Applied Thermal Engineering 37 (2012) 80–86

Contents lists available at SciVerse ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

Novel ammonia sorbents “porous matrix modified by active salt” for adsorptive heat transformation: 5. Designing the composite adsorbent for ice makers

Alexandra D. Grekova [a,b], Janna V. Veselovskaya [a], Mikhail M. Tokarev [a], Larisa G. Gordeeva [a,*]

[a] Boreskov Institute of Catalysis, Ac. Lavrentiev av. 5, Novosibirsk 630090, Russia
[b] Novosibirsk State University, Pirogova str. 2, Novosibirsk 630090, Russia

ARTICLE INFO

Article history:
Received 14 October 2011
Accepted 4 January 2012
Available online 10 January 2012

Keywords:
Adsorption cooling
Ice maker
Ammonia
Intent designing the adsorbent
Composite “barium halides/vermiculite”

ABSTRACT

The novel adsorbent of ammonia based on binary salt system $BaCl_2 + BaBr_2$ inside vermiculite pores was intently designed for adsorption cooling cycle specialized for ice-making. On the base of analysis of the working conditions of the cycle the requirement for the optimal adsorbent was formulated in terms of the equilibrium temperature of reaction between the salt and ammonia and the real composite adsorbent $(BaCl_2 + BaBr_2)$/vermiculite with required properties was prepared. The dynamics of ammonia adsorption on the composite was studied by a Large Temperature Jump method under working conditions of the ice-making cycle. The maximum cooling power W_0 realized at $t \to 0$ was estimated as 1.2 kW/kg. The composite allows the production of 2 kg/(kg h) of ice. Such a good performance demonstrates an advantage of the target-oriented design of the composite adsorbent with predetermined properties matching the particular conditions of the cooling cycle.

1. Introduction

Performance of cycles of adsorption heat transformation (AHT) is strongly affected by adsorption equilibrium of the working pair “adsorbent–adsorbate” [1–3]. The Coefficient Of Performance (COP) of adsorption chillers was shown to be a function of the amount of refrigerant exchanged per cycle [4]. The selection or synthesis of adsorbents, whose properties match the operating conditions of the particular heat transformation cycle, is one of encouraging ways to enhance the cycle performance [5–7]. The operating conditions of AHT cycles depend on the number of factors, in particular, the purpose of transformation, temperature of the heat source driving the cycle, climatic conditions of the area where the device is used, etc. Thus for each AHT cycle an adsorbent, which optimally fits its working conditions, can be selected or intently tailored [8].

The composite adsorbents “salt inside porous matrix” (CSPM) have recently been developed for AHT and other applications [9–12]. The adsorption equilibrium of CSPMs with the basic refrigerants (water, methanol and ammonia) can be intently modified that gives a wide scope for designing the composite optimal for the particular cycle [2,13]. The salt S, which is an “active component” of the composite, reacts with refrigerant vapor V forming the salt solvate S*NV that results in large sorption capacity. Recently the composite sorbent of ammonia based on $BaCl_2$ inside vermiculite pores has been proposed for adsorption air conditioning [14]. $BaCl_2$ forms complex with ammonia according to the reaction

$$BaCl_2 + 8\ NH_3 = BaCl_2 \cdot 8NH_3 \qquad (1)$$

that allows absorption of $w = 0.65$ g of ammonia per 1 g of the salt. Vermiculite is used as a matrix which disperses the salt and promotes the mass transport of the refrigerant to the salt. Furthermore, it damps the salt expansion during reaction and prevents the natural tendency of the salt particles to agglomeration. This composite can provide effective operation of the air conditioning cycles using a low potential heat source (353–363 K) giving COP as high as 0.54 ± 0.01 and Specific Cooling Power (SCP) ranging from 300 to 680 W/kg [14].

Adsorption ice makers have been proposed for food preservation, vaccine storage etc. [12,15–19]. The typical working pairs used in these cycles are following: composite LiCl/silica–methanol [12], LiBr/silica–water, zeolites 13X–water [15], activated carbon–methanol [16], $CaCl_2$/expanded graphite–ammonia [17], and activated carbon–ammonia [18]. The common temperature of the heat source driving the cycles ranges from 393 to 423 K [15,17,18]. The heat with lower temperature level of 353–373 like

---

* Corresponding author. Tel.: +7 383 326 9454; fax: +7 383 330 9573.
E-mail address: gordeeva@catalysis.ru (L.G. Gordeeva).

1359-4311/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.applthermaleng.2012.01.005

Nomenclature

C	salts molar content, mol/g
COP	coefficient of performance
C_p	heat capacity, J/(g K)
C_w	weight content, g/g
d_{av}	average pore diameter, μm
D_{gr}	grain diameter, mm
ΔH_{ev}	evaporation heat of ammonia, kJ/g
ΔH_{fr}	freezing heat of water, kJ/g
ΔH_r	reaction heat, kJ/mol
m_{ice}	mass of ice produced per cycle, g/g
m_0	adsorbent mass, g
M_{NH_3}	molar mass of ammonia, g
ΔN	amount of adsorbed/desorbed ammonia, mol/mol of Ba
ΔN_{max}	final amount of adsorbed/desorbed ammonia, mol/mol
P	pressure, kPa
P^*	equilibrium pressure of reaction, kPa
r	adsorption rate, g/(g s)
r_{ice}	specific rate of ice production, kg/(kg h)
R^2	coefficient of determination
S	area of heat exchange, m^2
SCP	specific cooling power, W/kg
S_{sp}	specific surface area, m^2/g
t	time, s
t(ads)	duration of adsorption stage, s
t(des)	duration of desorption stage, s
T	temperature, K
T_{ads}	reaction temperature at adsorption stages, K
ΔT_{ads}	driving temperature difference at adsorption stage, K
T_{con}	condenser temperature, K
T_{cool}	cooling water temperature, K (°C)
T_{env}	environment temperature, K
T_{ev}	evaporator temperature, K
T_{fr}	freezing temperature of water, K
T_{heat}	heating water temperature, K
T_{reg}	reaction temperature at regeneration stages, K
ΔT_{reg}	driving temperature difference at regeneration stage, K
V_m	ammonia molar volume, m^3/mol
V_p	pore volume, cm^3/g
V_{syst}	total volume of the rig, m^3
W	cooling power, W/g
w	ammonia sorption, g/g
Δw_{max}	final amount of adsorbed/desorbed ammonia, g/g
x	conversion
Greek letters	
α	heat transfer coefficient, W m^{-2} K^{-1}
τ	characteristic time, s

solar heat provided by simple flat plate or evacuated tube solar collectors and engine waste heat is widely available and the valorization of this heat seems to be attractive [12,20]. The cycle based on activated carbon as the adsorbent and methanol as refrigerant is driven by lower temperature heat of 373 K [21]. Theoretical analysis of single stage cycle with working pair LiBr/silica–methanol demonstrated that the desorption temperature can be as low as 353 K at evaporator temperature 271 K and condenser (adsorption) temperature 303 K [12].

The ammonia pressure under conditions of ice-making cycle is essentially higher than methanol pressure that results in better mass transport inside adsorber, evaporator and condenser and promotes higher cooling power. The aim of this communication is the intent design of composite adsorbent of ammonia, based on inorganic salts inside vermiculite pores, specialized for adsorption ice makers driven by low temperature heat source ($T_{heat} = 363$–373 K).

Firstly, the requirements of the ice-making cycle for the properties of the optimal adsorbent are formulated on the base of thermodynamic analysis of the operating conditions of the cycle and expressed in terms of equilibrium temperature of reaction between the salt and ammonia at pressure during adsorption and desorption stages. Then the data on the equilibrium between different salts and ammonia are analyzed to select the proper salts. Finally the new composites based on selected salts are synthesized. Their adsorption properties under operating conditions of the cycle are studied and the efficiency of the cycle is evaluated.

2. Theoretical consideration

The typical operating conditions of ice-making cycle driven by low temperature heat for moderate climatic conditions can be determined as follows: the temperature of cooling water T_{cool} equals the condenser temperature $T_{con} = 303$ K, the evaporator temperature $T_{ev} = 268$ K and the temperature of heating water $T_{heat} = 363$–373 K (Fig. 1). It was shown previously, that for the reaction between the salts and ammonia some overcooling of the adsorbent below the equilibrium reaction temperature $T_{ads}(P_{ev})$ is necessary at adsorption stage to provide a reasonable driving force for the reaction [22,23]. The reaction rate was quite high when the driving temperature difference $\Delta T_{ads} = T_{ads}(P_{ev}) - T_{cool} \geq 10$ K [24]. Thus the adsorbent for considered ice-making cycle has to sorb (or react with) ammonia at temperature $T_{ads}(P_{ev}) \approx 313$ K. To provide a driving force during the regeneration stage the overheating of the adsorbent by $\Delta T_{reg} = T_{heat} - T_{reg}(P_{con}) \geq 10$ K is necessary, where $T_{reg}(P_{con})$ is the equilibrium temperature of ammonia complex formation at the condenser pressure. Taking into account $T_{heat} = 363$–373 K, $T_{reg}(P_{con})$ can be evaluated as 353–363 K.

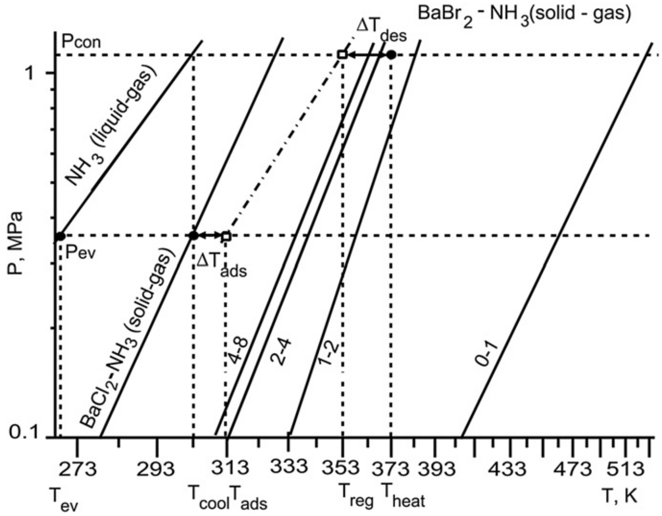

Fig. 1. The working conditions of ice-making adsorption cycle and the equilibrium isosters of ammonia sorption on the bulk $BaCl_2$ and $BaBr_2$, calculated from thermodynamic data on the equilibrium for reactions between the salts and ammonia [25]. The transitions between different complexes $BaBr_2 \cdot NNH_3$ are marked near the corresponding isosters.