

Microwave synthesized MOFs for CO₂ capture and stability study to acid gases with humid air

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INTRODUCTION:

The world is to look for new energy resources, because of the gradual decrease of petroleum and the rapid increase of energy consumption worldwide. Global warming and environmental concerns resulted from human activities with the rapid increase of population worldwide have attracted the attention of many researchers and scientists in the 20th century. Energy Information Administration (EIA) anticipated that the energy consumption will increase by 57 % by 2030[1]. The increasing atmospheric CO₂ concentration and its impact on the environment have led to increasing attention directed toward finding advanced materials/technologies suitable for efficient carbon capture and storage [2,3,4] while improving the efficiency of energy utilization and increasing the use of low-carbon energy sources are potential ways to reduce CO₂ emissions [5,6,7]. The Intergovernmental Panel on Climate Change (IPCC) pointed to anthropogenic CO₂ as a major contributor of global warming and climate change [8], which is now considered as a global problem. Thus, the challenge of reducing CO₂ emissions has become a crucial issue for the 21st century, leading to the expansion of renewable technologies, energy saving and carbon capture and sequestration (CCS) [9,10]. The CCS technology is an effective way to reduce CO₂ emissions [11,12] which includes four steps: CO₂ capture, compression, transportation and storage, while the cost for CO₂ capture accounts for about 75% of the total cost for CCS process. The most important factor is to develop cost-effective techniques for the capture and separation.

In this research, we report new MOF UTSA-16 (Zn) synthesized with the help of microwave irradiation. The synthesis procedure was inspected by changing synthesis time to determine a finest time for the UTSA-16 (Zn) formation. In our previous study we found that in as synthesis reaction time increases particle size of MOF UTSA-16 decreases but, in this study no significant difference in particle size was found as synthesis reaction time increases. The CO₂ and N₂ adsorption capacities as well as selectivities were measured by using a volumetric method and compared to detect the synthesis time dependence on the adsorption performance. The synthesized samples with different reaction times were characterized to identify crystal structure, surface area, particle size, and thermal stability by using XRD, BET, SEM, and TGA respectively.

In addition, we performed the stability test of the UTSA-16 (Zn) adsorbents under humid air and acid gases for practical applications because the humid air and acid gases in the exhaust gas of power plants decompose the adsorbents, causing significantly reduced performance. The material stability was evaluated by comparing the results of XRD data and adsorption capacity after samples conditioned in acid gases with humid air.

2. Experimental

2.1 Sample preparation:

Sample Preparation

The UTSA-16 (Zn) was synthesized at 90 °C for 1–6 h under microwave irradiation. Zn (NO₂)₃ 6(H₂O) (1.5365 g), C₆H₈O₇·H₂O (1.47 g), NaOH (1.17 g), were dissolved in 35 mL DMF solvent. The solution was transferred into a microwave glass reactor, sealed by using a Teflon cap and placed in a microwave oven (Discover SP). The white samples were collected by a centrifugation and washed with ethyl ether 2 times and methanol 3 times, then immersed in methanol which was decanted and replenished three times per day for three days. Finally, solvent was separated with the help of centrifuge (rpm 5000) and the powder sample was dried under vacuum for two hours and then to remove excess solvent heated at 90 °C for 6 h under vacuum.

Adsorption isotherm measurement

Adsorption equilibrium isotherms of CO₂ and N₂ for the microwave synthesized UTSA-16 (1–6h) were measured using a volumetric apparatus (BelSorp Mini II) at varying temperatures (298, 313, 323, 233, 343 and 353 K) under the pressure range of 0-1 bar. All temperatures were kept by using a Dewar equipped with a water-circulating jacket connected to a thermostatic bath with a precision of ± 0.01 °C. CO₂, N₂, and He gases with ultrahigh purity grade (>99.995%) were used. The free space of the sample holder was determined by dosing He. The specific surface area (S_{BET}) was calculated using multi-point adsorption data from the linear segment of the N₂ adsorption isotherms using Brunauer–Emmett–Teller (BET) theory. Before each measurement, the sample was evacuated at 90 °C for 12 h.

RESULTS AND DISCUSSION:

The X-ray diffraction (Fig. 1) patterns were measured to verify crystal structure formation depending on different reaction times.

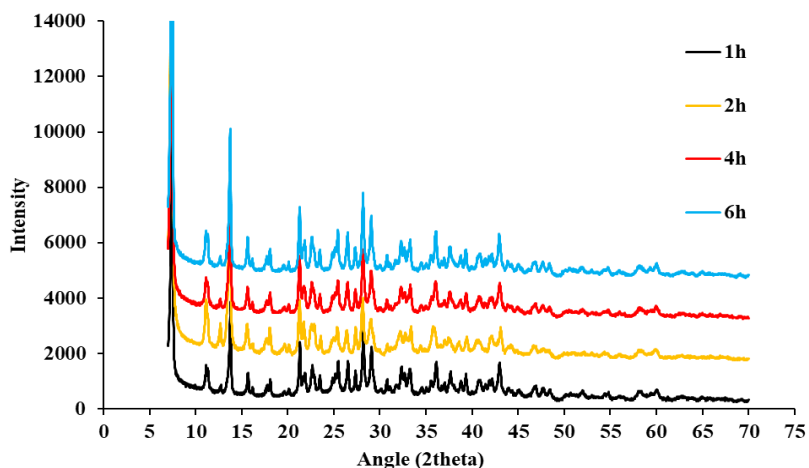


Fig.1 XRD spectra of UTSA-16 (Zn) for different reaction time of (1 h-6 h)

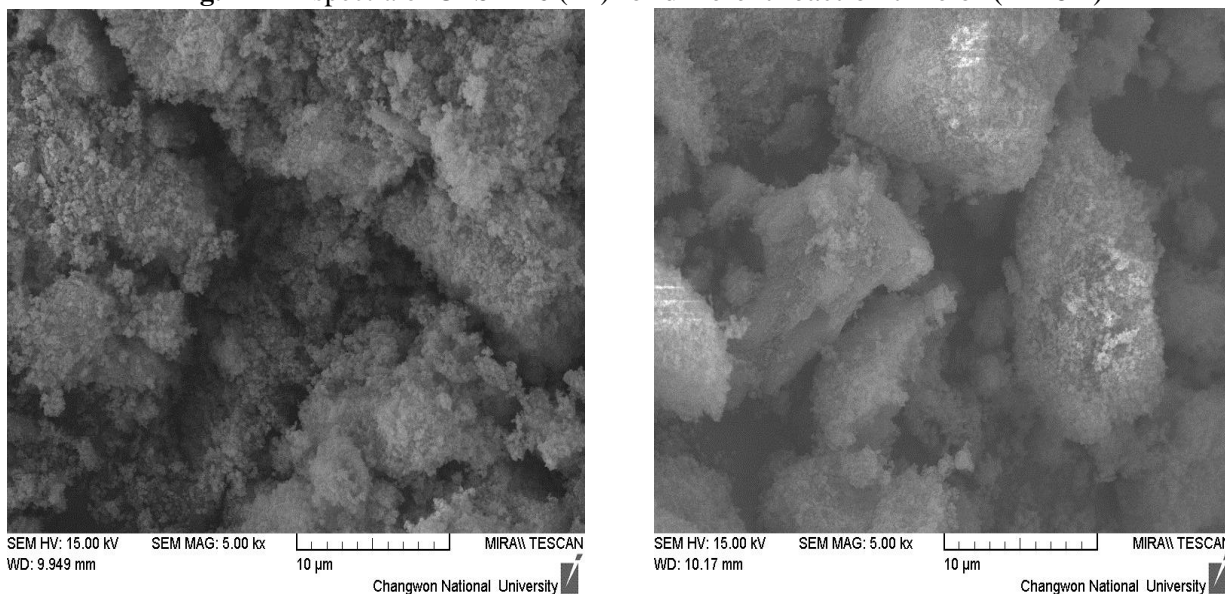


Fig .2 SEM image of UTSA-16 (Zn) 1 h and 4 h

In order to understand the effects of reaction time on the particle formation, particle images (Fig. 2) were taken using a scanning electron microscope (SEM). The thermal stabilities of the

UTSA-16 samples for different reaction times were evaluated by using a TGA (Fig.3). TGA instrument set up by opening gas and water flow. Measure the weight of empty pan samples were transferred to pan. Mantle was kept in upper position N₂ Gas flow rate was set at 50cc/min. The temperature was programmed and set at 28- 700 °C (20 °C/min)

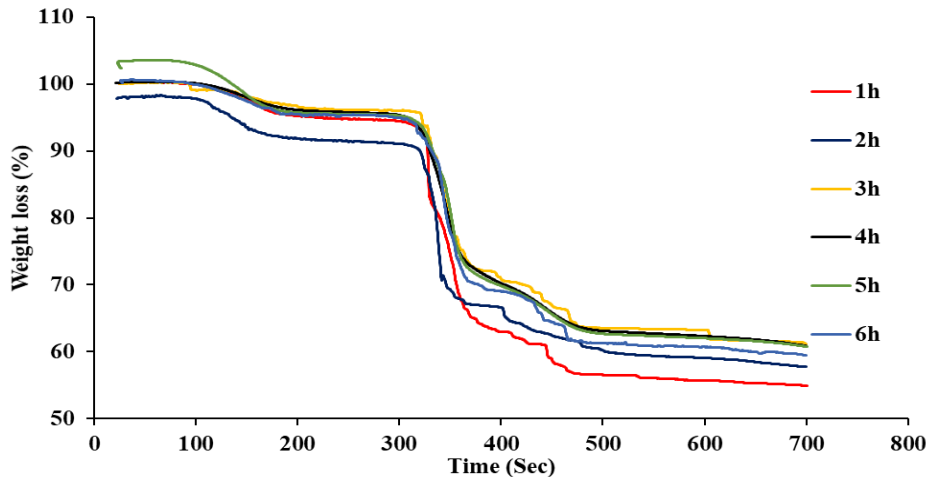


Fig.3 TGA weight loss UTSA-16 (Zn) (1 h -6 h)

CO₂ adsorption measurement:

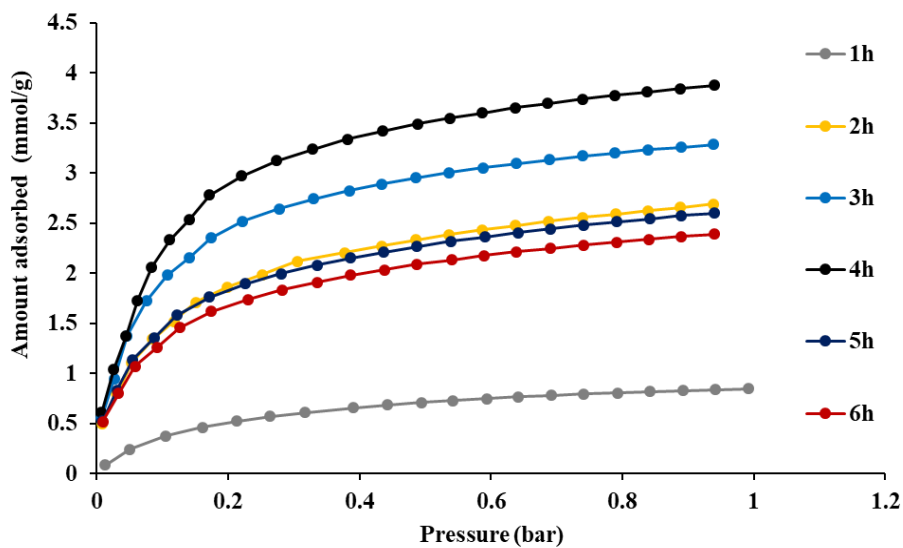


Fig.4 CO₂ adsorption in mmol/g at 298K and 1 bar

CO₂ adsorption isotherms of UTSA-16 (Zn) adsorbents with different reaction times are shown in Fig. 4. The CO₂ and N₂ adsorption measurements were carried out separately at 298 K under 0–1 bar using a volumetric method.

CONCLUSION:

UTSA-16 (Zn) were successfully synthesized with the help of microwave method. The synthesis procedure was investigated by varying synthesis time to determine an optimal time for the UTSA-16 formation. As synthesis time increases, surface area as well as pore volume increases from 1 to 4 h and then decreases after 5 h. CO₂ adsorption capacity was dependent on the reaction time.

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