

Attapulgite based LiCl composite adsorbents for cooling and air conditioning applications

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Abstract

A series of attapulgite-based LiCl composites were prepared with mixing method, incorporating hygroscopic LiCl into porous surface of attapulgite clay. Sorption properties of these composites were performed with high vacuum gravimetric method, desorption performance by TG-DTA analysis, and characterization by X-ray diffraction. The results show that both attapulgite structure and chloride content play prime roles in water adsorption on the AT–LiCl adsorbents, especially during lower water pressure, while at higher pressure, adsorption performances strongly depend on chloride content. At 1500 Pa, water loading on AT–LiCl (30%) can be as high as 0.44 kg/kg, while at 750 Pa, the loading is 0.31 kg/kg, which is higher than commonly used zeolite 13X and silica gel. Based on sorption equilibrium curves, isosteric heat is calculated. This study shows that intension of water sorption on composite adsorbent is intermediate between that on zeolite 13X and silica gel. The composites can be effectively regenerated during 170–190 °C. AT–LiCl (30%) seems to be an efficient candidate for cooling or air conditioning applications, specially when utilization of heat sources at temperatures lower than 170 °C.

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1. Introduction

As a good opportunity to replace vapor compression refrigeration, solid adsorption cycles have got intensified research efforts recently, specially their potential applications in waste heat recovery, and solar energy utilization etc. These systems are completely environmentally benign due to their using natural working media characterized by a zero ozone depletion potential and a zero global warming potential, as refrigerants. In addition, they have no moving parts, and are also less sensitive to shocks and the installation position [1,2]. However, much work still has to be done for large-scale applications of these adsorption machines. There are many possibilities to improve the performance of an adsorption machine. One of them is

linked with the advanced working pairs, i.e. increasing adsorption quantities of the adsorbate on the adsorbent and lowering desorption temperature of the pairs [3–8].

The most commonly investigated working pairs which involve water vapor as adsorbate, are zeolites and silica gels, which are of well-known limitations. Numerous researches have focused on modified zeolite, modified silica materials and composite sorbents [3,5,9–12]. Aristov et al. [3] has, for the first time, developed a family of composite sorbents, by impregnating hygroscopic promoter salts (inorganic salts in general, such as CaCl₂, LiBr, LiCl, etc.) into the pores cavities of host matrices (such as silica gels, porous carbons, aluminums, MCM-41, etc.), for multiple applications that include gas drying, thermal energy storage for low energy buildings and fresh water production, etc. Their studies show that composites based on CaCl₂ and LiBr as impregnated salts and different micro- and mesoporous silica gels as host matrices are able to

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absorb up to 0.75 g H₂O per 1 g of the dry sorbent, and those new materials can be operated with cycles whose maximum temperature is about 95 °C (for cooling) and 140 °C (for heating) that are lower than those for other pairs known so far. Also, similar work has been carried out by Jäenchen et al. [9,13,14] for heat storage, and by Daou et al. [10], Yefeng and Wang [15], Zhu et al. [16] for sorption air-conditioning, fresh water production and for heat storage.

Another promising material for these systems is clay or clay-based adsorbent, which is chemically inert, resistant to deterioration, commercially available in large quantities and has many industrial, catalytic and environmental applications [17]. Attapulgitic clay satisfies one of the main requirements for adsorption cycles, which has an ideal water loading of about 0.20 kg/kg as well as good containing ability for water due to its highly porous structures [18,19]. Work of Jäenchen et al. [9,13] shows that CaCl₂ impregnated attapulgitic presents similar performance as other mesoporous materials confined with hygroscopic salt hydrates have.

Recently, after Jäenchen, a series of attapulgitic clay-based CaCl₂ and SrCl₂ composites have been proposed by the authors and have shown advanced performance for cooling and air-conditioning systems driven by low temperature waste heat or solar energy [20–22]. The results show that: (1) At higher relative humidity, water loading on AT–CaCl₂ (20%) can be as high as 0.60 kg/kg, while at relative humidity 20%, the loading is 0.30 kg/kg, which is higher than commonly used 13X molecular sieve and silica gel. (2) The composites obtained can be effectively regenerated during 160–180 °C and reused. Though CaCl₂ is the most ordinary desiccant, LiCl is also well known for its particular hydrophilic property and has been widely used in the dehumidifier and in desiccant cooling systems [23]. Consequently, properties of attapulgitic-based LiCl composites deserve closer investigations.

In this paper, attapulgitic clay-based LiCl composites were prepared with previous proposed mixing method [20]. The obtained attapulgitic clay-based LiCl composite adsorbents are respectively named, with different content of LiCl, as AT–LiCl (10%) (where 10% means the content of lithium chloride in the composite adsorbent), AT–LiCl (20%), AT–LiCl (30%) and AT–LiCl (40%). Sorption properties of these composite adsorbents for water were performed with high vacuum gravimetric method, and desorption performance by TG-DTA analysis. Basing on the obtained data, a comparison of physico-chemical properties between the AT–LiCl composites and commonly used 13X molecular sieve and silica gel is made.

2. Experiments and materials

2.1. Materials

Main raw materials, used in this study, are shown in Table 1. The pore size distribution and specific surface area

Table 1
Pore size distribution and specific surface area of main materials

Adsorbent	S_{BET} (m ² /g)	Φ_{av} (nm)	Manufactory
The pure attapulgitic	113.17	9.87	Xuyi Botu Attapulgitic Clay Hi-tech Development Co., Ltd
AT–LiCl (30%)	95.23	13.4	Self-proposed
A type silica gel	673.12	2.4	Qingdao Haiyang Chemical Co., Ltd
13X molecular sieve	403	0.1	Nanjing Heyi Inorganic Chemical Co., Ltd

of the composites were determined by ASAP2020 device (Micromeritics Company).

2.2. Samples preparation

Four samples of attapulgitic-based LiCl composite adsorbents were prepared adopting mixing method, similar to previous composite materials [20].

2.3. Water adsorption on samples

The adsorption isotherms were measured gravimetrically with a common quartz spring balance proposed by the authors [5], equipped with a pressure sensor ranging from 0 to 13000 Pa continuously, made by Shanghai Zhen-tai Instruments Co., Ltd. Before application, the samples were calcined in high vacuum (<0.1 Pa) at 300 °C (for zeolite and AT–LiCl composite) and 120 °C (for silica gel) for 2 h, respectively. Both adsorption and desorption measurements were performed.

2.4. TG-DTA analysis

The desorption behavior of samples was investigated by thermogravimetry (TG)-differential thermal analysis (DTA) on a WCT-1 type thermal balance made by Beijing Optical Instrument Factory.

For determination of desorption temperature, the TG-DTA measurements were performed on the thermal balance at 20 °C with a heating rate of 10 °C/min to 410 °C in static air atmosphere.

To calculate activated energy of the adsorbents for desorption water, the desorption experiments were also performed, at different heating rates of 5–20 K/min to 350 °C (120 °C for silica gel). In each experiment, the sample mass was kept about 16.0–16.5 mg.

Before the TG-DTA measurement the sample was saturated with water at 30 °C at a relative humidity 0.751 “off-line” in a desiccator.

2.5. XRD analysis

The identification of the LiCl characterization in the composite adsorbents was performed by X-ray diffraction

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