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BET study of silver-doped silica based on an inexpensive method

Askwar Hilonga [a,b], Jong-Kil Kim [a,b,c], Pradip B. Sarawade [a,c], Dang Viet Quang [a], Godlisten N. Shao [a], Gideon Elineema [a], Hee Taik Kim [a,*]

[a] Department of Chemical Engineering, Hanyang University 1271 Sa 3-dong, Sangnok-gu, Ansan-si, Gyeonggi-do 426-791, Republic of Korea
[b] Nelson Mandela African Institute of Science and Technology in Arusha, Tanzania
[c] E & B Nanotech. Co., Ltd., Republic of Korea

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ABSTRACT

The aim of this study is to identify an acid precursor that is most desirable for the synthesis of sodium silicate-based silver-doped silica for large-scale industrial production. The final products were developed based on the presence of silver (silver-doped silica) or the absence of silver (pure silica). The properties of the obtained final products were examined using the BET method. This method involves characterization based on N_2 physisorption studies to determine the surface area, pore diameter, and pore volume. Various graphs were plotted using the obtained data to describe the pore size distribution, isotherms, and the properties of hysteresis loops. Silver-doped silica with a BET surface area of up to 357 m^2/g and a pore size of 5.4 nm was obtained using the most desirable precursors—sodium silicate and sulfuric acid. This is an unprecedented step toward synthesis of silver-doped silica from desirable precursors. This approach to the synthesis of silica with desirable properties without involving sacrificial templates (surfactants) will be convenient for many applications and suitable for large-scale economic industrial production.

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1. Introduction

Silver-doped silica is one of the effective antibacterial agents [1]. However, most of the reported previous works on the synthesis of sodium silicate-based, silver-doped silica were limited to the application of one type of acid, namely, hydrochloric acid [1–3]. The final products were acclaimed to be desirable for large-scale industrial production, but the conclusion was only based on the use of sodium silicate. While it is true that sodium silicates surpass all other silica precursors, because it is inexpensive and therefore suitable for large-scale industrial production [1–3], this benefit must be matched with the type of acid that is to be used during the polymerization reaction. The use of hydrochloric acid in most of the reported studies is an obstacle toward mass production since the acid is very expensive.

Inspired by the investigation of the effect of different acids on the structure and photocatalytic activity of mesoporous titania [4], in this work we explore the synthesis of silver-doped silica based on three types of mineral acids: hydrochloric, nitric, and sulfuric acids. We examine whether the properties of the final product are strongly dependent on the type of mineral acid used and when a sodium silicate is used as a silica precursor. This study will give insight into how various acids affect the properties of the silver-doped silica to qualify and/or recommend it for mass production. Moreover, aluminum ions were used to improve the properties of the final product. It was previously reported that the aluminum ions promoted the chemical durability of silver-doped silica gel [5]. They dramatically decrease the elusion of silica ions into an aqueous solution and induce a slow release of silver ions over a long period of time.

2. Experimental

2.1. Materials

Sodium silicate (24% SiO_2, 7.4% Na_2O) was obtained from Shinwoo Materials Co. Ltd., South Korea. Ammonia solution (28% NH_3), hydrochloric acid (36% HCl), nitric acid, sulfuric acid, and silver nitrate ($AgNO_3$) were purchased from Duksan Chemical. Aluminum isopropoxide ($Al(OC_3H_7)_3$) was obtained from ALDRICH.

2.2. Preparation

Generally, the method of preparation of silver-doped silica involves polycondensation of a silica precursor with a predetermined amount of $AgNO_3$ that was previously mixed with an ammonia solution. In this study, 4 g of sodium silicate (24% SiO_2, 7.4% Na_2O) and 0.204 g of aluminum isopropoxide ($Al(OC_3H_7)_3$) were dissolved in a relevant amount of an acid (e.g. 30 ml of 2 N HCl) and stirred for 10 min. Next, 10 ml of a 28% NH_3 solution containing 5×10^{-4} M of $AgNO_3$ was slowly added and then stirred for 2 h. The final products were named Ag–Al–Si–X, where X stands for a coded acid type,

* Corresponding author. Tel.: +82 31 400 5493; fax: +82 31 500 3579.
E-mail address: khtaik@yahoo.com (H.T. Kim).

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namely, hydrochloric acid (H), nitric acid (N), and sulfuric acid (S). After the final products were made, the samples were washed with water and dried at 110 °C for 2 h. Furthermore, the pure silica (without silver) samples were prepared and subjected to the same treatment to serve as a reference. They were named Pure Si–X, where X stands for a type of acid.

2.3. Characterization

The Brunauer–Emmett–Teller (BET) surface area and the porosity of the samples were studied using a nitrogen adsorption instrument (Micromeritics ASAP 2020). All samples were degassed at 250 °C for 1 h prior to actual measurements. The transmission electron microscopy (TEM) micrograph was obtained through JOEL 2000FX instrument.

3. Results and discussion

The literature reviewed suggests that Cl^-, Br^-, NO_3^-, and SO_4^{2-} are hydrated in the solution and that their hydrated ionic radii decreased in the following order: $1/2SO_4^{2-} > Cl^- > Br^- > NO_3^-$ [6]. Since the silica wall surface was negatively charged, it could be considered that the decrease of the ionic radii of the anionic ions will decrease their electrostatic force. This would make the two surfaces further and, thus the silica wall would have influenced the pore diameter. Therefore, the pore diameter increased with an increase in ionic radii. This is why different acids in the reaction system can affect the pore size of the silver-doped silica materials. Since the SO_4^{2-} ion is divalent, it is more highly repelled than Cl^- and NO_3^- in the reaction solution. Therefore the effect of the SO_4^{2-} ion on the pore diameter is more complex than that of Cl^-, Br^-, and NO_3^-. In the previous study, it was reported that the nature of the mineral acid, the use of TEOS versus TMOS, and the temperature of the polymerization had a strong influence on the textural properties of the obtained final product [6].

3.1. TEM micrograph

Fig. 1 shows the TEM micrograph of the representative sample of silver-doped silica products reported in this study (Ag–Al–Si–H). It should be noted that, in this study, the products were not calcined. Thus, silver nanoparticles that were reported in our previous studies [1–3] do not appear. Of course, after calcinations at higher temperatures (600 °C and above) there might be further developments that are beyond the scope of our present study. In this study, there is no significant difference between the micrographs of different products. This is the reason as to why BET method (the title of this study) was used for comparative purposes. This method clearly demonstrates the influence of each of the mineral acids in the properties of the final products. So the proceeding sections of this study will be only on BET method (nitrogen physisorption studies).

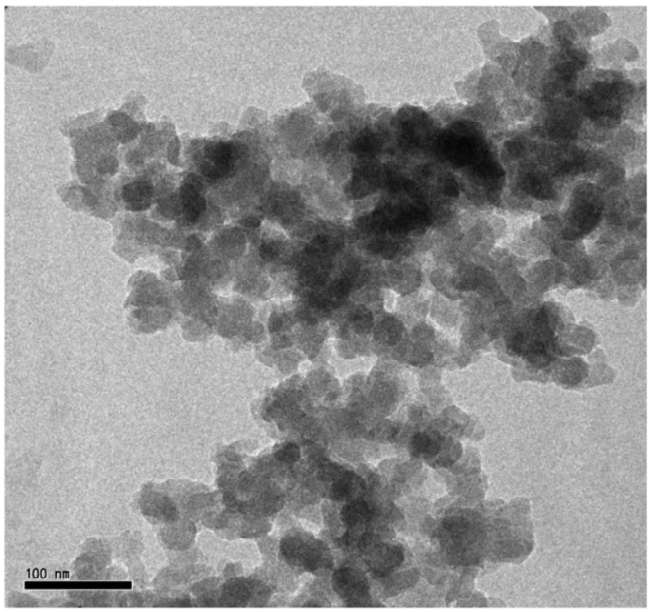


Fig. 1. TEM micrograph of the representative sample (Ag–Al–Si–H).

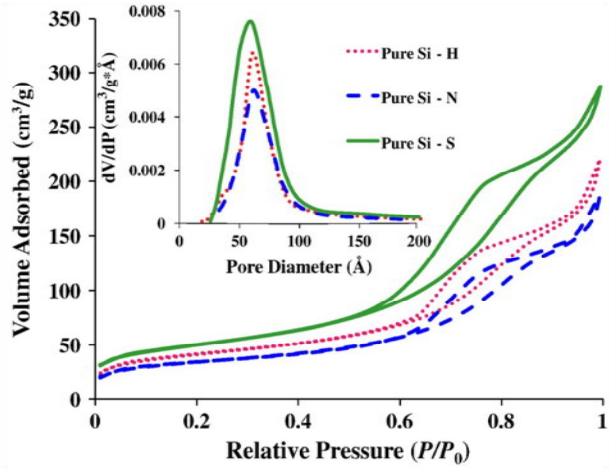


Fig. 2. Isotherms and pore size distribution (inset) of pure silica products.

3.2. Nitrogen physisorption studies

Nitrogen adsorption–desorption isotherms for all the samples are presented in Figs. 2 and 3. The conspicuous hysteresis loops at high relative pressures were observed. These, according to the IUPAC classification system [7], are related to capillary condensation associated with large pore channels and indicate the presence of mesopores. The pore size distribution calculated from the desorption branch of the isotherm is also presented in Figs. 2 and 3 as insets. Other data such as BET surface area, pore volume and average pore size are calculated and given in Table 1. The results show that all the samples synthesized in the present work are mesoporous in nature since the volume of the nitrogen adsorbed did not significantly increase until at relative pressures (P/P_0) position of reflection points exceeding 0.4. The isotherms of Pure-Si–X are all similar (type IV). Their hysteresis loops are type H3 and did not exhibit limiting adsorption at high P/P_0. This is attributed to the presence of aggregates of plate-like

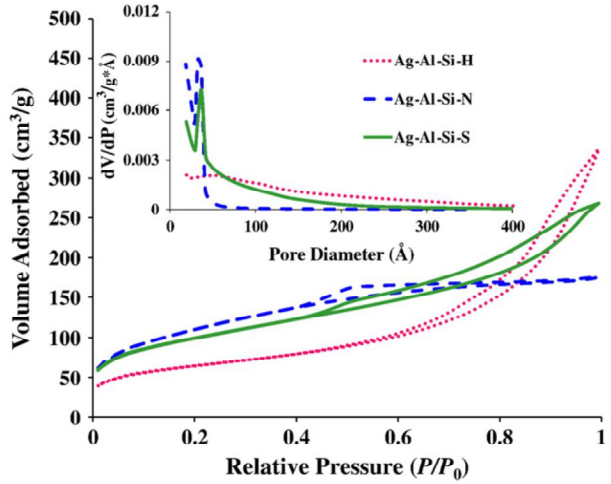


Fig. 3. Isotherms and pore size distribution (inset) of silver-doped silica products.

Table 1
Properties of silver-doped silica (Ag–Al–Si–X) and pure silica (Pure Si–X) products; "X" stands for type of acid — hydrochloric acid (H), nitric acid (N) or sulfuric acid (S).

	BET surf area (m^2/g)	Pore diameter (nm)	Pore volume (g/cm^3)
Pure Si–H	552	5.8	0.90
Pure Si–N	123	8.8	0.28
Pure Si–S	179	7.7	0.45
Ag–Al–Si–H	465	6.1	0.80
Ag–Al–Si–N	400	2.9	0.19
Ag–Al–Si–S	357	5.4	0.36

particles that gave rise to slit-shaped pores. The pore size distributions of the final products indicate that the Pure-Si–X samples have a wider pore size distribution than that of their silver-doped counterparts. In the previous study, the pure silica samples display a wider pore size distribution compared to the silver-doped samples, indicating the influence of silver on the properties of the final products [1–3]. Ag–Al–Si–S has shown optimum properties in both silver-doped and pure silica products.

It was also evident that the pure silica (without silver) sample has got larger porosities compared to those in the silver-doped silica (Figs. 2 and 3). In the previous report this tendency was attributed to the presence and coarsening of Ag particles within pore channels or between pores, which result in more and more isolated and unmeasured free spaces [8]. Only the larger particles located in the larger pores can continuously grow. The smaller particles and those located in the channels or pores with smaller dimensions will disappear. In our study, various properties of silica products were improved after doping them with silver as summarized in Table 1.

A closer look on the isotherms of the Ag–Al–Si–X (silver-doped silica) reveals significant difference in the types of isotherms. The Ag–Al–Si–N reveals a type I isotherm (which is thought to indicate the presence of micropores) [7] and has the smallest pore size (2.9 nm) compared to all the other products obtained in this study. This tendency was previously observed when HCl was used, and the final product was microporous [9]. Nevertheless, in our present study, none of the products was microporous although substituting hydrochloric acid with nitric or sulfuric acid leads to a lower BET value (Table 1). The silver-doped silica products reveal different types of isotherms and hysteresis loops. Also, their BET surface areas decreased in the order Ag–Al–Si–H (465 m^2/g) > Ag–Al–Si–N (400 m^2/g) > Ag–Al–Si–S (357 m^2/g).

The pore diameters of Ag–Al–Si–X were 6.1 nm, 2.9 nm, and 5.4 nm for the products synthesized with HCl, HNO_3, and H_2SO_4, respectively (shown in Table 1), which also confirmed that the type of anionic ions can significantly affect the pore sizes of silica products. The effect of different acids on the pore sizes of the silica products can be explained by the same reason with the counter ionic in the reaction systems [6]. Since the SO_4^{2-} ion is divalent and is surrounded by more positive ions, the effect of a SO_4^{2-} ion on the pore diameter is more complex than that of Cl^- and NO_3^-. The product silver-doped silica based on sulfuric acid (Ag–Al–Si–S) has shown optimum properties in all cases and it is highly recommended for the synthesis of silver-doped silica for economic industrial production.

4. Conclusion

The aim of this study is to identify an acid precursor that is most desirable for the synthesis of sodium silicate-based silver-doped silica for large-scale industrial production. Silver-doped silica with a BET surface area up to 357 m^2/g and pore size of 5.4 nm was obtained using the most desirable precursors—sodium silicate and the sulfuric acid. This approach to the synthesis of silica with desirable properties without involving sacrificial templates (surfactants) will be convenient for many applications and suitable for large-scale economic industrial production.

Acknowledgments

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