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Effects of Synthesis Parameters Towards Morphological Properties of Silica Xerogels

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ABSTRACT

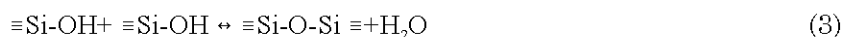
This study investigated the effects of synthesis parameters such as water to alcohol (water/alcohol) ratios, types of alcohol and catalysts towards morphological properties of silica xerogels which were prepared according to stober and conventional methods. The morphological properties of silica xerogels were determined using Scanning Electron Microscope (SEM). It was found that the silica xerogels tend to be spherical only in the presence of short chain alcohol as a co-solvent, increased particle size with decreasing water/alcohol ratios and increasing alcohol carbon atom number. There was no spherical morphology observed for butanol. As summary, the morphological properties of the silica xerogels formation depended on various experimental conditions used in the synthesis including types of catalyst, water/alcohol ratios and types of alcohol used.

Key words: Sol-gel preparation, silica xerogel, particles

INTRODUCTION

Silica is the most common substance on earth and a constituent of most rocks. It is a polymer of silicic acid, consisting of interlinked SiO₄ in tetrahedral fashion (Jal *et al.*, 2008; El-Nahhal and El-Ashgar, 2007). Silica materials offer several advantages over organic materials such as having high mechanical strength and thermal stability that can be used at high pressure operation, stable in solvent and acid and is also reusable (El-Nahhal and El-Ashgar, 2007). Silica particles with small particle size (2-5 nm) have an extraordinary large surface-to-volume ratio ($\approx 2 \times 10^9 \text{ m}^{-1}$) with high specific surface area ($\approx 900 \text{ m}^2 \text{ g}^{-1}$).

Silica materials can be prepared through sol-gel synthesis. The chemical reactions during sol-gel processing can be formally described by three equations (Doughty *et al.*, 1990):



In the first part of overall reaction, Si-OR group is hydrolyzed to produce a silanol group (Si-OH). Hydrolysis generally occurs under acidic or base catalyst. Hydrochloric acid is typically used as an acidic catalyst while ammonium hydroxide, sodium hydroxide and potassium hydroxide are used as the basic catalysts (Yu *et al.*, 2005; El-Nahhal and El-Ashgar, 2007). The Si-OH groups then undergo condensation polymerization reaction with another silanol (Eq. 2) or with an alkoxide group (Eq. 3) to produce a siloxane linkage with water or alcohol, respectively. As the polymeric network extends throughout the entire volume, the Sol turns to a gel (Doughty *et al.*, 1990; Jal *et al.*, 2008). After the gelation process, the product undergoes a drying process. Morphologies such as discoids and spheres are prepared by controlling silica hydrolysis and condensation through the adjustment of the synthesizing parameters. Several factors can affect the morphology and characteristics of the silica particles. These include the respective kinetics of the nucleation and aggregation processes where this competition depends on the quantity of nucleation seeds and the concentration of the reagent used (Boissiere *et al.*, 1999).

Although, several studies have been reported on the synthesis of silica gels, the actual control of such spherical silica xerogel morphology has not been fully elucidated so far. Thus, in this study the silica xerogels were synthesized using Tetraethoxysilane (TEOS) as the silica source in various experimental conditions (e.g., catalyst, ratio alcohol/water and types of alcohol) in order to control the silica hydrolysis and condensation processes and thus the morphological properties of the synthesized xerogels.

MATERIALS AND METHODS

The chemicals used for synthesis were ethanol (EtOH, 99.5%), methanol (MeOH, 99.9%) butanol (BuOH, 99.5%), tetraethyl orthosilicate (TEOS, 99%), ammonium hydroxide (NH₄OH, 25%), hydrochloric acid (HCl, 36.5-38.0%) and sodium hydroxide (NaOH, 99%) which were purchased from Merck (Germany) and Sigma-Aldrich (USA). All chemicals are of analytical grade and were used as received. Deionised water was used in all experiments from the Purite Water System (UK) that is available in our laboratory.

The silica xerogel was prepared according to Stober *et al.* (1968) (denoted as S1-S8) and conventional methods (denoted as S9, S10). According to the Stober method, the homogeneous alcohol, water and catalyst (acid or base) solution was first prepared. 6 mL of TEOS was then added drop-wise into the homogeneous solution and stirred for two hours at 600 rpm. On the other hand, the preparation of silica xerogel using conventional method was carried out by first mixing the alcohol, water and TEOS to form a homogeneous solution. The catalyst was then added drop-wise into the homogeneous solution. The hydrolysis and aging of silica xerogels for both methods were carried out at 30±1 and 50±1°C, respectively. After two days of aging, the produced precipitate was filtered, washed using deionized water and dried at ambient temperature (30±1°C). The final product was then ground into a powder form. The morphology properties of the synthesized silica xerogels were examined using Scanning Electron Microscope (SEM) model JEOL JSM-6390LV.

RESULTS AND DISCUSSION

Table 1 presents the experimental conditions used and morphological properties while Fig. 1 shows the SEM images of synthesized silica xerogels. The morphological properties of silica xerogels are strongly dependent of the synthesis parameters and method of preparation. It is observed that the particle size of silica xerogels prepared according to conventional method (S9) is found to be larger compared to Stober method (S7) for the same synthesis parameters used.

Table 1: Experimental conditions used and silica xerogel morphological properties

Sample code	Experimental conditions					Morphology	Particle sizes (μm)
	TEOS (mL)	H ₂ O:Alcohol (w/w)	NH ₃ OH (mL)	NaOH (mL)	HCL (mL)		
S1	6	1.00:0	-	-	4	Monolithic	-
S2	6	1.00:0	-	4	-	Monolithic	-
S3	6	0.50:0.50 MeOH	4	-	-	Spherical	0.06-0.18
S4	6	0.50:0.50 MeOH	-	4	-	Spherical	0.50-1.40
S5	6	0.50:0.50 EtOH	4	-	-	Spherical	0.28-0.35
S6	6	0.50:0.50 BuOH	4	-	-	Monolithic	-
S7	6	0.25:0.75 MeOH	4	-	-	Spherical	0.14-0.18
S8	6	0.75:0.25 MeOH	4	-	-	Monolithic	-
S9	6	0.25:0.75 MeOH	4	-	-	Spherical	0.22-0.30
S10	6	0.75:0.25 MeOH	4	-	-	Monolithic	-

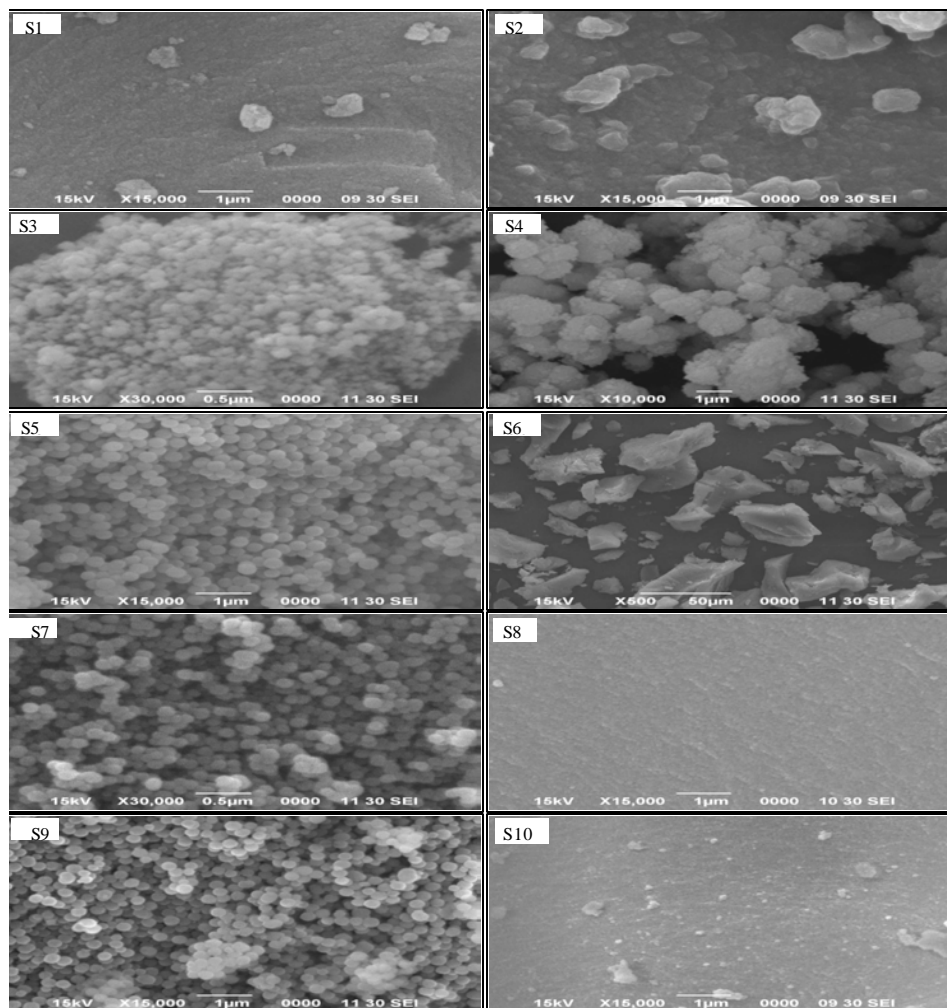


Fig. 1: SEM images of the silica gel samples: S1, S2, S3, S4, S5, S6, S7, S8, S9 and S10

The effects of catalyst towards silica xerogel formation were studied for (a) the absence of co-solvent (S1 and S2) and (b) the presence of co-solvent (S3 and S4). The S1 and S2 were prepared using acidic (HCl) and basic (NaOH) catalysts, respectively. In the absence of alcohol as a co-solvent, there was no spherical particle observed and the surface of the S1 (acidic) was smoother and clean compared to S2 (basic). This might be due to in acidic condition hydrolysis was faster than condensation and with a high number of siloxane linkages around, the central silicon atom formed a weakly branched polymeric network. In basic condition, the condensation was accelerated relatively to hydrolysis and more siloxane linkage was formed (Jal *et al.*, 2008). On the other hand, with the presence of a co-solvent (e.g., methanol) in basic condition, the morphology of silica particles tended to be spherical. The synthesized silica xerogel using NaOH (S4) as a catalyst produced spherical particles with rough surfaces having the particle sizes between 0.50-1.40 μm . As compared to NH_3OH as a basic catalyst, the silica xerogel particles (S3) were observed smoothly spherical having small particle sizes (0.06-0.18 μm). It was reported that the increase of the ammonia concentrations with constant other experiment conditions might form larger particles sizes (Stober *et al.*, 1968).

The effects of alcohol types as co-solvents were conducted using methanol (S4), ethanol (S5) and butanol (S6). The results show that the silica xerogel particles were observed to be smaller using methanol as a co-solvent and as the molecular weight of alcohol increased, the silica xerogel particles tended to be larger. In fact, there were no spherical xerogel particles formed in the presence of butanol (S6) and other higher molecular weight of alcohols like heptanol and octanol as co-solvents. In contrast, Stober *et al.* (1968) reported that by using butanol, the biggest spherical xerogel particles were formed. In the case of different alcohols as co-solvents, the reaction rates are the fastest using methanol and become the slowest by using butanol (Stober *et al.*, 1968). In the presence of higher molecular weight of alcohols, it was observed that the silica xerogel particles flocculated in irregular shape and no spherical shape xerogel particles formed.

Another, synthesis parameter found to be significant towards morphological properties of silica xerogels is water/alcohol ratios which are represented by low (S7), medium (S3) and high (S8) of the water/alcohol ratios. In this investigation, methanol solution was used as a co-solvent. The average size of spherical silica xerogel particles formed increased with the decrease of water/methanol ratios. In fact, at high water/alcohol ratio (S8), no spherical silica xerogel particle was formed which is similar to that of the result of no methanol used during the synthesis. Thus, the presence of alcohol as a co-solvent might result in the spherical silica xerogel particle formation and the amount could vary depending on the synthesis medium used.

CONCLUSIONS

Generally, the formation of silanol groups as a result from hydrolysis and condensation reaction is promoted by the addition of a catalyst. The acidic condition accelerates the hydrolysis process due to the increasing number of siloxane linkage. In contrast, in basic condition, the condensation process accelerates compared to the hydrolysis process. By changing the method and specific synthesis parameters during synthesis, the morphological properties of the silica xerogel particles can be varied. The presence of short chain alcohol as co-solvent is required for the formation of the spherical silica xerogel and the increase of alcohol concentration could result in the formation of a bigger particle size of silica xerogel. These results indicate the importance of the synthesis parameters towards morphological properties of the silica xerogel. A systematic study is thus required in order to further understand the effects of the synthesized parameters on other physical and chemical properties such as pore and surface characteristics of the synthesized silica xerogels.

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