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Micro-scale thermodynamic and kinetic analysis of a calcium chloride methanol system for process cooling

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Abstract

Calcium chloride methanol addition compounds are promising sorbent candidates, which can not only be used for thermal energy storage but also for providing evaporative cooling in industrial applications using low-grade heat. The methanolate dissociation occurs within the working temperature range of low temperature cooling systems. Methanol has a low freezing point and high operating pressure and is less toxic and corrosive than ammonia as refrigerant. In solid-gas reactions the overall specific cooling capacity mainly depends on the sorption rate of the reaction. In general the reaction pattern follows a complex mechanism, in which the formation of intermediate phases and structural changes might occur. In this study a comprehensive micro-scale analysis on the effect of the methanol partial pressure, the thermal history of the calcium chloride, the dissociation temperature and subsequent sorption-desorption cycling on the sorption rate has been carried out. Results show that thermodynamic conditions as well as the thermal history and physicochemical properties of the material have a great influence on the sorption rate, whereas only a marginal dependence between the regeneration temperature and the sorption process was observed.

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Keywords: Refrigeration, calcium chloride, methanol, TGA/DSC, kinetics, cycle stability

1. Introduction

Continuously increasing anthropogenic emissions contribute substantially to global warming. A major cause of rising global temperatures are CO₂ emissions emitted from industrial process refrigeration and air-conditioning. For process cooling conventional vapour compression refrigeration systems are most commonly being used, which are energy intensive and usually contain the environmentally critical and

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hazardous refrigerant hydrofluorocarbons (HFCs). In 2015, the European Union has adopted a new regulation on the restriction and limitation of the consumption of these fluorinated gases (F-gases) favouring the use of alternative, climate-friendly refrigerants [1]. The challenge of heat and fluorinated greenhouse gas reduction can be addressed by supplying cooling energy produced from waste heat-driven chemisorption systems. These systems, which are based on reversible chemical solid-gas reactions, demonstrate superior advantages compared with vapour compression, physisorption and absorption technologies [2,3]. The most widely and comprehensively studied alternative cooling systems have been adsorption refrigeration machines that use physisorption processes [2]. Physisorption or physical adsorption is generated by van der Waals forces. These are induced by dipole interactions between the molecules of the working fluid (adsorbate) and the surface of the polar substance (adsorbent). Physisorption results in weak, long-range attractive forces and low interaction energies and accordingly to low cooling capacities. Typical physisorption adsorbent materials are synthetic silica gels and zeolites. However, chemisorption is associated to strong chemical, short-range bonding resulting in the formation of stable adsorbate-adsorbent complexes. The observed enthalpies of formation and associated cooling capacities are comparatively high. The most common applied sorbents are metal halides such as calcium chloride. Chemisorption machines feature flexible operating conditions, low regeneration temperatures, non-delayed and time-decoupled supply of cooling [4]. Due to optional modular configuration and few moving parts these systems are easy-to-transport and highly attractive for both stationary and mobile applications. Additionally, the use of chemisorption systems can improve the energy efficiency by combining the production of heat and cold energy in integrated systems. At present no chemical-reaction-based refrigeration machine is commercially available [5]. Closed thermochemical sorption refrigeration machines basically consist of a sorption-desorption cycle. During the sorption phase, the refrigerant is chemically bound to the solid sorbent. This exothermic process is also referred to as discharging mode as the heat of reaction is released which causes a pressure drop within the system. As a result the fluid evaporates and absorbs surrounding heat below the ambient temperature producing a refrigerating effect. In the reverse process, which has an endothermic character, the sorption material can be regenerated by using low-level heat. Separation of the reaction products guarantees loss-free and infinite energy storage. Various reaction system types have been investigated in the last decades [3,6]. Data on the sorption-desorption characteristics of inorganic metal salt/ammonia systems are widely available at micro- and macro-scale, whereas the reaction of salts with alcohol has only been studied in casual manner. In cold energy storage the major system performance indicators for identifying and comparing different reaction system types at material level are the refrigerant uptake, the sorption rate, the energy storage capacity and the so-called specific cooling power (SCP). Systems using chemical reactions exhibit the highest cooling capacity among the various refrigeration systems as chemisorption involves higher energy compared to absorption and physisorption because of the associated formation of chemical bonds. Since chemical reactions generally follow a complex reaction mechanism proceeding via intermediate phases and are mainly affected by the reaction temperature, the partial pressure of the reactant and the alcoholate state, possible morphological and structural changes might occur during subsequent sorption-desorption cycling [7,8]. These changes might distinctively influence the kinetics and reversibility of the reaction. This paper will focus on a comprehensive micro-scale analysis of the dependency of the partial pressure, the dissociation temperature and the nature and thermal history of the reaction pair calcium chloride and methanol on the sorption kinetics under practical conditions. Cycle-dependent changes in the alcohol sorption and associated enthalpies of reaction were measured and compared. In a short-term cycling test the stability of the chosen reaction pair was evaluated.

2. Experimental section

2.1. Materials

The tested substances calcium chloride (Merck) and methanol (Merck) were waterfree and of high purity grade (Ph.Eur.). Methanol (CH_3OH) was selected as refrigerant due to its high operating pressure, low regeneration temperature and low freezing point, which are necessary for cold storage applications. Moreover, CH_3OH is a strong Lewis base with a high affinity to metal salts and less steric effects than other straight-chain primary alcohols such as ethanol or propanol. Calcium chloride (CaCl_2) was selected as it is inexpensive, easily available and chemically stable. The methanolate dissociation occurs within the working temperature range of low temperature cooling systems. Calcium halides are soft Lewis acids and hence form with alcohol, analogous to salt hydrates, strong salt-alcohol complexes.

2.2. Characterisation

Thermal behaviour, sorption kinetics and cycle stability of $\text{CaCl}_2\text{-CH}_3\text{OH}$ addition compounds were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques. A modified TGA/DSC 1 device from Mettler Toledo was used for all measurements. CH_3OH sorption and desorption involve changes in sample weight and enthalpy over time that can simultaneously be detected and recorded with high precision. The TGA/DSC was connected to a bubbler system in order to measure dynamic methanol vapour sorption. A thermostat maintained the water bath of the bubbler system at a constant temperature of 21 °C. For sorption experiments dry nitrogen was used as carrier gas and purged through the bubbler system to produce a CH_3OH -saturated nitrogen flux. The flow rates and hence the CH_3OH partial pressures ($p_{\text{CH}_3\text{OH}}$) were regulated by an external gas controller. During both sorption and desorption runs the whole apparatus was flushed with dry nitrogen. Specimen of 10 mg were evenly placed into a 70 μl alumina crucible and characterised with different temperature programmes. Sorption equilibrium tests were carried out at 25 °C at three different CH_3OH partial pressures ($p_{\text{CH}_3\text{OH}} = 6.8/8.2/9.1$ kPa) over 240 min. The dissociation pattern was studied by scanning the samples from 25 °C to 150 °C. In a quick multi-step screening the influence of the regeneration temperature on the CH_3OH sorption characteristics and sorption kinetics was determined. The discharging-charging process consisted of the following segments: (1) discharging at 25 °C, (2) charging at 90 °C, (3) discharging at 25 °C, (4) charging at 100 °C, (5) discharging at 25 °C and (6) charging at 150 °C. The discharging time was set to 60 min and the $p_{\text{CH}_3\text{OH}}$ was maintained at 6.8 kPa. The short-term cycling test was performed at the same sorption conditions as the multi-step screening. In the desorption behaviour study the temperature was elevated to 180 °C, which equals the maximum temperature available under field conditions. The same heating rates (3.0 K/min) were applied to each desorption measurement. The CH_3OH uptake and the specific cooling power were calculated from the weight gain and weight gain rate (in the following also referred to as sorption rate). The cooling capacity was derived from the manual integration of the heat fluxes as a function of time using the Mettler Toledo STARE. Software 11.00a.

3. Results and discussion

In sorption equilibrium tests the maximum sorption of CaCl_2 towards CH_3OH was determined. The total amount of sorbed CH_3OH was calculated to be around 3 mol per mol anhydrous CaCl_2 , wherein only 2 mol of CH_3OH are strongly coordinated to 1 mol of anhydrous CaCl_2 . About 1 mol is physically attached to the CaCl_2 surface. The experimental percentage weight losses are close to the theoretical values. The proposed chemical composition is therefore $\text{CaCl}_2\cdot 2\text{CH}_3\text{OH}$, which is in accordance with the literature [9,10]. CaCl_2 is a hygroscopic substance with a high deliquescence in an alcohol saturated atmosphere and therefore tends to an over-stoichiometric uptake of CH_3OH . A thermodynamic control of the reaction is mandatory and can be achieved by choosing an appropriate pressure-temperature

relationship and reaction time. The methanolate decomposition ranges from 80–143 °C. Between 75–85 % of the total weight is lost below 118 °C with peak temperatures around 100 °C. Two overlapping decomposition stages are observed. Tailing indicates the removal of both non-coordinated and coordinated methanol below 80 °C. By applying lower heating rates or working under vacuum, the peaks temperature could be shifted towards lower regeneration temperatures. The specific cooling power is defined as the capacity of a system to produce a refrigerating effect in relation to the initial sorbent weight and was estimated from the maximum sorption rate. The maximum sorption rate was derived from the first derivative of the weight loss curve. In Fig. 1 the sorption rate was plotted against the extent of conversion. For a better comparison the conversion is related to a total sorption of 2 mol of CH₃OH per mol CaCl₂ for each sample measured. It can be seen that the higher CH₃OH partial pressure, the higher the sorption rate. The reaction can be accelerated so that the maximum chemical sorption is reached in a shorter time. In the initial phase the sorption rate rapidly increases over a narrow time frame and drops quickly. In the further course of the reaction the sorption rate increases only slightly and finally gradually decreases until the chemical reaction is completed. The sorption of CH₃OH on CaCl₂ might follow a 2-step process as two sorption rate peaks can be observed. According to the experimental data a polynomial relation between the sorption rate and the CH₃OH partial pressure is assumed. The decelerated course of the sorption towards the end of the reaction might indicate a temperature gradient and heat transfer limitation. The sorption rate also depends on various other variables such as the sample's initial weight, structure, particle size, thermal history and porosity that might have different effects. In a comparative study the influence of the pre-treatment method on the CH₃OH uptake at 6.8 kPa was evaluated and is also shown in Fig. 1. Heating the sample slows down the sorption reaction resulting in a lower sorption rate and also a more stable final CaCl₂-CH₃OH-adduct as less physisorption is observed compared to the untreated starting material. For further investigations a CH₃OH partial pressure of 6.8 kPa was chosen as the corresponding temperature is equal to the condenser temperature.

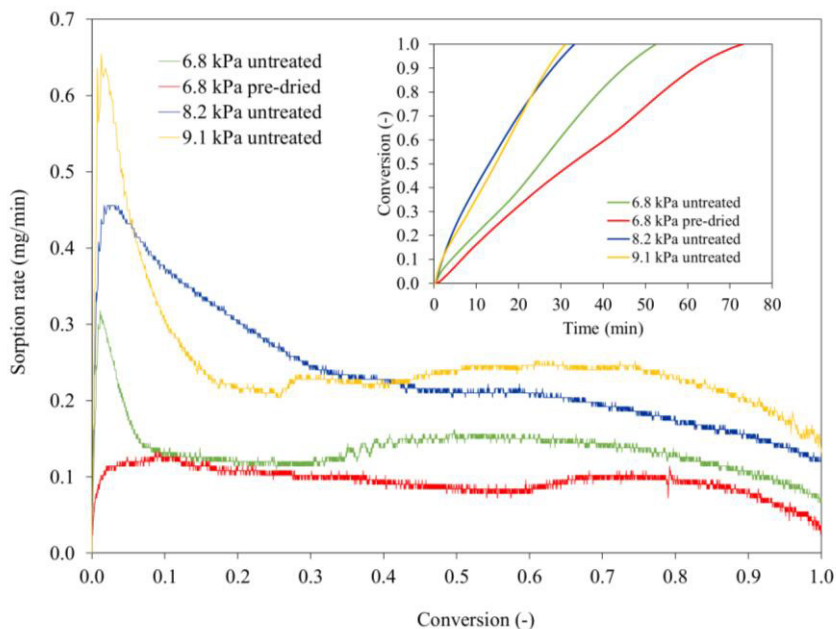


Fig. 1. The change in the sorption rate over the course of a reaction (extent of conversion) at different CH₃OH partial pressures.

The effect of the desorption temperature, also referred to as regeneration temperature, was examined in a quick multi-step screening. The sample as received without any thermal pre-treatment was used. The CH_3OH sorption is constant over the first two cycles. As part of the sorbed CH_3OH is released during stabilisation at 25 °C physical sorption seems to appear. In the last cycle a slightly lower CH_3OH uptake was measured. In total, sorption and desorption values are equal. Despite not being fully demethanolated the re-uptake of CH_3OH is the same in each cycle which leads to the assumption that an equilibrium state has been reached under the applied measurement conditions. Below 90 °C and 100 °C the $\text{CaCl}_2 \cdot n\text{CH}_3\text{OH}$ decomposes in one endothermic stage with a peak temperature at 83 °C and 99 °C, respectively, whereas above 100 °C two stages are present as aforementioned. The associated peak temperatures are 94 °C and 135 °C. The sorption rates (0.19/0.21/0.20 mg/min) are constant over three cycles, but appear to be slightly lower than the ones measured in the equilibrium test. Therefore the corresponding calculated cooling capacities were respectively lower. Other variables such as the initial sample mass and its porosity might also account for the lower value. The data reveals that the regeneration temperature affects the sorption rate only marginally. In order to validate this hypothesis a detailed characterization was carried out. The short-term performance of the CaCl_2 - CH_3OH -adduct was tested in a cycle stability test consisting of 18 consecutive sorption-desorption cycles. Information on the cycling behaviour is of great importance as changes in the morphology and coordination structure of the methanolate and physical effects such as solvation and aggregation might occur that probably affect the sorption kinetics. The sample was dried at 105 °C prior to cycling. Due to the thermal pre-treatment the sample had to be activated resulting in an increase of the CH_3OH -sorption over the first few cycles. As the amount of chemically and physically sorbed CH_3OH varies greatly at the beginning, the formation of metastable phases is assumed. Non-coordinated CH_3OH is evolved during stabilisation until a chemical equilibrium is reached and desorption begins. From the 10th cycle onwards sorption and desorption are constant and the amount of physically sorbed CH_3OH is reduced. Even though the sorption reaction proceeds fast at the beginning of the methanolation phase indicated as a steep curve. The reaction decelerates with time and with higher extent of conversion. The high desorption temperature of 180 °C probably has only a marginal effect on the sorption characteristics and the sorption rate as seen in Fig. 2.

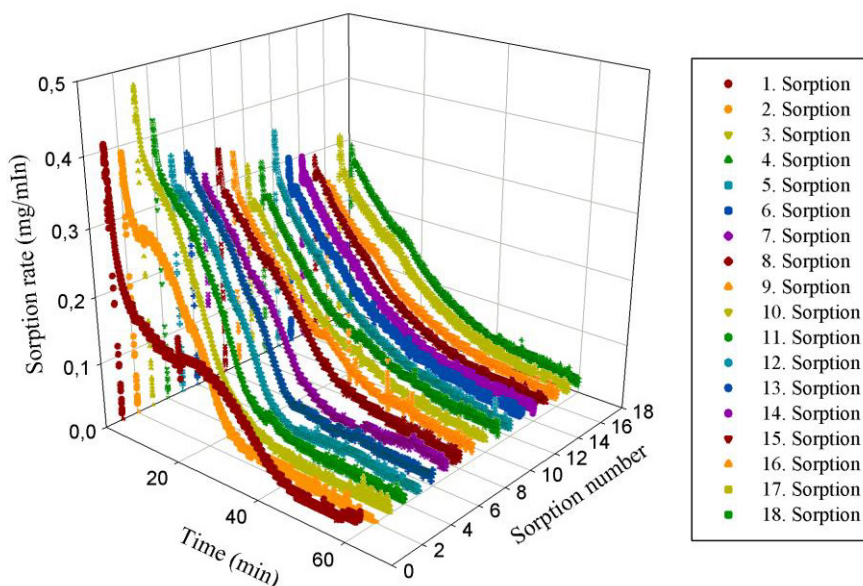


Fig. 2. Change of the sorption rate with subsequent short-term sorption-desorption cycling.

In the first and second sorption process the CH₃OH uptake is lower compared with the third one, in which the highest sorption rate is attained. The subsequent maximum methanolation rates are ranging from 37-29 mg/min and show apparently a decreasing tendency with increasing number of cycles despite constant initial sample. The results indicate that cooling can be provided at a constant level at least during the initial discharging-charging cycles. The decomposition pattern, however, is inconsistent. The decomposition peaks vary within a narrow range from cycle to cycle and seem to be shifted with further cycling.

4. Conclusion

The usability of calcium chloride methanolates has been tested under different experimental conditions. Performance criteria such as methanol uptake, cooling capacity, sorption rate and sorption cooling power remarkably depend on the material's physical properties, nature and thermal history, surface phenomena and process conditions. In solid-gas reactions the sorption rate can be lifted by applying higher methanol partial pressures. It could be shown that the sorption rate of the initial sample is slow and increases with cycling until a constant value with little deviation is reached and proceeds with a decreasing tendency. The desorption temperature seems to have no significant influence on the sorption rate. Substitution of coordinated methanol molecules by water molecules in salt methanolates was considered to be neglected at micro-scale in this study. In laboratory scale investigation the test reactor system should be hermetically sealed.

Acknowledgements

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Biography

Kathrin Korhammer is a PhD candidate at Leuphana University of Lüneburg. Her research focuses on the fundamentals of various salt-water and salt-alcohol systems as well as composite sorbents and binary mixtures for heating and cooling applications. She holds a degree in Chemical Engineering from KIT.