Journal of Ceramic Processing Research. Vol. 9, No. 3, pp. 302~306 (2008)

J O U R N A L O F
Ceramic Processing Research

Preparation of composite silica particles for the removal of formaldehyde at room temperature

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Silica/amine and silica/platinum composite particles were successfully prepared by a novel strategy including a water-in-oil (W/O) emulsion and self-hydrolysis by a one-step process. Amine groups and platinum nanoparticles were employed as a reacting group with formaldehyde. Thiol groups were employed as a chemical protocol to make a binding bridge between platinum nanoparticles and the silica surface. Because the composite particles have many reaction sites with formaldehyde molecules, the results showed a good ability for the removal of formaldehyde. In paticular, when the experiments were conducted using composite materials at room temperature, formaldehyde was removed efficiently. Detailed characterization of the composite particles and their applications were investigated by scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray spectrometry (EDX), and a UV-vis spectrophotometer.

Key words: Composite material, Silica, Amine, Platinum, Formaldehyde.

Introduction

Formaldehyde is a useful and widespread gas in many industries such as in paints, particle board, medium-density fiberboard, and wood burning appliances. However, due to the toxicity of environment formaldehyde in the environment, it is harmful to human health. In most indoor, formaldehyde is emitted from furniture and decorating materials. This chemical pollutant causes nasal tumors, skin irritation, and multiple subjective health complaints at home. Also, formaldehyde is frequently found in industrial waste-water. It harmfully affects the fish and other animals. Therefore, many researchers are dedicated to creating new advanced technologies to remove formaldehyde quickly and economically.

Nowadays, the development of composite particles is a subject of powerful interest in materials science [1, 2]. In many papers, composite particles have been used to remove formaldehyde. Tanada et al. made activated carbon materials functionalized by an amine group to apply to hospital waste [3]. Activated carbons were used as adsorbents of formaldehyde because of their high porosity and large surface area. Zhang et al. produced metal-coated composite materials for the oxidation of formaldehyde [4, 5]. These metal particles reacted with formaldehyde as a catalyst at room temperature. Also, Hayashi et al. reported the preparation of polyamine-intercalated zirconium phosphate [6]. Ammonium ions and polyamine interact with gaseous formaldehyde as a catalyst of a self-oxidation-reduction reaction with formaldehyde.

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Here, we report concerning easy and reproductive composite particles which have a many reaction sites on their surfaces to remove formaldehyde. To improve the physical properties of the composite particles such as density and solidity, silica was used as a substrate. Also, because silica material has environmentally friendly characteristics, it is useful to apply in environmental science. Because the removal of formaldehyde occurs at room temperature, there is no need to employ a heater in the reactor. The composite particles have micrometer-sizes and are easily separated in a system. The resulting composite particles and their application as a scavenger of formaldehyde were characterized by FE-SEM, EDX, and UV-vis analysis.

Experimentals

Materials

Tetraethyl orthosilicate (TEOS), N-[3-(trimethoxysilyl)propyl] ethylene diamine, N-[3-(trimethoxysilyl)propyl] diethylenetriamine, 3-mercaptopropyl trimethoxysilane (MPTMS), hydroxypropyl cellulose (HPC, average Mw 370,000), sorbitan monooleate (Span 80, nonionic surfactant), formaldehyde solution (37%), and Schiff's reagent were purchased from the Sigma-Aldrich Chemical Company. Ammonia hydroxide (NH_4OH, 25%) was obtained from the Wako Pure Chemical Industry. Hexachloroplatinate (IV) hydrate ($H_2PtCl_6 \cdot xH_2O$, x = 5.6) was purchased from Kojima Chemicals. Ethanol was purchased from the Yakuri Pure Chemicals Company. Polyvinylpyrrolidone (PVP K-15, MW. 10,000) and 1-octanol was obtained from the Junsei Chemical Company. Absolute ethanol (HPLC grade 99.9%) was purchased from the DUKSAN Pure Chemical Company as a washing reagent. All chemicals were used as received without further purification. Water was obtained from a Milli-Q water purification system (Millipore).

Preparation of amine-functionalized silica particles in a water/oil (W/O) emulsion

First of all, to prepare amine-functionalized silica particles, W/O emulsion was prepared as follows. An external oil phase was made by dissolving 1.26 g of HPC in n-octanol (90 g), and then kept at 80 °C for 6 h, and then the oil phase was kept at 40 °C. After 30 minutes, 3.6 g of Span 80 was added into the oil phase. The internal water phase was prepared by adding 0.2 g of NH_4OH as a catalyst into the water (10 g). As a final step of the preparation of the W/O emulsion, the water phase was added into the external oil phase. The weight ratio of water phase to oil phase in the emulsion was kept at 1:9. To disperse the water phase into the oil phase, agitation was performed using a magnetic stirrer at 40 °C for 1 h.

The sol-gel reaction for the formation of silica/amine particles was initiated by adding TEOS into the W/O emulsion. After 1 h reaction, the amine source was added into the reaction system in order to obtain silica particles with terminal amine groups at the surface of the silica. The weight ratios of water to TEOS and amine source were 1 and 4, respectively. Samples were prepared in a beaker and kept for 12 h. After the reaction was completed, the samples were centrifuged at 3000 rpm for 15 minutes to obtain the resulting silica particles. In order to remove the un-reacted materials such as polymer, n-octanol, and surfactant, the precipitates were washed with absolute ethanol twice. Then, these particles were dried at room temperature.

Preparation of silica/platinum composite particles

2 g of PVP were completely dissolved in 97 g of ethanol/water (1/1 w/w) solution. 0.0527 g of hexachloroplatinate (IV) hydrate was added into the solution and the solution was slowly stirred for 15 minutes in order to completely dissolve the platinum salt. Then the solution was heated with refluxity at a 120 °C. The nanoparticles of platinum were obtained through this polyol process.

10 g of MPTMS was added into 100 g of water with vigorous stirring until the oil (MPTMS) droplets has completely disappeared and a transparent solution was obtained. Then, Pt nanoparticles were added to the MPTMS-water solution with stirring. NH_4OH (0.1 ml) was added to the solution mixture (pH 11), and then the reaction was progressed for 12 h at room temperature. After completion of the reaction, the solution was kept at room temperature. The resulting precipitate was centrifuged and washed several times using alcohol.

Morphology and the removal of formaldehyde

Field emission scanning electron microscopy (FE-SEM, JEOL Co. Models JSA 840A and JSM-6700) was used to investigate the morphology of the composite particles. The chemical composition of the silica/platinum composite particles was investigated with an energy-dispersive X-ray (EDX) spectrometer attached to the FE-SEM. For the analysis of formaldehyde removal, a small plastic box was used. Formaldehyde was placed in the bottom of the plastic box and formaldehyde gas flowed through the filter paper coated with composite particles at room temperature. After the gas passed the filter paper, the formaldehyde in the gas reacts with the Schiff's reagent solution on the top of the plastic box. If the formaldehyde was scavenged completely by composite particles, there will be no Schiff's reaction. The UV-vis absorption spectra of the Schiff's solution from different conditions were measured by a UV-vis spectrophotometer (Agilent 8435, Agilent Technologies) and the maximum absorbance occurred at a wavelength of 550 nm.

Results and Discussion

Preparation and characterization of the AP (amine precursor)-functionalized silica spheres

To remove the formaldehyde, amine materials were adopted in the preparation of composite particles. In organic chemistry, an amine group reacts easily with an aldehyde group because the amine has many electrons which act as the nucleophilic parts. Generally, an amine attacks the double bond of the aldehyde group and it forms amide materials including formaldehyde-melamine and formaldehyde-urea in a liquid system [7]. Also, due to the good reactivity of the amine group with formaldehyde, there reactions occur in air. However, an amine contained in water has a toxicity which can badly influence human health or the health of animals. One promising strategy to solve this problem is a hybridization of an amine group on the surface of harmless materials. Also, the hybridization of amine groups at the surface of relatively large silica particles can make the easy removal of reaction products between amine groups and formaldehyde through simple filtration.

One representative harmless material is silica. After the Stöber-Fink-Bohn (SFB) process was introduced in 1968 for the preparation of silica particles [8], it has been generally used in the presence of silicon alkoxides containing an ammonia solution. For the preparation of spherical silica particles having a micrometer-size, the emulsion technique has occasionally been utilized as the basis of SFB synthesis. An emulsion is a class of dispersed systems consisting of two immiscible liquids. In our previous studies, silica particles with various surface shapes and morphologies were synthesized in a W/O emulsion [9, 10].

The reaction system is a W/O emulsion that is water containing the NH_4OH as a catalyst which is dispersed in n-octanol to form a droplet. TEOS and AP molecules as silica sources are dissolved into the continuous phase, n-octanol. When they contacted the interface of water

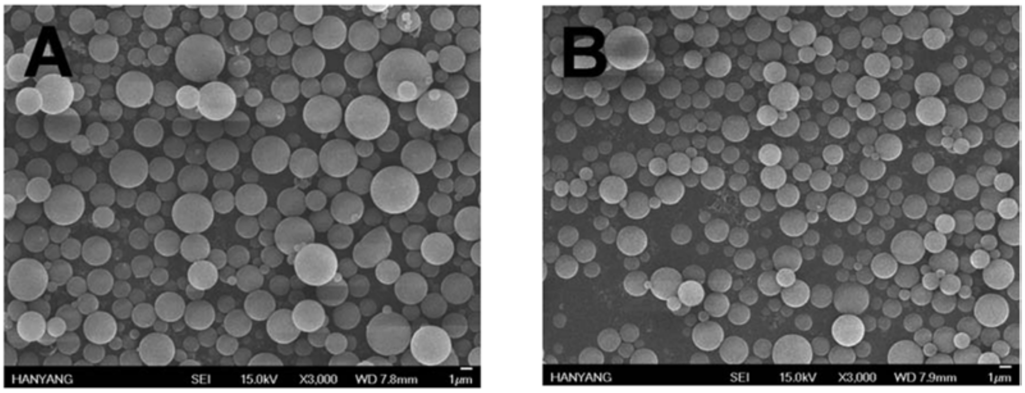

Fig. 1. SEM images of silica particles modified with amine organic groups; (A) N-[3-(trimethoxysilyl)propyl] ethylene diamine, Amine-2 (B) N-[3-(trimethoxysilyl)propyl] diethylenetriamine, Amine-3. Composite particles were made using W/O emulsion method.

droplets, a sol-gel reaction of TEOS and AP molecules takes place within the water droplets. As a result, amine molecule-modified silica particles can be synthesized. Hydroxyproply cellulose (HPC) plays an important role in preparing the spherical particles. The HPC polymer prevents separation of the water/oil phase and increases the stability of the W/O emulsion. Moreover, as the HPC polymer chains swell in the oil phase, they limit the excessively fast penetration of TEOS molecules and AP molecules at the interface of water droplets.

SEM images of silica particles functionalized with amine groups are shown in Fig. 1. It is clear from these images that the silica particles have a spherical shape and they are micrometre sized. Although numbers of amine group per one molecule of AP were increased from 2 to 3 as a surface modifier, all of the particles reveal a similar morphology.

To verify the elimination of formaldehyde, AP-functionalized silica particles were located in the experimental plastic box. In the experiment, Schiff's reagent was used because it reacts easily with aldehyde materials and is altered to a violet color. When 0.01 ml of formaldehyde was used without the composite particles, the UV intensity at 550 nm wavelength is 0.15. A further increase in the UV concentration of formaldehyde to 0.05 ml and 1 ml results in the absorbance of 0.35 and 0.53 as shown in Fig. 2. However, when a filter paper coated with composite particles was used, the intensity of the UV decreases to 0.24 and 0.06 Fig. 3. It is clear that the composite particles remove the formaldehyde and the remaining small amount of formaldehyde in the gas reacts with Schiff's reagent. Also, as the number of amine group increases from 2 (Amine-2) to 3 (Amine-3), the UV intensity decreases sharply. It is shown that N-[3-(trimethoxysilyl)propyl] diethylenetriamine (Amine-3) has a good reactivity with formaldehyde which is better than N-[3-(trimethoxysilyl)propyl] ethylene diamine (Amine-2) as shown in Fig. 3. As a result, the AP-functionalized composite particles help to remove the formaldehyde efficiently and as the number of amine groups in the amine precursor increases, a larger amount of formaldehyde was removed.

Preparation and characterization of silica/platinum composite particle

Monodispersed silica particles are a very applicable

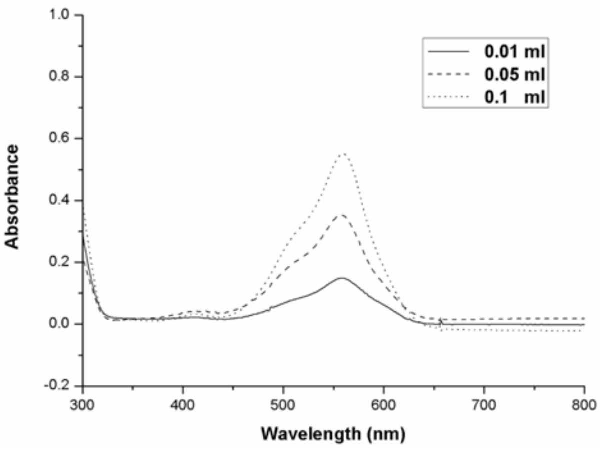

Fig. 2. UV-vis absorption spectra of the Schiff's reagent reacted with 0.01 ml, 0.05 ml, and 0.1 ml of formaldehyde.

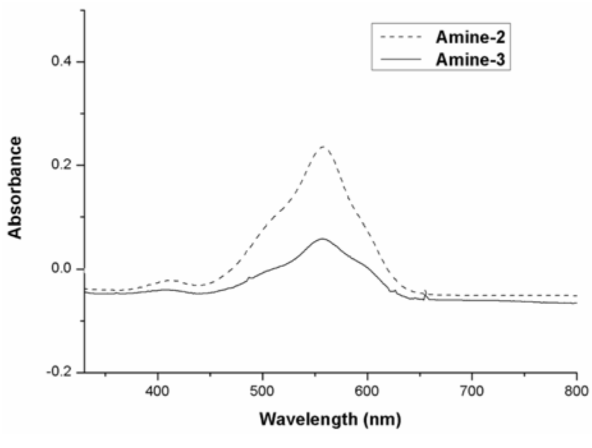

Fig. 3. UV-vis absorption spectra of the Schiff' reagent reacted with 0.1 ml of formaldehyde. Here, formaldehyde passed through the filter coated by the amine functionalized composite particles.

material. So, monodispersed silica material has been extensively used in industrial areas such as cosmetics, chromatographic adsorbents, and Chemical Mechanical Polishing (CMP) processing. Unfortunately, the SFB process needs a large amount of alcohol to generate the homogeneous phase offering a well-defined structure. Additionally, although silica particles prepared by the SFB synthesis route present a high monodispersity, it is difficult to obtain a high yield of silica materials from this route.

In particular, for the preparation of fine composite materials, surface modification is an important part [11]. Surface treatment has been used to immobilize useful materials in substrate materials by a chemical reaction. By changing the chemical composition on the silica surfaces, a variety of different types of materials can be prepared and used in several application fields. In our previous studies, a one-step preparation method for monodispersed hybrid silica particles was studied using organosilane chemicals in an aqueous solution [12]. Hybrid silica contains reactive thiol groups on the surfaces. So, platinum nanoparticles are easily attached to the thiol group on the surface of hybrid silica through the interaction between sulfur and the metal. This can be applied for fabricating silica/platinum composite particles.

It is well known that thiol groups strongly attach to metal particles by the cleavage of an S-H bond [13]. Because of the thiol property, it has been widely used as a chemical protocol to fabricate various composite materials. Therefore, the introduction of a thiol group using MPTMS is very important in these experiments because it was used as a chemical protocol to deposit metal nanoparticles on the silica surface.

Figure 4 gives an image of silica/platinum composite particles. The particle diameter is about 2 μm and the particles have a highly monodispersed shape. Contrary to the case of composite particles fabricated in the W/O emulsion, hybrid composite particles have a uniform particle size using the one-step fabrication process. MPTMS is easily hydrolyzed into organosilanetriol by self-hydrolysis. Although the MPTMS is not dissolved in water in the initial stage, the MPTMS droplets completely disappeared due to self-hydrolysis through stirring for 1 h. The self-hydrolysis phenomenon is related to the molecular of MPTMS structure. A MPTMS molecule has three short carbon chains which are suitable for changing from alkoxy groups to hydroxy groups. In addition, MPTMS released methanol as a byproduct during the hydrolysis reaction which helps the MPTMS precursor to be completely dissolved into water. Subsequently, MPTMS is reacted in an alcohol-free sol-gel system and the traditional co-solvent concept of the SFB method is unnecessary.

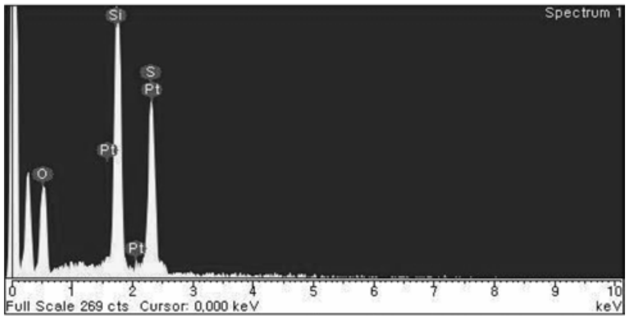

Fig. 5. EDX results of particles shown in Fig. 4.

Figure 5 shows the chemical elements in silica/platinum composite particles investigated by EDX analysis. The electron beam for EDX analysis was focused on the particles shown in Fig. 4, at a low magnification. In this pattern, Si, S, and Pt peaks clearly show that the platinum nanoparticles are successfully coated on the MPTMS-functionalized silica particles.

To prove the efficiency of silica/platinum composite particles for removal of formaldehyde, the reaction of Schiff's reagent with formaldehyde was conducted in the

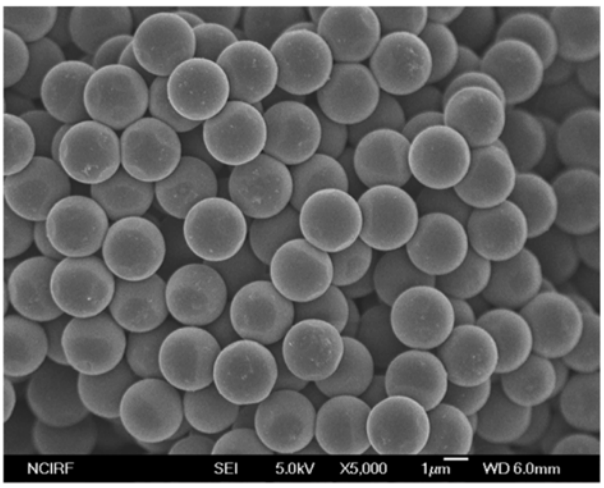

Fig. 4. SEM image of silica/platinum composite particles having a highly monodispersed shape and micrometre size. The particles were prepared using a one-step preparation method.

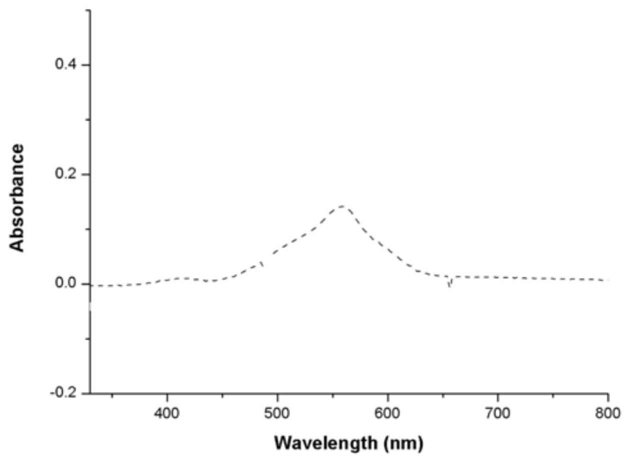

Fig. 6. UV-vis absorption spectra of the Schiff' reagent reacted with 0.1 ml of formaldehyde. Here, formaldehyde passed through the filter coated by the silica/platinum composite particles.

experimental plastic box. When silica/platinum composite particles were used, the UV intensity was extensively decreased compared with standard data Fig. 2. The maximum UV intensity was found to be 0.14 and this confirms that composite silica/platinum particles removed the formaldehyde as shown in Fig. 6.

Conclusions

To remove formaldehyde at room temperature, composite silica particles functionalized with amine groups and platinum nanoparticles were synthesized by a sol-gel reaction using a water-in-oil (W/O) emulsion and a self-hydrolysis one-step method. Composite particles reveal an excellent capacity for removing formaldehyde due to the reactivity of amine molecular and platinum nanoparitcles with formaldehyde. In environmental science, these composite particles have important applications especially as adsorbents and this approach can be extended to prepare other useful composite particles. The composite particles prepared in this study can be used to selectively remove formaldehyde chemicals, which are one of the major components causing the new house sick syndrome in air.

Acknowledgements

This work was supported by the research fund of Hanyang University (HY-2006-I)

References

1. J. Miranda-Hernández, S. Moreno-Guerrero, A.B. Soto-Guzmán, and E. Rocha-Rangel, J. Ceram. Process. Res. 7 (2006) 311-314.
2. S. Cui, J. Han, W. Li, S.H. Kang, and J.M. Lee, J. Ceram. Process. Res. 7 (2006) 371-374.
3. S. Tanada, N. Kawasaki, T. Nakamura, M. Araki, and M. Isomura, J. Colloid Interface Sci. 214 (1999) 106-108.
4. C. Zhang, H. He, and K. Tanaka, Catal. Commun. 6 (2005) 211-214.
5. C. Zhang and H. He, Catal. Today 126 (2007) 345-350.
6. A. Hayashi, Y. Fujimoto, Y. Ogawa, H. Nakayama, and M. Tsuhako, J. Colloid Interface Sci. 283 (2005) 57-63.
7. P. Girods, A. Dufour, Y. Rogaume, C. Rogaume, A. Zoulalian, and J. Anal. Appl. Pyrolysis 81 (2008) 113-120.
8. W. Stöber, A. Fink, and E. Bohn, J. Colloid Interface Sci. 26 (1968) 62-69.
9. Y.G. Lee, C. Oh, S.K. Yoo, S.M. Koo, and S.G. Oh, Microporous Mesoporous Mat. 86 (2005) 134-144.
10. Y.G. Lee, C. Oh, J.H. Park, S.M. Koo, and S.G. Oh, J. Ind. Eng. Chem. 13 (2007) 319-324.
11. M.J. Kim, B. Lim, Y.K. Jeong, Y.W. Cho, and Y.H. Choa, J. Ceram. Process. Res. 8 (2007) 293-295.
12. Y.G. Lee, J.H. Park, C. Oh, S.G. Oh, and Y.C. Kim, Langmuir 23 (2007) 10875-10878.
13. M. Tomonari, H. Sadohara, T. Yonezawa, K. Mori, and H. Yamashita, J. Ceram. Process. Res. 8 (2007) 195-198.