AIP - 20 April 2016

by Hartati Hartati

Submission date: 29-May-2019 09:45AM (UTC+0800)
Submission ID: 1137180662
File name: AIP-20_April_2016.pdf (347.32K)
Word count: 2786
Character count: 14799

Three-step Crystallization in Synthesis of ZSM-5 without Organic Template

Hartati[1,*], Alfa Akustia[1], Indra Permana[1], Didik Prasetyoko[2]

[1]Department of Chemistry, Faculty of Science and Technology, Universitas Airlangga, Surabaya, 60115, Indonesia

[2]Department of Chemistry, Faculty of Mathematics and Sciences, Institut Teknologi Sepuluh Nopember, Surabaya 60111, Indonesia

*Email: hartati@fst.unair.ac.id

Abstract. ZSM-5 was synthesized without organic template through three steps crystallization by adding seed solution. ZSM-5 crystals was characterized by X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy and nitrogen adsorption/ desorption technique. XRD and FTIR showed that this method produced the ZSM-5 and quartz as byproduct. Nitrogen adsorption/desorption technique was as certained the formulation of micro-meso porosity of hierarchical ZSM-5.

Keywords : *ZSM-5, without organic template, micro-meso porosity*

1 Introduction

Commonly, ZSM-5 is synthesized through the addition of organic template as organic structure-directing agent (SDA), namely TPAOH (Xue [1]; Wang [2], Zhu [3]; Tao [4]) or TPABr (Xiao [5]; Pan [6]; Schmid [7]). Prasetyoko [8] synthesized pure ZSM-5 from rice husk ash with the addition of silicalite-1 through the crystallization at 175 ° C for 24 hours. Pan [6] studied the synthesis of ZSM-5 from dealuminated metakaolin with crystallization at 180 °C for 72 hours organic template free. The results as well as ZSM-5 synthesized by using TPABr as a template.

Hence, much research has been directed to develop ZSM-5 synthesis method by the gradual crystallization. Kim [9] reported that ZSM-5 can be observed without the addition of the organic template through a two-step process of crystallization. Crystallization at high temperature (190 °C) were intended to accelerate the nucleation and crystallization at a lower temperature (150 °C) that aims to control the size of crystals and crystal size distribution. The results showed a rapid nucleation and crystallization at high temperatures can form large crystals. Xianliang [10] also studied about the control of crystallization condition, at temperature of 150 °C and 190 °C. They added a nucleation solution before crystallization. The results showed that crystal of ZSM-5 is formed if nucleation solution is made at high temperature (190 °C) and crystallization is done at a lower temperature (150 °C) with mole ratio of $SiO_2/Na_2O < 0.18$. The lower mole ratio of $SiO_2/Na_2O > 0,18$ produced a mordenit materual. Mostafa [11] synthesized ZSM-5 without organic template by gradual crystallization at 180-°C which continued at 120-°C and then at room temperature with the addition of ZSM-5 seed. The results showed that the ZSM-5 formed is partial microporous crystalline nanosize with high surface area. The gradual crystallization in synthesis of zeolite also intended to acquire mesoporous particles, as done by Xianliang [10] to gain a hierarchical porous zeolite NaY particles without organic matter as a mesoporous structure directing agent. The use of organic template and organic species as mesophase directing agent (usually use hexadecyltrimethyl ammonium bromide (CTAB)) have many problems, such as high production costs and the results of thermal decomposition of the species can cause environmental pollution.

In this study, we use three step crystallization in the synthesis of ZSM-5 using seed solution without the addition of an organic template. The results obtained are compared with the synthesis without seed solution and hierarchical ZSM-5 which was synthesized using TPAOH as organic template and CTAB as mesophase directing agent.

5th International Conference and Workshop on Basic and Applied Sciences (ICOWOBAS 2015)
AIP Conf. Proc. 1718, 060002-1–060002-8; doi: 10.1063/1.4943324

2 Experimental

2.1. Zeolite synthesis

All chemicals directly used without purification, include tetraethyl orthosilicates (TEOS, Merck, 99%); sodium aluminate, $NaAlO_2$ (Sigma Aldrich, $Al_2O_3 = 50 – 55\%$); sodium hydroxide (NaOH, Merck, ≥ 98%); tetrapropylammonium hydroxide (TPAOH, Merck, 40% wt solution in water), hexadecyltrimethyl ammonium bromide (CTAB, AppliChem).
The synthesis of ZSM-5 in gradual crystallization using seed solution (A) performed by dissolving NaOH with distilled water by stirring then sodium aluminate gradually add while stirring. Thereafter, the TEOS was incorporated into the mixture dropwise, so that obtained the molar composition of mixture: $10Na_2O$: $100SiO_2$:1, $25Al_2O_3$:$1800H_2O$. The mixture was divided in two parts (A1 and A2). The first mixture (A1) was allowed for 19 h at room temperature and then the mixture put in a stainless steel outoclave and heated in an oven at 190 °C for 4 h (Xianliang [10]). The second mixture (A2) was allowed at room temperature for 24 h. After that, A1 was blended with A2. The mixture was heated gradually at 100 °C for 24 h, 120 °C for 24 h, and 150 °C for 24 and 36 h. The product isolated by centrifugation, rinsed with distilled water, and then dried at 105 °C for 24 h.

As a comparison, the synthesis of ZSM-5 also carried out gradually without seed solutio with similar molar composition with synthesis ZSM-5 using seed solution. The mixture was stirred for 5 h without seed solution, then allowed for 24 h at room temperature. The mixture was inserted into stainless steel outoclave and then closed tightly and heated in an oven at 100 °C for 24 h, 120 °C for 24 h, and 150 °C for 24 h (B). Synthesis of zeolites in the gradual crystallization without seed solution also performed at low temperature, starting at 60 °C for 48 h and then at 80 °C for 48 h, and at 100 °C for 24 h (C). The solid obtained at each of the crystallisation washed up to neutral pH and dried overnight at 105 °C.

Hierarchical ZSM-5 (Hie-ZSM-5) also used as a comparison was synthesized following the modified method of Eimer [12] and Goncalves [13]. Sodium aluminate was mixed with TEOS through stirring for 30 min, then added TPAOH and aquades so obtained composition: $1SiO_2$: xAl_2O_3:0.2TPAOH: $38H_2O$ ($x = (SiO_2/Al_2O_3)^{-1}$, x-= 1/40 or mole ratio of Si/Al = 20). The mixture was stirred for 15 min, then hydrothermal process was conducted by entering the mixture into a polypropylene bottle, and heated in an oven at 80 °C for 48 h. The mixture was cooled to room temperature and then was added CTAB gradually up to a mole ratio of SiO_2/CTAB = 3.85. The mixture was stirred about 30 min then allowed for 3 h. The solids formed washed with distilled water until neutral pH, then dried at 60 °C for 48 h. The dried solid was calcined at 550 °C for 1 h in N_2 and continued in air for 6 h. The catalyst was previously reported by Hartati [20].

2.2. Characterization

X-ray diffraction patterns (XRD) was measured using a Philips X'pert XRD instrument with Cu Kα radiation in the 2θ range from 5 to 50° in steps of 0.02°. Infrared spectra measured on an infrared spectrophotometer (FTIR) Shimadzu using a KBr pellets techniques in range of wavenumbers of 400 − 4000 cm^{-1} with a spectral resolution of 4 cm^{-1}, 45 scans, at room tempetature. Nitrogen adsorption/desorpsi done at 77 K using Quantachrome Nova version 10. Sampels were degassed at 250 °C before measured. The micropore surface area of samples were measured using Brunauer – Emmett – Teller (BET) method on P/Po = 0.3, while the mesopore surface area, pore volume, and pore diameter were determined by Barrett – Joyner – Halenda (BJH) method.

3. Results and discussion

The crystalline phase and type of zeolite formed were identified by X- ray diffraction (XRD). Figure 1 shows the XRD pattern of samples synthesized by some variation of temperature in the gradual crystallization. It can be seen that the sample that synthesized without organic template and without the addition of seed solution (Figure. 1.A) clearly shows the characteristic peaks of MFI were detected on 2θ around 7-9 ° and 23 – 25° as well as the peaks of Hie-ZSM-5. However, in sample A appears peaks at 2θ = 20,92 ° and 26,72 ° corresponding to peaks of α-SiO_2 (quartz) (Wang [2]). The formation of quartz together in the results of the synthesis of ZSM-5 can be caused by a fairly high alkaline levels and weak template (Sang [14]; Yue-ming and Wang-ming, [15). The formation of the impurities such as quarts can also be occured when the synthesis is done in a long time (Guth and Kessler [16]), as was done in this study. Synthesis of zeolites through gradual crystallization was done using the same material composition with mixture used in synthesis using seed solution. The XRD patterns in Figure 1.B shows that the crystal of ZSM-5 has been formed, however there are other peaks at 2θ around 22 ° and at around 27.5 ° indicate α-cristobalite (Shinohara and Kohyama [17], Prasetyoko [8]). Difraction pattern in Figure 1.B also shows peak at 2θ near 26,72 ° indicate of α-SiO_2, while the peaks at 2θ around 6.5° and 10,5° show of mordenite (Xianliang [10]). The XRD pattern in Figure 1.C shows that the results of the synthesis of zeolites without the organic template and without the addition of seed solution a like big hum typically of the amorphous solids. This indicates that the ZSM-5 is not formed.

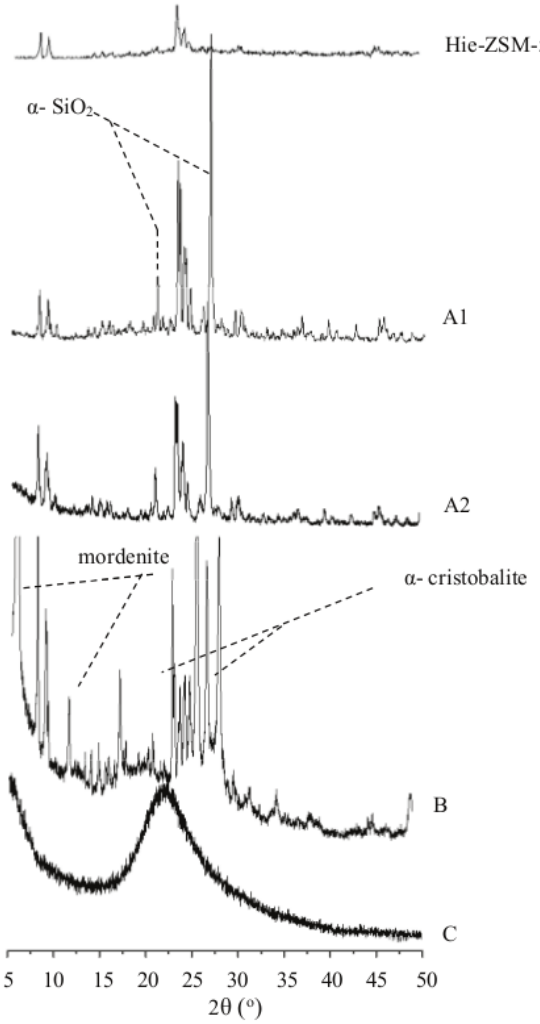

Figure 1. XRD pattern of samples

FTIR spectra at wavenumbers 400-2000 cm^{-1} is shown in Figure 2. Samples A and B in Figure 2 show a typical peak D5R at wavenumbers around 550 cm^{-1} and the vibration of external asymmetric at around 1223 cm^{-1} which became the structure identifier for MFI structure of ZSM-5 as also appear in Hie-ZSM-5 spectra. This is in accordance to the results of Kim [9] which shows that the gradual crystallization begins with warming at high temperature up to 190 °C can accelerate the formation of the crystal nuclei, so that it can generate ZSM-5. However, that peaks are not appear in sample C. The shoulder band at 1223 cm^{-1} is an asymmetric external vibration (← OTO →) which is characteristic peak of ZSM-5 (Khatamian [18]). A strong absorption at about 1100 cm^{-1} is an asymmetric internal vibration (← OTO →), a weak absorption at about 795 cm^{-1} shows the vibration of external symmetry (← OTO →), and absorption at about 450 cm^{-1} shows the vibrational of T-O from TO_4 (T = Si or Al) (Li and Wu [19]).

Table 1. Wavenumber of streching and bending vibration of FTIR spectra

Sample	Wavenumber (cm^{-1})				
	External Asimetry	**Internal Asimetry**	**External Simetry**	***D5R***	**T-O Bending**
A1	1223	1084	799	546	453
A2	1223	1084	799	546	453
B	1230	1086	783	544	445
C	-	1100	797	-	463
Hie-ZSM-5	1223	1110	797	545	453

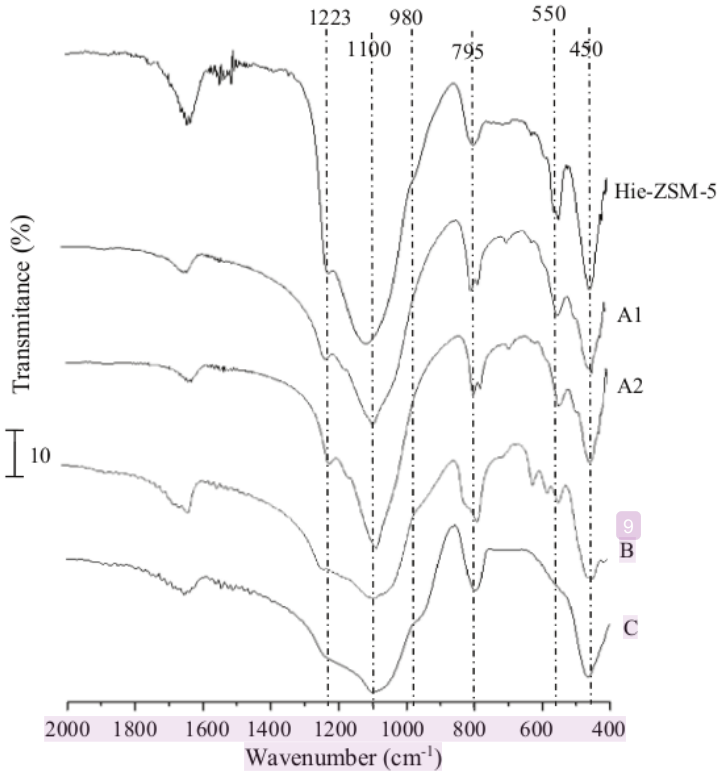

Figure 2. FTIR spectra of samples

The FTIR spectra support the XRD data that show the ZSM-5 can be synthesis by gradual crystalization at high temperature and by addition of seed solution. Figure 1.B shows FTIR spectra of sample C does not show clear peak at 2θ around 550 cm^{-1} and 1223 cm^{-1}. FTIR spectra at Figure 1.C does not show the bands at arround 550 cm^{-1} and 1223 cm^{-1} which are in accordance with the XRD pattern of an amorphous solid (Figure 1.C).

Figure 3 shows that isotherm curve of N_2 adsorption/desorption of zeolite ZSM-5 (A2) is lower than Hie-ZSM-5 which shows that A2 has a smaller porosity and surface area. This is consist with the data shown in Table 2. Table 2 also shows that the sample A2 has a hierarchical porous but the dominant of its surface is microporous. It is different from Hie-ZSM-5, which has a hierarchical porous with large meso-micro porous surface area. From the Figure 3 (insert), it can be stated that both samples showed hierarchical porous structure.

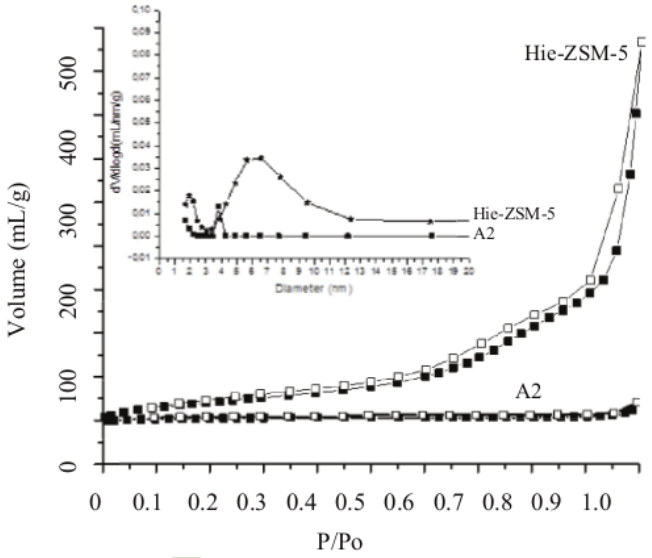

Figure 3. Isotherm N_2 adsorption/desorption of samples and pore diameter of samples (insert)

Table 2. Pore structure properties of samples

Sample	Surface Area Mesoporous[a] (m^2/g)	Surface Area Microporous[b] (m^2/g)	Pore Volume[a] (mL/g)	Pore Diameter[a] (nm)
Hie-ZSM-5*)	177.233	241.756	0.701	6.575
A2	13.015	213.844	0.031	3.808

a. determined by BJH
b. determined by BET method at $P/P_0 = 0.3$
*) as reported previously by Hartati [20]

4. CONCLUSIONS

Synthesis of ZSM-5 with step crystallization can be performed at a high temperature (100 ° C for 24 h, 120 ° C for 24 h, and 150 ° C for 24 or 36 h) with the addition of seed solution. ZSM-5 obtained has a hierarchical pore with the majority of micropores than ZSM-5 synthesized with the organic template and mesophase template. This method also produced the quartz mineral in small quantities.

Acknowledgement

The authors gratefully acknowledge the financial support from Ministry of Education and Culture, Indonesia, under "Unggulan" research.

References

[1] Xue,T., Chen,L., Wang, Y.M., He, M-Y, *Seed-induced synthesis of mesoporous ZSM-5 aggregates using tetrapropylammonium hydroxide as single template*, Microporous and Mesoporous Materials, 156, 97–105, 2012.

[2] Wang, P., Lv, A., Hu, J., Xu., and Lu, G., *In Situ Synthesis of SAPO-34 Grown onto Fully Calcined Kaolin Microspheres and Its Catalytic Properties for the MTQ Reaction,* Industrial & Engineering Chemistry Research, 50, pp. 9989 – 9997, 2011.

[3] Zhu, H., Liub, Z., Kong, D., Wang, Y., Yuan, X., Xie, Z., *Synthesis of ZSM-5 with intracrystal or intercrystal mesopores by polyvinyl butyral templating method*, Journal of Colloid and Interface Science , 331, 432–438, 2009.

[4] Tao,Y., Hattori,Y., Matumoto, A., Kanoh, H., dan Kaneko, K., *Comparative Study on Pore Structures of Mesoporous ZSM-5 from Resorcinol-Formaldehyde Aerogel and Carbon Aerogel Templating*, J. Phys. Chem. B., 109, 194-199, 2005.

[5] Xiao yun, L.I., Minghui, S., Claire, R.J., Lihua, C., Bao-Lian, S., Review: *Synthesis and Applications of Hirarkisly Porous Catalysts*, Chinese Journal of Catalysis, 34, 22–47, 2013.

[6] Pan, F., Lu, X., Wang, Y., Chen, S., Wang, T.X., Yan, Y., *Organic template-free synthesis of ZSM-5 zeolite from coal-series kaolinite*, Materials Letters, 15, 5–8, 2014.

[7] Schmidt, F., Lohe, Martin R., Büchner, B., Giordanino, F., Bonino, F., *Improved Catalytic Performance of Hirarkis ZSM-5 Synthesized by Desilication with Surfactants,* Microporous and Mesoporous Materials, 165, 148–157, 2013.

[8] Prasetyoko, D., Ayunanda, N., Fansuri, H., Hartanto, D., *Phase Transformation of Rice Husk Ash in The Synthesis of ZSM-5 Without Organic Template*, ITB Journal Sciences, 44 A, No. 3, 250-262, 2012.

[9] Kim, S.D., Noh, S.H., Park, J.W dan Kim, W.J., *Organic Free synthesis of ZSM-5 with Narrow Crystal Size Distribution Using Two Step Temperature Process*, Microporous and Mesoporous Materials, hal. 181-188, 2004.

[10] Xianliang, H., Rongrong, Z., Zhengbao, W., *Controlling Crystal Transformation between Zeolite ZSM-5 and Mordenite without Organic Structure-Directing Agent*, Chinese Journal of Catalysis, 33, 8, 2012.

[11] Mostafa, M.M., Rao, K.N., Harun, K.S., Basahel, S.K., Maksod, H.A., *Synthesis and characterization of partially crystalline nanosized ZSM-5 zeolites,* Ceramics International 39, 683–689, 2013.

[12] Eimer, G.A., Diaz, I., Sastre, E., Casuscelli, G.S., Crivello, M.E., Herrero, E.R, Periente, J., *Mesoporous Titanosilicates Synthesized from TS-1 Precursors with Enhanced Catalytic,* Applied Catalysis A: General 34, 77–86, 2008.

[13] Goncalves, M.L., Dimitrov, Ljubomir D., Jorda, M.H., Wallau, M., Urquieta-Gonzalez, E.A., *Synthesis of Mesoporous ZSM-5 by Crystallisation of Aged Gels in The Presence of Cetyltrimethylammonium Cations*. *Catalysis Today,* 133–135, 69–79, 2008.

[14] Sang, S., Chang, F., Liu, Z., He, C., He, Y., Xu, L., *Difference of ZSM-5 zeolites synthesized with various templates*, Catalysis Today, 93–95, 729–734, 2004

[15] Yue-ming, H., and Wang-ming, H., *Rapid synthesis of ZSM-5 zeolite catalyst for amination of ethanolamine*, Journal of Zhejiang University Science, 5(6):705-708, 2004.

[16] Guth, J.L and Kessler, H., *Synthesisi of Aluminosilicate Zeolites and Related Silica-Based Materials,* Catalysis and Zeolites: Fundamentals and Applications, Jens Weitkamp,Lothar Pupp (eds), Springer-Verlag, pp. 40, 1999.

AIP - 20 April 2016

ORIGINALITY REPORT

24%	18%	15%	2%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	repository.petra.ac.id Internet Source	5%
2	www.freepatentsonline.com Internet Source	1%
3	HUANG, Xianliang, Rongrong ZHANG, and Zhengbao WANG. "Controlling Crystal Transformation between Zeolite ZSM-5 and Mordenite without Organic Structure-Directing Agent", Chinese Journal of Catalysis, 2012. Publication	1%
4	Eshagh Moradiyan, Rouein Halladj, Sima Askari. "The beneficial use of ultrasound in rapid-synthesis of SAPO34/ZSM-5 nanocomposite and its catalytic performances on MTO reaction", Industrial & Engineering Chemistry Research, 2018 Publication	1%
5	oa.upm.es Internet Source	1%
	www.eco-ist.rs	

6	Internet Source	1%
7	Yin, Zhao Hua, Yong Chen, Zhong Wei Wang, Ying Xing, Xiu Juan Tian, Qing Yu, and Chang Gong Meng. "Synthesis of ZSM-5 Zeolite without Organic Template", Advanced Materials Research, 2015. Publication	1%
8	chemweb.com Internet Source	1%
9	bradscholars.brad.ac.uk Internet Source	1%
10	zdoc.site Internet Source	1%
11	Chi-Ying Hsieh, Yu-Yin Chen, Yu-Chuan Lin. "Ga-Substituted Nanoscale HZSM-5 in Methanol Aromatization: The Cooperative Action of the Brønsted Acid and the Extra-Framework Ga Species", Industrial & Engineering Chemistry Research, 2018 Publication	1%
12	Teng Xue, Sisi Li, Haihong Wu, Peng Wu, Mingyuan He. "Eco-Friendly and Cost-Effective Synthesis of ZSM-5 Aggregates with Hierarchical Porosity", Industrial & Engineering Chemistry Research, 2017	1%

	Publication	
13	pubs.acs.org Internet Source	1%
14	www.ingentaconnect.com Internet Source	1%
15	iptek.its.ac.id Internet Source	1%
16	www.arpnjournals.org Internet Source	1%
17	Ebrahim Mohiuddin, Yusuf Makarfi. Isa, Masikana M. Mdleleni, Nonyameko Sincadu, David Key, Themba Tshabalala. "Synthesis of ZSM-5 from impure and beneficiated Grahamstown kaolin: Effect of kaolinite content, crystallisation temperatures and time", Applied Clay Science, 2016 Publication	1%
18	www.intechopen.com Internet Source	1%
19	doaj.org Internet Source	1%
20	orca.cf.ac.uk Internet Source	<1%
21	Krisnandi, Yuni Krisyuningsih, Bimo Ary Pujangga Putra, Muhammad Bahtiar, Zahara,	<1%

Iman Abdullah, and Russell Francis Howe. "Partial Oxidation of Methane to Methanol over Heterogeneous Catalyst Co/ZSM-5", Procedia Chemistry, 2015.
Publication

---

22 mediatum.ub.tum.de <1%
Internet Source

---

23 Pan, Feng, Xuchen Lu, Yun Wang, Shiwei Chen, Tizhuang Wang, and Yan Yan. "Organic template-free synthesis of ZSM-5 zeolite from coal-series kaolinite", Materials Letters, 2014. <1%
Publication

---

24 Huihua Pan, Qunxiong Pan, Yuansheng Zhao, Yibin Luo, Xingtian Shu, Mingyuan He. "A Green and Efficient Synthesis of ZSM-5 Using NaY as Seed with Mother Liquid Recycling and in the Absence of Organic Template", Industrial & Engineering Chemistry Research, 2010 <1%
Publication

---

25 Didik Prasetyoko. "Characterization and Catalytic Performance of Niobic Acid Dispersed over Titanium Silicalite", Advances in Materials Science and Engineering, 2008 <1%
Publication

---

26 Roland Missengue, Pit Losch, Nicholas Musyoka, Benoit Louis, Patrick Pale, Leslie Petrik. "Conversion of South African Coal Fly <1%

Ash into High-Purity ZSM-5 Zeolite without Additional Source of Silica or Alumina and Its Application as a Methanol-to-Olefins Catalyst", Catalysts, 2018
Publication

---

27 Saeed Abbasizadeh, Ramin Karimzadeh. "Effect of Next-Nearest-Neighbor Aluminum Atoms in the HZSM-5 Framework Synthesized with Various Aluminum Sources on Liquefied Petroleum Gas Transformation to Light Olefins", Industrial & Engineering Chemistry Research, 2018 <1%
Publication

---

28 staff.uny.ac.id <1%
Internet Source

---

29 Zongtao Zhang, Yu Han, Lei Zhu, Runwei Wang, Yi Yu, Shilun Qiu, Dongyuan Zhao, Feng-Shou Xiao. "Strongly Acidic and High-Temperature Hydrothermally Stable Mesoporous Aluminosilicates with Ordered Hexagonal Structure", Angewandte Chemie International Edition, 2001 <1%
Publication

---

30 ltu.diva-portal.org <1%
Internet Source

---

31 H FENG, C LI, H SHAN. "In-situ synthesis and catalytic activity of ZSM-5 zeolite", Applied Clay <1%

Science, 2009
Publication

32	Aneliése L. Figueiredo, Antonio S. Araujo, María Linares, Ángel Peral et al. "Catalytic cracking of LDPE over nanocrystalline HZSM-5 zeolite prepared by seed-assisted synthesis from an organic-template-free system", Journal of Analytical and Applied Pyrolysis, 2016 Publication	<1%
33	Tao Pan, Zhijie Wu, Alex Yip. "Advances in the Green Synthesis of Microporous and Hierarchical Zeolites: A Short Review", Catalysts, 2019 Publication	<1%
34	Zihao Zhang, Hao Cheng, Hao Chen, Jing Li, Kequan Chen, Xiuyang Lu, Pingkai Ouyang, Jie Fu. "Catalytic Fast Pyrolysis of Rice Straw to Aromatics over Hierarchical HZSM-5 Treated with Different Organosilanes", Energy & Fuels, 2018 Publication	<1%
35	"Recent Trends in Materials Science and Applications", Springer Nature, 2017 Publication	<1%

Exclude quotes Off Exclude matches Off

Exclude bibliography On

AIP - 20 April 2016

GRADEMARK REPORT

FINAL GRADE

/0

GENERAL COMMENTS

Instructor

PAGE 1

PAGE 2

PAGE 3

PAGE 4

PAGE 5

PAGE 6

PAGE 7