# Novel ammonia sorbents "porous matrix modified by active salt" for adsorptive heat transformation: 2. Calcium chloride in ACF felt

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## ARTICLE INFO

## ABSTRACT

Novel composite sorbent "31 wt.% CaCl$_2$/ACF" was synthesised by dry impregnation of an ACF felt with a CaCl$_2$ aqueous solution. Apparent isosters of ammonia sorption were measured at $T = 20$–$90\,^\circ$C and $P = 0.1$–$9.0$ bar by an isosteric adsorption method. The method is based on the sorbent heating in a closed volume of an adsorber with registration of the ammonia equilibrium pressure $P$ as a function of temperature $T$. The uptake covered the range of 5.7–36.9 wt.%. The apparent enthalpy and entropy of the ammonia sorption as a function of ammonia uptake were obtained directly from the slop of isosteric lines $lnP(1/T)$. Appropriate correction to obtain the true sorption enthalpy was done by taking into account the "dead" volume of the adsorber. The new adsorbent was found to be an advanced material for adsorptive chilling.

## 1. Introduction

Modification of a porous adsorbent with an active salt is a promising way for improving its sorption ability [1,2]. On the other hand, use of a porous matrix helps to solve the problem of the salt swelling due to significant change in molar volume during the reaction with ammonia which causes a major decrease in the permeability of the fixed bed [3,4]. In [5] it was shown that the carbon fibers impregnated with MnCl$_2$ not only provide a very fast reaction with ammonia but also enable a complete conversion of the salt avoiding the agglomeration phenomenon. Indeed, in the impregnated carbon fibers the salt grains are protected by carbon fibers at the macromolecular scale and it is much more effective way of separation than simple mixture of the salt and carbon fibers.

In our previous papers we used CaCl$_2$ and BaCl$_2$ as active salt and expanded vermiculite, $\gamma$-alumina and carbonic material Sibunit as the host matrix for composite sorbent [6,7]. It was shown that modification of porous matrix by salt increased its sorption ability up to 0.7 g/g [6], while for pure matrices this value does not exceed 0.07 g/g. At the same time it was revealed that sorption properties of the active salt can be affected by porous structure of the host matrix. Thus, sorption equilibrium with ammonia for the salt confined to *mesopores* of $\gamma$-alumina and Sibunit was significantly different from that for the bulk one.

In this paper we used a *microporous* carbonic material, Active Carbon Fiber (ACF) felt, as a host matrix and calcium chloride as an active salt to tailor a new composite sorbent of ammonia. ACF has the large surface area (1000 m$^2$/g) and high micropore volume (1.2 cm$^3$/g), so we can expect that it has higher sorption capacity than the mesoporous matrices used in our previous works.

Carbon fibers impregnated with various chlorides have been suggested as ammonia adsorbents for heat pumping and refrigeration [8–10] as well as for ammonia scrubbing [11]. In [10] sorption equilibrium of the carbon fiber "Busofit" impregnated with calcium chloride with ammonia was investigated. The authors tested the prototype of solar refrigerator based on this material and obtained the *COP* for deep freezing as high as 0.43.

The aim of this paper was a detailed thermodynamic study of sorption properties of the new adsorbent CaCl$_2$/ACF, in particular, the measurement of isosters of the ammonia sorption and analysis of applicability of this material for adsorptive chilling.

## 2. Experimental

The ACF felt provided by the Nantong Tonghui Industrial & Trading Co., Ltd., China was filled with a saturated aqueous solution of calcium chloride and dried at 200 °C during 12 h. Salt content $\omega$ in the synthesised sorbent was 31 wt.%. SEM-photo of the sample synthesised (Fig. 1) demonstrates that the salt attached to the external fiber surface has a wide distribution on the particle size.

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**Nomenclature**

| | |
|---|---|
| $A, B, C, D$ | fitting coefficients |
| $COP$ | coefficient of performance |
| $C_p$ | specific heat, J/(g K) |
| $\Delta H$ | enthalpy of ammonia sorption, kJ/mol |
| $m_0$ | dry weight of the sorbent, g |
| $N$ | amount of ammonia in the adsorber, mol |
| $Q$ | heat, J/g |
| $P$ | pressure, Pa (bar) |
| $P_0$ | initial pressure in the buffer tank, Pa |
| $P_1$ | final pressure in the buffer tank, Pa |
| $R$ | universal gas constant, 8.31 J/(mol K) |
| $\Delta S$ | entropy of ammonia sorption, J/(mol K) |
| $T$ | temperature, K (°C) |
| $T_0$ | room temperature, K |
| $V$ | volume of the buffer tank, m³ |
| $V_1$ | "dead" volume in the adsorber (volume of gas phase in the adsorber), m³ |
| $V_m$ | molar volume of ammonia gas, m³/mol |
| $w$ | ammonia uptake, wt.% (g/g) |

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| $w_{max}$ | maximal ammonia uptake in the working cycle, wt.% (g/g) |

*Greek symbols*

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| $\alpha, \beta, \gamma$ | fitting coefficients |
| $\mu$ | molecular weight of ammonia, 17 g/mol |
| $\omega$ | salt content, wt.% (g/g) |

*Subscripts*

| | |
|---|---|
| *ads* | adsorber |
| *app* | apparent |
| *av* | average |
| *cond* | condenser |
| *eq* | equilibrium |
| *ev* | evaporator, evaporation |
| *i* | number of the ammonia transferring procedure, variable |
| *k* | total number of the ammonia transferring procedure repetitions |
| *reg* | regeneration |
| *tank* | buffer tank |

The ammonia uptake ($w$) was expressed as a wt.% of ammonia sorbed in respect to a dry weight of the sorbent. Isosters of the ammonia sorption were measured using an isosteric sorption (IS) technique described in details in [6,7]. The experimental equipment used is presented schematically in Fig. 2. The composite sorbent was placed in a stainless steel cylindrical adsorber of 4 cm in diameter with the volume 125.6 cm³. Temperature of the sorbent layer was measured by a thermocouple in the middle of the adsorber. The adsorber was placed into a water thermostat to maintain the sorbent at a constant temperature in the range of 20–90 °C. The temperature of the bath was maintained constant within a variation of ±0.1 K. The ammonia pressure over the composite sorbent was measured by the pressure gauge with accuracy of ±0.01 bar.

The sample was heated in an oven at 200 °C for 12 h and cooled down to room temperature in dry atmosphere. After that its dry weight $m_0$ was measured. The dry weight was 13.56 ± 0.01 g as the sample density was about 0.1 g/cm³. After that, the sample was placed in the adsorber and evacuated at 50 °C for 1 h down to the residual pressure 0.1 mbar. After that the certain amount of ammonia was transferred from the buffer tank to the adsorber with the composite sorbent. The ammonia sorption in the adsorber took place at the ambient temperature $T_0 \approx 20$ °C. The amount of ammonia $N$ (mol) transferred from the tank to adsorber was calculated as:

$$N = V \cdot \left( \frac{1}{V_m(P_0, T_{tank})} - \frac{1}{V_m(P_1, T_{tank})} \right) \tag{1}$$

where $V$ is the tank volume ($V = 1.256 \times 10^{-3}$ m³), $V_m$ is the molar volume of ammonia gas calculated as function of pressure and temperature using Soave modification of Redlich-Kwong equation of state for real gases [12], $P_0$ and $P_1$ are pressures in the buffer tank before and after the transferring procedure, $T_{tank}$ is the temperature of the buffer tank ($T_{tank} \approx T_0$).

Then the equilibrium NH₃ pressure $P_{eq}$ over the sorbent was measured as a function of temperature $T_{ads}$ at constant volume $V_1$.
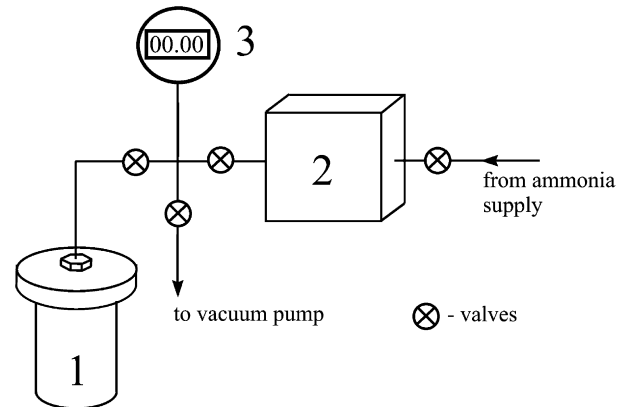


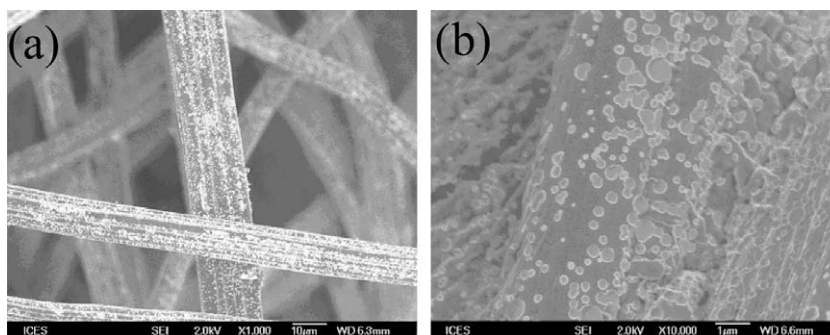**Fig. 2.** The scheme of experimental equipment for isosteric sorption measurements.



**Fig. 1.** SEM photos of ACF felt impregnated with CaCl₂: (a) 1000×, (b) 10,000×.