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Research Paper

Study of the hydration behavior of zeolite-$MgSO_4$ composites for long-term heat storage

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HIGHLIGHTS

- Hydration behavior of zeolite-$MgSO_4$ composites was investigated for long-term heat storage.
- Effects of various operation conditions on the hydration performance were revealed.
- The hydration enhancement of composites depended on zeolite properties.
- The hydration ability of composites decreased when the air temperature was above 50 °C.
- The tested composite showed a good cycling stability.

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ABSTRACT

Hydration behavior of composite adsorbents based on porous zeolite matrix and $MgSO_4$ hydrates was investigated experimentally for long-term heat storage. The composites were prepared by the infiltration method, and different zeolites were tested. Water sorption of composites in a constant temperature & humidity chamber was carried out first, and then the hydration of composites in a macro-scale reactor was performed. Special efforts were devoted to reveal the effects of various reaction conditions including temperature, relative humidity (RH) and air flow rate on the hydration performance of composites. The results showed that the prepared zeolite-$MgSO_4$ composites had larger hydration ability than pure zeolites, and zeolite 13X-$MgSO_4$ showed the best performance. Both the saturation adsorption amount and the hydration rate could be effectively increased by increasing the RH or the air temperature. However, the hydration ability of composites decreased significantly when the air temperature was above 50 °C. The air temperature lift during the reactor heat discharge was found to increase with the flow rate or RH of fed moist air. Besides, the reactor filled with the zeolite-$MgSO_4$ composites showed a high energy efficiency of 81.34% and a good cyclic stability.

1. Introduction

Utilization of solar energy for space heating provides an effective way to reduce the consumption of fossil fuels and concern of environmental pollution. However, solar energy is abundant in summer while it is not sufficient for heating in winter. Long-term heat storage, that stores solar energy for later use, can be used to overcome the issue of the mismatch between the supply and need of solar energy. Among various current long-term heat storage technologies, thermochemical heat storage has a great potential to be commercialized in the future due to its very high storage density (0.7–3.0 GJ/m^3) and negligible heat loss during storage [1]. Especially, thermochemical heat storage based on water sorption by salt hydrates has gained great worldwide attention, as water is the most feasible adsorbate considering safety, cost and availability [2,3]. The state of the art of the sorption heat storage by salt hydrates has also been reviewed recently [4–8].

The working principle of the thermochemical heat storage based on salt hydrates involves breaking and making of chemical bonds in the material, either by dehydrating the material during the heat charge or hydrating the material during the heat discharge. Presently, the thermochemical heat storage technology is still far from mature. Main efforts have been devoted to the screening and developing of promising salt hydrate thermochemical materials (TCMs), and the conceptual or prototype development of thermochemical reactors. When choosing a salt hydrate TCM, several factors should be considered, including reaction

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temperature, reaction enthalpy, reaction rate, material cycling stability, toxicity, and cost. Although potential candidates for water sorption heat storage are numerous, only some of salt hydrates have been identified, including: $MgSO_4 \cdot 7H_2O$ [9–12]; $MgCl_2 \cdot 6H_2O$ [13], $CaCl_2 \cdot 2H_2O$ [14], $SrBr_2 \cdot 6H_2O$ [15–16], $Al_2(SO4)_3 \cdot 18H_2O$ [14], $LaCl_3 \cdot 7H_2O$ [7]. Among them, $MgSO_4 \cdot 7H_2O$ is considered to be one of the most appropriates because of its high energy density, compatible storage temperature with solar collectors, availability of the chemical reaction compounds and non-toxicity [17].

Essen et al. [9,10] carried out extensive investigations on the characterization of $MgSO_4$ hydrate for thermochemical heat storage. It was found that dehydration of $MgSO_4 \cdot 7H_2O$ involves at least three steps, and most of water can be dehydrated at 150 °C. The reaction conditions, especially the water vapor partial pressure and the temperature, play great roles on the sorption ability and reaction rate of $MgSO_4$. The hydration reaction may become very slow, resulting in negligible temperature lift of moist air, under low temperature or low water vapor pressure. For the dehydration process, melting of $MgSO_4 \cdot 7H_2O$ particles was found, and the resulted crystal growth and bonding led to a reduction of particle porosity, which hindered the water vapor transport and reduced the reaction rate significantly. Besides, during the dehydration of $MgSO_4 \cdot 6H_2O$ above 55 °C, the structure of $MgSO_4 \cdot 6H_2O$ changed from crystal to amorphous, resulting in a great loss of water sorption ability and formation of cracks and pores on grains. The crystal growth and agglomeration could be avoided by performing the dehydration of $MgSO_4 \cdot 7H_2O$ in a packed bed reactor [11]. The hydration of $MgSO_4$ hydrates were also investigated by Posern and Kaps [12] using a humidity controlled calorimetry.

However, previous studies showed that the use of pure salt hydrate materials encountered some technical barriers, such as mass transport limitation of water vapor within salt hydrate grains, ineffective heat transport due to low conductivity of salt hydrate, performance degradation due to microstructure change, melting and agglomeration after over hydration, or decomposition of salt hydrates. Impregnating salt hydrates into porous matrix to form composite sorbent provides a viable solution to overcome these problems [6,18]. Recently, composite materials based on salt hydrates have gained increasing attentions. Various porous matrix have been used to form composites, including zeolite ($MgSO_4$-zeolite [17,19–21]; $MgCl_2$-zeolite [19,22]; $CaCl_2$-zeolite [20]), silica gel ($MgSO_4$-silica gel [20]; $MgCl_2$-silica gel [20]; $SrBr_2$-silica gel [23]), vermiculite ($MgSO_4$-vermiculite [20]; $CaCl_2$-vermiculite [20,24]; $SrBr_2$-vermiculite [25]), porous glass ($MgSO_4$-porous glass [26–27]), attapulgite ($CaCl_2$-attapulgite [28]; $MgSO_4$-$MgCl_2$-attapulgite [29]), and graphite or activated carbon foam (ACF) ($CaCl_2$-ACF [30]; $MgCl_2$-graphite [22]; LiCl-graphite [2]).

A new zeolite 13X-$MgSO_4$ composite was developed and characterized by Hongois et al. [17] for long-term heat storage. The composite hydration performance in a macro reactor was also investigated considering the effects of air flow rate and air humidity. It was shown that an optimized energy density of 0.18 W h/g was obtained, which was 45% of the theoretical energy density of the composite sorbent. Whiting et al. [21] carried out heats of water sorption studies on zeolite-$MgSO_4$ composites, and compared fours series of wide pore zeolite composites containing varying $MgSO_4$ quality (from 5 to 15 wt%). The results showed that micro structure of zeolite played a significant role on the heats of water sorption of composites. The influences of zeolite properties on heats of water sorption of zeolite-$MgSO_4$ and zeolite-$MgCl_2$ composites were also compared by Whiting et al. [19], and $MgCl_2$ composites offered a better heat release upon hydration in comparison to that of $MgSO_4$ composites. What's more, Posern and Kaps [29] studied the heat sorption of attapulgite granulate impregnated with mixture of $MgSO_4$ and $MgCl_2$ hydrates, which was to take advantages of high deliquescence relative humidity (DRH) of $MgSO_4$ to avoid salt melting and fast reaction rate of $MgCl_2$ to achieve high sorption ability and high temperature lift. Herein, the composite materials showed a better performance than any single material. The hydration behaviors of $MgSO_4$ hydrates impregnated in porous glass with different pore sizes were also investigated by Linnow et al. [26] and Posern et al. [27]. It was found that the mechanism and kinetics of water sorption depended highly on pore size, salt content, as well as climatic conditions.

Previous investigations based on salt hydrate-porous matrix composites mainly focused on hydration behaviors on small samples. Some important knowledge, which is valuable to understand the mechanism and develop the technology of sorption heat storage based on composites, has not been fully gained. Especially, the effects of reaction temperature and gas humidity on the composites hydration behavior, as well as the hydration performance of a macro-scale reactive bed using composites, need to be further investigated. This work thus set out to gain a deeper understanding of the hydration behavior employing zeolite-$MgSO_4$ composites for long-term heat storage under various reaction conditions. Zeolite is chosen as the supporting porous matrix due to its good water adsorption ability and its capability of working at high temperatures. The composites hydration behavior was first evaluated by measuring the water uptake in a constant temperature & humidity chamber under different reaction temperatures and humidity. Then the composites were tested in a macro-scale reactor to investigate the heat discharge performance under various flow rates and humidity. The cycling stability and the energy efficiency of the reactor were also analyzed.

2. Materials and methods

2.1. Sample preparation

The zeolite-$MgSO_4$ composites were prepared using the infiltration method, involving impregnation of magnesium sulfate into zeolite matrix using aqueous solutions of $MgSO_4$ ($MgSO_4$ dissolved in distilled water). The 13X, 3A, 4A zeolite molecular sieves (from Tianjin Guangfu Fine Chemical Research Institute, Q/12NK 4021-2013) were used, which were pelletized in beads of 2–3 mm diameter. The zeolite beads were immersed in $MgSO_4$ solutions with different mass fractions of 10% and 20%. After stirring thoroughly and immersing for 12 h, the zeolite beads were filtered and dried in air for 4 h. Then the impregnated zeolite beads were heated in a muffle furnace at 150 °C for 4 h and then 300 °C for 2 h, respectively. After the above treatment, the sample mass became stable and the materials were dehydrated completely.

After the above sample preparations, the composites were weighted, and the loaded mass fractions of $MgSO_4$ in the composites were calculated, as shown in Table 1. It can be seen that the mass contents of $MgSO_4$ depended on both the zeolites and the $MgSO_4$ solutions. With the same $MgSO_4$ solution, the mass content of $MgSO_4$ was the largest for zeolite 3A, while it was the smallest for zeolite 13X, which was most likely due to the different pore sizes of zeolites. The pore sizes of zeolite 3A, 4A, and 13X are 0.3 nm, 0.4 nm and 1 nm, respectively. Therefore, it seems that more $MgSO_4$ could be loaded by zeolite with smaller pore size. This is possibly due to that $MgSO_4$ is more difficult to enter into the pores with smaller size, and thus is mainly dispersed on the external surface of zeolite.

Table 1
Mass contents of $MgSO_4$ in different zeolites.

Mass fraction of $MgSO_4$ in solution	Zeolite 3A	Zeolite A	Zeolite 13X
10%	7.83%	3.92%	2.43%
20%	14.16%	10.17%	9.27%