Materials Science Forum
ISSN: 1662-9752, Vol. 948, pp 9-13
doi:10.4028/www.scientific.net/MSF.948.9

Submitted: 2018-04-10
Accepted: 2018-11-30
Online: 2019-03-15

Effect of Seed Amounts on the Synthesis of Zeolite ZSM-5 Using Coal Bottom Ash and Rice Husk as Sources of Silica and Alumina by Using Seeding Method

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Keywords: Coal Bottom Ash, Crystallinity, Rice Husk, Seed, Template Free, ZSM-5

Abstract. ZSM-5 has been successfully synthesized by seeding method using coal bottom ash and rice husk as the sources of silica and alumina.Synthesis ZSM-5 were performed by the hydrothermal method in autoclave autogenous at 180 ˚C for 36 h with molar ratio 10Na : 50SiO : 2Al2O3 : 500H2O with the addition of ZSM-5 commercial as seed. In this experiments, investigated variations seed amounts of 5, 10, 15, and 20% of weight silica. The product was characterized using X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM), and Brunauer-Emmet-Teller (BET). Resulted showed that ZSM-5 succeed formed in all variation of seed contain. At variation seed amount 5%, crystallinity obtained still low in which content of quartz phase still be high. Percent crystallinity highest obtained at the variation of seed amount 20% with the result percent crystallinity relative 106%. The experimental results revealed that phase transformation has occurred, in which an amorphous phase of coal bottom ash and rice husk has been transformed to the ZSM-5 crystal with addition seed as substitution organic template.

Introduction

Recently, material zeolite has been great demand for use in various industries. One type of zeolite is more used in industry is zeolite ZSM-5. ZSM-5 is one of type zeolite synthesis belonging to the MFI zeolite family. Zeolite MFI is one of type zeolite with silica structure most strong because of bond Si-O-Si nothing less than 140°.

ZSM-5 is one of synthesis zeolite is more used in industry which involves the catalyst as hydrocarbon conversion reaction [5], the catalyst in the petrochemical industry, and used as an adsorbent on liquids and gases [7].

ZSM-5 synthesized with a hydrothermal method using a mixture of silica and alumina. So far the source of the silica and alumina that used to synthesize ZSM-5 from commercial raw materials. Source of silica usually used were in the form of silica sol, silica gel, smoky silica and silica with organic derivatives such as Tetraethylorthosilicate [3]. Generally, a source of silica synthesis used because high levels of purity and reactivity. However, because of the high price from a source of silica synthesis then another alternative is to use a source of silica derived from nature. In Indonesia, the availability of raw materials sourced from nature is very abundant as well as to reduce environmental problems then in this research will utilize waste in the form of bottom ash coal and rice husk as a source of silica.

So far has many done studies about ZSM-5 synthesis by using a template as referring agent. Templates are used as filler structures or as structural stabilizing agents. However, the use of organic templates is considered inefficient in an economic and environmental perspective [2], then research about ZSM-5 synthesis without using organic template continues to be developed. In this research, the role of a template will be replaced by seed. The role of seed to help the formation of crystals and reduce the risk of impurity crystal synthesis results [1].

Meng et al. [4] has successfully synthesized ZSM-5 by using seed induction method from Tetraethylorthosilicate as the source of silica and silicalite-1 as the referring agent (seed). The use of seeds to assist crystallization process has also been carried out by Prasetyoko et al [6] by using rice husk as a source of silica and adding silicalite-1 as seed by studying the effect of crystallization time on synthesis results.
In this research that synthesis of ZSM-5 done using coal bottom ash and rice husk as the source of silica and alumina then adding commercial ZSM-5 as seed. The amount of seeds added will affect the properties of ZSM-5, thus in the research will be studied the influence of the amounts of seeds of synthesis results.

1. Experimental Section

1.1 Preparation of coal bottom ash

Granular coal bottom ash was mashed using a mortar and sieved with a sieve 200 mesh to obtain the powder

1.2 Preparation of silica from rice husk

Rice husk was washed using hot water to remove impurities on the surface of rice husk, and then dried in air. Rice husk was dissolved in KOH 1,5%, heated until boiling for 1h while stirring, and then in aging for 24h. The sample was filtered to obtain a brown filtrate containing dissolved silica and then added HNO3 10% so that the solution changed to gel (pH close to 7). The resulted gel is left aging for 24 hours. The obtained gel is washed with hot aquades repeatedly to remove the excess acid. The gel was washed and dried at 110 ° C for 6 hours to obtain a silica solid. Silica powder is calcined in the furnace at 550˚C for 3 hours because it still contains organic impurities so it needs to be purified. The raw material rice husk and obtained rice husk silica is shown in the figure 1.

Figure 1. Rice husk (left) and rice husk silica (right).

1.3 Preparation of synthesis ZSM-5 by seeding method

Synthesis of ZSM-5 by seeding method was done by the addition commercial ZSM-5 as seed. The mother liquor was reaction mixture with rice husk silica, coal bottom ash, NaOH, aquades, and commercial ZSM-5 was used as seed. The reaction mixture was prepared with a molar ratio of 10Na: 50SiO: 2Al2O3: 500H2O. The reaction was initiated by making two solutions A and B. Solution A consists of silica husk rice, NaOH, and aquades. Solution B consist of coal bottom ash, NaOH, and aquades. Both solutions are stirred for 2h. Then, the reaction mixture in solution B was added to solutions A and stirred for 6h until homogeneous. The resulting mixture was aged for 12h at room temperature. Then, the seed was added with variations of 5, 10, 15, and 20% of weight silica to the mixture while stirring until homogeneous. The resulting mixture has a Ph 12.4. To obtain ph 10, 1N H2SO4 was added drop by drop into a solution. The resulting mixture was being transferred to a stainless steel autoclave. The crystallization process was conducted at 180°C for 36h and autogenously pressure in an autoclave. After crystallization process completed, then as-synthesized product was washed using distilled water until the washing water became neutral, then

the solid was dried at 105 C for 2 hours to remove the water content from the product. Finally, to remove carbon the product was calcined process at 550°C for 5h with the increasing temperature 1°C/min.

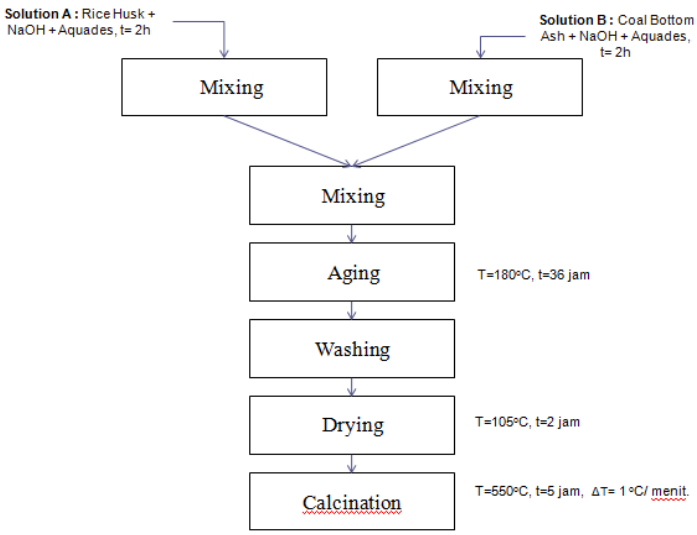

Figure 2. Diagram process manufacturing of zeolite ZSM-5.

1.4 Chararacterization

Coal bottom ash and rice husk silica were identified by using XRF (X-Ray Fluorescence) PANalytical Epsilon 3 to determine the chemical composition contained it. The product ZSM-5 was identified by X-ray diffraction (Sinar-X Pan Analytical X'Pert Powder) using Cu Kλ radiation at 30 Ma, 40 kV. The pattern was scanned in the 2θ ranges 5-50º. The infrared spectra of the product ZSM-5 were recorded on a Perkin Elmer FTIR wavenumber range of 1400-400 cm-1.

3 Results and Discussion

The silica has been produced from coal bottom ash and rice husk then was characterized using XRF (X-Ray Fluorescence) to determine the chemical composition contained it. Each of the composition of coal bottom ash and rice husk is shown in Table 1 and Table 2. The high content of SiO2 makes coal bottom ash and rice husk as a source of cheap, practical silica and can reduce environmental problems.

Figure 1 (a-e) presents the XRD pattern of the synthesized products of various amounts of seeds. The reference pattern XRD ZSM-5 is shown in Figure 1 (a). The XRD pattern with added amounts of seed 5% (Fig 1 (b)) indicates there a peak that appears at 2θ = 8,00˚, 8,94˚, 23,15˚ which are some peaks standard ZSM-5 but very small. Other peaks appear indicate samples still contain amorphous material, emerging various other phases such as silicon oxide, quartz, albite, analcime, ZSM-11, and Potassium Aluminum Silicate Hydroxide. The highest peak appears at 2θ = 26.1 which is the analcime phase. It was concluded that with added amounts of seeds 5%, ZSM-5 not much formed.

The XRD pattern with added amounts of seed 10% (Fig 1 (c)) indicates there full crystal phase with a peak that appears at 2θ = 7,91˚, 8,86˚, 10,56˚, 23,03˚ and 23,9˚. The XRD pattern indicates peaks standard ZSM-5, indicating that ZSM-5 has been formed. The highest peak appears at 2θ = 23,03 which is the characteristic ZSM-5 standard. However, there is still a peak other that appears at 2θ = 26.61˚ which shows the alpha quartz phase (Treacy, 2001), although the peak only slightly, the estimated alpha quartz phase appears because of the existence of coal bottom ash not finished reacting.

Meanwhile, the sample with added amounts of seed 15% (Fig 1(d)) indicating there peaks standard ZSM-5 but very small. The highest peak appears at 2θ = 26.1 which is the analcime phase.

The added amounts seed of 15% makes crystal ZSM-5the formed decreased again the estimated their presence of a collapsed seed due to an alkaline solution so that the ZSM-5 formed is not much. The XRD pattern with added amounts of seed 20% (Fig 1 (e)) indicates there full crystal phase with a peak that appears at 2θ = 7,98˚, 8,79˚, 22,95˚, and 23,94˚. The XRD pattern indicates peaks standard ZSM-5, indicating that ZSM-5 has been formed with the high-intensity relative. The highest peak appears at 2θ = 7,98 which is the characteristic ZSM-5 standard. Despite the high intensity, there appear peaks other indicating that the ZSM-5 product is not pure, the samples still contain amorphous materials, emerging various another phase such as alpha quartz, α-cristobalite, and Albite. The estimated appears other phases on the sample because there silica not reacting in the autoclave.

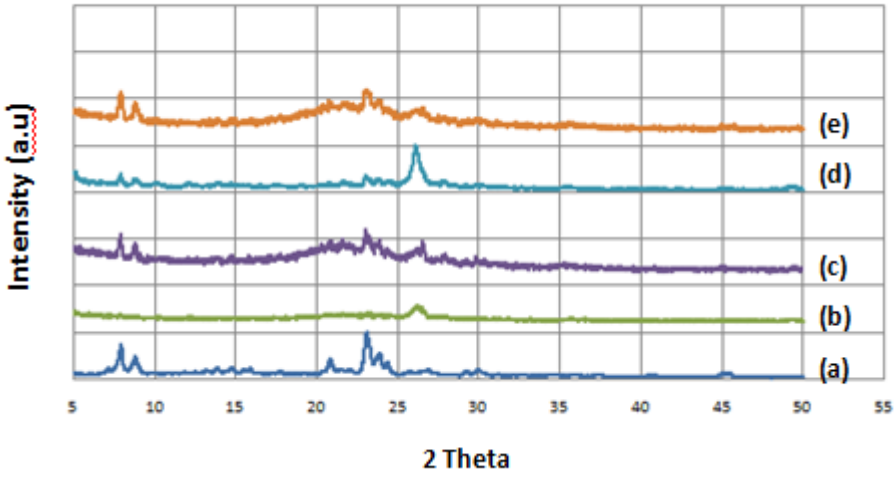

Figure 3. XRD patterns of (a) ZSM-5 standard, and samples at various amounts of seed: (b) 5%, (c) 10%, (d) 15%, (d) 20% of weight silica.

Has been calculated the percent of ZSM-5 crystallinity by comparing 2 theta peaks in each sample with 2 theta of ZSM-5 standard. The results of percent crystallinity at each run are shown in table 1.

Table 1. Percent crystallinity of the samples with various amounts seed.

STANDAR ZSM-5		RUN 1 SEED 5%		RUN 2 SEED 10%		RUN 3 SEED 15%		RUN 4 SEED 20%	
Pos. [°2Th.]	I real	Pos. [°2Th.]	I real	Pos. [°2Th.]	I real	Pos. [°2Th.]	I real	Pos. [°2Th.]	I real
7,94	74,19	7,94	15,217	7,94	81,964	7,94	40,203	7,94	94,118
8,8	49,74	8,8	16,071	8,8	65,331	8,8	28,378	8,8	63,051
9	30,83	9	13,665	9	42,685	9	20,946	9	54,228
23,08	96,98	23,09	19,099	23,09	86,974	23,09	32,179	23,09	92,647
23,12	100,00	23,12	18,789	23,12	85,772	23,12	27,703	23,12	95,221
23,14	97,53	23,14	23,37	23,14	80,361	23,14	29,476	23,14	94,85
23,16	92,84	23,157	21,506	23,157	72,144	23,157	27,787	23,157	91,544
23,18	89,40	23,174	20,419	23,174	76,553	23,174	27,618	23,174	90,074
23,2	88,12	23,2	19,332	23,2	81,764	23,2	26,943	23,2	89,154
23,22	81,13	23,22	20,703	23,22	78,156	23,22	26,858	23,22	84,375
	800,76		188,171		751,704		288,091		849,262
% Crystallinity			23,49%		93,87%		35,97%		106,05%

Percent crystallinity of ZSM-5 determine the amount of ZSM-5 contained in the product. The higher crystallinity in ZSM-5, indicating ZSM-5 is more stable and strength of structure so it is very well applied as a catalyst. The infrared spectra of the samples at various amounts seed were recorded at wavenumber in the range of 1400-400 cm-1 as shown in Table 3.

Table 2. Comparison of Wave Numbers FTIR on ZSM-5 with Various amounts seed with ZSM-5 Standard.

Samples	Asymmetric (Si-O-Si)	Symmetric	Vibration double ring	Vibration buckling bond (Si-O)
ZSM-5 standar	1250-950	720-650	650-500	500-420
Run 1 (5%)	1059,08	795,71	551,91	-
Run 2 (10%)	1055,82	799,38	548,66	-
Run 3 (15%)	1065,04	792,37	549,81	476,15
Run 4 (20%)	1063,3	798,84	521,39	-

4. Conclusion

ZSM-5 has been synthesis from coal bottom ash and rice husk as sources silica and alumina with operating conditions T = 180 C for 36h, Ph 10, and with added ZSM-5 commercial as seed. With investigating variations of seed amounts obtained synthesis best results on added amounts of seed 20% with crystallinity 106%. The higher crystallinity in ZSM-5, indicating ZSM-5 is more stable and strength of structure so it is very well applied as a catalyst.

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