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廢실리콘슬러지로부터 TMOS 및 실리카 나노粉末 製造†

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Synthesis of Tetramethylorthosilicate (TMOS) and Silica Nanopowder from the Waste Silicon Sludge†

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요 약

폐실리콘 슬러지로부터 테트라메틸오쏘실리케이트(TMOS)와 실리카 나노분말을 제조하였다. 먼저, 실리카 나노분말의 전구체인 TMOS를 폐실리콘 슬러지로부터 촉매 화학반응에 의해 합성하였다. TMOS의 합성실험에서 반응온도가 130°C 이상에서는 반응시간이 5시간 경과 시 반응온도에 무관하게 100%의 반응율을 나타내었다. 그러나 150°C 이상에서는 초기 반응속도가 빨라졌다. 메탄올 주입속도를 0.8 ml/min 에서 1.4 ml/min로 증가시에는 3시간 경과 후에는 반응율이 변화하지 않았다. 이와 같이 합성된 TMOS로부터 화염분무열분해법에 의해 실리카 나노분말을 제조하였다. 제조된 실리카 나노분말은 구형이며, 무응집 형태이었다. 평균입자크기는 전구체의 주입속도 및 농도변화에 따라 9 nm에서 30 nm로 변화하였다.

주제어 : 합성, 실리카 나노분말, 테트라메틸오쏘실리케이트, 실리콘 슬러지

Abstract

Tetramethylorthosilicate (TMOS) and silica nanopowder were synthesized from the waste silicon sludge containing 15% weight of silicon powder. TMOS, a precursor of silica nanopowder, was firstly prepared from the waste silicon sludge by catalytic chemical reaction. The maximum recovery of the TMOS was 100% after 5 hrs regardless of reaction temperature above 130°C. But the initial reaction rate became faster while the reaction temperature was higher than 150°C. As the methanol feedrate increased from 0.8 ml/min to 1.4 ml/min, the yield of reaction was not varied after 3 hrs. Then, silica nanopowder was synthesized from the synthesized TMOS by flame spray pyrolysis. The morphology of as-prepared silica nanopowder was spherical and non-aggregated. The average particle diameters ranged from 9 nm to 30 nm and were in proportional to the precursor feed rate, and precursor concentration.

Key words : Synthesis, Silica nanopowder, Tetramethylorthosilicate, Silicon sludge

1. Introduction

Silica (SiO_2) nanopowder have been widely used in various industrial applications, such as catalysis, pigments, pharmacy, electronic and thin film substrates, electronic and thermal insulators, and humidity sensors.[1)] SiO_2 nanopowder were also considered as nanometric fillers with potentially interesting reinforcing capabilities.[2)] In these applications, the particle morphology, average particle size or specific surface area, and surface characteristics are considered as the key characteristics of powders that must be controlled.[3)]

SiO_2 nanopowder is commercially fabricated by the

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flame synthesis method because of its high production rates and relative low cost and it can be operated as continuous processes. It is considered as a novel technique of producing fine, pure and single-phase particles in the as-prepared state.[4,5]

A flame assisted liquid droplet-to-particle conversion process called as flame spray pyrolysis (FSP) is an excellent method to prepare single to multi component metal oxide nanopowder directly from precursor solution which could be consisted of a lot of elements with controlled stoichiometry.

Many demands of those materials in Korea are dependent on import from the industrially advanced foreign nations. But fortunately, large amounts of domestic waste silicon sludge containing silicon are generated and that could be useful resources of SiO_2 nanopowder. Thus, it was greatly required to develop the advanced silicon-based materials from the existing domestic waste silicon resources. To do this, it was strongly recommended to develop a technology for SiO_2 nanopowder from waste silicon sludge.

In this study we present the synthesis of silica nanoparticles by the flame spray pyrolysis using the synthesized tetramethylorthosilicate (TMOS) from the waste silicon sludge. The effects of key variables such as the pressure of dispersion air, the feed rate of precursor solution, the flow rate of hydrogen, and precursor concentration on the particle morphology and size were investigated

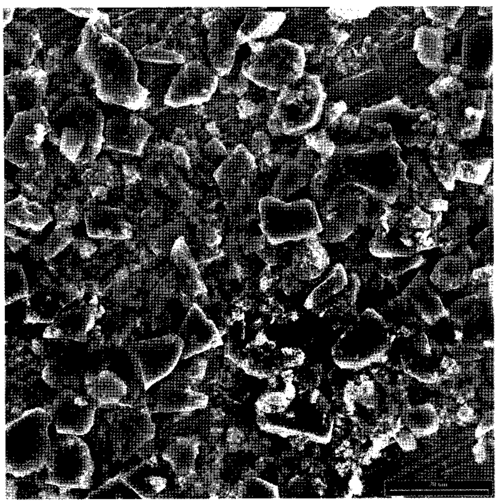

Fig. 1. SEM image of the dried waste silicon sludge.

2. Experimental

The waste silicon sludge consisted of silicon particles, silicon carbide particles and machine oil. The composition of silicon in the waste was 15 wt% and the average particle diameter of pure silicon was 2 μm (Fig. 1).

Tetramethylorthosilicate (TMOS) is widely used one of the metallic organic compounds as a precursor of silica based nanomaterials.[6-8] In this study, TMOS was prepared from the silicon particles in the sludge by the liquid-solid chemical reaction. The experimental apparatus consists of a round flask equipped with a heating mantle for a reactor, a condenser, and a TMOS reservoir. The Si powder and pure methanol was reacted to synthesize the TMOS with the addition of the potassium alkoxide catalyst. Reaction temperature, methanol feed rate, and pulp density of the dried sludge were chosen as key variable to synthesize the TMOS. In order to purify the TMOS, a Vigrux column of 10cm in height made of glass was used for the distillation.

A flame spray pyrolysis of TMOS was employed for the fabrication of SiO_2 nanopowder (Fig. 2). The experimental apparatus consists of an ultrasonic atomizer for aerosol precursor, a diffusion flame burner, and a particle collector. The precursor solution

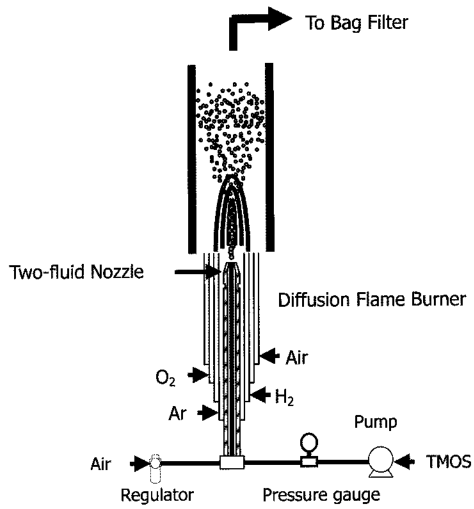

Fig. 2. A schematic of experimental apparatus for the synthesis of SiO_2 nanopowder by flame spray pyrolysis.

was atomized with an ultrasonic vibrator (1.7 MHz), and the atomized droplets were subsequently carried into the central tube of the burner by flowing dry Ar gas. H_2 was used as a fuel while O_2 and air were used as oxidants. The nanopowder generated were collected with a bag filter made of Teflon.

Purity of the TMOS was analyzed by a gas chromatography (GC, Donam Instument, Model DS6200). The particle morphology and size were characterized by a transmission electron microscopy (TEM, Philips Model CM12). The specific surface area of the particles was measured by nitrogen adsorption at -196°C using a BETmethod (Micrometrics Model ASAP 2400). An X-ray diffractometer (XRD, Rigaku Co. Model RTP 300 RC) was used to obtain the X-ray diffraction patterns of the synthesized particles.

3. Results and Discussion

3.1. Synthesis of TMOS

Before synthesizing the TMOS, potassium alkoxide catalyst was prepared with the reaction between potassium hydroxide and 2-(2-butoxyethoxy) ethanol at the 180°C under nitrogen atmosphere. Then, The TMOS was synthesized by the chemical reaction of the silicon sludge and methanol in the presence of the catalyst with respect to various process conditions.

Effect of reaction temperature on the yield of reaction was investigated. The recovery yield was changed with respect to variation of the reaction temperature, and the reaction time. The reaction temperature was varied from 130°C to 170°C. The injected weight of the catalyst was 5 g. The reaction time increased up to 300 minutes. Fig. 3 shows the effect of reaction temperature on the recovery of the TMOS with respect to reaction time. The maximum recovery of the TMOS was 100% after 5 hrs regardless of reaction temperature. But the reaction rate became faster while the reaction temperature was higher than 150°C. The purity of the initially produced TMOS was 35%. The TMOS was purified by the distillation and then 98% of purity was obtained.

Effect of methanol feed rate on the reaction yield was also investigated. As the methanol federate increased from 0.8 ml/min to 1.4 ml/min, the yield of reaction was not varied after 3 hrs (Fig. 4). 0.8 ml/min

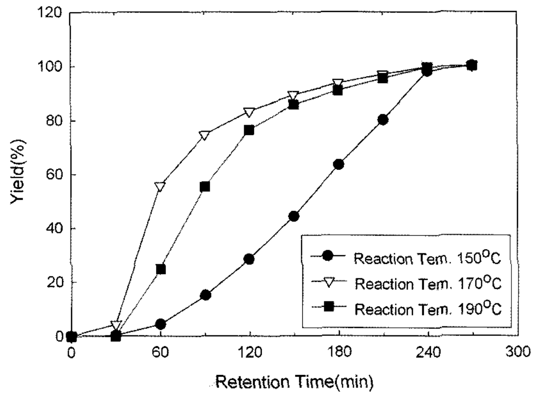

Fig. 3. Effect of reaction temperature on the reaction yield during the synthesis of TMOS from the waste silicon sludge.

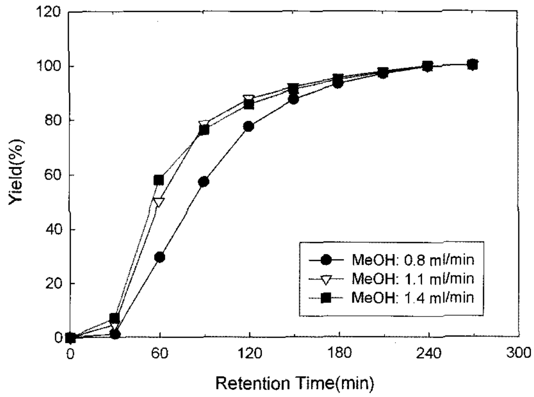

Fig. 4. Effect of methanol feed rate on the reaction yield during the synthesis of TMOS from the waste silicon sludge.

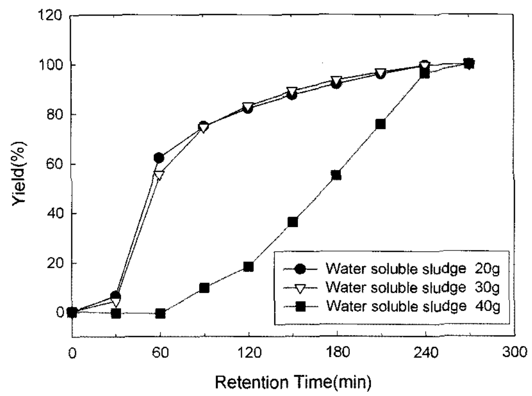

Fig. 5. Effect of the amount of sludge on the reaction yield during the synthesis of TMOS from the waste silicon sludge.

of the feed rate was found as optimum even though the yield was not much sensitive on the methanol feed rate.

In addition, effect of the amount of the silicon sludge on the yield of reaction was investigated. As the amount of the sludge increased from 20 g to 40 g, the 100% of yield of reaction obtained within 4 hrs while keeping the other experimental variables at constant (Fig. 5). But 30 g of the sludge was found as an optimum amount because of rapid reaction rate.

3.2. Fabrication of SiO_2 Nanopowder

The crystalline phase of as-prepared SiO_2 nano powder generated by the flame spray pyrolysis was found to be amorphous from the analysis of X-ray diffraction pattern which was not shown here. Fig. 6 shows TEM micrographs of the as-prepared SiO_2 nanopowder by flame spray pyrolysis at the different concentrations of the precursor (TMOS) at the fixed process condition (TMOS aerosol (8.3 lpm of dispersion air + 26.2 ml/min of TMOS), argon (5 lpm), hydrogen (4 lpm), oxygen (10 lpm) and air (35 lpm), and air (60 lpm)). The average particle diameters determined by BET analysis ranged from 9 nm to 13 nm as the TMOS concentration increased from 30 to 90% in volume.

The morphology of as-prepared silica nanopowder was spherical, non-hollow and there was no neck formation when the concentration of the precursor was higher than 50%. However, when the concentration was as low as 30%, chain-like aggregates were generated. When the liquid droplets size is small enough, the droplets are evaporated instantly due to the Kelvin effect.[9] The evaporated vapors undergo typical vapor-phase reaction described by oxidation, nucleation, condensation, collision, and coalescence, resulting in the chain-like aggregates finally. Besides, effect of precursor feed rate on the particle morphology and size was investigated by increasing the precursor feed rate from 18.3 ml/min to 35.8 ml/min while keeping the pressure of dispersion air and the other gas flow rates at constant. Even though precursor feed rate increased, morphology of the as-prepared powder kept spherical, non-hollow and non-aggregated, but particle size increased from 10 nm to 15 nm in average diameter.

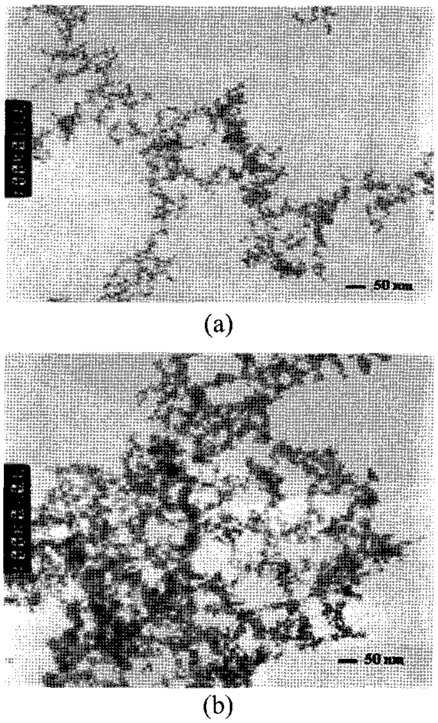

Fig. 6. TEM images of SiO_2 nanopowder synthesized from different TMOS concentration by flame spray pyrolysis ((a): 30 vol%, (b): 90 vol%)

4. Conclusions

TMOS was successfully synthesized from the waste silicon sludge by chemical catalytic reaction with methanol. Reaction temperature, methanol feed rate, and pulp density were chosen as key process variables to synthesize the TMOS by the chemical reaction. The optimum condition for the synthesis of the TMOS with the 100% of yield as follows; the reaction temperature: 170°C, the amount of the sludge: 30 g, the methanol feed rate: 0.8 ml/min.

Flame synthesis of silica nanopowder by a two-fluid nozzle was also successfully conducted from the synthesized TMOS solution. By controlling the experimental variables such as the pressure of dispersion air, the feed rate of precursor solution, the hydrogen flow rate, and the precursor concentration, the average particle size ranged from 9 to 30 nm and the morphology of as-prepared silica nanopowder was spherical, non-aggregated, and non-hollow. The average particle size was in proportional to the precursor feed rate, hydrogen flow rate, and precursor concentration.

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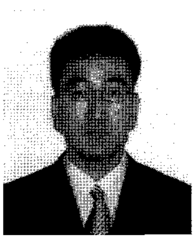

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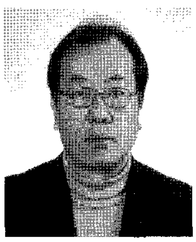

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