

## Synthesis of mesoporous silica from bottom ash and its application for CO<sub>2</sub> sorption

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**Abstract**—A supernatant solution of silicate species extracted from bottom ash in a power plant was used to prepare a mesoporous silica by the synthesis protocol of SBA-15. XRD, N<sub>2</sub> adsorption-desorption, and TEM confirmed a disordered mesopore structure. The pore volume and average pore size of the product were significantly larger than SBA-15 prepared using pure chemicals, and complementary textural mesoporosity was detected. When the mesoporous silica was tested for carbon dioxide sorption after polyethyleneimine (PEI) impregnation, substantially higher CO<sub>2</sub> sorption capacity (169 mg CO<sub>2</sub>/g-sorbent) was achieved than that of PEI-impregnated pure SBA-15 under the same test conditions. High CO<sub>2</sub> sorption capacity was maintained when the gas composition was changed to 15% CO<sub>2</sub>, and the hybrid material exhibited satisfactory performances during the 10 recycle runs.

Key words: Bottom Ash, Mesoporous Silica, SBA-15, Polyethyleneimine, Carbon Dioxide Capture

### INTRODUCTION

Coal combustion in power plants throughout the world produces large amounts of fly ash and bottom ash. Since improper disposal of these waste products is a serious burden to the environment and hence is a worldwide concern [1], conversion of them into useful products has been pursued [2-4]. In this regard, it would be beneficial if power plant waste products could be recycled as a sorbent for CO<sub>2</sub> generated on the same site. Capture and sequestration of CO<sub>2</sub> from power plant flue gases is being considered to be the most effective way to reduce the global warming by CO<sub>2</sub> emissions [5].

Large-scale separation of CO<sub>2</sub> via liquid phase amine-based absorption is currently in commercial operation among the various physico-chemical methods available for separation of CO<sub>2</sub> from gas mixtures [6]. During the chemical absorption of CO<sub>2</sub>, two molecules of amine species in various capturing agents react with one molecule of CO<sub>2</sub> to form a carbamate species ( $2R-NH_2 + CO_2 \rightarrow R-NH_3^+ + R-NHCOO^-$ ). However, a large amount of energy required for sorbent regeneration, equipment corrosion, and solvent degradation in the presence of oxygen remain as serious drawbacks [7]. Several research groups, as an alternative, recently reported promising performances of mesoporous silica materials impregnated with an amine-type CO<sub>2</sub> capturing agent for CO<sub>2</sub> removal [8-13]. Dispersion, immobilization, and confinement of the amine functional groups inside the mesoporous silica support produced a stable, mass transfer efficient, less toxic and less corrosive material than liquid amines.

In such applications, synthesis of mesoporous silica support materials using expensive TEOS as a silica source is not desirable. Accordingly, preparation of porous silica materials from coal fly ash has been proposed as a practical option [14-17]. Extra silica input is usually necessary during the synthesis steps in order to improve

the structural quality of the mesoporous silica product obtained. For amine-impregnated silica sorbent systems, however, we have shown recently that the pore volume and pore size of the support material are the governing factors to obtain a good CO<sub>2</sub> sorption performance, not high structural order. High pore volume can accommodate a greater amount of amine species in the pores, and a large pore size is desirable for enhanced diffusion of CO<sub>2</sub> in the channels [18].

In this work, we prepared a mesoporous silica from low grade bottom ashes under acidic condition following the synthesis procedure of SBA-15, but without adding any extra silica source. The mesoporous material after characterization of its textural properties was then tested as a sorbent for CO<sub>2</sub> after impregnation with PEI (polyethylenimine). An SBA-15 sample synthesized using pure chemical was also tested as a support material for PEI for comparison.

### EXPERIMENTAL

#### 1. Mesoporous Silica Synthesis from Bottom Ash

Silicate extraction was performed based on the procedure reported by Kumar et al. [15]. Bottom ash was mixed with NaOH powder at a 1 : 1.2 weight ratio. It was then fused at 550 °C for 1 h. The fused mixture was cooled to room temperature, ground to fine powder, and finally mixed with water at a weight ratio of 1 : 4. The extracted supernatant solution was used for the synthesis of mesoporous silica of SBA-15 type. For this purpose, 3.6 g of Pluronic P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, BASF) was dissolved in 150 g of 2 M HCl and stirred for 4 h. Thereafter, 100 mL of bottom ash supernatant was added and stirred for 1 h. To this reaction mixture, 25 g of 35 wt% HCl and 50 mL of distilled water were quickly added, and this was stirred for 24 h at room temperature. The resulting gel was aged at 100 °C for 72 h. The solid product was then filtered, washed, dried at 100 °C, and calcined in air at 550 °C for 24 h.

For pure SBA-15, 10 g of P123 was added to 380 ml of 1.6 M HCl (37%, Aldrich). After stirring for 1 h, 21.3 g of TEOS (98%, Aldrich) was added to the solution with vigorous stirring for 10 min.

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The resultant mixture was aged for 24 h at 35 °C and subsequently heated for 24 h at 100 °C. The solid product obtained was filtered and washed with ethanol. The product was dried overnight at 100 °C and calcined at 550 °C for 4 h [19].

## 2. Preparation of the PEI-loaded Mesoporous Silica

Polyethyleneimine (PEI) was introduced into mesoporous silica samples by wet impregnation as reported earlier [9]. In a typical preparation, PEI (Aldrich, average molecular weight of 600 by GPC, linear type, b.p of 250 °C) was dissolved in methanol with stirring for about 15 min, after which calcined mesoporous silica powder

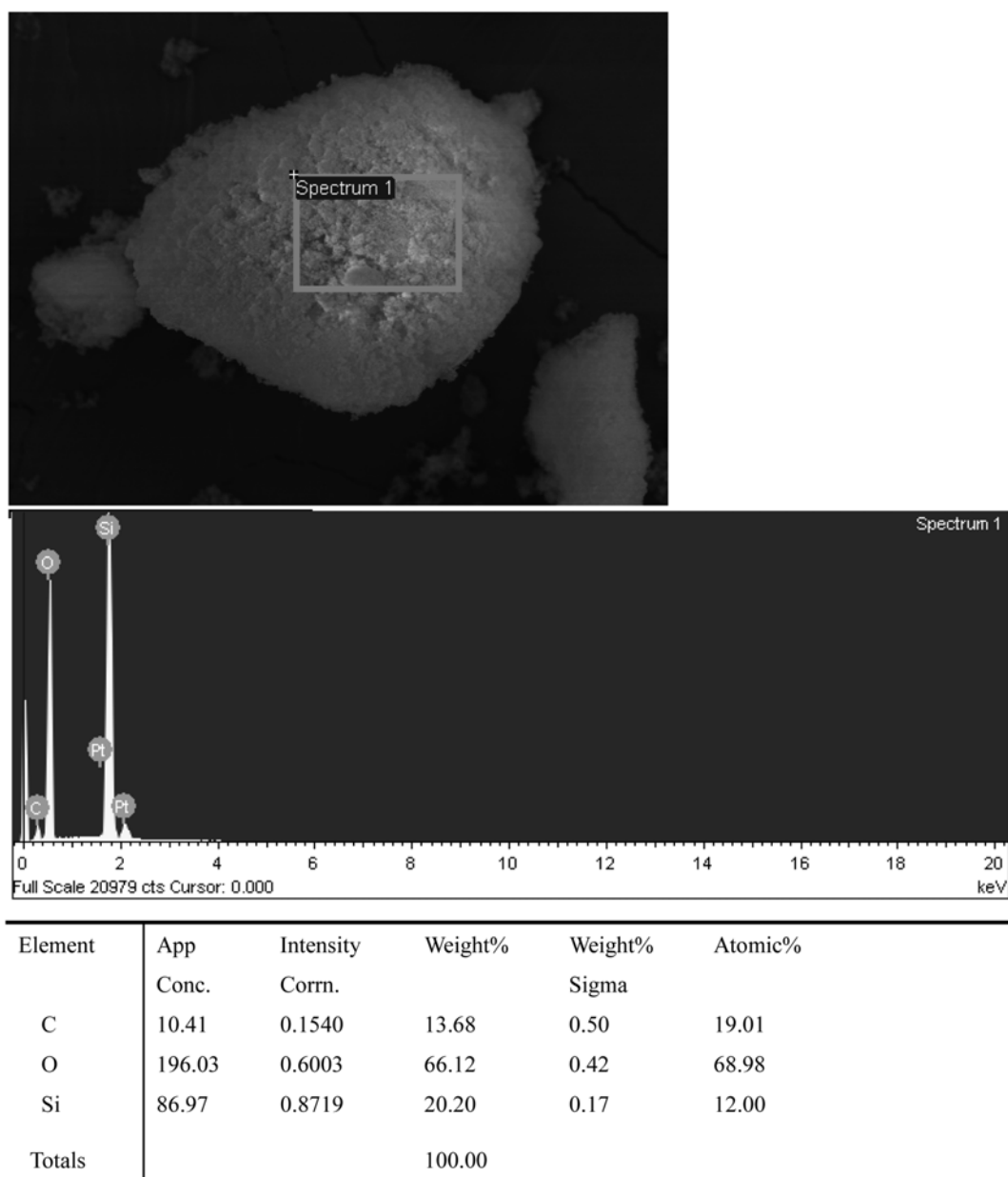
was added to the PEI/methanol solution in a glove box. The resultant slurry was continuously stirred for about 30 min and then was dried at 70 °C for 16 h under reduced pressure (700 mm Hg).

## 3. Characterization

The chemical composition of bottom ash was analyzed by X-ray fluorescence (XRF) (Phillips, Axios). The X-ray diffraction patterns of the mesoporous silica products were recorded on a Rigaku diffractometer using CuK $\alpha$  ( $\lambda=1.54$  Å) radiation. N<sub>2</sub> sorption isotherms were measured at liquid nitrogen temperature (Micromeritics ASAP-2000). The specific surface areas of these samples were calculated

**Table 1. Chemical composition of bottom ash (wt%)**

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	MnO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	SO <sub>3</sub>	SrO	ZrO <sub>2</sub>	BaO
47.7	18.9	17.4	1.32	0.145	7.33	0.648	1.27	2.43	1.04	4.02	0.144	0.212



**Fig. 1. EDXS of the mesoporous silica synthesized from the bottom ash extract.**

by the BET method, and pore diameter distributions were estimated from the desorption branch of the isotherms based on the BJH (Barratt-Joyner-Halenda) model. Energy dispersive X-ray spectroscopy (EDXS) was performed using a Hitachi S-4300 electron microscope for measuring the chemical composition. Transmission electron microscopy (TEM) measurement was taken on a JEOL JEM-2100F field emission electron microscope with an acceleration voltage of 200 kV. The amounts of PEI introduced to the mesoporous silica samples were measured by a thermogravimetric analysis (TGA, SCINCO thermal gravimeter S-1000) by heating the PEI loaded samples to 600 °C under air flow (50 mL/min).

#### 4. CO<sub>2</sub> Sorption-desorption Measurement

A sample weight of ca. 10 mg was loaded into an alumina sample pan in a TG unit (SCINCO thermal gravimeter S-1000) and tested for CO<sub>2</sub> sorption-desorption performances. The initial activation of the samples was carried out at 100 °C for 1 h in nitrogen environment (ultra high purity, U-Sung). The sorption run was carried out using both high purity (99.999%) and 15% CO<sub>2</sub> (N<sub>2</sub> as balance) gas, while the desorption run was conducted in N<sub>2</sub> flow. The feed flow rate was controlled to 30 mL/min by a mass flow controller (MFC) to the sample chamber. The sorption and desorption were both conducted at 75 °C under atmospheric condition for the PEI-loaded mesoporous silica samples.

## RESULTS AND DISCUSSION

The chemical composition of bottom ash was analyzed by XRF, and its composition in oxide form is summarized in Table 1; SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> are the most abundant species. Composition of the mesoporous silica synthesized from the bottom ash supernatant solution was then analyzed by EDXS, and the result shows that Si is the only chemical species incorporated (Fig. 1). Because of the strongly acidic synthesis conditions employed for SBA-15, other extracted metal species were kept in a dissolved state in the supernatant and were not incorporated to the solid product.

Fig. 2(a) shows the powder XRD pattern of the mesoporous silica sample prepared using bottom ash, and the XRD pattern of SBA-15 synthesized using pure chemicals is shown Fig. 2(b). The single

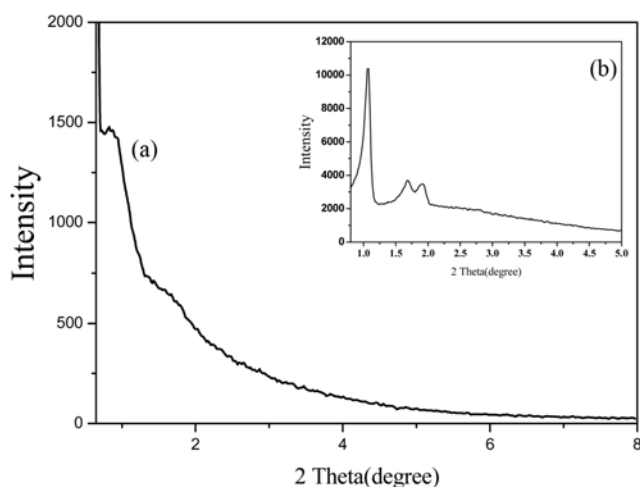


Fig. 2. XRD pattern of mesoporous silica prepared using (a) bottom ash and (b) pure chemicals.

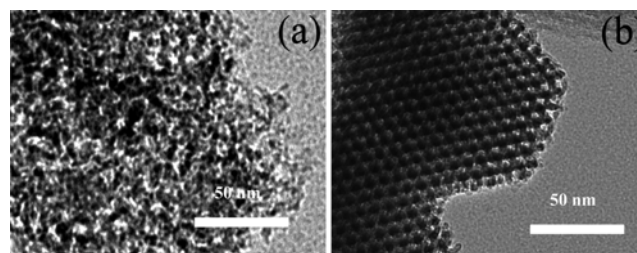


Fig. 3. TEM picture of mesoporous silica prepared using (a) bottom ash and (b) pure chemicals.

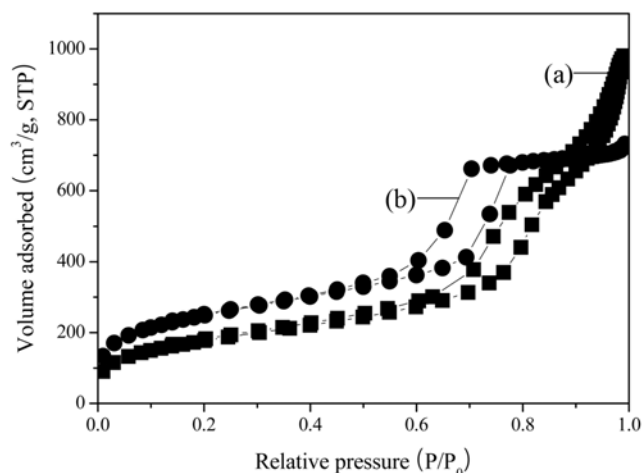


Fig. 4. N<sub>2</sub> adsorption-desorption isotherms of mesoporous silica prepared using (a) bottom ash and (b) pure chemicals.

Table 2. Textural parameters of mesoporous silica samples obtained

Samples	$S_{BET}$ (m <sup>2</sup> /g)	$V_p$ (cm <sup>3</sup> /g)	$D_p$ (nm)
Mesoporous silica from bottom ash	645	1.47	10.1
SBA-15 from pure chemicals	895	1.00	5.6

peak with smaller intensity accompanied by line broadening and the absence of the long range 2nd and 3rd peaks in Fig. 2(a) indicate the inferior structural order in the SBA-15 sample prepared using bottom ash. Transmission electron microscopy in Fig. 3(a) confirmed the disordered structure of the material, while well ordered SBA-15 having hexagonal pores was produced by pure chemicals as shown in Fig. 3(b).

Fig. 4 shows the nitrogen adsorption-desorption isotherms of the silica samples prepared, and the corresponding textural parameters are listed in Table 2. Both samples exhibited typical type IV isotherms with pronounced capillary condensation due to framework-confined mesopores (structural mesopores) near  $P/P_0=0.6-0.8$ . At  $P/P_0=0.9$ , however, another pronounced condensation step appears for the mesoporous silica prepared by bottom ash (isotherm a), which is ascribed to the interparticle voids between the primary particles (textural mesoporosity) [20]. These textural mesopores are important because they can facilitate efficient transport of CO<sub>2</sub> to its capturing sites located inside the structural mesopores [21]. On the other hand, no such

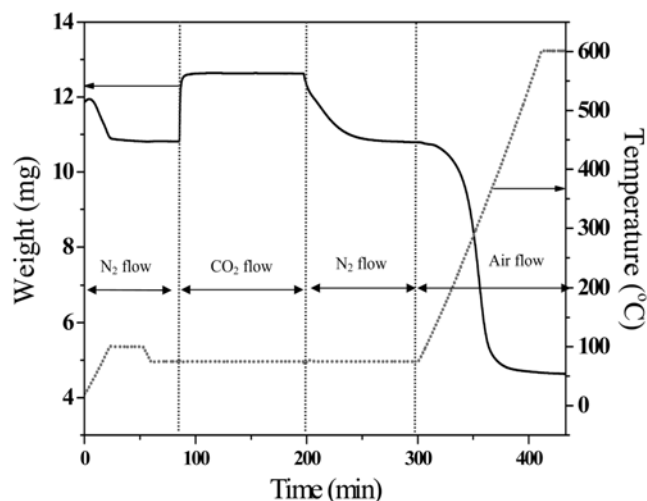


Fig. 5. Temperature steps programmed in TGA for CO<sub>2</sub> sorption/desorption runs.

textural mesoporosity was detected for the SBA-15 prepared by pure chemicals. According to Table 2, the sample pore volume measured by N<sub>2</sub> sorption is ca. 40% larger than SBA-15 prepared using pure chemicals (1.47 vs 1.0 cm<sup>3</sup>/g), and so was the average pore size (10.1 vs 5.6 nm). Substantially larger pore volume, larger pore size, and the presence of textural mesoporosity all make the SBA-15 prepared using bottom ash a desirable support material for amine impregnation.

As shown in Fig. 5, initially we pretreated the sorbent sample at 100 °C to remove moisture. N<sub>2</sub> was used as a purge gas. When no weight change was detected, the temperature was decreased to the sorption temperature (75 °C) and CO<sub>2</sub> was introduced into the chamber. After the CO<sub>2</sub> sorption run was completed, a desorption step followed using N<sub>2</sub> as a purge gas at the same temperature. Finally, temperature was increased to 600 °C to decompose amines inside the pores, and the amount of PEI introduced was measured. CO<sub>2</sub> sorption runs were conducted at 75 °C using high purity CO<sub>2</sub>, the selection of which is based upon previously reported optimization studies [9,12]. It is worth mentioning that this PEI-impregnated sorption system is different from those of amine-grafted mesoporous silica adsorption systems, which exhibited maximal CO<sub>2</sub> adsorption capacity at lower temperature (e.g., 25 °C). According to an earlier report by Xu et al. [9], as the temperature increases, the polymer PEI becomes more flexible and more CO<sub>2</sub>-affinity sites are exposed to CO<sub>2</sub> and thus CO<sub>2</sub> sorption capacity increases. Once efficient contact between CO<sub>2</sub> and sorption sites is established, the sorption process will be dictated by thermodynamics; too high a temperature will shift the equilibrium to the reverse direction and desorption will be favored.

Fig. 6 shows the loading effect of PEI on the CO<sub>2</sub> sorption performance. CO<sub>2</sub> sorption capacity increased with increases in amine loading amount, and 169 mg CO<sub>2</sub>/g sorbent was measured by 60 wt% PEI impregnated sample. This is a very high CO<sub>2</sub> sorption capacity compared to the amine-grafted system [22] and other amine impregnated systems reported earlier [8-13]. Sorption capacity decreased at higher PEI loadings, indicating that too much PEI introduced resulted in bad dispersion of PEI and lower sorption efficiency [9].

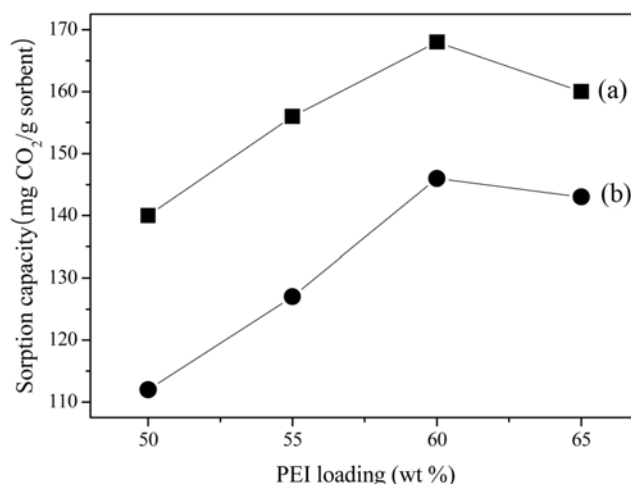


Fig. 6. CO<sub>2</sub> sorption performance of PEI impregnated mesoporous silica prepared by bottom ash: (a) high purity CO<sub>2</sub> and (b) 15% CO<sub>2</sub>.

To make a comparison, we introduced PEI on SBA-15 prepared using pure chemicals and tested it for CO<sub>2</sub> sorption as well. The highest sorption capacity was achieved at 50 wt% PEI loading (130 mg CO<sub>2</sub>/g sorbent). As before, CO<sub>2</sub> sorption capacity decreased when we increased the PEI loading beyond 50 wt%. Although the structural order of mesoporous silica prepared using bottom ash was inferior to that of SBA-15 synthesized by pure chemicals, its larger pore volume could accommodate larger amount of PEI within the pores; and textural mesopores facilitated mass transport of CO<sub>2</sub> into the framework mesopores [21], which brought it the better performance than that of PEI/SBA-15 prepared using pure chemicals.

For practical implementation, a sorbent should display good sorption capacity under a more realistic CO<sub>2</sub> concentration in a power plant. Hence, we also measured CO<sub>2</sub> sorption capacities of the sorbents using 15% CO<sub>2</sub> (balance N<sub>2</sub>). As shown in Fig. 6, for 60 wt% PEI impregnated mesoporous silica prepared using bottom ash, we obtained the highest sorption capacity (146 mg CO<sub>2</sub>/g sorbent) at

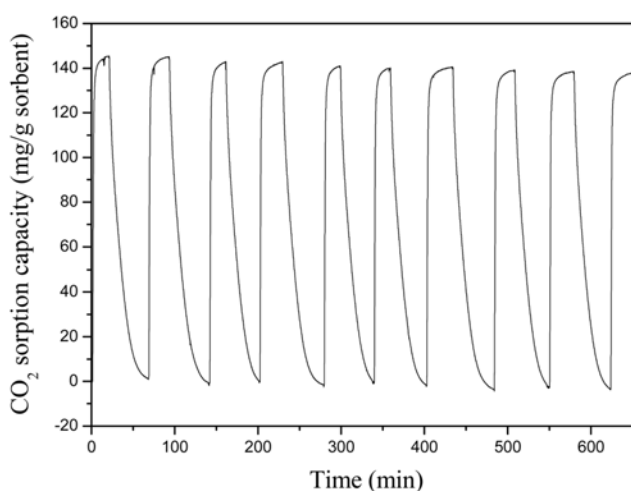


Fig. 7. Recycling performance of 60 wt% PEI-impregnated mesoporous silica prepared using bottom ash at 75 °C over 15% CO<sub>2</sub>.

75 °C, which is only slightly lower than that of the same sample when high purity CO<sub>2</sub> was used. This clearly demonstrates the advantage of chemisorptions. CO<sub>2</sub> sorption capacity decreases drastically by reduction in CO<sub>2</sub> partial pressure for the case of CO<sub>2</sub> removal induced by physisorption.

The stability of the sorbent is another important parameter to be considered. Thus, the performance of the 60 wt% PEI-impregnated sample in 10 consecutive sorption-desorption runs was tested for stability at 75 °C using 15% CO<sub>2</sub>. As shown in Fig. 7, its sorption capacity after the 10th cycle was ca. 139 mg/g, which has less than 5% decrease in CO<sub>2</sub> capturing capacity in 10 recycling runs (146 mg/g in the 1<sup>st</sup> run).

## CONCLUSIONS

A supernatant solution of silicate species extracted from bottom ash in a power plant was used to prepare a mesoporous silica following the synthesis procedure of SBA-15 without adding an extra silica source. The pore volume and pore size were found to be significantly higher than those of SBA-15 prepared by pure chemicals. At the same time, complementary textural mesoporosity in the resulting material was evidenced by the N<sub>2</sub>-sorption-desorption isotherm. The PEI-impregnated sample shows substantially higher CO<sub>2</sub> capacity than that achieved by PEI/SBA-15 made by pure chemicals. The CO<sub>2</sub> sorption capacity was closely maintained when the gas composition was changed to 15% CO<sub>2</sub> at 75 °C, and also performed well in the cyclic sorption-desorption performance during prolonged operation. These findings demonstrated the feasibility of recycling the industrial waste in a power plant into an excellent sorbent support material for CO<sub>2</sub>.

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