

# Synthesis of Li-Zr incorporated mesoporous TiO<sub>2</sub> and its application in CO<sub>2</sub> adsorption

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## TiO<sub>2</sub> 담지체에 합성된 Li-Zr 메조포러스 분자체 ; 이산화탄소 흡착 응용

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### Abstract

Li-incorporated mesoporous TiO<sub>2</sub> materials with various pore-sized distributions were synthesized by using triblockcopolymers via a sol-gel process in a aqueous solution. The properties of the materials were characterized by HR-TEM, XRD, and BET analysis. All particles have spherical morphology with a diameter range of 1 - 3  $\mu\text{m}$ . The mesoporous TiO<sub>2</sub> materials calcined at 400 °C and their specific surface area, average pore size and crystallite sizes were 210 m<sup>2</sup>g<sup>-1</sup>, 6.4 nm and 8.8 nm respectively. The Li-incorporated mesoporous TiO<sub>2</sub> were tested for CO<sub>2</sub> adsorption and its adsorption capacity is 90mg/g. The Li-incorporated mesoporous TiO<sub>2</sub> are observed to be thermally stable, recyclable and green or bent for CO<sub>2</sub> capture. The effect of bimetallic ZrLiTiO<sub>2</sub> is also studied for CO<sub>2</sub> adsorption.

Key words: mesoporous TiO<sub>2</sub>, Li-incorporation, CO<sub>2</sub> adsorption, bimetallic, LiZrTiO<sub>2</sub>.

### 1. Introduction

Elevation in greenhouse gas levels result in the anthropogenic warming. Extensive efforts have been devoted in reducing greenhouse gas emissions, especially for CO<sub>2</sub> capture and storage from coal power plant [1,2]. Solid sorbents adsorption is considered as one of the potential options for CO<sub>2</sub> capture process [3]. In recent years, CO<sub>2</sub> capture at high temperatures (450 - 700°C) based on regenerable sorbent materials has received increasing attention as an alternative to low temperature CO<sub>2</sub> capture adsorbents such as zeolite based adsorbents, activated carbon or molecular sieves [4 - 10]. The use of these high temperature sorbents provides both high CO<sub>2</sub> adsorption capacity and CO<sub>2</sub> selectivity at temperatures between 450 and 700

°C. Considering the wide range of materials tested, lithium silicate (Li<sub>2</sub>SiO<sub>4</sub>) has shown the largest CO<sub>2</sub> sorption capacity and the fastest CO<sub>2</sub> sorption rate over a wide range of temperatures and CO<sub>2</sub> concentrations [7,9,11,12]. In addition, Nakagawa et al. reported that lithium zirconate can theoretically hold CO<sub>2</sub> in amounts up to 28 acceptor weight percent at high temperatures [5]. The high capture capacity and stability at 723 - 873 K of lithium zirconate make it promising for application in both pre and postcombustion systems. This provoked us to synthesis Li-Zr incorporated mesoporous materials. Mesoporous TiO<sub>2</sub> (M-TiO<sub>2</sub>) has received considerable attention because of the distinguished mesostructure [13]. Hence, various strategies have been developed to successfully synthesize mesoporous TiO<sub>2</sub> [14 - 18]. However, the synthesis of mesoporous TiO<sub>2</sub> is

still challengeable due to the rapid hydrolysis of titanium sources, and thus the strong acid catalyst (HCl and HNO<sub>3</sub>) and ligand complexation (acetylacetone, oxalate and citrate) are conventionally used in the synthesis. Acetic acid aqueous solution (HAc AS), however, is a particularly interesting candidate as a typical nontoxic and environmental friendly organic acid with small molecular weight and strong chelating effect. Conventionally, acetic acid has been adopted to control the hydrolysis of titanium sources based on the slow release of water through the esterification reaction between acetic acid and alcohols [19–21]. However, the strong chelating effect of acetic acid [22,23] has been pitifully neglected in the synthesis of M-TiO<sub>2</sub>. Quite recently, Yu et al. [24] has successfully prepared M-TiO<sub>2</sub> ultrasonically by employing acetic acid as a modifying agent to slow down the hydrolysis rate and directly introducing water from the environment. Recently Liu et al. reported the synthesis of mesoporous TiO<sub>2</sub> by the the performance of weak acid solutions, e.g. HAc AS, in controlling the hydrolysis of titanium sources [25]. Based on this we attempted to synthesis metal incorporated mesoporous TiO<sub>2</sub> and to study its chemisorption of CO<sub>2</sub>.

## 2. Experimental

### 2.1 Synthesis of Li-Zr-TiO<sub>2</sub>

Li-Zr incorporated mesoporous TiO<sub>2</sub> was prepared using the hydrothermal assistant sol-gel method. In a typical synthesis, 5 g titanium butoxide (MW= 340.36, 98%, Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>), appropriate amount of lithium isopropoxide and zirconium isopropoxide was added dropwise to 30 mL HAc (A.R.) aqueous solution under vigorous stirring. The mixed solution was sealed and kept stirring for 4 h to obtain solution A. In order to investigate the effect of the HAc concentration, 10%, 20%, (v/v) HAc were adopted, respectively. In a separated beaker, 3 g block copolymer P123 (MW = 5800, purchased from Aldrich) was

dissolved in 20 mL ethanol (A.R.) thoroughly under vigorous stirring to obtain solution B. Solution B was then slowly added to solution A. The final solution mixture was sealed and further stirred for 24 h. All the above experiments were conducted at room temperature. The solution was then transferred into a Teflon sealed container which was then heated in an oven at 120 °C for 48 h, respectively. After reaction, the precipitation was collected and dried in air at 80 °C overnight without further washing. The as prepared samples were finally calcined at different temperatures of 400 °C for 4 h to remove organic surfactants and improve the crystallinity of the products. Deionized and doubly distilled water was used throughout the experiment. The sample is designated as Li-Zr-TiO<sub>2</sub>.

### 2.2. 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 0.5–5 ° at 0.02° step size and a 1 s step time. The nitrogen adsorption-desorption isotherms were measured at 196 °C on a Micromeritics ASAP 2010 volumetric adsorption analyzer. Prior to each adsorption measurement the samples were evacuated at 150 °C under vacuum ( $p<10^{-5}$  mbar) in the degas port. The specific surface area, SBET was determined from the linear part of the BET equation, and the pore volume was calculated using a BET plot based on the amount of nitrogen gas adsorbed at the last adsorption point ( $P/P_0 = 0.95$ ) and the pore size distribution using the Barrett-Joyner-Halenda (BJH) method. High-resolution transmission electron microscopy (HR-TEM) were captured on Tecnai G2 20S.

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

CO<sub>2</sub> adsorption-desorption measurements for Li-Zr-TiO<sub>2</sub> were performed using Thermo Gravimetric Analyzer. A sample weight of approximately 10 mg was loaded into an alumina sample pan in a

TG unit (SCINCO thermal gravimeter N 1000) and tested for CO<sub>2</sub> adsorption / desorption performance. The initial activation of the samples was carried out at 200 °C for 1 h in a nitrogen atmosphere. Then adsorption run was conducted using high purity CO<sub>2</sub> (99.999%) gas, and the desorption run was conducted in N<sub>2</sub> flow. The adsorption runs were conducted at 25, 50 and 75 °C under atmospheric conditions, and desorption was determined at 200 °C. Both the gases, CO<sub>2</sub> and N<sub>2</sub> were passed through an automatic valve, assisted with a timer for continuous adsorption and desorption profiles.

### 3. Results and Discussions

#### 3.1 Characterization

##### 3.1.1. XRD analysis

Fig. 1A shows one peak in low angle XRD pattern, which indicates the formation of mesoporous Li-Zr-TiO<sub>2</sub>. In the wide angle powder XRD pattern of the TiO<sub>2</sub> after calcination, as is shown in Fig. 1B, four crystal peaks at high 2 $\theta$  values of 25.3°, 38.1°, 48.1°, 54.5° and 62.6° appear which is consistent with the anatase phase of TiO<sub>2</sub> materials corresponding to those shown in the JCPDS card No. 21-1272. No reflections of rutile and brookite phases are observed in the prepared mesoporous Li-Zr-TiO<sub>2</sub>.

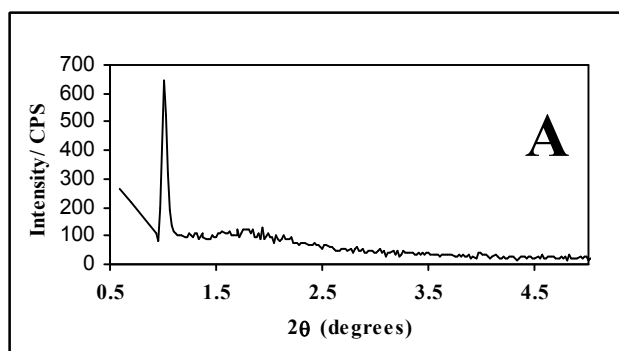


Fig. 1 (A) Small angle XRD pattern of Li-Zr-TiO<sub>2</sub> and (B) Wide angle XRD pattern of Li-Zr-TiO<sub>2</sub>

##### 3.1.2. BET analysis

The N<sub>2</sub> adsorption/desorption isotherms and Barrett - Joyner - Halenda (BJH) pore size

distributions of Li-Zr-TiO<sub>2</sub> sample is displayed in Fig. 2. The Li-Zr-TiO<sub>2</sub> exhibits type IV curve with a H1 hysteresis loop 2, which implies that the ordered cylindrical pore geometry with a high degree of pore size uniformity with the average size of 9.0 nm [26,27].

##### 3.1.3. TEM analysis

The TEM image of the Li-Zr-TiO<sub>2</sub> sample after calcination is presented in Fig. 3. The samples consist of the aggregation of nanoparticles with particle sizes of 100 nm. The particle size increases apparently with increasing the calcination temperature, agreeing with the results calculated from the XRD patterns.

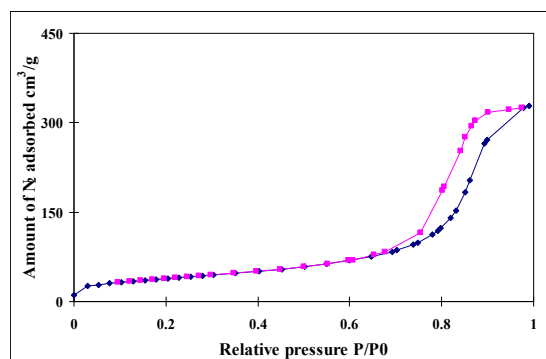


Fig. 2. N<sub>2</sub> adsorption / desorption isotherm of Li-Zr-TiO<sub>2</sub>

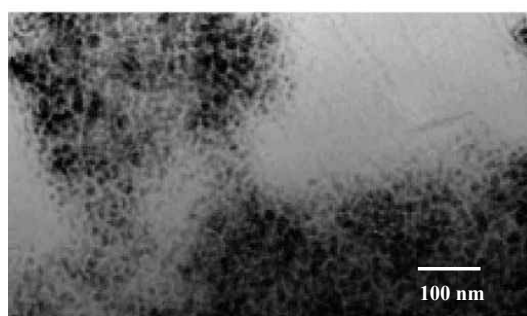
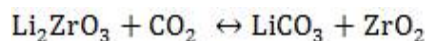


Fig.3. TEM image of Li-Zr/TiO<sub>2</sub>

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

Fig. 4 shows CO<sub>2</sub> adsorption/desorption profiles of mesoporous TiO<sub>2</sub> and Li-Zr-TiO<sub>2</sub> carried out at 25, 50 and 75 °C. a. CO<sub>2</sub> adsorption/desorption profiles illustrates the initial weight loss of approximately 5 wt% after preliminary activation at 300 °C in N<sub>2</sub> atmosphere is due to loss of moisture content and physisorbed CO<sub>2</sub> on

exposure to atmosphere. The maximum CO<sub>2</sub> adsorption capacity of Li-Zr-TiO<sub>2</sub> is 100mg/g at 25 °C, which is significantly higher than that of mesoporous TiO<sub>2</sub> (25 mg/g). The basic feature of Li<sub>2</sub>ZrO<sub>3</sub> acts as electron acceptor and could immediately react with CO<sub>2</sub> to Li<sub>2</sub>CO<sub>3</sub> according to the following reaction [16]:



Herein, the high CO<sub>2</sub> adsorption capacity of Li-Zr-TiO<sub>2</sub> is due to the high dispersion of Li<sub>2</sub>ZrO<sub>3</sub>.

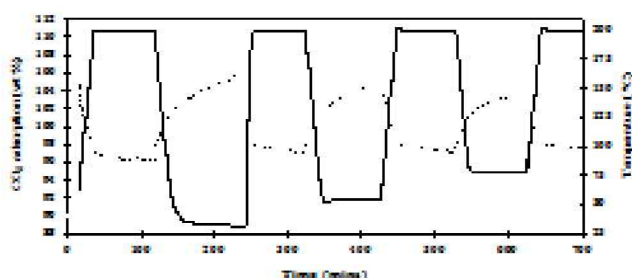


Fig. 4. CO<sub>2</sub> adsorption /desorption profiles for Li-Zr/TiO<sub>2</sub>

#### 4. Conclusions

Li incorporated mesoporous TiO<sub>2</sub> materials with various pore size distributions were synthesized by using triblock copolymers via a sol-gel process in aqueous solution. The XRD, BET, and TEM and SEM analysis reveals the mesoporosity of Li-Zr-TiO<sub>2</sub>. All particles have spherical morphology with a diameter range of 1-3 μm. The Li incorporated mesoporous TiO<sub>2</sub> were tested for CO<sub>2</sub> adsorption and its adsorption capacity is 90 mg/g. The Li incorporated mesoporous TiO<sub>2</sub> are observed to be thermally stable, recyclable and green sorbent for CO<sub>2</sub> capture

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