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## ORIGINAL ARTICLE

# One pot synthesized Li, Zr doped porous silica nanoparticle for low temperature CO<sub>2</sub> adsorption

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## KEYWORDS

Li;  
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**Abstract** Li, Zr doped porous silica was synthesized in one pot and investigated for low temperature CO<sub>2</sub> adsorption. The synthesized nanoparticle was characterized by X-ray diffraction (XRD), N<sub>2</sub> adsorption–desorption measurement, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The specific surface area, average pore diameter and pore volume were determined to be 962 m<sup>2</sup>/g, 2.3 nm and 0.56 cm<sup>3</sup>/g respectively. ICP-AES analysis revealed a metal content of 4 wt.% (Zr) and 3.42 wt.% (Li). Their CO<sub>2</sub> adsorption capacity was tested at room temperature and atmospheric pressure. An uptake of about 5 wt.% was observed and regenerable at a low temperature of 200 °C. This adsorption and desorption temperature of the sorbent is lower than the reported lithium silicate. The CO<sub>2</sub> adsorption–desorption cyclic performance studies illustrated that Li, Zr doped porous silica is a recyclable, selective and potential sorbent for CO<sub>2</sub> adsorption.

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## 1. Introduction

Carbon dioxide, a fatal green house gas and its accumulation into the atmosphere leads to climatic change followed by the destruction of the Earth's ecological system. For the global energy requirement, we solely depend on fossil fuel, which emits a large amount of CO<sub>2</sub> into air. Hence, it is a vital task to the scientific community to mitigate the emission of CO<sub>2</sub> before it reaches high concentration. The permanent sequestration of

CO<sub>2</sub> in deep sea and coal field may be effective. But they also have some serious adverse effects like cracking of the Earth's crust (Zoback and Gorelick, 2012) due to continuous gas permeation and decrease in pH in deep sea (Seibel and Walsh, 2001; Shirayama, 1998; Thistle et al., 2005; Zondervan et al., 2001) which ultimately leads to the destruction of the eco-system of sea. Recent studies on adsorption of CO<sub>2</sub> from atmosphere by the use of solid sorbents and biological system are of great interest.

Invention of MCM-41 by Mobil corporation scientist gave the breakthrough in new molecular sieve development (Beck et al., 1992; Monnier et al., 1993). These mesoporous molecular sieves have made a greater attraction in the fields like sorption science, catalysis (Sayari, 1996) and also as carrier for drugs and protein. By the incorporation of proper choice of metals, the mesoporous silica becomes a significant material for CO<sub>2</sub> adsorption from flue gas or from environment. In this

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regard metals like Mg, Ca, Fe, La, Ti etc., have been effectively incorporated into meso and microporous materials and studied for their efficiency for CO<sub>2</sub> adsorption (Barton et al., 1999; Ciesla and Schüth, 1999; Corma, 1997; Kosslick et al., 1998; Landmesser et al., 1998; On et al., 2003; Sayari, 1996; Tuel, 1999). High surface area and pore volume of mesoporous materials facilitate high loading of metal oxides on them than microporous materials. In this context, alkaline earth metal oxides, MgO and CaO were impregnated over mesoporous silica molecular sieves and studied for their CO<sub>2</sub> sorption capability (Chen and Ahn, 2011; Huang et al., 2010; Zhao et al., 2012).

Zirconium is one of the metals of choice for carrying out numerous organic and inorganic reactions (Bianchi et al., 2001; Carrión et al., 2005; Gontier and Tuel, 1996; Infantes-Molina et al., 2004; Piwonski et al., 1998; Rodríguez-Castellón et al., 2003, 2004; Wang et al., 2001; Wei et al., 2004). Nakagawa and Ohashi (1998, 1999) developed a promising inorganic lithium zirconate composite for CO<sub>2</sub> sorption based on non catalytic gas–solid adsorption and reported a capturing capability of about 4.5 mol/kg at high temperature (400–700 °C) with considerably large CO<sub>2</sub>/N<sub>2</sub> selectivity. Ida and Lin (2003) explained the mechanism of high temperature CO<sub>2</sub> adsorption over lithium zirconate. The kinetics of adsorption was drastically improved when it is used in nano crystalline form (Ochoa-Fernández et al., 2006). Till today, lithium zirconate is found to be a better choice of sorbent for CO<sub>2</sub> in flue gas from coal combustion plant, but it requires high adsorption temperature of >400 °C and still higher desorption temperature. Use of nano crystalline lithium silicate (Khomane et al., 2006) and sol–gel derived lithium zirconate (Ochoa-Fernández et al., 2006) greatly reduced the energy required for adsorption. Smaller particle size compared to natural lithium zirconate is the reason for such an effect. In this regard, an attempt was made to synthesize lithium, zirconium doped porous silica in one pot and study its CO<sub>2</sub> adsorption at low temperature.

## 2. Experimental

### 2.1. Materials

Cetyl trimethyl ammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), zirconium n-propoxide (70% in n-propanol), and lithium isopropoxide were received from Sigma Aldrich, Korea. Isopropyl alcohol, and sulfuric acid used were obtained from Daejung chemicals and metals, Korea. All the chemicals were used as received.

### 2.2. Synthesis of Li, Zr doped porous silica

In a typical synthesis, 4 g of CTAB was dissolved in 100 ml isopropyl alcohol to obtain a clear solution (the solution was heated if needed). Then 4.45 g of zirconium n-propoxide (70% in n-propanol) and 0.65 g of lithium isopropoxide were added followed by the addition of 16.6 g of TEOS to get clear sol. To the above sol about 5 ml of 2 M sulfuric acid was added with vigorous stirring. The obtained transparent jelly like product was aged at 100 °C for 12 h. The solid product was then filtered and washed with copious amount of DI water and dried at 100 °C and finally calcined in air at 550 °C for 6 h at a heating rate of 1 °C/min.

### 2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku Miniflex diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm). The diffraction data were recorded in the 2 $\theta$  range of 5–80° at 1° step size and 1 s step time. The nitrogen adsorption–desorption isotherms were measured at –196 °C by using a Belsorp mini II (Japan) volumetric adsorption analyzer. Before each adsorption measurement the samples were evacuated at 200 °C. The specific surface area,  $S_{\text{BET}}$ , was determined from the linear part of the BET equation. The average pore diameter and pore volume were also evaluated. The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) of the synthesized material was executed with a Jobin Yuon, JY-38 VHR spectrometer. The Li, Zr doped porous silica was examined by Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) spectroscopy by scanning 20 times at 4 cm<sup>-1</sup> resolution in the range of 4000–400 cm<sup>-1</sup> on a Nicolet IR 200 spectrometer. The morphologies of the samples were studied by a JEOL JSM 5600 (Japan) scanning electron microscope equipped with an energy dispersive X-ray (EDX) detector after gold sputter coating (Cressington, Sputter Coater-108 auto, Korea).

### 2.4. CO<sub>2</sub> adsorption–desorption study

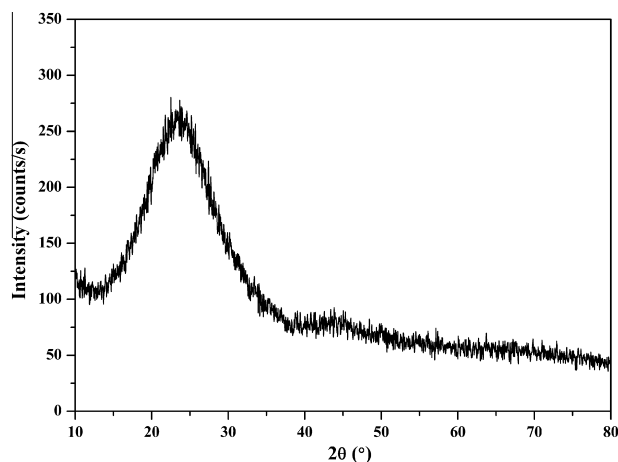
CO<sub>2</sub> adsorption–desorption measurements of the synthesized material were performed on a thermo gravimetric (TG) analyzer (SCINCO N-1000). The adsorption run was carried out using high purity CO<sub>2</sub> (99.9%) gas at 25, 50 and 75 °C under atmospheric pressure while the regeneration was carried out under N<sub>2</sub> flow at 200 °C. A sample weight of ca. 10 mg was loaded into a platinum sample pan in a TG unit and initial activation was carried out at 200 °C for 1 h in nitrogen atmosphere. Continuous CO<sub>2</sub> adsorption–desorption profile was obtained by heating, cooling and changing the gases, CO<sub>2</sub> (99.9%) and N<sub>2</sub> through automatic switching valve assisted with timer. A feed flow rate of 30 ml/min was controlled by a MFC to the sample chamber in TG unit.

## 3. Results and discussion

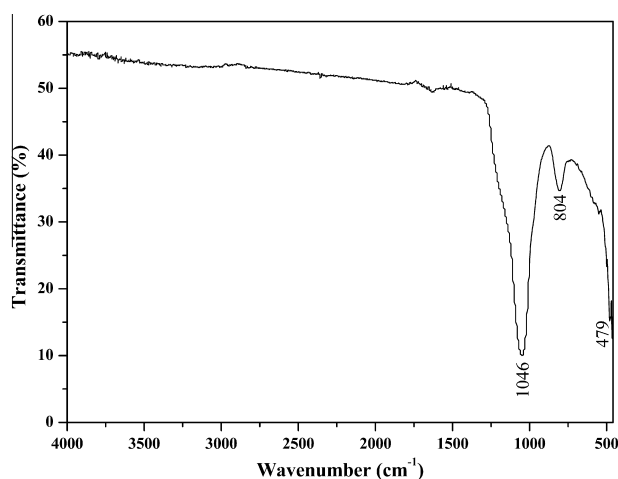
### 3.1. Characterization

The XRD patterns of Li, Zr doped porous silica are presented in Fig. 1. The presence of the tetragonal zirconia phase is evidenced by the peaks at 20, 30, 50° (20) (Arnal et al., 2006; Yamauchi et al., 2007). Due to a high content of amorphous silica compared to Li and Zr, the characteristic peaks pertaining to their respective oxide phases were not clearly resolved in the patterns. Fig. 2 depicts the FTIR spectrum of Li, Zr doped nanoporous silica. The sharp band at 1046 and 804 cm<sup>-1</sup> was assigned to the asymmetric and symmetric vibrations of Si–O–Si. The intense peak at 479 cm<sup>-1</sup> was due to stretching vibrations of Zr–O and Si–O–Si deformation vibrations (Tamas et al., 2005).

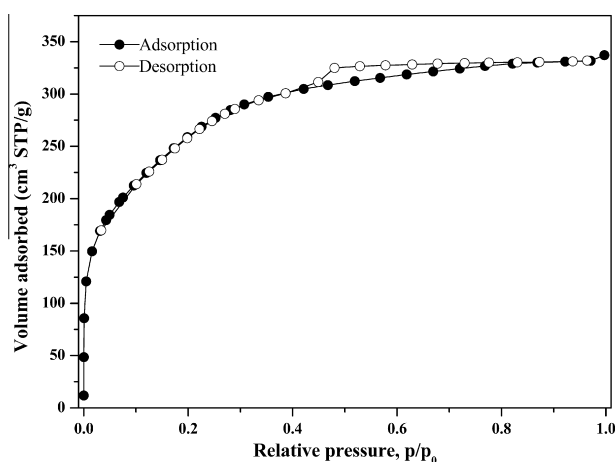
The N<sub>2</sub> adsorption–desorption isotherms of the synthesized Li, Zr doped nanoporous silica are illustrated in Fig. 3. The isotherms are of type-I confirming the characteristics of microporous materials with hysteresis. The presence of hysteresis proves the pores are enlarged to mesopore range. The  $S_{\text{BET}}$ ,



**Figure 1** XRD pattern of Li, Zr doped porous silica.

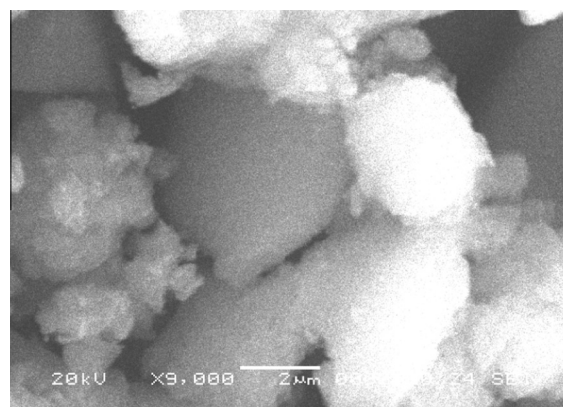


**Figure 2** FTIR spectrum of Li, Zr doped porous silica.



**Figure 3** N<sub>2</sub> adsorption-desorption isotherm of Li, Zr doped porous silica.

average pore diameter and pore volume were found to be 962 m<sup>2</sup>/g, 2.3 nm and 0.56 cm<sup>3</sup>/g respectively. The surface area was very high compared to previously reported nano crystal-



**Figure 4** SEM image of Li, Zr doped porous silica.

line lithium zirconate (Ochoa-Fernández et al., 2006). Even though CTAB was used during the synthesis, micropores were dominating over the mesopores. Similar type of isotherm was evidenced in the synthesized high surface area porous tin doped zirconium oxide (Ma et al., 2005). The SEM image of the nanoparticle is depicted in Fig. 4. The particles were spherical in shape with some deposits over them. The tiny deposits over the surface of the crystals may be due to formation of their respective oxides. The characteristic XRD patterns were not obtained illustrating insufficient dimension to yield peaks. The presence of Zr in the matrix is evidenced from the EDX analysis and was found to be 3.72 wt.% (Fig. 5). Absence of lithium in the EDX spectrum is due to its light mass (Teng et al., 2010). ICP-AES analysis showed presence of about 4 and 3.42 wt.% Zr and Li respectively.

### 3.2. CO<sub>2</sub> adsorption

CO<sub>2</sub> adsorption-desorption profile of porous Li, Zr doped silica nano particle at 25, 50 and 75 °C by TGA is shown in Fig. 6. Initial activation of the material was carried out at 200 °C for 1 h in N<sub>2</sub> atmosphere. A weight loss of about 5.5 wt.% was observed due to removal of water and pre-adsorbed gases. Thereafter when the temperature was reduced to 25 °C and simultaneous switching of gas to CO<sub>2</sub>, an uptake of about 5 wt.% (50 mg/g of sorbent) was noted. The adsorbed CO<sub>2</sub> was completely regenerated when the temperature was increased to 200 °C. This suggested the physical sorption of CO<sub>2</sub> into the micropores of the synthesized material. The temperature of adsorption is much less than that of the already reported nano crystalline lithium silicates (Khomane et al., 2006) and nano lithium zirconate (Ochoa-Fernández et al., 2006). With respect to mechanism of adsorption proposed for lithium zirconate by Ida and Lin (2003), high temperature is required for the melting of lithium over the zirconium particle. Hence the material requires high temperature for adsorption and desorption imposing high energy penalty. But in the present study, due to fine dispersion of lithium and zirconium in nano scale level over porous silica, the material required very less energy for its adsorption and desorption. In addition the porous nature of the silica support increases the surface coverage which in turn increases the contact of CO<sub>2</sub> with the lithium site. At 50 and 75 °C the adsorption capacity decreased due to decrease of adsorbent-adsorbate interactions (site-adsorbate) induced by an increase of the mobility of adsorbate

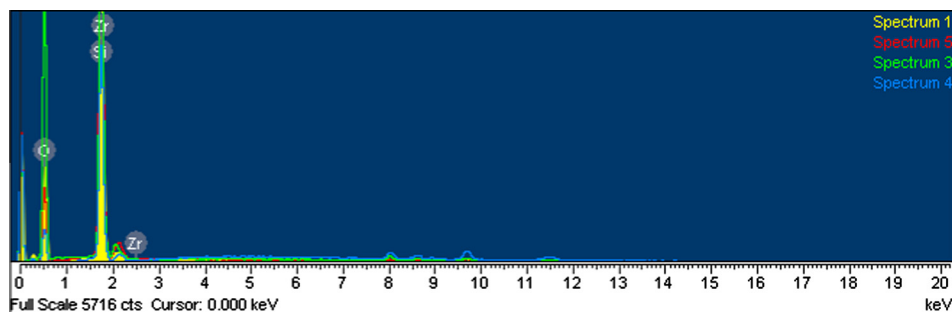


Figure 5 EDX spectrum of Li, Zr doped porous silica.

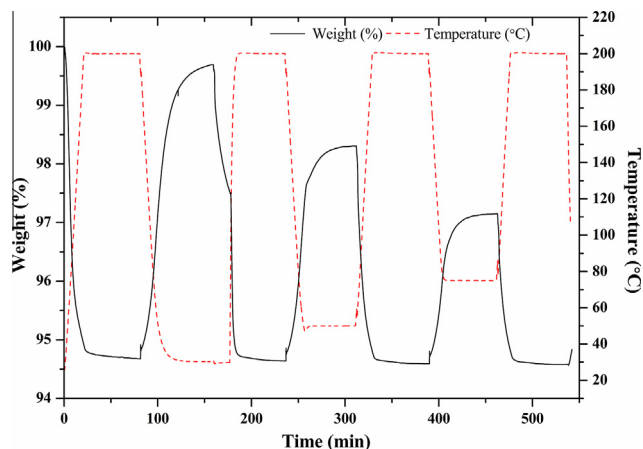


Figure 6 CO<sub>2</sub> adsorption-desorption profiles of Li, Zr doped porous silica at various temperature (25, 50 and 75 °C).

into the sorbent as a result of rise of thermal agitation. Fig. 7 illustrates the cyclical CO<sub>2</sub> sorption of the synthesized material at 25 °C. The material exhibited an uptake of 5 wt.% in the fourth cycle same as that of the first cycle. Hence, the material not only possesses a low temperature capturing capability but also displayed a perfect recycling property. In addition complete regeneration was observed when the temperature was

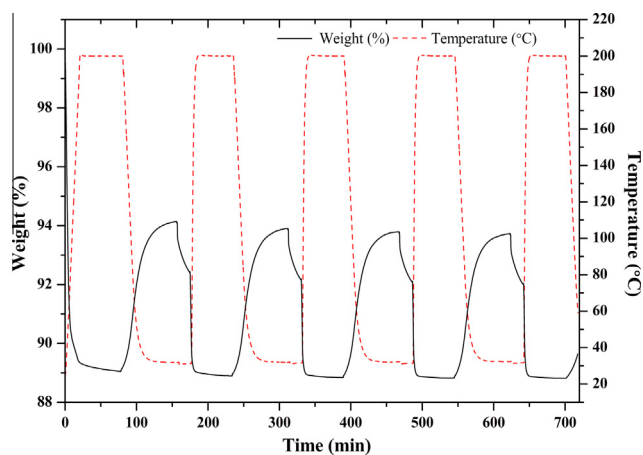


Figure 7 CO<sub>2</sub> adsorption-desorption recycle profile of Li, Zr doped porous silica.

increased from 25 to 200 °C. Hence the synthesized material is also a better choice of sorbent for capturing of CO<sub>2</sub> at low temperature.

#### 4. Conclusions

Li, Zr doped porous silica nanoparticle was synthesized successfully and studied for its CO<sub>2</sub> adsorption. The incorporation of the target metals into the pores of silica is clearly evident from the SEM-EDX analysis. The ICP-AES results confirm the doping of Zr and Li on silica. A CO<sub>2</sub> uptake of about 5 wt.% at a low temperature of 25 °C was noted and also displayed complete desorption and recyclability. Hence, it is concluded that the Li, Zr doped nanoporous silica is one of the better candidates for the adsorption of CO<sub>2</sub>.

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