Synthesis of Template-Free ZSM-5 from Rice Husk Ash at Low Temperatures and Its CO₂ Adsorption Performance

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ABSTRACT: In this paper, a green synthesis method for ZSM-5 zeolite is explored to reduce the synthesis cost, environmental hazard, and reaction temperatures. For the ZSM-5 samples prepared at low temperatures, the influence of factors such as the hydrothermal temperature, crystallization time, and the number of seeds is systematically investigated. The adsorption isotherm of CO₂ is used for fitting analysis of adsorption models and determination of the adsorption selectivity. The results show that the best one among the three samples presents the highest CO₂ adsorption capacity of 2.39 mmol/g at 273 K and 15 bar. It is prepared with a hydrothermal temperature of 393 K, crystallization time of 7 days, and a seed crystal of 1 wt %. The dual-site Langmuir model can well describe the experimental data, indicating that double adsorption sites rather than the simple single-layer adsorption are dominant in samples. As the pressure increases, the adsorption capacity calculated by the model is much lower than the actual value with a deviation index of 12.5%. At a pressure of 1 bar, the optimal selectivity is attained with sample L-20, viz., CO₂/N₂ of 34.3 and CO₂/O₂ of 70.2. The green synthesis method reported in this research can be used to successfully prepare ZSM-5 zeolite, and it shows excellent CO₂ adsorption performance. In addition, the use of low-cost raw materials and template-free synthesis methods will facilitate the large-scale application of green synthesis processes in the future.

1. INTRODUCTION
Zeolite Socony Mobil 5 (ZSM-5) is a typical MFI-type zeolite with two kinds of open-framework structures: one consists of eight five-membered rings as the basic structural unit and the other is a three-dimensional channel system of ten-membered rings as the main channel window. It has great thermal stability, intrinsic acidity, and coking resistance. Its unique open-framework structure makes it suitable for both catalysis and CO₂ adsorption. Newsome et al. believed that the lower the Si/Al ratio of a zeolite, the more favorable is its CO₂ adsorption capacity. Therefore, the preparation of ZSM-5 with a low Si/Al ratio will have more significance in the field of CO₂ adsorption.

The synthesis of ZSM-5 zeolite has been explored for many years, especially in terms of the synthesis of silicon sources, templating agents, and synthesis temperature. In terms of silicon sources, ZSM-5 was mostly synthesized from chemical silicon sources, such as tetraethyl orthosilicate. To reduce the synthesis cost and protect the environment, it was found that kaolin and rice husk in the waste are rich in silicon, and the calcined rice husk ash (RHA) is rich in SiO₂. Due to the low packing density of RHA, disposal in landfills or open spaces may cause serious problems related to the environment and human health. Therefore, using RHA as a silicon source not only reduces the synthesis cost but also eases the environmental pressure. Barbosa et al. successfully synthesized ZSM-5 with RHA as a silicon source. In terms of templating agents, although ZSM-5 has been synthesized by RHA, the use of a template could not be avoided. A template usually plays an important role of structure-directing...
in the synthesis process of ZSM-5. The typical templates are always tetrapropyl ammonium hydroxide (TPAOH) and tetrapropyl ammonium bromide (TPABr). Both of them are organics and harmful to the environment and very expensive. So, it is necessary to explore a template-free method to synthesize ZSM-5. In addition, the absence of a template means that the sample does not require calcination to remove the template, which saves cost in terms of energy consumption. In recent years, many researchers have synthesized template-free ZSM-5, but the hydrothermal reaction temperature was high, around 443 K. Generally, high temperatures mean high energy consumption; therefore, in terms of synthesis temperature, much work has been done to reduce the hydrothermal reaction temperature of ZSM-5. Barakov et al. and Kadja et al. have both successfully synthesized ZSM-5 at 373 and 363 K, respectively. Table 1 shows the synthetic conditions of ZSM-5 zeolite in previous studies. Although the synthesis of ZSM-5 has a history of several decades, there are still shortcomings in its current synthesis process, such as high synthesis cost, use of chemical raw materials as silicon or aluminum sources, addition of organic templates, and high synthesis temperatures.

In this work, RHA and pseudo-boehmite were used as silicon and aluminum sources to synthesize ZSM-5, aiming at saving the synthesis cost. At the same time, ZSM-5 was successfully synthesized by the template-free method at a low temperature. This method reduced both energy consumption and environmental pollution. Then, the CO$_2$ adsorption performance of ZSM-5 synthesized at a low temperature was studied at 15 bar. This work is new with respect to the synthesis method and adsorption performance analysis. In terms of the synthesis method, this work used RHA as the silicon source, successfully synthesized ZSM-5 zeolite under the conditions of no organic template and a low temperature, and explored a green synthesis route for ZSM-5 zeolite. In terms of performance testing, this work explored the CO$_2$ adsorption performance of ZSM-5 zeolite under high-pressure conditions (0–15 bar), which will be of great significance for its use in the field of high-pressure adsorption of CO$_2$.

### Table 1. Synthetic Conditions of ZSM-5 Zeolite in Earlier Studies

| sample | silicon source (RHA, kaolin, or chemical silicon source) | template | synthesis temperature (K) |
|--------|--------------------------------------------------------|----------|----------------------------|
| ZSM-5  | chemical silicon source                                | TPAOH    | 443                        |
| ZSM-5  | chemical silicon source                                | TPAOH    | 438                        |
| ZSM-5  | RHA                                                    | TPAOH    | 453                        |
| ZSM-5  | chemical silicon source                                | TPABr    | 413                        |
| ZSM-5  | chemical silicon source                                | free     | 463                        |
| ZSM-5  | chemical silicon source                                | free     | 463                        |
| ZSM-5  | RHA                                                    | TPABr    | 383                        |
| ZSM-5  | RHA                                                    | TPABr    | 423                        |
| ZSM-5  | chemical silicon source                                | free     | 438                        |
| ZSM-5  | kaolin                                                 | TPABr    | 453                        |

Figure 1 shows the X-ray diffraction (XRD) patterns of the three samples. As can be seen, these three samples have the same characteristic diffraction peaks at 2θ = 8.0, 8.9, 13.3, 14.1, 14.9, 16.0, 23.2, 24.0, 24.4, 25.9, 26.9, 29.4, and 30.2°, which are in agreement with the MFI-type framework structure (ICDD PDF No. 44-0003). Crystallinity is calculated by dividing the diffraction peak intensity by the total intensity. The crystallinities of samples L-20, L-30, and L-40 are 84.1, 77.3, and 69.9%, respectively. The crystallinity decreases with the increase of the Si/Al molar ratio. Between 20 and 25°, samples L-30 and L-40 also have a clear amorphous hump of SiO$_2$, which is attributed to the increase in the crystallization time of ZSM-5 zeolite with the increase in the ratio of silicon/aluminum and part of the SiO$_2$ not been fully converted. The XRD pattern indicates that ZSM-5 zeolite with different Si/Al ratios can be successfully synthesized under the chosen conditions. However, the incomplete reaction of excessive SiO$_2$ in the raw material will adversely affect the finished product of ZSM-5 zeolite.

Figure 2 shows the Fourier transform infrared (FTIR) spectra of the three samples. All three samples were dried under vacuum at 100 °C for 2 h before the FTIR measurement.
to avoid signal interference caused by the adsorbed water. The transmission bands of the three samples synthesized at 393 K are almost at the same wavenumbers as that of the seed sample R-20, which indicates that the four samples contain similar functional groups, further verifying the successful synthesis of ZSM-5 zeolite at low-temperature conditions. The presence of the bands at 3447 and 1634 cm$^{-1}$ are mainly attributed to the tensile vibration and bending vibration bands of the O−H bond in the water molecules absorbed in the samples. The presence of the bands at 1080 and 799 cm$^{-1}$ is mainly attributed to the symmetric and asymmetric tensile vibration of Si−O−Si and Si−O−Al tetrahedral structures. The presence of the band at 550 cm$^{-1}$ is considered to represent the double-loop vibration of the five-membered ring. With the increase of the Si/Al ratio, the intensity of the transmission bands at 550 and 799 cm$^{-1}$ decreases significantly, indicating that the amount of ZSM-5 zeolite in the sample is reduced, which is consistent with the XRD characterization results.

Figure 3 shows the scanning electron microscopy (SEM) images of the three samples. In appearance, all samples showed the standard prismatic morphology of ZSM-5, with consistent grain size and uniform distribution, indicating the successful preparation of ZSM-5. The average diameters of ZSM-5 zeolite in samples L-20, L-30, and L-40 are 0.80, 0.83, and 0.71 μm, respectively. With the increase of the Si/Al molar ratio, the ZSM-5 with the prismatic morphology in the samples gradually decreases.

Figure 4 shows the N$_2$ adsorption–desorption isotherm at 77 K and the pore size distribution (calculated by the 2D-NLDFT model) of L-m analyzed in Table 2. The N$_2$ adsorption amount of all three samples at 77 K increases rapidly in the low-pressure zone ($P/P_0 < 0.1$), which is mainly due to microporous adsorption. The adsorption amount first increases steadily and then increases rapidly in the high-pressure zone ($P/P_0 > 0.1$), and a loop representing the mesoporosity is exhibited in each adsorption–desorption diagram, which is mainly due to mesoporous adsorption, macroporous adsorption, and adsorption between microparticles. So, both microporous and mesoporous structures are present in all three samples, which can also be seen in the pore size distribution maps of the three samples. All three samples contain micropores of about 0.58 nm and extensive mesoporous structures. With the increase of the Si/Al molar
ratio, the specific surface area of the sample, calculated by the t-plot method, decreases. At the same time, the total pore volume, micropore volume, and the micropore volume ratio of the samples also decrease. This is because with the increase of the Si/Al molar ratio, the formation of microporous structures takes more time. Besides, the sample L-40 contains an obvious mesoporous structure, which is mainly due to the unreacted amorphous SiO2 in the sample. The results show that the zeolite obtained in this study has excellent pore size uniformity, which is very conducive to the adsorption of CO2 with a specific size of molecules.

2.2. Adsorption Performance of L-m Zeolites. According to the investigation results, ZSM-5 zeolite samples with Si/Al molar ratios of 20, 30, and 40 were synthesized with a synthesis temperature of 393 K, crystallization time of 7 days, and a seeding ratio of 1 wt %. They are named L-m (m = 20/30/40).

2.2.1. Adsorption Regeneration Property. The adsorption regeneration property of the three samples was studied in this work. Without removing or reactivating the samples, cyclic adsorption and desorption were directly performed to observe the change in the adsorption amount of the samples. The relationship between the adsorption index of each sample and the number of cycles is given in Figure 5a. According to the results, for the L-20 zeolite, the adsorption amount in the vicinity of 15 bar for the fifth cycle was 2.39, 2.23, 2.21, 2.21, and 2.03 mmol/g, respectively. From the second cycle of adsorption and desorption, the adsorption indices of the sample were 93.43, 92.59, 92.28, and 85.01%. For the L-30

Table 2. Textural Properties of L-m Zeolitesa,b,c

| sample | S_BET (m²/g) | S_micropore (m²/g) | S_external (m²/g) | V_total (cm³/g) | V_micropore (cm³/g) | R_micropore (%) |
|--------|--------------|--------------------|------------------|----------------|---------------------|-----------------|
| L-20   | 284.8        | 211.8              | 73.0             | 0.157          | 0.110               | 70.1            |
| L-30   | 246.3        | 185.7              | 60.6             | 0.154          | 0.098               | 65.6            |
| L-40   | 182.9        | 133.0              | 49.9             | 0.138          | 0.071               | 51.4            |

*aS_BET: specific surface area calculated by the Brunauer–Emmett–Teller model. *bS_micropore: micropore area calculated by the t-plot model. *cS_external: external surface area calculated by the t-plot model.
zeolite, the adsorption amounts were 2.11, 1.92, 1.91, 1.73, and 1.74 mmol/g, respectively, and the adsorption indices of the sample were 91.15, 90.68, 82.25, and 82.69%. For the L-40 zeolite, the adsorption amounts were 1.92, 1.58, 1.54, 1.75, and 1.60 mmol/g, respectively, and the adsorption indices of the sample were 82.49, 80.11, 91.35, and 83.43%. The cyclic adsorption–desorption performance of L-40 exhibited first a decrease and then an increase owing to the presence of a large amount of amorphous silica in L-40, which has not been converted into ZSM-5 zeolite crystals. According to the pore size distribution test result of sample L-40, the sample contains many large pores, which makes the cyclic desorption performance of the sample not sufficiently stable under high-pressure conditions. Furthermore, we conduct an error analysis.
on the cyclic adsorption performance of the three samples in Figure 5b. The results show that the cyclic adsorption performance of the L-20 sample is significantly better than those of the other two samples, which is mainly due to the perfect crystallization of the L-20 zeolite.

2.2.2. Measurement of CO2 Adsorption Capacity. The CO2 adsorption isotherm of samples L-20, L-30, and L-40 was measured at temperatures of 273, 303, and 333 K in the pressure range of 0–15 bar. It is necessary to predict the equilibrium relationship between the adsorbent and the adsorbate to explore its interaction and adsorption mechanism. The Langmuir, Freundlich, and dual-site Langmuir models were used to carry out the fitting analysis with the measured data.

Figure 6 shows the CO2 adsorption isotherm fitted by models of L- m zeolites at 273, 303, and 333 K. Table 3 gives the CO2 adsorption isotherm parameters of the three models of L- m at 273, 303, and 333 K. The adsorption amounts of the three samples decrease with the increase of the adsorption temperature. The adsorption amounts at a pressure of 1 bar of the CO2 adsorption isotherm parameters of the three samples decrease with the increase of the adsorption temperature. The adsorption amounts at a pressure of 1 bar of the three samples decrease with the increase of the adsorption temperature. The adsorption amounts at a pressure of 1 bar of the three samples decrease with the increase of the adsorption temperature. The adsorption amounts at a pressure of 1 bar of the three samples decrease with the increase of the adsorption temperature.

Table 3. CO2 Adsorption Isotherm Parameters of the Models of L-m at 273, 303, and 333 K

| model              | parameter          | L-20     | L-30     | L-40     |
|--------------------|--------------------|----------|----------|----------|
| Langmuir           | \( q_a \) (mmol/g) | 2.148    | 1.789    | 1.509    |
|                    | \( b_a \) (bar\(^{-1}\)) | 0.001    | 0.001    | 2.996    |
|                    | \( Q \) (kJ/mol)  | 22.878   | 22.439   | 28.763   |
|                    | \( R^2 \)         | 0.924    | 0.919    | 0.926    |
| Freundlich         | \( k \) (mmol/(g·bar\(^{1/2}\))) | 1.622    | 1.217    | 0.981    |
|                    | \( n_1 \)         | 13.087   | 16.464   | 14.126   |
|                    | \( R^2 \)         | 1855.3   | 1688.3   | 182.3    |
| dual-site Langmuir | \( q_{a,A} \) (mmol/g) | 1.244    | 1.075    | 0.968    |
|                    | \( b_{a,A} \) (bar\(^{-1}\)) | 4.595 \times 10^{-5} | 2.519 \times 10^{-5} | 4.068 \times 10^{-5} |
|                    | \( Q_a \) (kJ/mol) | 25.090   | 24.439   | 22.968   |
|                    | \( q_{a,B} \) (mmol/g) | 1.092    | 0.958    | 0.751    |
|                    | \( b_{a,B} \) (bar\(^{-1}\)) | 1.861 \times 10^{-4} | 6.425 \times 10^{-4} | 8.047 \times 10^{-4} |
|                    | \( Q_b \) (kJ/mol) | 53.681   | 26.829   | 56.280   |
|                    | \( R^2 \)         | 0.995    | 0.980    | 0.991    |

According to Table 4, compared with ZSM-5 zeolites reported in other references, the L-20 sample described herein has a higher CO2 adsorption capacity with a lower synthesis cost.

Table 4. Comparison of CO2 Adsorption Capacity of ZSM-5 Zeolite at 1 bar

| sample | Si/Al | adsorption temperature (K) | CO2 adsorption capacity (mmol/g) |
|--------|-------|-----------------------------|----------------------------------|
| ZSM-5  | 25    | 273                         | 2.03                             |
| ZSM-5  | 50    | 208                         | 1.79                             |
| ZSM-5  | 130   | 308                         | 1.45                             |
| ZSM-5  | 27    | 323                         | 1.75                             |
| ZSM-5  | 27    | 303                         | 1.34                             |
| ZSM-5  | 20    | 273                         | 2.02                             |
| ZSM-5  | 303   | 1.76                         |
| ZSM-5  | 333   | 1.50                         |

"This work."
that the adsorption amount of the sample calculated by the model is much lower than the actual value. It is necessary to measure the real adsorption capacity of samples at high pressures rather than calculate it.

2.3.3. Selectivity Measurements. To know more about the adsorption performance of samples synthesized at low temperatures, the selectivity of CO2/N2 and CO2/O2 was predicted in this paper. Due to the differences in size, polarity, and quadrupole moment of the CO2 and N2 or O2 molecules, they were selectively adsorbed by adsorbents. To obtain the selectivity of CO2/N2 and CO2/O2, the adsorption capacities of CO2, N2, and O2 for L-m zeolites of three silicon/aluminum ratios were first measured at 273 K. The obtained adsorption isotherm was fitted, and the fitting formula was used to calculate the selectivity of CO2/N2 and CO2/O2. The dual-site Langmuir model with the highest fitting degree of CO2 adsorption isotherms was selected to fit the adsorption isotherms of N2 on the three samples. The CO2/N2 adsorption isotherm parameters of the three samples are shown in Table 6. It can be seen that all of the correlation coefficients ($R^2$) are beyond 0.999, meaning that the dual-site Langmuir model’s excellent fit in the low-pressure region provides the necessary accuracy for predicting selectivity.

The selectivity of CO2/N2, calculated by eq 8, of the three samples are shown in Figure 8. It can be seen that the selective adsorption capacity of the three samples decreases with the increase of pressure. When the pressure is 1 bar, the selective adsorption capacities of samples L-20, L-30, and L-40 are 34.3, 30.3, and 30.5, respectively. So, the selective adsorption capacity of sample L-20 is much better than those of the other two samples. As the pressure increases, the selective adsorption capacity of the sample tends to be stable. For sample L-20, the selective adsorption capacity of CO2/N2 is around 15, and those of samples L-30 and L-40 are around 14 and 16, respectively.

The dual-site Langmuir model was also selected to fit the adsorption isotherms of O2 on the three samples. The CO2/O2 adsorption isotherm parameters of the three samples are shown in Table 7. It can be seen that all of the correlation coefficients ($R^2$) are beyond 0.999, meaning that the selectivity of CO2/O2 predicted by the dual-site Langmuir model was also reasonable.

The selective adsorption capacities of CO2/O2 calculated by eq 8 of the three samples are shown in Figure 9. It can be seen that the selective adsorption capacities of the three samples decrease with the increase of pressure. When the pressure is 1 bar, the selective adsorption capacity of samples ZSM-5-L-20, ZSM-5-L-30, and ZSM-5-L-40 are 70.2, 49.7, and 52.8, respectively. So, the selective adsorption capacity of sample ZSM-5-L-20 is far better than those of the other two samples. As the pressure increases, the selective adsorption capacity of the sample tends to be stable. For sample ZSM-5-L-20, the selective adsorption capacity of CO2/O2 is around 18, and those of samples ZSM-5-L-30 and ZSM-5-L-40 are around 14 and 15, respectively.

3. CONCLUSIONS

This paper explored the synthesis of ZSM-5 zeolite under low-temperature and template-free conditions using an inexpensive silicon source (rice husk ash) and aluminum source (pseudoboehmite) and verified the feasibility of the green synthesis strategy. Based on the findings, ZSM-5 zeolite samples with Si/Al molar ratios of 20, 30, and 40 were finally synthesized at 393 K, with a crystallization time of 7 days and a seeding ratio of 1 wt %. Based on the characterization and performance measurement results of the three samples, the L-20 zeolite has better adsorption and selectivity performance. From the measurement results, when the temperatures were 273, 303, and 333 K, the adsorption amounts of sample L-20 near 15 bar were 2.39, 2.26, and 2.16 mmol/g, respectively. Through the fitting of the three models (Langmuir, Freundlich, and dual-site Langmuir), it is found that the ZSM-5 zeolite with three silica/alumina ratios synthesized at a low temperature is more biased toward adsorption with double sites. As the pressure increases, the adsorption capacity predicted by the model is lower than the actual measured value. For sample L-20, the selective adsorption capacities of both CO2/N2 and CO2/O2 decrease with increasing pressure, and the selective adsorption capacity at 1 bar is 34.3 and 70.2, respectively. In addition, the excellent regeneration capacity of ZSM-5 obtained in this work will also become a significant advantage for large-scale applications in the future.

Table 5. CO2 Adsorption Isotherm Parameters of the DSL Model of L-20 at 1 bar

| parameter | $q_{0,A}$ (mmol/g) | $b_{0,A}$ (bar$^{-1}$) | $Q_A$ (kJ/mol) | $q_{0,B}$ (mmol/g) | $b_{0,B}$ (bar$^{-1}$) | $Q_B$ (kJ/mol) | $R^2$ |
|-----------|-------------------|----------------------|----------------|-------------------|----------------------|----------------|--------|
| L-20      | 1.235             | 9.599 x 10$^{-5}$    | 25.460         | 0.868             | 6.285 x 10$^{-4}$    | 32.316         | 0.998  |

Figure 7. Deviation indices of sample L-20.
4. MATERIALS AND METHODS

4.1. Materials. The silicon source was from rice husk bought from a local farm. RHA was obtained by burning the rice husk (973 K, 6 h), and its chemical composition analysis (X-ray fluorescence, XRF) is shown in Table 8. Using RHA as a silicon source not only reduces the synthesis cost but also eases the environmental pressure. The alkali-dissolving acid extraction method reported in a prior study was used to obtain the silica solid powder from RHA with a SiO2 content of about 98.5 wt % (Table 8). The silica solid powder was used directly as a silicon source for the synthesis of ZSM-5. Pseudo-boehmite purchased from Guizhou Morui New Material Technology (China) was also chosen as an aluminum source in this paper, and its chemical composition analysis (XRF) is shown in Table 8. Besides, tetrapropyl ammonium hydroxide (TPAOH, 25 wt % in H2O), sodium chloride, sodium hydroxide, and hydrochloric acid (36−38%) were purchased from Sinopharm.

4.2. Synthesis Methods. The hydrothermal method was used for the synthesis of the ZSM-5 zeolite seed crystals. The ZSM-5 zeolite seed was synthesized with the raw material in the molar ratio of 20SiO2:8TPAOH::xAl2O3:400H2O:2.6xNaCl:0.5xHCl (x = 0.5/0.375/0.25) and was named R- (m = 20/30/40). The hydrothermal method was used for the synthesis of the ZSM-5 zeolite seed crystals. The ZSM-5 zeolite seed was synthesized with the raw material in the molar ratio of 20SiO2:8TPAOH::xAl2O3:400H2O:2.6xNaCl:0.5xHCl (x = 0.5/0.375/0.25) and was named R-m (m = 20/30/40). Pseudo-boehmite was completely dissolved with stirring in deionized water, and HCl was dropped into the solution to obtain sol particles of pseudo-boehmite. Then, TPAOH, NaCl, and SiO2 were added into the solution sequentially. Four hours later, the solution was transferred into a Teflon-lined stainless steel reactor at 438 K for 48 h. Finally, it was calcined at 773 K for 6 h to remove the organic template.

Then, ZSM-5 zeolite samples were synthesized under low-temperature and organic template-free conditions and were named L-m (m = 20/30/40). Different from the synthetic process above, the silicon and aluminum source solutions were prepared separately. Then, the silicon source solution was added to the aluminum source solution. After that, the above synthesized seed crystals were added to the solution an hour later. Other steps are similar except for calcination. By the addition of 0.5 g of seed crystals, about 4 g of ZSM-5 zeolite is synthesized and so the cost of using an organic template can be reduced by 87.5%.

4.3. Synthesis Parameters. The three main factors affecting the synthesis of ZSM-5 are synthesis temperature, crystallization time, and the dosages of seed crystals. To determine the influence of the temperature on the synthesis of ZSM-5 zeolite, samples were synthesized with a Si/Al molar ratio of 20 at different temperatures of 363, 378, and 393 K and were named L-20-t (t = 363/378/393). To
determine the influence of crystallization time, ZSM-5 samples were synthesized with a Si/Al molar ratio of 30 at different crystallization times of 3, 5, and 7 days and were named L-30-xD (x = 3/5/7). To determine the influence of the dosage of seed crystals, samples were synthesized with a Si/Al molar ratio of 20 at different seeding ratios of 0, 1, 2, and 5 wt % and were named L-20-n (n = 0/1/2/5). Then, ZSM-5 zeolite samples with Si/Al ratios of 20/30/40 were synthesized at a low temperature, named L-m (m = 20/30/40), and their adsorption performance was studied.

**4.3. Characterization Methods.** The chemical composition analysis of RHA silica was performed by X-ray fluorescence (XRF) with a ZSX Primus ii spectrometer (Rigaku, Japan). A powder X-ray diffractometer (XRD-7000, Shimadzu) equipped with a Cu anticathode was used to measure the crystal phases of the samples. The measuring range was from 5 to 40° with a step of 0.02°. A Fourier infrared spectrometer (Cary 660 FTIR, Agilent) was used to measure the functional groups of samples in the range of 500−4000 cm⁻¹. A scanning electron microscope (Ultra Plus, ZEISS) was used to observe the microcrystal morphology of samples. The nitrogen adsorption/desorption isotherms of the samples were recorded using a Physical adsorption apparatus (ASAP 2460, Micromeritics) at 77 K. The Brunauer−Emmett−Teller (BET) and T-plot models were used to analyze the specific surface area, pore size distribution, and the micropore volume.

**4.4. Gas Adsorption Measurements.** The adsorptive properties of samples were measured using a high-pressure physical adsorption apparatus (3H-2000PH, Beishide). Two pressure sensors are placed in the high-pressure physical adsorption apparatus: one for the 200 bar model US381-2-200BA and the other for the 10 bar model US381-2-10BA. Before installing in the sample tube, all samples were dried in a vacuum drying oven at 423 K for about 6 h. Then, 1 g of the sample was placed in the sample tube. Before the measurements, the samples were heated to 573 K for 12 h to degas for accurate measurements.

**4.4.1. CO₂ Adsorption Isotherm.** In this paper, CO₂ adsorption isotherms of samples L-20, L-30, and L-40 were measured at temperatures of 273, 303, and 333 K in the pressure range of 0−15 bar. The Langmuir, Freundlich, and dual-site Langmuir models were used to carry out the fitting analysis with the measured data.

**Table 8. Chemical Composition Analysis of RHA and Pseudo-Boehmite (wt %)**

| samples   | RHA   | SiO₂ from RHA | pseudo-boehmite |
|-----------|-------|---------------|-----------------|
| SiO₂      | 91.6726 | 98.2956       | 0.3053          |
| Al₂O₃     | 0.6033  | 0.2274        | 99.4150         |
| K₂O       | 3.9910  | 0.0704        | 99.7650         |
| CaO       | 1.1797  | 0.0261        | 99.7950         |
| P₂O₅      | 0.9358  | 0.0178        | 99.3920         |
| MgO       | 0.5845  |               |                 |
| Fe₂O₃     | 0.5809  | 0.0580        | 99.3600         |
| MnO       | 0.2812  |               |                 |
| Cr₂O₃     | 0.0912  |               |                 |
| SO₃       | 0.0342  | 0.0408        | 99.4850         |
| Ga₂O₃     | 0.0137  | 0.0085        | 99.0700         |
| Cl        | 0.0117  | 0.6401        |                 |
| Na₂O      | 0.0081  | 0.6127        | 0.0026          |

*Figure 9. CO₂/O₂ adsorption isotherm and adsorption quantity ratio of L-m zeolites at 273 K: (a) L-20, (b) L-30, and (c) L-40.*
has a constant enthalpy and adsorption activation energy and the adsorbate does not migrate onto the surface plane.\(^\text{39}\) It is expressed by the following equations

\[
q = \frac{q_b p}{1 + b_p p}
\]

\[
b_L = b_{L,0} \exp \left(\frac{-Q}{RT}\right)
\]

where \(q\) is the adsorption quantity (mmol/g) at the absolute pressure \(p\) (bar), \(q_b\) is the complete monolayer adsorption constant (mmol/g), \(b_L\) is the Langmuir model constant \((\text{bar}^{-1})\), \(Q\) is the same amount of adsorption heat that is required for physical adsorption (kJ/mol), \(T\) is the reaction temperature (K), and \(b_{L,0}\) is a constant (bar\(^{-1}\)).

Compared to the Langmuir model, the Freundlich model is an empirical model applied to multilayer adsorption.\(^\text{42}\) It is expressed by the following equations:

\[
q = k p^{1/n}
\]

\[
n = n_1 + \frac{n_2}{T}
\]

where \(q\) is the adsorption quantity (mmol/g) at the absolute pressure \(p\) (bar), \(k\) is the Freundlich model constant \((\text{mmol/}(\text{g-bar}^{1/\text{n}}))\), \(n\) is the heterogeneous adsorption surface coefficient calculated by eq 4, \(T\) is the reaction temperature (K), and \(n_1\) and \(n_2\) are constants.

The dual-site Langmuir model is a type of four-parameter model developed from the two-parameter Langmuir model, which is used to fit the adsorption isotherm. In the building of this model, it is considered that the heterogeneous surface of the adsorbent is a collection of different energy locations,\(^\text{40}\) and it is expressed by the following equations:

\[
q = \frac{q_{m,\text{A}} b_p}{1 + b_p p} + \frac{q_{m,\text{B}} b_p}{1 + b_p p}
\]

\[
b_A = b_{0,\text{A}} \exp \left(\frac{-Q_A}{RT}\right)
\]

\[
b_B = b_{0,\text{B}} \exp \left(\frac{-Q_B}{RT}\right)
\]

where \(q\) is the adsorption quantity (mmol/g) at the absolute pressure \(p\) (bar), \(q_{m,\text{A}}\) and \(q_{m,\text{B}}\) are the maximum saturated adsorption quantities of the two different adsorption sites considered (mmol/g), \(b_A\) and \(b_B\) are the Langmuir model constants of the two different adsorption sites \((\text{bar}^{-1})\), which are calculated by eqs 7 and 8, respectively, \(Q_A\) and \(Q_B\) are the same amount of adsorption heat that is required for physical adsorption (kJ/mol), \(T\) is the reaction temperature (K), and \(b_{0,\text{A}}\) and \(b_{0,\text{B}}\) are constants \((\text{bar}^{-1})\).

In this paper, the deviation index \((D)\) is defined to express the adsorption quantity calculated by the model \((q_0\), mmol/g) and that measured practically \((q_i\), mmol/g) and is expressed as follows

\[
D = \frac{q_0 - q_i}{q_i} \times 100\%
\]

4.4.2. Selectivity. To determine the selective adsorption capacity \((S)\) of CO\(_2\)/N\(_2\) and CO\(_2\)/O\(_2\) of the three samples, we measured the adsorption isotherms of CO\(_2\), O\(_2\), and N\(_2\) at 273 K. The obtained adsorption isotherms are fitted, and the fitting formula is used to calculate the selective adsorption capacity of CO\(_2\)/N\(_2\) and CO\(_2\)/O\(_2\) of the corresponding sample combined with the actual working conditions to predict the effect of the sample used in industrial flue gas separation. The industrial flue gas usually consists of N\(_2\) and CO\(_2\) in a volume ratio of 9:1.\(^\text{51}\) The selective adsorption capacity of CO\(_2\)/N\(_2\) is calculated by the following equation

\[
S = \frac{q_i/q_b}{p/p_i}
\]

where \(q\) is the adsorption quantity (mmol/g) at the partial pressure \(p\) (bar), \(i\) represents CO\(_2\), and \(j\) represents N\(_2\) or O\(_2\).

4.4.3. Adsorption Regeneration Property. To measure the adsorption regeneration property, the CO\(_2\) cyclic adsorption performance was measured at 273 K. The percentage of the regenerated adsorption amount and the initial adsorption amount was defined as the adsorption index.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.0c05842.

Characterization results of the process of synthesis conditions of ZSM-5 zeolite at low temperatures: XRD patterns (Figure S1); SEM images (Figure S2); pore size distribution (Figure S3); and textual properties (Table S1) (PDF)

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Notes
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