Li, Zr doped mesoporous silica: One pot synthesis and its application to CO_2 adsorption at low temperature

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Li, Zr 담지 메조포러스 실리카 합성 : One pot 합성 및 저온 이산화탄소 흡착 응용

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Abstract

Li, Zr doped mesoporous silica was synthesized in one pot and investigated for low temperature CO_2 adsorption. Herein CTAB and TEOS are used as structural directing agent and silica source respectively. The characteristics of the material was obtained from FT IR, XRD, SEM, TG and BET results. ICP AES results revealed the presence of lithium and zirconium. The material possesses high surface area ($962.22 m^2 g^{-1}$) with mono dispersed particles of about 2 nm. The maximum CO_2 adsorption capacity is 5 wt % (50 mg/g) of CO_2/g of sorbent at 25 °C, which is regenerable at 200 °C. This regeneration temperature of the adsorbent is lower than the reported lithium zirconium silicate powder. Until now, there is no report for the synthesis of Li, Zr doped mesoporous silica. The performance studies illustrate that Li, Zr doped mesoporous silica is tunable, regenerable, recyclable and selective sorbent and hence found to be a promising candidate for CO_2 adsorption.

1. Introduction

Carbon dioxide a fatal green house gas (GHG), its accumulation into the atmosphere leads to the climatic change which is followed up by the destruction of earth's ecological system. For the global energy requirement we solely depend on fossil fuel, which emits large amount of CO_2 into air, hence it is vital task to the scientific community to mitigate the emission CO_2 before it reaching its higher concentration or finding new renewable energy source. The permanent sequestration of CO_2 in deep sea and coal field may be effective. But, the recent literature proved even though this method give permanent solution for CO_2 removal, they also have some serious adverse effect like cracking of earth crust due to continuous gas permeation and pressure in coal field and increase in pH in deep sea which ultimately leads to the destruction of eco system. Recently studies on adsorption of CO_2 in 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 sieves development. These mesoporous molecular sieves have made a greater attraction in the fields like sorption science, catalysis, biologicals as an adsorbent, catalyst for chemical reaction, solid support for other catalyst and as carrier for drug and protein. Mesoporous materials ensnare the scientist due to their uniform and tunable pores,

high surface areas and tunable acid base, redox properties (1 7). It is very easy to tune the acidic property of defected hydroxyl group by incorporating alkaline, transitional metal and amines. By the incorporation proper choice of metals we can make the mesoporous silica to become a valuable material for CO_2 adsorption from flue gas or from environment. In this regards metals like Mg, Ca, Fe, La, Ti etc have been effectively incorporated into meso and microporous materials and studied for their efficiency for CO_2 adsorption .

Zirconium is one of the metal of choice for carrying out numerous organic and inorganic reaction as in the form of its oxides and as mesoporous zirconia. Recent past, zirconium doped mesoporous silica materials attracted scientist's interest due to their easiest way of synthesis and applications to extensive range of reactions like vapor and liquid phase organic transformations, oxidation reactions with hydrogen peroxide, C60 fullerene adsorption, gas phase hydrogenation of acetonitrile, as catalyst support in Fischer – Tropsch synthesis, hydrogenation and ring opening of aromatic hydrocarbons (tetralin) [9 18]. Recently, Nakagawa et al developed a promising inorganic lithium zirconate composite for CO_2 sorption based on non catalytic gas – solid adsorption and showed that it adsorb a large amount of CO_2 (about 4.5 mol/kg) at high temperature (400 – 700 °C) with considerably large CO_2/N_2 selectivity compared to ion exchanged ZSM 5 zeolite (limited CO_2/N_2 selectivity). Ida and Lin postulated the unique double shell mechanism for it's CO_2 adsorption based on the results of the structural and thermal analysis[19 25]. Till today, though lithium zirconate are said to be best choice for CO_2 adsorption from flue gas from coal combustion plant, it suffers drawback of high temperature (400 °C) adsorption and desorption still at higher temperature. Recent study on nano crystalline lithium silicate, sol gel derived lithium zirconate revealed that the energy required for adsorption is greatly reduced in case of smaller particles than the natural lithium silicates. Herein we synthesized Li Zr doped mesoporous silica in one pot and studied the CO_2 adsorption capacity at low temperature.

2. Experimental

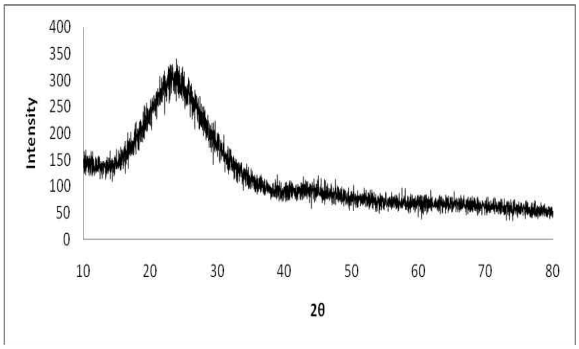
2.1. Synthesis of lithium zirconium doped porous silica

Zirconium n propoxide and lithium acetate were used as source for zirconium and lithium respectively. In a typical synthesis, 4 g of CTAB was dissolved in 100ml isopropanol to make 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 lithium isopropoxide was added followed by addition of 6.6 g of TEOS to get clear sol. To the above sol about 5 ml 2M sulphuric acid was added with vigorous stirring. The obtained transparent jelly like product aged at 100 °C for 12h. 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 with a heating rate of 1°C/min.

3. Results and Discussion

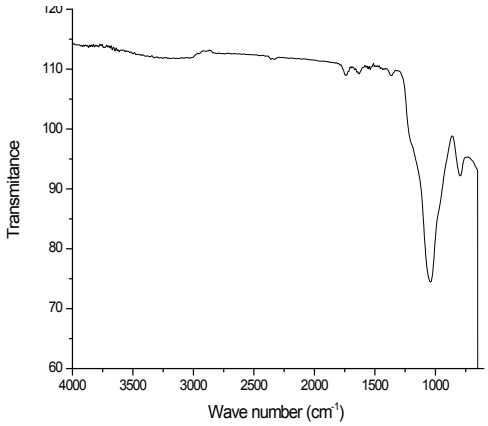
3.1. Characterization

The synthesized material was characterized by XRD, SEM, EDX, FT IR and ICP AES. Powder X ray diffraction patterns were recorded using a Rigaku Miniflex diffractometer with Cu Kα radiation (λ = 0.154 nm). The diffraction data were recorded in the 2Θ range 0.5 – 10° with 0.02° step size and 1 s step time. Fig.1. illustrates the presence of tetragonal zirconium phase at 20° (2 Θ). The absence of characteristic patterns for Zr confirms the incorporation of Zr into the pores.



[Fig 1] XRD pattern of Li, Zr doped porous silica

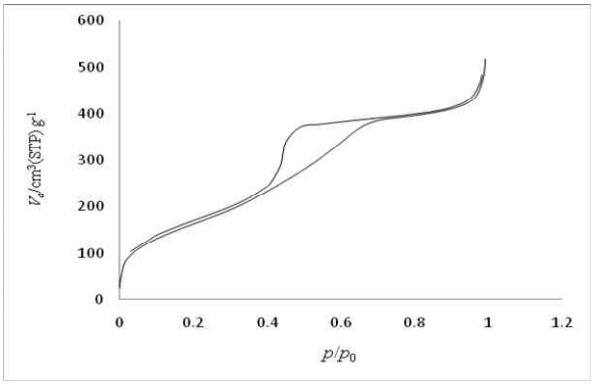
Figure 2 depicts the FT IR spectrum of Li,Zr porous silica. The band at 720 cm ^{1} is due to the presence the tetragonal phase of zirconia. The sharp band at around 1030 cm ^{1} is assigned to Si – O – Zr. The absence of band at 800 cm ^{1} pertaining to ring structure of Si – O clearly evidences the incorporation of Zr into the mesoporous structure.



[Fig.2] FTIR spectrum of Li, Zr doped porous silica

3.2. BET

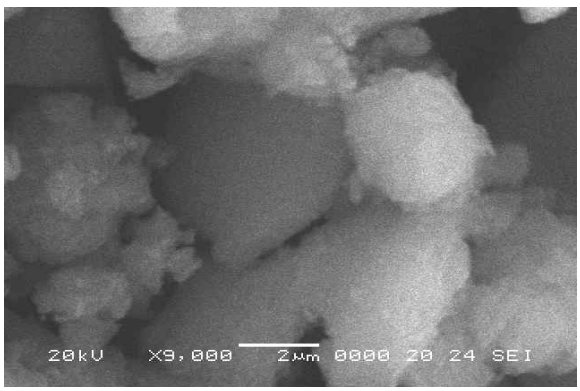
With reference to IUPAC classification of N_2 adsorption – desorption isotherms, the synthesized Li, Zr doped mesoporous silica (Fig. 3) possess type IV isotherm, with a sharp capillary condensation step at relatively high pressure with H2 hysteresis loop indicating the presence of well defined mesopores. The BET surface area and mean pore diameter obtained by BJH method was found to be 962.22 m^2g^{1} and 1.2 nm respectively. The surface area was very high compared to previously reported nano crystalline lithium zirconate [26].



[Fig 3] N_2 adsorption-desorption isotherm of Li,Zr doped porous silica

3.3. SEM and EDX

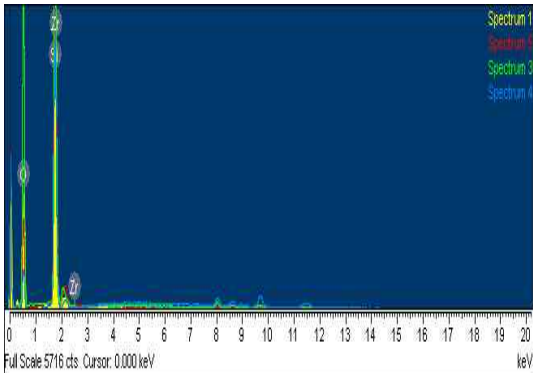
The morphology of the synthesized material was studied using JEOL scanning electron spectrophotometer equipped with EDX system. The particles are spherical in shape (Fig.3.). The presence of Zr is evidenced from the EDX analysis and was found to be 3.72 % wt. The presence of lithium is not detectable as it is of low atomic weight (Fig 4).



[Fig. 3] SEM image of Li,Zr doped porous silica.

3.4. ICP AES

The presence of Zr and Li is further confirmed from ICP AES analysis. The weight percent of Zr and Li was found to be 4% and 3.42% respectively.

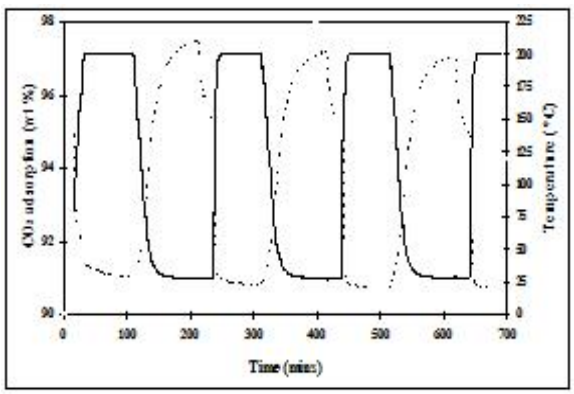


[Fig.4] .EDX spectrum of Li, Zr doped porous silica

3.5. CO_2 adsorption

CO_2 adsorption – desorption measurements of the synthesized material was performed on thermo gravimetric analyzer (SCINCO thermal gravimeter N 1000). The adsorption run was carried out using high purity CO_2 (99.9%) gas at 25 °C under atmospheric pressure while the regeneration was carried out under N_2 flow at 200 °C. A sample weight of ca. 10 mg was loaded into an alumina sample pan in a TG unit and initial activation was carried out at 200 °C for 1 h in nitrogen atmosphere. Continuous CO_2 adsorption – desorption profile was obtained by heating, cooling and changing the gases CO_2 (99.9%) and N_2 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. CO_2 adsorption result shows an adsorption capacity of 5 wt% and remained the same even upto 3 repeated cycles (Fig 5).



[Fig. 5] CO_2 adsorption/desorption of Li/zr doped meso silica (three cycles)

4. Conclusions

The incorporation of the target metals into the pores of silica is clearly evident by the characteristic pattern of the tetragonal phase of Zr. The EDX and ICP AES results confirm the presence of Zr inside the pores of silica. The maximum adsorption capacity of Li,Zr doped porous silica was found to be 5 wt%. The effect of particles alters the adsorption of CO_2. Increased surface area and reduced particles attributes to adsorption of CO_2 at low temperature of 25 °C and desorption at 200°C. Hence, the Li, Zr doped silica, a promising candidate for the adsorption CO_2.

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