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Experimental study on the kinetics of water vapor sorption on the inner surface of silica nano-porous materials

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ABSTRACT

An experiment of kinetic water vapor adsorption of inner surface of silica nano-porous materials is performed by using the thermal gravimetrical method in a relative humidity range from 0.15 to 0.9 at different temperature levels of 25, 35, 45, 55, 65 °C, respectively. The temperature and humidity environment was supplied by a hygrothermostat. This experiment work shows that the water vapor adsorption equilibrium on silica nano-porous materials belongs to Type IV according to Brunauer's classification and could be well correlated by BET (Stephen Brunauer, Paul Hugh Emmett and Edward Teller) equation. The exponential-decay-2 model proposed in this work could fit the full kinetic adsorption process while the pseudo models failed. Under the same relative humidity, although the water vapor concentration increases significantly with temperature, the saturated water uptake decreases slightly with the increase of temperature for the adverse effect of temperature on adsorption.

1. Introduction

Silica aerogels have been used extensively in many engineering practices. They are characterized by extremely high porosity (up to 99%), large specific surface area and complicated microscopic structure. These structural properties result in a few interesting physical properties, for example extremely low thermal conductivity and high optical transparency [1]. But the pure silica aerogels are fragile and transparency to thermal radiation at high temperature and these two defects limit the application area of silica aerogels as thermal insulation materials. Reinforced fibers and opacifiers are usually doped in the aerogels to improve both the mechanic strength property and thermal insulation property. The composite silica aerogels are named silica nano-porous materials and they have the similar space structure and have superior insulation at high temperature and higher mechanic strength properties compared with the pure silica aerogels [2–6]. The silica nano-porous materials have broad applications or applications prospect in the fields where have strict limit of space, weight or thermal insulation, for example in aeronautics and aerospace, transportation of offshore oil and gas, and buildings energy saving [1,7].

Like silica aerogels, one of their severe drawbacks of unmodified silica porous materials is concerned on their long term stability under a humid atmosphere because a large number of hydroxyl groups on the inner surface of the material introduced during the manufacturing process will absorb water vapor, drastically deteriorating their thermal insulation performance [8–10]. For example, when the silica nano-porous materials are stored or used in high humid environment, it will absorb the water vapor from the air inevitably in the process of storage and service, leading to its thermal conductivity being 1 or 2 times higher than that of dry material [8]. Thus the study of the water vapor kinetic adsorption, saturated adsorption amount and thermal conductivity of silica nano-porous materials at different temperature and humidity is an urgent need for predicting and optimizing the adsorption property and thermal insulation of silica nano-porous materials in temperature and humidity environment.

Many studies of water vapor sorption on silica gel and other adsorbate have been conducted, and they are mainly concerned on the adsorbing capacity and rates of the adsorbents [11–18]. Various methods can be used for the adsorption of water vapor: gravimetric method with adsorption in the hygrothermostat [14,17] or enclosed space containing saturated solutions of appropriated salts [11,15,16,18], and volumetric method that isothermally changes the vapor pressure in a vacuum system [12]. Yang and Al-Duri [13] studied the liquid-phase adsorption of reactive dyes on activated carbon. They fitted the kinetic adsorption process and the adsorption equilibrium with several generalized kinetics and equilibrium models and proposed a modified pseudo-first-order kinetic

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Nomenclature

a	isotherm constant, $(mg/L)^{-b_2}$
B,c	isotherm constants
b_2	Fritz–Schlüder isotherm constant
C	water vapor concentration, mg (water)/L (moist air)
D	BET mean pore diameter, nm
k	isotherm constant; rate constant
N	number of points
n	adsorption layer
p	water vapor pressure, Pa
q	water uptake, mg/g
R	correlation coefficient
S	BET surface area, m^2/g
W	weight of sample, g

Greek symbols

β	isotherm constant
ϕ	porosity, %
φ	relative pressure, relative humidity
ρ	apparent density, kg/m^3

Subscripts

cal	calculation
dry	dry sample
e	equilibrium
ei	equilibrium value of *i* point
exp	experiment
F	Freundlich isotherm constant
L	Langmuir isotherm constant
wet	wet sample
m	mass
R	Redlich–Peterson isotherm constant
s	Fritz–Schlünder isotherm constant
t	time

model which fits the experiment data well. BP neural network was adopted to model the water sorption isotherm for corn starch [19]. From the above brief review it can be seen that there are few works on the kinetics of water vapor sorption on the inner surface of silica nano-porous materials, which is of great significance for the practical application of silica nano-porous materials. This study gives the kinetics of water vapor sorption on the silica nano-porous materials at different temperature and humidity under ambient pressure. The objective of this paper is threefold: first, to obtain the kinetics and equilibrium data of water vapor adsorption under different temperature and humidity environment; second, to test the validity of the kinetic models and the adsorption equilibriums and to propose a new kinetic model to fit the experimental kinetic values; last, to investigate the influence of temperature and relative humidity on the water vapor sorption rate and capacity. To the best of our knowledge, there is no experimental study which reveals the influences of temperature and humidity on the adsorption rate and adsorption amount of nano-porous materials with different porosity comprehensively.

2. Experimental apparatus, procedures and materials

Five silica nano-porous materials with different porosity are presented in this paper. The silica nano-porous materials are manufactured by the sol–gel process and supercritical drying method and the detailed preparation information can be referred to [20–22]. The geometry parameters of the bulk samples are shown in Table 1. The adsorption isotherms and porous structures of the samples are determined by the adsorption of nitrogen at 77 K using ASAP 2020 specific surface area and porosity analyzer.

In this work, the thermal gravimetrical method is adopted to measure the equilibrium and dynamic adsorption data of water vapor adsorbent system under atmospheric pressure. The picture of the test apparatus is shown in Fig. 1. The temperature and humidity environment is supplied by a HS-800 (Nanjing Test Sky, China) hygrothermostat with space of 0.8 m^3 inside and uncertainties of ±0.5 °C for temperature and ±3% for relative humidity. Kinetic adsorption of water vapor on the inner surface of silica nano-porous materials is conducted within relative humidity range of 0.15–0.9 at five temperature levels of 25, 35, 45, 55 and 65 °C.

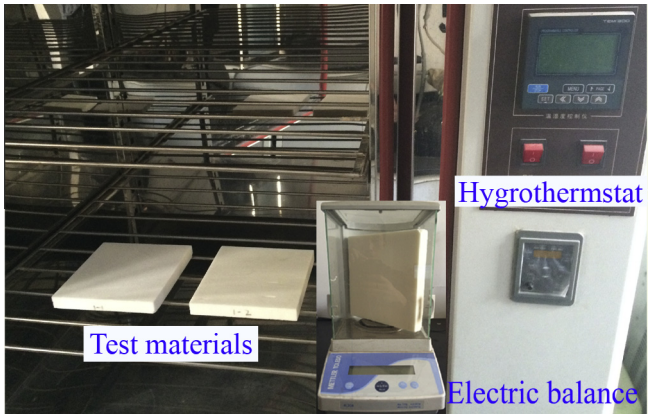

Fig. 1. Test picture of the water vapor adsorption apparatus.

The amount of water vapor adsorbed by the samples per unit mass was calculated by the following formula:

$$\text{water uptake} = (W_{wet} - W_{dry})/W_{dry}\ (\text{mg/g}) \quad (1)$$

where W_{wet} and W_{dry} are the mass of the moist and the dried nano-porous materials, respectively. The test procedures are as follows. First the dry weight of the samples is obtained by drying it in the hygrothermostat at 150 °C under atmosphere pressure. Then its

Table 1
Geometric parameter of the silica nano-porous material.

Sample	Apparent density ρ (g/cm^3)	Porosity ϕ (%)	BET mean pore diameter D (nm)	BET surface area S (m^2/g)
1	0.3795	77.7	8.05	185.5
2	0.4292	74.8	8.10	200.9
3	0.4143	75.6	9.87	210.0
4	0.3648	78.5	8.85	236.9
5	0.1403	91.7	NA	NA