Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 2153–2157

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

Organic template-free synthesis of ZSM-5 zeolite particles using rice husk ash as silica source

Kartick Prasad Dey, Sourav Ghosh, Milan Kanti Naskar*

Sol–Gel Division, CSIR—Central Glass and Ceramic Research Institute, Kolkata 700 032, India

Received 18 June 2012; accepted 24 July 2012
Available online 10 September 2012

Abstract

ZSM-5 zeolite particles were synthesized through *in-situ* extraction of silica from rice husk ash in the absence of organic template by a simple hydrothermal condition at 150 °C/72–96 h. The powders were characterized by XRD, TGA, DTA, FTIR, N_2 physisorption studies, and field emission scanning electron microscopy (FESEM). Crystallization of ZSM-5 started at 150 °C/72 h. The vibration bands at around 540 and 1220 cm^{-1} indicated the presence of characteristic double 5-ring of ZSM-5. The BET surface area and pore volume increased with increase in synthesis time from 72 to 96 h at 150 °C. FESEM images showed coffin-shaped morphology of ZSM-5 particles.

Keywords: B. Porosity; Microstructure; Rice husk ash; ZSM-5 zeolite

1. Introduction

Zeolites are hydrated crystalline aluminosilicates composed of tetrahedral TO_4 units (T = Si or Al) which are linked together by sharing oxygen atoms to form regular intracrystalline cavities and channels of atomic dimensions. The framework of ZSM-5 contains two intersecting channel systems composed of sinusoidal (zigzag) and straight channels with 10-membered ring openings [1] of diameter ~5.5 Å. Because of its unique structure with good catalytic activity and shape selectivity [2], it finds several applications in petrochemical processing, fine chemical production, and liquid and gas separation. ZSM-5 zeolites are commonly prepared by the hydrothermal method of the gel containing precursors of silica, alumina, nonbridging metal cations, and organic template as structure directing agents (SDAs). Tetrapropyl ammonium hydroxide (TPAOH) or tetrapropyl ammonium bromide (TPABr) is generally used as SDA for the synthesis of ZSM-5; however, different amines instead of TPAOH or TPABr have also been used as structure directing agents (SDAs) [3–6]. The use of organic templates can cause many adverse problems such as high production cost, contamination by waste water, air pollution arising from thermal decomposition, and coke deposit due to incomplete decomposition. Therefore, to overcome such detrimental effects, many researchers have made great effort to synthesize ZSM-5 in the absence of organic templates [7,8]. Kim et al. [7] synthesized ZSM-5 in the absence of organic templates under stirring conditions. Cheng et al. [8] obtained ZSM-5 sans using organic template at 180 °C.

Synthesis of ZSM-5 from low cost silica sources becomes important for industrial production. Rice husk is an abundantly available agricultural waste material containing maximum amount of siliceous ash. Burning of rice husk in air produces rice husk ash (RHA) containing 85–98% silica. The burnt rice husk causes environment pollution and health hazard [9]. Therefore, useful applications of rice husk are desirable to mitigate environment pollution and health hazard. Recently, we have reported the utilization of RHA for the synthesis of hydroxy sodalite [10], and ZSM-5 zeolite [11] in the presence of organic templates (tetrapropyl ammonium hydroxide (TPAOH)).

In this communication, we have synthesized ZSM-5 zeolite powders using RHA as a silica source and other

---

*Corresponding author. Tel.: +91 33 24733496x3516; fax: +91 33 24730957.
E-mail address: milan@cgcri.res.in (M.K. Naskar).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.07.083

low cost water-based precursors, in the absence of any organic template following a single step hydrothermal process at relatively low temperature (150 °C) under static condition; to the best of our knowledge, it has not yet been reported before. As the present method for the preparation of ZSM-5 zeolite powders starts with the agricultural waste material, RHA, and avoids use of any organic precursors, it will be advantageous as a low cost and environment friendly process.

2. Experimental

2.1. Material and preparation of ZSM-5 particles

RHA locally collected followed by its calcination at 700 °C for 6 h with a heating and cooling rate of 4 °C min^{-1} each in air atmosphere, having the composition (wt%) SiO_2 (95.54%), Al_2O_3 (0.78%), K_2O (0.72%), P_2O_5 (1.45%), MgO (0.60%), CaO (0.29%), Fe_2O_3 (0.23%), Na_2O (0.10%), MnO (0.05%), TiO_2 (0.02%) and SO_3 (0.22%), sodium hydroxide (G.R., Merck, India, purity > 98%), aluminum metal foil (A.R., s.d. Fine-chem Ltd., India, purity > 99%), and deionized water (DI) were used as the starting materials. Fig. 1 shows schematically the preparation of ZSM-5 particles. Sodium aluminate solution as prepared by dissolving aluminum metal foil (0.08 g) with NaOH solution (4.8 g in 20 mL water), was mixed proportionately with RHA (18.9 g) and water (142 mL) under stirring with the molar composition of $100SiO_2$:$0.5Al_2O_3$:$20Na_2O$:$3000H_2O$. The stirring was continued for 20 h to obtain dispersion. The above dispersion was poured into Teflon-lined stainless steel autoclaves and heated at 150 °C for 48–96 h under autogenic pressure. After hydrothermal reaction, the as-prepared powders were collected by centrifugation (9000 rpm) followed by washing with water repeatedly until the washing liquid became almost neutral. The powders were dried at 80 °C for 4 h followed by calcination at 550 °C for 5 h with heating rate of 1 °C min^{-1} and cooling rate of 2 °C min^{-1}.

2.2. Material characterization

The crystal phases of the powders were identified using powder diffraction technique by a Philips X'Pert Pro XRD (Model: PW 3050/60) with Ni-filtered Cu-K$_\alpha$ radiation (λ=0.15418 nm), operating at 40 kV and 30 mA. The thermal behaviors of the as-prepared powders were studied by differential thermal analysis (DTA) and thermogravimetry (TG) (Shimadzu 50, Japan) from 30 to 800 °C in air atmosphere at the heating rate of 10 °C min^{-1}. The characteristic vibration bands of the particles were confirmed by FTIR (Nicolet 5PC, Nicolet Analytical Instruments, Madison, WI) with KBr pellets at a resolution of 4 cm^{-1}. Nitrogen adsorption and desorption measurements were performed at liquid nitrogen temperature (77 K) with a Quantachrome (Autosorb 1) instrument. The samples were outgassed in vacuum at 300 °C for 4 h prior to measurement. The total surface area was determined by the BET method [12]. Micropore (pore size < 20 Å) volume was calculated by the *t*-plot method [13]. The total pore volume was estimated from the amount of nitrogen adsorbed at the relative pressure (p/po) of ~0.99. The Barrett–Joyner–Halenda (BJH) method [14] was employed to calculate the pore size distribution in the mesopore range while the HK method [15] was applied for pore size distribution in micropore range. The morphology of the synthesized particles was examined by FESEM (Model: Zeiss, Supra™ 35VP, Oberkochen, Germany) operating with an accelerating voltage of 10 kV.

3. Results and discussion

Fig. 2 shows the XRD patterns of the powders obtained hydrothermally at 150 °C for (a) 48, (b) 72, and (c) 96 h. It was observed that for 48 h of reaction time the crystallization of

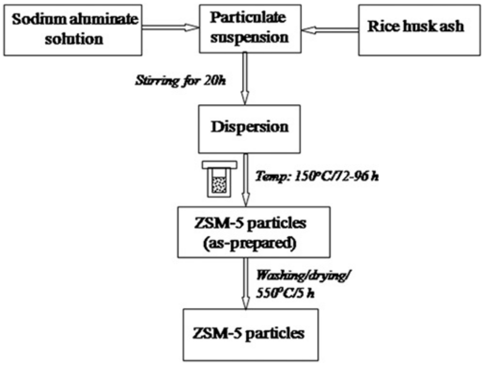

Fig. 1. Schematic representation for the synthesis of ZSM-5 zeolite powders using rice husk ash as a silica source and in the absence of organic templates.

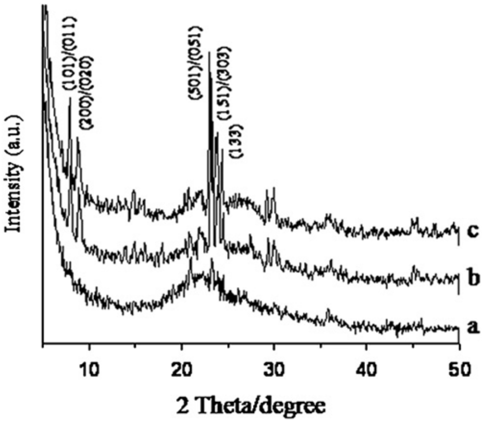

Fig. 2. XRD patterns of ZSM-5 powders synthesized using rice husk ash as a silica source and in the absence of organic templates at 150 °C for (a) 48, (b) 72, and (c) 96 h.

ZSM-5 particles did not take place. The crystallization of ZSM-5 started at 150 °C/72 h. With increasing reaction time from 72 h to 96 h, the degree of crystallization increased due to increase in nucleation with time.

Fig. 3 shows the FTIR spectra of the powders prepared at 150 °C for (a) 48, (b) 72, and (c) 96 h. The characteristic absorption bands of ZSM-5 were found at around 450, 540, 788, 1099 and 1220 cm^{-1}. The bending vibration of TO_4 (T=Si, Al) in ZSM-5 was recorded at around 450 cm^{-1}. It is to be noted that the vibration bands at around 540 and 1220 cm^{-1} indicated the presence of double 5-rings in ZSM-5. The internal asymmetric stretching vibration and external symmetric stretching of Si–O–T linkage were evidenced from the absorption bands at around 1099 and 788 cm^{-1} respectively. The characteristics bands of 540 and 1220 cm^{-1} of double 5-rings were practically absent for the powders prepared for the reaction time of 48 h, which corroborated the XRD results.

TG and DTA analyses of ZSM-5 were performed with the as-prepared powders synthesized at 150 °C/96 h. The TG curve (Fig. 4a) of ZSM-5 particles shows about 8.5% mass losses up to 200 °C which was attributed to the removal of water. The DTA curve (Fig. 4b) of ZSM-5 indicates a sharp endothermic peak at around 114 °C along with some small endothermic peaks at around 70, 142 and 176 °C. The endothermic peaks indicated the removal of water molecules.

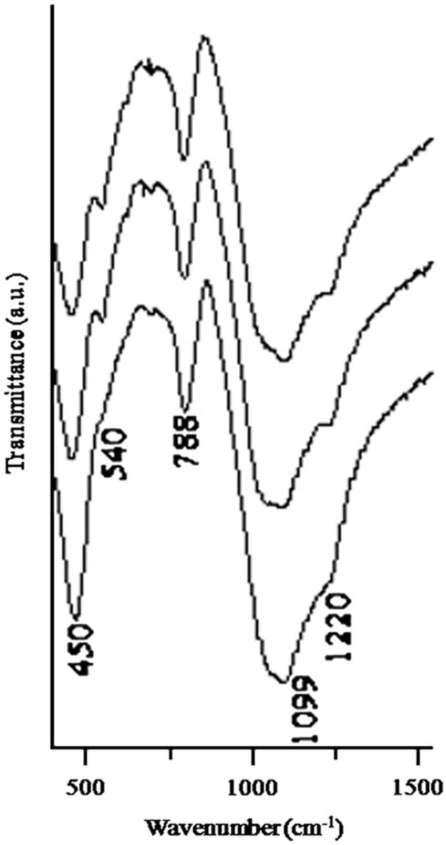

Fig. 3. FTIR spectra of ZSM-5 powders synthesized using rice husk ash as a silica source and in the absence of organic templates at 150 °C for (a) 48, (b) 72, and (c) 96 h.

The textural properties (BET surface area, micropore surface area, external surface area, total pore volume, and average pore size) of the samples synthesized at 150 °C for 72 and 96 h are shown in Table 1. It was noticed that with increase in reaction time, BET surface area increased. The average pore size decreased with increase in reaction time. It is to be pointed out that the micropore surface area could be due to the presence of structural pores of ZSM-5 zeolite (zeolitic pores), and the higher external surface area was due to the formation of textural mesoporosity [16] of ZSM-5 zeolite crystals. Fig. 5 shows the N_2 adsoption and desorption isotherms of ZSM-5 powders prepared at 150 °C/96 h. The pore size distributions (PSD) in the micropore range as evaluated by the HK method and those in the mesopore range as determined by the BJH method are depicted in the insets (I) and (II) respectively of Fig. 5. The adsorption/desorption isotherm indicated that the initial steep micropore uptake took place at about $p/p_o < 0.02$. The uptake of nitrogen increased steeply above the relative pressure of about 0.8. It shows an IUPAC type IV isotherm; the hysteresis loops were due to the formation of textural mesoporosity originated from the crystal intergrowth [16]. The inset (I) of Fig. 5 shows the micropore size distribution. The sharp peak at around 5.6 Å corresponds to the zeolitic pore of ZSM-5. BJH pore size distribution curve of the sample is shown in the inset (II) of Fig. 5. The prominent peak at around 38 Å indicates the mesopores generated in the ZSM-5 zeolite crystals.

Fig. 6 shows the FESEM microstructures of ZSM-5 powders obtained at 150 °C/96 h. It reveals the characteristic coffin-shaped particles of ZSM-5. It can be explained that under alkaline medium in the presence of NaOH, silica in RHA started dissolving to form silicate. The silicate and aluminate ions ($Al(OH)_4^-$) rearranged with Na^+ ions to form channel-type structure of ZSM-5. The Na^+ ion acted as a templating agent [8] for the formation of ZSM-5. During *in-situ* extraction of SiO_2, the RHA particles became smaller, which acted as nucleating sites for seeding growth of ZSM-5 particles. The seeds were grown to smaller particles. The smaller particles because of their high surface energy started aggregating. Under a certain reaction condition, the intergrowth of the particles took place leading to the formation of well crystalline coffin-shaped ZSM-5 particles.

4. Conclusions

ZSM-5 zeolite particles were synthesized through *in-situ* extraction of silica from RHA in the absence of any organic template by static hydrothermal condition at 150 °C/72–96 h. Degree of crystallization increased with increase in reaction time from 72 to 96 h. Average mesopore (textural mesoporosity) size decreased with increase in reaction time. Inter-growth of the seed particles

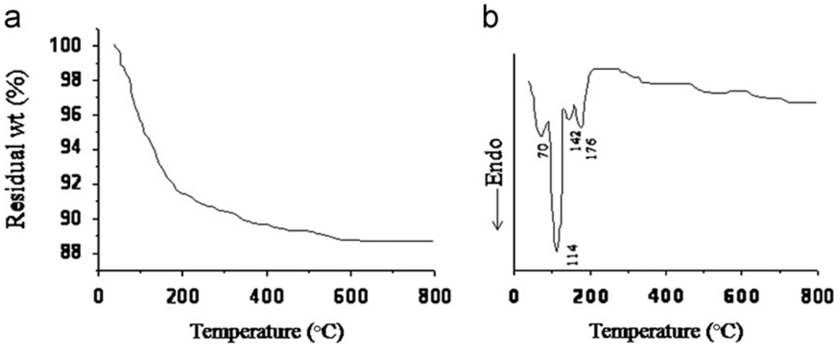

Fig. 4. Thermogravimetry (a) and differential thermal analysis (b) of ZSM-5 powders synthesized using rice husk ash as a silica source and in the absence of organic templates at 150 °C/96 h.

Table 1
Textural properties of ZSM-5 particles synthesized using rice husk ash as a silica source and in the absence of organic templates at 150 °C.

Synthesis time	S_{BET} ($m^2\,g^{-1}$)[a]	$S_{\text{micropore}}$ ($m^2\,g^{-1}$)[b]	S_{external} ($m^2\,g^{-1}$)[c]	$V_{\text{p-total}}$ ($cm^3\,g^{-1}$)[d]	d_p (nm)[e]
72 h	54.38	28.27	26.11	0.0545	4.01
96 h	73.99	43.84	30.15	0.0704	3.81

[a] BET surface area.
[b] Micropore surface area.
[c] External surface area.
[d] Total pore volume.
[e] Average pore size.

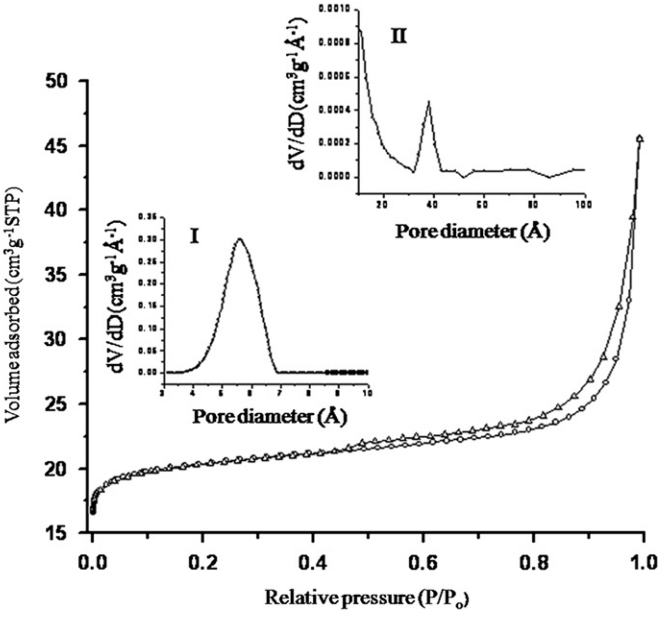

Fig. 5. Nitrogen adsorption and desorption isotherm of ZSM-5 powders synthesized using rice husk ash as a silica source and in the absence of organic templates at 150 °C/96 h. Inset: pore size distributions by (I) HK method and (II) BJH method.

led to coffin-shaped ZSM-5 powders. The present method of synthesis of ZSM-5 is a low cost and environmentally friendly process.

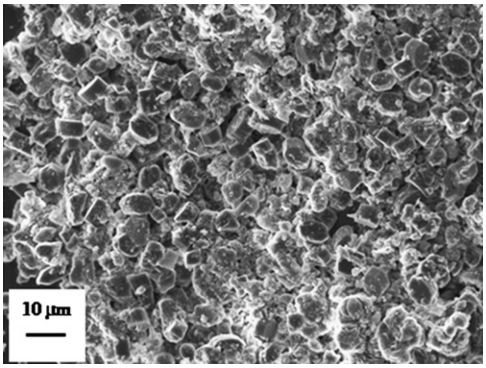

Fig. 6. FESEM image of ZSM-5 powders synthesized using rice husk ash as a silica source and in the absence of organic templates at 150 °C/96 h.

Acknowledgments

The authors would like to thank the director of this institute for his kind permission to publish this paper. They also acknowledge the help rendered by Sensor and Actuator Division, X-ray Characterization and Electron Microscopy Sections of the Institute for Material Characterization. The work was funded by the Institute's project of CSIR—Central Glass and Ceramic Research Institute, under Project no. OLP 299.

References

[1] G.T. Kokotailo, S.L. Lawton, D.H. Olson, W.M. Meier, Structure of synthetic zeolite ZSM-5, Nature 272 (1978) 437–438.
[2] A. Das, N. Das, M.K. Naskar, D. Kundu, M. Chatterjee, H.S. Maiti, Influence of process parameters on the formation of silicalite-1 zeolite particles, Ceramics International 35 (2009) 1799–1806.
[3] L.W. Beck, P. Lu, W.P. Weber, M.E. Davis, Investigation of organosilanes as structure-directing agents in zeolite synthesis, Microporous Materials 12 (1997) 361–368.
[4] L. Chen, S.Y. Zhu, Y.M. Wang, M.-Y. He, One-step synthesis of hierarchical pentasil zeolite microspheres using diamine with linear carbon as single template, New Journal of Chemistry 34 (2010) 2328–2334.
[5] C. Falamaki, M. Edrissi, M. Sohrabi, Studies on the crystallization kinetics of zeolite ZSM-5 with 1, 6-hexanediol as structure-directing agent, Zeolite 19 (1997) 2–5.

[6] M.K. Naskar, D. Kundu, M. Chatterjee, Synthesis of ZSM-5 zeolite particles using triethanol amine as structure-directing agent, Journal of the American Ceramic Society 95 (2012) 449–452.

[7] S.D. Kim, S.H. Noh, K.H. Seong, W.J. Kim, Compositional and kinetics study on the rapid crystallization of ZSM-5 in the absence of organic template under stirring, Microporous and Mesoporous Materials 72 (2004) 185–192.

[8] 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.

[9] S. Chandrasekhar, K.G. Satyanarayana, P.N. Pramada, P. Raghavan, T.N. Gupta, Review processing, properties and applications of reactive silica from rice husk—an overview, Journal of Materials Science 38 (2003) 3159–3168.

[10] M.K. Naskar, D. Kundu, M. Chatterjee, Coral-like hydroxy sodalite particles from rice husk ash as silica source, Materials Letters 65 (2011) 3408–3410.

[11] M.K. Naskar, D. Kundu, M. Chatterjee, A facile hydrothermal conversion of rice husk ash to ZSM-5 zeolite powders, Journal of the American Ceramic Society 95 (2012) 925–930.

[12] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecules layers, Journal of the American Chemical Society 60 (1938) 309–319.

[13] J.H. de Boer, B.C. Lippens, B.G. Linsen, J.C.P. Broekhoff, A. van den Heuval, T.J. Osinga, The *t* curve of multimolecular N_2 adsorption, Journal of Colloid and Interface Science 21 (1966) 405–414.

[14] E.P. Barrett, L.G. Joyner, P.P. Halenda, The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms, Journal of the American Chemical Society 73 (1951) 373–380.

[15] J. Schmidt, A. Boisen, E. Gustavssion, K. Stahl, S. Pehrson, S. Dahl, A. Carlsson, C.J.H. Jacobsen, Carbon nanotube templated growth of mesoporous zeolite single crystals, Chemistry of Materials 13 (2001) 4416–4418.

[16] G. Majano, A. Darwiche, S. Mintova, V. Valtchev, Seed-induced crystallization of nanosized Na-ZSM-5 crystals, Industrial and Engineering Chemistry Research 48 (2009) 7084–7091.