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Experimental study of the synthesis and characterisation of silica nanoparticles via the sol-gel method

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Abstract. Silica nano-particles were synthesised by chemical methods from tetraethylorthosilicate (TEOS), ethanol (C2H5OH) and deionized water in the presence of ammonia as catalyst at room temperature. The morphology and structure of colloidal silica particles formed depend on the molar ratio of reagents. The formation of silica particles has been investigated using different solvents: ethanol and ethanol-glycerol. The nature and morphology of particles was investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD).

1. Introduction
Interest in the sol-gel processing of inorganic ceramic and glass materials began as early as the mid-1800s with Ebelman [1], and Graham’s [1] studies on silica gels. The sol–gel technique is the most common method of synthesising silica nano-particles. It involves the simultaneous hydrolysis and condensation reaction of the metal alkoxide [1]. However, the physical properties of nanosized spherical colloidal silica, prepared from tetraethylorthosilicate (TEOS) in ethanol, are difficult to reproduce in that they often depend on the method of isolation of the product. Kolbe [2] in 1956 observed formation of silica particles by reacting TEOS in alkali solution with water in the presence of certain bases.

In 1968 Stöber and Fink developed a system of chemical reactions which controlled the growth of spherical silica particles. The importance and advantages of mono-dispersed nanometre-sized particles were shown not only scientifically, but also in various industrial applications, e.g. as catalysts, pigments or pharmaceuticals [3]. Of these particles, SiO2 nano-particles are used to make electronic substrates, thin film substrates, electrical insulators, thermal insulators and humidity sensors. The silica particles play a different role in each of these products. The quality of some of these products is highly dependent on the size and size distribution of the silica particles. Commercial silica has a broad size distribution and varying levels of metal contaminants. It is imperative to have silica particles of a narrow size distribution and a high purity [4]. Depending on the synthesis process parameters, the structure of colloidal particles may vary from isolated spherical particles to agglomerates of complex...
structures [5]. Therefore, a major concern associated with obtaining colloidal silica particles is the control of structural features, such as average diameter and morphology of particles. Silica particles are suitable candidates for application in chemo-mechanical polishing (CMP) because silica can be directly precipitated as monodispersed spheres, their narrow size distribution being an important requirement. The synthesis of a wide range of mono-dispersed silica particles with various mean particle sizes will be helpful for modern polishing manufacturers in producing a series of polish grades optimized to a particular application.

The purpose of the present study is to investigate different solvents and their effects in preparing mono-dispersed silica particles. Different solvents such as ethanol, ethanol-glycerol were considered.

2. Experimental
TEOS, NH₄OH aqueous solution and ethanol (EtOH) were used (Merck Co.) and the water used for the sample preparation was purified by both ion-exchange and distillation. Reagents were mixed into the two starting time solutions of ethanol: (I) TEOS/EtOH; and (II) NH₄OH/H₂O/EtOH. The contents of the solutions (I) and (II) were adjusted so that the concentrations of TEOS, H₂O, and NH₄OH would be at the prescribed concentrations. The solutions were prepared in a glove box at room temperature under dry air. The humidity in the glove box was kept below a few percent [5]. The solutions (I) and (II) were mixed with each other at 298 K, and the mixture was stirred vigorously by hand for approximately 6s. The glycerol was added directly to the water/ammonia/ethanol mixture prior to the addition of TEOS.

Depending on different molar ratio of reagents, the condensation reaction began after various times. This could be easily observed, because, after the invisible hydrolysis reaction forming silicic acid, the condensation of the supersaturated silicic acid was indicated by an increasing opalescence of the mixture starting 2-10 minutes after adding the TEOS. After this transformation, a turbid white suspension formed after a few minutes more. Samples for SEM and TEM observation were prepared by diluting the sample liquid with ethanol and dispersing with ultrasound.

3. Results & Discussion
Colloidal silica nano-particles are based on the hydrolysis reaction of silicon alkoxide where the resulting particle size and morphology depend strongly on the hydrolysis kinetics. In the selected constituent concentrations, spherical, silica particles can be obtained. The reaction time of this synthesis required 15 minutes. The reaction continues until the solution is super-saturated [4]. To investigate the possibility of tailoring the particle size and maybe the particle size distribution, a kinetic study of the particle size evolution as a function of reaction time was carried out. X-ray diffraction using CuKα radiation (Philips X’pert) was used to determine the crystalline structure of silica particles [7]. The silica particles were amorphous according to XRD with peaks less than 2θ=10º conforming to the JCPDS file (79-1711). This demonstrates that a high percentage of these particles are amorphous, but a few of them are crystalline, as the energy of amorphous silica is very close to that of crystalline silica [2]. Vacassy and Flatt [4] reported that when one is interested in fine particles, the water concentrations should be fixed at 0.2 - 3.2 M, also the molar ratio of ammonia and TEOS should be the same. Silica nano-particles were prepared taking into account these considerations. Fig. 2 shows these particles and also the narrow size distribution of these particles.

The final product was analysed by XRF. The result of this analysis is shown in Table 1.

| Table 1: The result of XRF analysis. |
|-------------------------------------|
| LOI  | SiO₂ | Cl | Zn | Br |
| wt % | 18.096 | 81.854 | 0.04 | 0.01 | 0.015 |

In this table, LOI (Loss on Ignition) could consist of water, CO₂, sulfur etc. Pure reagents (99.9+% pure Merck) were used for synthesizing this particles. Table 1 shows that the purity of silica nano-particles is high, but some impurities could arise from the experimental fabrication process.
Vasconcelos and Campos [8] have considered the effect of different molar ratios of reagents on the structure and morphology of silica particles at room temperature. When the reaction was conducted at 60º C, silica nano-particles were also obtained. This temperature was based upon a limitation of the boiling point of the reagents.

Fig. 1: X-ray spectra of colloidal silica particles.

Fig. 2: TEM image of silica particles (TEOS : water : ammonia molar ratio = 0.2 : 1 : 0.2).

(Figure 3) (Figure 4)

Figs. 3, 4: SEM micrographs of silica particles obtained from a molar ratio of Water : TEOS : Ammonia : Ethanol = (Fig. 3) 1 : 4 : 6 : 6; (Fig. 4) 1 : 4 : 6 : 24, respectively.

Figures 3 and 4 show spherical and agglomerated silica nano-particles, which were obtained using different molar ratios of reagents; the molar ratio of the solvent is also important. With a lower molar
ratio of solvent (ethanol), agglomerated silica particles were obtained. Park and Kim [6] have shown when a narrow size distortion is required, a small molar ratio of ethanol should be employed. The optimum conditions for synthesizing silica nano-particles were considered to be with the same molar ratio of TEOS and ammonia and a higher molar ratio of ethanol giving rise to smaller silica nano-particles with a broad distribution of particle sizes [5].

Stober and Fink [3] have shown the different solvent effects on the size of particles [3]. Using different solvents such as methanol, ethanol, propanol, butanol and ethanol-glycerol, different structures were obtained. From methanol and ethanol-glycerol, a stable sol could be obtained, but when butanol and ethanol were used, precipitation could be easily observed. Different experiments show that the presence of glycerol during synthesis affects the precipitation.

4. Conclusion
Spherical silica particles with a very narrow particle size distribution have been synthesised by the hydrolysis reaction of TEOS in ethanol containing water and ammonia. The morphology and the average diameter of colloidal silica particles depend on the proportion of the reactants. Silica nanoparticles were obtained via the same molar ratio of TEOS, ammonia and also a high molar ratio of ethanol. Different solvents have different effect on the size of the silica particles. Using methanol and ethanol-glycerol, a stable sol could easily be obtained.

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