VOLUME 52
ISSUE 6, 2017

ISSN 1314-7471 (print)
ISSN 1314-7978 (on line)
www.uctm.edu

JOURNAL OF CHEMICAL TECHNOLOGY AND METALLURGY

SOFIA 2017

Volume 52, Iss. 6, 2017

Journal of Chemical Technology and Metallurgy

52, Iss. 6, 2017
ISSN 1314-7471 (print)
ISSN 1314-7978 (on line)

EDITOR-IN- CHIEF
Prof. Dr. Bogdana Koumanova
Tel: (+ 359 2) 81 63 302
University of Chemical Technology and Metallurgy
8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: journal@uctm.edu

SELECTED ARTICLES

International Conference

“Collaboration Seminar of Chemistry and

Industry (CoSCI-2016)”

5-6 October, 2016

Surabaya, Indonesia

Invited Editor

Dr. Purkan Purkan

Home

Editorial Board

University "Babeş -Bolyai", Cluj-Napoca, Romania

S. Kalcheva,

University of Chemical Technology and Metallurgy, Bulgaria

F. Keil,

Hamburg University of Technology, Germany

T. Koinov,

University of Chemical Technology and Metallurgy, Bulgaria

T. Komatsu,

Nagaoka University of Technology, Japan

J.M. LeLann,

Institut National Polytechnique,École nationale supérieure des ingénieurs en arts chimiques et technologiques, France

S.N. Lezhnev,

Rudny Industrial Institute, Rudny, Kazakhstan

A. Mavrova,

University of Chemical Technology and Metallurgy, Bulgaria

Lipetsk State Technical University, Russia

G. Radeva,

University of Chemical Technology and Metallurgy, Bulgaria

A. Di Schino,

University of Perugia, Italy

M. Simeonova,

University of Chemical Technology and Metallurgy, Bulgaria

V. Stefanova,

University of Chemical Technology and Metallurgy, Bulgaria

D. Stoilova,

Bulgarian Academy of Sciences

N. Tsarevsky,

Southern Methodist University, Dallas, Texas, USA

I. Turunen,

Lappeenranta University of Technology, Finland

L. Vezenkov,

University of Chemical Technology and Metallurgy, Bulgaria

Journal of Chemical Technology and Metallurgy

Country Bulgaria - SIR Ranking of Bulgaria

Subject Area and Category Chemical Engineering
Chemical Engineering (miscellaneous)

Engineering
Industrial and Manufacturing Engineering

Publisher University of Chemical Technology and Metallurgy

Publication type Journals

ISSN 13143859, 13147471

Coverage 2013-ongoing

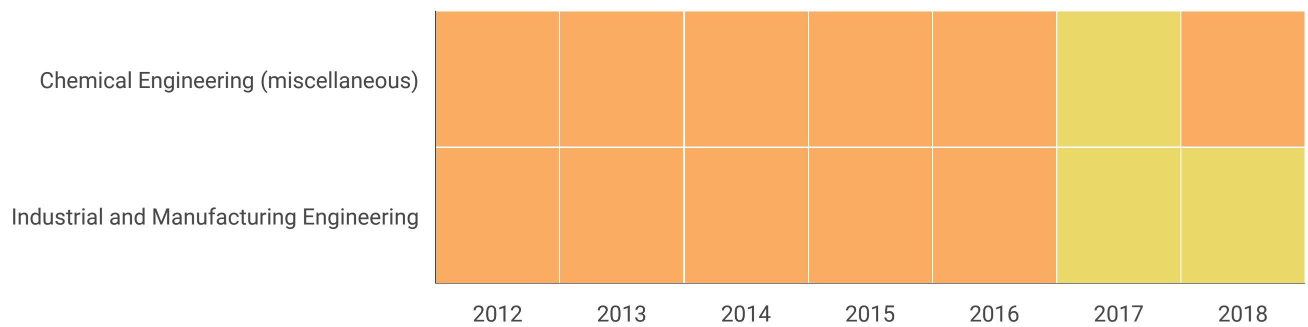
15

H Index

How to publish in this journal

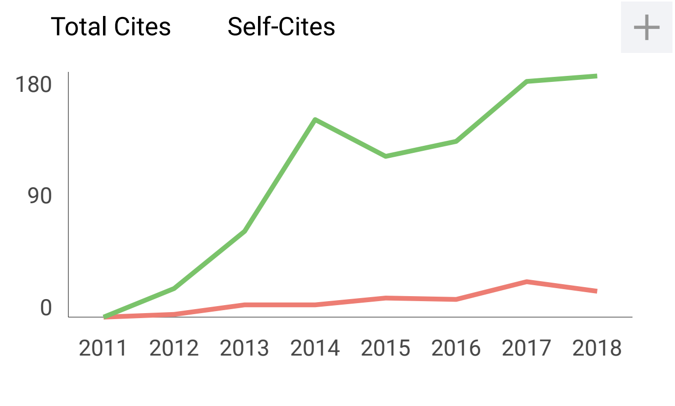
Join the conversation about this journal

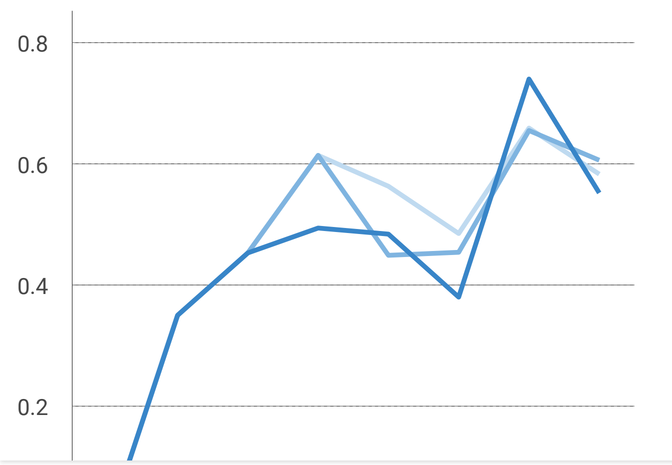
Quartiles

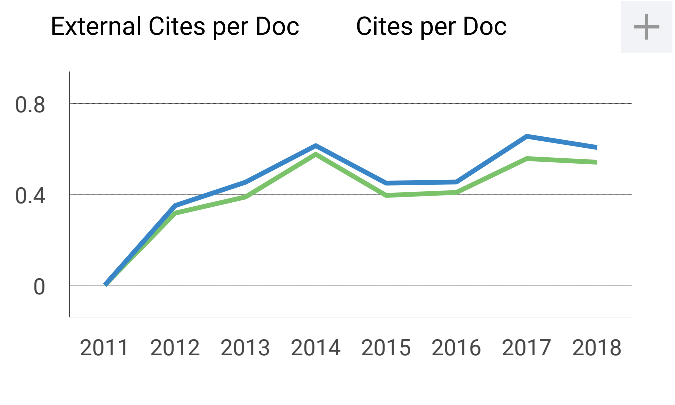


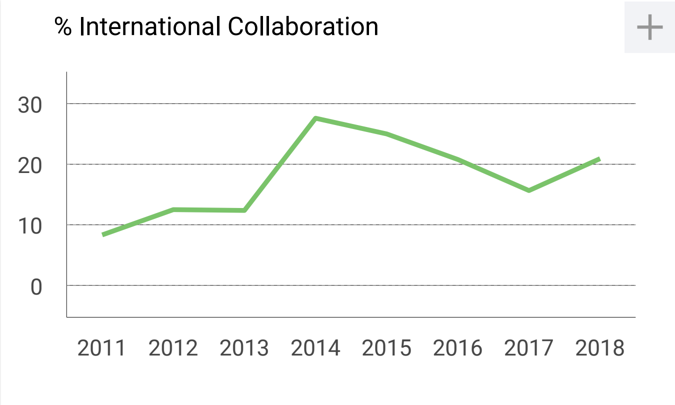
SJR

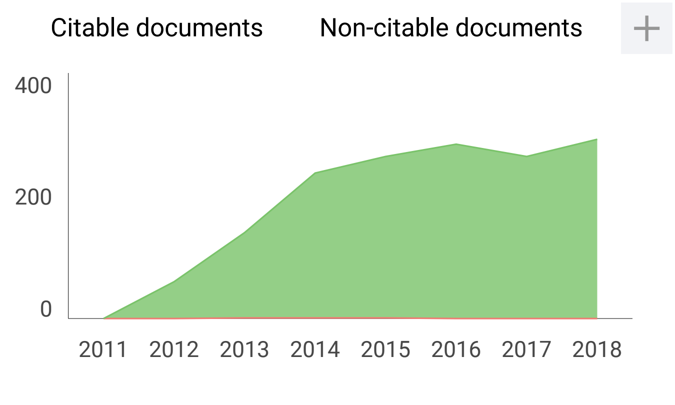
Citations per document

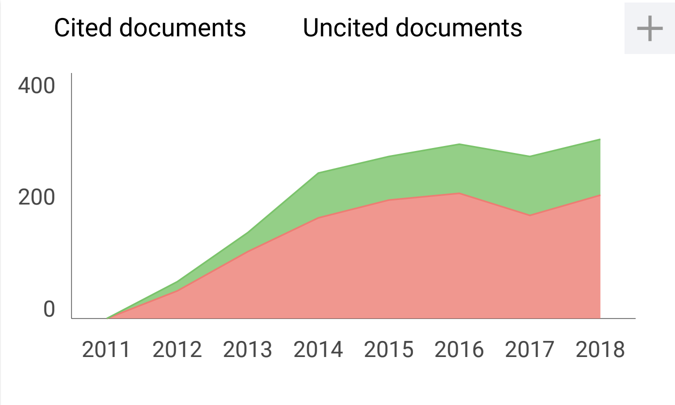












← Show this widget in your own website

Just copy the code below and paste within your html code:

<a href="https://www.scimag

B

Bilal 1 year ago

Dear Sir/M'am,

Can you please let me know why ı can't open the website of the journal?

reply

Elena Corera 1 year ago

Dear Bilal,

sorry, but unfortunately we cannot help you with your request, SJR has no relation with journal's website.

Best regards,
SCImago Team

S

Salim Kaiser 1 year ago

let me know the present status of my manuscript“Corrosion behaviour of Al-12Si-1Mg automotive alloy in acidic, alkaline and salt media with trace of Zr”

reply

S

Salim Kaiser 1 year ago

Dear Sir
Please let me know the present status of my manuscript entitle
“Corrosion behaviour of Al-12Si-1Mg automotive alloy in acidic, alkaline and salt media with trace of Zr”
kind regards.
Salim Kaiser

reply

Elena Corera 1 year ago

Dear Salim, we suggest you contact the journal directly. Best Regards, SCImago Team

V

Vinay 1 year ago

Dear Sir/M'am,

Can you please let me know the procedure for publishing a research paper in your journal.

Regards

Vinay

reply

Elena Corera 1 year ago

Dear Vinay, in the link below you will find the information corresponding to the author's instructions of this journal. Best regards, SCImago Team http://dl.uctm.edu/journal/node/61

Leave a comment

Name

Email
(will not be published)

I'm not a robot
reCAPTCHA
Privacy - Terms

Submit

Journal of Chemical Technology and Metallurgy, 52, 6, 2017, 1145-1149

ORGANIC TEMPLATE FREE HIERARCHICAL ZSM-5 PREPARED BY DESILICATION

Hartati, Alfa Akustia Widati, Aning Purwaningsih, Alfinda Novi Kristanti, Anggarani Nur Oktavia

Department of Chemistry, Faculty of Science and Technology
Universitas Airlangga, Kampus C UNAIR, Jl. Mulyorejo
Surabaya, 60115, Indonesia
E-mail: hartati@fst.unair.ac.id

Received 05 January 2017
Accepted 20 July 2017

ABSTRACT

Organic template free hierarchical ZSM-5 were synthesized using desilication. X-Ray Diffraction (XRD), Fourier Transform Infra Red (FTIR) spectrometry, and N_2 adsorption/desorption analytical techniques were applied to characterize the physicochemical properties of the solid synthesized. Hierarchical ZSM-5 of a molar composition of $100SiO_2$:$1.25Al_2O_3$:$1800H_2O$ was obtained at a hydrothermal temperature of 175°C for 36 h. The analytical results showed that the hierarchical ZSM-5 had a mesopore surface area, a pore volume, and a pore diameter of 42.752 m^2/g, 0.186 cc/g, and 3.810 nm, respectively.

Keywords: hierarchical ZSM-5, desilication, organic template free.

INTRODUCTION

Zeolites are microporous crystalline solids of unique properties such as a thermal stability, a high acidity, a good selectivity, and a high ion exchange capacity. Therefore, they can be used as catalysts, adsorbents, and ion exchange agents [1]. Natural zeolites often contain impurities that can cover the pores or active sites, so activation is required for their elimination [2].

Synthetic zeolites are generally made through a crystallization process of sodium aluminosilicates gels. In this case, a mixture of sodium silicates and sodium aluminates [3] is the source of silica and alumina for zeolites synthesis. Synthetic zeolites are commonly applied in industries because of their high purity and uniformity of particle size.

In general, ZSM-5 zeolites are synthesized using structure directing agents (SDA). Tetraprophylammonium hydroxide (TPAOH) is the most effective substance as a SDA [4]. Although TPAOH provides a good crystal structure, it also causes economical, health, and enviromental problems because it is expensive, toxic [5], and promotes air pollution in the the course of the calcination process [6, 7].

Most of ZSM-5 zeolites are prepared of a micropore size. Microporous ZSM-5 has limitations in respect to molecular diffusion due to steric effects, especially in case of bulky molecules [8]. There are many attempts to overcome this problem referring to the development of mesoporous ZSM-5 and hierarchical (microporous and mesoporous) ZSM-5. Meso-sized pores are expected to facilitate the reactants mass transport into the active site of the zeolite.

Mesopores can be obtained in zeolites with the addition of a cationic surfactant as a mesophase template. The surfactant can be eliminated, as is done by Goncalves et al. [9], Barakov et al. [10], Hartati et al. [11], or Jian et al. [12] upon completion of the synthesis process. However, the use of cationic surfactant results in air pollution, and which is why alternative methods are needed. Desilication is an easy method applied to the synthesis of various types of mesoporous zeolites, for example Mobile Five-1 (MFI) [13], Mordenite (MOR) [14], and Beta Polymorph A (BEA) [15]. Desilication can provide a controlled mesoporous structure maintaining Bronsted acidity [13].

In this research, ZSM-5 was synthesized using tetraethylorthosilicate (TEOS) and sodium aluminosilicate without structure direchting agent or seeds. The resulting microporous ZSM-5 was then converted into a hierarchical (mesoporous and microporous) ZSM-5 through a desilication process.

EXPERIMENTAL

Anhydrous sodium aluminate ($NaAlO_2$, Sigma Aldrich, 50 %), tetraethylorthosilicate (TEOS, Merck, 99 %), sodium hydroxide (NaOH, Merck, 99 %), ethanol (C_2H_5OH, Sigma Aldrich, 99.8 %) and distilled water were used. Approximately 0.375 g of NaOH were dissolved in 10 mL of distilled water and then gradually mixed with 0.256 g of $NaAlO_2$ in a plastic beaker. The solution was then added dropwise to 14.1 mL of TEOS as a silica source and 10 mL of distilled water. Thus a mixture of a molar composition of $10Na_2O$: $100SiO_2$: $1.25Al_2O_3$: $1800H_2O$ was obtained. It was stirred for 5 h and aged for 19 h. Subsequently, it was transferred to a stainless steel autoclave. The latter was sealed and heated at 175°C of a varying time (24 h, 36 h, 48 h, and 72 h). Then the solids obtained were washed with distilled water to pH 7 using centrifugation techniques and dried in an oven for 24 h at 100°C. Thus microporous ZSM-5 was obtained.

The desilication process was carried out by introducing 0.176 g of microporous ZSM-5 to a mixture of 20 mL of water and 10 mL of ethanol placed in a plastic beaker. Then 20 mL of 0.125 M NaOH were added dropwise. During this process the plastic beaker was covered with aluminum foil to prevent evaporation. The mixture was transferred to a polypropylene bottle and heated for 24 h at 100°C [16]. The product obtained was washed with distilled water until pH 7 and dried for 24 h at 80°C.

The structure of ZSM-5 was determined by X-Ray Powder diffraction (XRD) at a wavelength 1.54056 Å using a Philip Analytical X'Pert PRO of 2θ = 5 - 50° and Cu Kα radiation. FT-IR spectra (Shimadzu IR Prestige 21 spectro-photometer) were used to identify the structure of ZSM-5 and the functional groups present. The pore properties prior to and following the desilication were studied using nitrogen absorption/ desorption (Nova Quanthacrome 1200E).

RESULTS AND DISCUSSION

The X-ray diffraction patterns of ZSM-5 synthesized in absence of an organic template with hydrothermal time varying at 175°C is shown in Fig. 1. It is evident that no ZSM-5 but an amorphous solid is formed within 24 h. The time increase to 36 h results in ZSM-5 synthesis. This is verified by the sharp peak at 2θ of about 7° - 9° and 22° - 25° (Fig. 1b). Fig. 1b shows a peak at ca 6° - 7° which is characteristic peak of mordenite [14]. The sample obtained within 48 h (Fig. 1c) shows a diffraction pattern similar to that in Fig. 1.b, but with an additional peak at ca 27° indicating the formation of quartz 17]. At 72 hours, Quarts dominates ZSM-5 in case of 72 h hydrothermal time as evident from Fig. 1d.

The data presented shows that the hydrothermal time increase leads to a lower crystallinity of MFI structure and promotes the formation of quartz and modernit. This is so because no structure directing agent of MFI is used [18]. Furthermore, quartz formation is facilitated by high NaOH concentrations of NaOH as reported by Prasetyoko et al. [19]. The characterization by FTIR spectra is aimed at determining the constituent bonds of the zeolite framework. Peaks appear at 468.67 cm^{-1}, 796.55 cm^{-1}, 1097.4 cm^{-1} and 1629.74 cm^{-1} appear in

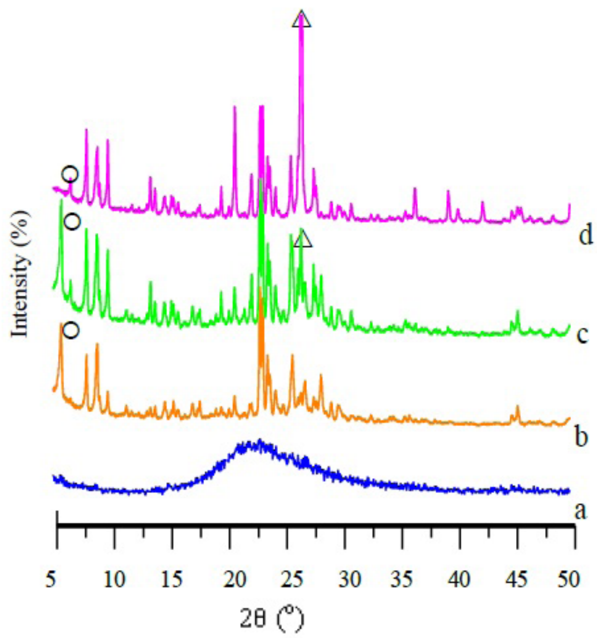


Fig. 1. XRD pattern of ZSM-5 synthesized at 175°C for a) 24 h; b) 36 h; c) 48 h; d) 72 h (○ - mordenite, △ - quartz).

Table 1. FTIR data referring to ZSM-5 synthesized.

Hidrothermal Time	Wavenumber (cm^{-1})					
	Bending vibration of Si-O and Al-O	Five membered ring	Symetric stretching vibration of Si-O-Si	Asymmetry stretching vibration of Si-O-Si	TO4 tetrahedron units	bending vibration of –OH
24 h	468.67	-	796.55	1097.42	-	1629.74
36 h	445.53	545.82	781.12	1080.06	1236.29	1629.74
48 h	457.10	545.82	781.12	1083.92	1238.21	1629.74

case of hydrothermal time of 24 h. Peaks appear at 445.53 cm^{-1}, 545.82 cm^{-1}, 781.12 cm^{-1}, 1080.06 cm^{-1}, 1236.29 cm^{-1} and 1629.74 cm^{-1} when the treatment is within 36 h. The peaks in the spectra recorded in case of hydrothermal time of 48 and 72 h are outlined at identical wave numbers, i.e. at 457.10 cm^{-1}, 545.82 cm^{-1},781.12 cm^{-1}, 1083.92 cm^{-1}, 1238.21 cm^{-1} and 1629.74 cm^{-1}. These results are similar to those reported by Cheng et al. [5]. The band at around 450 cm^{-1} illustrated in Fig. 2 shows the bending vibration of Si-O and Al-O, the band at around 1100 cm^{-1} is indicative of the asymmetry stretching vibration of Si-O-Si, that at around 800 cm^{-1} is ascribed to the symmetric stretching vibration of Si-O-Si, while the band at around 550 cm^{-1} is typical for the five membered ring of the pentasil structure. All FTIR data obtained is listed in Table 1. It is evident that no ZSM-5 ris synthesized within hydrothermal time of 24 h, i.e. no bands at around 550 cm^{-1} and 1200 cm^{-1} characteritic of MFI structure are seen. Thus the FTIR data obtained support those of XRD analysis.

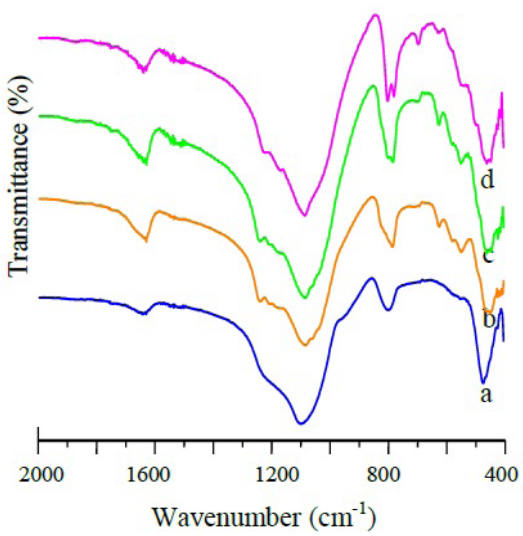


Fig. 2. FTIR spectra of ZSM-5 synthesized at 175°C for a) 24 h; b) 36 h; c) 48 h; and d) 72 h.

Desilication is a post-treatment of a zeolite aimed at a selective extraction of silicon atoms from the zeolite framework. It is worth adding that the the aluminum framework does not disrupt during this process because of the basicity provided by NaOH presence. In this research, the desilication is carried out using NaOH solution. Sodium hydroxide is a good desilicating agent when compared to organic bases such as tetrapropil ammonium hydroxide (TPAOH) and tetrabutyl ammonium hydroxide (TBAOH) because the desilication process with their participation is considered less selective [20].

The XRD diffraction patterns in Fig. 3 show specific peaks at ca 7° - 9° and 23° - 25°. This provides the conclusion that the process conducted decreases the zeolite cryrallinity but still preserves ZSM-5 MFI structure. The NaOH treatment affects crystal morphology through facilitation of mesopores formation. In fact the morphological changes of the zeolite crystals increase with NaOH concentration increase [21]. According to Groen et al. [22], the optimum conditions of desilication refer to 0.2 M NaOH, temperature of 338 K and duration of 30 min.

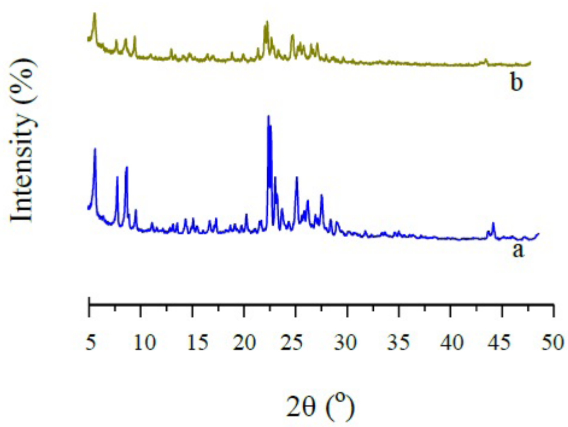


Fig. 3. XRD pattern of ZSM-5 a) prior to desilication and b) after desilication.

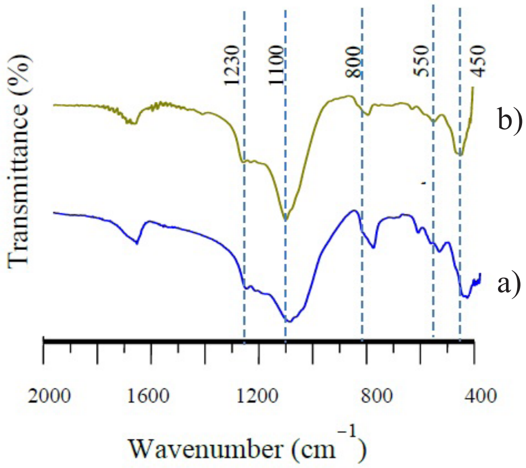


Fig. 4. FT-IR spectra of ZSM-5: a) prior to desilication and b) after desilication.

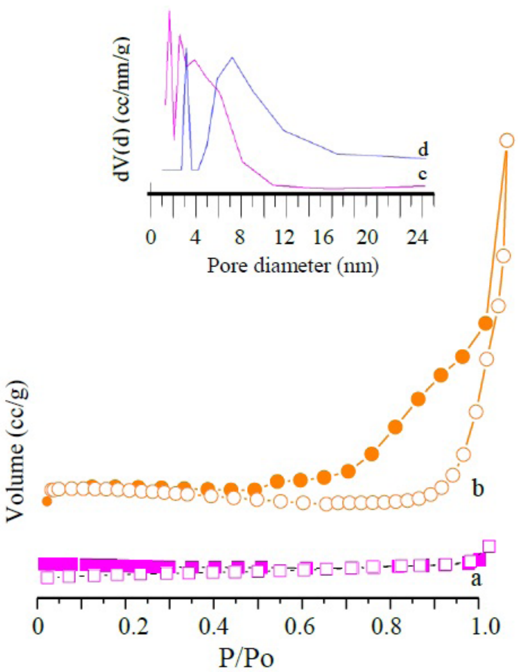


Fig. 5. Nitrogen absorption/desorption isotherm of ZSM-5 a) prior to desilication and b) after desilication ; pore diameter curve: c) before desilication and d) after desilication).

The FTIR spectra are shown in Fig. 4. A similarity of the pattern is observed in Figs. 4a and 4b. This indicates that the framework structure is not changed during the desilication process.

The nitrogen absorption/desorption curves of a sample of ZSM-5 prior to and after desilication are shown in Fig. 5. In Fig. 5 was also listed about curves of pore size distribution of ZSM-5 after desilication process. It is evident that the curve of ZSM-5 prior desilication is of type I, which is typical for microporous solids. The insert in Fig. 5c shows that the pore diameter is ca 3.436 nm, while the surface area of the mesopores is ca 65.797 m^2/g (69.44 % of total surface area). It is also evident that the pore volume is ca 0.232 cc/g, while the micropores surface area is ca 28.954 m^2/g. Fig. 5b indicates that the curve of ZSM-5 after desilication corresponds to type IV. The latter is typical for mesoporous solids (Groen et al., 2005). The distribution of the pore diameter is between 3.8 nm and 8 nm (Fig. 5d), while the mesopores surface area is ca 42.752 m^2/g (86.84 % of total surface area). The pore volume is 0.186 cc/g, while the micropores surface area is found equal to 6.475 m^2/g. It is small but nevertheless it shows that ZSM-5 considered differs from that prior desilication.

CONCLUSIONS

Hierarchical ZSM-5 can be synthesized without organic templates by the hydrothermal method at 175^o C for 36 h. Quartz is evidenced as an impurity by the XRD diffraction pattern in case of a longer synthesis (72 h). The formation of ZSM-5 is also supported by the FT-IR spectra obtained. The formation of mesoporous ZSM-5 is proved by nitrogen absorption/ desorption and pore size distribution curves recorded.

Acknowledgements

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

REFERENCES

1. S. Wang, Y. dan Peng, Natural zeolites as Effective Adsorbents in Water and Wastewater Treatment, Chemical Engineering Journal, 156, 2010, 11-24.
2. M.W. Ackley, S.U. Rege, H. dan Saxena, Application of Natural Zeolites In The Purification and Separation of Gases, Microporous and Mesoporous Materials, 61, 1-3, 2003, 25-42.
3. C. Rovario, Javier, P. dan Ramires, Mesoporous ZSM-5 Zeolites Prepared by a Two Step Route Comprising

Sodiumaluminat and Acid Treatment, Microporous and Mesoporous Materials, 128, 2009, 91-100.
4. O.A. Fouad, R.M. Mohamed, M.S. Hassan, I.A. Ibrahim, Effect of Template Type and Template/silica Mole Ratio on The Crystallinity of Synthesized Nanosized ZSM-5, Catalysis Today, 116, 1, 2006, 82-87.
5. Y. Cheng, L.J. Wang, J.S. Li, Y.C. Yang, X.Y. Sun, Preparation and Characterization of Nanosized ZSM-5 Zeolites in The Absence of Organic Template, Materials Letters, 59, 2005, 3427-3430.
6. Li, G., Kikuchi, E., dan Matsukata, M., ZSM-5 Zeolite Membranes Prepared From A Clear Template-Free Solution, Microporous and Mesoporous Materials, 60, 1-3, 2003, 225-235
7. S. Stefan, T. Melin, J.L. Falconer, R.D. dan Noble, Transport of C6 Isomers Through ZSM-5 Zeolite, Journal of Membrane Science, 224, 1-2, 2003, 51-67.
8. A.M.P. Van Donk, P.J. Kooyman, J.C. dan Jansen, The Introduction of Carbon Oligomers Into The Framework of Silicalite-1, Studies in Surface Science and Catalysis, 158, 2005, 351-358.
9. M.L. Goncalves, L.D. Dimitrov, M.H. Jordao, M. Wallau, E.A.U. Gonzales, Synthesis of Mesoporous ZSM-5 by Crystallisation of Aged Gels in The Presence of cetyltrimethylammonium cations, Elsevier Catalysis Today, 133-135, 2008, 69-79.
10. R. Barakov, N. Shcherban, P. Yaremov, I. Bezverkhyy, A. Baranchikov, V. Trachevskii, V. Tsyrina, V. Ilyin, Synthesis of micro-mesoporous aluminosilicates on the basis of ZSM-5 zeolite using dual-functional templates at presence of micellar and molecular templates, Chinese Journal of Catalysis, 35, 10, 2016, 1727-1739.
11. H. Hartati, A. Widati, H. Setyawati, S. Fitri, Preparation of Hierarchical ZSM-5 from Indonesian Kaolin by Adding Silica, Chemistry & Chemical Technology, 10, 1, 2016, 87-89.
12. Y. Jian, Y. Wang, W. Zhao, J. Huang, Y. Zhao, G. Yang, Y. Lei, R. Chu, Effect of (Si+Al)/CTAB ratio on crystal size of mesoporous ZSM-5 structure over methanol to olefin reactions, Journal of the Taiwan Institute of Chemical Engineers, 61, 2016, 234-240.
13. J.C. Groen, L.A.A.A. Peffer, J.A. Moulijn, J.P. Ramirez, Role of Intrinsic Zeolite Properties on Mesopore Formation by Desilication of MFI Structures, Studies in Surface Science and Catalysis, 156, 2005, 401-408.
14. J.C. Groen, T. Sano, J.A. Moalijn, J. Perez-Ramirez, Alkaline-mediated mesoporous mordenite zeolites for acid catalyzed conversions, Journal of Catalysis, 251, 2007, 21-27.
15. J.C. Groen, S. Abello, L.A. Villaescusa, J. Perez-Ramirez, Mesoporous beta zeolite obtained by desilication, Microporous and Mesoporous Materials, 114, 2008, 93-102.
16. W.C. Yoo, X. Zhang, M. Tsapatsis, A. dan Stein, Synthesis of Mesoporous ZSM-5 Zeolite Through Desilication and re-assembly Processes, Microporous and Mesoporous Materials, 149, 2012, 147-157.
17. M.M.J. Treacy, J.B. dan Higgins, ZSM-5, Calcined, Collection of Simulated XRD Powder Patterns for Zeolites, 2001, 236-237.
18. F.Z. Zhang, X.W. Guo, X.S. Wanga, Li, G.Y. Zhao, X.H. Bao, X.W. Han, L.W. dan Linb, Preparation and Characterization of Titanium Containing MFI From Highly Siliceous ZSM-5: Effect of Precursors Synthesized With Different Templates, Materials Chemistry and Physics, 60, 1999, 215-220.
19. D. Prasetyoko, N. Ayunanda, H. Fansuri, D. Hartanto, Z. Ramli, Phase Transformation of Rice Husk Ash in the Synthesis of ZSM-5 without Organic Template, ITB J. Sci., 44 A, 3, 2012, 250-262.
20. S. Abello, A. Bonilla, J.P. Ramirez, Mesoporous ZSM-5 Zeolite Catalysts Prepared by Desilication With Organic Hydroxides and Comparison With NaOH Leaching, Applied Catalysis A: General, 364, 1-2, 2009, 191-198.
21. V.V. Ordomsky, V.Y. Murzin, Y.V. Monakhova, Y.V. Zubavichus, E.E. Knyazeva, N.N. Nesterenko, I.I. dan Ivanova, Nature, Strength and Accessibility of Acid Sites in Micro/Mesoporous Catalysts Obtained by Recrystallization of Zeolite BEA, Microporous and Mesoporous Materials, 105, 1-2, 2007, 101-110.
22. J.C. Groen, L.A.A.A. Peffer, J.A. Moulijn, J.P. Ramirez, On The Introduction of Intracrystalline Mesoporosity in Zeolites Upon Desilication in Alkaline Medium, Microporous and Mesoporous Materials, 69, 1-2, 2004, 29-34.