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Reaction of calcium chloride and magnesium chloride and their mixed salts with ethanol for thermal energy storage

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Abstract

The use of thermochemical energy storage systems increasingly gains interest in order to meet the energy targets of the European renewable energy directive. In this study the suitability of calcium chloride, magnesium chloride and mixed salt ethanolates as heat storage materials for practical implementation was determined by investigating specific thermodynamic properties and estimating the materials' lifetime at various operating conditions. It was proven that the reaction of the before mentioned metal salts with ethanol depends on the applied ethanol vapour pressure. The ethanol sorption increased in the following order: $MgCl_2 < CaCl_2 < 2CaCl_2{*}MgCl_2$. The enthalpies followed the same sequence. Over-stoichiometric ethanol uptake, in particular for $CaCl_2$ and $2CaCl_2 * MgCl_2$ with increasing C_2H_5OH vapour pressure, was observed. However, the reaction systems $CaCl_2$-C_2H_5OH and $2CaCl_2{*}MgCl_2$ -C_2H_5OH showed the best sorption properties and cycle stability and thus have a great potential for low-grade thermal energy storage as well as cold storage due to their low reaction temperatures in comparison with salt-water-systems. In general, physically mixing of single salts from the same family with different chemical properties leads to superior thermal behaviour with higher heat storage capacities and material stabilities.

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Keywords: Thermal energy storage; TCM; calcium chloride; magnesium chloride; mixed salts, ethanol, TGA; sorption; cycle stability; reaction kinetics

1. Introduction

In the transformation process to a more environmentally friendly heat energy conservation and recovery the advancement of clean technologies can help meet the stricter government regulations on carbon dioxide emissions.

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Low-grade heat storage systems using reversible chemical gas-solid reactions have the advantage of balancing weather-driven supply fluctuations and time-decoupled demand of heat, which is for instance produced as by-product during power generation from renewable energy sources. The operating temperature usually ranges from 30-150 °C. In the building sector the excess heat can be recovered and re-used for domestic space heating or hot water production. Compared to conventional technologies such as sensible and latent heat storage applications, thermochemical heat storage ensures loss-free, long-term, compact and cost-efficient storage of low-carbon heat.

In the last decades different binary reaction systems have been investigated by numerous scientists. In the low-temperature range inorganic metal salts and alcohols have been identified as potential working pairs. The underlying reaction scheme is given in equation (1):

$$MX(s) + nR - OH(g) \rightleftharpoons MX \cdot nR - OH(s) + \Delta_R H \tag{1}$$

During the exothermic discharging reaction the solid inorganic metal salt MX reacts with the gaseous alcohol $R - OH$ forming the salt alcoholate $MX \cdot nR - OH$, where n is the stoichiometric number of alcohol molecules sorbed, and releasing the stored heat $\Delta_R H$. The reverse reaction (charging reaction) is endothermic. Heat energy must be supplied to surpass the activation energy. Fast reaction kinetics, precise temperature control and high reaction enthalpies make salt-alcohol-pairs an advantageous option. Moreover, in comparison to reaction systems with water as reaction partner they exhibit lower charging temperatures.

Up to now, the reaction of inorganic salts with alcohol for thermal energy applications has only drawn a few researchers' attention. Most research articles and publications report on the synthesis of salt alcoholates of different stoichiometric ratios and their characterisation via calorimetric and thermogravimetric analysis and X-ray diffraction. For instance, calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$ form various ethanolates with ethanol (C_2H_5OH), in particular $CaCl_2 \cdot 1C_2H_5OH$, $CaCl_2 \cdot 2C_2H_5OH$, $CaCl_2 \cdot 3C_2H_5OH$, $CaCl_2 \cdot 4C_2H_5OH$ and $MgCl_2 \cdot C_2H_5OH$ according to Iyimen-Schwarz and Lechner, Mar and Carling and Parker et al. [1,5,6]. The research group around Aristov at the Moscow State University has mainly carried out studies on the ethanol/methanol sorption and desorption behaviour of modified salt-porous-carrier-composites in gram-scale experiments [2,3]. Micro-scale thermogravimetric analysis has been conducted by Iyimen-Schwarz and Lechner, they have made pioneering scientific contributions to the usability of salt alcoholates based on $CaCl_2$ and$MgCl_2$ and ethanol for thermal energy storage. They have calculated the energy storage density from the forward and reverse reaction enthalpy determined in dynamic differential calorimetric measurements under vacuum with controlled temperature and alcohol vapour pressure. The total energy yield of the above mentioned reactions of $CaCl_2$ with C_2H_5OH decreased to 65 % after 10 operation cycles, while for the $MgCl_2$- C_2H_5OH -system the total energy yield remained constant at 99 % [1].

However, fundamental and systematic studies on the reaction of $CaCl_2$ and $MgCl_2$ and their mixed salts with C_2H_5OH are still lacking. By physically mixing two different salts of the same family, the overall performance can be improved compared to single untreated salts. Focus of this study is the characterisation of thermodynamic properties and reaction mechanisms as well as the successive cycling behaviour of above mentioned materials by thermal analysis. C_2H_5OH uptake and release and the associated reaction enthalpies have been calculated from single thermogravimetric analysis (TGA) measurements. The C_2H_5OH vapour pressure dependence of the sorption rate has been analysed by applying different flow rates during the sorption process. Preliminary results of desorption kinetics are presented. The model-free Kissinger method has been used to determine the activation energy and pre-exponential factor. A major requirement for use in heat storage systems is a good cycling performance under periodic operation. Thus, the stability of the materials has been examined in cycling tests.

Nomenclature

DSC	differential scanning calorimetry
DTG	differential thermogravimetry
TGA	thermogravimetric analysis
TG/MS	thermogravimetric mass spectrometry

k_{max}	maximum sorption rate (mg/min)
$mass\%$	change in mass (%)
t_{50}	time required to reach a degree of conversion of 50 % (min)
t_{90}	time required to reach a degree of conversion of 90 % (min)
T_{max}	maximum temperature / peak temperature (K)
T	reaction temperature (°C)

Greek symbols

$\alpha(t)$	conversion (1)
β	heating rate (K/min)

2. Experimental section

2.1. Materials

Anhydrous $CaCl_2$ (Ph Eur, Merck), water-free $MgCl_2$ (>98.5 %, Roth) and C_2H_5OH (99.8 %, max. 0.01 % H_2O, Merck) stored over 4 Å binderless molecular sieves Köstrolith® 4ABFK (Chemiewerk Bad Köstritz) were used in this study. $CaCl_2$ and $MgCl_2$ have been chosen because of their environmental benignity, satisfactory C_2H_5OH sorption capacity, low production costs and good economic procurement. C_2H_5OH has been favoured due to its low boiling point, high vapour pressure compared to water and low toxicity. The mixed salt ($2CaCl_2{*}MgCl_2$) was prepared by physically mixing $CaCl_2$ and $MgCl_2$ in the ratio of 2:1 in a glove-box in an inert He-atmosphere. The mixture was thoroughly homogenised using pestle and mortar to ensure a perfect blend, dried under vacuum and stored in sealed sample vials over 4 Å binderless molecular sieves. It is assumed that the mixed salt is a mixture and does not form any compounds during preparation.

2.2. Methods

The sorption and desorption properties, the reaction temperature range, the reaction enthalpies and the cycle stability were determined by using a simultaneous thermogravimetric and differential scanning calorimetric analysis device (TGA/DSC 1) from Mettler Toledo. Open alumina crucibles with a volume of 70 µl were used. All experiments were performed with small milligram quantities (10-12 mg), which were evenly distributed with no packing at the bottom of the crucible. The experimental setup is illustrated in Fig. 1

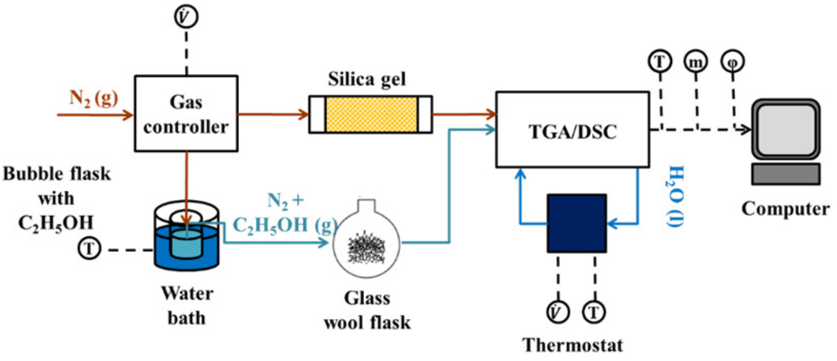

Fig. 1. Experimental setup.

The sorption process (discharging) was performed with an ethanol saturated carrier gas (nitrogen) under atmospheric pressure at 25 °C. The carrier gas was fed with C_2H_5OH by passing it through a bubble flask filled with liquid C_2H_5OH (bubbler system). The water bath temperature of the bubbler system was set to 21 °C to produce ethanol vapour of an equilibrium pressure of 6.2 kPa. For the study on the dependence of the ethanol vapour on the sorption behaviour measurements with different carrier gas flow rates (50 ml/min, 75 ml/min and 100 ml/min) were carried out. During the measurement the reaction chamber was additionally purged with silica-gel dried nitrogen (50 ml/min) to remove released gaseous reaction products and to avoid any side reactions. The time-dependent C_2H_5OH uptake was studied by variation of the ethanolation time. For the kinetic studies and cycling tests the sample was exposed to a C_2H_5OH -saturated gas flux of 50 ml/min for 120 min, which is equivalent to an alcohol partial pressure of 3.1 kPa. Between the sorption and desorption phase the sample was stabilised for 60 min at 25 °C. In the desorption process the sample was heated to 180 °C with a heating rate of 3 K/min and stabilised at the final temperature for about 30 min while flushing it continuously with silica-gel dried nitrogen. In the last step the sample was cooled down to the initial temperature with a temperature ramp of -10 K/min. Kinetic data have been obtained under non-isothermal conditions using different heating rates (1 K/min, 3 K/min, 5 K/min and 10 K/min). Measurements with more than 20 cycles of operation were carried out for life cycle analysis. Prior to each measurement the specimen were thermally pre-treated to remove any residual moisture and impurities. The pre-treatment of the sample has a tremendous impact on its sorption behaviour towards the reactant, in particular in the first number of cycles.

Changes in mass and heat flux were recorded online as a function of time and temperature. The precision of the microbalance is given as ± 1.0 µg. Temperature and heat flux referring to a reference material were simultaneously detected. The heat power can be determined to a precision of ± 0.1 mW. Experimental data were analysed by the Mettler Toledo STARe® software 11.00a. The reaction enthalpies were obtained by integrating the reaction peak area and were also referred to one mole of anhydrous sample. All measurement curves presented in this study were blank curve corrected in order to compensate buoyancy effects. The C_2H_5OH sorption in mole was calculated from the difference of the initial and final sample mass and was referred to one mole of anhydrous sample. The standard uncertainties of the calculated mass and enthalpy are 10-20 %. The change in mass $mass\%$ was calculated as follows:

$$mass\% = \frac{m_t}{m_0} \times 100\% \tag{2}$$

where m_0 is the initial sample mass and m_t the mass at the reaction time t. The total conversion $\alpha(t)$ was calculated using the following equation:

$$\alpha(t) = \frac{m_0 - m_t}{m_0 - m_1} \tag{3}$$

where m_0 is the initial sample mass, m_t the mass at the reaction time t and m_1 the finial sample mass.

3. Results

As the samples might undergo slight changes during storage and handling the pure salts as received and mixed salts were heated to 400 °C with a temperature ramp of 10 K/min to gain information on the actual water content and decomposition pattern. As assumed the water content measured was slightly higher than given by the supplier. Traces of coordinated water cannot properly be avoided in technical applications and thus were neglected for the evaluation of the materials sorption behaviour. The chemical formula of the received water-free $CaCl_2$ and $MgCl_2$ were calculated to be $CaCl_2 \cdot 0.5H_2O$ and $MgCl_2 \cdot 0.6H_2O$, respectively. The mixed salt $2CaCl_2{*}MgCl_2$, prepared by physically mixing, contained 1.0 mole of H_2O.

3.1. Influence of C_2H_5OH vapour pressure on sorption properties

Both chemicals $CaCl_2$ and $MgCl_2$ and their mixed salts possess good sorption abilities towards C_2H_5OH. The sorption mechanism strongly depends on the C_2H_5OH vapour pressure. The given C_2H_5OH vapour pressures associated to the different flow rates are theoretical values and have been derived from the Antoine-equation. The following results are summarised in Table 1. All values are average values of 5 runs. The results on the time-dependent C_2H_5OH sorption on $CaCl_2$ and $MgCl_2$ at a C_2H_5OH vapour pressure of 3.1 kPa showed that an ethanolisation time of 60 min is not sufficient to reach a sorption equilibrium state. With a total amount of C_2H_5OH sorbed per mole anhydrous $CaCl_2$ or $MgCl_2$ of 0.6 for $CaCl_2$ ethanolates and 0.7 for $MgCl_2$ ethanolates these values are considerably lower than obtained in stoichiometric gram-scale salt ethanolate synthesis or mentioned in the literature. The associated sorption enthalpy of $CaCl_2$ ethanolates (-20 kJ/mol) is lower than the average desorption enthalpy (32 kJ/mol). The sorption enthalpy of $MgCl_2$ ethanolates is -29 kJ/mol, more heat energy is required to induce the decomposition of $MgCl_2$ ethanolates resulting in a higher desorption reaction enthalpy (45 kJ/mol).

Extension of the ethanolation segment resulted in higher ethanol/salt ratios and reactions enthalpies. An average sorption of 1.0 mole C_2H_5OH per mole anhydrous $CaCl_2$ was reached. This value is lower than the theoretical stoichiometric value of 2 moles C_2H_5OH per mole $CaCl_2$ due to the applied measuring method varying from the conditions given in the literature [1,4-5]. By doubling the ethanolation time double the sorption enthalpy (-44 kJ/mol) could be measured. An average desorption enthalpy of 57 kJ/mol was calculated. The energy yield was less than 61 %. Iyimen-Schwarz calculated an average energy yield of 65 % over 10 cycles [7]. Applying vacuum can potentially improve the sorption performance of this reaction system. Working at a higher C_2H_5OH vapour pressure of 3.7 kPa, which equals a flow rate of 75 ml/min, had a low impact on the total amount of C_2H_5OH sorbed by $CaCl_2$. The C_2H_5OH uptake was only 0.3 mole C_2H_5OH per mole $CaCl_2$ higher than at 3.1 kPa. At 4.1 kPa a slight increase in the uptake to a value of 1.7 could be observed. Mar and Carling have suggested the possible existence of both $CaCl_2 \cdot 1C_2H_5OH$ and $CaCl_2 \cdot 2C_2H_5OH$.

Table 1. Sorption characteristics of $CaCl_2$ and $MgCl_2$ and their mixed salt $2CaCl_2{*}MgCl_2$ tested under different measurement conditions. C_2H_5OH sorption and reaction enthalpies are referred to one mole of C_2H_5OH for better comparison.

	$CaCl_2$				$MgCl_2$				$2CaCl_2{*}MgCl_2$		
C_2H_5OH vapour pressure (kPa)	3.1	3.1	3.7	4.1	3.1	3.1	3.7	4.1	3.1	3.7	4.1
Sorption											
Sorption time (min)	60	120	120	120	60	120	120	120	120	120	120
C_2H_5OH uptake (mol C_2H_5OH /mol salt)	0.6	1.0	1.3	1.7	0.7	0.9	0.7	1.2	3.2	3.7	4.4
Enthalpy (kJ/mol salt)	-20	-44	-73	-79	-29	-59	-40	-65	-181	-201	-205
Enthalpy (kJ/mol C_2H_5OH)	-33	-44	-56	-46	-41	-66	-57	-54	-57	-54	47
Desorption											
C_2H_5OH release (mol C_2H_5OH /mol salt)	-0.5	-0.8	-1.0	-1.2	-0.7	-0.8	-0.6	-1.1	-2.8	-3.0	-3.0
Enthalpy (kJ/mol salt)	32	57	63	59	45	36	32	48	149	145	159
Enthalpy (kJ/mol C_2H_5OH)	64	72	63	49	64	45	53	44	53	48	53
Energy yield (%)	52	61	89	94	64	146	108	122	108	113	89

The normalised desorption reaction enthalpies are also listed in Table 1. They are partially higher than the sorption reaction enthalpies. At 3.1 kPa, the maximum amount of C_2H_5OH sorbed by anhydrous $MgCl_2$ was only 0.9 in the extended sorption test. The prolonged exposure of $MgCl_2$ to C_2H_5OH resulted in an increased sorption enthalpy of -59 kJ/mol. The calculated energy yield was with 145 % surprisingly high. Due to its chemical nature $MgCl_2$ has a higher binding affinity towards C_2H_5OH than $CaCl_2$ and thus stronger intermolecular interaction between these reactants are assumed. The data proposes that $MgCl_2$ forms with C_2H_5OH only $MgCl_2 \cdot 1C_2H_5OH$ compounds. A decline of the sorption capacity at 3.7 kPa compared to a lower C_2H_5OH vapour pressure of 3.1 kPa, and a jump at 4.1 kPa might be explained by an emerging drop in the sorption capacity and associated reaction enthalpy with increasing number of cycles at 3.1 kPa. The formation of gaseous side products is assumed. Iyimen-Schwarz has gained a sorption reaction enthalpy of -17 kJ/mol for both $MgCl_2$ and $CaCl_2$ mono-ethanolates in TGA analysis experiments over 10 cycles [7]. The desorption enthalpies measured were with 19 kJ/mol and 26 kJ/mol much lower than reported in this study as the measurements were performed under vacuum at different conditions. Reactions are accelerated under vacuum and peak temperatures of desorption steps are shifted towards lower temperatures.

The sorption reaction enthalpy for $CaCl_2 \cdot 2C_2H_5OH$ and the enthalpy of decomposition for $CaCl_2 \cdot 1C_2H_5OH$ calculated by Carling et al. (-44 kJ/mol) and Mar and Carling (51 kJ/mol) are in closer agreement with the values of this work, which are ranging between -44 and -79 kJ/mol [4,5].The latter enthalpy was derived from second-law analysis. The ethanolation and deethanolation enthalpies referred to one mole of C_2H_5OH for $MgCl_2$ ethanolates measured by thermal analysis differ from enthalpies obtained from laboratory experiments, which were significantly lower. The mixed salt $2CaCl_2{*}MgCl_2$ showed an excellent C_2H_5OH uptake. The C_2H_5OH capacity exceeded a value of 3.0 mole C_2H_5OH per mole anhydrous $2CaCl_2{*}MgCl_2$. The sorption enthalpy was remarkable. It is 6-9 times higher than the sorption enthalpy of pure $CaCl_2$ and $MgCl_2$. The overall energy yield of 108 % is satisfying. The variation in the sorption and desorption enthalpy for $MgCl_2$ and $2CaCl_2{*}MgCl_2$ and given efficiencies over 100 % might be due to deviations in the enthalpy integration. The C_2H_5OH sorption increased at higher C_2H_5OH vapour pressure. During stabilisation at 25 °C between 0.4-1.4 mole C_2H_5OH were lost, which was probably non-coordinated C_2H_5OH. The higher the C_2H_5OH vapour pressure the more C_2H_5OH was released. Therefore, the total amount of coordinated, chemically sorbed C_2H_5OH was about 3.0 and seemed pressure independent.

Mass loss observed during the subsequent stabilisation phase regarding $CaCl_2$ ethanolates indicates that an ethanolation time of 60 min might be too short for the C_2H_5OH to be incorporated into the crystal lattice and to be strongly bonded to the $CaCl_2$. Extended ethanolation at higher C_2H_5OH vapour pressure led to an even higher C_2H_5OH desorption during stabilisation. A steric hindrance is considered to occur between the C_2H_5OH and the calcium ion due to its higher cation size compared with the magnesium ion and thus a slower solvation process is assumed. However, the release of small amounts of C_2H_5OH from $MgCl_2$ ethanolates at 25 °C is negligible. At lower temperatures mainly non-coordinated physically sorbed C_2H_5OH is given off. For proper validation of the reproducibility of above mentioned results repeated measurements have to be carried out.

3.2. Kinetic analysis of sorption process

The effect of the C_2H_5OH vapour pressure on the sorption behaviour of the pure and mixed salts was studied by applying different C_2H_5OH flow rates (Table 2). In order to compare the reaction kinetics of these substances the time required to achieve a conversion of 50 % (t_{50}) and 90 % (t_{90}) was calculated.

Table 2. Dependence of the sorption kinetics of the tested salts on the C_2H_5OH vapour pressure.

	3.1 kPa			3.7 kPa			4.1 kPa		
	t_{50} (min)	t_{90} (min)	k_{max} (mg/min)	t_{50} (min)	t_{90} (min)	k_{max} (mg/min)	t_{50} (min)	t_{90} (min)	k_{max} (mg/min)
$CaCl_2$	35	77	0.14	27	61	0.16	25	62	0.26
$MgCl_2$	38	100	0.07	33	92	0.12	52	106	0.11
$2CaCl_2{*}MgCl_2$	27	72	0.12	25	68	0.14	28	83	0.16

In the thermograms of the tested materials are shown in Fig. 2 to Fig. 4. The sorption behaviour of the pure salts $CaCl_2$ and $MgCl_2$ and the mixed salt $2CaCl_2{*}MgCl_2$ were varying in terms of the applied C_2H_5OH vapour pressure. Despite a higher C_2H_5OH uptake at higher C_2H_5OH vapour pressure (see Table 1), the sorption of C_2H_5OH on $CaCl_2$ could be speed up as the C_2H_5OH vapour pressure increased resulting in a higher maximum sorption rate k_{max}. The sorption rate is defined as the amount of C_2H_5OH (mg) sorbed in one unit of time (min).

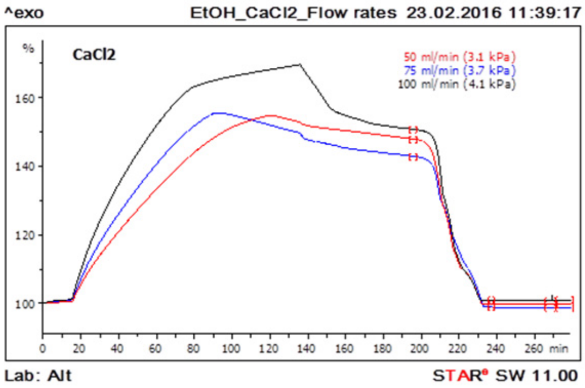

Fig. 2. Dependence of C_2H_5OH vapour pressure on C_2H_5OH sorption on $CaCl_2$. The sorption referred to the mass of the anhydrous salt (%) is plotted versus the reaction time (min).

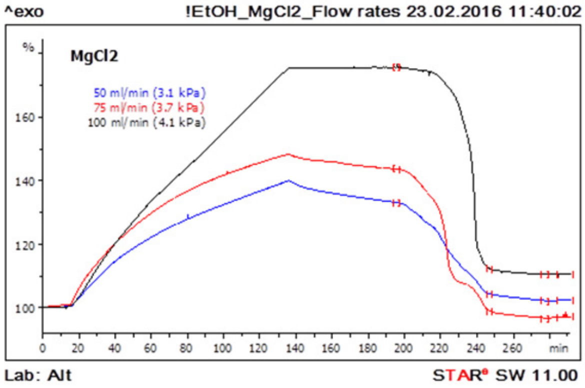

Fig. 3. Dependence of C_2H_5OH vapour pressure on C_2H_5OH sorption on $MgCl_2$. The sorption referred to the mass of the anhydrous salt (%) is plotted versus the reaction time (min).

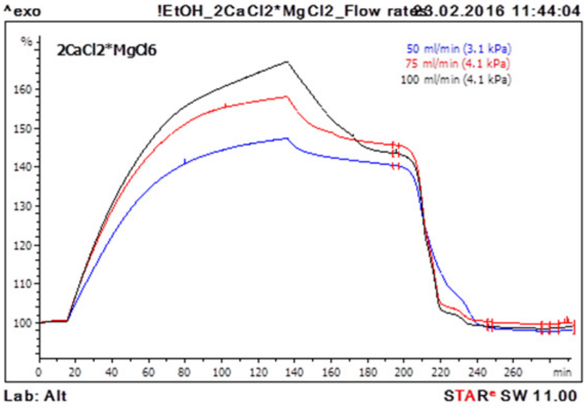

Fig. 4. Dependence of C_2H_5OH vapour pressure on C_2H_5OH sorption on $2CaCl_2{*}MgCl_2$. The sorption referred to the mass of the anhydrous salt (%) is plotted versus the reaction time (min).

Maximum sorption capacity was reached in less than 100 min in experiments at 3.1 kPa and 3.7 kPa. An over-stoichiometric uptake of C_2H_5OH was observed. This physically sorbed C_2H_5OH was immediately released. $CaCl_2$

showed the fastest reaction with the highest sorption rate compared to $MgCl_2$ and $2CaCl_2{*}MgCl_2$. For $MgCl_2$ the fastest reaction occurred at 3.7 kPa as less C_2H_5OH was sorbed (0.7 mole C_2H_5OH per mole $MgCl_2$) in comparison to the C_2H_5OH uptake at 3.1 kPa (0.9 mole C_2H_5OH per mole $MgCl_2$) and 4.1 kPa (1.2 mole C_2H_5OH per mole $MgCl_2$). The mixed salt possesses properties which are between the properties of its individual elements. The sorption rate was increasing with increasing pressure. However, at a pressure of 4.1 kPa the reaction proceeded the slowest.

3.3. Desorption behavior and kinetics

A literature study revealed that information about the thermal desorption behaviour and kinetics of $CaCl_2$ and $MgCl_2$ ethanolates is scarce. The release of C_2H_5OH from $CaCl_2$ and $MgCl_2$ ethanolates proceeded in three overlapping stages, which cannot be separated. The deethanolation process was completed below 150 °C. The deethanolation of $2CaCl_2{*}MgCl_2$ followed a complex mechanism. C_2H_5OH is lost in up to 4 stages which are not clearly separable. In the first few cycles the stepwise desorption temperatures were varying over a small temperature interval, while with increasing cycle number C_2H_5OH was desorbed at similar peak temperatures. DTG plots were taken into account for the division of the stages. For $2CaCl_2{*}MgCl_2$ ethanolates the desorption steps and hence desorption peaks varied in the first few cycles, but at higher cycle numbers the peaks and peak temperatures were congruent.

As demonstrated in Fig. 5 the heating rate affects the pattern of the reaction. The increase of the heating rate resulted in the shift of the desorption peaks towards higher temperatures (Fig. 5). Data on desorption reaction kinetics is of great importance for the determination of the material's thermal behaviour and the prediction of its stability in applications under periodic conditions. Results from non-isothermal differential thermal analysis measurements carried out at multiple heating rates β were used to calculate the activation energy E_A and the pre-exponential factor A by model-free Kissinger method as follows:

$$ln\frac{\beta}{{T_{max}}^2} = ln\frac{A \cdot R}{E_A} - \frac{E_A}{R \cdot T_{max}} \tag{4}$$

where T_{max} is the maximum or peak temperature corresponding to the maximum mass loss peak. R is the universal gas constant. The maximum or peak temperature was gained by integrating the first derivative of the mass curve. The Kissinger method is based on the assumption that the maximum temperature of the maximum mass loss rate is a function of the heating rate. By plotting $ln\frac{\beta}{{T_{max}}^2}$ against $\frac{1}{T_{max}}$ and fitting a linear regression line to the data values (Fig. 6) E_A and A can be derived from the slope and intercept of equation (4).

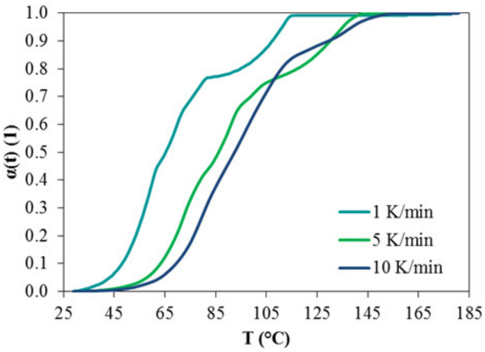

Fig. 5. Example of the degree of conversion over temperature at different heating rates for $CaCl_2{\cdot}1.2C_2H_5OH$.

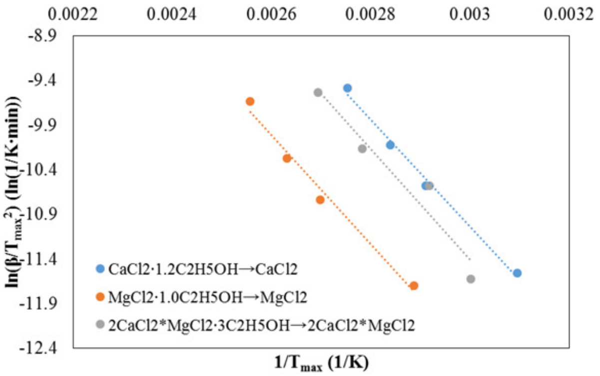

Fig. 6. Determination of desorption kinetic parameters by Kissinger analysis.

For desorption of 1.2 moles C_2H_5OH from 1 mole anhydrous $CaCl_2$ an activation energy of 50 kJ/mol was needed. The corresponding pre-exponential factor was calculated to be 6.48·10^6 1/min. Activation energies of 46 kJ/mol and 52 kJ/mol were obtained for $MgCl_2 \cdot 1C_2H_5OH$ and $2CaCl_2{*}MgCl_2{\cdot}3C_2H_5OH$, respectively. The pre-exponential factors were 3.13·10^5 1/min and 7.52·10^6 1/min. The activation energies for desorbing C_2H_5OH are mostly congruent to the deethanolation enthalpies stated in 3.1. In general, the activation energy is equal to the minimum heat that can be stored or liberated. The activation energy obtained from the Kissinger equation is mainly valid for the rate-determining step. As the desorption of C_2H_5OH from salt ethanolates is a multi-step process as mentioned before, the activation energy changes in the course of the reaction with the degree of the conversion. A comparative study using different determination methods is currently ongoing.

3.4. Cycle stability

One of the most important parameters for determining the suitability of thermochemical materials for heat storage applications is the material's lifespan. The runtime performance of a storage material can be predicted on micro-scale by long-term cycling tests. First stage cycling experiments have shown that the used substances possess stable ethanol uptakes over 5 sorption-desorption cycles. Thus, further experiments with extended cycles have been performed.

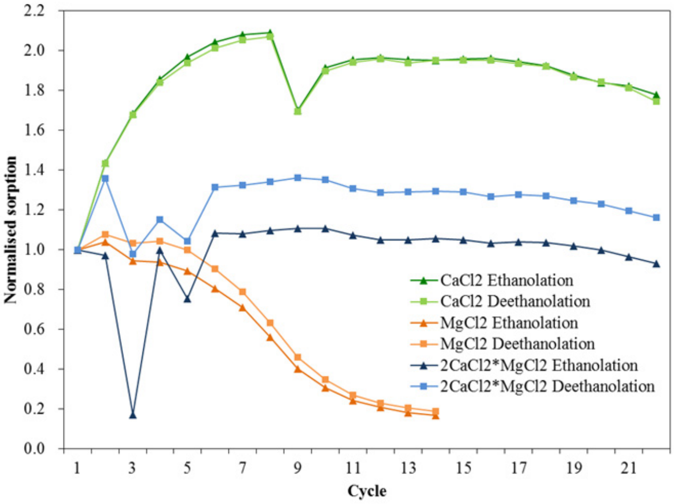

Fig. 7. Cycle stability of tested samples referred to the initial sample mass.

For a better comparison of the different salt-ethanol-systems the sorption and desorption have been normalised to the initial sorption value. In Fig. 7 the normalised sorption is plotted versus the number of operation cycles. The $CaCl_2$-C_2H_5OH -ystem had remarkable cycle stability over 36 successive cycles despite being tempered to 400 °C for pre-treatment prior to the measurement. Pre-treatment highly affects the reaction. It is assumed that baking-out might cause a change in the chemical structure and hence decrease the material's reactivity in the first cycles. The overall performance decreased only slightly by 15 % (referred to cycle number 8). Cycle stability can at least be guaranteed for a total amount of C_2H_5OH of 1.1-1.6 sorbed by one mole of $CaCl_2$. Stable $CaCl_2$ ethanolates only exist up to $CaCl_2 \cdot 1C_2H_5OH$. However, $CaCl_2$ was not fully ethanolated in order to prevent the material from forming crystalline ethanol solvates, which might cause a sharp performance decline.

Irreversible decomposition of $MgCl_2$ with increasing cycle numbers probably strongly reduced the sample's sorption ability resulting in a poor reversibility. The performance starts already to drop in early stages and is continuously reduced so that the total degradation is about 85 % referred to the initial sorption. Thus, the cycling test was stopped after 15 cycles. Actually this is not the fully ethanolated state. $MgCl_2$ can adsorb up to 4 moles of C_2H_5OH molecules. But with increasing number of molecules the result would probably be worse.

$2CaCl_2{*}MgCl_2$ exhibited only a marginal performance decline during cycling. The depicted amplitudes within the first 5 cycles are due to cooling problems of the system. Addition of 2 $CaCl_2$ to 1 $MgCl_2$ resulted in reversible and stable sorption-desorption cycles. From the 5th cycle onwards the performance declined only by 14 %.

During desorption gaseous degradation products such as ethylene chloride might be released regarding $MgCl_2$ ethanolates and maybe also for $2CaCl_2{*}MgCl_2$ ethanolates. In additional experiments, which are part of another study, the formation of ethylene chloride in high temperature regions could be confirmed by TG/MS and Raman. The degradation of $MgCl_2$ ethanolates and production of ethylene chloride would explain the drastic decline in performance with increasing number of operation cycles. We assume that the alcohol forms complexes with the salts consisting of both build-in and free C_2H_5OH molecules as reported in other publications [4,7].

4. Conclusions

The sorption behaviour of $CaCl_2$, $MgCl_2$ and their mixed salt $2CaCl_2 * MgCl_2$ strongly depends on the experimental conditions and can be controlled by variation of the C_2H_5OH vapour pressure, the discharging and charging temperature, the run time and temperature ramp of the desorption process. The experimental values on sorption and desorption ability and associated reaction enthalpies were coherent with literature and theoretical values. The molar C_2H_5OH /salt ratio referred to the anhydrous salt increased in the following order: $MgCl_2 < CaCl_2 < 2CaCl_2{*}MgCl_2$. The desorption enthalpies followed the same sequence. It could be proven that C_2H_5OH sorption is a function of the C_2H_5OH vapour pressure. Substances tend to over-stoichiometric ethanol uptake, in particular $CaCl_2$ and $2CaCl_2{*}MgCl_2$ with increasing C_2H_5OH vapour pressure. The reaction systems $CaCl_2$-C_2H_5OH and $2CaCl_2{*}MgCl_2$-C_2H_5OH showed the best sorption properties and long-term stability and thus have a great potential for low-grade thermal energy storage as well as cold storage due to their low reaction temperatures in comparison to salt-water-systems. Physically mixing of salts from the same family with different chemical properties leads to superior thermal behaviour with higher heat storage capacities compared with the single salts.

A comprehensive understanding of the thermal behaviour of salt ethanolates to be used in technical applications is required in order to forecast the material's stability. Reaction kinetic parameters of salt ethanolates are affected by various factors such as pre-treatment method, ethanolisation state and chemical composition. Future studies will focus on a detailed kinetic analysis using different mathematical models. A systematic study on the effect of the pre-treatment and history of the substance on the sorption ability is planned. During desorption irreversible decomposition of the materials might occur resulting in the production of chloride-based gaseous side products. Thus, the chemical composition of the gases given off will be analysed by combining thermogravimetric and mass spectrometer analysis. As salt ethanolates tend to solvation and agglomeration in bulk state during consecutive sorption-desorption cycles, optimization and modification methods will be addressed also.

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