Using one waste to tackle another: preparation of a CO₂ capture material zeolite X from laterite residue and bauxite

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Abstract

In this work, zeolite X, a benchmark adsorbent for carbon capture, has been successfully prepared from low cost waste minerals namely laterite residue and bauxite using alkali fusion process followed by hydrothermal treatment. The structure and morphology of the as-synthesized zeolite X were verified and characterized with a range of experimental techniques such as x-ray diffraction, scanning electronic microscopy and infrared spectroscopy. The surface area and (N₂ and CO₂) gas adsorption isotherms of this product were found comparable to that of commercial ones, demonstrating the effectiveness of synthesizing zeolite X from laterite and bauxite. Further improvement of the product purity was also accomplished by optimizing the process conditions.

Key words: Zeolite X, preparation, laterite residue, bauxite, CO₂ capture

1. Introduction

Nickel is a strategic metal and widely used in stainless steel, batteries, fuel cells, electroplating, catalyst, and etc [1-3]. Currently, the world’s recoverable nickel resources can be divided into two main categories, respectively sulfide ores and laterite ores, depending on the geological compositions [4]. The global nickel supply has been predominantly from sulfide deposits, although laterite ores comprise approximately 70% of the continental nickel resources [5, 6]. The reason is that the recovery process of nickel from the laterite ores is quite costly, because of the complex mineralogy and low nickel content of laterite [7]. Recently,

1 however, the laterite exploitation has received extensive attentions, due to the reduction of
2 nickel sulfide reserves as well as significant increase in nickel demands [8, 9]. Therefore,
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4 there is an increasing interest in the utilization of laterite.
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7 In general, nickel can be recovered from the laterite by using pyrometallurgical,
8 hydrometallurgical or combined (pyro-hydrometallurgical) techniques [10, 11].
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10 Pyrometallurgical process comprises of reduction roasting, electric furnace for ferronickel
11 production, and rotary kiln carbon reduction, etc [12, 13]. Nevertheless, the
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13 hydrometallurgical processes consist of ammonia leaching, acid leaching, high-pressure acid
14 leaching and bacteria leaching, etc [14, 15]. However, these processes can generate large
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16 amount of solid waste, which causes serious environmental pollution. Large volumes,
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18 approximately 40 million tons, of laterite residue are generated annually in China alone [16].
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20 Current metallurgical processes usually focus on the recovery of Ni and/or Co, whereas
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22 laterite residue containing other waste minerals are all discarded, which brings enormous
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24 burden to the environment [17]. Therefore, converting laterite residue into useful commodity
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26 could offer a number of benefits from both economic and environmental aspects.
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28 Nevertheless, to our best knowledge, little information is available in literature on the
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30 effective utilization of the laterite residue. Laterite residue consists essentially of SiO_2 , Al_2O_3
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32 and Fe_2O_3 [3], presenting a similar composition to that of natural zeolites, which makes it
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34 possible to use laterite residue as source materials in zeolites production. Zeolite X is one of
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36 the zeolites that have been widely used in adsorption, separation, ion exchange and catalysis,
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38 due to its large surface areas, molecular sieving ability and acidity [18, 19]. Particularly,
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40 zeolite X is also a well-known adsorbent for CO_2 capture from flue gas streams owing to its
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42 high selectivity of CO_2 against N_2 [20, 21]. In this paper, we report the synthesis of zeolite X
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44 using laterite residue as raw materials, in which another common mineral bauxite was added
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46 to the starting material to maintain an appropriate Si/Al ratio during the hydrothermal
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treatment, because otherwise the large ratio of Si/Al in the laterite residue would inhibit the formation of zeolite X during the hydrothermal reactions.

The ultimate aim of this work was to develop a new route to utilize the laterite residue for the production of zeolites that can be used for CO₂ capture from flue gas streams. To obtain high purity of zeolite X, the molar ratios of the components in the starting materials and during the hydrothermal treatment should be carefully controlled. The optimum synthesis procedure was established in this study, and the carbon capture potential of our as synthesized products was also investigated.

2. Experimental

2.1 Synthesis

Laterite residue and bauxite was obtained from Sichuan Province (China) and Indonesia, respectively. The chemical compositions of laterite residue, bauxite and prepared zeolite X were analyzed by XRF (ZSX100e, Rigaku) and described in Table 1 showing 39.1wt.% Si and 1.2wt% Al in laterite residue and 8.7wt.% Si and 31.5wt.% Al in bauxite. For comparison purposes, commercial zeolite X beads were also purchased from Sinopharm Chemical Reagent Co., Ltd.

The synthesis procedure for zeolite X is summarized schematically in the flow diagram Fig. 1, which involved two steps *viz.* fusion and hydrothermal treatment. In a typical procedure, 5 g of laterite residue was mixed with bauxite using different molar ratios of SiO₂/Al₂O₃ mole ratios such as 3, 3.2, 3.5, and 3.8. Then, NaOH was added into the resulting mixture to adjust the Na₂O/SiO₂ mole ratio to a desired value in the range of 1.4-2.6. The mixture was fused in a tube furnace at 600 °C for 2 h. Then, the resulting product was dissolved in water with various H₂O/Na₂O ratio (35, 40, 43, 48, 55, and 60 mol•mol⁻¹), followed by ageing of different time (0, 8, 12, 24, and 48 h). The mixture was transferred into an autoclave and heated at 100 °C for different hydrothermal reaction time (0.5, 3, 6, 12, and 24 h) under static

conditions. After cooling to the room temperature, the resultant solid was filtered, washed three times with deionized water, and dried at 100 °C overnight. The synthesis conditions used with different samples are presented in Table 2 (Group A-E). Note that the optimal synthesis conditions determined from the experiments of Group A was carried on to the experiments of Group B, likewise finally to group E.

2.2 Measurement and characterization

The crystalline properties of the raw materials and the synthesized samples were examined by X-ray diffraction (XRD) using a Shimadzu X-ray diffractometer, with a scanning rate of 2°/min from 4° to 50°. FE-SEM (Field Emission Scanning Electron Microscopy) analysis was conducted by employing a Hitachi S-3400N scanning electron microscope operated at 15 kV. All samples were platinum coated prior to measurement. BET surface areas were measured on an ASAP2020 analyzer (Micromeritics, USA) using N₂ as probe gases at 77 K in the relative pressure range of 0.05-0.25. CO₂ and N₂ adsorption isotherms were measured on ASAP2020. Prior to analysis, all the samples were degassed under vacuum at 330 °C for 8 h. Infrared spectroscopy was performed using an Agilent Cary 600 FTIR instrument, and samples were mixed with KBr using a mortar before the measurement.

3. Results and discussion

3.1 Raw materials characterization

The X-ray diffraction pattern of laterite residue (Fig. 2) indicates that the crystalline phases are mainly SiO₂, Mg₃[Si₂O₅(OH)₄], Mg₃Si₄O₁₀(OH)₂, and Mg_{1.8}Fe_{0.2}[SiO₄], identified by their characteristic sharp peaks at the corresponding positions. The X-ray diffraction pattern for bauxite (Fig. 3) indicates the major crystalline phase is gibbsite, with coexistence of anatase, α-quartz, kaolinite, and hematite [22].

The chemical compositions of the raw materials (Table 2) by XRF show that they are impure in nature. The Si/Al ratio of the laterite residue and bauxite are about 29.034 and

0.248, respectively, indicating that laterite residue and bauxite are rich in silica and alumina, respectively, a favorable combination as raw materials for synthesizing zeolite X. Furthermore, XRF data reveals that the raw materials contain a very small amount of impurity, which suggests high purity of zeolites X could be obtained using laterite residue and bauxite.

3.2 Zeolite X synthesis and characterizations

3.2.1 Effect of $\text{Na}_2\text{O}/\text{SiO}_2$ mole ratios

The effect of $\text{Na}_2\text{O}/\text{SiO}_2$ mole ratios on zeolite X formation was determined by mixing NaOH, laterite residue and bauxite at the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio range of 1.4 to 2.6 at 600°C for 2 h. The XRD spectra of the zeolite products obtained at different $\text{Na}_2\text{O}/\text{SiO}_2$ ratio were shown in Fig.3 (A1-A6). At the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio of 1.4, strong peaks of zeolite X along with weak ones of zeolite P were observed, suggesting a minor contamination by zeolite P byproduct. When a $\text{Na}_2\text{O}/\text{SiO}_2$ ratio of 1.6 was used as the synthesis condition, the peaks of zeolite P disappeared, indicating any latent zeolite P was transformed into zeolite X completely during the hydrothermal reaction. When the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio was increased to 1.8 or higher, a large fraction of zeolite P contaminant was found in the product, while at the ratio of 2.6, a secondary contaminant sodalite was observed in addition to zeolite P. According to the XRD results of products in Group A, the optimal $\text{Na}_2\text{O}/\text{SiO}_2$ ratio for attaining high purity zeolite X (product A2) is 1.6, and this optimal ratio was used throughout the entire experiments.

3.2.2 Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratios

Adjusting $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the starting materials prior to hydrothermal reaction is an important aspect to obtain pure zeolites. Fig. 4 shows the X-ray diffraction patterns for products prepared at the ratio range from 3 to 3.8. The XRD results show that zeolite X was the main phase at this ratio range. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 3.2 was a critical ratio to synthesize pure zeolite X. At the ratio of 3, zeolite X and amorphous impurity phase were

obtained. However, when $\text{SiO}_2/\text{Al}_2\text{O}_3$ increased to 3.5 or higher, the peaks of zeolite P also appeared, indicating that a higher ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ results in the formation of zeolite P. These findings show that $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is a key factor for the preparation of different types of zeolites, which is in good agreement with earlier report [23]. Thus, the optimum $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was 3.2, wherein high purity zeolite X was obtained. Therefore, this ratio was used in the following study.

3.2.3 Effect of $\text{H}_2\text{O}/\text{Na}_2\text{O}$ mole ratios

Crystallization of zeolites occurs through nucleation and crystal growth, depending a lot on alkalinity. The effect of $\text{H}_2\text{O}/\text{Na}_2\text{O}$ mole ratios of the starting materials, in the range of 35 to 60, was investigated by XRD examination on the corresponding samples, and the results were shown in Fig.5. The XRD analysis showed that crystallinity of synthesized zeolite decreases with increase in $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio. Zeolites could be obtained when the $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios were less than 55. At a $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio of 35, the peaks of sodalite appeared indicating sodalite was the main phase. When the $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio increased to 40, pure zeolite X was obtained indicating the transformation of sodalite into zeolite X. When $\text{H}_2\text{O}/\text{Na}_2\text{O}$ mole ratio further increased to 43, the peaks of zeolite P appeared, suggesting a high $\text{H}_2\text{O}/\text{Na}_2\text{O}$ mole ratio could induce the formation of zeolite P. However, XRD patterns of the sample at the $\text{H}_2\text{O}/\text{Na}_2\text{O}$ mole ratio of 55 clearly show broad amorphous peaks combined with quartz and small peaks of zeolite X indicating only a few zeolite X particles were nucleated. This reveals that higher $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios may inhibit the formation of zeolite X from laterite residue and bauxite, probably because low alkalinity reduces dissolution of silicate and leads to a poor conversion to zeolites. The best zeolite X was obtained from the starting materials with $\text{H}_2\text{O}/\text{Na}_2\text{O}$ mole ratio of 40, and thus, this $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio was able to be used in the following experiments.

3.2.4 Effect of aging time

Aging is also an important factor for the zeolite synthesis process. In order to investigate the influence of aging time on zeolite X preparation, time-dependent synthesis was carried out and the purity of the products was examined by XRD analysis (Fig.6). Extended aging time from 0 h to 24 h can improve the purity of the product zeolite X. In particular, pure zeolite X with high crystallinity could be obtained at the aging time of 24 h. However, further prolonging the aging time to 48 h, zeolite X was again heavily contaminated with zeolite P impurity. It suggests that aging time plays a significant role in the formation of zeolites prepared from laterite residue and bauxite. Thus, an optimal aging time of 24 h was determined for obtaining high purity zeolite X, and the aging time of 24 h was used through the rest of the study.

3.2.5 Effect of hydrothermal reaction time

XRD patterns of the products obtained at different reaction time were shown in Fig.7. In the first 0.5 h, the XRD pattern of the product exhibits a very broad peak located around at 27° in 2θ , combined with some small peaks of zeolite X, suggesting the formation of amorphous aluminosilicate and a small amount of zeolite X. However, the evolution from amorphous phase into zeolite X occurred in a short time period. Zeolite X with very low impurities of amorphous phase was produced, by extending to 3 h of reaction time. Further increasing reaction time to 6 h, highly crystalline and pure zeolite X was obtained. When the reaction time was lengthened to 12 h, pure phase of zeolite X was still observed. Nevertheless, longer time crystallization also caused the transformation of zeolite X into sodalite. At the crystallization time of 24 h, the diffraction pattern of zeolite sodalite appeared. This is probably because sodalite is more thermodynamically stable than zeolite X, and longer reaction time favors the formation of more stable sodalite type zeolite. Therefore, a reaction time of 6 h is sufficient for the formation of high purity zeolite X.

According to the experiments above, the optimal synthesis conditions for zeolite X were

found as follows: $\text{H}_2\text{O}:\text{Na}_2\text{O}:\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of 204.8:5.12:3.2:1, and the product obtained at the optimal conditions was used in the following experiments.

3.3 Morphological and structural analysis

The morphologies of the laterite residue, bauxite and zeolite X were presented in Fig. 8. SEM images for laterite residue and bauxite (Fig.8a, b) show particles with a wide size distribution and irregular shape. Figure (8c-d) show the low and high resolution SEM micrographs of as-synthesized zeolite X with typical octahedral structure and uniform distribution. In addition, amorphous material was hardly noticeable in the SEM images of as-synthesized zeolite X, suggesting the formation of highly crystalline zeolite X. Furthermore, the XRF results show that the prepared zeolite X consists of Na, Al, Si, Fe, Mg, with a wt. % of 9.9, 14.6, 23.9, 2.6, and 1.2, respectively, and the molar ratio of Na/Al/Si falls in the region of theoretical formula of pure zeolite X, which means most of the trace impurities were removed during the fusion and hydrothermal reaction process. The N_2 adsorption isotherm at 77K and pore size distribution of prepared zeolite X are shown in Fig.9. BET surface area of as-synthesized zeolite X was around $486 \text{ m}^2/\text{g}$, a little smaller than that of the commercial one ($596 \text{ m}^2/\text{g}$), which may be attributed to the small fraction of impurities. Furthermore, the pore size of as-synthesized product was approximately $7 \text{ \AA}$. All these findings suggest that high purity zeolite X was obtained at the optimum reaction conditions.

FT-IR spectra can be useful in obtaining crucial information about the structure of zeolites. Fig.10 presents the spectra of commercial zeolite X and the as-synthesized one. It can be seen that our synthesized zeolite X has almost identical spectra to the commercial one. All these observations further confirm successful preparation of high purity zeolite X.

3.4 Adsorption Properties

The representative adsorption isotherms measured at 0°C and 30°C for pure CO_2 and N_2 on the prepared zeolite X were shown in Fig.11. The adsorption loadings of CO_2 and N_2 on

prepared zeolite X are well comparable to that of the commercial one [18]. Furthermore, the prepared zeolite X is very selective to carbon dioxide at 0 °C and 30 °C through the whole pressure range, and the equimolar selectivities of CO₂/N₂ were shown in Fig.12. For example, in the partial pressure region of 5-15 kPa (for individual component), the equilibrium adsorption capacity of CO₂ is about 60-115 times higher than those for N₂ at 30 °C, suggesting zeolite X prepared from laterite residue and bauxite can be a very good adsorbent for postcombustion carbon capture by vacuum swing adsorption where the partial pressure of CO₂ in the flue gases is around 10 kPa only [24, 25]. In addition, it may also be used for CO₂ removal in the process of air purification [26].

The adsorption isotherms of CO₂ and N₂ on our zeolite X material were fit by classical Langmuir equations:

$$N = \sum_{i=1}^j \frac{M_i B_i P}{1 + B_i P} \quad (1)$$

$$B_i = b_i \exp\left(\frac{Q_i}{RT}\right) \quad (2)$$

where N is the adsorbed amount (mol·kg⁻¹), M_i the maximum monolayer adsorption capacity for site i , b_i the gas-solid affinity coefficient (kPa⁻¹), Q_i the enthalpy of adsorption (J·mol⁻¹), P the pressure (kPa), R the gas constant (J·mol⁻¹·K⁻¹) and T the temperature (K). N , P and T are variables. We used a dual sites model for CO₂ (i.e. $i = 2$) to characterize its surface heterogeneity and a single site model for N₂ adsorption ($i = 1$). The results of the fitted parameters are shown in Table 3 with a very high goodness of fitting. The enthalpy of adsorption values derived from our model are in very close match of that reported in literature [25]. We further calculated the isosteric heat of adsorption by applying the Clausius-Clapeyron equation with the Langmuir model parameters we obtained. As shown in Fig. 13, CO₂ has a much higher heat of adsorption than that of N₂, with a difference from 12.2 kJ/mol at low surface coverage to 11 kJ/mol at high coverage, which is responsible for the high

selectivity of CO₂ over N₂ on our synthesized zeolite X. These information will complement the design and simulation of vacuum or pressure swing adsorption (VSA/PSA) processes while applying our adsorbents.

4. Conclusion

Laterite residue and bauxite have been successfully utilized for the production of zeolite X for the first time. The optimal synthesis conditions for zeolite X were found as follows: H₂O:Na₂O:SiO₂:Al₂O₃ ratio of 204.8:5.12:3.2:1; aging time of 24 h, and hydrothermal reaction time of 6 h. SEM images of as-synthesized zeolite X particles exhibit typical octahedral morphology with uniform size distribution. The prepared zeolite X shows similar surface areas to that of commercial ones. Furthermore, the adsorption properties of our prepared X are comparable to the commercial ones in terms of CO₂ and N₂ adsorption equilibrium capacities. This study may bring a new and alternative approach for large scale recycling of laterite residue wastes for making valuable zeolite X that are highly in demand for adsorption based carbon capture processes.

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References

- [1] X. Li, B. Li, S. Wu, J. Li, Q. Xu, Z. Yang, Y. Liu, S. Wang, D. Chen, Silica-based iminodiacetic acid functionalized adsorbent for Ni Hydrometallurgical extraction of nickelferous laterite, *AIChE*. 58(2012) 3818-3824.
- [2] F. Cheng, J. Liang, Z. Tao, J. Chen. Functional materials for rechargeable batteries, *Adv Mater*. 23(2011) 1695-1715.

- [3] J. Li, D. Xiong, H. Chen, R. Wang, Y. Liang. Physicochemical factors affecting leaching of laterite ore in hydrochloric acid.,Hydrometallurgy. 129-130(2012) 14-18.
- [4] K.H. Park, C.W. Nam, Status and prospect of nickel resources and processing, Trending Metals Mater.Eng. 21(2008) 1-9.
- [5] B. Wang, Q. Guo, G. Wei, P. Zhang, J. Qu, T. Qi, Characterization and atmospheric hydrochloric acid leaching of a limonitic laterite from Indonesia, Hydrometallurgy. 129-130 (2012) 7-13.
- [6] S. Sudol, The thunder from down under: everything you wanted to know about nickel laterites but were afraid to ask, Can. Min. J. 126 (2005) 8-12.
- [7] K.B. Hallberg, B.M. Grail, C.A. du Plessis, D.B. Johnson. Reductive dissolution of ferric iron minerals: a new approach for bio-processing nickel laterites, Miner.Eng. 24(2011) 620-624.
- [8] D.Q. Zhu, Y. Cui, K. Vining, S. Hapugoda, J. Douglas, J. Pan, G.L. Zheng, Upgrading low nickel content laterite ores using selective reduction followed by magnetic separation, J.Miner.Process. 106-109(2012) 1-7.
- [9] T.Norgate, S. Jahanshahi, Assessing the energy and greenhouse gas footprints of nickel laterite processing, Miner.Eng. 24(2011) 698-707.
- [10]J.Lu, S.Liu, J.Shangguan, W. Du, F. Pan, S. Yang, The effect of sodium sulphate on the hydrogen reduction process of nickel laterite ore, Minerals Engineering. 49(2013) 154-164.
- [11]M.Z. Mubarak, J. Lieberto, Precipitation of nickel hydroxide from simulated and atmospheric-leach solution of nickel laterite ore, Procedia. 6(2013) 457-464.
- [12]M. Jiang, T. Sun, Z. Liu, J. Kou, N. Liu, S. Zhang, Mechanism of sodium sulfate in promoting selective reduction of nickel laterite ore during reduction roasting process, International Journal of Mineral Processing. 123(2013) 32-38.
- [13]G. Li, M. Rao, Q. Li, Z. Peng, T. Jiang, Extraction of cobalt from laterite ores by citric acid in presence of ammonium bifluoride, Trans.Nonferrous Met.Soc.China. 20(2010) 1517-1520.
- [14]C.Y. Cheng, G. Boddy, W. Zhang, M. Godfrey, D.J. Robinson,Y. Pranolo, Z. Zhu, L. Zeng, W. Wang, Recovery of nickel and cobalt from laterite leach solutions using direct solvent extraction: Part 2: Semi- and fully-continuous tests, Hydrometallurgy. 104(2010) 53-60.
- [15]T. Norgate, S. Jahanshahi, Low grade ores-smelt, leach or concentrate, Miner.Eng. 23

(2010) 65-73.

- [16]P. Zhang, Q.Guo, Y.Song, J.Qu, T. Qi, Separation and recovery of Ni and Cr from ferronickel slag of nickel laterite, The Chinese Journal of Process Engineering. 13(2013) 608-614.
- [17]W.N. Mu, Y.C. Zhai, Y.Liu, Leaching of magnesium from desiliconization slag of nickel laterite ores by carbonation process. Trans.Nonferrous Met.Soc.China. 20(2010) s87-s91.
- [18]D.W. Breck, Zeolite Molecular Sieves, Wiley-Interscience, New York, 1974.
- [19]L. Liu, R. Singh, G. Li, G. Xiao, P. Webley, Y. Zhai, Synthesis of hydrophobic zeolite X@SiO₂ core-shell composites, Materials Chemistry and Physics. 133(2012) 1144-1151.
- [20]S. Cavenati, C.A.Grande, A.E.Rodrigues, Adsorption Equilibrium of Methane, Carbon Dioxide, and Nitrogen on Zeolite 13X at High Pressures, J. Chem. Eng. Data. 49(2004), 1095-1101.
- [21]L.Liu, R.Sing, P.Xiao, P.A.Webley, Y. Zhai, Zeolite synthesis from waste fly ash and its application in CO₂ capture from flue gas streams, Adsorption. 17(2011) 795-800.
- [22]S.J.Palmer, R.L.Frost, Characterisation of bauxite and seawater neutralised bauxite residue using XRD and vibrational spectroscopic techniques, Journal of materials science. 44(2009) 55-63.
- [23]C.W.Purnomo, C.Salim, H. Hinode, Synthesis of pure Na-X and Na-A zeolite from bagasse fly ash, Microporous and mesoporous materials. 162(2012) 6-13.
- [24]G. Li, P. Xiao, P. Webley, J. Zhang, R. Singh, M. Marshall, Capture of CO₂ from high humidity flue gas by vacuum swing adsorption with zeolite 13X, Adsorption. 14 (2008) 415-422.
- [25]P. Xiao, J. Zhang, P. Webley, G. Li, R. Singh, R. Todd, Capture of CO₂ from flue gas streams with zeolite 13X by vacuum-pressure swing adsorption, Adsorption. 14(2008) 575-582.
- [26]A. Goeppert, M. Czaun, R. B. May, G. K. Surya Prakash, G. A. Olah, and S. R. Narayanan, Carbon dioxide capture from the air using a polyamine based regenerable solid adsorbent, J. Am. Chem. Soc. 133 (2011) 20164-20167.

Table.1 Chemical compositions (wt. %) of raw materials

Materials	Composition					
	SiO ₂	Al ₂ O ₃	Na ₂ O	Fe ₂ O ₃	MgO	Others
Laterite residue	83.8	2.3	0	4.6	2.8	6.5
Bauxite	18.5	59.5	0.5	18.4	0	3.0
As-synthesized zeolite X	51.3	27.6	13.3	3.7	2.0	2.1

Table.2 List of zeolite X products from this work and their synthesis conditions

Samples	Na ₂ O/SiO ₂	SiO ₂ /Al ₂ O ₃	Laterite :	H ₂ O/Na ₂ O	Aging time	Hydrothermal reaction time
	ratio	ratio	bauxite ^a	ratio	(h)	(h)
A1	1.4	3.5	0.576	48	24	8
A2	1.6	3.5	0.576	48	24	8
A3	1.8	3.5	0.576	48	24	8
A4	2.0	3.5	0.576	48	24	8
A5	2.3	3.5	0.576	48	24	8
A6	2.6	3.5	0.576	48	24	8
B1	1.6	3	0.459	48	24	8
B2	1.6	3.2	0.506	48	24	8
B3	1.6	3.5	0.576	48	24	8
B4	1.6	3.8	0.647	48	24	8
C1	1.6	3.2	0.506	35	24	8
C2	1.6	3.2	0.506	40	24	8
C3	1.6	3.2	0.506	43	24	8
C4	1.6	3.2	0.506	48	24	8
C5	1.6	3.2	0.506	55	24	8
C6	1.6	3.2	0.506	60	24	8
D1	1.6	3.2	0.506	40	0	8
D2	1.6	3.2	0.506	40	8	8
D3	1.6	3.2	0.506	40	12	8
D4	1.6	3.2	0.506	40	24	8

D5	1.6	3.2	0.506	40	48	8
E1	1.6	3.2	0.506	40	24	0.5
E2	1.6	3.2	0.506	40	24	3
E3	1.6	3.2	0.506	40	24	6
E4	1.6	3.2	0.506	40	24	8
E5	1.6	3.2	0.506	40	24	24

^a The ratio of laterite to bauxite in weight is calculated from the SiO₂/Al₂O₃ ratios of individual mineral and that in their mixture.

Table.3 Model fitting parameters for CO₂ and N₂ adsorption isotherms

Gas	Langmuir parameters						Goodness of fitting	Root mean square error
	M_1 (mol/kg)	b_1 (kPa ⁻¹)	Q_1 (kJ/mol)	M_2 (mol/kg)	b_2 (kPa ⁻¹)	Q_2 (kJ/mol)		
CO ₂	2.11	4.79×10 ⁻⁸	33.07	2.03	4.88×10 ⁻⁷	34.54	0.9997	0.0228
N ₂	4.13	9.96×10 ⁻⁸	22.13	-	-	-	0.9992	0.0071

Fig.1. Flowchart for synthesizing zeolite X from laterite residue and bauxite.

Fig.2. XRD pattern: (a) laterite residue, (b) bauxite.

Fig.3. XRD patterns of zeolites X synthesized at the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio of (A1) 1.4, (A2) 1.6, (A3) 1.8, (A4) 2.0, (A5) 2.3, (A6) 2.6, where X represents zeolite X, P corresponds to zeolite P, and S represents zeolite sodalite.

Fig.4. XRD patterns of X zeolites synthesized at the SiO₂/Al₂O₃ ratio of (B1) 3, (B2) 3.2, (B3) 3.5, (B4) 3.8, where X represents zeolite X, and P corresponds to zeolite P.

Fig.5. XRD patterns of products synthesized at the H₂O/Na₂O ratio of (C1) 35, (C2) 40, (C3) 43, (C4) 48, (C5) 55, (C6) 60, where X represents zeolite X, P corresponds to zeolite P, S represents zeolite sodalite, Q denotes quartz.

Fig.6. XRD patterns of zeolite products synthesized at the aging time of (D1) 0 h, (D2) 8 h, (D3) 12 h, (D4) 24 h, (D5) 48 h, where X denotes zeolite X and P corresponds to zeolite P.

Fig.7. XRD patterns of zeolites synthesized at the crystalline time of (E1) 0.5 h, (E2) 3 h, (E3) 6 h, (E4) 12 h, (E5) 24 h, where X represents zeolite X, S represents zeolite sodalite and Q corresponds to quartz impurity.

Fig.8. SEM images for: (a) laterite residue, (b) bauxite, (c, d) as-synthesized zeolite X at high and low magnifications respectively.

Fig.9. (a) N₂ adsorption isotherm, and (b) pore size distribution of prepared zeolite 13X.

Fig.10. FTIR spectra of commercial and as-synthesized zeolite X.

Fig.11. Adsorption (filled) and desorption (hollow) isotherms of CO₂/N₂ on zeolite X at 0 °C and 30 °C.

Fig.12. Equimolar selectivities of CO₂/N₂ on zeolite X at 0 °C and 30 °C.

Fig.13. Calculated isosteric heat of adsorption of CO₂ and N₂ on zeolite X at 0 °C.