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SELECTIVE WATER SORBENTS FOR MULTIPLE APPLICATIONS, 4. CaCl₂ CONFINED IN SILICA GEL PORES: SORPTION/DESORPTION KINETICS

M.M. Tokarev and Yu.I. Aristov

Federal Scientific Center, Boreskov Institute of Catalysis,
Novosibirsk 630090, Russia

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Abstract

This paper presents experimental data on water sorption/desorption kinetics on composite SWS-1L and SWS-1S materials, bulk aqueous CaCl₂ solutions and pure KSKG silica gel. Desorption kinetic curves are measured in the temperature range of 328-363 K at different vapor pressures. First order kinetics is found for both SWS materials and the bulk aqueous solution with the apparent activation energies of the water desorption equal to 23.5 kJ/mol and 48.6 kJ/mol, respectively. The difference in the kinetic behavior of the bulk and disperse systems is discussed.

Keywords: Water desorption kinetics, calcium chloride/silica gel composites, small size effect

INTRODUCTION

Recently we have reported some thermodynamic properties of new selective water sorbents SWS-1L and SWS-1S, which appear to possess a high water sorption capacity and several other properties promising for practical applications [1-6]. In addition to the thermodynamic aspects, the kinetics of water sorption/desorption by these materials is expected to be of great importance for their practical use. The kinetics defines the amount of absorbed water that is really involved in drying or energy accumulating process with a finite residence time of a vapor-containing gas mixture.

Here we present experimental data on the water sorption/desorption kinetics in a composite SWS-1L material at different temperatures T and partial water vapor

pressures $P(\text{H}_2\text{O})$. For comparison, similar measurements were performed for separate components of the composite system, namely, bulk aqueous solutions of CaCl_2 and KSKG silica gel. Kinetic equations and apparent activation energies for these three materials were obtained in the temperature range of 328-363 K. A difference in the kinetic behavior of the bulk and disperse systems was found. The kinetic data indicate that the sorption equilibrium in the confined system is likely to be limited under these experimental conditions by internal diffusion of water molecules.

EXPERIMENTAL

Procedure of the composite sample preparation has been described elsewhere [1]. Pure calcium chloride of spectroscopic grade and KSKG and KSM silica gels (both from Reachim) were used without additional purification.

The sample was placed into a glass container with two taps for entry and exit of an air flux. The air flux saturated with water vapor up to the desired partial pressure $P(\text{H}_2\text{O})$ passed through a container placed into the furnace with a fixed temperature T . The air flow rate was $8.33 \text{ cm}^3/\text{s}$. The container was weighed every 10 min to record the water loss. A single experimental run was finished when a constant sample weight was reached. The measurements were conducted at $T = 328\text{-}363 \text{ K}$ and $P = 23.6\text{-}31.7 \text{ mbar}$. An isothermal dependence of the sample weight on time gave a dehydration kinetics, the final points of the kinetic curves determined the equilibrium water content at fixed temperature and vapor pressure $m_{\text{eq}}(P(\text{H}_2\text{O}), T)$.

RESULTS AND DISCUSSION

Isothermal kinetic curves of water desorption from the composite SWS-1L material are presented in Fig. 1. Each curve corresponds to fixed $P(\text{H}_2\text{O})$ and T and demonstrates a monotonic decrease of the sorbed water amount down to its equilibrium value $m_{\text{eq}}(P(\text{H}_2\text{O}), T)$. Sections of this function at constant $P(\text{H}_2\text{O})$ and T give isobaric and isothermal charts, respectively, described in Ref. [1,2].

The kinetics of water removal at $P(\text{H}_2\text{O}) = \text{const.}$ and $T = \text{const.}$ may be satisfactorily described by the first-order equation

$$m(t) = \Delta m \exp(-kt) + m_{\text{eq}} \quad (1)$$

where $\Delta m = \Delta m(t=\infty) = [m(0) - m_{eq}]$ is the final loss of sorbed water at $t \gg 1/k$, k is the first-order rate constant of the desorption process. The latter value may

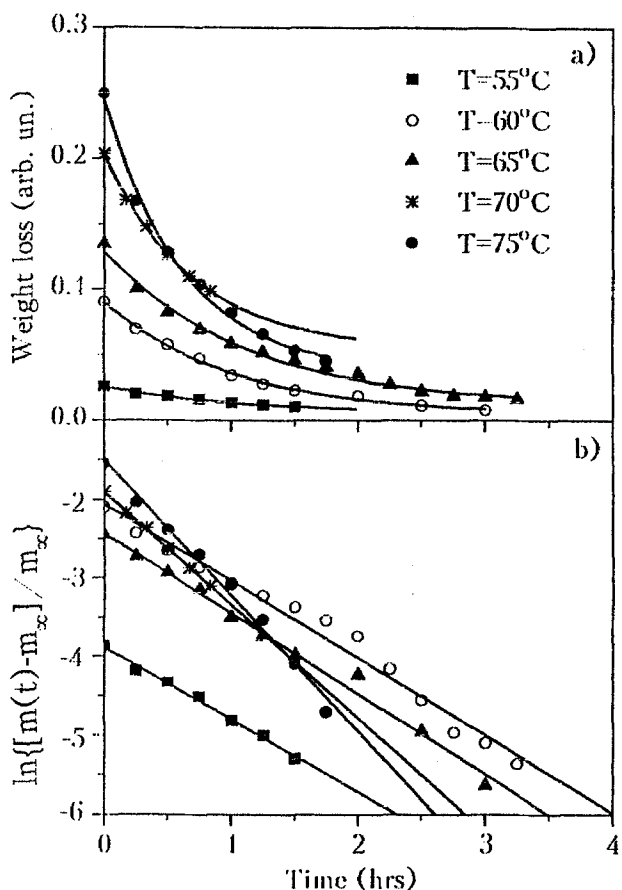


Fig. 1. Experimental kinetic curves of water desorption from the SWS-1L (a) and their presentation as $\ln\{(m(t) - m_{eq})/[m(0) - m_{eq}]\}$ vs. t plots at various temperatures and a partial vapor pressure $P(H_2O) = 31.7$ mbar (b)

be obtained from the slope of the kinetic curves presented in the $\ln[(m(t) - m_{eq})/(m(0) - m_{eq})]$ vs. t coordinates (Fig. 1b). The first several points of the curves demonstrate faster water removal and somewhat deviate from first-order kinetics. Indeed, the first portions of water evaporate from less concentrated solutions with a desorption heat lower than that of more concentrated solutions and/or crystalline hydrate [7]. This facilitates desorption and increases its rate.

Since the absolute value of the constant depends on a variety of factors including the air flow rate and the sample geometry, all the influencing parameters were maintained constant during experimental runs. This allowed to find a temperature dependence $k(T)$ which appeared to have the Arrhenius form (Fig. 2) with an apparent activation energy of water desorption equal to 23.5 kJ/mol and independent of the partial vapor pressure.

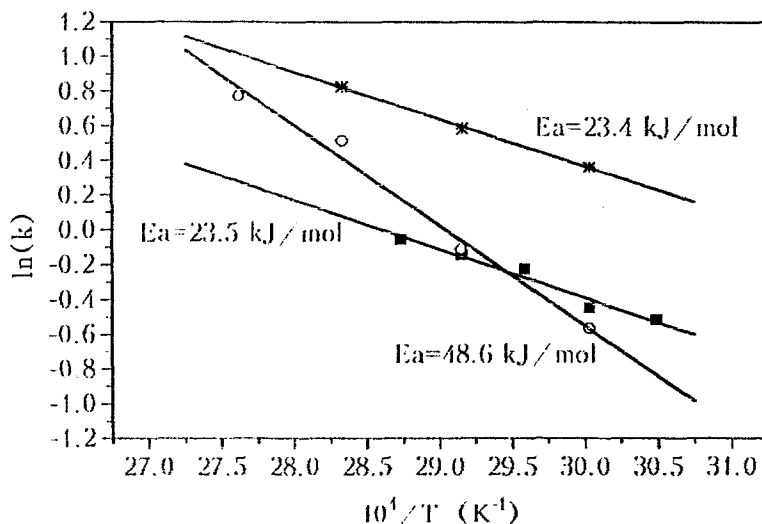


Fig. 2. Arrhenius plots for determination of the activation energy of water desorption from the SWS-1L at $P(\text{H}_2\text{O}) = 31.7$ mbar (■) and 23.6 mbar (○) as well as from bulk CaCl_2 at $P(\text{H}_2\text{O}) = 31.7$ mbar (*)

The first-order kinetic equation of the type (1) also satisfactorily describes the water desorption from pure bulk CaCl_2 solutions (Fig. 3). The bulk monomolecular kinetics can be equally explained by two different approaches: (1) water removal is limited by water evaporation from the liquid phase, thus giving first-order kinetics like in the case of pure water evaporation; (2) dehydration is accompanied by the formation of solid crystalline hydrates ($\text{CaCl}_2 \cdot n\text{H}_2\text{O}$, $n \leq 4$) [1], and creation of a critical nucleus of the solid phase is the rate-limiting stage of phase transformation [8].

An Arrhenius behavior of the rate constant for the bulk solution allows to determine the apparent activation energy, which has been found to be equal to 48.6 kJ/mol (Fig. 2). This value is close to the typical energy required for water removal from the bulk aqueous solution of CaCl_2 [9]. Thus, it supports the first

dehydration model mentioned above, and it is reasonable to consider the removal of water molecule from the liquid solution as the rate-determining step for the bulk system, so that the process occurs in the kinetic mode.

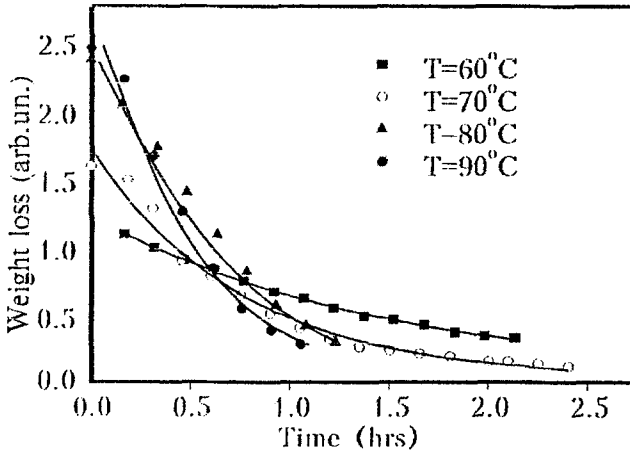


Fig. 3. Experimental kinetic curves of water desorption from bulk CaCl₂ solutions at P(H₂O) = 31.7 mbar and various temperatures

Note that the activation energy of the latter is approximately twice higher than that of the composite SWS-1L material. In our opinion, this indicates that dehydration in the confined state is also limited by water diffusion inside the silica gel pores or in the confined solution. Indeed, if a kinetically controlled chemical reaction of an arbitrary order n follows the rate equation

$$\{\text{reaction rate}\} = k_o \exp(-E_a/RT) C^n$$

then the apparent kinetics under internal diffusion control may be written as [10]

$$\{\text{reaction rate}\} = (k_o D_{\text{eff}})^{1/2} \exp[-E_a/(n+1)RT] C^{(n+1)/2}$$

where C is the reagent concentration, D_{eff} is the effective diffusion coefficient. For a first-order reaction ($n = 1$), it leads to a monomolecular law with the apparent activation energy two times lower than its real value.

Isothermal desorption kinetics from the pure host material – the KSKG silica gel – shows a quite different behavior giving a linear function $m(t)$ (Fig. 4). The

specific equilibrium water sorption by pure silica gel is much lower than that of the composite sorbent SWS-1L. This indicates a predominant role of confined CaCl_2 in the water sorption process, which is consistent with our previous findings [1] and the results of Ref. [11].

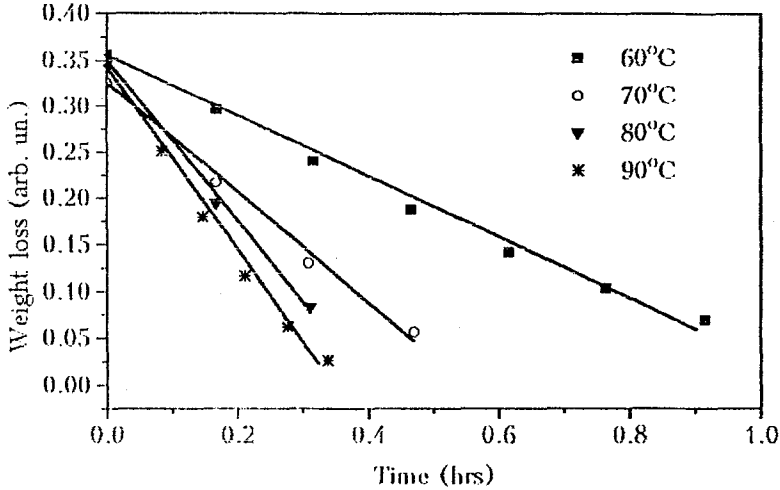


Fig. 4. Kinetic curves of water removal from pure KSKG silica gel at $P(\text{H}_2\text{O}) = 31.7$ mbar

The kinetics of the reverse process (water sorption) has been found to follow first-order too. Our study has shown that the kinetics of water sorption by bulk CaCl_2 solution and the composite SWS-1L and SWS-1S materials appeared to be a simple function (Fig. 5)

$$\Delta m(t) = \Delta m_{\infty} [1 - \exp(-t/t_0)] \quad (2)$$

where t_0 is the characteristic time of the water sorption, $\Delta m(t)$ the sample weight increase, and $\Delta m_{\infty} = [m_{\text{eq}} - m(0)]$ is the final increase of sample weight at $t \gg t_0$. The typical time required for reaching the sorption equilibrium has been found to depend strongly on the dispersity of the confined salt (or its solution). Indeed, at fixed external conditions, the sorption equilibrium is established much faster in the microporous material SWS-1S, where the salt is in the most dispersed state, which provides a highly active surface for water sorption (Table 1). This table demonstrates that the confinement of $\text{CaCl}_2\text{-H}_2\text{O}$ system into KSM silica gel leads to a more than 10-fold reduction of t_0 in comparison with the bulk sample.

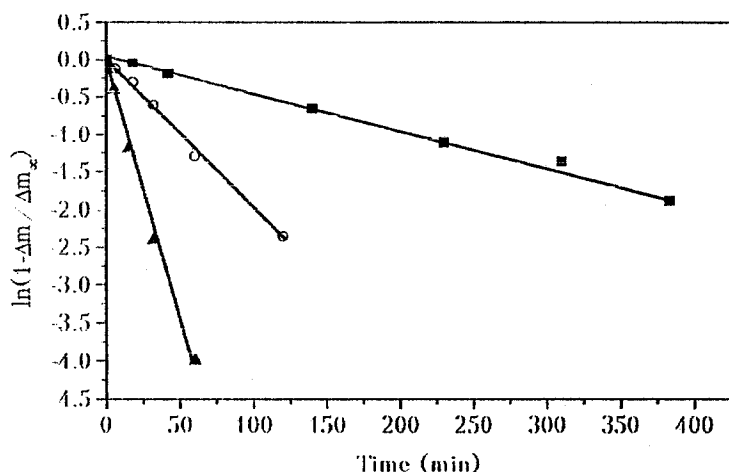


Fig. 5. Experimental kinetics of water sorption on the SWS-1L (O), SWS-1S (▲) and pure CaCl₂ solution (■) at T = 25°C and relative humidity 33% presented as a ln[1 - Δm(t)/Δm_∞] dependence on time

Table 1

Characteristic time t₀ of reaching water sorption equilibrium for bulk and confined calcium chloride solutions at T = 25±1°C and relative humidity of 33±2%

Sample:	bulk CaCl ₂	confined salt dispersity (nm)	
		15	3.5
t ₀ (min)	211	50	16

The similarity of sorption and desorption kinetics (eqs 1 and 2) indicates that both processes are restricted by diffusion of water in the silica pores or in the confined liquid solution. In the absence of air this equilibrium sets in much faster. It takes only 0.5-2 min at 30-70°C, which clearly proves the crucial role of the water diffusion.

Kinetic data obtained here as well as sorption equilibrium data reported in Ref. [1,2] can be used for analysis of multiple applications of the SWS materials in air conditioning, gas drying, fresh water production from air, adsorption heat pumps, etc.

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