

# Effect of secondary template polarity to the properties of mesoporous ZSM-5 zeolites

T. M. Karim, R. Nuzuliyah, D. A. Nurani, and Y. K. Krisnandi

Citation: [AIP Conference Proceedings](#) **1862**, 030086 (2017); doi: 10.1063/1.4991190

View online: <http://dx.doi.org/10.1063/1.4991190>

View Table of Contents: <http://aip.scitation.org/toc/apc/1862/1>

Published by the [American Institute of Physics](#)

---

## Articles you may be interested in

[Carbon dioxide capture by activated methyl diethanol amine impregnated mesoporous carbon](#)

[AIP Conference Proceedings](#) **1862**, 030090 (2017); 10.1063/1.4991194

[Synthesis of ZSM-5 zeolite using Bayat natural zeolite as silica and alumina source](#)

[AIP Conference Proceedings](#) **1862**, 030094 (2017); 10.1063/1.4991198

[Sensitivity differences between microporous NaY and hierarchical ZSM-5 modified electrodes as ammonia gas sensor](#)

[AIP Conference Proceedings](#) **1862**, 030081 (2017); 10.1063/1.4991185

[Classification of right-hand grasp movement based on EMOTIV Epc+](#)

[AIP Conference Proceedings](#) **1862**, 030069 (2017); 10.1063/1.4991173

[Design of early warning system for nuclear preparedness case study at Serpong](#)

[AIP Conference Proceedings](#) **1862**, 030067 (2017); 10.1063/1.4991171

[Organic shale analysis using geochemical data and seismic attributes: Case study of Talang Akar formation, South Sumatera Basin](#)

[AIP Conference Proceedings](#) **1862**, 030178 (2017); 10.1063/1.4991282

---

# Effect of Secondary Template Polarity to the Properties of Mesoporous ZSM-5 Zeolites

T. M. Karim, R. Nuzuliyah, D. A. Nurani and Y. K. Krisnandi<sup>a)</sup>

*Department of Chemistry, Faculty of Mathematics and Natural Science (FMIPA),  
Universitas Indonesia, Depok 16424, Indonesia*

<sup>a)</sup>Corresponding author: yuni.krisnandi@sci.ui.ac.id

**Abstract.** Synthesis and characterization of mesoporous ZSM-5 using two kinds of secondary templates with different polarity, polydiallyldimethylammonium chloride (PDDA-Cl) or cetyltrimethylammonium bromide (CTABr) were studied. The weight lost after calcination at 550 °C for 5 hours were 30.93 wt% and 25.87 wt% for PDDA-Cl-templated ZSM-5 (ZSM-5<sub>pc</sub>) and CTABr-templated ZSM-5 (ZSM-5<sub>cs</sub>), respectively. Both as-synthesized mesoporous ZSM-5 zeolites then were characterized by XRD, FTIR, SEM, and EDX. Based on wide angle XRD analysis that both mesoporous ZSM-5 showed similar diffraction patterns and the typical peaks of ZSM-5 in which  $2\theta = 7^\circ\text{-}9^\circ$  (doublet peaks) and  $22^\circ\text{-}25^\circ$  (triplet peaks) appeared. For the analysis of functional group, FTIR analysis showed that both mesoporous ZSM-5 gave strong band at  $550\text{ cm}^{-1}$ , which is attributed to asymmetric stretching vibration of the double 5-rings from MFI zeolites. Meanwhile, the result of EDX calculation showed mesoporous ZSM-5<sub>pc</sub> had Si/Al ratio of 26.69 and ZSM-5<sub>cs</sub> had Si/Al ratio of 12.62. Furthermore, the SEM images exhibited mesoporous ZSM-5<sub>pc</sub> had morphology of hexagonal (coffin-like) while ZSM-5<sub>cs</sub> had ellipse form.

**Keywords:** mesoporous ZSM-5, functional group, Si/Al ratio, morphology, secondary template

## INTRODUCTION

Energy source that being used today primarily comes from petroleum, a non-renewable energy source. So, that it is a very necessary effort to reduce the dependency on petroleum. One way to do that is to utilize the natural potential of more abundant but renewable sources, such as methane gas that obtained from natural gas, feedstock, landfill, and biomass. However, methane is one of greenhouse gases [1] so that the utilization of methane to methanol directly is less environmentally friendly. Therefore, conversion of methane to methanol is one of many solutions to utilize the natural potential as environmentally friendly energy source. Furthermore, methanol can be used in conventional combustion engines without requiring major adjustments [1] and also as fuel of direct methanol fuel cell (DMFC) [2,3]. However, direct methane conversion to methanol is quite difficult due to the thermodynamic obstacles. To overcome that problem, attempts to convert methane to methanol have been done by other groups and among others using ZSM-5 zeolite impregnated with cobalt as catalyst [4,5]. ZSM-5 is a zeolite which has MFI-type framework, which is composed of straight channels and zigzag channels [6]. Therefore, ZSM-5 allows to perform high shape and size selectivity toward reactant and/or product molecules [6,7].

Since the mesoporous addition to conventional microporous ZSM-5 is important, in order to keep mass transport to and from active site and to extend the catalyst lifetime, the choice of secondary template as mesoporous directing agent becomes important. One of the secondary template that often used as mesoporous directing agent is cationic polymer, as reported by Wang *et al.* [8]. It is show that the cationic polymers can interact effectively with inorganic silicate species resulting in (mesoporous structure) in which the pore size can be tuned by changing the amount of cationic polymers [8]. Although the cationic polymer could reduce the phase separation and interact with inorganic silicate species effectively, but the obtained mesoporous form was still poorly ordered, as shown by Meng *et al.* [9] and Xiao *et al.* [10]. Mesoporous disorder is highly influenced by the interaction which takes place between

secondary template and silicate species at step of the mesoporous structure formation. In this case, the most important factor is template polarity. Therefore, in the present work synthesis and characterization of mesoporous ZSM-5 using two kinds of secondary templates that the different in polarity i.e. PDDA-Cl (having polar site) and CTABr (having polar and non polar site) were carried out, with aim to know the effect of template polarity toward the formed mesoporous structure and the characteristics of the obtained mesoporous ZSM-5. Furthermore, we also aim to synthesize mesoporous ZSM-5 with well-ordered mesoporous structure as MCM-41 by using CTABr as mesoporous directing agent.

## MATERIALS AND METHODS

### Materials

Materials are used in this experiment i.e. tetraethyl orthosilicate (TEOS) 98% (Sigma Aldrich), tetrapropylammonium hydroxide (TPAOH) 1 M (Sigma Aldrich), sodium aluminate (Sigma Aldrich), polydiallyldimethylammonium chloride (PDDA-Cl 35%), cetyltrimethylammonium bromide (CTABr) 98% (Sigma Aldrich), and distilled water.

### Mesoporous ZSM-5 Preparation Using PDDA-Cl

This synthesis followed the procedure developed by Krisnandi *et al.* [4] with (slightly) modification. First, sodium aluminate (0,3 g), TPAOH (36.9 g), and TEOS (25.1 g) were dissolved in 87.6 g of distilled water. Afterward, the mixture solution was adjusted pH until ~11 and then aged for 3 h. All steps took place under stirring condition at 100 °C with total molar ratio of gel: 1 Al<sub>2</sub>O<sub>3</sub> : 64.3 SiO<sub>2</sub> : 10.1 (TPA)<sub>2</sub>O : 3571.7 H<sub>2</sub>O. Then, 3 g of PDDA-Cl was added into the mixture solution at room temperature and stirred for 15 h. The obtained suspension was placed in autoclave for hydrothermal process for 144 h at 150 °C. The solid product was collected by filtered, then washed with distilled water, dried at 60 °C for 12 h and calcined at 550 °C for 5 h. The obtained sample was labelled as ZSM-5<sub>pc</sub>. Subsequently, the ZSM-5<sub>pc</sub> was characterized by XRD, FTIR, SEM, and EDX instruments.

### Mesoporous ZSM-5 Preparation Using CTABr

This synthesis was done by following the previous procedure [4,11]. Briefly, the resulted gel after mixing all reagents had composition of molar ratio: 1 Al<sub>2</sub>O<sub>3</sub> : 64.3 SiO<sub>2</sub> : 10.1 (TPA)<sub>2</sub>O : 3571.7 H<sub>2</sub>O : 4.4 CTABr and all steps carried out at room temperature. The obtained suspension then was placed in autoclave for hydrothermal process for 72 h at 120 °C. Then, the product was filtered, washed with distilled water, dried at 60 °C for 12 h and calcined at 550 °C for 5 h. The obtained sample was labelled as ZSM-5<sub>cs</sub>. Afterward, the ZSM-5<sub>cs</sub> was characterized by XRD, FTIR, SEM and EDX instruments.

## RESULTS AND DISCUSSION

Figure 1a and 1b showed the wide angle XRD patterns of both mesoporous ZSM-5. All samples exhibited the presence of typical peaks of ZSM-5-type structure which are located at  $2\theta = 70^\circ\text{-}90^\circ$  (doublet peaks) and  $22^\circ\text{-}25^\circ$  (triplet peaks) [4]. Furthermore, both mesoporous ZSM-5 using PDDA-Cl and CTABr also showed high intensity on the typical peaks which indicates that the ZSM-5 structure possesses high crystallinity. However, the regularity of mesoporous structure which expected to be formed on ZSM-5<sub>cs</sub> was not occurred. It showed by Fig. 1c in which the absence of diffraction patterns at  $2\theta = 2.5^\circ, 4.25^\circ$  and  $4.81^\circ$  which is attributed to the (100), (110), and (200) plane reflection of two-dimensional hexagonal structure of MCM-41 [11]. This indicates that the formed mesoporous structure was disorder [12].

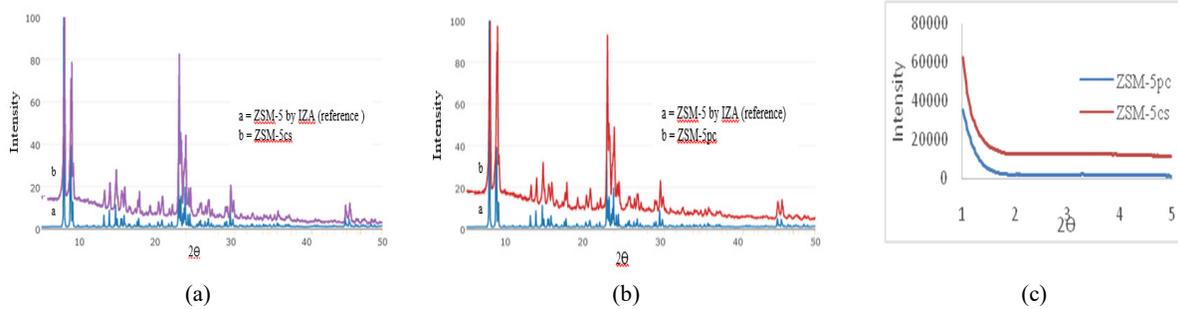


FIGURE 1. Powder XRD patterns of wide angle (a) ZSM-5<sub>cs</sub>, (b) ZSM-5<sub>pc</sub> and low angle (c) ZSM-5<sub>pc</sub> and ZSM-5<sub>cs</sub>.

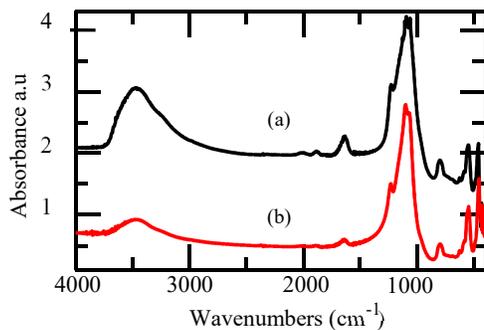


FIGURE 2. FTIR spectra of (a) ZSM-5<sub>pc</sub> and (b) ZSM-5<sub>cs</sub>.

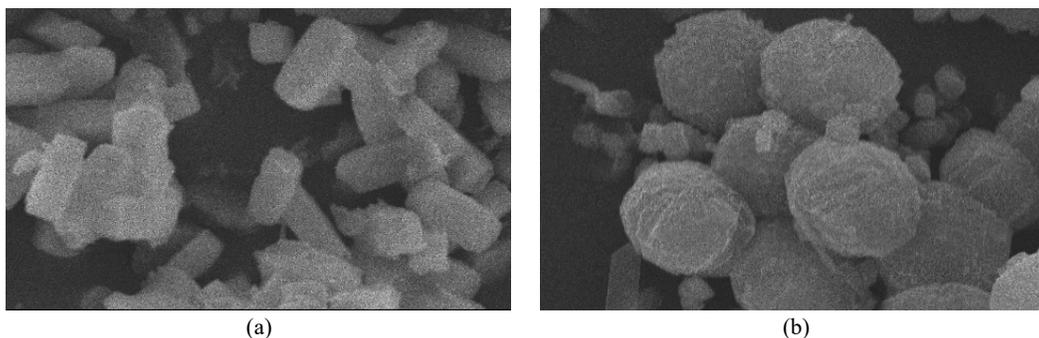


FIGURE 3. SEM images of (a) mesoporous ZSM-5<sub>pc</sub> (magnification of  $\times 2,500$ ) and (b) ZSM-5<sub>cs</sub> (magnification of  $\times 5,000$ )

Figure 2 showed FTIR spectra of both mesoporous ZSM-5. According to the spectra, ZSM-5<sub>pc</sub> and ZSM-5<sub>cs</sub> contain MFI structure which is the typical structure belongs ZSM-5. It showed by the presence of strong band around  $550\text{ cm}^{-1}$ , in which the band is assigned to asymmetric stretching vibrations of double 5-ring from MFI structure [12]. Moreover, asymmetric stretching vibrations of the external and internal structure of T-O (T = Si or Al) were also observed which showed by the presence of band at around  $1225\text{ cm}^{-1}$  and  $1093\text{ cm}^{-1}$ , respectively [13-14]. The band at around  $795\text{ cm}^{-1}$  also appeared, which is attributed to symmetric stretching vibrations of internal tetrahedron structure nor external tetrahedron structure [13-15]. Whereas, the band at around  $450\text{ cm}^{-1}$  assigned to bending vibrations of T-O [13-15], was not clearly observed since stacked with the band at around  $420\text{-}300\text{ cm}^{-1}$  (attributed to pore vibrations [13]).

SEM images of ZSM-5<sub>pc</sub> and ZSM-5<sub>cs</sub> are shown in Fig. 3. Image of ZSM-5<sub>pc</sub> exhibited hexagonal-shaped crystal which is typical shape of ZSM-5 [4]. The presence of rough structure on the crystal surface is caused by the mesoporous formation on zeolite framework. While image of ZSM-5<sub>cs</sub> exhibited ellipse-shaped crystal with the

**TABLE 1.** EDX elemental analysis of ZSM-5 zeolite

Name	2 <sup>nd</sup> Template	Mass percent of Si	Mass percent of Al	Si/Al molar ratio
ZSM-5 <sub>pc</sub>	PDDA-Cl	48.32	1.81	26.69
ZSM-5 <sub>cs</sub>	CTABr	45.55	3.61	12.62

crystal surface roughly and staircase steps indicating the mesoporous formation. The morphology of ZSM-5 with ellipse shape also was observed by Zhu *et al.* [6] and Jiang *et al.* [11]. According to Jiang *et al.* [11], the morphology of mesoporous ZSM-5 depends on the amount of CTABr (mesoporous direction) used. Meanwhile, Zhu *et al.* [6] explained that the crystal morphology with ellipse shape is not resemble the typical morphology of conventional ZSM-5 crystal. They also explained that the cubic-shaped crystal morphology is morphology that similar to conventional ZSM-5 zeolite, and to change the morphology from ellipse shape to cubic shape could be carried out by adding the amount of CTABr that used [6,11]. So that, the morphology of ZSM-5<sub>cs</sub> which ellipse-shaped supposed due to little amount of CTABr used.

Si/Al ratio of ZSM-5<sub>pc</sub> and ZSM-5<sub>cs</sub> was shown in Table 1. Based on EDX measurement, ZSM-5<sub>pc</sub> had Si/Al ratio of 26.69 with the mass percent of Si and Al of 48.32% and 1.81%, respectively. Meanwhile, ZSM-5<sub>cs</sub> had Si/Al ratio of 12.62 with the mass percent of Si and Al of 45.55% and 3.61%, respectively. The lower Si/Al ratio in ZSM-5<sub>cs</sub> compared ZSM-5<sub>pc</sub> was caused due to the Al content in ZSM-5<sub>cs</sub> (3.61%) higher than ZSM-5<sub>pc</sub> (1.81%). This is might be due to the percent of aluminum-substituted mesoporous silicate when synthesized by CTABr as mesoporous directing agent [6]. This phenomena occurred since the effect of sodium ions and the cationic head groups of CTABr which supported the incorporation of tetrahedral aluminum into the zeolite framework [16]. Moreover, the role of tetraalkylammonium base that acting as an aluminum directing agent also supported the incorporation of the aluminum species [16]. Therefore, the mass percent of Si in ZSM-5<sub>cs</sub> (45.55%) lower than ZSM-5<sub>pc</sub> (48.32%) which is the consequence of the substitute phenomena.

## CONCLUSIONS

Both mesoporous ZSM-5 have been successfully synthesized using two kinds of secondary templates, PDDA-Cl (cationic polymer) and CTABr (cationic surfactant), that different in polarity. Moreover, the mesoporous structure also formed which is marked by the presence of the rough crystal surface. However, the well-ordered mesoporous structure which expected to be formed by using CTABr was not occurred. For Si/Al ratio, ZSM-5<sub>cs</sub> had the ratio (12.62) lower than the one of using PDDA-Cl (26.69). The lower Si/Al ratio of ZSM-5<sub>cs</sub> indicates that the negative charge of ZSM-5<sub>cs</sub>, is high enough, so that it has the potential to be modified into a mesoporous M/ZSM-5 (M = metal) which is reactive and selective catalyst toward the conversion of methane to methanol.

## ACKNOWLEDGMENTS

This research was partially funded by TWAS Grant No. 13-034 RG/CHE/AS\_I-UNESCO FR: 3240277703, Osaka Gas Foundation for International Cultural Exchange year 2016-2017 and Hibah PUPT BOPTN No. 1136/UN2.R12/HKP/05.00/2016

## REFERENCES

1. A. Bill, A. Wokaun, B. Eliasson, E. Killer, and U. Kogelschatz, *Energy Conversion and Management* **38**, S415– S422 (1997).
2. A. S. Aricò, V. Baglio, and V. Antonucci, in *Electrocatalysis of Direct Methanol Fuel Cell: From Fundamental to Application*, edited by J. Zhang and H. Liu (Willey-VCH, Weinheim, 2009), pp. 1-78
3. B. Gurau and E. S. Smotkin. *J. Power Sources* **112**, 339-352 (2002).
4. Y.K. Krisnandi, *et al.*, *Procedia Chem.* **14**, 508–515 (2015).
5. N. V. Beznis, B. M. Weckhuysen, and J. H. Bitter, *Catal. Letters* **136**, 52–56 (2010).
6. Y. Zhu, *et al.*, *Chem. Eur. J.* **17**, 14618-14627 (2011).
7. K. Zhang and M. L. Ostraat, *Catal. Today* **264**, 3-15 (2015)
8. L. Wang, Z. Zhang, C. Yin, Z. Shan, and F. S. Xiao, *Microporous Mesoporous Mater.* **131**, 58–67 (2010).
9. X. Meng, F. Nawaz, and F. S. Xiao. *Nano Today* **4**, 292-301 (2009).
10. F. S. Xiao, *et al.*, *Angew. Chem. Int. Ed.* **45**, 3090-3093 (2006).

11. Y. Jiang, et al., *J. Taiwan Inst. Chem.* **61**, 234-240 (2016).
12. L. Jin, et al., *React. Kinet. Mech. Cat.* **113**, 575–584 (2014).
13. E. M. Flanigen, H. Khatami, and H. A. Szymanski, in *Advances in Chemistry Series 101: Molecular Sieve Zeolites-I*, edited by E. M. Flanigen and L. B. Sands (American Chemical Society, Washington D. C, 1971), pp. 201–229.
14. G. Coudurier, C. Naccache, and J. C. Vedrine, *J. Chem. Soc. Chem. Commun.* **24**, 1413–1415 (1982).
15. M. L. Goncalves, L. D. Dimitrov, M. H. Jordão, M. Wallau, and E. A. Urquieta-González. *Catal. Today* **133-135**, 69-79 (2008).
16. K. R. Kloetstra, H. W. Zandbergen, and H. V. Bekkum. *Catal. Lett.* **33**, 157-163 (1995).