



## Mesoporous Materials Synthesized by Novel Reflux Synthesis Method

Open  
Access

Thiam Leng Chew<sup>1,2,\*</sup>, Cheng Kong Choy<sup>1</sup>, Yin Fong Yeong<sup>1,2</sup>, Jun Wei Lim<sup>3</sup>, Abdul Latif Ahmad<sup>4</sup>, Chii Dong Ho<sup>5</sup>

- <sup>1</sup> Department of Chemical Engineering, Faculty of Engineering, Universiti Teknologi Petronas, 32610 Bandar Seri Iskandar, Perak, Malaysia  
<sup>2</sup> CO<sub>2</sub> Research Centre (CO2RES), Institute of Contaminant Management, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia  
<sup>3</sup> Department of Fundamental and Applied Sciences, Universiti Teknologi Petronas, 32610 Bandar Seri Iskandar, Perak, Malaysia  
<sup>4</sup> School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Penang, Malaysia  
<sup>5</sup> Department of Chemical and Materials Engineering, Tamkang University, New Taipei City 25137, Taiwan

### ARTICLE INFO

#### Article history:

Received 27 February 2018  
Received in revised form 10 April 2018  
Accepted 29 May 2018  
Available online 23 July 2018

#### Keywords:

Mesoporous silica materials, MCM-48, porous characteristic, Reflux synthesis method

### ABSTRACT

MCM-48 is an important mesoporous silica material for current large-scale applications in key fields of the chemical industry including CO<sub>2</sub> separation. Despite conventional hydrothermal synthesis used to produce mesoporous silica materials, but there is still research efforts needed to seek for the alternative for the production of mesoporous silica materials. In the current project, reflux synthesis method was studied and compared with conventional hydrothermal synthesis for the synthesis of MCM-48 samples. The synthesis temperature was varied (60 – 100 °C) at constant 2 days for both methods. The synthesized samples were characterized for its property using different analytical techniques including scanning electron microscope (SEM), x-ray powder diffraction (XRD), Fourier transform infrared microscope (FTIR), Thermogravimetric Analysis (TGA) and Brunauer-Emmett-Teller (BET). In current project, spherical particles of MCM-48 were successfully synthesized by reflux synthesis method at 100 °C for 2 days as well as conventional hydrothermal synthesis at 100 °C for 2 days, as observed from SEM and XRD analysis. From the BET analysis, the MCM-48 samples produced by reflux synthesis and conventional hydrothermal synthesis at 100 °C for 2 days displayed comparable pore characteristic with the commercial MCM-48 and MCM-48 reported by other researchers.

Copyright © 2018 PENERBIT AKADEMIA BARU - All rights reserved

## 1. Introduction

Nanoporous materials are extremely important as the backbone of current large-scale applications in key fields of the chemical industry [1]. These materials consist of high specific surface areas, regular organic or inorganic framework supporting a regular, well-defined pore sizes and structure, and functional sites [2]. Nanoporous materials are widely used in the field of molecular adsorption, molecular storage and CO<sub>2</sub> separation, sensing, catalysis, drug delivery, and so forth [3].

\* Corresponding author.

E-mail address: [thiamleng.chew@utp.edu.my](mailto:thiamleng.chew@utp.edu.my) (Thiam Leng Chew)

According to IUPAC, nanoporous materials can be divided into 3 categories which are microporous materials (0.2 – 2nm), mesoporous materials (2 – 50nm), and macroporous materials (50 – 1000nm)[4]. Mesoporous materials have gained great interest and research effort in the synthesis, characterisation, functionalization, molecular modelling and design since first procedure of formation of mesoporous silica materials was patented around the year of 1970, followed by production of mesoporous materials by Japan researchers and Mobil Corporation laboratories, respectively [5-11]. Mesoporous silica material is a mesoporous molecular sieves form of silica. There are few common types of mesoporous silica material, such as MCM-41, MCM48 and MCM-50, which composed of amorphous silica wall, and consisted of long range ordered framework with constant mesopores and large surface area. In recent nanotechnology development, it is getting much attention in different fields, such as sorption, gas sensing and ion exchange. Henceforth, the field of mesoporous silica materials, has undergone significant developments and steadily grown in the past decades.

Conventional hydrothermal synthesis is the common method to produce MCM-48. This method involves heating of the solution precursor under certain temperature and autogenous pressure in a closed reactor. However, there is still research efforts in exploring for alternative synthesis method for MCM-48, with the aim to produce MCM-48 with better quality. To the best of our knowledge, there is no works reported on the synthesis of MCM-48 by using reflux synthesis method. Hence, the current study focused on synthesis of MCM-48 materials using reflux synthesis method as well as conventional hydrothermal synthesis. The synthesis temperature was varied from 60 to 100 °C to study its effect on the properties of the formed MCM-48. The formed materials were characterised for its property using different analytical techniques including scanning electron microscope (SEM), X-ray powder diffraction (XRD), Fourier transform infrared microscope (FTIR), Thermogravimetric Analysis (TGA) and Brunauer-Emmett-Teller (BET). MCM-48 materials formed by reflux synthesis method and conventional hydrothermal synthesis in current study were compared.

## 2. Methodology

### A. Materials

The chemical materials used are deionised water (H<sub>2</sub>O), hexadecyltrimethylammonium bromide, CTAB (≥99%), sodium hydroxide, NaOH and tetraethyl orthosilicate, TEOS (≥98%).

### B. Synthesis of the Samples

The solution precursor was prepared according to the mole ratio recipe which is 1TEOS:0.59CTAB:0.5NaOH:61H<sub>2</sub>O. CTAB and NaOH were dissolved into deionised water. The mixture solution was stirred at 35 °C for 2 hours and followed by addition of TEOS. The resultant mixture was stirred for another 30 minute. The final solution precursor was subjected to conventional hydrothermal synthesis and reflux synthesis methods separately for the synthesis of MCM-48. For heating via conventional hydrothermal synthesis, the solution precursor was loaded and sealed in a stainless steel vessel. This vessel was heated up to the desired synthesis temperature for 2 days in an oven. However, for heating through reflux synthesis method, the solution precursor was loaded into three head round bottom flask with condenser set. This flask was heated at the desired synthesis temperature for 2 days in a heating mantle. The planned synthesis temperature studied for synthesis of MCM-48 via conventional hydrothermal synthesis and reflux synthesis methods, with the names of the samples, are shown in Table 1. Afterwards, the precipitate was filtered and rinsed with deionised water, and then dried at 100 °C temperature overnight by using an oven. Lastly, the sample was calcined at 550 °C for 6 hours by using a furnace.

**Table 1**

Planned Experimental Set of Synthesis Conditions (Synthesis Temperature) for Synthesis of Samples via both Synthesis Methods for 2 Days

Conventional Hydrothermal Synthesis Method [H]	Synthesis Temperature (°C)				
	60	70	80	90	100
Name of the samples	H2,60	H2,70	H2,80	H2,90	H2,100

Reflux Synthesis Method [R]	Synthesis Temperature (°C)				
	60	70	80	90	100
Name of the samples	R2,60	R2,70	R2,80	R2,90	R2,100

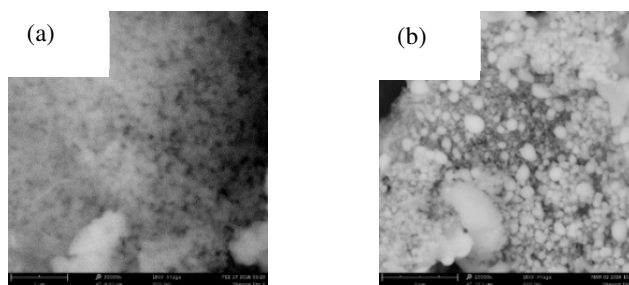
### C. Characterization of the Samples

Different characterization methods were used in this research project for the analysis of properties of the samples. FTIR analysis on the samples was performed using the FTIR model of Spectrum One or BX. The wave range for FTIR was between 450 – 4000  $\text{cm}^{-1}$ . The samples were subjected to  $\text{N}_2$  adsorption studies at 77K using BET machine (BEL JAPAN, INC, Japan, model: Belsorp). TGA analysis of the samples was performed using TGA model of PYRIS 1. The TGA was operated under the flow of nitrogen gas, with temperature between 25°C and 800°C. The heating rate for the operation condition of TGA was 10°C/ min. SEM model of SUPRA 55VP was used to study the morphology of the samples. The samples were tested for XRD analysis by using D8 Discover Advance model manufactured by Bruker, Germany. The diffraction angles were in the range of 1° to 50°.

## 3. Results and Discussion

### A. Scanning Electron Microscope (SEM)

Figure 1 show the SEM images of sample synthesised by conventional hydrothermal synthesis and reflux synthesis methods at 100 °C for 2 days in current project. The presence of spherical particles is observed in the SEM images of the samples. The spherical particles are believed to be MCM-48 particles, as the similar spherical MCM-48 particles [12]. Therefore, MCM-48 particles were successfully synthesised by reflux synthesis method as well as conventional hydrothermal synthesis in current project.



**Fig. 1.** SEM images of samples (a) H2,100 and (b) R2,100

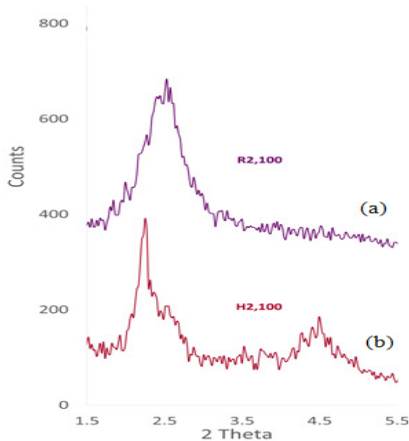
### B. X-Ray Powder Diffraction (XRD)

Tables 2 shows the matching of XRD's  $2\theta$  values between the samples synthesised in current project and the MCM-48 samples synthesised from previous researchers [13,14]. It is observed from Tables 2 that only the samples H2,90, H2,100, and R2,100 partially or completely matched the reported XRD's  $2\theta$  values of MCM-48. The XRD result shows the partial or complete formation MCM-48 for the samples H2,90, H2,100, and R2,100. The XRD patterns illustrated Bragg peaks in the  $2\theta$  between  $1^\circ$  and  $50^\circ$  range which reflected the various Miller Indices and its interplanar spacing was indicated by MCM-48 arrangement of plane in cubic  $la3d$  structure. The XRD patterns of calcined mesoporous silica particles, especially of the samples H2,100 and R2,100, were comprised of the significant MCM-48's peak between  $2.25^\circ$  and  $2.53^\circ$  range (211).

**Table 2**

Matching Calcined Sample with Past Researches Data based on MCM-48's Miller Indices and Approximated Degrees  $2\theta$ .

DATA	SAMPLES	MCM-48 MILLER INDICES [h,l,k] (APPROXIMATED DEGREES $2\theta$ )							
Past Researches Data from Other Researcher	[12]	[2 1 1] ( $\sim 2.70^\circ$ )	[2 2 0] ( $\sim 3.00^\circ$ )	[3 2 1] ( $\sim 3.35^\circ$ )	[4 0 0] ( $\sim 3.60^\circ$ )	[4 2 0] ( $\sim 4.05^\circ$ )	[3 3 2] ( $\sim 4.20^\circ$ )	[4 2 2] ( $\sim 4.40^\circ$ )	[4 3 1] ( $\sim 4.60^\circ$ )
Matching Miller Indices based on approximated degree $2\theta$									
Data of Current Project	R2,60	X	X	X	X	X	X	X	X
	R2,70	X	X	X	X	X	X	X	X
	R2,80	X	X	X	X	X	X	X	X
	R2,90	X	X	X	X	X	X	X	X
	R2,100	√	√	√	√	√	√	√	X
	H2,60	X	X	X	X	X	X	X	X
	H2,70	X	X	X	X	X	X	X	X
	H2,80	X	X	X	X	X	X	X	X
	H2,90	√	√	X	X	X	X	X	X
	H2,100	√	√	√	√	√	√	√	√



**Fig. 2.** XRD pattern for samples (a) R2,100 and (b) H2,100

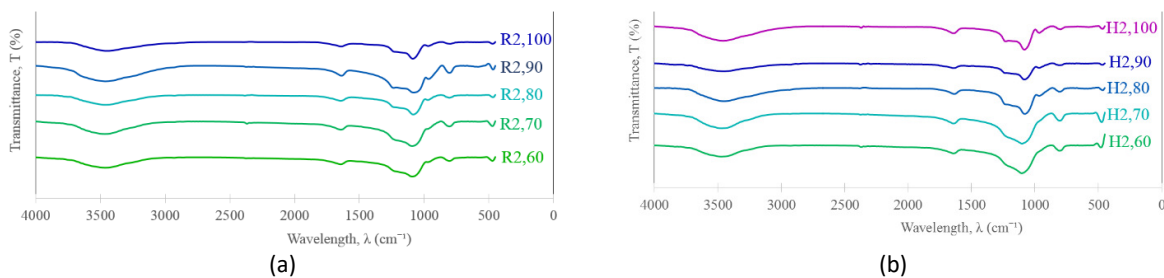
Figure 2 shows XRD pattern for samples (a) R2,100 and (b) H2,100. It is an interesting finding that MCM-48 samples were obtained for H2,100 and R2,100 samples due to the matching of XRD's 2 $\theta$  values as shown in Table 2 [15]. The R2,100 sample also displayed comparable XRD peak intensity with H2,100 samples as shown in Figure 2. Hence, it was proved that reflux synthesis method at 100 °C for 2 days was able to produce high quality MCM-48 particles [14].

### C. Fourier Transform Infrared Spectroscopy (FTIR)

Table 3 shows the list of type of bonding represented by the FTIR spectrum. The FTIR spectrum for all the samples produced in current project matched with the spectrum of MCM-48 reported in the literature [16-19]. The symmetric and asymmetric of CH<sub>2</sub> stretching vibration, which is attributed to CTAB's FTIR bands characteristic, in the range of 2850 – 2950 cm<sup>-1</sup>[20], was not found in the samples' FTIR spectrum. This is because the CTAB was removed from the samples by calcination process prior to the FTIR analysis of the calcined samples. Figure 3 show the FTIR spectrum of calcined samples synthesised by conventional hydrothermal synthesis and reflux synthesis methods, respectively at different synthesis temperature for 2 days. It is observed that all the samples displayed similar FTIR spectrums.

**Table 3**  
 Type of Bonding Represented by the FTIR Spectrum

Characteristic Band of FTIR Spectrum (Wavelength [ $\lambda$ ], cm <sup>-1</sup> )	Type of Bonding	Reference
451 – 480	Si-O [Bending]	
795 – 810	Si-O-Si [Asymmetric Stretching]	
959 – 980	Si-OH [Symmetric Stretching]	[16-19]
1061 – 1104	Si-O-Si [Symmetric Stretching]	
1630 – 1647	H <sub>2</sub> O	
3444 – 3471	Si-OH	



**Fig. 3.** FTIR spectrum of calcined samples which were synthesised by using (a) reflux synthesis method and (b) conventional hydrothermal synthesis method at various synthesis temperature for 2 days

### D. Thermogravimetric Analysis (TGA)

Table 4 shows the weight percentage loss of samples produced by both methods in the current project. The weight loss of the samples was due to (1) desorption of physically adsorbed water at 30-120 °C and (2) condensation of silanol groups (Si-OH) region to form siloxane at 120-768 °C. The TGA

weight loss curves for the samples produced in the current studies are comparable with the previous work [21].

**Table 4**  
Weight Percentage Loss of Samples for both Methods at Different Synthesis Temperature

Samples	Weight Percentage Loss, wt%		Total Weight Loss
	Desorption of Physically Absorbed Water At 30°C – 120°C	Condensation of Surface Silanol Group (Si-OH) At 120°C – 768°C	
R2,60	2.66 – 16.88	2.29 – 5.49	4.95 – 20.84
R2,70			
R2,80			
R2,90			
H2,60	5.21 – 12.31	2.11 – 6.17	7.32 – 16.48
H2,70			
H2,80			
H2,90			
H2,100			

#### E. Brunauer-Emmett-Teller (BET) analysis

Table 5 shows the comparison of pore characteristic of calcined samples produced in current project with MCM-48 of commercial specification and of past researches data. The pore diameter of R2,100 and H2,100 is 2.41 nm and 2.43 nm, respectively, indicating comparable pore diameters of two samples which were produced by reflux synthesis method and conventional hydrothermal synthesis method. Furthermore, synthesis temperature of MCM-48 materials' does not have significant effect on MCM-48's pore diameter, but it does affect significantly the thickness of silica wall because the reaction rates of hydrolysis and condensation of silicate source are highly temperature dependent [22]. In current project, the calcined samples R2,100 and H2,100 displayed comparable pore characteristic with the commercial MCM-48 and MCM-48 reported in past researches data as shown in Table 5.

**Table 5**  
The Comparison of Pore Characteristic of Calcined Samples Produced in Current Project with MCM-48 of Commercial Specification and of Past Researches Data

DATA	SAMPLES	PORE CHARACTERISTICS	
		Specific Surface Area, $a_{\text{SBET}}$ ( $\text{m}^2/\text{g}$ )	Pore Diameter, $d_p$ (nm)
Commercial MCM-48	[24]	1214	3.70
	[15]	1171	2.69
Past Researches Data (MCM-48)	[23]	-	2.43
	[21]	1290	2.58
	[25]	1389	2.90
	[26]	1332	2.70
	[27]	1202	-
	[28]	1166	3.60
	[29]	921	2.60
	[30]	1291	-
Current Project	R2,100	1230	2.41
	H2,100	1316	2.43

## 4. Conclusion

In current project, the synthesis of MCM-48 samples via conventional hydrothermal synthesis and reflux synthesis method was investigated by changing the synthesis temperature (60 – 100 °C) for 2 days. The synthesized samples were characterised for its properties using different analytical techniques including FTIR, BET, SEM, TGA and XRD. The SEM and XRD analysis shows that spherical particles of MCM-48 samples were successfully synthesised by conventional hydrothermal synthesis as well as reflux synthesis methods. MCM-48 sample with pore diameter of 2.43 nm and 2.41 nm was obtained, via conventional hydrothermal synthesis for 2 days at 100 °C and reflux synthesis for 2 days at 100 °C respectively, which is comparable to the pore diameter of commercial MCM-48 samples. It can be concluded that hydrothermal synthesis and reflux synthesis methods for 2 days at 100 °C in current project, were able to produce MCM-48 samples with properties comparable to the MCM-48 reported by other researchers, as results of analysis from different characterisation methods.

## Acknowledgement

The authors acknowledge the support provided by LRGS grant (grant number: 304/PJKIMIA/6050296/U124). The financial and technical support from LRGS grant (cost centre: 0153AB-L12), KURITA WATER ENVIRONMENT FOUNDATION, KWEF (cost centre: 0153AB-M10), Institute of Contaminant Management, Universiti Teknologi PETRONAS and CO<sub>2</sub> Research Centre (CO2RES), Universiti Teknologi PETRONAS are also acknowledged.

## References

- [1] Gordon Research Conferences [GRC]. Nanoporous materials and their applications, 2015. Available: <https://www.grc.org/programs.aspx?id=15022>.
- [2] Russo, P. A., MML Ribeiro Carrott, P. J. M. Carrott, J. M. Lopes, F. Ramôa Ribeiro, and João Rocha. "Structure and catalytic activity of Al-MCM-48 materials synthesised at room temperature: influence of the aluminium source and calcination conditions." *Microporous and Mesoporous Materials* 114, no. 1-3 (2008): 293-302.
- [3] Xu, Qiang. *Nanoporous materials: synthesis and applications*. CRC Press, 2013.
- [4] Rouquerol, J., D. Avnir, C. W. Fairbridge, D. H. Everett, J. M. Haynes, N. Pernicone, J. D. F. Ramsay, K. S. W. Sing, and K. K. Unger. "Recommendations for the characterization of porous solids (Technical Report)." *Pure and Applied Chemistry* 66, no. 8 (1994): 1739-1758.
- [5] Beck, Jeffrey Scott, J. C. Vartuli, W. Jelal Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu et al. "A new family of mesoporous molecular sieves prepared with liquid crystal templates." *Journal of the American Chemical Society* 114, no. 27 (1992): 10834-10843.
- [6] Hanns, Biegler, and Kallrath Gottfried. "Process for producing silica in the form of hollow spheres." U.S. Patent 3,383,172, issued May 14, 1968.
- [7] Chiola, Vincent, Joseph E. Ritsko, and Clarence D. Vanderpool. "Process for producing low-bulk density silica." U.S. Patent 3,556,725, issued January 19, 1971.
- [8] Max, Lu GQ, and Zhao Xiu Song, eds. *Nanoporous materials: science and engineering*. Vol. 4. World Scientific, 2004.
- [9] Le Page, Madeleine, Raymond Beau, and Jacques Duchene. "Porous silica particles containing a crystallized phase and method." U.S. Patent 3,493,341, issued February 3, 1970.
- [10] Trewyn, Brian G., Igor I. Slowing, Supratim Giri, Hung-Ting Chen, and Victor S-Y. Lin. "Synthesis and functionalization of a mesoporous silica nanoparticle based on the sol-gel process and applications in controlled release." *Accounts of chemical research* 40, no. 9 (2007): 846-853.
- [11] Sang, Wong Yean, and Pei Ching Oh. "Tailoring MCM-41 mesoporous silica particles through modified sol-gel process for gas separation." *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* 42, no. 1 (2018): 46-56
- [12] Zhao, Dongyuan, Jianglin Feng, Qisheng Huo, Nicholas Melosh, Glenn H. Fredrickson, Bradley F. Chmelka, and Galen D. Stucky. "Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores." *science* 279, no. 5350 (1998): 548-552.
- [13] Kresge, Charles T., and Wieslaw J. Roth. "The discovery of mesoporous molecular sieves from the twenty year perspective." *Chemical Society Reviews* 42, no. 9 (2013): 3663-3670.



- [14] Nishiyama, Norikazu, Dong Huy Park, Akihiro Koide, Yasuyuki Egashira, and Korekazu Ueyama. "A mesoporous silica (MCM-48) membrane: preparation and characterization." *Journal of Membrane Science* 182, no. 1-2 (2001): 235-244.
- [15] Zhao, Wei, Ming Qin, Lina Wang, Jinglong Chu, Jingkui Qu, Shaohua Li, Quanzhi Li, and Tao Qi. "Synthesis of submicron spherical Fe-MCM-48 with actual gyroid like structure." *Journal of colloid and interface science* 384, no. 1 (2012): 81-86.
- [16] Galeener, Frank L., A. J. Leadbetter, and M. W. Stringfellow. "Comparison of the neutron, Raman, and infrared vibrational spectra of vitreous Si O 2, Ge O 2, and Be F 2." *Physical Review B* 27, no. 2 (1983): 1052.
- [17] Kalita, Banani, Prodeep Phukan, and Anup K. Talukdar. "Oxidation of anisole over MCM-48 materials modified by incorporation of transition and inner transition metals." *Catalysis Science & Technology* 2, no. 11 (2012): 2341-2350.
- [18] Romero, Antonio A., Maria D. Alba, and Jacek Klinowski. "Aluminosilicate mesoporous molecular sieve MCM-48." *The Journal of Physical Chemistry B* 102, no. 1 (1998): 123-128.
- [19] Wangcheng, Z. H. A. N., L. U. Guanzhong, G. U. O. Yanglong, G. U. O. Yun, W. A. N. G. Yanqin, W. A. N. G. Yunsong, Zhigang ZHANG, and L. I. U. Xiaohui. "Synthesis of cerium-doped MCM-48 molecular sieves and its catalytic performance for selective oxidation of cyclohexane." *Journal of Rare Earths* 26, no. 4 (2008): 515-522.
- [20] Kim, Wun-gwi, Sunho Choi, and Sankar Nair. "Swelling, functionalization, and structural changes of the nanoporous layered silicates AMH-3 and MCM-22." *Langmuir* 27, no. 12 (2011): 7892-7901.
- [21] Kim, Sangil, Junichi Ida, Vadim V. Guliants, and Y. S. Lin. "Tailoring pore properties of MCM-48 silica for selective adsorption of CO<sub>2</sub>." *The Journal of Physical Chemistry B* 109, no. 13 (2005): 6287-6293.
- [22] Nishiyama, Norikazu, Dong-Huy Park, Yasuyuki Egashira, and Korekazu Ueyama. "Pore size distributions of silylated mesoporous silica MCM-48 membranes." *Separation and purification technology* 32, no. 1-3 (2003): 127-132.
- [23] Zhao, Wei, Zhengping Hao, and Chun Hu. "Synthesis of MCM-48 with a high thermal and hydro-thermal stability." *Materials research bulletin* 40, no. 10 (2005): 1775-1780.
- [24] Klinthong, Worasaung, Kuei-Jung Chao, and Chung-Sung Tan. "CO<sub>2</sub> Capture by as-synthesized amine-functionalized mcm-41 prepared through direct synthesis under basic condition." *Industrial & Engineering Chemistry Research* 52, no. 29 (2013): 9834-9842.
- [25] Huang, Helen Y., Ralph T. Yang, Daniel Chinn, and Curtis L. Munson. "Amine-grafted MCM-48 and silica xerogel as superior sorbents for acidic gas removal from natural gas." *Industrial & Engineering Chemistry Research* 42, no. 12 (2003): 2427-2433.
- [26] Huo, Cheng, Huidong Zhang, Hongyu Zhang, Houyu Zhang, Bing Yang, Ping Zhang, and Yue Wang. "Synthesis and assembly with mesoporous silica MCM-48 of platinum (II) porphyrin complexes bearing carbazol groups: spectroscopic and oxygen sensing properties." *Inorganic chemistry* 45, no. 12 (2006): 4735-4742.
- [27] Schumacher, K., M. Grün, and K. K. Unger. "Novel synthesis of spherical MCM-48." *Microporous and Mesoporous Materials* 27, no. 2-3 (1999): 201-206.
- [28] Vallet-Regí, María, Luisa Ruiz-González, Isabel Izquierdo-Barba, and José M. González-Calbet. "Revisiting silica based ordered mesoporous materials: medical applications." *Journal of Materials Chemistry* 16, no. 1 (2006): 26-31.
- [29] Wang, Shuguo, Dong Wu, Yuhan Sun, and Bing Zhong. "The synthesis of MCM-48 with high yields." *Materials research bulletin* 36, no. 9 (2001): 1717-1720.
- [30] Xia, Yongde, and Robert Mokaya. "Mesoporous MCM-48 aluminosilica oxynitrides: synthesis and characterization of bifunctional solid acid-base materials." *The Journal of Physical Chemistry C* 112, no. 5 (2008): 1455-1462.