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Influence of drying technique on physicochemical properties of bimodal meso-macropore structure of silica support

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Abstract

Drying process directly affect in structure of the silica support for catalysts . Therefore, we herein prepared bimodal meso-macropore structure of silica by sol-gel method and investigated the silica support obtained from various drying techniques, namely, hot air drying (HA), microwave drying(MW)and freeze drying (FD)by means of BET and BJH N_2-sorption, and SEM. The results showed a significant effect of drying technique on the textural properties of the dried bimodal porous silica support. In addition, it was found that freeze drying could enhance surface area of silica support with higher than 500 m^2/g.

Keywords: *bimodal meso-macropore structure silica support: drying technology: freeze drying: hot air drying: microwave drying*

1. Introduction

Silica supports are widely used in field of catalysis. High surface area, large pore size and large pore volume of silica are often desired for catalyst supports in many reactions. Bimodal meso-macropore structure of silica is suitable for use as support in aspect of high dispersion of metal catalyst and good mass and heat transfer [1]. Generally, akyl orthosilicates are used as a silica source for the preparation of silica support. Moreover, organic surfactant are also used as the pore structure-directing agent (template) of silica support. However, they are not appropriate in term of commercial, safety and green approach production due to their high cost, flammability, difficulties in handling or storage, and toxic to environment [2-3]. Therefore, sodium silicate is an interesting as silica source and chitosan is an alternative bio-template, in aspect of lower cost and cleaner production of silica support. In order to modify the textural properties of silica support, especially in preparing the meso-macro struacture of silica, is always conducted by chemical techniques. For example, Li et al. [4] had prepared meso-macroporous structure of silica by using tetrametoxysilane (TMOS) as silica source and polyethylene glycol (PEG) as template, Blin et al. [5] proposed the usage of decane as an effective expander to enlarge the pore size of mesoporous silica. It is found that these techniques are not only use more expensive chemicals but also impractical in green processing which effected to the environment. Besides, it is found that the preparation methods are more complicated for industrial scale [6].

However, many previous researches have been suggested that drying is a physical process that directly affects on structure of the prepared silica support [7-9]. The hot air drying is the process that thermal energy is transferred to the interior of the wet-gel silica via conduction, depends on the thermal conductivity of the wet-gel silica [2]. While, in the microwave drying, water, presented in the wet-gel silica, absorbs the microwave throughout the entire mass, causing molecular vibration with respect to the oscillating electric field of the microwave and the generated heat is transferred homogenously to a molecular scale throughout the bulk [2,10]. Whereas, freeze drying, moisture is removed by sequentially freezing the water/solvent and subliming it at low pressure [10]. As per the abovementioned, we interested and attempt to apply the drying techniques in term of physical techniques to modify textural properties of silica support instead of those chemical techniques. Due to the drying is easier and effective method with lower cost [6].

Therefore, we herein prepared bimodal meso-macropore structure of silica supports by sol-gel method using sodium silicate as a silica source and chitosan as a template, and investigated comprehensively the properties of silica support obtained from various drying techniques, namely, hot air drying (HA), microwave drying (MW) and freeze drying (FD).

2. Materials and Methods

The silica supports were prepared using sol-gel method. Firstly 0.4 g of chitosan was dissolved in 100 mL of 2% v/v acetic acid in deionized water under continuously stirred at 300 rpm and control temperature using water bath at 40 °C for 30 min. Then, 5.4 g of sodium silicate solution (based on 1 g of SiO_2) were primarily diluted with 10 mL of deionized water and added to the chitosan solution. The solution was adjusted to pH of 6 by dropwise addition of 2 M hydrochloric solution. After that, the hydrolysis-condensation reaction was carried out at 40 °C with continuously stirred for 3 h, and then the resulting mixture was aged in the Teflon-lined autoclave at 100 °C for 24 h. The precipitated wet-gel silica products were filtered, washed several times with distilled water. Then, the washed wet-gel silica cake was dried using different drying techniques (hot air drying, microwave drying and freeze drying). Dried-gel silica were finally ground and calcined at 600 °C with the heating rate of $2°Cmin^{-1}$ for 4 h in order to remove chitosan template. The obtained white silica powder was kept in vacuum container. Hot air drying was carried out in a hot air dryer (Binder GmbH, RedLine RF115, Tuttlingen, Germany) at the operating temperature of 80, 100 and 120 °C for 120, 90 and 60 min, respectively. Microwave drying was carried out in a microwave oven (Samsung, MS28H5125BK, Seoul, Korea). The oven was operated at a frequency of 2.45 GHz and a power of 600, 850 and 1000 W for 40, 30 and 20 min, respectively. Freeze drying was carried out in a freeze dryer (Thermo Fisher Scientific, Supermodulyo-230, Waltham, MA) with vacuum pressure for 24 h. Pior to use the freeze dryer, the wet-gel silica cake was freeze in the freezer at -20°C for 24 h. The prepared silica support obtained from various drying techniques were characterized by means of Brunauer, Emmett and Teller (BET) and BJH N_2-sorption (Quantachrome Instruments, Autosorb-1C, Boynton Beach, FL) and Scanning electron microscopy (SEM) (FEI, Quanta 450, Hillsboro, OR).

3. Results and discussion

The results of textural properties (BET specific surface area, average pore diameter and cumulative pore volume) of silica supports prepared by various drying techniques were summarized in Table 1. It was clearly noticed that the largest BET specific surface area was obtained for dried silica support by using freeze dryer. Whereas, silica supports, dried by using hot air and microwave dryer, were relative lower BET surface area. In addition, the average pore diameter and cumulative pore volume for freeze dried silica support were much grater than those of hot air and microwave dried silica support.

Table 1. Textural properties for silica supported dried by using microwave, hot air and freeze drying

Sample	Surface area[a] (m^2g^{-1})	Pore diameter (nm)		Pore volume (cm^3g^{-1})
		Mesoporous[b]	Macroporous[c]	
HA80	376	13.1	~400	1.23
HA100	401	12.6	~250	1.24
HA120	406	12.4	~150	1.28
MW600	414	12.6	~150	1.30
MW850	390	13.3	~350	1.30
MW1000	413	12.5	~250	1.30
FD	700	17.0	171.6, 500<	2.18, 4.05

[a] Specific surface area calculated by BET method.
[b] Pore diameter (mesopore) measured by BJH desorption method.
[c] Pore diameter (macropore) estimated from SEM.

The N_2-sorption isotherm results for silica supports dried by using MW, HA and FD were given in Fig.1. It was found that HA and MW dried silica sample showed similar isotherm although differences in surface area, pore volume and pore size were observed. These isotherms exhibited hysteresis loop which correspond to the type IV isotherms at high relative pressure range of 0.75-0.9. It was due to the capillary condensation of N_2 gas occurring in the mesopores. Therefore, the type IV isotherm was considered as the characteristic of mesoporous materials [2,11]. In addition, it was clearly noticed that the isotherm for freeze dried silica support exhibited significant difference hysteresis loop, which corresponded to the composite isotherm type IV-II. The sharp increase of N_2, at relative pressure range of 0.8 to above 0.9, indicated the presence of large meso-macropores or interparticle adsorption and condensation [3,12].

Pore size distribution of silica supports dried by using various drying methods were presented in Fig.2. It was found that the pore size distribution for silica supports corresponded to the results of pore size of silica listed in Table 1. It can be seen that hot air and microwave dried silica supports also showed similar and uniform pore size distribution with mesopores diameter of around 12 nm. While freeze dried silica support showed broader pore size distribution with mesopores diameter of 17 nm and clearly showed macropores diameter of 171.6 nm. The SEM image for silica support obtained by different drying techniques were

presented in Fig.3. It was clearly observed that the texture of HA dried silica support are closely packed particles when drying temperature increased from 80 to 120°C. It was due to the water molecules were constantly eliminated during the drying process. It led to the increasing of sol concentration, increasing in the capillary force and also created fluid drag which caused the particles to come closer to each other and forms aggregate to achieve greater stability [2,6,13]. In comparison with MW drying found that, the MW dried silica support had the higher porous of structure with larger pore size and pore volume. This could be due to fusion of some of the smaller particles during microwave drying [10]. The freeze dried silica support exhibited the lossely packed, highly porous and sponge-like particles with the macropore of interparticle voids. In the FD process, the effect of capillary force was avoided due to it involves solid-gas transition. The volume expansion occurred during the liquid water transformation to solid in the freezing process also could contribute to the loose packing [13]. In addition, the macropore diameter estimated by SEM images (Fig.3) for all of silica samples listed in Table 1.

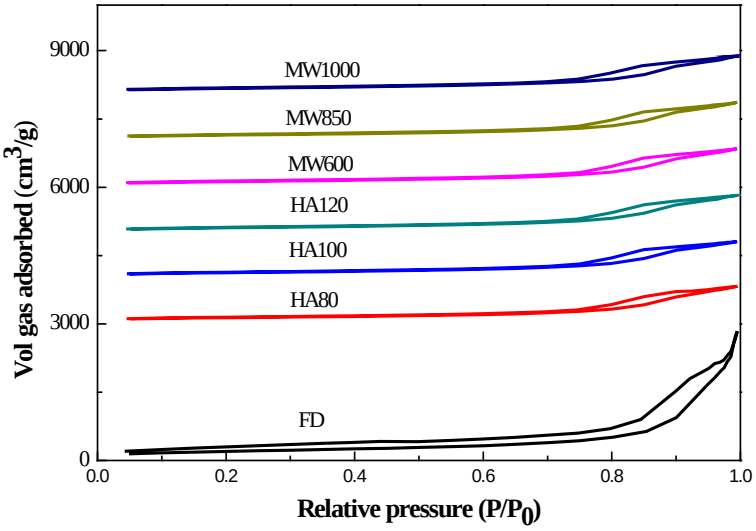

Fig. 1 N_2-sorption isotherm for silica supports dried by using microwave, hot air and freeze drying.

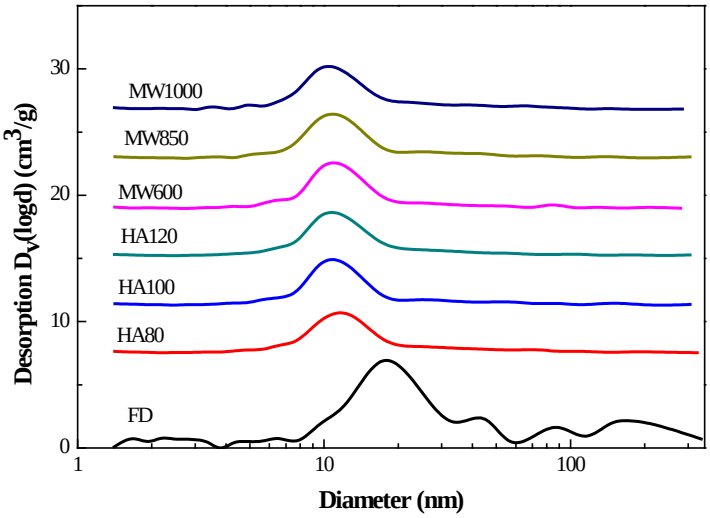

Fig. 2 Pore size distribution for silica supports dried by using microwave, hot air and freeze drying.

4. Conclusion

The bimodal meso-macropore structure of silica supports were successfully prepared by sol-gel method using sodium silicate as a silica source and chitosan as a template. The textural properties of the prepared silica supports obtained from various drying techniques were investigated comprehensively. The freeze drying technique led to the highest surface area, largest pore size and pore volume of silica support among the hot air and microwave drying techniques. In addition, the application of the prepared bimodal porous silica support in catalysis field is based on kind of reaction, that should be further studied.

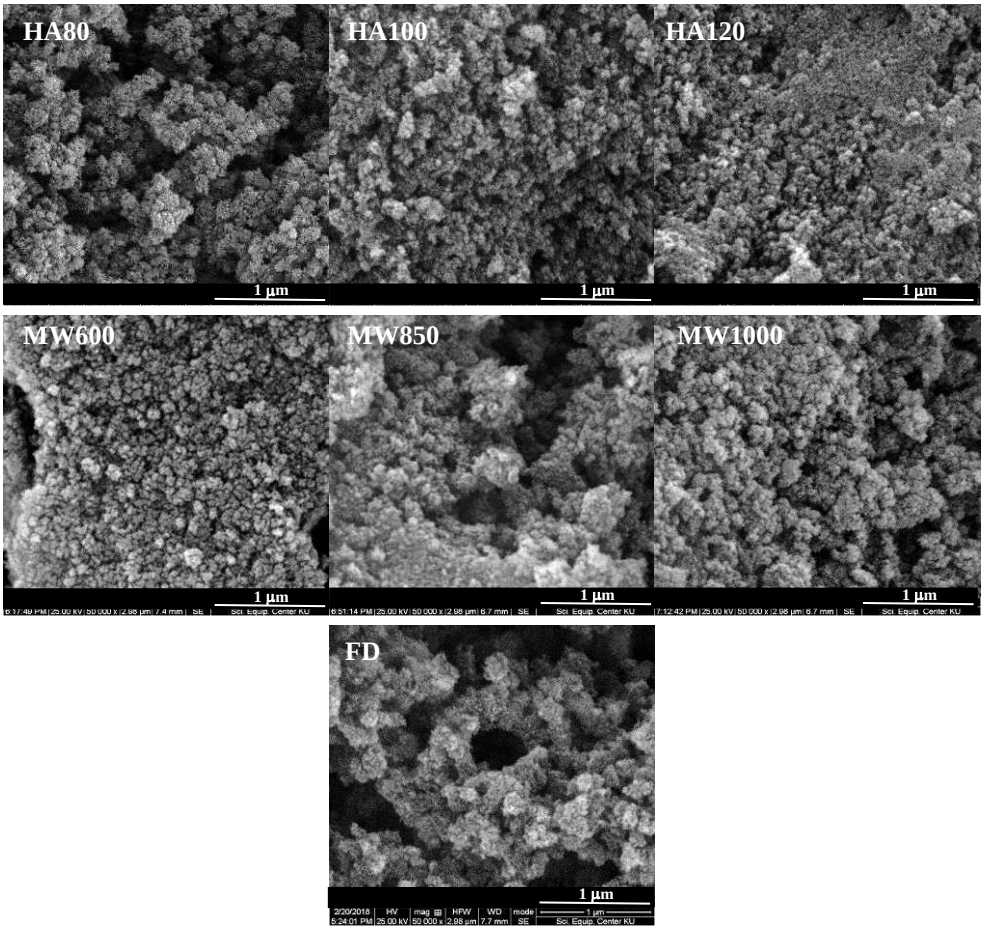

Fig. 3 SEM images for silica support dried by using microwave, hot air and freeze drying.

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