Proceedings of the IConSSE FSM SWCU (2015), pp. BC.97–102
ISBN: 978-602-1047-21-7

Direct synthesis of mordenite from kaolin and rice husk ash

Sari Rahmawati[*], Ratna Ediati, Didik Prasetyoko

Chemistry Department, Sepuluh Nopember Institute of Technology, Surabaya 60111, Indonesia

Abstract

Mordenite with a Si/Al molar ratio of approximately 20 was synthesized from natural material such as kaolin and rice husk ash. The synthesis of mordenite was conducted under the following reaction condition $6Na_2O$:$0.75Al_2O_3$:$30SiO_2$:xH_2O (*x*= 710, 780 and 850) at 175 °C for 24-72 hours. The products were then identified by X-ray diffraction, FTIR, and SEM. The results showed that batch composition of the starting gel $6Na_2O$:$0.75Al_2O_3$:$30SiO_2$:$710H_2O$ with 36 hours synthesis time formed a high crystalline mordenite.

Keywords mordenite; kaolin; rice hush ash; H_2O amount; synthesis time

1. Introduction

Mordenite is a high silica zeolite with orthorhombic structure. With a Si/Al molar ratio equal to 5, the completely hydrated sodium form has the ideal composition of $Na_8Al_8Si_{40}O_{96}\cdot 24H_2O$. Mordenite consists of parallel 12-membered ring (MR) channels (0.67 0.70 nm) with 8 MR side pockets (0.34 0.48 nm). Mordenite has been used as catalyst for various industrially important reactions due to its high thermal and acid stability (Mignoni et al., 2008). Mordenite is one of the most important industrial catalysts for the conversion of hydrocarbons, for instance in hydroisomerization, alkylation, dewaxing, reforming and cracking (Zhang et al., 2009). The concentration of active sites and the catalytic activity are related to the zeolite structure formation and the increasing degree of crystallinity (Pirutko et al., 1996).

Mordenite are commonly prepared by hydrothermal method of the gel containing precursors of silica, alumina, metal cations and H_2O. Most of works on the synthesis of mordenite, the starting materials for silica and alumina were from chemical sources. It was reported that for the synthesis of mordenite using reactive and amorphous silica from natural material rice husk ash, relatively lesser Na_2O or greater SiO_2 content in the starting mixture was required compared to that of using silica from chemical source (Bajpai & Rao, 1981). In addition, natural material Kaolin showed to be a promising source of Si and Al for mordenite synthesis (Mignoni et al., 2008). In a country such as Indonesia, rice husk ash and kaolin are available in very large quantities and at low cost. It will have advantages as a low cost and environmental friendly process.

Some studies show that compounds with high-crystallinity have higher activity. For example an amorphous PtRuIr/C catalyst with high-crystallinity was found to have a higher electrocatalytic activity for methanol oxidation reaction. These results show that control of

[*] Corresponding author. Tel.: +62 857 313 49426; E-mail address: sari@chem.its.ac.id

crystallinity of the catalyst can play an important role in activity (Ma et al., 2013). Since the crystallinity of mordenite are strongly determined by the nucleation and crystal growth rate, the H_2O amount in the starting gel could affect the concentration of reactive species in liquid phase. Besides, synthesis time is also can affect crystallinity, zeolite phases and morphology (Mousavi et al., 2013). In this study, we report the crystallinity-controlled synthesis of mordenite by hidrothermal technique with various parameters such as synthesis time and H_2O content using kaolin and rice husk ash (RHA) as alternative source of raw material.

2. Materials and methods

2.1 *Materials*

Materials used for synthesis of mordenite were sodium hydroxide, deionized water and natural materials such as rice husk ash (94 wt% Si) obtained from Gresik, Indonesia and Kaolin from Bangka Indonesia (22 wt% Al, 46 wt% Si) used as silica and alumina source.

2.2 Methods

The mordenite were synthesized through a hydrothermal method with synthesis conditions as shown in Table 1. At first, a certain amount of sodium hydroxide and rice husk ash were mixed and was calcined at 723 K for 4 hours. To obtain the final batch gel compositions of $6Na_2O:0.75Al_2O_3:30SiO_2:xH_2O$ (x= 710, 780 and 850), deionized water and kaolin were added to calcinated mixture. The gel was then transferred to a stainless steel autoclave and left to crystallize at 448 K using time variation as shown in Table 1.

Table 1. Synthesis conditions and crystallinity data of synthesized mordenite.

Sample name	H_2O content (molar)	Synthesis time (hour)
MA-24	710	24
MA-36	710	36
MA-48	710	48
MB-24	780	24
MB-36	780	36
MB-48	780	48
MC-24	850	24
MC-36	850	36
MC-48	850	48

The products were identified and their crystallinity was determined using X-ray diffraction pattern, recorded on a Philips Expert (30 mA, 40 kV) with CuKα radiation and a 2θ range of 5-55°. For calculation of the crystallinity, the intensity of the main peak in each sample was compared with the sample which has the highest peak intensity. Morphology of the crystals was examined by Scanning Electron Microscopy (SEM) using a scanning electron microscope.

FTIR experiments were done on a Shimadzu 8201 PC FTIR spectrometer to characterize the framework structure of the mordenites. The samples were dissolved in KBr pellets and were analyzed in the range 2000–400 cm^{-1}.

3. Results and discussion

From the Match phase identification software analysis, all of the samples gave characteristics identical to mordenite with five most intense reflection at 2θ = 10.8; 20.6; 23.2; 26.6; 27.3 (Mignoni et al., 2008). The results exhibited that rice husk ash and kaolin as starting material can lead to the production of mordenite. Fig. 1 shows XRD pattern of samples with the highest crystallinity synthesized using H_2O amount of 710, 780 and 850, respectively. The sample with the lowest water amount (e.g., MA-36) shows the highest crystallinity. Conversely, when the H_2O amount was increased, the crystallinity of mordenite reduced as a consequence of decreasing supersaturation degree and nucleation rate (Mousavi et al., 2013).

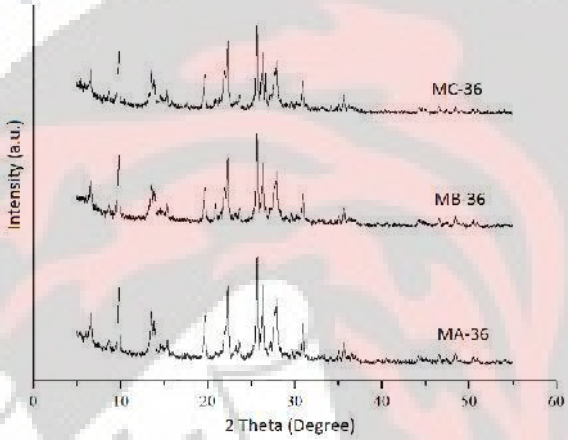

Figure 1. XRD pattern of the MA-36, MB-36 and MC-36 (H_2O amount of 710, 780 and 850 molar, respectively).

Table 2. Synthesis conditions and crystallinity data of synthesized mordenite.

Sample name	H_2O content (molar)	Synthesis time (hour)	Intensity (a.u)	Crystallinity (%)*
MA-24	710	24	1066.76	97.25
MA-36	710	36	1096.98	100.00
MA-48	710	48	1059.00	96.54
MB-24	780	24	829.76	75.64
MB-36	780	36	952.87	86.86
MB-48	780	48	930.59	84.83
MC-24	850	24	783.19	71.40
MC-36	850	36	878.51	80.08
MC-48	850	48	877.70	80.01

* Crystallinity calculated using the ratio of the intensity of the main peak (2θ = 25,67 with the same main peak of sample which has the highest peak intensity MA-36 and multiplied by 100.

Table 2 shows the crystallinity of mordenite obtained at different parameters (H_2O amount and synthesis time). As is shown in Table 2, the materials synthesized for 36 hours exhibited the highest crystallinity. It means that 36 hour of synthesis time is the best condition for the gel synthesis. This may be due to the fact that the crystals were being formed and were growing, and the particles were converting to the crystals as synthesis time goes on (Araki et al., 2012). But, when the reaction time was increased up to 48 hours, the product with lower crystallinity was obtained.

Keeping the composition ratio of $6Na_2O$:$0.75Al_2O_3$:$30SiO_2$:$710H_2O$, the mordenites were synthesized at longer synthesis time, i.e., 60 and 72. Surprisingly, it was found that mordenite with highest crystalline phase was obtained with synthesis time of 72 (see Figure 2). Araki et al. (2012) pointed to a four step zeolite synthesis mechanism: (1) formation of aluminosilicates, (2) particle growth and aggregation, (3) crystallization and crystal growth and (4) gentle crystal growth. It seems that within 72 hours the aggregates are going to convert to the crystals, according to the fourth step. Although 72 hours of synthesize time gave the highest crystallinity, but the gap of the crystallinity degree between 72 hours and 36 hours was slight. So, 36 hours of synthesis time was still the best condition to form high crystallinity mordenite, considering the low of reaction time.

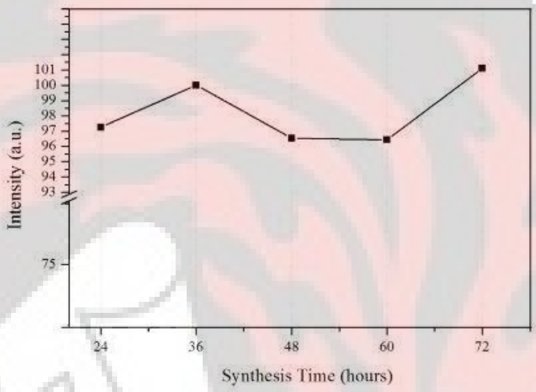

Figure 2. Graphic of the MA samples with synthesis time 24, 36, 48, 60 and 72 hours, respectively.

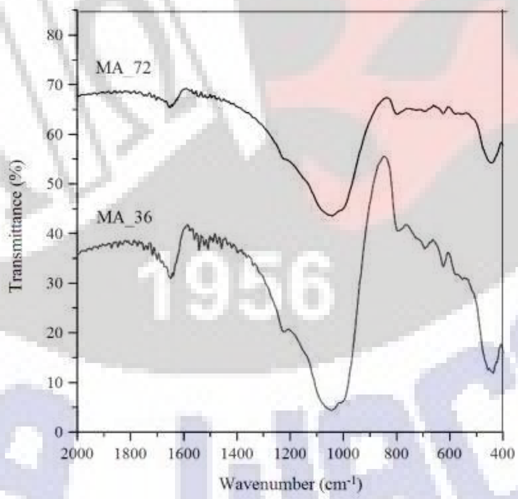

Figure 3. FTIR spectra of mordenites with different synthesis time: 36 hours (MA_36) and 72 hours (MA_72).

FTIR spectra of mordenites with the highest crystallinity (MA_60 and MA_72) are shown in Figure 3. The spectra shows the bands at 1621 and 1386 cm^{-1} due to bending vibration of (H-OH) and –(O-H-O)- band respectively. Typical vibrations for mordenite are observed: the absorbance of T–O (T = Si or Al) bending near 450 cm^{-1}, the peaks between 700-850 cm^{-1} and 1000-1150 cm^{-1} are assigned to symmetric Al-O and antisymmetric Si-O stretching vibration (Bhadauria et al., 2011).

Figure 4 represents the SEM micrograph of the synthesized material MA_72 which has the highest crystallinity among other samples. In this figure, it is clear that two phases are formed: sphere form of zeolite mordenite and amorphous aggregates. Since the size and morphology of zeolite crystals are mainly determined by the relative rates of nucleation and growth, the H_2O amount in the starting gel could affect the resultant crystal sizes by its effect on the reactivity of the aluminosilicate gel. a lowered supersaturation degree results in the formation of fewer nuclei, which would grow slowly and larger in the diluted gel (Zhang et al., 2009). From the SEM images, the crystal size of mordenite MA_72 was measured approximately 7.27 µm. According to the results reported by Araki et al. the products may already exist in steps 2 and 3 (particle growth and aggregation, and crystallization and crystal growth). So by further extending synthesis time using water content of 710, mordenite with higher crystallinity can be formed.

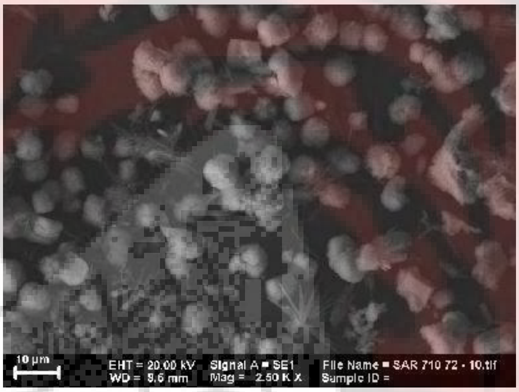

Figure 4. Scanning electron micrograph of sample containing 710 molar of H_2O with synthesis time 72 hours.

4. Conclusion and remarks

The study showed that the rice husk ash and kaolin as starting material can lead to the production of mordenite. With those materials, the batch composition $6Na_2O$:0,75Al_2O_3:30SiO_2: 710H_2O with 36 hours of synthesis time was the best condition to obtain the highest crystallinity of mordenite.

Acknowledgment

The authors gratefully acknowledge Kimia Material dan Energi laboratory (Chemistry Department) for providing library facilities, Laboratorium Energi LPPM-ITS and Laboratorium Divisi Karakterisasi Material FTI-ITS for the characterization of the synthesized material.

References

Araki, S., Kiyohara, Y., Tanaka, S., & Miyake, Y. (2012). Crystallization process of zeolite rho prepared by hydrothermal synthesis using 18-crown-6 ether as organic template. *Journal of Colloid and Interface Science*, *376*, 28–33.

Bajpai, P.K., & Rao, M.S. (1981). Synthesis of mordenite type zeolite using silica from rice husk ash. *American Chemical Society*, 721–725.

Bhadauria. J. Singh, B.K., Tomar, A., & Tomar, R. (2011). Synthesis and characterization of analogue of mordenite and its role as a catalyst for Friedel-Crafts acylation of anisole. *J. Chem. Pharm. Res., 3*, 245–257.

Ma, Y., Wang, R., Wang, H., Liao, S., Key, J., Linkov, V., & Ji, S. (2013). The effect of PtRuIr nanoparticle crystallinity in electrocatalytic methanol oxidation. *Materials*, *6*, 1621–1631.

Mignoni, M.L., Petkowicz, D.I, Machado, N.R.C.F., & Pergher, S.B.C (2008). Synthesis of mordenite using kaolin as Si and Al source. *Applied Clay Science*, *41*, 99–104.

Mousavi, S.F., Jafari, M., Kazemimoghadam, M., & Toraj, M. (2013). Template free crystallization of zeolite rho via hydrothermal synthesis: Effects of synthesis time, synthesis temperature, water content and alkalinity. *Ceramics International*, *39*, 7149–7158.

Pirutko, L.V., Dubkov, K.A., Solovyeva, L.P., & Panov, G.I., (1996). Effect of ZSM-11 crystallinity on its catalytic performance in benzene to phenol oxidation with nitrous oxide. *React. Kinet. Catal. Lett.*, *58*(1), 105–110.

Zhang, L., van Laak, A.N.C., de Jongh, P.E., & de Jong, K.P. (2009). Synthesis of large mordenite crystals with different aspect ratios. Microporous and Mesoporous Materials. *126*, 115–124.