Research Article

Hartati Hartati*, Aning Purwaningsih, Tjitjik Srie Tjahjandarie, Nastiti Heru Saputri, Ika Septiani Puspitasari, Christina Natalia Lamanele, Amalia Ayu Sa’adah, Arini Sabilal Haque, Dea Zaqiatul Mardho

Synthesis of amorphous aluminosilicate from impure Indonesian kaolin

https://doi.org/10.1515/chem-2020-0033
received November 27, 2018; accepted November 12, 2019.

Abstract: Synthesis of amorphous aluminosilicates from high impurities in Indonesian kaolin were carried out in several ways, directly from kaolin and indirectly from metakaolin (calcined kaolin), both with silica addition and without silica addition. Synthesis was conducted in a gradual temperature hydrothermal reaction and in a constant temperature hydrothermal reaction. Before being synthesized, kaolin impurities were separated according to density and/or particle size by centrifugation. X-Ray Diffraction and FTIR Spectrometry characterization of the synthesized product showed that the results of synthesis of aluminosilicates from metakaolin via hydrothermal with gradual temperature or constant temperature produced aluminosilicates with high quartz impurities, while synthesis with the addition of silica in hydrothermal conditions at 80°C for 12 hours can produce aluminosilicate with a low quartz content. Direct synthesis from kaolin with the addition of silica could produce pure aluminosilicates.

Keywords: aluminosilicate; Indonesian kaolin; metakaolin; silica addition; hydrothermal.

1 Introduction

The application of inorganic porous material has a great contribution in several fields: industry (catalysis [1, 2, 3, 4], wastewater treatment [2]), gas storage [2], drug delivery [5], environmental catalysis [6], etc. Its wide range and high potential application is due to its unique physicochemical properties, and controllable surface area, particle size, and pore size. Aluminosilicate is an inorganic porous material, a polymer of alumina and silica which has high mesoporous porosity and large surface area. Aluminosilicates have been widely used as a catalyst in organic reactions, such as addition [7], cracking [8], acetalization reaction [9, 10], etc. As a catalyst, aluminosilicate has some superiority due to its mesoporosity, high surface area, good ion exchange capability, thermal stability, and selectivity [11, 12]. Hartati, et al [13] successfully synthesized hierarchical aluminosilicate nanoparticles and analyzed their catalytic activity towards acetalizations of some aldehyde and propylene glycol, compared to PTSA as a homogeneous catalyst. The results of her research showed that all synthesized hierarchical aluminosilicate nanoparticles showed a higher selectivity than the PTSA catalyst. In general, aluminosilicate is synthesized from chemicals such as TMOS (Tetra Methyl Ortho Silicate), TEOS (Tetra Ethyl Ortho Silicate) and sodium aluminate [9, 10, 14, 15] as raw materials. The use of chemicals as raw materials is relatively expensive and toxic, therefore many researchers have substituted the use of chemicals by the natural ones, such as fly ash [16], rice husk [17], kaolin [10, 18, 19], etc. Kaolin is abundant silica-alumina based natural minerals. Aluminosilicate synthesis from kaolin can be carried out directly from kaolin [18, 20, 21] or from kaolin’s reactive form (metakaolin) [22, 23], which is obtained through calcination. Kaolin pre-treatment can be carried out in the presence of alkaline solution [24], such as potassium hydroxide [25], sodium hydroxide [21], sodium fluoride [26], etc. Hydroxide (OH−) could stimulate SiO2 and
Al\textsubscript{2}O\textsubscript{3} hydrolysis and to form 2Al(OH)\textsuperscript{−}\textsubscript{4} and [SiO(OH)]\textsuperscript{−}\textsubscript{4} free species of silicate and aluminate, and promote its polymerization [27]. The use of a fluorinated medium could produce fewer metastable phases [28] and catalyze the formation of Si-O-Si [29] as depicted in Figure 1. Dealumination, additional silica source, and desilication could be used to achieve the desired mole ratio of Si:Al. The addition of colloidal silica has some advantages, it contains nanometer scale silica dispersed in water; it has high stability, high binding capacity, narrow particle distribution and is less toxic than TEOS. This advantage would make the polymerization go well [30].

The use of high impurity Indonesian kaolin as a raw material to synthesize pure aluminosilicate was investigated in this research. The effects of prior calcinations, silica addition and base activator were examined. Aluminosilicate was synthesized by two synthesis routes. The first route was done by direct synthesis from kaolin with and without silica addition. The second route was done from metakaolin, with and without the silica addition. Sodium hydroxide and sodium fluoride were used as an activator base. The goal of this research was to produce a pure amorphous aluminosilicate catalyst from low grade impure Indonesian kaolin. The synthesized amorphous aluminosilicate was expected to be used as esterification catalyst.

2 Methods

2.1 Materials

Kaolin (Blitar Kaolin); sodium hydroxide (NaOH, Merck, 99%); hydrochloride acid (HCl, Merck, 37%); sodium fluoride (NaF, Merck, 99%); Colloidal Silica (LUDOX® 40 wt.% SiO\textsubscript{2} dalam H\textsubscript{2}O; Aldrich, destilled water).

2.2 Kaolin Preparation

Kaolin Blitar was grinded and added to distilled water in beaker glass with ratio 1:3. The mixture then stirred for 3 hours, then aged for 24 hours. Afterwards kaolin was separated from the impurities based on its particle size by centrifugation. The mixture was poured into a centrifuge tube and centrifuged for 20 minutes. After centrifugation, the mixture formed 3 layers: filtrate (top), yellowish white (middle) and black (bottom). The middle layer was kaolin, and the bottom layer was the impurities. The middle layer was collected and centrifuged again for 3 times until it formed 3 layers: filtrate, white layer, yellowish layer. The white layer was clean kaolin; it was collected and dried in an oven at a temperature of 100°C for 2 hours. Half of the dried
clean kaolin was then calcined in the furnace at 650°C for 6 hours. The result of the calcinations process was metakaolin. Then the metakaolin was dealuminated, the metakaolin was mixed with HCl (6M, 8M, 10M) in a ratio of 1: 5 (b/v) then refluxed at 80°C for 2 hours. The dealuminated metakaolin was washed with distilled water using a centrifuge until neutral. The filtrate from the mixture was removed by decantation, and the solids were dried in an oven at 100°C for 2 hours. The results were MD-8 (metakaolin dealuminated in HCl 8M), MD-9 (metakaolin dealuminated in HCl 9M), MD-10 (metakaolin dealuminated in HCl 10M).

### 2.3 Synthesis of Aluminosilicate

Samples AFM-1, AFM-2, and AFM-3 were synthesized with 0.8 g of NaOH dissolved into 68.4 mL of distilled water in plastic beaker. Plastic beakers were used instead of glass because NaOH causes a corrosive environmental effect on glass [31]; in certain temperatures and concentrations NaOH could react with glass (SiO₂) to form sodium silicate. This might impact the gel composition. The mixture of 0.0375 g MDA-8 and 3.2547 g MDA-10 added to NaOH solution, stirred using a magnetic stirrer for 15 hours at room temperature for aging. Afterwards, the mixture was transferred to a polypropylene bottle and heated in an oven at 60°C (24 hours). Afterwards the mixture was separated and washed with distilled water by centrifugation. Collected solids were then dried in an oven at 60°C for 24 hours. The desilication process was carried out with 0.8811 g of synthesized products, dissolved in a mixture of 54 g NaOH in 90 mL distilled water. The mixture was then heated at 100°C for 24 hours. Afterwards, the mixture was separated and washed with distilled water by centrifugation. The collected solids were then dried at 80°C for 24 hours. Based on FTIR study by Holm [32] alkali treatment can cause the loss of the internal Si-OH group and silanol group, resulting in the increase in Si-OH concentration.

Samples AFM-4, AFM-5 and AFM-6 were synthesized with similar procedures, but different starting materials and hydrothermal conditions. The starting materials were 3/4/17 grams of dealuminated metakaolin (MD-10), Hydrothermal conditions: 60°C (24 hours)- 80°C (24 hours)- 100°C (24 hours) for AFM-4, 80°C (24 hours)- 100°C (24 hours)- 120°C (24 hours)- 140°C (24 hours) for AFM-6. Sample AFM-7, AFM-8, and AFM-9 were synthesized by similar procedures with AFM-1 but with an addition of 1 ml peptin to the mixture of MD-10 and NaOH, and with a different hydrothermal condition. Hydrothermal conditions: 120°C (24 hours) for AFM-7, 140°C (24 hours) for AFM-8, 150°C (24 hours) for AFM-9. Sample AFM-10 synthesized with 0.2469 g metakaolin mixed with 11.3 mL colloidal silica, and 61.6 mL NaOH 1.33 M. Hydrothermal reaction carried out at 80°C for 12 hours.

Sample AFK-1 was synthesized based on a method by Qoniah [18] modified in the variation of base used in preparation. Synthesis was carried out with 0.2488 g kaolin, mixed in 18 mL of NaF 1.33 M at the plastic beaker, then added 11.3 mL colloidal silica, stirred for 1 hour. NaF act as activator. After the solution is homogeneous, 0.8 g NaOH and 43.6 mL H₂O were added. The mol ratio of the mixture was 15SiO₂: 0.00625Al₂O₃: 0.2NaOH: 38H₂O. Afterwards, the mixture was moved to a polypropylene bottle and heated in an oven with a gradual temperature, at 60°C (24 hours), and 80°C (48 hours). Afterwards the mixture was separated and washed with distilled water by centrifugation. Collected solids were then dried in an oven at 60°C for 24 hours.

Table 1 shows the details of the aluminosilicate synthesis process. Synthesized samples were characterized by X-ray diffractometry (XRD), infrared spectrophotometry (FTIR), nitrogen adsorption/desorption and scanning electron microscopy (SEM).

Ethical approval: The conducted research is not related to either human or animal use.

### 3 Results and Discussion

Blitar kaolin had a high quartz content as the kaolin diffractogram shows in Figure 2. Kaolin showed typical kaolinite peaks at 2θ around 12°, 20°, 25°, 35-40°, 45°[19] and quartz peak at 2θ = 26.74°. In order to reduce quartz and other impurities, kaolin was washed with distilled water by centrifugation. By the centrifugal force field, the components will separate according to their particle size [33]. For variation of starting materials, half of kaolinite was calcined to produce a more reactive phase: metakaolin. The metakaolin diffractogram showed an irregular intensity, its characteristic pattern of amorphous material. A trace of typical peak kaolinite peak was detected, but quartz peak was still detected, same as
A broad irregular hump-shaped peak at 2θ around 20° to 30° is the typical peak of amorphous materials [34]. AFM-1 and AFM-2 diffractogram showed a similar pattern with a metakaolin diffractogram, there were no typical amorphous phase of aluminosilicate. While sample AFM-3 showed a slight broad irregular peak at 2θ around 20° to 30°, the quartz peaked at 2θ around 27° (IZA). The result of first route synthesis method (sample AFM-1, AFM-2 and AFM-3), with increasing hydrothermal time, showed the development of an aluminosilicate formation, although it’s not perfectly formed. A longer hydrothermal time or higher hydrothermal temperature was needed to form amorphous phase of aluminosilicate.

Sample AFM-4 to AFM-6 synthesized by a similar route but with a higher gradual temperature and longer hydrothermal time, while samples AFM-7 to AFM-10 were synthesized with a constant temperature. Samples AFM-4 to AFM-9 diffractograms show the formation of amorphous aluminosilicate peaks, with an increased intensity at 2θ around 20° - 30°, but the typical peak of quartz was still detected. This was caused by pH of NaOH being too high, so the less stable aluminosilicate might be dissolved and produced more stable phase: quartz [17]. Other peaks around 20° were identified as nepheline and tridymite, while some peaks that appeared around 35-45° were identified as mullite, anatase, gibbsite, and illite [35]. The formation of this crystalline phase might be caused by thermal transformation during the synthesis.

Table 1: Synthesis route of the samples.

| Sample code | Raw material | Base         | Colloidal silica addition | Hydrothermal Temp (°C) | Time(h) |
|-------------|--------------|--------------|--------------------------|------------------------|---------|
| AFM1        | MDA          | NaOH         | -                        | 40-60-80               | 12-12-12|
| AFM2        | MDA          | NaOH         | -                        | 40-60-80               | 12-12-24|
| AFM3        | MDA          | NaOH         | -                        | 40-60-80               | 24-24-24|
| AFM4        | MDA          | NaOH         | -                        | 60-80-100              | 24-24-24|
| AFM5        | MDA          | NaOH         | -                        | 80-60-100              | 24-24-24|
| AFM6        | MDA          | NaOH         | -                        | 100-120-140            | 24-24-24|
| AFM7        | MDA          | NaOH         | -                        | 120                    | 24      |
| AFM8        | MDA          | NaOH         | -                        | 140                    | 24      |
| AFM9        | MDA          | NaOH         | -                        | 160                    | 24      |
| AFM10       | MDA          | NaOH         | -                        | 80                     | 12      |
| AFK1        | Kaolin       | NaF+NaOH     | -                        | 40-60-80               | 24-24-48|

MDA: Dealumated Metakaolin

Figure 2: XRD pattern of synthesized aluminosilicates.
process. Sample AFM-10 showed the formation of a typical amorphous phase of aluminosilicate peak with a slight quartz peak. The AFK-1 diffractogram showed a typical amorphous phase of aluminosilicate peak at 2θ around 20° to 30° without any trace of quartz or other impurities peaking. From the result, it can be concluded that the synthesis method of AFM-10 and AFK-1 (with the addition of silica) could produce amorphous aluminosilicate with minimum impurities. From the synthesis routes of this research, the addition of colloidal silica became the key factor to produce pure amorphous aluminosilicate. Besides as a silica source, colloidal silica could act as a seed that could trigger the growth of crystal core. Colloidal silica is very labile and reactive, so it can form crystal core easily [36]. Sample AFM-10 synthesized from metakaolin with NaOH as activator, while sample AFK-1 synthesized directly from kaolin with NaF and NaOH. Although AFK-1 synthesized from kaolin (less reactive than metakaolin), the use of NaF could promote aluminosilicate formation [28].

Spectra FTIR of samples were shown in Figure 3. Spectra AFK1, AFK2, and AFK3 didn’t show a significant difference. The pattern were same with metakaolin spectra, with bands at 476,42; 796,60 cm⁻¹ and 966 cm⁻¹. Band at 476,42 cm⁻¹ was indicated as bending vibrations of Si-O and Al-O. The band at 796,60 cm⁻¹ was indicated as vibrations of Si-O-Si asymmetry stretching and Si-O-Si symmetry stretching [15]. The band at 966 cm⁻¹ indicates the presence of asymmetry stretching the vibration of the silanol group (Si-O-H) [32]. Other samples (AFM 1-9) had similar patterns. All showed typical bands of aluminosilicate at 472, 798, 966 and 1066 cm⁻¹. The band around 1066 cm⁻¹ indicated as asymmetric stretch vibration and 798 cm⁻¹ indicated as Si-O-Si symmetrical stretch vibration. 472 cm⁻¹ band indicated as the vibration of Si-O and Al-O stretches. Bands at 472 and 1066 cm⁻¹ were indicated as the characteristics of the silica framework in aluminosilicate samples [18].

Physiosorption analysis were done with sample AFM-4 (representing all the amorphous aluminosilicate produced with high quartz impurities), and AFK-1 as the best product. The isothermic adsorption-desorption graphic of samples shown in Figure 4, had the characteristics of IUPAC isotherm graphic type 4. The hysterisis loop indicates mesopores, caused by the difference amount of adsorbed and desorbed N₂ molecules in the sample’s relative pressure [37]. Further analysis by the BET and BJH method were done to analyze average pore diameter and pore volume. The results of the analysis were summarized in Table 2, sample AFM-4 had S₁₀⁰⁰₂ 44,0081 m²/g, average pore diameter 3.7 nm with volume 0.1161 cm³/g. Sample AFK-1 had S₁₀⁰⁰₂ 23,7680 m²/g, average pore diameter 3.9 nm with volume 0.0696 cm³/g. Further analysis to sample AFK-1 was done by SEM-EDX to analyze the morphology and composition. The sample’s micrographs were shown in Figure 5. From the micrograph could be observed aluminosilicate particle with irregular shape and irregular size. Based on the result of EDX, sample AFK-1 had Si:Al molar ratio 57.
Figure 4: \( \text{N}_2 \) isothermic adsorption-desorption graphic.

Figure 5: Micrograph of Sample AFK-1 (magnification A: 5000x, B: 10000x), C: EDX of Sample AFK-1.
4 Conclusions

From all synthesized samples, the best products were AFK-1 and AFM-10, which produced amorphous aluminosilicate with the lowest (AFM-10) and no (AFK-1) quartz content. Both AFK-2 and AFM-10 were synthesized with the addition of colloidal silica and a low temperature (60-80°C) hydrothermal process. The best product (AFK-1) was synthesized with NaF as activator, and this proved that NaF could promote aluminosilicate synthesis.

Acknowledgement: This research was supported by funding of Ministry of Research and Technology, Republic of Indonesia, PDUPT, 2018-2019.

Conflict of interest: Authors state no conflict of interest.

References

[1] Perez-Ramirez J, Christensen CH, Egeblad K, Christensen CH, Groen JC. Hierarchical Zeolites: Enhanced Utilisation of Microporous Crystals in Catalysis by Advances in Materials Design. Chem. Soc. 2008;37:2530-42.
[2] Logar NZ, Kaucic V. Nanoporous Materials: From Catalysis and Hydrogen Storage to Wastewater Treatment. Acta Chim. Slov. 2006; 53:117-35.
[3] Hartati, Prasetyoko D, Santoso M, Bahruji H, Triwahyono S. Highly Active Aluminosilicates with a Hierarchical Porous Structure for Acetalization of 3,4-dimethoxybenzaldehyde. Jurnal Teknologi. 2014;69(5):25-30.
[4] Partlett CMA, Lee AF, Wilson K. Hierarchical porous materials: Catalytic application. Chemical Society Reviews. 2013;42:3876-93.
[5] Sayed E, Haj-Ahmad R, Ruparelia K, Arshad MS, Chang MW, Ahmad Z. Porous Inorganic Drug Delivery Sistem a Review. American Association of Pharmaceuticals Scientist. 2017;18:1507-25.
[6] Lan-Yi W, Xue-Hua Y, Zhen Z. Synthesis of Inorganic Porous Materials and Their Application in the Field of Environmental Catalysis. Acta Phys.-Chim. Sin. 2017;33(12):2359-76.
[7] Diwakar J, Viswanadh N, Saxena SK, Kumar S, Al-Muhtaseb AH. Liquid-phase solvent-less reactions for value addition of glycerols and phenols over nano porous aluminosilicates. CSIR-Indian Institute of Petroleum; 2018.
[8] Goyal G, Kuhn JN, Philippidis GP. Light alkene production by cracking picocolchorum, oculatum microalgae using aluminosilicate catalyst. Biomass and Bioenergy. 2018;108:252-7.
[9] Hartati, Prasetyoko D, Santoso M. Cyclic acetalization of furfural on porous aluminosilicate acid catalysts, Indonesian Journal Chemistry. 2016;16:289-96.
[10] Hartati, Prasetyoko D, Santoso M, Bahruji H, Triwahyono S. Highly active aluminosilicate with a hierarchical porous structure for acetalization of 3,4-dimethoxybenzaldehyde. Journal Teknologi. 2014;69:25-30.
[11] Lopes AC, Martins P, Lancers-Mendez S. Aluminosilicate and aluminosilicate based polymer composites: Present status, applications and future trends. Progress on Surface Science. 2014;89:239-77.
[12] Podvalov GP. On the role of acidity in amorphous silica-alumina based catalysts (Sub: On the Nature of the Sulfur Tolerance of ASA-Supported NiMo(W) sulfide and Pt hydrogenation catalys). Eindhoven: Technische Universiteit Eindhoven; 2001.
[13] Hartati, Santoso M, Nur H, Loon LW, Bahruji H, Qoniah I, Prasetyoko D, Selective Hierarchical Aluminosilicate for Acetalization Reaction with Propylene Glycol. Indonesian Journal of Chemistry. 2019;19(4):975-84.
[14] Liu H, Shen T, Li T, Yuan P, Shi G, Bao X. Green Synthesis of Zeolites from A Natural Aluminosilicate Mineral Rectorite: Effect of Thermal Treatment Temperature, Applied Clay Science. 2014;90:53-60.
[15] Sun C, Zhang F, Wang A, Li S, Cheng F. Direct synthesis of aluminosilicate using natural clay from low-grade potash ores of a salt lake in Qinghai China, and its use in octodecylamine adsorption. Applied Clay Science. 2015;108:123-7.
[16] Alzeer MIM, MacKenzie KJD. Synthesis and Catalytic Properties of New Sustainable Aluminosilicate Heterogeneous Catalyst Derived from Fly Ash. ACS Sustainable Chemistry & Engineering. 2018;6(4):5273-82.
[17] Prasetyoko D, Ayunanda N, Fansuri H, Hartanto, D. Phase Transformation of Rice Husk Ash in The Synthesis of ZSM-5 Without Organic Template, J. Math. Fund. Sci. 2012;3:250-62.
[18] Qoniah I, Prasetyoko D, Bahruji H, Triwahyono S, Jalil AA, Suprapto, Hartati, Purbaningtias, TE. Direct synthesis of mesoporous aluminosilicate from Indonesian kaolin without calcinations. Applied Clay Science. 2015;118:290-4.
[19] Ayele L, Pérez-Pariente J, Chebude Y, Díaz I. Conventional Versus Alkali Fusion Synthesis of Zeolite A From Low Grade Kaolin. Applied Clay Science. 2016;132-133:485-90.
[20] Du C, & Yang H. Investigation of Physicochemical Aspects from Natural Kaolin to Al-MCM-41 Mesoporous Materials. Journal of Colloid and Interface Science. 2012;369:216-22.
[21] Diffo BBK, Elimbi A, Cyr M, Manga JD, & Kouamo HT. Effect of the Rate of Calcination of Kaolin on the Properties of Metakaolin-based Geopolymers. Journal of Asian Ceramic Societies. 2015;3:130-8.
[22] Hartati H, Widiati A, Setyawati H, Fitri S. Preparation of Hierarchical ZSM-5 from Indonesian Kaolin by Adding Silica, Chemistry and Chemical Technol. 2016;10(1):87-90.
[23] Hartati H, Widiati AA, Kristanti AN, Purwaningsih A, Alfiani. Organic template free synthesis of ZSM-5 from calcinated Indonesian Kaolin. AIP Conference Proceedings. 2017;1888:020024.
[24] Davidovits J. Geopolymer Chemistry and Applications. 4th ed. SanQuintin, France: Institud Géopolymerè; 2008.
[25] Bouguermouh K, Bouzidi N, Mahtout L, Pérez-Villarejo L. Transformation of Rice Husk Ash in The Synthesis of ZSM-5 Versus Alkali Fusion Synthesis of Zeolite A From Low Grade Kaolin. Applied Clay Science. 2015;108:123-7.
[26] Gu X, Jiang T, Tao H, Zhou S, Li X, Ren J, Wang Y, Lu G, Schmidt W. Hydrothermally highly stable acidic mesoporous aluminosilicate spheres with radial channels. Journal of Material Chemistry. 2010;21:880-6.
[27] Masoudian SK, Sadighi S, Abbasi A. Synthesis and characterization of high aluminum zeolite X from technical
grade materials. Bulletin of Chemical Reaction Engineering and Catalysis. 2013;8(1):54–60.

[28] Louis B, and Kiwi-Minsker L. Synthesis of ZSM-5 Zeolite in Fluoride Media: an Innovative Approach to Tailor Both Crystal Size and Acidity. Microporous and Mesoporous Materials. 2004;74:171-8.

[29] Villaescusa LA, Wheatley PS, Bull I, Lightfoot P, Morris RE. The Location and Ordering of Fluoride Ions in Pure Silica Zeolites with Framework Types IFR and STF: Implications for the Mechanism of Zeolite Synthesis in Fluoride Media. J A Chem. Soc. 2001;123:8797-805.

[30] Anbia M, Bandarchian F. Optimization of Nanocrystals NaX Zeolite Synthesis with Different Silica Sources. Journal of Applied Chemical Research. 2015;9(4):71-80.

[31] Amaro A, Reis PNB, Neto MA, Louro C. Effect of Alkaline And Acid Solutions on Glass/Epoxy Composites, Polymer Degradation and Stability. 2013; 10.1016/j.polymdegradstab.2012.12.029.

[32] Holm MS, Svelle S, Joensen F, Beato P, Christensen CH, Borgida S, Bjorgen M. Assessing the Acid Properties of Desilicated ZSM-5 by FTIR using CO and 2,4,6-trimethylpyridine (collidine) as Molecular Probes, Applied Catalysis A: General. 2009;356:23-30.

[33] Taulbee DN, Maroto-Valer MM, Centrifugation. Encyclopedia of Separation Science. Chemistry, Molecular Science and Chemical Engineering. 2000;17-40.

[34] Peta S, Zhang T, Dubovoy V, Koh K, Hu M, Wang X, Asefa T. Template-free synthesis of highly selective amorphous aluminosilicate for toluene alkylation. Applied Catalysis A. General. 2018;556:155-9.

[35] Tiffo E, Mbah JBB, Belibi PDB, Djobo JNY, Elimbi A. Physical and mechanical properties of unheated and heated kaolin based-gel polymers with partial replacement of aluminium hydroxide. Materials Chemistry and Physics. 2020;239:122103.

[36] Cundy SC, Cox PA. The hydrothermal synthesis of zeolite: Precursors, intermediates and reaction mechanism. Microporous and Mesoporous Materials. 2005;82:1-78.

[37] Sing KSW, Everett DH, Haul RAW, Moscou L, Pierotti RA, Rouquerol J, Siemieniewska T. IUPAC-Surface Chemistry Including Catalysis-Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. Pure & Appl. Chem. 1985;57:603-19.