

# Adsorption of Water Vapor on Silica, Alumina, and Their Mixed Oxide Aerogels

Željko Knez\* and Zoran Novak

University of Maribor, Faculty of Chemistry and Chemical Engineering,  
Smetanova 17, SI-2000 Maribor, Slovenia

---

SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> aerogels and mixed SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> aerogels exhibit excellent adsorption capacities of water vapor in the range above 1.0 kg of water/kg of aerogel. Adsorption properties of mixed SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> aerogels remain stable even after 25 repeated adsorption/desorption cycles.

---

## Introduction

Aerogels based on silica and other metal oxides (alumina, titania, zirconia, stannic or tungsten oxide, or a mixture of these oxides) are extremely porous materials with high specific surface areas. They possess ultrafine pore sizes (<100 nm) and due to their high porosity (up to 99% for SiO<sub>2</sub>) show interesting physicochemical properties, including very high specific surface areas (500 to 1000) m<sup>2</sup>·g<sup>-1</sup>, low bulk densities (0.003 to 0.35) g·cm<sup>-3</sup>, low thermal conductivities (0.014 W·m<sup>-1</sup>·K<sup>-1</sup> at 1 atm and 0.004 W·m<sup>-1</sup>·K<sup>-1</sup> at reduced pressure), and refractive indices between 1.008 and 1.4.

Due to these remarkable properties, aerogels could, besides other well-known applications,<sup>1</sup> serve as good adsorbents for water vapor and pollution gases.<sup>2</sup> Zeolites and silica gels are the most common adsorbents today, exhibiting adsorption capacities of water vapor around (0.3 to 0.4) kg of water/kg of adsorbent.<sup>3</sup>

The research and development of new, more effective adsorbents for water vapor, focusing on adsorption characteristics of three different aerogels, is reported.

## Experimental Section

Samples were prepared by sol–gel synthesis followed by supercritical drying with carbon dioxide. The final step was calcining at 400 °C for 3 h in air.

**Sol–Gel Synthesis.** Table 1 shows all the data for sol–gel syntheses. The apparatus used for sol–gel synthesis is already presented in previous articles.<sup>4</sup> It consists of a two-piece glass reactor with a water-cooled condenser for the reflux of a solvent and a dropping funnel for the addition of reactants during sol–gel synthesis. To perform a sol–gel synthesis in an inert atmosphere, nitrogen was supplied from a gas cylinder.

**Supercritical Carbon Dioxide Drying.** The second step in the production of aerogels was the drying of gels. In supercritical carbon dioxide drying, alcohol from the structure of the gel was replaced by carbon dioxide at 40 °C and 100 bar.<sup>5</sup>

The extractor was completely filled with cold solvent (alcohol) in order to minimize evaporation of the solvent from the alcogel and to avoid cracks developing during pressure build up. CO<sub>2</sub> was pumped into the extractor to

a pressure above its critical pressure, that is, 100 bar. Before entering the extractor, CO<sub>2</sub> was heated to a temperature above its critical temperature, that is, 40 °C. During drying, the flow of CO<sub>2</sub> to the extractor was held constant at 0.54 kg·h<sup>-1</sup> and controlled independently of pressure. In the separator, the solvent was separated from carbon dioxide by expansion. When the solvent was completely replaced, the extractor pressure was slowly reduced to ambient pressure.

**Adsorption Isotherms.** Water vapor adsorption isotherms were measured gravimetrically at 293 K. Hystereses were not investigated because step-by-step desorption was not included in the experiments. The measurements of adsorption/desorption isotherms of nitrogen at 77 K were carried out using the Micromeritics, ASAP 2010 MP volumetric adsorption instrument.

For investigation of specific surface areas while repeating ads/des cycles, BET surface areas were measured using a gas mixture of 30% nitrogen and 70% argon with a Micromeritics Flowsorb II 2300 instrument. Prior to the measurements, each sample was dried for 24 h in a vacuum at 70 °C and then degassed for 15 min in the apparatus at the same temperature.

Aerogel adsorbents were also viewed with transmission electron microscopy (TEM) to define both the morphology and porous texture.

## Results and Discussion

From Figure 1 the affinity of different adsorbents (aerogels and commercial silica gels) for water vapor can be seen. The adsorption capacities of all aerogels were between 1.1 and 1.4 kg of water/kg of adsorbent at relative pressures approaching 1.0.

The adsorptivity of water vapor was relatively low at low relative pressures for all single- and mixed-oxide aerogels. To compare water vapor affinity, two commercial silica gels were included (SiGel 10–40 with mean particle sizes between 10 and 40 μm and SiGel 2–4 with mean particle sizes between 2 and 4 μm).

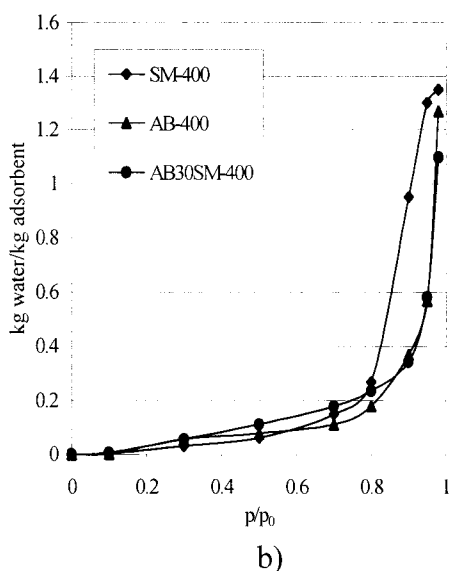
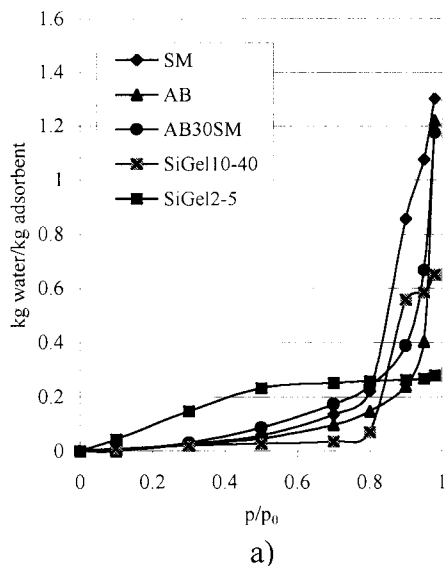
Adsorption isotherms of water vapor for both silica aerogels (raw and calcined) are type V, having a noticeable uptake near the relative pressure  $p/p_0 = 0.8$ . All adsorption isotherms for other aerogels (alumina and mixed silica–alumina) are similar up to this value. After that a sharp increase is evident for all aerogels at higher  $p/p_0$  ratios than those for SiO<sub>2</sub> aerogels.

\* Phone: +386 2 2294 463. Fax: +386 2 2516 750. E-mail: zeljko.knez@uni-mb.si.

**Table 1. Oxide Aerogel Designations and Corresponding Sol–Gel Synthesis Conditions**

aerogel	composition/mass %	sol–gel system, <sup>a</sup> alkoxide–solvent	water <sup>b</sup>	appearance	aging/days
SM	100% SiO <sub>2</sub>	Si(OMe) <sub>4</sub> –MeOH	4	transparent gel	3
AB	100% Al <sub>2</sub> O <sub>3</sub>	Al( <i>s</i> -OBu) <sub>3</sub> – <i>s</i> -BuOH	3	precipitate	3
AB30SM	30% Al <sub>2</sub> O <sub>3</sub> <sup>–</sup>	Si(OMe) <sub>4</sub> –MeOH	4	gel	3
	70% SiO <sub>2</sub>	Al( <i>s</i> -OBu) <sub>3</sub> – <i>s</i> -BuOH	3		

<sup>a</sup> 10 mass % solutions of alkoxides in solvent. <sup>b</sup> Mole of water/mole of alkoxide.

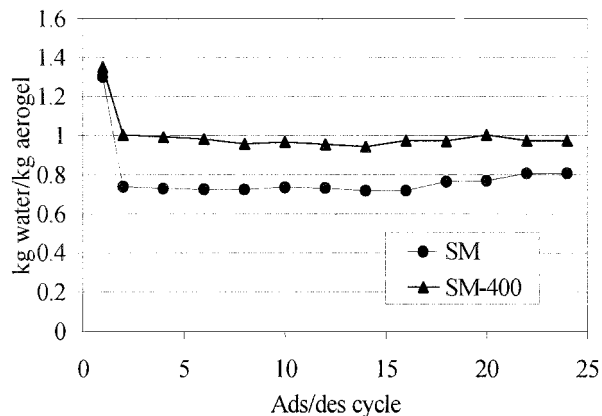


**Figure 1.** Water vapor adsorption on different aerogels and silica gels at 293 K: (a) uncalcined; (b) calcined at 400 °C.

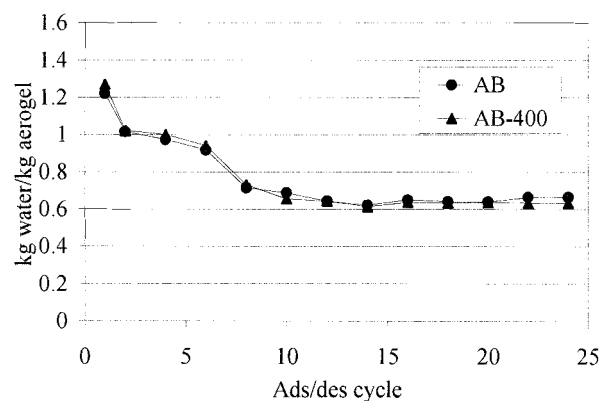
The type of adsorption isotherm for commercial SiGel 10–40 is the same as that for SiO<sub>2</sub> aerogels (type V), but the saturated amount of water adsorbed is much lower and it is around 0.6 kg of water/kg of adsorbent.

The saturated amount of water adsorbed on aerogels is the highest in the case of single SiO<sub>2</sub> aerogels (≈1.35 kg/kg). This amount is 1.25 kg/kg for Al<sub>2</sub>O<sub>3</sub> aerogels and 1.15 kg/kg for mixed SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> aerogels. Raw and calcined aerogels do not show much difference in the saturated amount of water adsorbed. The differences appear when adsorption/desorption cycles are repeated. In this case the situation is different, depending on the type of aerogels.

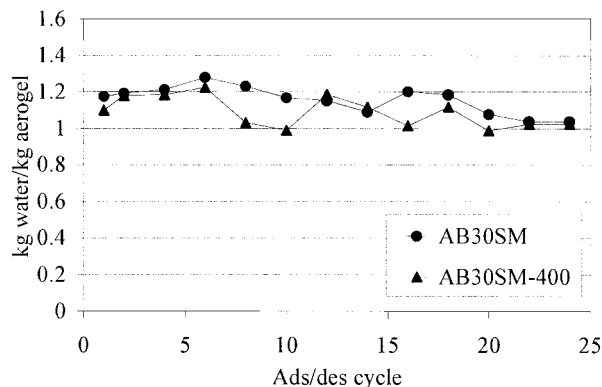
The adsorptive capacity of aerogels compared to commercial silica gels is markedly high on a mass basis and



a)



b)



c)

**Figure 2.** Adsorption of water vapor on aerogels (raw and calcined at 400 °C) during repeated ads/des cycles: (a) single silica aerogel; (b) single alumina aerogel; (c) mixed silica–alumina aerogel.

low on a volume basis (0.136 kg of water/L of aerogel compared to 0.209 kg of water/L of silica gel). With calcination the bulk density of aerogels increases but the adsorptive capacities remain almost the same (Figure 1),

**Table 2. BET Surface Areas,  $S_{\text{BET}}$ , Determined by the Adsorption of a Gas  $\text{N}_2$ -Ar Mixture**

aerogel	$S_{\text{BET}}$ $\text{m}^2\cdot\text{g}^{-1}$	$S_{\text{BET}}$ (after first cycle) $\text{m}^2\cdot\text{g}^{-1}$	decrease %	$S_{\text{BET}}$ (after 20th cycle) $\text{m}^2\cdot\text{g}^{-1}$
SM	783	578	26.18	595
SM-400	664	610	8.13	558
AB	453	324	28.47	332
AB-400	296	270	8.78	170
AB30SM	577	382	33.79	293
AB30SM-400	376	274	27.12	236

that is, the differences in saturated amount of water vapor on a volume basis become even smaller.

The reproducibility of the isotherms in Figure 1 was very good. Each isotherm was measured at least twice, and relative errors range from 0.2% to 3.6%.

Figure 2 shows results of repeated ads/des cycles of water vapor. In the repeated adsorption/desorption experiments the adsorption steps were performed after complete desorption by thermal treatment.

The adsorptivity of single silica aerogels decreased markedly after the first cycle (42% for raw silica aerogel and 26% for the calcined sample), but after this drop, adsorptivity remained more or less stable in the next 25 cycles. The adsorptivity of calcined silica aerogels was higher than that of the raw aerogels because of their strengthened structure produced during calcining.

A similar drop in adsorptivity was also evident for single alumina aerogels but not so great as in the case of silica aerogel. Adsorptivity slowly decreased to a value between 0.6 and 0.7 kg of water/kg of aerogel adsorbent, after which it remained stable. The comparison between raw and calcined single alumina aerogels (Figure 2) showed that there is no difference in amount of adsorbed water vapor.

The best stability and the highest adsorptivity of water vapor were exhibited by the mixed silica-alumina aerogels. Adsorptivity remained stable for at least 25 repeated ads/des cycles in the range between 1.0 and 1.2 kg of water vapor/kg of adsorbent. There was no loss of ability of adsorption after the first cycle and no difference between raw and calcined aerogels.

BET surface areas of different aerogel adsorbents were measured twice during the repeated ads/des cycles. The first measurements were done immediately after the first ads/des cycle and after the 20th cycle. For the adsorptivity of water vapor for all single silica and alumina aerogel adsorbents, the first ads/des cycle was the most stressful, which is evident from Table 2 and Figure 2. The same reduction was also evident for BET surface areas after the first ads/des cycle for both single aerogels. The decrease in BET surface areas was greater for the raw, uncalcined aerogels. This is consistent with the theory that the

**Table 3.  $\text{N}_2$  Physisorption Results for Two Different Silica Aerogels**

aerogel	$S_{\text{BET}}$ ( $S_{\text{mic}}$ ) <sup>a</sup> / $\text{m}^2\cdot\text{g}^{-1}$	$V/\text{cm}^3\cdot\text{g}^{-1}$ meso/micro	$d^b/\text{nm}$ meso/micro
SM	1065 (170)	6.3/0.072	10–20/1.5
AB30SM	620 (243)	1.1/0.117	10–15/1.5

<sup>a</sup>  $S_{\text{mic}}$  in parentheses is the specific micropore area derived from t-plot analyses. <sup>b</sup> Cylindrical pore geometry.

calcination process strengthens the structure of aerogels; hence, the possibility of damaging the structure is lower when adsorption and desorption processes take place.

Some main characteristics of the porous texture of two different silica aerogel samples obtained by  $\text{N}_2$  physisorption are presented in Table 3. Both samples consist of micropores and mesopores. A single silica aerogel has a large pore volume but a low level of microporosity, as confirmed by both low micropore area and volume.

TEM images show the compact morphology and porous texture of all aerogel samples. The structure is quite open and, because of this, easily accessible for water vapor.

## Conclusions

The investigation of adsorption of water vapor on silica, alumina, and mixed silica-alumina aerogels, prepared by supercritical  $\text{CO}_2$  drying, resulted in two important facts:

All three aerogels exhibit adsorption capacities in the range between 1.0 and 1.2 kg of water/kg of aerogel, which is markedly higher than that of any known adsorbent today.

The adsorptivity of a mixed silica-alumina aerogel is higher than the adsorptivities of both single aerogels in repeated ads/des cycles and remains practically unchanged after 25 cycles.

## Literature Cited

- (1) Fricke, J., Ed. *Aerogels*, Proceedings of the 1st International Symposium on Aerogels, ISAI, Würzburg, 1985; *Springer Proceedings in Physics*, Vol. 6; Springer-Verlag: Berlin, 1986.
- (2) Attia, Y. A.; Ahmed, M. S.; Zhu, M. In *Sol-Gel Processing and Applications. Proceedings of the International Symposium on Advances in Sol-Gel Processing and Applications*; Attia, Y. A., Ed.; Plenum: New York, 1993; pp 311–321.
- (3) Ruthven, D. M. *Principles of adsorption and adsorption processes*; Wiley: New York, 1984.
- (4) Novak, Z.; Knez, Z. Sol-gel transition for production of silica aerogels. *Chem. Tech.* **1997**, *49*, 106–108.
- (5) Novak, Z.; Knez, Z. Diffusion of methanol-liquid  $\text{CO}_2$  and methanol-supercritical  $\text{CO}_2$  in silica aerogels. *J. Non-Cryst. Solids* **1997**, *221*, 163–169.

Received for review July 5, 2000. Accepted March 19, 2001.

JE000201I