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Effect of preparation parameters on the texture of SiO_2 aerogels

Yuan-Yang Wang [*], Yin-Ben Gao, Yu-Han Sun, Song-Ying Chen

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China

Abstract

SiO_2 aerogels with good properties were prepared by the sol–gel method involving supercritical drying. The effects of preparation parameters, including solution, gelation and supercritical condition, upon the textural properties of SiO_2 aerogels were investigated.

Keywords: SiO_2; Aerogels; Sol–gel; Supercritical drying; Preparation

1. Introduction

NiO/SiO_2-Al_2O_3 catalysts (prepared by the sol–gel route with supercritical drying) appeared to be very active in CO oxidation. Among these catalysts, NiO/SiO_2 produced by impregnating SiO_2 aerogels with a precursor solution was shown to be comparable with noble metal catalysts (such as Pt/Al_2O_3) in its catalytic performance [1]. In order to have a full understanding of their differences, the effects of the preparation parameters on the texture of SiO_2 aerogels are in the first instance investigated in terms of sol–gel chemistry.

A number of parameters, such as the initial solution, gelation and the supercritical condition, are important factors for the preparation of SiO_2 aerogels [2], in which the amount of water added and the pressure of pre-added nitrogen appeared to seriously influence the texture of the SiO_2 aerogels. Therefore, the effect of parameters on SiO_2 aerogels prepared by two routes is investigated in this paper.

2. Experimental

2.1. Preparation

Two routes were employed for colloid preparation. One (M1) is that the tetraethoxy-silicane (TEOS), ethanol, water and acetic acid were mixed at a certain mole ratio into a solution and then stirred at a certain temperature until the sol formed. The sol was then introduced into an autoclave for supercritical drying. As a contrast to M1, via route M2, the precursors were mixed at the same mole ratio and then introduced into an autoclave without any stirring, the colloid formation occurred in the autoclave when supercritical conditions were reached.

2.2. Supercritical drying (SCD)

When the sol or the solution was introduced into the autoclave, nitrogen was pumped into the autoclave to replace the air at a flow rate of 20 ml/min (if the effect of pre-added nitrogen pressure was to be investigated, the nitrogen was introduced into the autoclave with a certain

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[*] Corresponding author.

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pressure at this moment), the autoclave was then heated to 533 K at a heating rate of 3 K/min under 7.5 MPa, then kept for 30 min. After the ethanol vapour was evacuated quickly (usually 5 min), the autoclave was cooled to room temperature (RT) under a dry nitrogen flow of 20 ml/min, which gave the SiO_2 aerogels.

2.3. Characterization

The SiO_2 aerogels were characterized by TEM (H-600 II) and texture measurement (ASAP-2000).

3. Results

3.1. Solution

In the sol–gel process of TEOS, hydrolysis and condensation take place simultaneously [3]:

$$Si(OC_2H_5)_4 + xH_2O \rightarrow Si(OH)_x(OC_2H_5)_{4-x} + C_2H_5OH$$

$$\text{-Si-OH} + \text{Si-OH} \rightarrow \text{-Si-O-Si} + H_2O$$

$$\text{-Si-}OC_2H_5 + \text{Si-OH} \rightarrow \text{-Si-O-Si} + C_2H_5OH$$

i.e. water is both a reactant and condensation product. The ratio of H_2O/TEOS is therefore very important for sol formation. Here, acetic acid was selected as the acid catalyst for the formation of cross-linked hydrogels which gave SiO_2 aerogels with a highly porous structure.

Table 1 shows that the BET surface area decreases with increasing TEOS concentration. Considering the low density of SiO_2 aerogels, however, the proper concentration appears to be around 1 mol/l. In this case, the H_2O/TEOS ratio is critical and its influence is dependent on the sol–gel routes: the surface area reaches a maximum at 4.00 of H_2O/TEOS for the M1 route, but it increases with increasing H_2O/TEOS ratio for the M2 route (see Table 1), which is closely related to their morphologies (see Fig. 1). Furthermore, the H_2O/TEOS ratio greatly changes the pore structure (see Fig.

Table 1
The effect of solution on texture of SiO_2 aerogels [a]

Sample no.	H_2O/ TEOS	Concentration of TEOS (M)	Surface area (m^2/g)	Average pore size (nm)	Pore volume (cm^3/g)
M1-1	7.00	0.5	1101		
M1-2	7.00	1.0	918		
M1-3	7.00	1.5	878		
M1-4	2.00	1.0	955.99	10.98	2.62
M1-5	4.00	1.0	1274.09	11.16	3.56
M1-6	8.00	1.0	584.30	14.34	2.10
M1-7	22.0	1.0	439.71	13.57	1.49
M2-1	2.06	1.0	37.49		
M2-2	4.00	1.0	529.82		
M2-3	7.78	1.0	767.92		
M2-4	22.3	1.0	904.04		

[a] CH_3COOH/TEOS = 0.1, stirring time = 120 min, gelation temperature = RT.

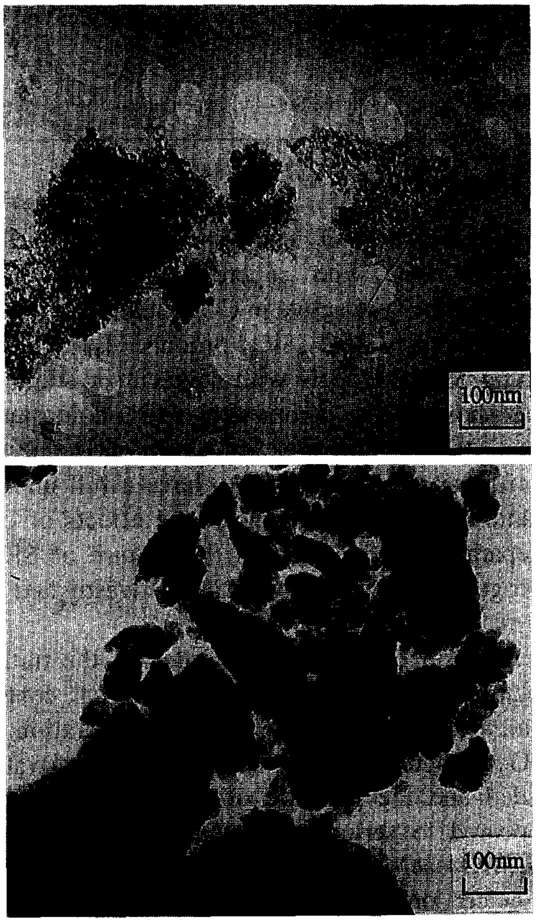

Fig. 1. TEM of typical M1 (top) and M2 (bottom) samples.

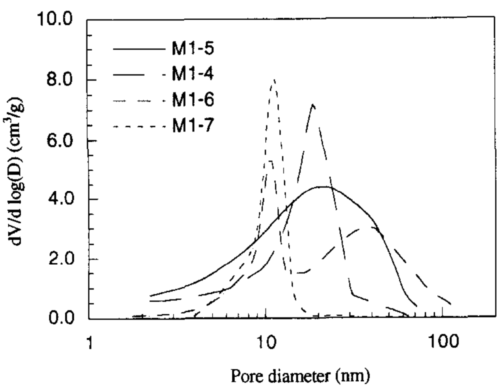

Fig. 2. The effect of H_2O/TEOS ratio on the pore distribution of SiO_2 aerogels prepared via the M1 route.

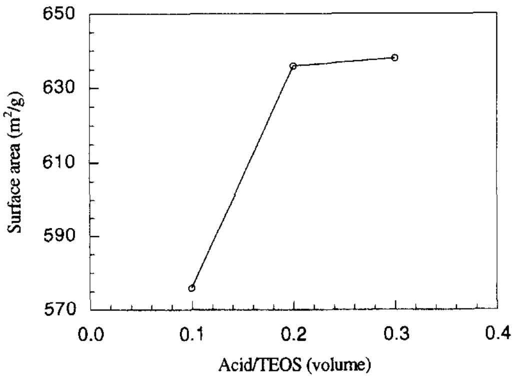

Fig. 3. The effect of acetic acid amount on the surface area of SiO_2 aerogels.

2). In addition, the presence of acid catalyst improves the surface area of SiO_2 aerogels (see Fig. 3).

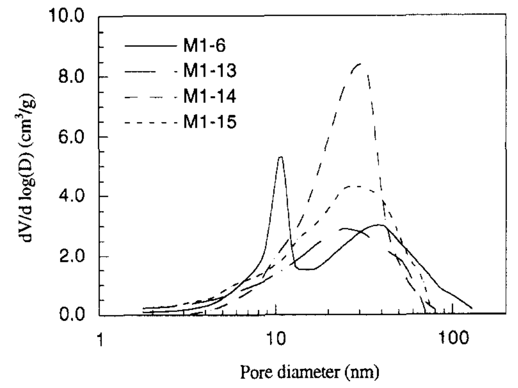

Fig. 4. The effect of initial N_2 pressure on the pore distribution of SiO_2 aerogels prepared via the M1 route.

3.2. Gelation and ageing

Gelation and ageing strongly affect the structure of sol–gel derived SiO_2 in which the temperature is crucial to the final surface area of the aerogels [4]. Comparing sample M1-8 with sample M1-9 in Table 2, it can be seen that M1-9 aged at 343 K has a higher surface area than M1-8. In contrast, samples (M1-10 and M1-12) gelled and aged at 343 K had a lower surface area in relation to those (M1-9 and M1-11) gelled at room temperature and aged at 343 K. The data in Table 2 also indicates that their surface area changes with the state of the wet gels no matter what the gelation temperature is. This suggests that the sol should be introduced into the autoclave as soon as it starts gelling if a high surface area is expected.

Table 2

The effects of gelation temperature and ageing degree on texture of SiO_2 aerogels [a]

Sample no.	Gelation and ageing temperature	Appearance		Surface area (m^2/g)
		Before SCD	After SCD	
M1-8	stirred and aged at RT	semifluid	translucent, monolith	681
M1-9	stirred at RT, aged at 343 K	semifluid	translucent, monolith	912
M1-10	stirred at RT, aged at 343 K	peptone	opaque, powder	653
M1-11	stirred and aged at 343 K	semifluid	translucent, monolith	858
M1-12	stirred and aged at 343 K	peptone	opaque, powder	518

[a] TEOS concentration = 1 M, H_2O/TEOS = 6.19, CH_3COOH/TEOS = 0.4, stirring time = 120 min.

Table 3
The effect of initial N_2 pressure on texture of SiO_2 aerogels [a]

Sample no.	Initial pressure (MPa)	Appearance	Surface area (m^2/g)	Average pore size (nm)	Pore
M1-6 [b]	0.0	fragment	584.30	14.34	2.10
M1-13	2.0	fragment	580.41	14.57	2.11
M1-14	4.0	few fragment	570.02	24.57	3.50
M1-15	6.0	monolith	732.81	15.74	2.88

[a] TEOS concentration = 1 M, $H_2O/TEOS = 8.00$, $CH_3COOH/TEOS = 0.2$. Ratio is 0.1, stirring time = 120 min, gelation temperature = RT.
[b] $CH_3COOH/TEOS = 0.1$.

3.3. *Supercritical drying*

The condition selection for supercritical drying is based on critical parameters of solvent, and the drying is usually carried out over the critical point in order for all of the solvent in the autoclave to be in a fluid state [5]. In the case of ethanol, parameters were selected to be $P = 7.5$ MPa and $T = 533$ K (because its critical point is $P_c = 6.36$ MPa and $T_c = 513$ K). Fig. 4 illustrates that the presence of pre-added nitrogen pressure strongly influences the pore distribution of SiO_2 aerogels, and with increase of the initial nitrogen pressure, their surface area increases but their pore size and pore volume show a maximum (see Table 3).

4. Discussion

4.1. *Effect of $H_2O/TEOS$ ratio on texture of SiO_2 aerogels prepared by two routes*

Fig. 2 illustrates that the pore distribution of SiO_2 aerogels greatly changes with the $H_2O/TEOS$ ratio. At a ratio of 2.00, the pores are shown to be concentrated around 20 nm; when the ratio reaches 4.00, a bimodal pore distribution appeared, and this change becomes much clearer at a ratio of 8.00 where some pores tend to be about 10 nm, with others at 40 nm. At a ratio of 22.00, only small-sized pores survive. This reveals that the mechanism for sol–gel formation greatly depends on the $H_2O/TEOS$ ratios. It is clear that less water slows down TEOS hydrolysis, which produces a number of small clusters such as tetramers and chains, and then improves cluster–cluster polymerization [6]. This leads to the formation of a cross-linked network and the production of small particles with concentrated pores and high surface area (see Table 1 and Fig. 2). With more water (especially at a stoichiometric ratio of 4.00), part of the TEOS transformed into large colloidal clusters due to its fast hydrolysis and then gave rise to a bimodal pore distribution, which becomes more significant at higher ratio (for instance, $H_2O/TOES = 8.00$). However, the situation greatly changes when much more water is added. At a ratio of 22.00, the bimodal distribution disappears because the hydrolysis is too fast to form a highly cross-linked network. In this case, the hydrolysis–condensation may follow a colloidal mechanism and therefore the aerogels with small concentrated pores and a lower surface area are produced.

The $H_2O/TEOS$ effect on the texture of the samples prepared via M2, however, shows totally different patterns: the surface area increases with the water amount (see Table 1). This indicates that the M2 route follows a different mechanism from M1, which may be caused by the fast hydrolysis–condensation of TEOS and replacement of water by ethanol simultaneously taking place with the increased temperature of the system. This also indicates that stirring is very important so that the gelation could be carried out at the molecular-level in homogeneous solution. Fig. 1 shows that the samples prepared via M1 are highly dispersed at a nano-sized level, but those via M2 consist of large particles. The detailed mechanism for M2 route is still under investigation.

4.2. *Effect of initial nitrogen pressure on the pore structure of SiO_2 aerogels*

Capillary pressure is the main reason for the collapse of the pore network of oxides on drying, which can be expressed as follows:

$$\Delta P = 2\gamma \cos \theta / r$$

with $r = 20$ nm, $\gamma = 22.75 \times 10^{-5}$ N/cm, $\theta = 90°$, ΔP would be 2.25 MPa, which is large enough to destroy the network formed in the sol–gel process [7]. However, the pressure produced by the surface tension could be reduced to zero under supercritical conditions, and then the original network would be maintained to a great extent. The introduction of nitrogen into autoclave is not only to produce monoliths [8], but also balances the capillary pressure before the system reaches the supercritical conditions.

Table 3 and Fig. 4 indicate that even with an initial N_2 pressure of 2.0 MPa, bimodal pore distribution of the aerogels disappears although its surface area and pore volume does not show any significant changes compared with the sample produced without initial nitrogen pressure. It is interesting that with the initial pressure increased, the average pore size and the pore volume show a maximum but the surface area is minimum at 4.0 MPa, which is reasonable if the change in the phase of the system is considered in the autoclave. Obviously, with higher N_2 pressure, more ethanol remains in the liquid phase and more water stays in the pores during drying, this induces the collapse of small pores due to the high capillary pressure, leading to large pore formation without any significant changes in the supercritical sol–gel mechanism. At 6.0 MPa, which approaches the critical pressure of ethanol, only a little ethanol but more water could evaporate into the gas phase, the polymerization mechanism may predominate and smaller particles are formed. This improves the surface area, although both pore size and pore volume decrease because the high initial pressure may compress the network of aerogels thus produced.

5. Conclusions

1. The sol–gel method involving supercritical drying is one of the most useful routes for the preparation of nano-sized highly porous oxides.
2. With an increase of TEOS concentration, the BET surface area of SiO_2 aerogels decreases, but the presence of CH_3COOH appears to be critical to produce high surface area aerogels.
3. The H_2O/TEOS ratio strongly influences the texture as well as sol–gel formation, leading to different pore distributions.
4. Relatively low gelation temperature and suitable ageing appear to benefit the production of high surface area aerogels, and stirring is very important to form a well-distributed colloidal system.
5. The presence of initial N_2 pressure improves the formation of SiO_2 aerogels with large pore structure.

Acknowledgements

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