	gar	-	3.03
ZIF-6	$Zn(Im)_2$	gis	GIS	8.80
ZIF-7	$Zn(bIm)_2$	sod	SOD	4.31
ZIF-8	$Zn(mIm)_2$	sod	SOD	11.60
ZIF-9	$Co(bIm)_2$	sod	SOD	4.31
ZIF-10	$Zn(Im)_2$	mer	MER	12.12
ZIF-11	$Zn(bIm)_2$	rho	RHO	14.64
ZIF-12	$Co(bIm)_2$	rho	RHO	14.64
ZIF-14	$Zn(eIm)_2$	ana	ANA	2.20

[a] For definitions of three-letter abbreviations, see the Reticular Chemistry Structure Resource.
[b] Structure of zeolites which are defined by the International Zeolite Association.
[c] Diameter of the largest sphere that will fit into the framework.

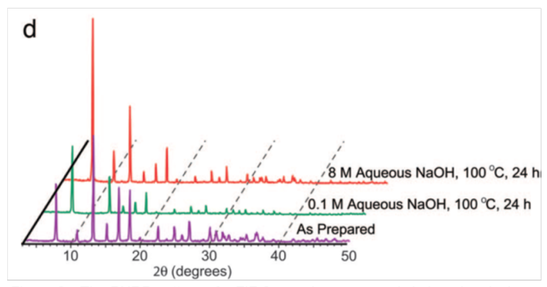


Figure 2. The PXRD patterns for ZIF-8 samples measured during chemical stability tests. (d) In refluxing aqueous NaOH solution for up to 1 day.

Yaghi, O. M. *et al. PANS.* **2006**, *103*, 10186-10191.
Yaghi, O. M. *et al. Acc. Chem. Res.* **2010**, *43*, 58-67.
Yaghi, O. M. *et al. Science.* **2008**, *319*, 939-943.
Li, Y. *et al. ACS Sustainable Chem. Eng.* **2019**, *7*, 3632-3646.

Stability of ZIF-8 under acidic conditions

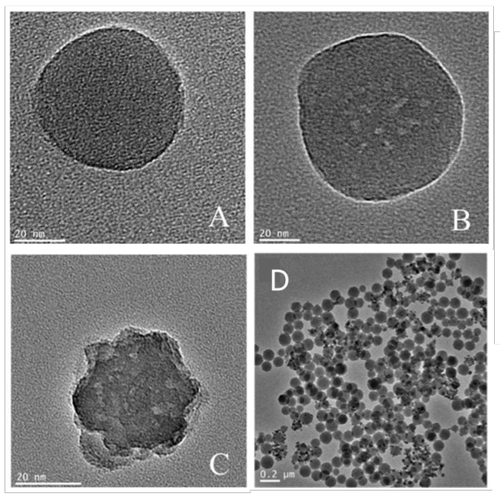


Figure 3. TEM images on single particle when ZIF-8 immersed in pH 6.0 buffer for (A) 0 hr; (B) 0.5 hr; (C) 1 hr; (D) in PBS (pH7.4) for one day.

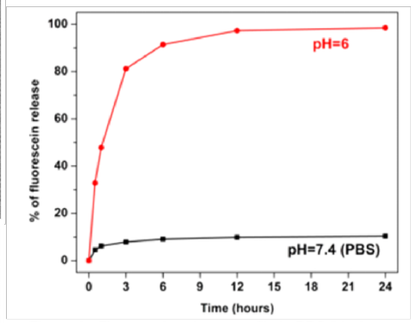


Figure 4. Fluorescein release profile in PBS (black squares) and pH 6.0 buffer solution (red circles)

Zhuang, J. *et al. ACS Nano.* **2014**, *8*, 2812-2819.
Nair, S. *et al. Chem. Mater.* **2018**, *30*, 4089-4101.

Curing of epoxy resin with ZIF-8

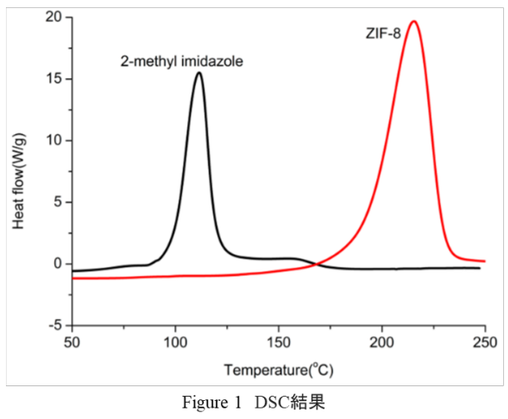
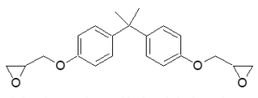
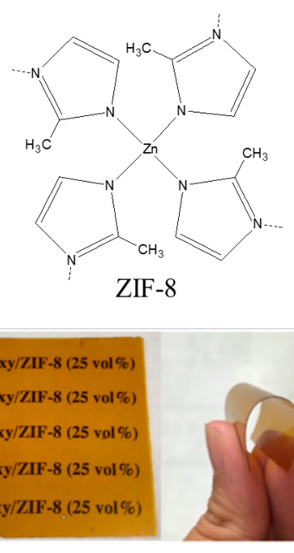


Figure 1 DSC結果



bisphenol A diglycidyl ether
(D.E.R. 383)



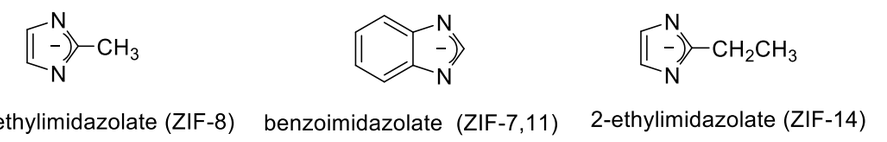
Liu, C.; et al. *ACS Apple. Mater. Interfaces,* 2018, 10, 1250-1257.

潜在性硬化剤

○ モノマー → 通常の硬化剤 → ポリマー

○ モノマー → 潜在性硬化剤（反応が進まない）→ モノマー + 潜在性硬化剤 → 外部刺激（熱や光など）→ ポリマー

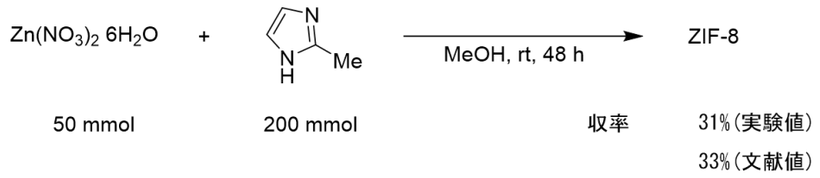
ZIF (Zeolitic Imidazolate Framework)



2-methylimidazolate (ZIF-8)　benzoimidazolate (ZIF-7,11)　2-ethylimidazolate (ZIF-14)

Fig. Ligands of zeolitic imidazolate frameworks (ZIFs)

Preparation of ZIF-8



参考文献：*J. Am. Chem. Soc.* **2014**, *136*, 1702.

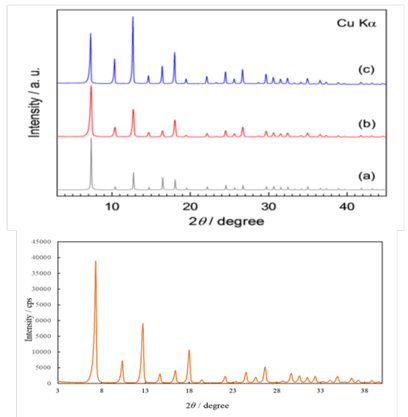
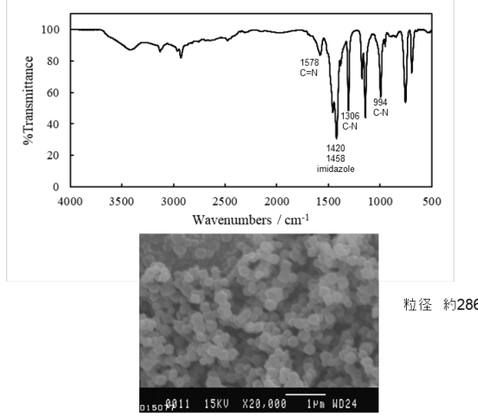


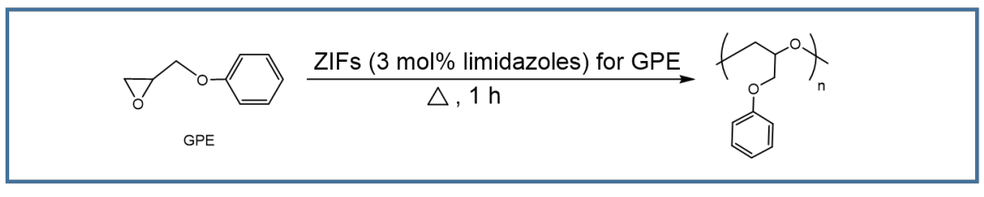
Fig. 上図: 文献値(a) 計算値, (b) 実験値
下図: 合成したZIF-8のXRD

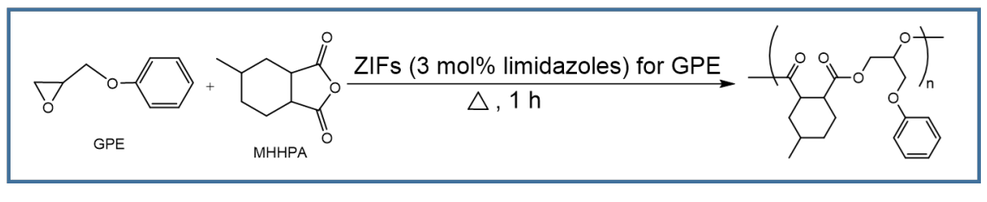


粒径　約286nm

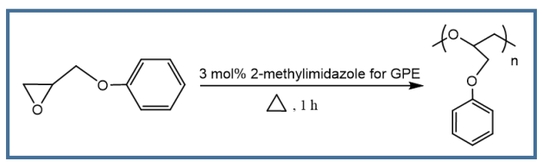
Fig. 上図: 合成したZIF-8のIR　下図:合成したZIF-8のSEM画像

Reaction scheme





Reaction of GPE with ZIF-8



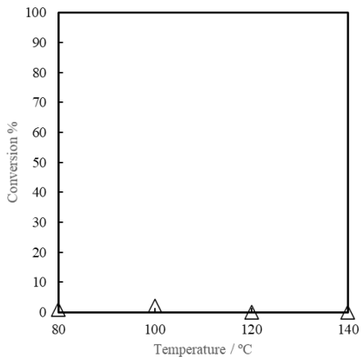
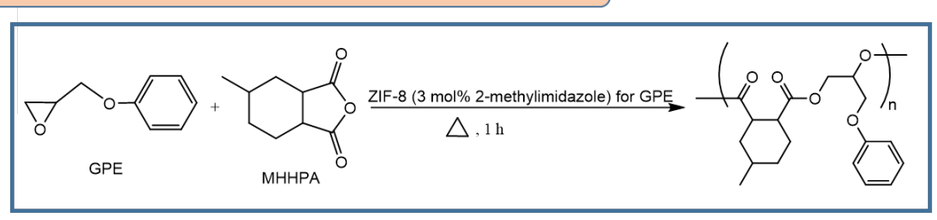


Fig. The conversion of GPE after 1h as a function of temperature during reaction of GPE with ZIF-8.

加熱条件下、140℃では
全く反応しない

Reaction of GPE-MHHPA with ZIF-8



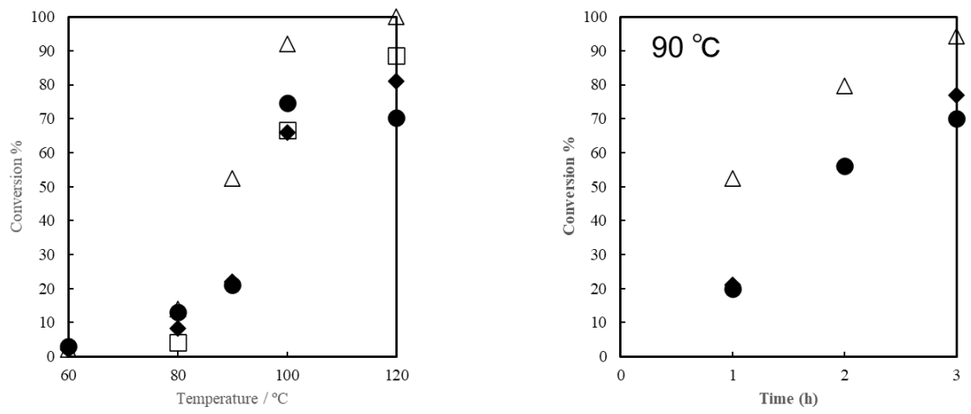
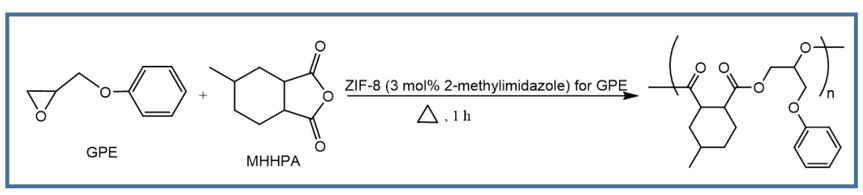


Fig. The conversion of GPE after 1h as a function of temperature during reaction of GPE-MHHPA with ZIF-8 (Δ) α-ZrP·2MIm (□), HX-3088 (◆), and HX-3722 (●).

HX-3088, HX-3722 (●): 旭化成潜在性硬化剤
α-ZrP·2MIm (□): 2-methylimidaoleの層状リン酸ジルコニウム

Storage stability of GPE-MHHPA with ZIF-8



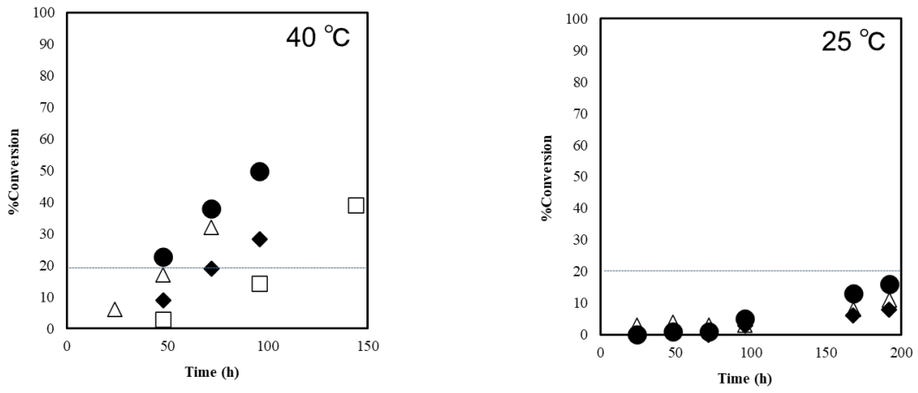


Fig. The conversion of GPE as a function of time during reaction of GPE-MHHPA with ZIF-8 (Δ) α-ZrP·2MIm (□), HX-3088 (◆), and HX-3722 (●).

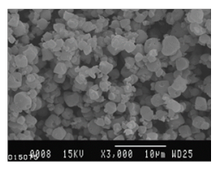
HX-3088, HX-3722 (●): 旭化成潜在性硬化剤
α-ZrP·2MIm (□): 2-methylimidaoleの層状リン酸ジルコニウム

Preparation of ZIFs

$Zn(NO_3)_2 \cdot 6H_2O$ + 2-ethylimidazole → ZIF-14

H_2O / 1-octanol, rt, 2.5 h

5 mmol　20 mmol　**収率** 47%



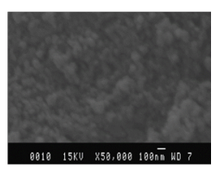
粒径 約1.8 μm

参考文献: *Chem. Matter.* **2018**, *30*, 4089.

$Zn(NO_3)_2 \cdot 6H_2O$ + benzimidazole → ZIF-7

DMF, rt, 48 h

10 mmol　85 mmol　**収率** 49%



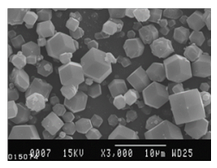
粒径 約50 nm

参考文献: *Mol. Pharmaceutics.* **2015**, *12*, 3158.

$Zn(OAc)_2 \cdot 2H_2O$ + benzimidazole → ZIF-11

MeOH / toluene, NH_3aq, rt, 3 h

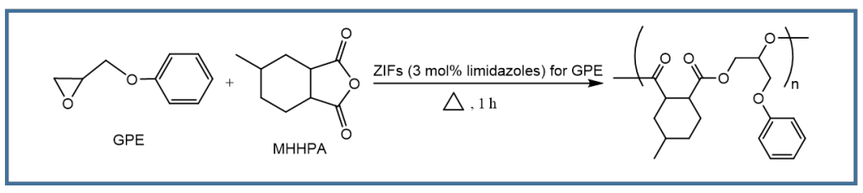
3.2 mmol　6.4 mmol　**収率** 99%



粒径 約6 μm

参考文献: *J. Am. Chem. Soc.* **2017**, *139*, 453.

Reaction of GPE-MHHPA with ZIFs



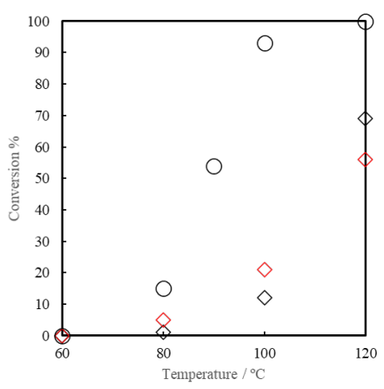
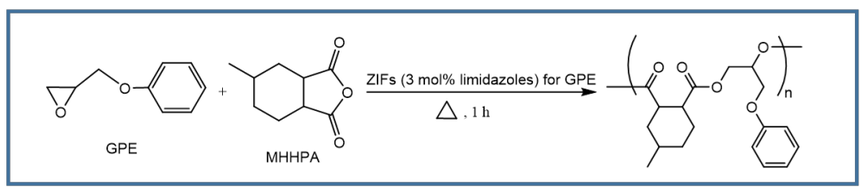


Fig. The conversion of GPE after 1h as a function of temperature during reaction with ZIF-7 (◇) ZIF-11 (◇), ZIF-14 (○).

反応性
ZIF-8 , ZIF-14 ＞ ZIF-7, ZIF-11

Storage stability of GPE-MHHPA with ZIF-7,11 and 14



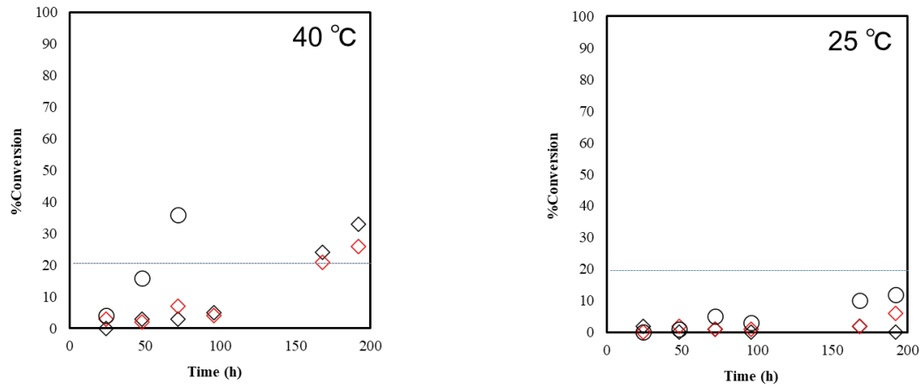
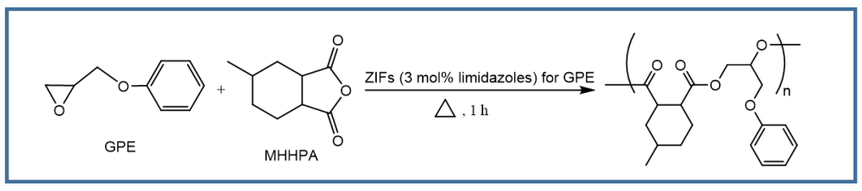


Fig. The conversion of GPE as a function of time during reaction of GPE-MHHPA with ZIF-7 (◇), ZIF-11 (◇), and ZIF-14 (○).

Summary

・ZIFs(Zeolitic Imidazolate Frameworks)をエポキシモノマー(GPE)と酸無水物(MHHPA)との反応に利用すると100℃以下で硬化できる熱潜在性硬化剤として機能した。

・25℃の貯蔵条件では、安定に保存できることが分かった。



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https://doi.org/10.1021/acsomega.1c02619

■お問い合わせ先
大阪工業大学　研究支援社会連携推進課
〒535-8585 大阪市旭区大宮 5-16-1
TEL：06-6954-4140　FAX：06-6954-4066
E-mail：OIT.Kenkyu@josho.ac.jp
https://www.research.oit.ac.jp/liaison-step/