SHC 2012

Low temperature chemical reaction systems for thermal storage

Baerbel Egenolf-Jonkmanns, Stefano Bruzzano, Goerge Deerberg, Matthias Fischer, Thomas Marzi, Maria Tyukavina, Jorge Salazar Gomez, Holger Wack, Barbara Zeidler-Fandrich

Fraunhofer UMSICHT, 46535 Oberhausen, Germany

Abstract

This paper presents recent research works regarding the development of materials for thermal storage at temperatures below 200°C. The main idea is to utilize reversible chemical reaction systems to enable high storage densities. Current work focuses on the retrofitting of CO₂ hydrates through selected additives for climate and cooling purposes and the activation of thermoreversible organic reaction systems for the waste heat utilization at low temperatures.

1. Motivation

Proper energy storage becomes more and more a key issue in future energy supply systems. Today’s thermal storage materials and systems mainly rely on sensible and latent heat storage approach. In theory energy storage densities of thermochemical heat storage materials are up to 10 times higher than those of sensible and phase change materials respectively. Current developments of thermochemical heat storage materials concentrate on the high temperature range up to 800 °C and there is a lack of materials for temperature applications below 200 °C [1]. The aim of our research is therefore to develop and optimize cost-efficient thermochemical heat storage materials with energy densities above average. The activities are focused on two development lines:

- improving the efficiency of existing and future hydrate-based technologies through additive enhanced CO₂ hydrates with optimized reaction kinetics for cooling and climatization purposes,
- and elaborating new organic thermochemical reaction systems with high storage densities for the utilization of waste heat.

2. CO₂ hydrates for cooling and climatization purposes

Gas hydrates are crystalline structures that trap a large amount of guest compounds such as CO₂ in the polyhedral cavities formed by a water-based host matrix. Hydrate formation is an exothermic crystallization process and dissociation takes place endothermically. Comparing ice and different hydrates reveal that hydrate slurries have generally higher energy storage capacity and can also be applied above temperatures of 0°C. Therefore hydrates are already used in cooling and climatization industries e.g. on the basis of hydrates with TBAB (Tetra-n butylammonium bromide) [2]. Our research activities focus on CO₂ hydrates as coolant since CO₂ is widely available, less expensive and less harmful to water than TBAB. CO₂ hydrates offer additionally promising perspectives in other domains, such as water purification, gas separation, gas storage and transportation.

CO₂ hydrates form at moderate temperature and pressure conditions (e.g. 1 °C and 15 bar), while at room temperature and ambient pressure they decompose again. However, due to the heterogeneous process of CO₂ hydrate formation, the specific kinetic is slow and only few technical applications have been realized yet.

Controlling the process of hydrate formation and dissociation by adding specific agents is well known. The past developments of additives focused on inhibitors and (anti) agglomerates which restrain the formation of undesired hydrate structures, and thus were mostly intended to assure a smooth transport of natural gas [4]. Otherwise, the targeted use of additives (nucleating agents, agglomerates) can favour both, kinetics and thermodynamics of the hydrate formation and dissociation and can so significantly minimize
the time and energy demand of hydrate-based technologies. The question is: How can we identify an adequate promoter and what are the crucial agent parameters, e.g. chemical structure, morphology?

2.1. Experiments on CO₂ hydrate formation adding hydrogels

Hydrate formation is an exothermic crystallization process. After a stochastic nucleation step hydrate growth follows. First visible hydrate structures in aqueous solution define the turbidity point, where typically the pressure drops and the temperature increases. The pressure drop shows that gas molecules are enclosed in water cages. The gas consumption versus time can be used to evaluate growth kinetics.

In our lab experiments we use a small glass reactor for visual observation of the formation process. Pressure and temperature data were recorded. The time interval between the establishment of supersaturation and the turbidity point is called induction time [5], which is an important characteristic parameter for hydrate formation.

To increase the reproducibility of hydrate formation a so called "multi-cycle procedure" was used [6] for the reference procedure applying just CO₂ and ultrapure water. Further experiments were carried out with an add-on of 0.01 wt.-% PA hydrogels with variable particle diameters. PA hydrogels are cross-linked sodium (Na) salts of Polyacrylic Acid (PA), known from super absorbent polymers.

![Fig. 2. Induction times of CO₂ hydrate formations using ultrapure water and hydrogels with different diameters](image)

If we compare the induction times of hydrogels with smaller diameter (cf. K100 in Fig. 2) we observe an inhibiting effect that means prolonging of induction time. On the contrary, the experiments with hydrogels with coarser particles (cf. K300 in Fig. 2), lead to nearly sudden hydrate formation. These
results can be verified by thermoanalysis and high-pressure Differential Scanning Calorimetry (HP-DSC), respectively.

2.2. **CO$_2$ hydrate formation observed by DSC measurements**

The results of the high-pressure Differential Scanning Calorimeter (µDSC 7 Evo, Setaram) experiments are presented in Fig. 3. The procedure for these experiments refers to [7] and [8] as an established method to evaluate kinetic inhibitors in the oil and gas industry. At first the sample is cooled down rapidly to -25 °C. During the following dissociation, heat is increased very slowly. Ultrapure water was used again as reference medium. The dissociation of the sample from ultrapure water (black curve) shows two peaks. The first sharp peak is associated to ice melting at nearly 0 °C. The second peak is smaller and assigned to dissociation of CO$_2$ hydrates. Using an aqueous solution with an add-on of K100 (hydrogel with a particle diameter of 98 µm), no hydrate dissociation was observed. The corresponding curve (red curve) shows only one peak assigned to ice melting. This inhibiting effect matches with the results obtained from the experiments with the glass reactor.

![Fig. 3. High-pressure DSC measurement and thermogram with heatflows](image)

In the case of K300 we obtain once again a thermogram with two peaks, similar to the reference measurement applying just ultrapure water. However, we observed an enlarged second peak, which represents the amount of dissociated CO$_2$ hydrates. The peak maximum is shifted to the right hand side (higher temperature) and show an improved stability of the CO$_2$ hydrate. Further experiments will be executed to combine additive effects due to morphological and chemical structure of the applied hydrogel.
3. Organic thermochemical reaction systems

Investigations on thermochemical systems focus on reactions between gases or between solids and gases at temperatures above 200 °C [10]. Only sorption storage units work at lower temperatures [11]. Systems with solid reactants will usually need thermofluids to transfer the thermal energy from storage unit to heat production and heat demand, respectively, accompanied by energy losses during heat exchanges at the storage [12]. Our aim is to identify liquid thermoreversible chemical reaction systems which combine high storage densities with the low temperature working range.

3.1. Choice of substances and reaction type

To avoid high pressures liquid organic substances with boiling points above the potential working temperature are considered. Moreover promising thermochemical storage materials have to comply with further prerequisites:

- Thermoreversibility in the low temperature range
- Long-term stability; absence of side reactions
- High energy densities (high reaction enthalpy per unit volume)
- Cheap and non-toxic substances

For several reasons we chose the Diels-Alder cycloaddition as reaction type. These reactions require reactants that carry two functional groups, a 1,3-Diene and a double bond. Product building takes places under the formal transformation of two double bonds into two single bonds which indicates high reaction enthalpies. Reaction enthalpies and rates can be influenced by additives like solutes, antisolutes or acid catalysts [12]. Diels-Alder reactions are generally thermoreversible and work for a huge variety of substances. The most simple but kinetically hindered system is the reaction between 1,3-butadiene and ethene to cyclohexene. The enthalpy of this hypothetical reaction, based on the heats of formation of all reactants [13], is calculated to 179.4 kJ/mol and correlates to a maximum heat density of 1.765 GJ/m³ (based on the volume of Cyclohexene). This value exceeds the potential heat densities of most other storage systems in the low temperature range [1].

In our case 2-n-butylfuran and N-tert-butylmaleimid was selected (Fig. 4) as a model Diels-Alder system. Since both reactants and product are mutual miscible liquids, no solvent is needed and a dilution of energy density can be avoided. The applicable temperature range at atmospheric pressure is limited to values lower than 140 °C due to the boiling point of 153 °C of 2-n-butylfuran.

3.2. Experiments and results

Thermal reversibility and long-term stability are two of the most important requirements for using a system of substances as thermochemical storage material in the considered temperature range. Both prerequisites were tested by infrared-monitoring while running the Diels-Alder reaction and Retro-Diels-Alder reaction, respectively. Due to the assumed reversibility and the lack of solutes ATR spectroscopy is one of only few possibilities to determine reactant concentrations at specific reaction times.
In this case every reactant has at least one specific signal in the infrared spectrum where other reacting agents barely absorb (Fig. 4). According to the Beer-Lambert law, specific absorptions are a measure for the concentrations of associated reactants. The product consists of a mixture of four isomers with similar physical properties. Slightly different bonding energies of the shown exo- and endo-isomers lead to a broadened specific signal, while their not shown regio-isomers are not distinguishable.

Fig. 5 shows the development of all reactant concentrations of our Diels-Alder system while executing a temperature program. For 2-n-butylfuran and N-tert-butylmaleimide peak areas under the specific absorptions are plotted against reaction time. In case of the product only absorptions (peak heights) were recorded because of slight overlaps with neighboring signals. Both measures are proportional to concentrations of related substances. Additionally the temperature program is mapped.

Equimolar amounts of both educts were mixed at 0 °C. An ATR-IR probe was immersed into the mixture before the reaction vessel was sealed. During a first heating step to 70 °C an initial reaction is observable via an increase of product concentration and a corresponding decrease of reactant concentrations. Further heating to 120 °C induces a Retro-Diels-Alder reaction where the product decomposes into 2-n-butylfuran and N-tert-butylmaleimide. The concentration profiles during a following temperature cycle (cooling down from 120 °C to 0 °C and heating back to 120 °C) indicate reversibility.

A further test of thermal stability was carried out by thermogravimetric analysis where the Diels-Alder product of our system was heated up to 600 °C in an open vessel under nitrogen. In Fig. 6 the relative sample mass is plotted against temperature (blue line; heating rate: 10 K/min). Its derivative with respect to temperature (black line) indicates two major steps of mass losses. The absolute mass losses of each step are denoted (Initial sample weight: 12.489 mg).
Fig. 5. Reaction monitoring via specific IR signals for an equimolar mixture of reactants

Fig. 6. Thermogravimetric analysis (TGA) of the Diels-Alder product in a vessel with perforated lid under nitrogen
One might have assumed that major mass losses occur around the boiling points of the reactants (153 °C and 189 °C) after the Retro-Diels-Alder reaction took place. However, fig. 6 indicates a mass loss of more than 50% with a maximum rate at 127 °C that might be caused by formation of an azeotropic mixture. Application of the considered reaction mixture in open processes is therefore limited to lower temperatures.

Another important prerequisite for heat storage materials is a high enthalpy of reaction per unit volume. The determination of the enthalpy of reaction was carried out via isothermal calorimetry (ITC). For this reason N-tert-butylmaleimid was filled in the sample cell and furan was added stepwise in increments of the same volume. Each step leads to a temporarily increase of the heat flow (spikes in upper diagram of Fig. 7) between sample cell and reference cell. Integration of the area under a single spike leads to the heat energy being produced by a single titration step (values plotted in the lower diagram of Fig. 7 with respect to the molar ratio). The intersection of fitted curve and ordinate axis indicates the heat that one incremental amount of 2-n-butylfuran produces if it is completely consumed by the reaction and thereby reveals the molar heat of reaction $\Delta_{\text{R}}H$ of -47 kJ/mol or an energy density of 165 MJ/m$^3$.

Fig. 7. Isothermal titration of N-methylmaleimide (M) with 2-n-butylfuran (F) at 60 °C
2-n-butylfuran and N-tert-butylmaleimid form a thermoreversible Diels-Alder system that consists of liquid reactants only. It is stable in closed applications up to 120 °C while exposed to air and too volatile for use in open applications at temperatures above 100 °C. Since the possible energy density is not competitive at the moment our system needs further improvement. As shown above Diels-Alder reactions own the potential for much higher reaction enthalpies. Due to their huge variety of possible reactant substances (electroincal and steric influences of residues) and additives (solutes, anti-solutes or catalysts), Diels-Alder systems offer ways to an optimized thermochemical storage material. This optimization is going to be the focus for our future work.

Acknowledgements

We gratefully acknowledge financial support of the German Federal Ministry of Economics and Technology (BMWi), the scientific assistance of Prof. A. Laschewsky, University of Potsdam and Prof. D. Dalmazzone, ENSTA ParisTech, and the assistance of Mettler-Toledo GmbH and TA Instruments.

References