

FSM-16: A Recyclable Mesoporous Acid Promoter for *meso*-Tetraarylporphyrin Synthesis

Tomotaka Shinoda,^a Yusuke Izumi^a and Makoto Onaka^{*b}

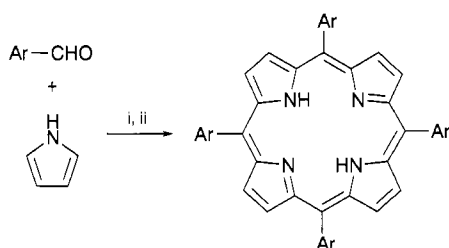
^a Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464-01, Japan

^b Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153, Japan

A new porous silicate, FSM-16 with a pore size of 2.8 nm in diameter is remarkably effective for *meso*-tetraarylporphyrin synthesis and can be used repeatedly without any efficiency loss after calcination at 500 °C in air.

Recently, highly ordered mesoporous materials, FSM-16,¹ MCM-41² and Ti-HSM³ have been discovered and used as reaction media where photoinduced electron transfer reactions proceed⁴ and as catalysts in the oxidation of aromatic compounds.³ We previously reported that montmorillonite K10 (commercially available sulfuric acid-treated montmorillonite) gave *meso*-tetraalkylporphyrins in high yields from aliphatic aldehydes and pyrrole⁵ because the mesopores of K10 are capable of forming the cyclic intermediate porphyrinogen from the linear precursor tetrapyrromethane.⁶ In comparison, in the synthesis of *meso*-tetraalkylporphyrin K10 was not adequately porous and resulted in low synthetic yields.⁷ We have thus been focusing our attention on discovering alternative porous solids to provide *meso*-tetraarylporphyrins in higher efficiency than K10. We have studied FSM-16 because of its uniform, honeycomb-like pore structure with controllable pore sizes in the range 1.5–10 nm as well as tunable acid properties depending on the content of alumina included.¹

At first, three kinds of FSM-16 containing 4 mass% of Al₂O₃ with pore sizes of 2.0, 2.8 and 3.4 nm in diameter [abbreviated as FSM-16 (2.0 nm) FSM-16 (2.8 nm) and FSM-16 (3.4 nm), respectively] were used in the *meso*-tetraphenylporphyrin (TPP) synthesis from benzaldehyde and pyrrole as shown in Scheme 1.[†] These FSM-16's were found to have almost the same acid site density of $(24 \pm 5) \times 10^{-5}$ mmol m⁻² with $H_0 \leq -5.6$ in CH₂Cl₂ by using Hammett indicators. Apparently, the difference in the pore diameter of the FSM-16 reflected the efficiencies in the porphyrin formation as shown in Table 1: FSM-16 (2.8 nm) gave a higher TPP yield of 38% in comparison with FSM-16 (2.0 nm) (18%) and FSM-16 (3.4 nm) (28%) as well as K10 (30%) which has a broad mesopore



Scheme 1 *meso*-Tetraarylporphyrin synthesis. Reagents and conditions: i, solid acid, CH₂Cl₂, room temp.; ii, *p*-chloranil, reflux, 1 h.

Table 1 TPP Synthesis^a

Solid acid	<i>t</i> /h	Yield (%)
FSM-16 (2.0 nm)	1	18
FSM-16 (2.8 nm)	1	38
FSM-16 (3.4 nm)	1	28
K10	2	30

^a PhCHO (1 mmol, 10⁻² mol dm⁻³), pyrrole (1 mmol, 10⁻² mol dm⁻³), solid acid (1 g) in CH₂Cl₂ (100 ml).

diameter distribution of 2–10 nm.⁶ These results indicate that the uniform mesopores in a certain nanometer range are suitable reaction media for TPP formation.

FSM-16 (2.8 nm) was used in the synthesis of a variety of *meso*-tetraarylporphyrins.[†] The comparison of a porous solid acid, FSM-16 (2.8 nm) with a conventional liquid acid, BF₃·OEt₂⁸ is summarized in Table 2. Irrespective of the kind of substituted functionalities and their positions on the benzene ring, it was found that the *meso*-tetraarylporphyrin yields on FSM-16 (2.8 nm) were almost comparable to the yields by BF₃·OEt₂ except in the case of Ar = *o*-ClC₆H₄.

Although FSM-16 (2.8 nm) can be recovered by filtration on a suction funnel after the porphyrin formation reactions, the surface of the dark purple FSM-16 inevitably adsorbed by-products, such as polypyrromethanes and polypyrromethenes, in addition to excess *p*-chloranil and its reduction products. If the FSM-16 can be recycled, its use in porphyrin synthesis will be increased. When BF₃·OEt₂ and CF₃CO₂H are used as acid promoters for porphyrin synthesis they have to be neutralised with bases to get the product, and it is impossible to reuse the acids. In order to regenerate FSM-16, we treated the recovered FSM-16 (2.8 nm) with calcination in air at 500 °C for 3 h. After calcination, the surface of the FSM-16 turned white, like the unused FSM-16. We used the regenerated FSM-16 as an acid promoter in the same TPP synthesis. Fig. 1 indicates that FSM-16 (2.8 nm) could be used repeatedly in constant yields of 38–45% during 6 successive runs. As a control experiment, K10 was also treated with the same calcination procedure as in the case of FSM-16, and applied repeatedly to the TPP synthesis. Interestingly, the K10 had no activity in the second run. After calcination of K10 in air at 500 °C for 3 h, both the acid strength and the acid site density of the regenerated K10 decreased, compared with the unused K10.[‡] This high temperature-durable property of FSM-16 leads to the recyclable use of the silicate in the preparation of *meso*-tetraarylporphyrin in a preparative scale.

This report is the first successful application of a new mesoporous material, FSM-16, to fine-chemicals synthesis, making the best use of the hexagonal channels as reaction media in nano dimensions where the copolymerisation of aldehydes

Table 2 *meso*-Tetraarylporphyrin syntheses^a

Ar	Yields (%)	
	FSM-16 (2.8 nm)	BF ₃ ·OEt ₂
<i>o</i> -MeC ₆ H ₄	31	45 ^b
<i>p</i> -MeC ₆ H ₄	37	28
<i>o</i> -MeOC ₆ H ₄	41	20 ^b
<i>p</i> -MeOC ₆ H ₄	Trace	Trace
<i>o</i> -ClC ₆ H ₄	3	28 ^b
<i>p</i> -ClC ₆ H ₄	7	Trace

^a Aldehyde (1 mmol, 10⁻² mol dm⁻³), pyrrole (1 mmol, 10⁻² mol dm⁻³), FSM-16 (2.8 nm) (1 g), BF₃·OEt₂ (0.1 mmol, 10⁻³ mol dm⁻³) in CH₂Cl₂ (100 ml). ^b Data were quoted from ref. 8.

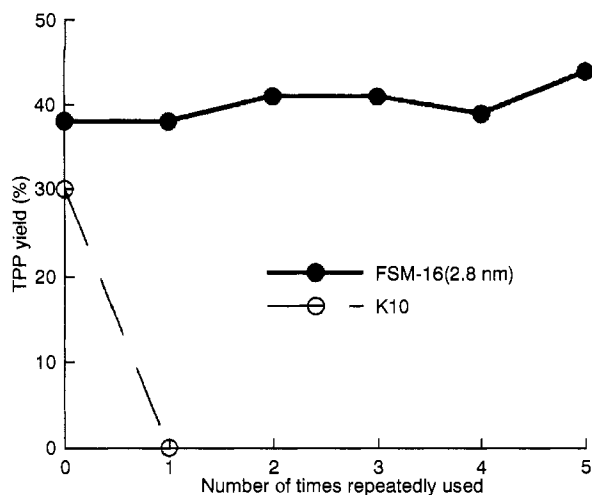


Fig. 1 Repeated use of FSM-16 (2.8 nm) and K10 in TPP synthesis

and pyrroles and the subsequent intramolecular cyclisation to porphyrinogens are directed to proceed predominantly.⁶

We thank Mr Shinji Inagaki of Toyota Central R & D Laboratories for the kind supply of FSM-16.

Received, 13th June 1995; Com. 5/03833B

Footnotes

† A typical procedure is as follows. FSM-16 containing 4 mass% of Al_2O_3 (1 g) was activated in a 200 ml flask at 120 °C and below 0.5 Torr for 3 h. To the activated FSM-16 were added dry CH_2Cl_2 (100 ml), aromatic aldehyde (1 mmol), and pyrrole (1 mmol) in an N_2 atmosphere. The stirring

was continued for 1 h at room temp. without exposure to light. Then solid *p*-chloranil (0.75 mmol) was added and the mixture was gently refluxed at 45 °C for 1 h. Solid materials were removed through a glass filter and washed with EtOAc (60 ml). The combined filtrate was condensed and adsorbed on Florisil (2 g). The adsorbate was placed on the top of an Al_2O_3 (Merck neutral aluminum Oxide 90, Activity II-III, 100 g) column and developed with hexane- CH_2Cl_2 . The purple crystals of porphyrin were precipitated by methanol addition to the condensed porphyrin fraction, collected, and dried at 80 °C and below 0.5 Torr for 6 h.

‡ After the calcination, the regenerated FSM-16 (2.8 nm) still kept almost the same maximum acid strength of $H_0 \leq -8.2$ in CH_2Cl_2 , and the acid site density of $(24 \pm 5) \times 10^{-5} \text{ mmol m}^{-2}$ with $H_0 \leq -5.6$ in CH_2Cl_2 as unused FSM-16. As for K10, however, the maximum acid strength of the calcined K10 was weakened to $-8.2 < H_0 \leq -5.6$ in CH_2Cl_2 and the acid site density with $H_0 \leq -5.6$ was diminished to $(28 \pm 5) \times 10^{-5} \text{ mmol m}^{-2}$ in CH_2Cl_2 , while unused K10 originally had $H_0 \leq -8.2$ in acid strength and $(49 \pm 8) \times 10^{-5} \text{ mmol m}^{-2}$ in the acid site density.

References

- 1 S. Inagaki, Y. Fukushima, A. Okada, T. Kurauchi, K. Kuroda and C. Kato, *Proc. 9th Int. Zeolite Conf. Vol. 1*, ed R. von Ballmoos, J. B. Higgins and M. M. J. Treacy, Butterworth-Heinemann, Montreal 1992, p. 305; S. Inagaki, Y. Fukushima and K. Kuroda, *J. Chem. Soc., Chem. Commun.*, 1993, 680.
- 2 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
- 3 P. T. Tanev, M. Chibwe and T. J. Pinnavaia, *Nature*, 1994, **368**, 321.
- 4 A. Corma, V. Fornés, H. García, M. A. Miranda and M. J. Sabater, *J. Am. Chem. Soc.*, 1994, **116**, 9767.
- 5 M. Onaka, T. Shinoda, Y. Izumi and E. Nolen, *Chem. Lett.*, 1993, 117.
- 6 T. Shinoda, M. Onaka, and Y. Izumi, *Chem. Lett.*, 1995, **493**, 495.
- 7 M. Onaka, T. Shinoda, Y. Izumi and E. Nolen, *Tetrahedron Lett.*, 1993, **34**, 2625.
- 8 J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney and A. M. Marguerettaz, *J. Org. Chem.*, 1987, **52**, 827; J. S. Lindsey and R. W. Wagner, *J. Org. Chem.*, 1989, **54**, 828.