Swelling-agent-free synthesis of rice husk derived silica materials with large mesopores for efficient CO\textsubscript{2} capture

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**Highlights**

- Biporous MS-400(25) with large mesopores was prepared without swelling agents.
- Using silicate waste of rice husk as precursor reduces the chemical costs.

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**Abstract**

Swelling-agent-free synthesis of silica materials with large mesopores were developed using silicate from rice husk ash (RHA) as an alternative silica precursor in this study. Unlike the conventional methods for preparing large-pore silica materials in which toxic and expensive additives were employed as swelling agents, the obtained silica materials with large mesopores could be facilely prepared via a simple temperature-controlled approach without adding pore expanders. The fusion and hydrothermal temperature effects on the structural properties of obtained mesoporous silicas were investigated by the XRD, nitrogen adsorption–desorption, SEM and TEM analyses. The obtained mesoporous MS-400(25), which was fabricated using rice husk fused at 400 °C and treated with sodium hydroxide at 25 °C, exhibited bimodal meso-porosities (2.7 and 24 nm) and large pore volume (1.92 cm\textsuperscript{3}/g). The bi-porosities mainly originated from the intra-particle mesostructure within silica particles and the inter-particle porosity between the aggregated nano-sized silica particles, respectively. The synthesized silicas were applied as the supports of adsorbents for CO\textsubscript{2} capture. The adsorption tests clearly revealed that the tetraethylenepentamine (TEPA) impregnated MS-400(25) material could achieve CO\textsubscript{2} adsorption capacity of 173 mg/g under 10% CO\textsubscript{2} at 75 °C, which was the best sorbents among all samples due to its relatively large pore volume.

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**1. Introduction**

The mitigation of global warming due to CO\textsubscript{2} emission is of great importance in environmental protection. Among available technologies, the use of amine-based solid sorbents for controlling CO\textsubscript{2} emission has attracted considerable attention, particularly in post-combustion processes where CO\textsubscript{2} is captured at low temperature and low pressure [1–4]. In comparison with conventional amine-based solvent scrubbing, the use of solid sorbents shows great potential to reduce the cost of capture process and lessen the energy penalty [5,6]. Therefore, the development of efficient and low-cost CO\textsubscript{2} sorbents will undoubtedly enhance the competitiveness for CO\textsubscript{2} capture applications [7,8].

Recently mesoporous silicas with tunable pore texture and unique surface chemistry via functionalization are considered as promising adsorbents for CO\textsubscript{2} capture [9]. Progress has been made by functionalizing various amine-based polymers on several supports including MCM-41, SBA-15, HMS, KIT, MSU, mesoporous silica spherical particles and mesocellular foams [10–16]. And high sorbent capacity and selectivity have been achieved for CO\textsubscript{2} capture. More recently, research works have shown that the pore size and pore volume of silica support play important roles in sorbent performance [17–19]. Supports with high pore volume can accommodate a greater amount of amines in the pores, and a large pore size is desirable for rapid diffusion of CO\textsubscript{2} in the pores. In this regard, mesocellular foams and mesoporous silica with large pore size and good pore interconnection appear to be more efficient than the other mesoporous silica supports [19–21].

Silicon alkoxide and sodium silicate are common silica sources [22,23]. However, the commercial fabrications of silica sources are...
highly energy-consumed and associated with high temperature, high pressure and strong acidity process [24,25], which is expensive and unfriendly to the environment. In addition, in the preparation of silica supports with large pores and hierarchical structures for efficient CO₂ capture, the use of toxic and expensive swelling agents such as trimethylbenzene (TMB) and ammonium fluoride are required [26,27]. Thus the industrial applications of current methods would have certain limitations in terms of environment, energy and economic concerns.

The recycling of silicon or silica-containing wastes as alternative precursors for preparing mesoporous silica instead of using commercial agents may provide an excellent opportunity to prepare the sorbents economically and minimize the waste production as well. Rice husk (RH) is one of the major agricultural wastes around the world, and it has been demonstrated to be a potentially feasible resource for synthesizing silica-based materials [28–30]. With the aim of lowering manufacturing cost and green synthesis for CO₂ adsorbent, a series of polyethyleneimine-immobilized uni-modal and/or bi-modal porous silicas were prepared from rice husk ash with biopolymer of chitosan as a pore structure-directing agent [31]. However, the maximum pore volume of their prepared silica support was only 1.08 cm³/g, which could only accommodate ca. 50 wt.% amines. From the viewpoint of both lowering cost and green synthesis, it is highly desirable to develop a simple and scalable approach to prepare silica supports with large pore volume and large pore size.

In this study, the fabrication of mesoporous silica materials with different mesopore sizes and large pore volumes were prepared by using sodium silicate solution as silica source via a simple temperature-controlled approach. The sodium silicate solution, which is extracted from rice husk ash (RHA), has been demonstrated to be a potentially feasible resource for synthesizing silica-based materials. The synthetic process is simple, cost-effective and environmentally benign since no extra pore expander and post-pore-expansion treatment are necessary, which significantly simplifies the scale-up synthesis. The pore structure and morphology of the obtained silica materials are presented and discussed. Moreover, an attempt has also been made to apply these mesoporous silica for immobilization of tetraethylpentamine (TEPA) as sorbents and investigate their structure vs. performance relationship for CO₂ capture.

2. Experimental section

2.1. Silica extraction and material preparation

In order to figure out the effect of fusion temperature on structural properties of the obtained MS materials, the rice husk (RH) was fused under 400, 550 or 700 °C, respectively, and the obtained rice husk ash (RHA) was then mixed with aqueous NaOH solution at 25 °C for 24 h for the extraction of silica. The resulting mixture was then centrifuged to separate supernatant and sediment. The silica supernatant was then utilized as the silica precursor for the synthesis of mesoporous silica materials. Mesoporous silicas were synthesized by the hydrothermal treatment method using the silica supernatant extracted from RHA as the silica precursor and cetyltrimethylammonium bromide (CTAB) as employed as the structure-directing template in the synthesis. The molar composition of the gel mixture was 1 SiO₂: 0.2 CTAB: 0.89 H₂SO₄: 120 H₂O. In a typical procedure, 63 ml of waste silicate solution was acidified by adding approximately 40 ml of 4N H₂SO₄ to bring down the pH to 10.5 with constant stirring to form a gel. After stirring, 7.28 g of CTAB (dissolved in 25 ml of DI water) was added drop by drop into the above mixture and the combined mixture was stirred for three additional hours. The resulting gel mixture was transferred into a Teflon coated autoclave and kept in an oven at 145 °C for 36 h. After cooling to room temperature, the resultant solid was recovered by filtration, washed with DI water and dried in an oven at 110 °C for 8 h. Finally, the organic template was removed by using a muffle furnace in air at 550 °C for 6 h. The synthesized mesoporous silica was denoted as MS-X(25), where X corresponds to the fusion temperature of raw RH under 400, 550 or 700 °C, with the following silica extraction temperature at 25 °C.

On the other hand, for studying the effect of extraction temperature on structural properties of the obtained MS materials, the RH was fused under a fixed temperature of 400 °C, the fused RHA was then mixed with aqueous NaOH solution at different hydrothermal temperatures of 25, 40, or 105 °C, respectively, to extract silica from fused RHA. The resulting mixture was then centrifuged to separate supernatant and sediment. The silicate supernatant was then utilized as the silica precursor for the synthesis of mesoporous silica, with similar procedures described above. The synthesized mesoporous silica was denoted as MS-400(Y), where 400 denotes the fusion temperature and Y corresponds to the silicate extraction (hydrothermal) temperature of either 25, 40, or 105 °C.

For comparison purpose, the preparation of MCM-41(NaSi) and SBA-15(NaSi) from commercial silica precursors via conventional hydrothermal process was presented as well [8]. The synthesis of MCM-41(NaSi) was carried out using pure chemicals of sodium metasilicate nanohydrate (Na₂SiO₃·9H₂O) with CTAB as the structure-directing template. The molar composition of the gel mixture was 1SiO₂: 0.2 CTAB: 120 H₂O: 0.89 H₂SO₄. Mesoporous SBA-15 was synthesized using a tri-block copolymer, EO₃₀–PO₇₀–EO₃₀ (Pluronic P123, BASF) as the template and sodium silicate solution (~14% NaOH, ~27% SiO₂, Aldrich) as the silica source. The molar composition of the gel mixture was 1SiO₂: 0.01 P123: 286 H₂O: 0.7 H₂SO₄.

2.2. Characterization

The specific surface area, specific pore volume and average pore diameter (BJH method) of the samples were measured by N₂ adsorption–desorption isotherms at 77 K using a surface area analyzer (Micromeritics, ASAP 2000). All the samples were degassed for 6 h at 350 °C under vacuum (10⁻⁶ mbar) prior to the adsorption experiments. The powder X-ray diffraction (XRD) analyses were made to reveal the crystalline structure of mesoporous materials, and the diffractograms of the mesoporous samples were recorded in the 2θ range of 2–80° in steps of 0.6 degree with a count time of 60 s at each point. The morphology of the materials was observed via the SEM (HITACHI-S4700) images. TEM images of the samples were observed with a JEOL JEM 1210 TEM instrument operated at 120 kV, prior that the samples (5–10 mg) were ultrasonicated in ethanol and dispersed on carbon film supported on copper grids (200 mesh).

2.3. Functionalization and CO₂ adsorption tests

The above mesoporous silica materials were functionalized with amine reagent of tetraethylpentamine (TEPA) via the wet impregnation method to enhance their CO₂ capture capacity. In a typical process, all silica supports were thermally pretreated at 120 °C for 1 h. Meanwhile, TEPA was mixed with ethanol and the resulting solution was stirred for 30 min. After pretreatment, the silica adsorbents were dispersed into a flask containing TEPA solution and the mixture was then refluxed at 80 °C for 2 h. After cooling to room temperature, the obtained materials were dried at 100 °C for 2 h. The nitrogen loading of the aminated material was evaluated by a thermo-gravimetric analyzer (TGA, Netzsch TG209 F1, Germany).
To obtain the adsorption capacity and breakthrough curve of the adsorbent, CO₂ adsorption experiment was carried out by a dynamic packed column method. Prior to the adsorption, the pre-weighed adsorbent (1.0 g, 16–30 mesh powder, packing height ≈ 5 cm) was packed in a Pyrex quartz tube with an internal diameter of 0.75 cm, and placed in a temperature-controlled oven. In a typical process, the adsorbents were pretreated under a N₂ flow of 0.1 L/min at 110 °C for 1 h, and then cooled to the adsorption temperature of 75 °C. Subsequently, the gas flow was switched to 10% (v/v) CO₂ gas stream (balanced with N₂) under a flow rate of 0.1 L/min. The concentration of CO₂ was continuously measured by a CO₂ analyzer (Molecular Analytics AGM 4000 Gas Analyzer).

3. Results and discussion

3.1. Characterization of MS-X(25) and MS-400(Y) materials

The pore structures of the calcined MS-X(25) and MS-400(Y) materials are analyzed by the nitrogen adsorption–desorption measurement and the results are shown in Fig. 1a. All samples exhibited isotherms of type IV of the IUPAC classification which featuring a narrow step due to capillary condensation of nitrogen within the primary mesopores [32]. It is noted that MS-400(25) and MS-550(25) showed two uptakes of nitrogen adsorption under relative pressures of 0.25–0.40 and 0.80–1.0, respectively. Such observation revealed the presence of bimodal porosity [33] as also observed in Fig. 1b. The first hysteresis loop at p/p₀ = 0.25–0.40 is related to capillary condensation of nitrogen within small intraparticle mesopores that are originated from CTAB templates. The second hysteresis loop, which lifted up sharply in the p/p₀ region of 0.85–1.0, demonstrated the presence of an additional appreciable amount of secondary mesopores. As the fusion temperature further increases to 700 °C, the MS-700(25) did not show observable hysteresis loop located at relative lower pressures of 0.25–0.40, it only show the hysteresis loop in the p/p₀ region of 0.80–1.0. This suggests that there is no well-defined intraparticle mesopores within MS-700(25). Furthermore, it is noteworthy that when the fusion temperature increases, the hysteresis loop and N₂ adsorption capacity at relative pressures of 0.85–1.0 decreased significantly, which reflected the decrease in the amounts of large pores of the materials.

On the other hand, as the extraction temperature increases from 25 to 40 °C and 105 °C, it is seen for MS-400(40) and MS-400(105) materials that the capillary condensation step at relative lower pressures of 0.25–0.40 with type H1 hysteresis loop became more pronounced, along with increased adsorption volume. Such phenomenon revealed the enhanced uniformity of cylindrical pore channels with higher specific surface area that were templated by CTAB [34]. Meanwhile, the hysteresis loop and adsorption capacity at relative pressures of 0.80–1.0 diminished gradually, which reflected the decrease in the amounts of large pores of the materials.

The pore size distributions of the HRA-derived MS-X(25) and MS-400(Y) samples were estimated from the BJH method with results shown in Fig. 1b. It can be seen that only MS-400(25) and MS-550(25) displayed bimodal mesopore structure consisting of small mesopores at ca. 2.7 nm as well as large mesopores at 10–50 nm. This is probably due to the presence of large inter-particle mesopores, which are derived from the aggregated silica particles. But when fusion temperature increases to 700 °C, the MS-700(25) exhibited only a broad pore size distribution at 10–50 nm. On the other hand, when the extraction temperatures were 40 and 105 °C (MS-400(40) and MS-400(105)), there appears to have only one pore size distribution at small pore range (2.7–3.0 nm) as observed in Fig. 1b.

The structural parameters of BET specific surface area (S_{BET}), total pore volume (V_{tore}) and average pore diameter (D_{pore}) as derived from nitrogen adsorption–desorption measurements are summarized in Table 1. It is seen that the MS-X(25) materials possessed mesoporous structure with specific surface area (S_{BET}) in the range of 211–518 m²/g. The specific surface area was slightly increased with increasing fusion temperature from 400 °C to 550 °C. However, the surface area decreased drastically as fusion temperature was increased further to 700 °C. The decrease in surface area could be associated with the extensive growth and aggregation between the individual silica particles, resulting in the lower surface area of the materials. On the other hand, it is noteworthy that the specific surface areas of the MS-400(X) materials is enhanced significantly from 484 m²/g to 945 and 1063 m²/g as the extraction temperature increases from 25 °C to 40 °C and 105 °C.

The crystalline structure of MS-X(25) and MS-400(X) samples were revealed by the powder XRD patterns as shown in Fig. 2. It is observed from Fig. 2a that all MS-X(25) samples exhibited one main intensive peak at 2θ of ca. 22°, which are characteristic of silica materials with randomly arranged pore structures [24, 35]. When the extraction temperature was increased from 25 °C to 40 and 105 °C, it is seen from Fig. 2b that one main intensive (100) peak at 2θ of ca. 2° and another peak (110) diffraction peak at 2θ of ca. 3.7° appeared for MS-400(40) and MS-400(105), indicating the presence of hexagonal array and one-dimensional channel structure [36]. With a further increase of extraction temperature to 105 °C, the (100) peak shifted slightly to a higher angle, which
could be associated with the slightly diminished pore diameter of MS-400(105). This is in line with nitrogen physisorption results in which MS-400(40) shows larger pore diameter than that of MS-400(105) as showed in Table 1.

The morphologies of MS-400(25) and MS-400(105) samples are revealed by the SEM images, as illustrated in Fig. 3a and b. It can be clearly observed that aggregated nanoparticles with ca. 50–100 nm particle size are formed for the MS-400(25); on the contrary, MS-400(105) is mainly consisted of tubular and irregular shapes. The textural mesostructure of the MS-400(25) and MS-400(105) are further characterized by TEM images and the results are shown in Fig. 3c and d. The TEM image of MS-400(25) material consists of both small and large mesopores. The mesostructure is composed of unidirectional pore orientation within tubular particles, which is

<table>
<thead>
<tr>
<th>Sample name</th>
<th>°Fusion temperature (°C)</th>
<th>°Extraction temperature (°C)</th>
<th>( S_{\text{BET}} ) (m²/g)</th>
<th>( d_{\text{BJH}} ) (nm)</th>
<th>( V_\theta ) (cm³/g)</th>
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<tr>
<td>MS-400(25)</td>
<td>400</td>
<td>25</td>
<td>484</td>
<td>14.4</td>
<td>1.92</td>
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<tr>
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<td>550</td>
<td>25</td>
<td>518</td>
<td>11.8</td>
<td>1.71</td>
</tr>
<tr>
<td>MS-700(25)</td>
<td>700</td>
<td>25</td>
<td>211</td>
<td>25.8</td>
<td>1.36</td>
</tr>
<tr>
<td>MS-400(40)</td>
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<td>40</td>
<td>945</td>
<td>4.4</td>
<td>0.97</td>
</tr>
<tr>
<td>MS-400(105)</td>
<td>400</td>
<td>105</td>
<td>1063</td>
<td>3.4</td>
<td>1.00</td>
</tr>
<tr>
<td>MCM-41(NaSi)</td>
<td>–</td>
<td>–</td>
<td>1064</td>
<td>3.0</td>
<td>1.00</td>
</tr>
<tr>
<td>SBA-15(NaSi)</td>
<td>–</td>
<td>–</td>
<td>801</td>
<td>6.5</td>
<td>1.02</td>
</tr>
</tbody>
</table>

a °Fusion temperature of raw rice husk.

b °Extraction (hydrothermal) temperature for the extraction of silicate from pre-heated rice husk ash.

Fig. 2. XRD patterns of MS-400(25), MS-550(25), MS-700(25), MS-400(40) and MS-400(105).

Fig. 3. SEM images of mesoporous silica materials: (a) MS-400(25), (b) MS-400(105); and TEM images of mesoporous silica materials: (c) MS-400(25) and (d) MS-400(105).
similar with the characteristic of MCM-41 synthesized via conventional aqueous route [36].

### 3.2. CO₂ adsorption over TEPA-impregnated mesoporous silica-based adsorbents

The nitrogen loadings on 50 wt.% TEPA-impregnated adsorbents were evaluated by the thermo-gravimetric analyses (TG/DTG) with results shown in Fig. 4a and b. All aminated adsorbents show a broad temperature range of their weight losses as seen from Fig. 4a. The first weight loss region at <120 °C is mainly from the evaporation of the physically adsorbed water on the surface of the adsorbents. The weight losses at second regions of around 120–200 °C are very significant. It is observed from the DTG profile (Fig. 4b) that the maximum mass change rates appeared at around 170–200 °C, and this is mainly attributed to Hofmann elimination of trimethylamine in TEPA-impregnated adsorbents [37,38]. The third weight loss regions (200–700 °C) are due to the carbon chain (C–H2) decomposition by oxidation processes [18].

The CO₂ adsorption capacities of all 50 wt.% TEPA-impregnated adsorbents were evaluated by the thermo-gravimetric analyses (TG/DTG) with results shown in Fig. 4a and b. All aminated adsorbents show a broad temperature range of their weight losses as seen from Fig. 4a. The first weight loss region at <120 °C is mainly from the evaporation of the physically adsorbed water on the surface of the adsorbents. The weight losses at second regions of around 120–200 °C are very significant. It is observed from the DTG profile (Fig. 4b) that the maximum mass change rates appeared at around 170–200 °C, and this is mainly attributed to Hofmann elimination of trimethylamine in TEPA-impregnated adsorbents [37,38]. The third weight loss regions (200–700 °C) are due to the carbon chain (C–H2) decomposition by oxidation processes [18].

The TEPA contents were calculated based on the mass losses observed in the temperature range of 120–700 °C and the results were expressed as N loading and summarized in Table 2. The N loadings were calculated to be 9.85, 10.39, 10.13, 9.17 and 9.86 mmol of nitrogen adsorption sites per gram of silica, respectively, for TEPA-MS-400(25), TEPA-MS-550(25), TEPA-MS-700(25), TEPA-MS-400(40) and TEPA-MS-400(105). It can be observed that all aminated sorbents exhibited similar S BET and N loadings after 50 wt.% TEPA impregnation.

Fig. 5a displays the breakthrough curves of 10% CO₂ adsorption on TEPA-impregnated MS materials at 75 °C via the packed column reactor. For comparison basis, mesoporous MCM-41(NaSi) and SBA-15(NaSi) silica materials synthesized from commercial sodium silicate solution via conventional hydrothermal process were also used as supports for their CO₂ adsorption performance. Their structural properties including specific surface area, pore size and total pore volume are summarized in Table 1. It is seen that CO₂ gas could be effectively adsorbed on all adsorbents with capture efficiency of near 100% at the beginning. But the CO₂ concentration using TEPA-SBA-15(NaSi) raised first (C eff/C in > 0.0), while the TEPA-MCM-41(NaSi) reached the saturated point (C eff/C in = 1.0) first. On the other hand, both the breakthrough time (t eff/C in = 0.05) and the saturated time (t eff/C in = 1.0) of the TEPA-MS-400(25) adsorbent were the longest among all tested adsorbents. This indicated that TEPA-MS-400(25) is the best CO₂ adsorbent among all tested materials.

Fig. 5b shows the saturated adsorption capacities of all 50 wt.% TEPA-impregnated adsorbents. The CO₂ adsorption capacities of all tested adsorbents were in the range of 113–155 mg/g-adsorbent which followed the order of TEPA-MS-400(25) > TEPA-MS-550(25) > TEPA-MS-700(25) > TEPA-MS-400(40) ≈ TEPA-MS-400(105) ≈ TEPA-MCM-41(NaSi) ≈ TEPA-SBA-15(NaSi). There are many parameters determining the sorbent capacity, e.g. support textural property and surface density of amines. It is generally accepted that supports with high-surface-area are beneficial for a better dispersion of amines on the support and high sorbent capacity [10,39]. As observed from Tables 1 and 2, however, there is no relationship between S BET and CO₂ uptake. It is well-known that the adsorption of CO₂ over TEPA-impregnated adsorbents was carried out between the acidic CO₂ molecules and the basic amino groups within TEPA molecules. Generally, the following chemical reactions are expected to take place when CO₂ molecules react with TEPA under anhydrous conditions [14]:

![Fig. 4. (a) TG profiles; (b) DTG profiles of 50 wt.% TEPA-impregnated mesoporous silica adsorbents.](image_url)

### Table 2

<table>
<thead>
<tr>
<th>Sample name</th>
<th>S BET (m²/g)</th>
<th>Vₐ (cm³/g)</th>
<th>N loading (mmol/g)</th>
<th>N surface density (N atom/nm²)</th>
<th>CO₂ capacity (mg/g) at 10% CO₂, 75 °C</th>
<th>Amine efficiency (CO₂/N) (mmol/mmol)</th>
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<tr>
<td>TEPA-MS-400(25)</td>
<td>33</td>
<td>0.30</td>
<td>9.85</td>
<td>12.25</td>
<td>155 ± 5</td>
<td>0.72</td>
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<td>TEPA-MS-550(25)</td>
<td>31</td>
<td>0.25</td>
<td>10.39</td>
<td>12.07</td>
<td>141 ± 4</td>
<td>0.62</td>
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<tr>
<td>TEPA-MS-700(25)</td>
<td>28</td>
<td>0.19</td>
<td>10.13</td>
<td>28.90</td>
<td>124 ± 6</td>
<td>0.56</td>
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<td>TEPA-MS-400(40)</td>
<td>30</td>
<td>0.13</td>
<td>9.17</td>
<td>5.85</td>
<td>116 ± 3</td>
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<tr>
<td>TEPA-MS-400(105)</td>
<td>40</td>
<td>0.15</td>
<td>9.86</td>
<td>5.59</td>
<td>113 ± 3</td>
<td>0.52</td>
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<tr>
<td>TEPA-MCM-41(NaSi)</td>
<td>53</td>
<td>0.15</td>
<td>11.28</td>
<td>6.38</td>
<td>114 ± 3</td>
<td>0.46</td>
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<td>TEPA-SBA-15(NaSi)</td>
<td>40</td>
<td>0.11</td>
<td>10.61</td>
<td>7.97</td>
<td>114 ± 3</td>
<td>0.48</td>
</tr>
</tbody>
</table>

*Calculated based on the mass loss in the temperature of 120–700 °C.

*Calculated based on the amount of nitrogen per 1 nm² of the parent mesoporous silica support.*
capacity was almost unchanged. Adsorption capacity is adsorbed on adsorption performance. They concluded that the amine was introduced into the pore channels. Liu et al. [41] also concluded that the key parameter influencing uptake. This result is similar with a recent work of Liu et al. [44] found that the enlargement of pore diameter of the silica support would enhance the CO₂ adsorption performance. They concluded that the amine was introduced into the pore channels more easily as the pore diameter of the mesoporous silica support increases. As seen from Fig. 6b, the sorbent capacity increased linearly with increasing pore size in the range of 3.0–14.4 nm. However, the adsorption capacity decreased drastically for the largest pore size of 25.8 nm (TEPA-MS-700(25) sorbent). The results shown in Fig. 6a and b may suggest that although higher amine surface density and larger pore size of the silica support could enhance the CO₂ adsorption, their positive influence is limited to a certain degree.

\[
\text{CO}_2 + 2\text{RNH}_2 \rightarrow \textRNHCOO^- + \text{RNH}_3^+ \\
\text{CO}_2 + 2\text{R}_1\text{R}_2\text{NH} \rightarrow \text{R}_1\text{NHCOO}^- + \text{R}_2\text{NH}_2 + (\text{R}_2\text{NCOO}^- + \text{R}_1\text{NH}_2^+) \\
\]

In the absence of moisture, one mole of CO₂ is adsorbed on TEPA-impregnated sorbents through formation of carbamate ion, where two moles of nitrogen atoms in the amine are consumed. In an earlier study, CO₂ adsorption capacity was demonstrated to be strongly dependent on the surface density of amine species [40]. They found that densely amino groups are more effective as adsorption sites than those isolated on bare silica supports. Liu et al. [41] also concluded that the key parameter influencing the CO₂ adsorption is not surface area but might be the surface density of amines on the sorbents.

The influence of surface density of amines on the sorbent capacity is plotted in Fig. 6a. It is seen that the sorbent capacity increased linearly with increasing surface density of amine in the range of 5–13 N-atom/nm². This may reveal that higher surface density of amine groups is beneficial for enhancing the CO₂ adsorption performance. This result is similar with a recent work of Liu et al. [42], who conducted the CO₂ adsorption over amine-impregnated mesoporous silica materials and found that the CO₂ adsorption is in proportion to the surface density of amine groups in the range of 4–23 N-atom/nm². However, it is noted from both Fig. 6a and Table 2 that as N surface density increases from 5.59 N-atom/nm² to 7.97 N-atom/nm², the CO₂ capacity was almost unchanged. While as further increasing the surface density of amine groups to 28.9 N-atom/nm² (TEPA-MS-700(25) sorbent), a drastic decline in the CO₂ adsorption capacity was observed (124 mg/g-adsorbent). The above observations may reveal that the N surface density is not the only parameter affecting CO₂ adsorption performance in these aminated sorbents. The pore texture of the mesoporous silica support may significantly influence the dispersion and accessibility of the impregnated amines, and thus affect the CO₂ uptake.

In addition to amine surface density, structural properties of silica support such as pore size and pore volume might also be influencing factors on CO₂ adsorption. Zelený et al. [43] and Son et al. [44] found that the enlargement of pore diameter of the silica support would enhance the CO₂ adsorption performance. They concluded that the amine was introduced into the pore channels more easily as the pore diameter of the mesoporous silica support increases. As seen from Fig. 6b, the sorbent performance increased linearly with increasing pore size in the range of 3.0–14.4 nm. However, the adsorption capacity decreased drastically for the largest pore size of 25.8 nm (TEPA-MS-700(25) sorbent). The results shown in Fig. 6a and b may suggest that although higher amine surface density and larger pore size of the silica support could enhance the CO₂ adsorption, their positive influence is limited to a certain degree.
The sorbent capacity, on the other hand, correlated well to the total pore volume of the parent silica support as observed in Fig. 7a. A high correlation coefficient of $R^2 = 0.97$ is observed between the total pore volume of the parent silica supports and the CO$_2$ capacity (Fig. 7a). This is in line with the work by Yan et al. [45], who reported that the total pore volume of the parent mesoporous SBA-15 support played a predominated role in CO$_2$ adsorption rather than pore diameter. Yan et al. [45] conducted CO$_2$ adsorption tests over SBA-15 based materials of similar pore properties. Furthermore, the total pore volume of sorbents after impregnated with 50 wt.% TEPA was also measured to study on their correlation with the CO$_2$ sorbent capacity and the result is shown in Fig. 7b. It is interesting to see that a high correlation ($R^2 = 0.95$) still appeared between the CO$_2$ capacity and total pore volume of aminated sorbents. This clearly indicates that the more residual space left inside the pores of the silica support after loading with the same amount of amine, the more efficient contact between the CO$_2$ molecules and the impregnated amines. This prevents the blockage of pores from effective adsorption and thus favors higher sorbent capacity and amine utilization.

To further determine the optimal amine loading on the silica support for CO$_2$ adsorption and the relationship between the CO$_2$ capacity and amine loadings, MS-400(25) support impregnated with various TEPA contents was used for CO$_2$ adsorption. Fig. 8 shows the saturated adsorption capacities and total pore volume as a function of TEPA loaded content for the MS–400(25) sorbents, and their structural properties are summarized in Table 3. It is seen from Table 3 that both the surface area and total pore volume decrease significantly with increasing TEPA loading amount in the range of 20–70 wt.%. And a linear increase in adsorption capacity with increasing TEPA loading in the range of 20–60 wt.% is observed. The highest capacity for the MS-400(25) sample was 173 mg/g-adsorbent at 60 wt.% TEPA as observed in Fig. 8. However, a further increase in the TEPA content to 70 wt.% leads to a decrease in the adsorption capacity of MS-400(25) sorbent. The density of TEPA is 0.99 cm$^3$/g and the total pore volume of MS-400(25) is 1.92 cm$^3$/g. Thus the maximum theoretical TEPA amounts loaded inside the pore channels is calculated to be 66%. When the TEPA content is beyond 65 wt.%, the pores of MS-400(25) were nearly filled. Therefore, this may easily result in the blockage of effective adsorption sites within the pores, leading to the decrease in adsorption capacity. It is also noteworthy from Table 3 that the total pore volume of 65 wt.% TEPA-impregnated MS-400(25) is 0.15 cm$^3$/g, which is similar to those of MS-400(105), MCM-41(NaSi) and SBA-15(NaSi) sorbents at 50 wt.% TEPA (Table 2), but it has a much higher CO$_2$ uptakes than these three sorbents. This clearly implies that larger pore volume is beneficial for accommodating and dispersing more TEPA molecules inside the pore channels without pore blockage. Taking into account the above structure-sorbent capacity relationship, it may conclude that the mesoporous silica support with high specific surface area and uniform mesostructures are not key parameters affecting the CO$_2$ sorbent performance. The amine surface density, pore diameter and total pore volume of the support seem to largely

![Fig. 7. Relationship between the total pore volume of mesoporous silicas and their CO$_2$ uptakes as expressed based on (a) the pore volume of parent mesoporous supports; and (b) the remaining pore volume of TEPA-impregnated mesoporous adsorbents. Sorbents: 50 wt.% TEPA-impregnated silicas; adsorption temperature: 75 °C; CO$_2$ inlet concentration: 10%.](image)

![Fig. 8. Effect of amine loading on sorbent capacity of TEPA-MS-400(25). Adsorption temperature: 75 °C; CO$_2$ test concentration: 10%.](image)

<table>
<thead>
<tr>
<th>Sample name</th>
<th>TEPA loading (wt.%)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_p$ (cm$^3$/g)</th>
<th>N loading (mmol/g)</th>
</tr>
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<tbody>
<tr>
<td>20</td>
<td>217</td>
<td>1.2</td>
<td>5.45</td>
<td></td>
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<tr>
<td>33</td>
<td>190</td>
<td>0.96</td>
<td>6.96</td>
<td></td>
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<tr>
<td>TEPA-MS-400(25)</td>
<td>50</td>
<td>33</td>
<td>0.30</td>
<td>9.85</td>
</tr>
<tr>
<td>60</td>
<td>22</td>
<td>0.22</td>
<td>13.92</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>15</td>
<td>0.15</td>
<td>15.14</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>9</td>
<td>0.09</td>
<td>16.72</td>
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</table>
influence the adsorption capacity, and among which the total pore volume of the mesoporous silica support appears to play a dominant role in determining the CO₂ adsorption performance.

The capture of CO₂ has been studied over various sorbents during past years. Table 4 summarizes the comparison of TEPA-related sorbents for CO₂ capture. All supports listed in Table 4 were obtained from published experimental results. Among them the TEPA-impregnated MCFs exhibited the highest CO₂ adsorption capacity of 191 mg/g, which can be considered as a high efficient adsorbent for CO₂ capture. However, both of the cost and environmental hazard for the production of MCFs materials are high because it requires the use of pure silica chemicals and pore expander as well. On the other hand, the TEPA-impregnated MS-400(25), which CO₂ adsorption capacity (173 mg/g adsorbent) was only second to and slightly less than that of TEPA-MCFs. The MS-400(25) material can be facilely prepared using rice husk wastes as silica precursor through a simple temperature-controlled method. The MS-400(25) with large pore size and large pore volume was obtained under mild conditions without the use of expensive pore expanders and/or post-pore-expansion treatments, which can reduce the cost and significantly simplify the scale-up synthesis.

4. Conclusions
A simple method for preparing silica support materials with large pore size and large pore volume has been demonstrated in this study using rice husk waste as the silica source. By altering the fusion and hydrothermal temperatures, the silica materials with adjustable mesoporosities can be easily obtained. The nitrogen physisorption measurements, SEM and TEM results suggested that the obtained MS-400(25) exhibits pore volume (1.92 cm³/g) larger than that of the MCM-41 material, and bimodal mesopores (2.7 and 14.4 nm) which make it a desirable support material of amine immobilization for CO₂ capture. The TEPA-impregnated MS-400(25) adsorbent appeared to be more efficient and lower cost than other supports reported in the literature, it achieved a good CO₂ adsorption capacity of 173 mg/g adsorbent under 10% CO₂ at 75 °C. The above results might suggest that MS-400(25) could be considered as a potential support of adsorbent in terms of CO₂ adsorption, which performs several advantages of simple and cost-effective synthesis as well as superior adsorption performance.

Acknowledgment
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Table 4
Comparison of TEPA-related sorbents for CO₂ capture.

<table>
<thead>
<tr>
<th>Support</th>
<th>Precursors</th>
<th>Test conditions</th>
<th>TEPA amount (wt.%)</th>
<th>Capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared MSU-1</td>
<td>Sodium silicate + alcohol polyoxyethylene ether</td>
<td>10% CO₂, 75 °C</td>
<td>50</td>
<td>172</td>
<td>[14]</td>
</tr>
<tr>
<td>KIT-6</td>
<td>TEOS + P123</td>
<td>10% CO₂, 75 °C</td>
<td>50</td>
<td>128</td>
<td>[46]</td>
</tr>
<tr>
<td>SBA-15</td>
<td>TEOS + P123</td>
<td>10% CO₂, 75 °C</td>
<td>60</td>
<td>153</td>
<td>[47]</td>
</tr>
<tr>
<td>Silica aerogels</td>
<td>TEOS + P123</td>
<td>10% CO₂, 75 °C</td>
<td>80</td>
<td>154</td>
<td>[48]</td>
</tr>
<tr>
<td>MCFs</td>
<td>TEOS + P123 + TMB + NH₄F</td>
<td>10% CO₂, 75 °C</td>
<td>70</td>
<td>191</td>
<td>[38]</td>
</tr>
<tr>
<td>MS-400(25)</td>
<td>Waste derived silica [RHA] + CTAB</td>
<td>10% CO₂, 75 °C</td>
<td>60</td>
<td>173</td>
<td>This study</td>
</tr>
</tbody>
</table>

References


