



Research paper

Direct synthesis of mesoporous aluminosilicates from Indonesian kaolin clay without calcination



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ABSTRACT

The transformation of kaolin to amorphous mesoporous aluminosilicate was investigated in this study. We demonstrated the use of kaolin as silica and alumina sources without prior pretreatment. Two steps synthesis method were carried out; hydrothermal reaction at 80 °C, followed by addition of mesoporegen cetyltrimethylammonium bromide (CTABr) surfactant. We observed that prolonging the synthesis period improves the surface area of the aluminosilicate with enhances mesopore volume and surface acidity.

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1. Introduction

There is a growing challenge for developing robust materials based on aluminosilicate framework mainly to be used as catalyst for the synthesis of fine chemicals. Considerable effort has been dedicated to achieve desired mesoporous aluminosilicate materials with high surface area and hydrothermal stability as acid catalyst. Mesoporous structure in aluminosilicate is beneficial in catalytic application; the unique mesopores improve the mass transport and the diffusion of chemical reactant that subsequently accelerates the catalytic process (Pérez-Ramírez et al., 2008). Mass transport is faster in the catalyst cavity that offers shorter diffusion pathway between the reactant and the active site of the catalyst (Na et al., 2013).

Although the synthesis of aluminosilicates are well-established, commercial silica and alumina for example tetraethylorthosilicate (Li et al., 2013; Enterría et al., 2014; Li et al., 2010), colloidal silica (Xue et al., 2012), aluminum isopropoxide (Rownaghi et al., 2012; Jian et al., 2013), aluminum nitrate nonahydrate (Gonçalves et al., 2008) and sodium aluminate (Petushkov et al., 2011; Liu et al., 2014) are often used as starting material. Natural minerals provides alternative green and sustainable silica and alumina sources to replace the used of

synthetic chemicals. Many researchers have explored the potential of silica from rice husk ash (Prasetyoko et al., 2012), palygorskite (Jiang et al., 2014), and kaolin (Pan et al., 2013) for aluminosilicate synthesis. However, these materials must undergo calcination and acid leaching pretreatment to eliminate impurities that have significant influences on the physical properties of the synthesized materials. Kaolin is a clay mineral with the chemical composition of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. It consists of high Si and Al contents that is beneficial for aluminosilicate synthesis. The Si and Al in kaolin however exist in inactive states, which make the transformation into aluminosilicate is a challenging process (Chandrasekhar and Pramada, 2008). Conversion of kaolin into silica-based materials such as Ln-ZSM-5/MCM-41 (Li et al., 2010), mesoporous Al_2O_3 (Liu and Yang, 2010; Pan et al., 2013), Al-MCM-41 (Du and Yang, 2012) requires calcination at high temperature to activate the kaolin. Soft-template such as surfactant is added into the gel mixture or after crystallization period, which control the pore structure and the particle size of the intercrystalline powder (Li et al., 2013; Enterría et al., 2014).

Here, we report direct synthesis of amorphous mesoporous aluminosilicate using raw kaolin clay as the Si and Al sources without prior pre-treatment. Silicalite-1 seed was used as structure-directing agent (SDA) to obtain MFI-type framework, while cationic surfactant, CTABr was used as mesoporegen. We studied the transformation of kaolin into mesoporous aluminosilicate by monitoring the changes in porosity,

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acidity and surface area of the synthesized materials at various hydrothermal synthesis periods.

2. Experimental

2.1. Materials

Mesoporous aluminosilicate was prepared by kaolin (kaolinite, $\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8$) from Bangka Belitung, Indonesia with the composition of (wt%) Al_2O_3 (22%), SiO_2 (57%), P_2O_5 (3.9%), K_2O (3.22%), CaO (1.8%), TiO_2 (2.2%), V_2O_5 (0.15%), Fe_2O_3 (8.89%), CuO (0.31%), Ga_2O_3 (0.074%), ZrO_2 (0.22%), and BaO (0.77%); NaOH (sodium hydroxide, pelet, Applichem, >99.5%); LUDOX (colloidal silica, SiO_2 , Aldrich, 30%); distilled water; CTABr (cetyltrimethylammonium bromide, $\text{C}_{19}\text{H}_{42}\text{BrN}$, Applichem, 99%); and seed silicalite-1.

2.2. Synthesis

For the synthesis of mesoporous aluminosilicate, kaolin (3.7 g) was mixed thoroughly with NaOH solution (3.2 g in 40 mL of distilled water) followed by gradual addition of ludox (73 g) to the mixture. The mixture was stirred for 15 min before 40 ml of distilled water was added to give final chemical composition ratios of $10 \text{ Na}_2\text{O} : 100 \text{ SiO}_2 : 2 \text{ Al}_2\text{O}_3 : 1800 \text{ H}_2\text{O}$ (Prasetyoko et al., 2012). The stirring was continued for 8 h to obtain gel mixture and leave to age for another 12 h. The silicalite-1 seed (0.29 g) was subsequently added to the mixture followed by 30 min stirring.

The resulting mixture was then transferred into stainless steel autoclave and placed in oven at 80°C for 12, 24 and 48 h. The autoclave was brought immediately to room temperature by quenching with cold water. The CTABr (12.6 g, $\text{SiO}_2/\text{CTABr} = 3.85$) were slowly added and stirred for 1 h to obtain homogenous gel. The mixture was left to age at room temperature for 4 h. The solid products were separated by centrifugation (5000 rpm) and thoroughly washed with distilled water until the pH of supernatant is neutral. The final product was dried at 60°C for 24 h. The resulting powder was calcined at 550°C under continuous flow of N_2 for 1 h, followed by air calcination for another 6 h.

2.3. Characterization

X-ray powder diffraction patterns of crystal phase were recorded on a Philips Expert with $\text{Cu K}\alpha$ (40 kV, 30 mA) radiation in the range $2\theta = 5\text{--}40^\circ$. The infrared spectra (range $400\text{--}1400 \text{ cm}^{-1}$) of characteristic

vibration bands were monitored by FTIR Shimadzu Instrument Spectrum One 8400S. Total surface area, pore size distribution and total pore volume were determined from N_2 adsorption-desorption using a Quantachrome Instruments Nova 1200. Total surface area was determined by the BET and pore size distribution and volume in the mesopore were determined from the BJH method. The t -plot method was employed to calculate the micro-mesopore surface area and micropore volume while HK method was applied to calculate the pore size distribution in the micropore range. The acidity was measured by pyridine adsorption using FTIR spectrometer. Samples (13 mg) were pressed into wafer, placed in the homemade glass transmission cell and outgassed at 400°C for 3 h under N_2 flow. Pyridine was adsorbed at room temperature for 1 h and subsequently evacuated at 150°C for 3 h. FTIR Spectra were recorded in the $1600\text{--}1400 \text{ cm}^{-1}$. For TEM images, high resolution images and selected area electron diffraction patterns were recorded using a JEM 1400 instrument operating at 120 kV.

3. Results and discussion

XRD patterns of fresh kaolin and amorphous mesoporous aluminosilicates produced after 12, 24, and 48 h of crystallization period are shown in Fig. 1A. As observed, the kaolin precursor consists of a well-crystallized kaolinite. For the synthesized mesoporous aluminosilicates, the diffraction patterns consist of a big hump at $2\theta = 20\text{--}30^\circ$ indicating the amorphous aluminosilicate framework, as reported by Du and Yang (2012) and Dang et al. (2013). The transformation of kaolin crystalline phase to amorphous aluminosilicate have occurred at ~ 12 h of hydrothermal synthesis which the process presumably involves the dissolution of kaolin sheet-structure of amorphous silica (Chandrasekhar and Pramada, 2008; Liu and Yang, 2010).

We used infrared spectroscopy analysis to investigate the transformation of kaolin to mesoporous aluminosilicates framework. The infrared spectra of the fresh kaolin shows band appeared at $428, 470$ and 541 cm^{-1} which are corresponded to the vibrations of Si-O-Al framework. The bands appeared at $696, 754$ and 790 cm^{-1} were assigned to the vibrations of gibbsite-like layers of kaolinite. Peak at 917 cm^{-1} is Al-OH vibration and the peaks at 1033 , and 1110 cm^{-1} are the vibrations of in plane Si-O stretching (Olejnik et al., 1968; Dang et al., 2013) (Fig. 1B). Product obtained after 12 h of synthesis shows the peaks corresponded to kaolinite has disappeared together with the appearance of the peaks at $1090, 796$, and 470 cm^{-1} that were characteristics of the silica-based materials framework. The shoulder peaks at

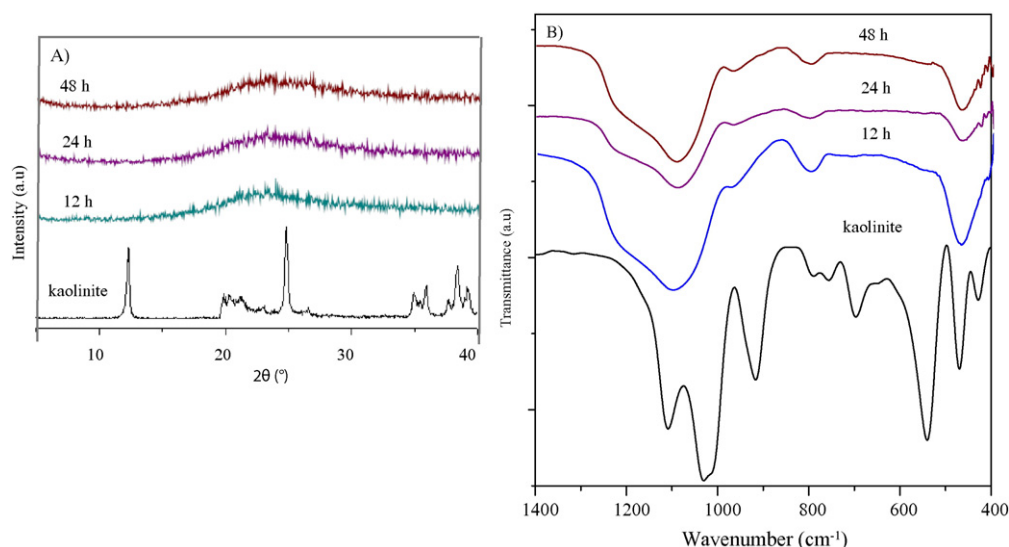


Fig. 1. A) XRD pattern and B) FTIR spectra of the synthesized amorphous mesoporous aluminosilicates at 12, 24 and 48 h.

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