The influence of the ammonia concentration and the water content on the water sorption behavior of ambient pressure dried silica xerogels

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Abstract

Porous silica xerogels were synthesized within 10 h by a two-step sol–gel process under atmospheric conditions. In the first step, tetraethylorthosiloxane (TEOS) was hydrolyzed with water using sulfuric acid as a catalyst. In the second step, water and ammonia were added to the prehydrolyzed silica sol prior to the drying of the samples at 150 °C. The influence of the ammonia concentration and the water content on the physicochemical properties and the water sorption behavior of silica xerogels produced in the aforementioned way was investigated. The resulting silica xerogels were characterized by helium pycnometry, scanning electron microscopy, fourier-transform infrared spectroscopy, nitrogen sorption, and water sorption. It was shown that a higher ammonia concentration leads to an increased pore size of the silica xerogel which starts to adsorb water at a higher relative pressure. With an increased water content during gelation, the silica xerogel has a higher specific surface area and a higher water sorption capacity. Furthermore, silica xerogels can be tailored by a controlled addition of ammonia and water to have a higher water sorption capacity than the reference silica gel over the whole range of relative pressure.

Graphical Abstract

Keywords Adsorption · Silica gel · Xerogel · Water sorption · Sorben

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Highlights

- Silica xerogels were synthesized within 10 h by a hydrolysis-condensation sol–gel process.
- An increased ammonia concentration during the condensation reaction leads to a higher porosity and larger average pore size of the silica xerogel.
- A higher water content during the condensation reaction increases the specific surface area and the water sorption capacity of the silica xerogel.

1 Introduction

Adsorption heat pumps (AHPs) have gained a lot of interest in the past couple of decades since they are considered an environmentally friendly and cost-effective alternative to compressor-based heat pumps. AHPs utilize waste heat rather than electrical energy to provide space heating and cooling. Conventional AHPs are equipped with silica gel as an adsorbent, however, the widespread application of AHPs has not been achieved due to the low water adsorptivity and the poor mass and heat transport properties of silica gels [1]. The synthesis and structural characterization of porous solids, such as zeolites, metal-organic frameworks, activated carbons, or silica gels, have received a growing interest and an increase in research studies [2–7]. In order to maximize efficiency, the amount of cycled water within the operation window has to be maximized meaning that the sorbent has to be tailored for its application. To address this issue, silica gels with tailored porosity and pore size have been proposed to enhance mass transport properties.

An attractive method to tailor the pore size of the silica xerogel is by varying the concentration of acid or base used for hydrolysis or condensation respectively. It was found that xerogels synthesized with a low concentration of acid and base have smaller particle and pore size than those synthesized with a high concentration of acid and base [8, 9]. Alcañiz et al. [2] investigated the influence of the pore size distribution of silica xerogels on the water sorption behavior. It was found that essentially microporous silica gels adsorb water at low and medium relative pressures ($0 < P/P_{\text{sat}} < 0.6$) whereas silica gels which contain micro- and mesoporosity adsorb water in the whole pressure range ($0 < P/P_{\text{sat}} < 0.95$).

The mechanism of adsorption of water on silica gels has been investigated intensively within the last decades [10–16]. This mechanism is rather complex due to the polarity of the water molecule. It is known that the surface of amorphous, hydroxylated silica is covered with silanol ($\equiv\text{Si}-\text{OH}$) groups. When the dried silica surface is exposed to water vapor, the water molecules start to adsorb, presumably by direct interaction with the silanols [17]. However, the sequence of the adsorption of water on the silica surface is not yet clear. One option for the water molecule to adsorb is “oxygen down” and by the formation of a 1:1 complex in which the surface OH groups are donors and the water

molecules are acceptors of the hydrogen bond [18]. Another option is the water interacts with SiOH as a hydrogen acceptor which means that the water molecule is doubly hydrogen bonded to the surface [19–21]. At high relative humidity, the water molecules condense at the entrance to the pores before the condensed liquid will migrate into the pores, a process known as capillary condensation [13, 22, 23].

Water vapor adsorption on silica gel has been investigated intensively owing to the fact that silica gel is used in industry as a drying agent, catalyst support, or filler [11, 24–26]. Those studies focus on the cycle stability towards water, diffusion times, or the kinetics of water adsorption on silica gel. Other studies focus on the synthesis of the silica gels and the subsequent characterization by density measurements, fourier-transform infrared spectroscopy, and nitrogen sorption analysis [8, 9]. There exists only a few studies that investigate the influence of the pore size on the water sorption behavior through inhouse synthesis of silica gels [2, 27].

In this work, we report the synthesis of silica xerogels derived from tetraethylorthosiloxane (TEOS) within 10 h including hydrolysis, gelation, aging and drying. The effect of the ammonia concentration and the water content on the porosity, pore size, surface area, and the water sorption behavior were examined. It was found that a higher concentration of ammonia during the condensation reaction leads to a bigger pore size and shifts the water sorption isotherm to high relative pressure. The water sorption capacity can be increased by increasing the amount of water during the condensation reaction. By a controlled addition of ammonia and water, silica xerogels can be tailored to have a higher water sorption capacity than the reference silica gel over the whole range of relative pressure.

2 Experimental

2.1 Materials

Ethanol (A15-A ethanol denatured with 2% methyl ethyl ketone) was obtained from Alcosuisse. Ammonium hydroxide (29 wt.%) and sulfuric acid (95–98 wt.%) were received from Sigma Aldrich. Tetraethylorthosiloxane (TEOS, $\geq 98\%$) was received from Evonik. All solutions

Table 1 Table of experiments

Sample	Prehydrolyzed silica sol [ml]	H ₂ O [ml]	Ammonia [mM]
XGW1	41	4.04	18.3
XGW2	41	4.04	36.6
XGW3*	41	4.04	61.1
XGW4	41	4.04	91.6
XGW5	41	4.04	122.1
XGA6	41	2.04	61.1
XGA7	41	3.04	61.1
XGA8*	41	4.04	61.1
XGA9	41	5.04	61.1
XGA10	41	6.04	61.1

XGW: silica xerogels series synthesized with the same content of water

XGA: silica xerogels series synthesized with the same concentration of ammonia

*XGW3 and XGA8 are the same sample

were prepared from ultrapure water (double distilled quality, $>18\text{ M}\Omega\cdot\text{cm}$). As reference adsorbents, commercial silica gel beads (RD-type) with a diameter between 1.8 and 2.0 mm were received from Fuji Silysia Chemical Ltd.

2.2 Preparation of the xerogels

The synthesis of the silica xerogels consists out of three steps: hydrolysis, condensation, and drying. For the hydrolysis, 18 g of ethanol were mixed with 0.256 g of concentrated H₂SO₄. This solution was added to 308 g of TEOS and stirred vigorously for 1 h at room temperature. Then, the temperature was increased to 35 °C before 41.62 g of water was added over the course of 2 h using a syringe pump. The obtained prehydrolyzed silica sol was then used for the condensation reaction.

For condensation, 41 ml of the prehydrolyzed silica sol was mixed with water before the addition of ammonia (Table 1). The silica sol was poured into plastic containers and sealed before being put in an oven at 65 °C. The gelation onset was after about 5–10 min from the addition of the last reagent. After the gelation, the gels were covered with 10 ml of Ethanol and placed back in the oven for 6 h of aging. Then, the gels were removed from the plastic mold and dried in a ventilation oven at 150 °C for 2 h. Before the characterization, the dried xerogels were placed in an 80% relative humidity chamber for 10 days in order to exchange the ethoxy groups by hydroxyl groups.

2.3 Characterization

The envelope density (ρ) was measured by a Geopyc 1360 from Micromeritics. In this characterization method, the

silica xerogel (2–4 mm in diameter) was placed in a bed of DryFlo® granular medium, which was agitated and carefully consolidated around the scaffold using a piston [28]. The sample was getting consolidated by agitation and rotation of the cylindrical chamber since the piston was gradually pushed into the chamber until the consolidation force was reached, followed by retraction and recompression. A 12.7 mm diameter chamber was used to measure with a conversion factor of 0.1246 and a consolidation force of 4 N. For each measurement, 10 cycles were carried out. The skeleton density (ρ_{skeleton}) was determined with an AccuPyc II 1340 helium pycnometer (Micromeritics, helium purity of 99.999%). The skeleton volume of the sample was measured by detecting the change in pressure owing to the volume of helium that was displaced by the silica xerogel within the sealed and pressure-equilibrated chamber. Each measurement consisted of 10 purge cycles and 10 analysis cycles. Prior to all density measurements, the silica xerogels were dried for 12 h at 150 °C. The porosity Φ was calculated from the envelope density ρ and the skeleton density ρ_{skeleton} using Eq. (1):

$$\Phi = 1 - \frac{\rho}{\rho_{\text{skeleton}}} \quad (1)$$

The pore volume (V_{pore}) was determined from Eq. (2):

$$V_{\text{pore}} = \frac{1}{\rho} - \frac{1}{\rho_{\text{skeleton}}} \quad (2)$$

Scanning electron microscopy (SEM) was performed for microstructural investigation after coating with 15–20 nm of Platinum. SEM images have been recorded with a FEI Nova NanoSEM 230 at an acceleration voltage of 7 kV and a working distance of 5 mm.

N₂ adsorption and desorption isotherms at 77 K were collected on a Micromeritics 3flex Surface Area and Porosity Analyzer. Prior to the experiments, approximately 150 mg of small silica pieces were degassed at 150 °C for 40 h at a pressure of 1.6×10^{-2} mbar. The total surface area of the materials was calculated by the Brunauer-Emmet-Teller (BET) method [29]. A Physi ViewCalc tool from Micromeritics was used to calculate the micropore volume (V_{Micro}) with the t-plot method [30]. The total pore volume (V_{total}) was calculated from the volume of nitrogen adsorbed (V_{ads}) converted to liquid V_{liq} at a pressure close to $P/P_0 = 1$ [31]. The mesopore volume (V_{Meso}) was calculated by subtracting the value of V_{Micro} from V_{total} [32]. The average pore diameter (D_{pore}) was calculated from the total pore volume (V_{total}) of the xerogel and its specific surface area (S_{BET}) by $D_{\text{pore}} = 4V_{\text{pore}}/S_{\text{BET}}$. The pore size distributions were determined by the Barrett-Joyner-Halenda (BJH) method based on the desorption branch [33].

Fourier-transform infrared spectroscopy (FTIR) was performed on a Bruker Tensor 27 spectrometer in attenuated total reflectance (ATR) mode with a diamond analyzer crystal. Each spectrum was collected in the range from 4000 to 600 cm^{-1} with 32 scans. The spectra were obtained using the OPUS software provided by the instrument manufacturer (Bruker Optics GmbH, Ettlingen, Germany). Prior to the measurements, the samples were degassed in a vacuum oven (10 mbar) at 50 °C for 16 h.

Dynamic vapor sorption (DVS) isotherms were measured by an isothermal gravimetric DVS apparatus (TA Instruments VTI-SA+). The amount of adsorbed water vapor was continuously recorded by a high-precision microbalance with an accuracy of 10 μg . The amount of sample material placed in the experiment chamber was 10–30 mg. Prior to the actual measurement, the sample was heated to 90 °C under nitrogen atmosphere for 1 h and the resulting mass was taken as the dry reference mass. For the subsequent measurement, the sample was cooled down to 50 °C. Adsorption/desorption cycles were performed at a constant temperature of 50 °C. The material is exposed to relative pressure (P/P_{sat}) steps between 0 and 0.6 in 0.05 intervals and between 0.6 and 0.8 in 0.1 intervals in a controlled flow of a mixture of nitrogen and water vapor while the sample mass is recorded every 60 s. At 50 °C, the saturation pressure of water is 124 mbar ($P/P_{\text{sat}} = 1$). For each step, the pressure was kept constant until the rate of mass change became negligible (less than 0.08 %/5 min) and the corresponding pressure and mass values were recorded until the entire adsorption and desorption isotherms were completed.

3 Results and discussion

3.1 Density and porosity

The influence of the catalyst concentration and the content of water on the envelope density, skeleton density, porosity,

and calculated pore volume is shown in Table 2. It can be observed that a higher concentration of ammonia leads to a lower density and an increase in porosity as well as pore volume. These results are in agreement with the observations from Fidalgo et al. [8]. An increase in the ammonia concentration during gelation leads to a decrease in envelope density and an increase in porosity. Chan et al. [31] found that the pore volume is increasing when the gel is synthesized with a higher concentration of NaF which is in agreement with our observed data.

A decrease in the density is usually accompanied by a lower volume shrinkage during the drying of the material. The shrinkage is influenced by the responses of the structures to the removal of the solvent upon drying. Gels with a large bulk modulus are more likely to withstand the capillary pressure which leads to a lower density of the dried xerogel [8]. Possibly, gels which were synthesized with a high concentration of ammonia have a stronger network which leads to a lower shrinkage and, therefore, to a lower density of the dried xerogel.

Furthermore, an increase of the water content for the condensation reaction also leads to a reduction of the envelope density. According to Milea et al. [34], an increase in water content leads to a corresponding increase in condensation rate. A higher degree of condensation leads to a stronger silica network and, therefore, to a lower shrinkage during drying [35].

3.2 Xerogel microstructure

Figure 1 shows the SEM micrographs of the xerogels after drying at 150 °C. It can be observed that the xerogels reveal a 3-dimensional network of primary particles [36]. A higher concentration of ammonia leads to a bigger particle size. This observation is consistent with the measurement of the envelope density. Increasing the ammonia concentration induces the formation of larger and more cross-linked polymers with a stronger network and a larger particle size.

Table 2 Effect of catalyst and water concentration on envelope density, skeleton density, porosity and, pore volume

Sample	ρ [g/cm^3]	ρ_{skeleton} [g/cm^3]	Porosity Φ [%]	V_{pore} [cm^3/g]
XGW1	1.149 ± 0.017	1.978 ± 0.001	41.9	0.365 ± 0.013
XGW2	1.065 ± 0.011	1.946 ± 0.002	45.3	0.425 ± 0.010
XGW3	1.001 ± 0.008	1.973 ± 0.002	49.3	0.492 ± 0.008
XGW4	0.985 ± 0.006	1.945 ± 0.001	49.3	0.501 ± 0.006
XGW5	0.925 ± 0.005	1.944 ± 0.001	52.4	0.567 ± 0.006
XGA6	1.083 ± 0.007	1.925 ± 0.001	43.8	0.404 ± 0.006
XGA7	1.078 ± 0.007	1.927 ± 0.001	44.1	0.409 ± 0.006
XGA8	1.001 ± 0.008	1.973 ± 0.002	49.3	0.492 ± 0.008
XGA9	0.935 ± 0.008	1.962 ± 0.001	52.3	0.560 ± 0.009
XGA10	0.940 ± 0.004	1.967 ± 0.001	52.2	0.555 ± 0.005
Reference silica gel	1.249 ± 0.019	2.060 ± 0.002	38.9	0.315 ± 0.012

Fig. 1 Scanning electron microscopy images of the silica xerogels after drying

A low concentration of ammonia leads to the formation of smaller particles which are more susceptible to capillary pressure and can cause the network to deform and impinge one another. The result is a denser dry gel without any macropores [8].

A small water content leads also to the formation of smaller particles. With an increase in the water content, the particles of the xerogel become bigger which may be caused by an enhanced condensation rate [34, 36].

3.3 Surface properties

Figure 2a, b illustrate the N_2 adsorption and desorption isotherms of the silica xerogels prepared with different ammonia concentration and different water content. The N_2 isotherms of the silica xerogels show a high nitrogen uptake at low relative pressures ($P/P_0 < 0.1$) and a plateau at high relative pressures which indicates the presence of

microporosity. All samples (except XGW1) show an additional uptake at relative pressures ($P/P_0 > 0.2$) and a hysteresis, which reflects the presence of mesoporosity. The nitrogen sorption capacity increases with a higher ammonia concentration as well as with a higher water content (Fig. 2a, b). According to the BJH pore size distribution (Fig. 2c, d), the concentration of ammonia and the content of water increases the fraction of all pores indicating an increasing porosity.

The influence of the ammonia concentration and the water content on the BET surface area, micropore volume, mesopore volume, and the average pore size is shown in Table 3. It can be observed that the BET surface area increases with a higher concentration of ammonia or a higher amount of water. With an increase in the ammonia concentration, the mesopore volume significantly increases. An increase in water content during the condensation reaction increases the micropore volume as well as the

Fig. 2 Low-temperature nitrogen adsorption (open symbols)/desorption (closed symbols) isotherms of silica xerogels with (a) different ammonia concentration and (b) different water content and its corresponding BJH pore size distributions (c, d)

Table 3 BET surface area, micropore volume, mesopore volume, total pore volume and average pore size of the silica xerogels

Sample	S_{BET} [m ² /g]	V_{Micro} [cm ³ /g]	V_{Meso} [cm ³ /g]	V_{total} [cm ³ /g]	D_{pore} [Å]
XGW1	738	0.175	0.212	0.387	21.0
XGW2	879	0.143	0.358	0.501	22.8
XGW3	968	0.113	0.452	0.565	23.4
XGW4	976	0.088	0.509	0.597	24.5
XGW5	991	0.075	0.564	0.639	25.8
XGA6	856	0.165	0.313	0.478	22.3
XGA7	903	0.125	0.405	0.530	23.5
XGA8	968	0.113	0.452	0.565	23.4
XGA9	995	0.057	0.567	0.624	25.1
XGA10	1039	0.038	0.651	0.689	26.5

mesopore volume of the silica xerogels. These results are in agreement with the observations from Alcañiz et al. [2]. With an increase in the water:TEOS ratio, the micropore and mesopore volume increases whereas an increase in pH leads to a significant increase in the mesopore volume. The average calculated pore size increases with a higher

concentration of ammonia and with a higher content of water. The pore volume calculated by the envelope and skeleton density (Table 2) is close to the total pore volume determined by the nitrogen sorption analysis. These results are in agreement with the observations from Fidalgo et al. [8] and Chan et al. [31]. An increase in the concentration of ammonia respectively NaF during gelation leads to an increase in average pore size and a higher total pore volume.

The full FTIR spectra (4000 cm⁻¹–600 cm⁻¹) of all samples present in this study are shown in Fig. S1. The broad peak around 3400 cm⁻¹ is ascribed to an O–H stretching region where some freely vibrating OH groups and a majority of hydrogen-bonded OH groups are apparent [37]. Silica gels which contain physisorbed water show a small peak at 1630 cm⁻¹ [38]. Since the silica xerogels in this study were degassed in a vacuum oven prior to the measurement, this feature is not visible. The FTIR spectra of the fingerprint region (1400 cm⁻¹–600 cm⁻¹) of the silica xerogels synthesized with different ammonia concentrations are shown in Fig. 3a whereas the silica xerogels synthesized with different water contents are shown in Fig. 3b. The spectra look very similar. The adsorption band at 1090 cm⁻¹ is related to asymmetric stretching modes of Si–O–Si bonds

Fig. 3 FTIR spectra of silica xerogels with (a) different ammonia concentration and (b) different water content

[39]. The band at about 800 cm^{-1} is associated with the symmetric stretching modes of these bonds [40]. The band at 960 cm^{-1} reveals the presence of surface silanol groups on these samples [38, 40–42]. The intensity of the band at 960 cm^{-1} is higher for xerogels synthesized with a high concentration of ammonia and for xerogels which were synthesized with a high water content. Xerogels which were synthesized with a higher concentration of ammonia, respectively, with a higher content of water have a higher specific surface area and are therefore expected to have a

greater number of nonbridging surface —SiOH groups [38]. The presence of these bands in the collected FTIR spectra confirms that sol–gel silica samples were successfully obtained in this study.

3.4 Water sorption behavior

The effect of the ammonia concentration on the water sorption behavior of the silica xerogels is shown in Fig. 4. A low concentration of ammonia leads to a higher water sorption at lower relative pressure and a small hysteresis, which might be due to the smaller pore size. However, the total water sorption capacity is relatively low, which is in good correlation with the BET surface area. A higher concentration of ammonia shifts the water sorption isotherm to higher relative pressure, which might be caused by the increasing pore width and the higher fraction of mesopores. Silica gels prepared with a higher content of water show an increase in water sorption capacity. These results are in agreement with findings from Ibrahim et al. [43] who found an increased water sorption capacity when the silica xerogels were synthesized with a higher $\text{H}_2\text{O}/\text{TEOS}$ ratio. The increased water sorption capacity is consistent with the N_2 sorption measurements which exhibited a larger BET surface area and a higher total pore volume for xerogels which were synthesized with a higher water content. Furthermore, it can be deduced that silica gels containing a higher mesopore volume exhibit a larger hysteresis of the water sorption isotherms.

The silica gel which was synthesized with the lowest concentration of ammonia (XGW1) has a higher water sorption capacity over the whole range of relative pressure compared to the reference silica gel (Fig. S2). The combination of a short processing time with the high water sorption capacity might be very interesting for industrial applications such as desiccants or AHPs.

4 Conclusions

Silica samples with promising applications as water sorbents were successfully obtained in this work. The total processing time, including hydrolysis, gelation, aging and ambient pressure drying is 10 h. It was found that an increasing concentration of ammonia or a higher content of water leads to a significant reduction of the envelope density. Silica gels prepared from a higher concentration of ammonia exhibit a higher average pore size whereas the silica gels prepared from a higher content of water have an increased BET surface area. From the comparative analysis of nitrogen and water sorption isotherms, it was observed that water adsorption at low relative pressure mainly occurs in micropores. Silica gels containing a high fraction of

Fig. 4 Water vapor adsorption (open symbols) and desorption (closed symbols) isotherms of silica gels prepared with different concentration of ammonia (XGW1–XGW5) and different amount of water (XGA6–XGA10)

mesopores exhibit water adsorption at higher relative pressures compared with those containing a low fraction of mesopores. By a controlled addition of ammonia and water,

silica xerogels can be tailored to have a higher water sorption capacity than the reference silica gel over the whole range of relative pressure.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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