CrystEngComm

COMMUNICATION

View Article Online View Journal | View Issue

Cite this: *CrystEngComm*, 2013, **15**, 9360

Received 9th June 2013, Accepted 24th August 2013

DOI: 10.1039/c3ce41072b

www.rsc.org/crystengcomm

Morphological diversity of Mn(III) metalloporphyrinbased nano- and microsized CPAs assembled *via* kinetic and thermodynamic controls and their application in heterogeneous catalysis[†]

Kyung Yeon Lee,^a Young Sun Lee,^a Sundol Kim,^a Hoang Mai Ha,^{ac} Sang-Eun Bae,^b Seong Huh,^b Ho Gyeom Jang^a and Suk Joong Lee^{*a}

A series of narrowly dispersed nano- and microsized CPAs has been prepared from a (porphyrin)M(III) biscarboxylic acid and $Co(OAc)_2$. The morphologies have been diversified from amorphous spheres to crystalline cubes by varying reaction periods. In addition, their heterogeneous catalytic olefin oxidations are successfully demonstrated.

Porous coordination polymers (PCPs), also called metalorganic frameworks (MOFs) for three-dimensional (3D) PCPs, have received much attention due to their potential applications in catalysis, gas storage, molecular recognition, separation, and optics.1 Currently, nano- and microsized PCPs (nPCPs or mPCPs) have often been reported with promising applications.² They could possess numerous advantages over both the PCPs and inorganic nanomaterials.³ Their novel and/or enhanced performances are frequently reported with potential applications in catalysis,⁴ separation,⁵ gas storage,⁶ drug delivery,⁷ biosensing, and imaging.⁸ Although a variety of nPCPs or mPCPs can be successfully obtained by controlling the growth conditions,⁹ their fabrication is still a major challenge because of the lack of information regarding the crucial factors for the precise control of particles during the synthesis. Furthermore, the translation of building blocks into well-defined structures, whose properties and functions are regulated at the building block level, still remains very challenging.¹⁰ In this regard, metalloporphyrins would be good building blocks for the construction of such functional materials because of their unique structure evidenced by a wide range of molecular architectures, such as molecular boxes, self-assembled arrays, and CPs with various applications in catalysis,¹¹ gas storage¹² and separation.¹³ In particular for the catalysis application, the utilization of CPs and MOFs would be the best strategy¹⁴ in order to avoid catalyst degradation *via* μ -oxo dimer formation of metalloporphyrinbased homogeneous catalysts.¹⁵

So, we describe herein the preparation and use as heterogeneous catalysts of Mn(m) metalloporphyrins that contain sizecontrolled amorphous and crystalline nano- and microsized coordination polymer aggregates (CPAs). Particularly, we focused on the conversion of kinetically controlled amorphous assemblies into thermodynamically controlled crystalline structures based on the self-assembly of a (porphyrin)Mn(m)biscarboxylic acid and Co(OAc)₂.

The Mn(III) metalloporphyrin has been prepared according to the literature procedure by the condensation between the corresponding dipyrromethane and aldehyde followed by hydrolysis and oxidative metallation (Scheme S1 in the ESI[†]).¹⁶ We employed a high-temperature stirring method for the selfassembly of nano- and microsized CPAs.17 A solution of the (porphyrin)Mn(III) biscarboxylic acid (1.9 mg) and Co(OAc)₂ (1.0 mg) in 0.5 mL of distilled dimethylformamide (DMF) was vigorously stirred at 90 °C for approximately 30 min, and a dark brown suspension was obtained. After cooling the end product, it was analyzed by scanning electron microscopy (SEM), which revealed that the suspension was a collection of fairly uniform microsized spheres with an approximate dimension of 850 \pm 70 nm in diameter. When the reaction is initiated in DMF at 90 °C, seeds are generated due to the fast interaction between the (porphyrin)Mn(III) biscarboxylic acid and the $Co(\pi)$ ion and they continue to grow until they are in a solution phase, and these microspheres become less soluble and start to precipitate from the DMF medium. IR spectroscopy analysis of this microsphere showed characteristic

^a Department of Chemistry, Korea University, 5 Anam-dong, Sungbuk-gu, Seoul 136-701, Republic of Korea. E-mail: slee1@korea.ac.kr; Fax: +82 2 925 4284; Tel: +82 2 3290 3145

^b Department Chemistry and Protein Research Center for Bio-Industry, Hankuk University of Foreign Studies, Yongin 449-791, Republic of Korea

^c Institute of Chemistry, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

[†] Electronic supplementary information (ESI) available: Complete experimental details of syntheses, compound characterization, catalysis details, additional SEM images, EDX, TGA, and adsorption/desorption isotherms. See DOI: 10.1039/c3ce41072b

View Article Online

bands of carboxyl at 1535 cm⁻¹ for the antisymmetric stretch and 1384 cm⁻¹ for the symmetric stretch with Δv_{as-sym} of 151 cm⁻¹, indicating the bidentate complex¹⁸ between the carboxylic acid and Co(π) ions (Fig. S2 in the ESI†). However, unreacted metalloporphyrins were identified from the dark purple solution that was obtained after the microsphere isolation.

Therefore, we have increased the reaction time to attempt to complete the reaction during the particle growth. By allowing longer reaction time, we would extend the assembly time of particles in DMF to offer a potential to obtain larger objects while maintaining the narrow particle size distribution.¹⁹ Therefore, we increased the reaction time by 45, 60, 75, 90, 120, and 200 min, respectively, and we obtained dark brown suspensions as expected. SEM analysis revealed that these suspensions were collections of uniform structures showing systematically modulated morphologies and sizes (Fig. 1, S3 and S4 in the ESI[†]). For example, when the reaction mixture was vigorously stirred at 90 °C for 45 min, the applelike structures (Fig. 1b), i.e., spheres with a small opening at the surface with approximately 650 ± 60 nm average diameter were obtained. This small opening grew bigger in size, and eventually, the morphology of structure changed into donuts (Fig. 1c) and stretched rubber bands (Fig. 1d) when the reaction time was increased.

Interestingly, the dark brown suspension became clear with no indications of particle formation, when the reaction time was extended to 300 min. However, a new dark brown suspension was again observed after cooling it at ambient temperature. SEM analysis revealed that the suspension was a collection of uniform nanospheres (Fig. 1e) with



Fig. 1 SEM images of (porphyrin)Mn(μ) biscarboxylic acid- and Co(OAc)₂-based nano- and microsized CPAs obtained at various reaction periods: (a) 30 (microsphere), (b) 45 (apple), (c) 60 (donut), (d) 90 (rubber band), (e) 300 (nanosphere), and (f) ~450 min (microcube).

approximately 120 ± 25 nm average diameter. When the reaction is initiated in DMF at 90 °C, the seeds are immediately generated and quickly grow into large microspheres until they are in a solution phase. As the reaction time is extended, the surfaces of microspheres are redissolved and a small opening is formed at the surface, thus producing "apples". The dissociated building blocks, (porphyrin)Mn(III) biscarboxylic acid and Co(II) ions, from microspheres are redeposited on the surface of particles, and thus, donuts and stretched rubber band structures are formed. This process continues until all the components are completely dissolved in the hot DMF. After cooling, redissolved building components become less soluble, precipitate from the DMF medium, and quickly generate nanospheres. As expected, these materials exhibit similar powder X-ray diffraction (PXRD) patterns with undetermined peaks, showing typical amorphous characteristics despite their difference in morphologies (Fig. S6 in the ESI[†]).

Remarkably, the dark brown suspension was again obtained upon extending the reaction time to 450 min at 90 °C, and narrowly dispersed microcubes, approximately $2.02 \pm 0.5 \mu m$ in length, were confirmed by SEM analysis (Fig. 1f). PXRD analysis revealed that these microcubes showed better crystallinity compared with other aggregates (Fig S6 in the ESI†). Redissolved building components from amorphous spheres are systematically assembled to produce stable crystalline microcubes with a longer reaction time. However, when the assemblies were carried out at 120 °C, morphologically polydispersed particles were obtained (Fig. S5 in the ESI†).

Thermogravimetric analysis (TGA) of the samples obtained at various reaction periods was performed to analyze the thermal stability of all the particles. The TGA curves show an initial weight loss due to solvent liberation and a high thermal stability up to 300 °C. They show continuous weight loss in the range from 300 °C to 600 °C due to the decomposition of frameworks (Fig. S7 in the ESI†). Furthermore, the samples of nanospheres and the microcubes show relatively large initial solvent-mediated weight losses, presumably due to somewhat large surface areas.

Therefore, the extreme cases of samples, i.e., microspheres, and microcubes were selected to investigate their surface area and gas sorption properties. Their volumetric gas sorption measurements were carried out using N2 and H2 at 77 K and CO2 at 196 K. As illustrated in Fig. 2, the N2 and H₂ adsorption isotherms of the microsphere sample show surface areas of 6.4 and 6.2 m² g⁻¹, respectively, while the sorption of CO_2 reveals an uptake value of 40.5 cm³ g⁻¹. The smaller surface area and gas uptake are attributed to the nonporous nature of the microspheres. In the microcube sample, the N₂ and H₂ adsorption isotherms reveal surface areas of 22.6 and 44.8 m^2 g⁻¹, respectively, while the sorption of CO_2 shows an uptake value of 61.8 cm³ g⁻¹. The surface area has been significantly increased due to the formation of crystalline particles, although the particle size has also been increased dramatically. However, the relatively small values of crystalline microcubes are presumably due to the



Fig. 2 Adsorption (filled symbols) and desorption (open symbols) isotherms of CO_2 (red) at 196 K and N_2 (black) and H_2 (green) at 77 K measured with microcubes (squares) and microspheres (circles).

decomposition of frameworks during the CHCl_3 exchange and/or evacuation processes.²⁰

With the easily accessible Mn(m) metalloporphyrin, microspheres, nanospheres and microcubes have been chosen to test their catalytic abilities in the oxidation of selected olefins with different sizes. The catalyst was prepared by immersing the corresponding particles in CH₂Cl₂ for 48 h followed by brief drying to prevent their frameworks from breaking down. As shown in Table 1, the particles provide effective catalytic performances for oxidations of most of the olefins. However, as expected, they display significant differences in conversion due to their surface area. For example, the conversion decreases dramatically with an increase in the size of spherical particles (micro vs. nano) because of the dramatic changes in surface areas which are attributed to the size of amorphous particles. This finding suggests that the reactions occur only at the external surfaces of amorphous and nonporous micro- and nanospheres whose surfaces provide easy accessibility for substrates. Therefore, the number of reaction sites mainly depends on the external surface area, which is inversely proportional to

Table 1Epoxidation a of olefins using CPAs of microspheres, nanospheres,and microcubes obtained from various reaction conditions

R^{1} CPA R^{1} R^{2} R^{2}					
Entry	1	2	3	4	5
Olefin	1-Hexene	1-Octene	Styrene	(Z)-Stilbene	(E)-Stilbene
Microsphere	63.7^{b}	40.5	48.42	16.6	10.2
	(86.8) ^c	(89.5)	(100)	(68.2)	(81.5)
Nanosphere	79.5	54.9	82.7	71.0	63.2
	(71.5)	(87.1)	(92.2)	(51.9)	(95.7)
Microcube	78.1	51.7	93.9	60.0	57.4
	(78.0)	(92.4)	(100)	(76.4)	(94.8)

^{*a*} Reaction conditions—substrate: 35 μmol, oxidant (2-(*tert*-butylsulfonyl) iodosylbenzene): 50 μmol, CPA: 5 mg, solvent (CH₂Cl₂): 1 mL, reaction time: 30 min, room temperature. ^{*b*} Conversion (%) determined by GC with hexadecane as an internal standard. ^{*c*} Epoxide selectivity (%).

the size of the particles.²¹ Crystalline microcubes display catalytic performance similar to that of nanospheres, suggesting that the reactions not only take place at the external surface of the particles but may also occur inside the cavities generated by the formation of PCP microcubes. This porosity is confirmed by N₂ sorption experiments, which reveal that they display higher surface area than amorphous spheres do, even though the size of crystalline microcubes is larger than that of spheres. These cavities were further verified when relatively bigger substrates were employed. For example, when stilbenes (entries 4 and 5, Table 1) are used with microcubes, significantly lower conversions are observed and similar values to nanospheres are observed for all other substrates. Apparently, the microcube provides relatively small cavities that do not permit the large substrates, such as stilbenes, to enter, and therefore, the reaction takes place only at the external surface.

Furthermore, the particles were separated after the reaction by centrifugation and reused four times. They showed outstanding reusability without significant catalytic activity losses (Table S1 in the ESI†), and the morphology of particles was retained after multiple oxidations (Fig. S8 in the ESI†). In addition, the catalyst lifetime was dramatically enhanced by the incorporation of Mn(m) metalloporphyrin catalyst into CPA from approximately 2 hours to more than 6 hours (Fig. S9 in the ESI†), suggesting that the degradation of catalysts *via* oxobridged dimer formation was successfully blocked by the immobilization of catalysts in CPAs.¹⁴

In summary, we have prepared a new class of narrowly dispersed nano- and microsized CPAs from (porphyrin)Mn(m) biscarboxylic acid and $Co(OAc)_2$. Diverse morphologies— amorphous microspheres, nanoapples, nanodonuts, nanospheres, and crystalline microcubes—have been prepared by changing the reaction times. PXRD patterns indicated that kinetically controlled structures, for example, microspheres, apples, donuts, and nanospheres, have amorphous natures, while the thermodynamically controlled microcube shows relatively high crystallinity. Furthermore, the oxidation of olefins has been successfully demonstrated with these Mn(m) metalloporphyrin-based CPAs, and they showed good reusability without losing their catalytic activity after reuse four times.

Acknowledgements

The authors acknowledge the financial support from the KRF programs (No. NRF2013R1A1A2007429 and NRF20100020209) of Korea funded by the MEST.

Notes and references

 (a) T. Lee, Z. X. Liu and H. L. Lee, *Cryst. Growth Des.*, 2011, 11, 4146; (b) Y. Ikezoe, G. Washino, T. Uemura, S. Kitagawa and H. Matsui, *Nat. Mater.*, 2012, 11, 1081.

- 2 (a) S. Diring, S. Furukawa, Y. Takashima, T. Tsuruoka and S. Kitagawa, *Chem. Mater.*, 2010, 22, 4531; (b) J. Reboul, S. Furukawa, N. Horike, M. Tsotsalas, K. Hirai, H. Uehara, M. Kondo, N. Louvain, O. Sakata and S. Kitagawa, *Nat. Mater.*, 2012, 11, 717.
- 3 A. Carne, C. Carbonell, I. Imaz and D. Maspoch, *Chem. Soc. Rev.*, 2011, **40**, 291.
- 4 S. Zhang, Q. Liu, M. Shen, B. Hu, Q. Chen, H. Li and J.-P. Amoureux, *Dalton Trans.*, 2012, 41, 4692.
- 5 A. J. Nunez, L. N. Shear, N. Dahal, I. A. Ibarra, J. Yoon, Y. K. Hwang, J.-S. Chang and S. M. Humphrey, *Chem. Commun.*, 2011, 47, 11855.
- 6 J. Duan, CrystEngComm, 2012, 14, 5381.
- 7 J. D. Rocca, D. Liu and W. Lin, Acc. Chem. Res., 2011, 44, 957.
- 8 D. Liu, R. C. Huxford and W. Lin, Angew. Chem., 2011, 123, 3780.
- 9 A. Umemura, S. Diring, S. Furukawa, H. Uehara, T. Tsuruoka and S. Kitagawa, *J. Am. Chem. Soc.*, 2011, 133, 15506.
- 10 S.-W. Kim, M. Kim, W. Y. Lee and T. Hyeon, *J. Am. Chem. Soc.*, 2002, 124, 7642.

- 11 D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2012, 51, 10307.
- 12 Z. Zhang, W.-Y. Gao, L. Wojtas, S. Ma, M. Eddaoudi and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2012, **51**, 9330.
- 13 C. Y. Lee, O. K. Farha, B. J. Hong, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, *J. Am. Chem. Soc.*, 2011, 133, 15858.
- 14 D. E. De Vos, M. Dams, B. F. Sels and P. A. Jacobs, *Chem. Rev.*, 2002, 102, 3615.
- 15 M. L. Merlau, M. d. P. Mejia, S. T. Nguyen and J. T. Hupp, *Angew. Chem., Int. Ed.*, 2001, 40, 4239.
- 16 S. Matsunaga, N. Endo and W. Mori, *Eur. J. Inorg. Chem.*, 2012, 30, 4885.
- 17 F. Xing, Y. Bai, X. He, J. Jia, D. Zhou, M. Shao and S. Zhu, *CrystEngComm*, 2012, 14, 4312.
- 18 H. Shahroosvand, F. Nasouti, A. Sousaraei, E. Mohajerani and A. Khabbazi, *Phys. Chem. Chem. Phys.*, 2013, 15, 9899.
- 19 D.-S. Moon and J.-K. Lee, Langmuir, 2012, 28, 12341.
- 20 D. H. Lee, S. Kim, M. Y. Hyun, J.-Y. Hong, S. Huh, C. Kim and S. J. Lee, *Chem. Commun.*, 2012, 48, 5512.
- 21 A. Carne, C. Carbonell, I. Imaz and D. Maspoch, *Chem. Soc. Rev.*, 2011, 40, 291.