

Microwave Irradiation-Assisted Synthesis of Zeolites from Coal Fly Ash: An Optimization Study for a Sustainable and Efficient Production Process

Boitumelo Makgabutlane, Lebea N. Nthunya, Edward N. Nxumalo, Nicholas M. Musyoka, and Sabelo D. Mhlanga*



Cite This: *ACS Omega* 2020, 5, 25000–25008



Read Online

ACCESS |



Metrics & More



Article Recommendations

ABSTRACT: Class F South African coal fly ash was used as a precursor for the synthesis of zeolite A via complete microwave irradiation. To attain optimal conditions for the synthesis of zeolite A with minimum impurities, the microwave synthesis time, irradiation power, and Si/Al ratio were varied. Sodalite with fly ash phases were obtained when the Si/Al ratio in the coal fly ash was not adjusted and when the microwave irradiated coal fly ash slurry was used instead of the extract solution. Increased microwave irradiation time power and time favored the crystallization of zeolite A phase due to sufficient energy needed to ensure the dissolution of Al and Si from coal fly ash. A Brunauer–Emmett–Teller surface area of 29.54 m²/g and a cation exchange capacity of 3.10 mequiv/g were achieved for zeolite A, suggesting its potential application as an adsorbent and cation exchange material for environmental remediation. Complete microwave irradiation offers a greener approach toward zeolite synthesis from coal fly ash compared to conventional hydrothermal and fusion methods that consume a lot of energy and require longer reaction times.



1. INTRODUCTION

Coal fly ash is a byproduct of coal combustion generated in large quantities by thermal power plants such as Eskom in South Africa (SA). It is freely available and usually discarded as a waste material.¹ This waste material is a disposal challenge for countries such as SA whose primary source of power generation remains coal combustion. The rate at which the coal fly ash is produced is greater than its application, rendering it environmentally unsustainable. Nonetheless, coal fly ash has been used as a zeolite precursor because of its prevalent alumina and silica content.^{2,3} The type of zeolite produced from coal fly ash depends on but is not limited to: (i) the source of alumina and silica, (ii) the Si/Al ratio, (iii) loading ratio (volume of the alkali solution to weight of CFA), (iv) the synthesis procedure, and (v) reaction conditions (i.e., reaction time and temperature).^{4–11} The synthesis of zeolites from coal fly ash has been proposed to follow three steps, which involves the *dissolution* of SiO₂ and Al₂O₃, especially from the glass phase into an alkaline solution (e.g., NaOH); the *condensation* of silicate and aluminate ions in alkali solution to make aluminosilicate gel; and the *crystallization* of aluminosilicate gel to make the zeolite crystal.⁴

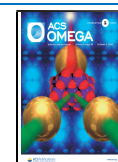
Several methods have been used to synthesize zeolites from coal fly ash. These include the hydrothermal method,⁵ alkali fusion-assisted hydrothermal treatment,⁶ microwave-assisted

hydrothermal treatment,⁷ molten salt method,⁸ solvent-free method,⁹ and ultrasonic-assisted method.¹⁰ The above-mentioned synthesis methods have produced different types of zeolites with varied purity levels, such as zeolite A, sodalite, zeolite X, and zeolite Na–P.^{11,12} The type and purity level of zeolites produced informs its application. Synthetic zeolites have been applied as adsorbents,¹³ cation exchange materials,¹⁴ and catalysts¹⁵ using various methods. However, the challenge with some of these methods is the long reaction time and the employment of high reaction temperatures. The hydrothermal synthesis of zeolite is a long reaction method typically performed for up to 48 h because of the high activation energy required to dissolve the coal fly ash glassy phase of Si and Al.¹⁶ The alkali fusion-assisted methods which have been extensively used due to their production of highly pure and crystalline zeolites require the employment of high temperatures (~550 °C).¹⁷ Although, these methods successfully

Received: March 2, 2020

Accepted: May 26, 2020

Published: September 22, 2020



produced zeolites from coal fly ash, they are not economically viable nor environmentally benign. Researchers have made great efforts in assisting the conventional synthesis methods with greener methods such as microwave and ultrasound irradiation energy to reduce the synthesis time and temperature.^{18,19} Ojumu et al.¹⁰ replaced the energy consuming fusion step with an ultrasonic treatment prior to hydrothermal heating, which afforded the production of the pure zeolite-A phase at lower energies and shorter reaction times.¹⁰ Belviso²⁰ recently compared the effect of direct sonication and conventional hydrothermal method to investigate the crystallization mechanism of zeolites from fly ash. It was observed that the hydrothermal process is a slower mechanism of crystallization in comparison with ultrasonic treatment.²⁰ Ultrasonic waves have been shown to induce a rapid zeolite synthesis and significantly reduced crystallization temperature below that observed when conventional hydrothermal synthesis is employed.¹⁸

Several studies have focused on the microwave-assisted hydrothermal treatment in order to reduce the reaction time and energy consumption.⁷ In this method, the coal fly ash reaction mixture is irradiated with microwave energy to reduce the dissolution time followed by crystallization using hydrothermal heating. During hydrothermal heating, the reaction mixture is placed in either a high temperature oven, autoclave, or a heated oil bath for crystallization to occur.²¹ The complete microwave synthesis of zeolites employed in this study, entailing both dissolution and crystallization being performed using microwave energy, has received little attention. Inada et al.⁷ were not successful in the synthesis of zeolite using a complete microwave irradiation process. Although, the fly ash-based materials obtained showed improved cationic exchange capacity, they did not crystallize into zeolite phases. They observed that continuous microwave irradiation without conventional heating prevented the formation of zeolites.⁷ An optimization study was not performed and hence the reaction conditions might have not been favorable for the crystallization of zeolite. The main limitation of zeolite synthesis is the slow reaction time and high temperatures required to dissolve Si and Al from coal fly ash, conditions under which high cation exchange capacity (CEC) and porous zeolites such as zeolite A cannot be synthesized. When the reaction temperature is decreased, the synthesis yield decreases and long activation time is required.²² Complete microwave irradiation employed in this study offers a synthesis method of zeolites using less energy at short reaction times. To the best of our knowledge, no zeolites have been successfully crystallized from coal fly ash using a complete microwave synthesis method without the assistance of conventional methods such as the hydrothermal and alkali fusion.

The main focus of this work was to study the effect of microwave irradiation energy on the physicochemical properties of zeolites synthesized from coal fly ash. Microwave irradiation conditions, such as irradiation power and time, required to optimize the synthesis of zeolite materials were studied. This greener approach of complete microwave irradiation will open further research directions for the synthesis and application of cost-effective and efficient high-quality zeolitic materials derived from environmentally concerning coal fly ash.

2. EXPERIMENTAL PART

2.1. Materials. Coal fly ash was supplied by Rosherville Eskom Research Station (Johannesburg, South Africa). This fly ash was a waste product from Duvha Thermal Power Plant in Mpumalanga (SA). Sodium hydroxide (NaOH, ACS reagent $\geq 97.0\%$ pellets) and sodium aluminate (NaAlO_2 , ACS Reagent Grade, 90%) were obtained from Sigma-Aldrich and used as received without further purification.

2.2. Microwave Synthesis of Zeolites from Coal Fly Ash Slurry with No Al Adjustment. Raw coal fly ash was used as a silica and alumina source and NaOH was used as a mineralizing agent. Typically fly ash (20 g) was added into a round bottom flask filled with 100 mL of distilled water. To this solution, 5 M NaOH was added and the mixture was shaken to homogeneity. The resulting solution mixture was subjected to microwave irradiation using Sineo UWave-1000 at a constant temperature of 100 °C, varied power (300, 600 and 900 W), and time (5, 10, and 15 min). Thereafter, it was centrifuged to separate the slurry (solid component) and clear extract (liquid component), which were further crystallized in additional steps described in Sections 2.3 and 2.4, respectively, to produce the final zeolite products.

2.3. Microwave Synthesis of Zeolites with Al Adjustment in the Coal Fly Ash Slurry. Typically, 72 mL of slurry from the microwave irradiated coal fly ash solution was used as Al and Si sources. A 28 mL NaAlO_2 solution was added to the slurry as an additional Al source to adjust the Si/Al ratio.²³ The adjustment of the Si/Al ratio is important to facilitate the type of zeolite that is produced. The resulting solution of the slurry was further subjected to microwave irradiation at various power settings (300 and 600 W) and time (10 and 20 min). The solid product was centrifuged, oven-dried, and kept for analysis.

2.4. Microwave Synthesis of Zeolites with Al Adjustment in the Extract Solution. The extract obtained by centrifuging the microwave irradiated coal fly ash slurry solution was used as a precursor for zeolite synthesis. Approximately 72 mL of the recovered extract was used as Al and Si sources. Typically, 28 mL of NaAlO_2 solution was added to the extract solution as an additional Al source to adjust the Si/Al ratio. The resulting solution was further subjected to microwave irradiation at various power settings (300 and 600 W) and time (20 and 30 min). On a different set of the experiment, the extract was placed in an oven for 1 h (hydrothermal heating). The resulting product was centrifuged, followed by crystals oven drying, and analysis. Figure 1 presents the steps followed in synthesizing the zeolites.

The following equation was used to calculate the percentage yield of synthesis products

$$\text{yield} = \frac{\text{obtained mass (g)}}{\text{theoretic mass (g)}} \times 100\%$$

2.5. Characterization. X-ray fluorescence (NEX CG Rigaku) was used for the elemental analysis of the raw material and its products. X-ray diffraction spectroscopy (XRD, Rigaku 124 Ultimate IV X-ray diffractometer) was conducted to evaluate the crystallinity. Furthermore, scanning electron microscopy (SEM, JOEL STM-IT300) was used to determine the morphology. The chemical functional groups on the materials were analyzed by a PerkinElmer model RZX FTIR, while a Brunauer–Emmett–Teller (BET, 3Flex surface area analyzer) was used to measure their surface area and porosity.

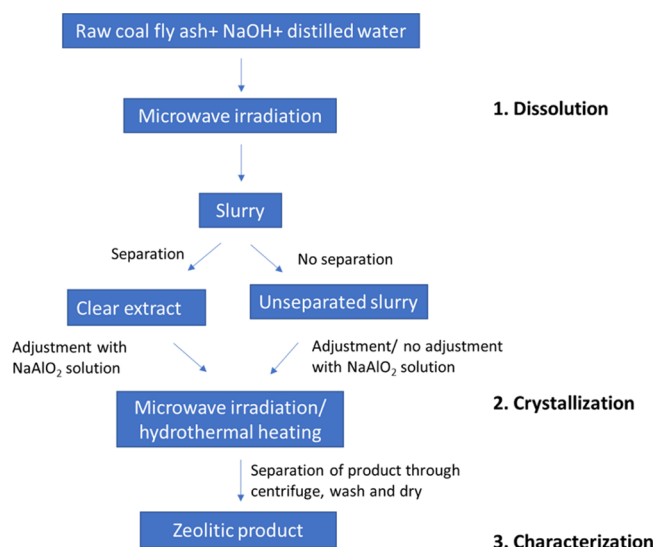


Figure 1. Schematic representation for synthesis and characterization of zeolites.

A procedure adopted from the study reported by Musyoka et al.,²⁴ was used to measure the CEC. Finally, a 930 Compact IC Flex Metrohm ion chromatography was used to determine the concentrations of exchangeable cations (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) in the final solution.

3. RESULTS AND DISCUSSION

3.1. Zeolitic Products Obtained from Microwave Irradiation of the Unadjusted Slurry. This section describes the physicochemical properties of the materials obtained in Section 2.2. The coal fly ash used was class F and the elemental composition results are presented in our previous study.²⁵ Figure 2 shows XRD patterns of coal fly ash products obtained after microwave synthesis at different power settings (300, 600, and 900 W) and time (5, 10, and 20 min). No zeolite materials were formed at shorter irradiation

times (i.e., 5–10 min) for all power settings used (i.e., 300, 600, and 900 W). A similar observation was reported in the previous literature.²⁶ This phenomenon was attributed to the energy of irradiation of the reaction mixture which is a function of both irradiation time and microwave power.²⁶ The energy was insufficient for zeolites to crystallize from the coal fly ash. The dissolution and depolymerization of the silica and alumina polymeric groups in coal fly ash have been reported to be the driving mechanism for the crystallization of zeolites.¹⁶ Dissolved oligomers in the liquid phase appear to form stable nuclei capable of inducing crystal growth.¹⁶ However, crystal growth will not be observed if the amount of energy transferred to the reaction mixture is inadequate. At longer irradiation time (20 min), sodalite began to form and the phase was more distinct at an elevated power of 900 W (Figure 2c). The broad hump observed at an irradiation time of 20 min with 600 W and 900 W was attributed to amorphous phases, which signifies the dissolution of glassy crystal phases of coal fly ash. The oscillating electromagnetic field in the microwave oven was active for longer with increasing power, resulting in a stronger dissolution effect.²⁷ This means more silica and alumina were available to crystallize into sodalite at elevated power. Owing to the formation of the undesired phase (sodalite) even at a higher reaction power (900 W), 300 and 600 W were chosen to study the effect of power and time on the Al adjusted slurry and extract solution.

SEM was used to determine the surface morphology of the coal fly ash products after being subjected to microwave irradiation at various power and time (Figure 3a–c). The shape of the products was mostly spherical with some being irregular shaped. At low power and shorter reaction times, the surfaces of the materials were still smooth and similar to that of coal fly ash, indicating that coal fly ash was still the dominant phase (Figure 3a–c). As the irradiation time and power were increased, zeolite crystals began to deposit on the activated coal fly ash surfaces (Figure 3c). These findings were similar to those reported in the previous literature.^{7,28} The deposition of zeolite crystals on the surface of fly ash has been found to

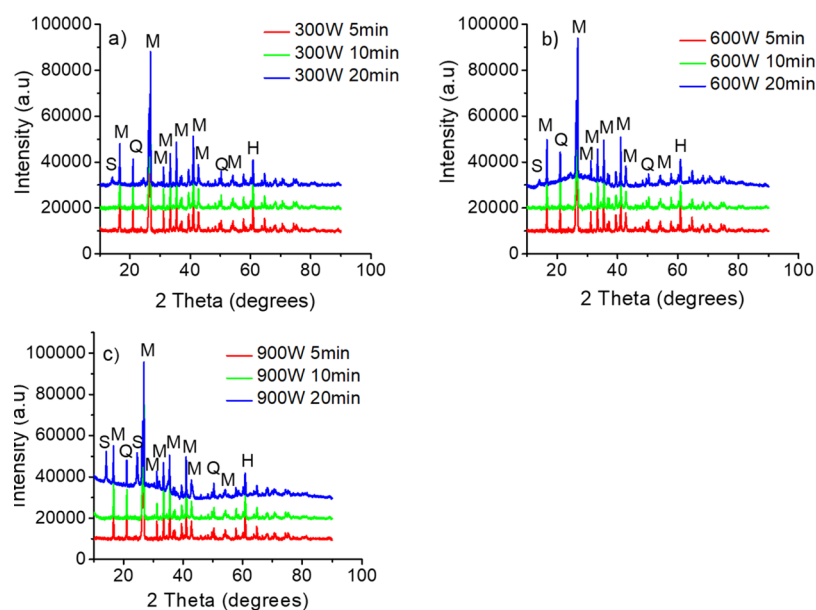


Figure 2. XRD patterns of coal fly ash products synthesized at various power settings; (a) 300, (b) 600, and (c) 900 W and various reaction time (5, 10, and 20 min). S = sodalite, M = mullite, Q = quartz, and H = hematite.

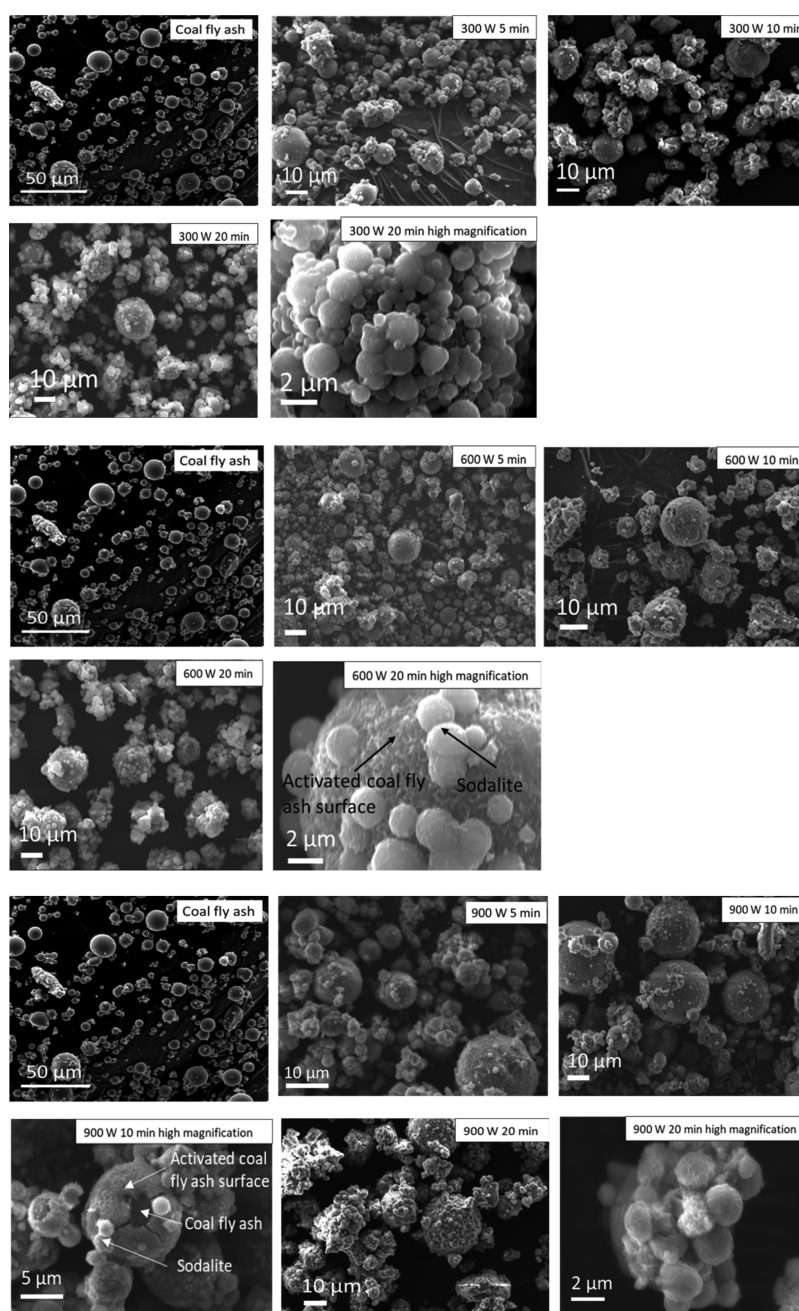


Figure 3. (a) SEM images of coal fly ash and its zeolitic products synthesized at 300 W for 5, 10, and 20 min. (b) SEM images of coal fly ash and its zeolitic products synthesized at 600 W for 5, 10, and 20 min. (c) SEM images of coal fly ash and its zeolitic products synthesized at 900 W for 5, 10, and 20 min.

restrict the access of hydroxyl ions that would have enhanced the dissolution of Si and Al from the coal fly ash.²⁹ The SEM images showed a gradual transformation of coal fly ash at low irradiation power and time to the formation of the sodalite phase at higher power and longer times which is also confirmed by XRD results.

3.2. Zeolitic Products Obtained from Microwave Irradiation of the Al Adjusted Slurry. The effect of microwave irradiation power and time on the synthesis of zeolite from the Al-adjusted coal fly ash slurry (Section 2.3) was studied and the resulting XRD plots of the products obtained are shown in Figure 4. Sodalite in the presence of fly ash phases was formed at varied irradiation power and time. The products were crystallized from the slurry. Hence, the

crystalline phases of fly ash were still present (mullite, quartz, and hematite). Similar results were obtained with the unadjusted coal fly ash slurry (Section 2.2). The low intensity peaks of sodalite in Figure 4 were attributed to the resistance in the dissolution of the coal fly ash phases. At 300 W 20 min, the sample was more crystalline and the sodalite peaks became more distinct compared to a higher microwave irradiation power of 600 W. Sodalite phases were still formed at longer reaction times and increased power. This observation showed that sodalite was favorable when the slurry was used even though the Al ratio which is said to promote the formation of zeolite A was adjusted.²³

Figure 5 shows SEM images of coal fly ash and the products synthesized from the coal fly ash slurry at various microwave

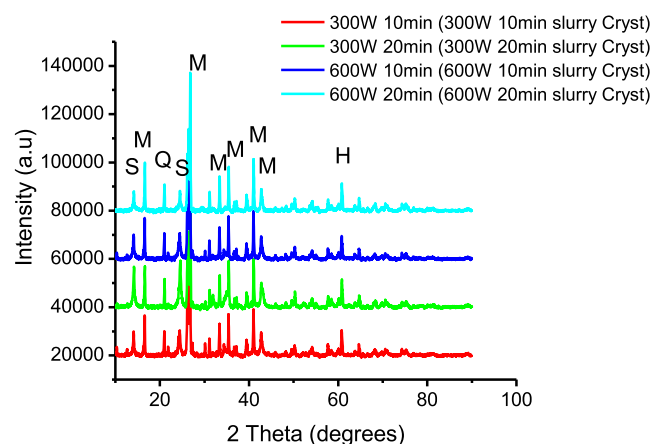


Figure 4. XRD plots of products obtained from microwave irradiation of coal fly ash using the slurry at various power settings (300 and 600 W) and reaction time (10 and 20 min). S = sodalite, M = mullite, Q = quartz, and H = hematite.

irradiation power and time. Owing to their amorphous and glassy phases, coal fly ash particles were spherical and smooth.³⁰ However, after alkaline microwave activation, the morphology of the coal fly ash was transformed. Sodalite crystals were formed on the smooth surface of coal fly as the microwave irradiation time was increased. Zeolite crystallization appeared to take place at the interface between the undissolved coal fly ash and the alkaline solution which led to the deposition of zeolite crystals. This meant that the nucleation mechanism of the coal fly ash zeolitization is heterogeneous.²² At 300 W and 20 min of irradiation, more sodalite crystals were formed and similar results were observed with XRD results. Sodalite phases were still formed even at high microwave irradiation power. This meant that the coal fly ash residue in the slurry promoted the formation of sodalite phases.

3.3. Zeolite A Obtained from Microwave Irradiation of the Al-Adjusted Extract. Figure 6 shows XRD plots for zeolites synthesized from the coal fly ash extract solution at various irradiation power and time settings according to the method presented in Section 2.4. It is noteworthy that zeolite crystals were not formed when the extract solution was unadjusted. This was attributed to the insufficient extraction of Si/Al from the fly ash slurry for zeolitization to occur. The filtration of the fly ash solution resulted in the removal of undissolved components remaining in the solution. Highly

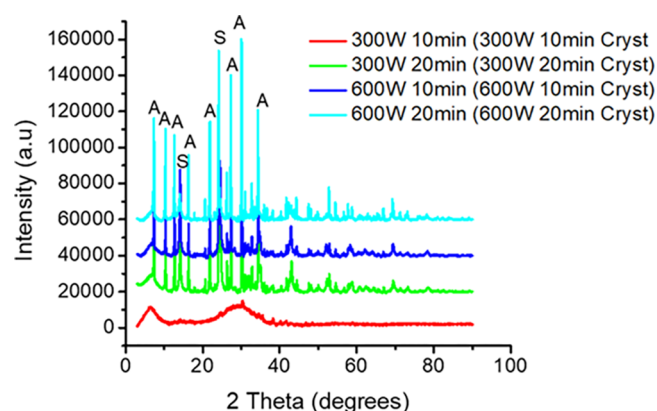


Figure 6. XRD plots of products obtained from the microwave irradiation of coal fly ash using the filtered clear extract at various power settings (300 and 600 W) and irradiation time (10 and 20 min). A = zeolite A and S = sodalite.

crystalline zeolite A and sodalite phases were formed at different irradiation times and power. This was observed by the highly intense and narrow peaks without an elevated baseline. At 300 W and after 10 min no crystal phase was obtained, the produced material was amorphous. This was due to the low power and time which subsequently failed to promote zeolite crystallization. As the microwave irradiation time increased to 20 min while the power setting was maintained at 300 W, the amorphous phase decreased and crystalline phases of zeolite A and sodalite were observed. Interestingly, an increase in microwave irradiation power (600 W) resulted in an increase in zeolite A crystal phases. This was also confirmed by the SEM image (Figure 7), which showed cubic shape crystals associated with zeolite A to be more dominant. Sodalite peaks at $2\theta = 14^\circ$, $2\theta = 24^\circ$, and $2\theta = 43^\circ$ began to disappear at 600 W 20 min, zeolite A peaks became more pronounced and new peaks appeared at $2\theta = 53^\circ$. Complete zeolite phases (sodalite and zeolite A) were crystallized in the absence of fly ash phases as compared to the samples prepared using the slurry which still had fly ash phases (mullite and quartz). This is because the zeolites were crystallized using the extract which contained only the Si/Al extract without coal fly ash residues.

Figure 7 shows SEM images of coal fly ash and its zeolitic products at various microwave irradiation power and time. The coal fly ash spheres were deformed, and the smooth surfaces changed into various crystal shapes upon alkaline microwave activation. At 300 W and after 10 min of microwave

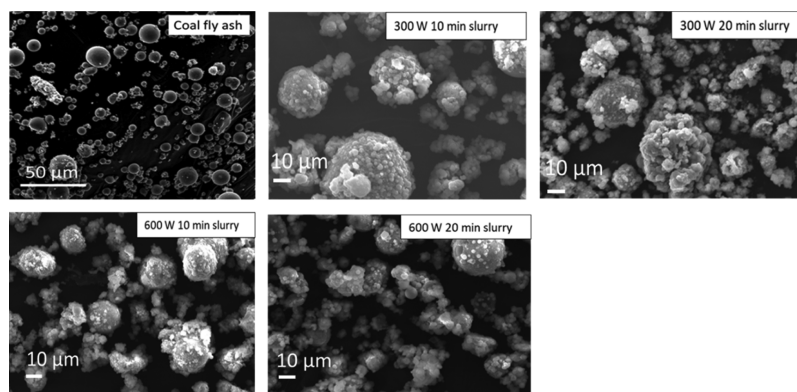


Figure 5. SEM images of products obtained from the microwave irradiation of coal fly ash using the slurry at various power and time.

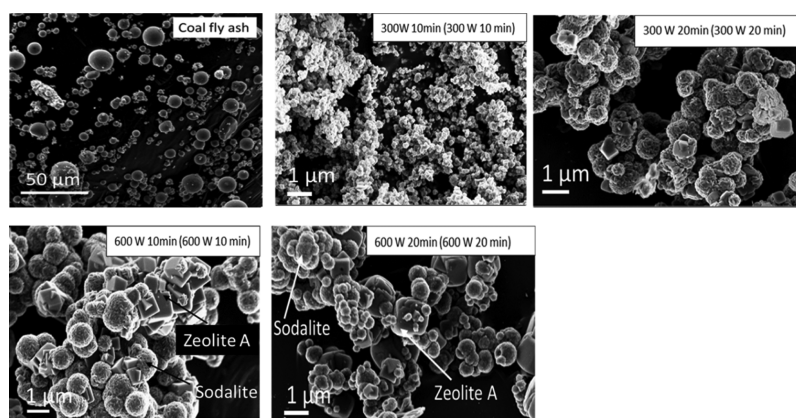


Figure 7. SEM images of products obtained from microwave irradiation of the coal fly ash extract at various power and time.

irradiation, the materials were amorphous and no zeolite products were formed, which is also confirmed by XRD. This was attributed to insufficient energy required to dissolve silica and alumina in coal fly ash to ensure zeolitization. At an elevated time of 20 min (same power—300 W), a mixture of zeolite A and sodalite crystals began to form. The crystals were flower-like spheres (sodalite) and cubic (zeolite A) in shape.¹⁰ At an elevated power of 600 W, more cubes (zeolite A) were formed, meaning zeolite A required more energy to crystallize. However, the synthesis of zeolites is a metastable processes where the least stable phases (e.g., zeolite A) are transformed to more stable phases (sodalite). In the quest to find the optimum reaction conditions for pure phase zeolite A, the reaction time should not be increased beyond the phase formation of sodalite.

3.4. Zeolitic Products Obtained from Microwave-Assisted Hydrothermal Heating of the Al Adjusted Extract. Figure 8 shows XRD plots of zeolite A and sodalite

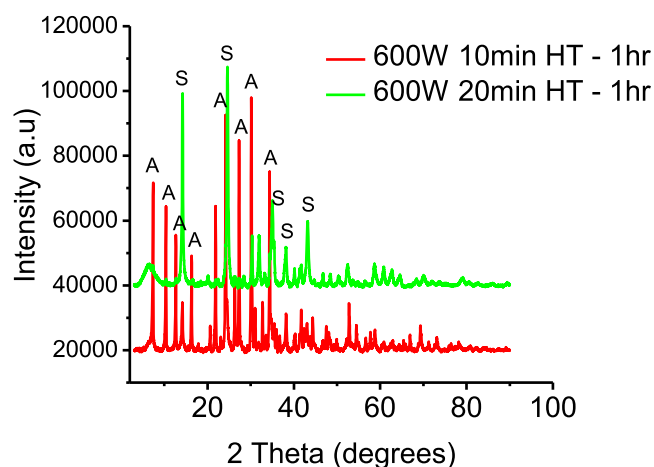


Figure 8. XRD plots of microwave-assisted hydrothermal synthesis of zeolitic products from coal fly ash using the extract at various irradiation time (10 and 20 min). A = zeolite A, S = sodalite.

synthesized from the coal fly ash extract by a microwave hydrothermal-assisted method (Section 2.4). The effect of microwave irradiation time was studied on the hydrothermally crystallized products. The results indicated that the microwave irradiation time influenced the synthesis of zeolite. At 10 min, almost pure phase zeolite A was formed with minimal impurities of the sodalite phase. An increase in irradiation

time (~20 min) resulted in the phase transformation of zeolite A to a pure phase sodalite. Zeolites are thermodynamically metastable phases. The law of the Ostward successive reaction is followed in zeolite synthesis. The metastable phases appear first, followed by successively more stable phases.¹⁰ This observation is explained by the transformation of zeolite A phase into a sodalite phase at a longer reaction time. Owing to the formation conditions of crystal zeolite A with a complete microwave irradiation method, 600 W was chosen as the optimum irradiation power to study the effect of irradiation time on the synthesis of zeolite A on the microwave-assisted method.

SEM images for zeolites synthesized from coal fly ash by the microwave-assisted hydrothermal method are presented in Figure 9. The smooth spherical shape of coal fly ash was transformed into cubes, which was associated with zeolite A after 600 W and after 10 min of microwave irradiation and 1 h hydrothermal heating. At longer microwave irradiation times, the spheres associated with the sodalite phase were formed as was the case in the XRD results. A similar observation was seen with the complete microwave synthesis method (Section 2.4). Aldahri et al.,³¹ synthesized zeolite-P with low crystallinity and low purity dominated by coal fly ash phases at 6 h conventional heating times.³¹ While in this study, a shorter conventional heating time of 1 h resulted in the formation of highly crystalline zeolite A with little sodalite phases.

3.5. Characterization of Optimum Synthetic Sodalite and Zeolite A. The results presented in this section are for the synthesized sodalite and zeolite A obtained at optimum conditions using complete microwave irradiation at 300 W and 20 min for the Al-adjusted slurry (Section 3.2) and 600 W and 30 min for the Al-adjusted extract (Section 3.3), respectively.

3.5.1. Fourier Transform Analysis of Coal Fly Ash and Its Synthesized Products. The functional groups present in coal fly ash and the synthesized products were studied using FTIR and the results are presented in Figure 10. The asymmetrical stretching modes associated with T–O–T stretching (T = Al, Si) observed at 1062 cm⁻¹ for coal fly ash shifted to 968 cm⁻¹ for sodalite and zeolite A.⁶ This shift was due to the formation of crystalline sodalite and zeolite A phases. The intensity of the zeolite A peak was higher than that of sodalite because of the highly crystalline formed zeolite A as confirmed by the XRD. Remarkably, the new vibrational bands observed at 1444 cm⁻¹ were attributed to C–O stretching, the 1651 and 3363 cm⁻¹ vibrations were due to OH bonding in the zeolite structure.³² Furthermore, Al–O–Si symmetrical vibrations shifted from

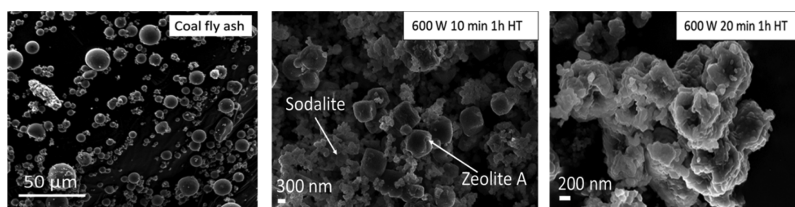


Figure 9. SEM images of the microwave-assisted hydrothermal synthesis of zeolitic products from the coal fly ash extract.

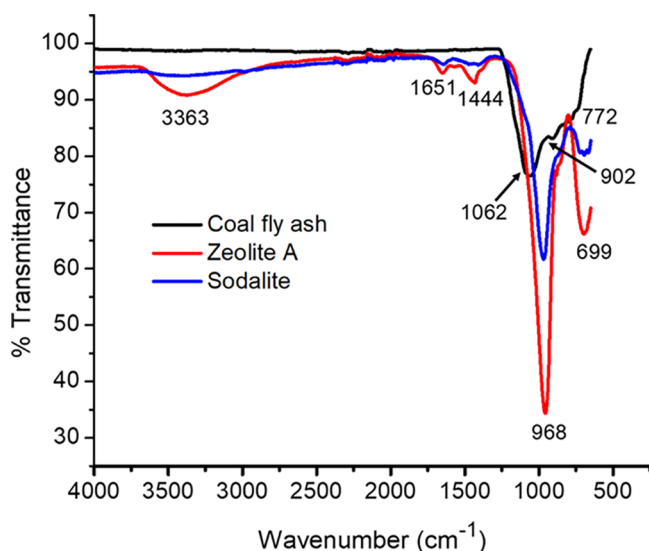


Figure 10. Fourier transform infrared spectra of synthesized zeolite A and sodalite.

772 cm^{-1} and appeared more pronounced at 699 cm^{-1} for the synthesized sodalite and zeolite A.³³ The vibrational peaks were displaced to a lower wavenumber compared to coal fly ash and new peaks were formed during zeolitization.

3.5.2. Surface Area and Porosity Analysis of Synthesized Sodalite and Zeolite A. The surface areas of synthesized zeolitic materials (sodalite and zeolite A) obtained at optimum conditions using a complete microwave irradiation method determined by BET measurements are presented in Figure 11.

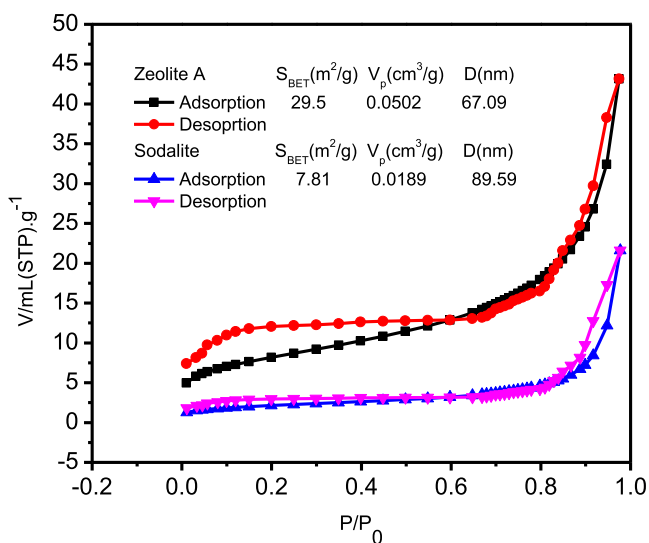


Figure 11. Nitrogen sorption isotherms of sodalite and zeolite A.

The surface area of coal fly ash was reported elsewhere.²⁵ Under the optimized conditions, the surface area of sodalite and zeolite A was found to be 7.81 and 29.5 m^2/g , respectively. These results are comparable to commercial zeolite A studied by Iqbal et al.,³⁴ which showed a surface of 36.6 m^2/g .³⁴ Muriithi et al.,³⁵ synthesized zeolite A using a fusion-assisted hydrothermal method and recorded a higher BET surface area of 43 m^2/g because of the synthesis of a pure phase.³⁵ The remarkable increase in surface area, pore volume, and pore width were observed upon the zeolitization of the coal fly ash. The improved surface area was due to the growth of zeolitic crystals with smaller particles compared to that of coal fly ash particles. Zeolite A had the highest surface area because of the improved quality and relatively higher crystallinity as shown by XRD results compared to sodalite. Similarly, the high porosity of the zeolitic products was confirmed by SEM micrographs. The presence of the hysteresis loop confirms the presence of mesopores in the pore structure of sodalite and zeolite A (Figure 11). The absence of a well-defined type I isotherm which is associated with zeolites was due to the pore blocking effect of the cations that are dispersed in the channels of the zeolite. Additionally, it is believed that the applied degassing temperature resulted in the structural reorganization of the zeolite. Thus, the BET results should be interpreted together with CEC and XRD results.

3.5.3. Cation Exchange Capacity and Yield of Synthesized Sodalite and Zeolite A. The CEC of coal fly ash was reported on our previous study.²⁵ Under optimized conditions, the CECs of sodalite and zeolite A were 0.98 and 3.10 mequiv/g, respectively (Table 1). Owing to their high number of readily

Table 1. Cation Exchange Capacity and Yield of Sodalite and Zeolite A

material	CEC (mequiv/g)	yield (%)
sodalite (300 W, 20 min)	0.98	87
zeolite A (600 W, 20 min)	3.10	22

exchangeable cations within the framework, zeolitic products were characterized by higher CEC values compared to their counterpart raw coal fly ash.²⁵ Behin et al.²² obtained a CEC of 1.82 mequiv/g for zeolite A synthesized using a microwave-hydrothermal method. The complete microwave synthesis method used in the study gave relatively higher CEC for zeolite A compared to the hydrothermal-assisted method. It is evident that the microwave irradiation improved the CEC, which makes the materials applicable for adsorption purposes.²⁵

The yield was inclusive of coal fly ash and zeolite phases present in the synthesis products. The yield of sodalite and zeolite A were 85 and 22%, respectively. The zeolite A yield was lower than that of sodalite because zeolite A was synthesized from the filtered extract. It was predominately

zeolite A with some sodalite as confirmed by XRD and SEM. The sodalite product consisted of coal fly ash phases which were not present in zeolite A because it was synthesized from the unfiltered slurry.

4. CONCLUSIONS

Zeolite A and sodalite were synthesized via a complete microwave irradiation method and a microwave-hydrothermal assisted method using a noxious waste—South Africa class F coal fly ash as a precursor. The complete microwave synthesis using the coal fly ash slurry led to the production of sodalite, while zeolite A was produced from the filtered clear extract. Remarkably, irradiation time, power, and Si/Al ratio were found to influence the synthesis of zeolite A. Longer reaction times with an adjusted Si/Al ratio resulted in the formation of more crystalline zeolite A phases. Zeolite formation was shown to be a thermodynamically metastable process, where zeolite A was transformed into a more stable sodalite phase. Hence, the formation of pure-phase zeolite A without sodalite phases would need more optimization studies using the complete microwave technique. In essence, the complete microwave irradiation synthesis of zeolites demonstrated better results compared to conventional hydrothermal heating. This method significantly reduced the reaction time and temperature compared to conventional synthesis methods. Thus, providing a greener approach for the synthesis of zeolite with a higher yield within shorter reaction times. Hence, it offers an economically viable utilization of a waste coal fly ash for industrial applications while simultaneously minimizing environmental pollution.

AUTHOR INFORMATION

Corresponding Author

Sabelo D. Mhlanga – SabiNano Research and Innovation and the DSI/MINTEK Nanotechnology Innovation Centre, Mintek, 2194 Johannesburg, South Africa; orcid.org/0000-0003-4985-2418; Phone: (+2711) 709 4798; Email: smhlanga@sabinano.co.za

Authors

Boitumelo Makgabutlane – Nanotechnology and Water Sustainability Research Unit, College of Science, Engineering and Technology, University of South Africa, 1709 Johannesburg, South Africa; SabiNano Research and Innovation and the DSI/MINTEK Nanotechnology Innovation Centre, Mintek, 2194 Johannesburg, South Africa

Lebea N. Nthunya – Department of Chemical, Metallurgical and Material Engineering, Tshwane University of Technology, Pretoria 0001, South Africa; orcid.org/0000-0002-1838-6365

Edward N. Nxumalo – Nanotechnology and Water Sustainability Research Unit, College of Science, Engineering and Technology, University of South Africa, 1709 Johannesburg, South Africa

Nicholas M. Musyoka – HySA Infrastructure Centre of Competence, Centre for Nanostructures and Advanced Materials (CeNAM), Chemicals cluster, Council for Scientific and Industrial Research (CSIR), Pretoria 0001, South Africa; orcid.org/0000-0001-9830-9265

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsoomega.0c00931>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The financial support received from the University of South Africa and access to laboratory space and microwave reactor from SabiNano and the DSI/Mintek NIC is gratefully acknowledged.

REFERENCES

- (1) Alzeer, M. I. M.; Mackenzie, K. J. D. Synthesis and catalytic properties of new sustainable aluminosilicate heterogeneous catalysts derived from fly ash. *ACS Sustain. Chem. Eng.* **2018**, *6*, 5273–5282.
- (2) Koshy, N.; Singh, D. N. Fly ash zeolites for water treatment applications. *J. Environ. Chem. Eng.* **2016**, *4*, 1460–1472.
- (3) Rashidi, N. A.; Yusup, S. An Overview on the potential of coal-based bottom ash as low-cost adsorbents. *ACS Sustain. Chem. Eng.* **2016**, *4*, 1870–1884.
- (4) Inada, M.; Tsujimoto, H.; Eguchi, Y.; Enomoto, N.; Enomoto, J. Microwave-assisted zeolite synthesis from coal fly ash in hydrothermal process. *Fuel* **2005**, *84*, 299–304.
- (5) Derkowski, A.; Franus, W.; Beran, E.; Czimerová, A. Properties and potential applications of zeolitic materials produced from fly ash using simple method of synthesis. *Powder Technol.* **2006**, *166*, 47–54.
- (6) El-Naggar, M. R.; El-Kamash, A. M.; El-Dessouky, M. I.; Ghonaim, A. K. Two-step method for preparation of NaA-X zeolite blend from fly ash for removal of cesium ions. *J. Hazard. Mater.* **2008**, *154*, 963–972.
- (7) Inada, M.; Tsujimoto, H.; Eguchi, Y.; Enomoto, N.; Hojo, J. Microwave-assisted zeolite synthesis from coal fly ash in hydrothermal process. *Fuel* **2005**, *84*, 299–304.
- (8) Park, M.; Choi, C. L.; Lim, W. T.; Kim, M. C.; Choi, J.; Heo, N. H. Molten-salt method for the synthesis of zeolitic materials I. Zeolite formation in alkaline molten-salt system. *Microporous Mesoporous Mater.* **2000**, *37*, 81–89.
- (9) Liu, Y.; Yan, C.; Zhao, J.; Zhang, Z.; Wang, H.; Zhou, S.; Wu, L. Synthesis of zeolite P1 from fly ash under solvent-free conditions for ammonium removal from water. *J. Clean. Prod.* **2018**, *202*, 11–22.
- (10) Ojumu, T. V.; Du Plessis, P. W.; Petrik, L. F. Synthesis of zeolite A from coal fly ash using ultrasonic treatment – a replacement for fusion step. *Ultrason. Sonochem.* **2016**, *31*, 342–349.
- (11) Tauanov, Z.; Shah, D.; Inglezakis, V.; Jamwal, P. K. Hydrothermal synthesis of zeolite production from coal fly ash: A heuristic approach and its optimization for system identification of conversion. *J. Clean. Prod.* **2018**, *182*, 616.
- (12) Belviso, C.; Giannossa, L. C.; Huertas, F. J.; Lettino, A.; Mangone, A.; Fiore, S. Synthesis of zeolites at low temperatures in fly ash-kaolinite mixtures. *Microporous Mesoporous Mater.* **2015**, *212*, 35–47.
- (13) Tauanov, Z.; Lee, J.; Inglezakis, V. J. Mercury reduction and chemisorption on the surface of synthetic zeolite silver nanocomposites: Equilibrium studies and mechanisms. *J. Mol. Liq.* **2020**, *305*, 112825.
- (14) Chen, X.; Wendell, K.; Zhu, J.; Li, J.; Yu, X.; Zhang, Z. Synthesis of nano-zeolite from coal fly ash and its potential for nutrient sequestration from anaerobically digested swine wastewater. *Bioresour. Technol.* **2012**, *110*, 79–85.
- (15) Babajide, O.; Musyoka, N.; Petrik, L. Novel zeolite Na-X synthesized from fly ash as a heterogeneous catalyst in biodiesel production. *Catal. Today* **2012**, *190*, 54–60.
- (16) Belviso, C. State-of-the-art applications of fly ash from coal and biomass: A focus on zeolite synthesis processes and issues. *Prog. Energy Combust. Sci.* **2018**, *65*, 109–135.
- (17) Belviso, C.; Cavalcante, F.; Lettino, A.; Fiore, S. Zeolite synthesised from fused coal fly ash at Low temperature using seawater for crystallization. *Coal Combust. Gasif. Prod.* **2009**, *1*, 7–13.

- (18) Belviso, C.; Cavalcante, F.; Fiore, S. Ultrasonic waves induce rapid zeolite synthesis in a seawater solution. *Ultrason. Sonochem.* **2013**, *20*, 32–36.
- (19) Tanaka, H.; Fujii, A.; Fujimoto, S.; Tanaka, Y. Microwave-assisted two-step process for the synthesis of a single-phase Na-A zeolite from coal fly ash. *Adv. Powder Technol.* **2008**, *19*, 83–94.
- (20) Belviso, C. Ultrasonic vs hydrothermal method: Different approaches to convert fly ash into zeolite. How they affect the stability of synthetic products over time? *Ultrason. Sonochem.* **2018**, *43*, 9–14.
- (21) Yan, F.; Jiang, J.; Tian, S.; Liu, Z.; Shi, J.; Li, K.; Chen, X.; Xu, Y. A green and facile synthesis of ordered mesoporous nano-silica using coal fly ash. *ACS Sustain. Chem. Eng.* **2016**, *4*, 4654.
- (22) Behin, J.; Bukhari, S. S.; Dehnavi, V.; Kazemian, H.; Rohani, S. Using coal fly ash and wastewater for microwave synthesis of LTA zeolite. *Chem. Eng. Technol.* **2014**, *37*, 1532–1540.
- (23) Musyoka, N. M. Zeolite A, X and cancrinite from South African coal fly ash: mechanism of crystallization, routes to rapid synthesis and new morphology. Ph.D. Thesis, University of the Western Cape, 2012.
- (24) Musyoka, N. M.; Petrik, L. F.; Balfour, G.; Misheer, N.; Gitari, W.; Mabovu, B. Removal of Toxic Elements from Brine Using Zeolite Na-P1 Made from a South African Coal Fly Ash. *Int. Mine Water* **2009**, *5*, 680–687.
- (25) Makgabutlane, B.; Nthunya, L. N.; Musyoka, N.; Dladla, B. S.; Nxumalo, E. N.; Mhlanga, S. D. Microwave-assisted synthesis of coal fly ash-based zeolites for removal of ammonium from urine. *RSC Adv.* **2020**, *10*, 2416–2427.
- (26) Bukhari, S. S.; Behin, J.; Kazemian, H.; Rohani, S. Conversion of coal fly ash to zeolite utilizing microwave and ultrasound energies: A review. *Fuel* **2015**, *140*, 250–266.
- (27) Musyoka, N. M. Hydrothermal synthesis and optimisation of zeolite Na-P1 from South African coal fly ash. Ph.D. Dissertation, University of the Western Cape, 2009.
- (28) Aldahri, T.; Behin, J.; Kazemian, H.; Rohani, S. Synthesis of zeolite Na-P from coal fly ash by thermo-sonochemical treatment. *Fuel* **2016**, *182*, 494–501.
- (29) Visa, M. Synthesis and characterization of new zeolite materials obtained from fly ash for heavy metals removal in advanced wastewater treatment. *Powder Technol.* **2016**, *294*, 338–347.
- (30) Sathupunya, M.; Gulari, E.; Wongkasemjit, S. Microwave preparation of Li-zeolite directly from aluminosilicate. *Mater. Chem. Phys.* **2004**, *83*, 89–95.
- (31) Aldahri, T.; Behin, J.; Kazemian, H.; Rohani, S. Effect of microwave irradiation on crystal growth of zeolitized coal fly ash with different solid/liquid ratios. *Adv. Powder Technol.* **2017**, *28*, 2865–2874.
- (32) Jiang, Z.; Yang, J.; Ma, H.; Ma, X.; Yuan, J. Synthesis of pure NaA zeolites from coal fly ashes for ammonium removal from aqueous solutions. *Clean Technol. Environ. Policy* **2016**, *18*, 629–637.
- (33) Thuadaij, P.; Nuntiya, A. Effect of the SiO₂/Al₂O₃ ratio on the synthesis of Na-x zeolite from Mae Moh fly ash. *ScienceAsia* **2012**, *38*, 295–300.
- (34) Iqbal, A.; Sattar, H.; Haider, R.; Munir, S. Synthesis and characterization of pure phase zeolite 4A from coal fly. *J. Clean. Prod.* **2019**, *219*, 258–267.
- (35) Muriithi, G. N.; Petrik, L. F.; Doucet, F. J. Synthesis, characterisation and CO₂ adsorption potential of NaA and NaX zeolites and hydrotalcite obtained from the same coal fly ash. *J. CO₂ Util.* **2020**, *36*, 220–230.