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Composites $CaCl_2$/SBA-15 for adsorptive transformation of low temperature heat: Pore size effect

Ivan Glaznev [a,*], *Ilya Ponomarenko* [b,1], *Sergei Kirik* [b,1], *Yuriy Aristov* [a]

[a] *Boreskov Institute of Catalysis, Pr. Lavrentieva 5, 630090 Novosibirsk, Russia*
[b] *Institute of Chemistry and Chemical Technology, K. Marx Street 42, 660036 Krasnoyarsk, Russia*

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ABSTRACT

Each specific cycle for adsorptive heat transformation (AHT) requires appropriate adsorbent which ensures the best realization of precisely this cycle. This paper addresses a synthesis of novel composite sorbents "$CaCl_2$ confined to a meso-structured silicate SBA-15" with variable properties which appear to depend on the SBA pore size (8.1 and 11.8 nm). The equilibrium and dynamics of water sorption have been studied under typical conditions of isobaric stages of AHT cycle. Steep sorption isotherms are found, the pressure at which the sharp increase of water sorption is observed being higher in larger pores. This allows fine adjustment of sorbent properties to cycle boundary temperatures: the stronger water bounding by the salt confined to smaller pores results in the appropriate enhancement of the desorption and condensation temperatures.

Comparison of the new composites with other adsorbents promising for AHT showed that mono-sized matrices are encouraging for both tailoring step-like sorption isotherms, managing the step position to fit given AHT cycle and fast water sorption.

Adsorbants composites au $CaCl_2$/SBA-15 pour la transformation de la chaleur par adsorption à une température relativement basse: Effet de la taille des pores

Mots clés : Système à adsorption ; Adsorption-équilibre ; Composite ; Adsorbant ; Cycle thermodynamique

1. Introduction

New effective adsorbents for transformation of low temperature heat are a subject of numerous studies over the last decade. These systems would allow utilization of huge amount of industrial waste heat as well as the low-grade solar energy and fit the requirements of the Zero Ozone Depletion and the Global Warming Potentials (Ziegler, 1999; Critoph and Zhong, 2005; Wang et al., 2009).

Booming progress in the material science allows the formulation of advanced concept of nanotailoring novel adsorbents with predetermined properties adapted to particular

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[*] *Corresponding author*. Tel.: +7 (383) 3269454; fax: +7 (383) 330 80 56.
E-mail address: glaznev@catalysis.ru (I. Glaznev).
[1] Tel.: +7 (391) 2273831; fax: +7 (391) 2238658.

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Nomenclature

Ad-HE	adsorbent-heat exchanger
AHT	adsorptive heat transformation
C	salt content
D_{av}	average pore diameter (nm)
h_{fg}	latent heat of water vaporization (2478 kJ kg^{-1})
m	mass of adsorbent sample (g)
m_{dry}	mass of dry adsorbent sample (g)
N	water uptake $(mol_{H_2O} \bullet (mol_{CaCl_2})^{-1})$
PSD	pore size distribution
P	water vapor pressure (kPa)
P_0	pressure of saturated water vapor (kPa)
R	universal gas constant (8.31 J mol^{-1} K^{-1})
S_{BET}	specific pore surface area defined by BET method (m^2 g^{-1})
T	temperature (K)
t	time (s)
V	volume (m^3)
V_{pore}	specific pore volume (cm^3 g^{-1})
W	specific power
w	water uptake (g g^{-1})
μ	molecular weight (kg mol^{-1})
τ	characteristic time (s)

Subscripts

c	condenser
d	desorption
e	evaporator
0.5	corresponding to 50% of the equilibrium sorption
0.8	corresponding to 80% of the equilibrium sorption
max	maximal

AHT cycles (Aristov, 2007). A new family of composites "salt in porous matrix" (CSPMs) is exemplified this approach (Aristov et al., 2002, 2008a; Gordeeva et al., 2002). More than 60 novel sorbents of water, methanol, ethanol and ammonia have been synthesized and characterized. Confined salt is an active component of CSPMs, while the matrix acts as a media that disperses the salt and provides efficient heat and mass transfer.

Great potential of CSPMs is associated, first of all, with the opportunity of purposeful modification (or even tailoring) of their sorption properties. It can be made by a plenty of tools, among which are controllable varying a) chemical nature of the confined salt, b) its particle size inside the matrix pores, c) amount of the confined salt, and d) synthesis conditions, as was demonstrated by Aristov (2007), Aristov et al. (2008a). Several CSPMs have been tested by Aristov et al. (2002), Restuccia et al. (2004), Jänchen et al. (2004), Zhu et al. (2006), Daou et al. (2008), Saha et al. (2009) for heat transformation (heat pumping, chilling) and demonstrated promising performance, especially at low regeneration temperature (70–90 °C).

One of the most important findings is a tuning of the hydration temperature of the confined salt as it appears to depend on the pore size of the host matrix. Indeed, this temperature is higher if the salt is located in smaller pores, however, the hydration/dehydration transition gets less sharp (Simonova and Aristov, 2005). One can expect that confinement of a guest salt to a host matrix with a narrow pore size distribution (PSD) may lead to narrowing the hydration/dehydration transition that may improve both AHT efficiency and dynamics (Aristov, 2009). This exciting opportunity is provided by nano-structured silicates of MCM and SBA types with mono-sized pores (Beck et al., 1992; Corma, 1997).

Composites $CaCl_2$/MCM-41 and $CaCl_2$/SBA-15 have recently been synthesized keeping in mind application for adsorptive heat transformation. The average pore size of these composites was 3.8 and 7.5 nm, respectively. The isotherms, isobars and isosters of water sorption were measured and analyzed for application in adsorption heat pumps by Tokarev et al. (2002) and Ponomarenko et al. (2010). For $CaCl_2$/MCM-41, the water uptake at $P/P_0 \approx 0.7$ reached 0.7–0.75 g sorbed by 1 g of the dry composite. For the bulk salt, the water sorption equilibrium is mono-variant, while for $CaCl_2$/MCM-41 it was found to be bi-variant. This indicated a considerable change of the salt properties due to its confinement within the small MCM-41 pores. For $CaCl_2$/SBA-15, isotherms and kinetics of water adsorption/desorption were measured at temperature 50 °C and vapor pressure of 0–5 kPa. A mono-variant type of sorption equilibrium was revealed. The equilibrium pressure over the dispersed $CaCl_2$ dihydrate was found to be 2.5–4 times lower relative to the bulk one. The reason of this effect may be an increase of the surface energy of the salt caused by its confinement as discussed in Ponomarenko et al. (2010). The Knudsen diffusion in the SBA mesopores was found to be a rate limiting stage of water sorption on the $CaCl_2$/SBA-15 composite.

The aim of the present study is a detailed analysis of the pore size effect on the water sorption properties of composites $CaCl_2$/SBA-15 applied to AHT cycles. For this aim, we have synthesized expanded SBA-matrices with the pores of 8.1 and 11.8 nm diameter that is larger than for common SBA-15 (7.5 nm). The newly synthesized materials were compared with a famous composite adsorbent SWS-1L which has been considered as promising for AHT units (Aristov et al., 2002). It contains the same salt (33.7 mass% $CaCl_2$), however, the host matrix is a commercial silica gel KSK. In contrast to mono-sized SBA-matrices, this silica has mesopores which size is distributed over a wide range of 3–22 nm (15 nm, in average). Brief comparison with other promising adsorbents, namely, a functional adsorbent material FAM-Z02 (Kakiuchi et al., 2005) and a Fuji silica gel of type RD (Chua et al., 2002; Saha et al., 2007), has also been made.

2. Experimental

2.1. Samples preparation

Two $CaCl_2$/SBA-15 samples have been synthesized, namely, $CaCl_2$/SBA (8.1 nm) and $CaCl_2$/SBA (11.8 nm). Pure matrices SBA (8.1 nm) and SBA (11.8 nm) were synthesized as described elsewhere (Zhao et al., 1998).

The initial components for synthesis of silicate matrices were Pluronic P123 from Aldrich, (M.W. = 5800, Cat:43,546-5,