Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 23 Oct 2006.

To cite this article: Ph. Touzain & M. Moundanga-iniamy (1994): Thermochemical Heat Transformation: Study of The Ammonia/Magnesium Chloride-Gic Pair in A Laboratory Pilot, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 245:1, 243-248

To link to this article: http://dx.doi.org/10.1080/10587259408051696

Mol. Cryst. Liq. Cryst. 1994, Vol. 245, pp. 243–248
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Printed in the United States of America

THERMOCHEMICAL HEAT TRANSFORMATION : STUDY OF THE AMMONIA/MAGNESIUM CHLORIDE-GIC PAIR IN A LABORATORY PILOT

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Abstract An improved thermochemical heat exchange system is herein described. It uses an ammonia/magnesium chloride graphite intercalation compound couple which is alternately heated and cooled. The stored energy can be restituted in the form of heat or cold. The use of graphite intercalation compounds increases the mass and heat transfers, and thus improves the heating /cooling energy and power.

INTRODUCTION

The working of the thermotransformer (chemical heat pump) is based on reversible adsorption or absorption solid or liquid/gas reactions. The stored energy released by the absorption reactions of ammonia on metal chlorides[1] is very important. We have studied the reversible reaction which uses the magnesium chloride - graphite intercalation compounds (GIC) :

$$C_xMgCl_2(NH_3)_2 + 4\ NH_3 \underset{2}{\overset{1}{\rightleftharpoons}} C_xMgCl_2(NH_3)_6 + Q_{cal.} \qquad (1)$$

in a laboratory pilot in order to determine the kinetic and thermodynamic parameters required for a heat storage or a cold generation. The use of GIC has been adopted only to improve the mass and heat transfers of the solid reactant[2]. Graphite does not directly participate to the chemical reaction.

EXPERIMENTAL TECHNIQUES

The laboratory reactor mainly consists of two parts connected by a tube through which the ammonia gas can flow in either way (figure 1).

The first part is the stainless steel reactor. It initially contains a certain amount of $MgCl_2$-GIC powder so that the porosity will be around 50-60 % when the reaction has been completed. The ammonia gas can penetrate the whole powder through a diffuser placed in the reactor core. A coolant

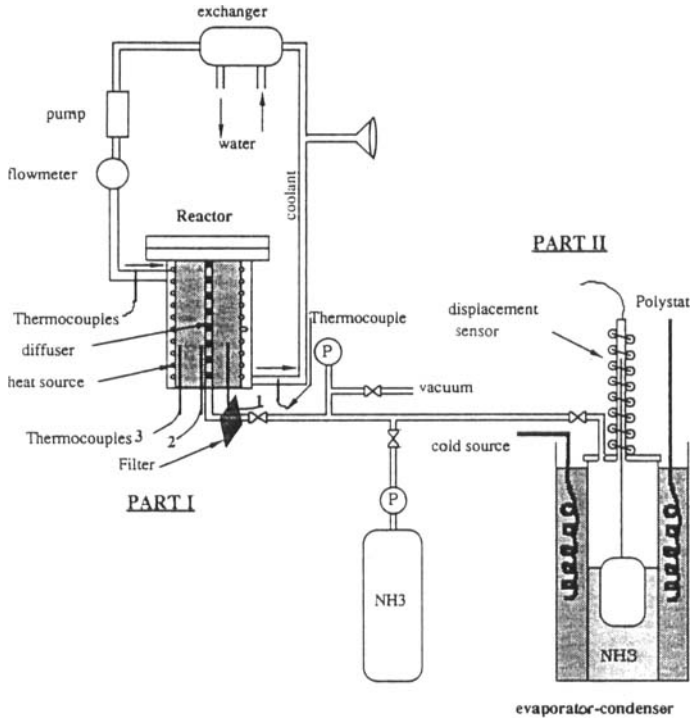

FIGURE 1 Laboratory pilot (simplified)

circulates around the reactor to collect the reaction (1) heat Q and prevent the increase of the sample temperature. An electrical heating unit supplies the energy required to run the reaction in the opposite way. Several thermocouples are placed inside the GIC powder and the fluid, so as to supervise the reaction progress.

The second part is the condenser-evaporator which contains the liquid ammonia. The level measurement - owing to a magnetic displacement float - allows to determine the absorbed or disorbed ammonia quantity during the reaction. The evaporator temperature can be set between -40 and +20 °C in order to keep the vapor pressure of the ammonia gas constant in all the system.

The reaction in direction 1 releases about 60 kJ per NH_3 mole[3]. The laboratory pilot can recover this energy, in the form of heat collected by the coolant. The heat evolution can be recorded by the computer by means of thermocouples at the same time as ammonia pressure, rate of coolant flow and float displacement. The reaction advancement and power are directly calculated by the computer.

The magnesium chloride-GICs (C_xMgCl_2) have been prepared according to the usual methods for C_7MgCl_2 [4] – a relatively poor first stage compound – and to a new method based on a cointercalation technique for $C_5(MgCl_2)_{0.8}(CoCl_2)_{0.2}$ [5] –a saturated first stage compound.

RESULTS AND DISCUSSION

The first reaction which is carried out in the reactor :

$$C_xMgCl_2 + 6\ NH_3 \rightleftharpoons C_xMgCl_2(NH_3)_6 \quad (2)$$

is not completely reversible. Only reaction (1) is reversible after several cycles and is used for the results described below. Its advancement degree X = 1/4 ($NH_3/MgCl_2$) is represented on figure 2, as a function of the actual temperature (Ts : strain temperature). In fact, the kinetic is a function of the

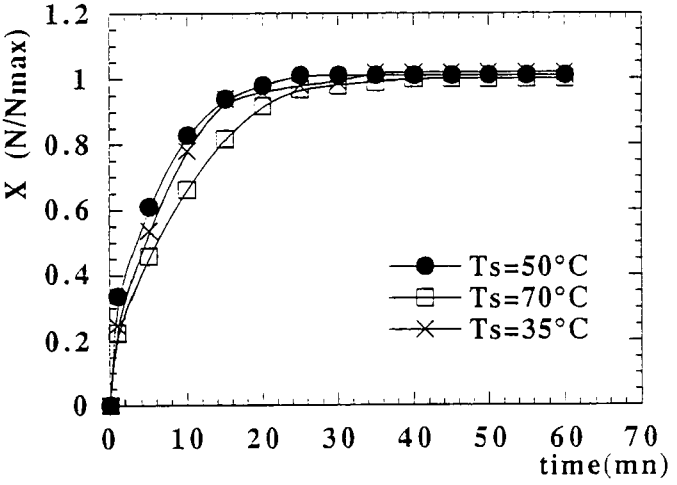

FIGURE 2 Advancement degree of synthesis reaction (1) for $C_7MgCl_2(NH_3)_{2\text{-}6}$

equilibrium drop, i.e. the difference between the equilibrium temperature (corresponding to the effective pressure on the equilibrium curve given by the Clapeyron equation [6]) and this strain temperature. Figure 3 shows the differences in the reaction rates for pure $MgCl_2$ and $MgCl_2$-GIC, and figure 4 indicates the reactor temperature variations during the synthesis phase of reaction (1) in these two cases. The reaction kinetic depends a lot on the form of these last curves : if the temperature stays high for too long a time (in the case of pure salt), the reaction rate slows down. In order to obtain a high power, it is necessary to have a fast reaction due to a good heat transfer which is provided by the use of graphite.

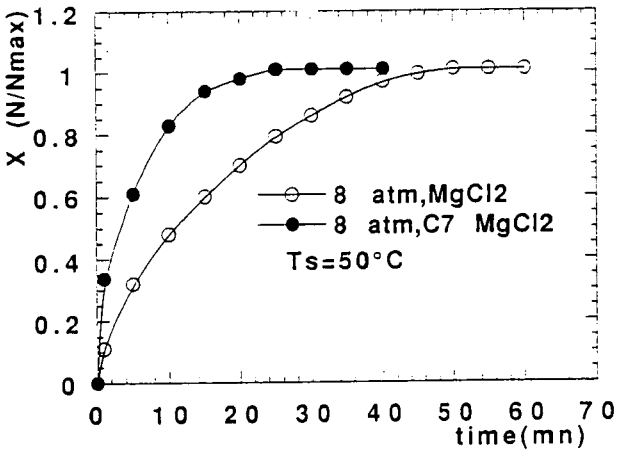

FIGURE 3 Comparison of the advancement degrees of the synthesis reactions for pure $MgCl_2(NH_3)_{2\text{-}6}$ and $C_7MgCl_2(NH_3)_{2\text{-}6}$

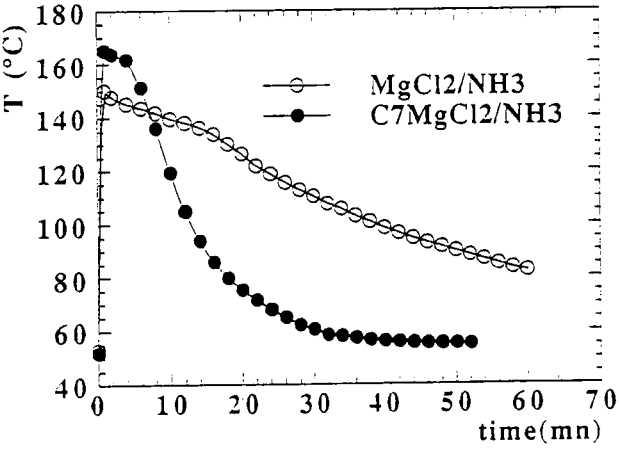

FIGURE 4 Comparison of the temperature evolution during the synthesis reactions for pure $MgCl_2(NH_3)_{2\text{-}6}$ and $C_7MgCl_2(NH_3)_{2\text{-}6}$

The influence of the ammonia pressure is indicated on figure 5 : too low a pressure is unsuitable for the reaction rate. The kinetic is here also a function of the equilibrium drop between the strain and the equilibrium pressures.

The regeneration of the reaction (phase 2 of reaction (1)) always takes more time than in phase 1. But, here too, the use of graphite is advisable in view of a greater efficiency (figure 6).

The power extracted from the experimental reactor can be estimated according to the formula $P = f\rho C_p \Delta T/V$ (f : coolant flow, ρ : coolant density, C_p : coolant specific heat capacity, ΔT : inlet/outlet reactor temperature difference and V : reactor volume). During the first two minutes of the reaction

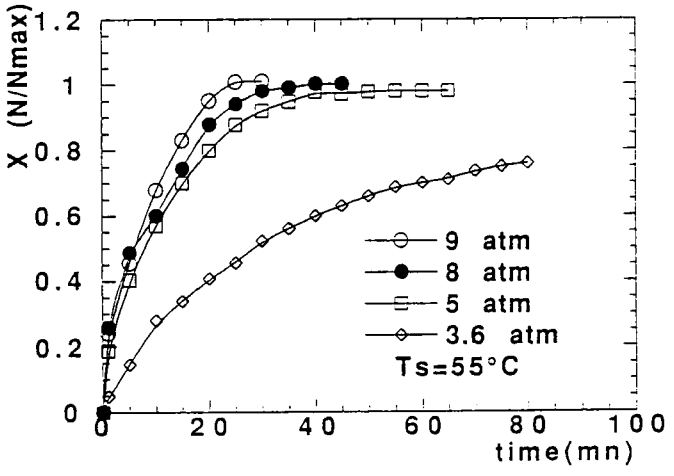

FIGURE 5 Ammonia pressure influence on the synthesis reaction for $C_5(MgCl_2)_{0.8}(CoCl_2)_{0.2}(NH_3)_{2\text{-}6}$

(which lasts about 20 minutes), the average supplied powers are respectively 125,160 and 205 kWm^{-3} for $MgCl_2$, C_7MgCl_2 and $C_5(MgCl_2)_{0.8}(CoCl_2)_{0.2}$. The corresponding energies represent approximately 20-25 % of the total recovered energy.

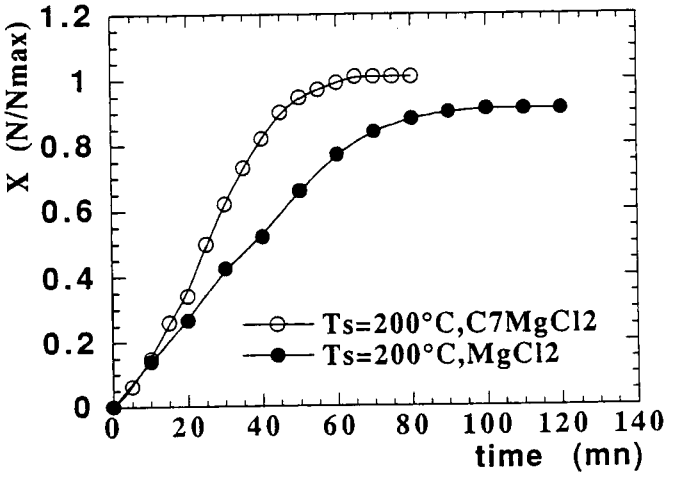

FIGURE 6 Advancement degrees of decomposition reactions (1) for pure $MgCl_2(NH_3)_{6\text{-}2}$ and $C_7MgCl_2(NH_3)_{6\text{-}2}$

CONCLUSION

Mass transfer and heat transfer are essential to a high yield for energy storage. Our experiments have shown that the use of graphite intercalation compounds increases these transfers, and thus, improves the heating/cooling energy and power.

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