

Synthesis of Spherical Silica by Sol-Gel Method and Its Application as Catalyst Support

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In this present study, the spherical silica support was synthesized from tetraethoxysilane (TEOS), water, sodium hydroxide, ethylene glycol and n-dodecyltrimethyl ammonium bromide (C₁₂TMABr). The particle size was controlled by variation of the ethylene glycol co-solvent weight ratio of a sol-gel method preparation in the range of 0.10 to 0.50. In addition, the particle size apparently increases with high weight ratio of co-solvent, but the particle size distribution was broader. The standard deviation of particle diameter is large when the co-solvent weight ratio is more than 0.35 and less than 0.15. However, the specific surface area was similar for all weight ratios ranging from 1000 to 1300 m²/g. The synthesized silica was spherical and has high specific surface area. The cobalt was impregnated onto the obtained silica to produce the cobalt catalyst used for CO₂ hydrogenation.

Keyword: Spherical silica, Sol-gel Method, Carbon dioxide hydrogenation

INTRODUCTION

Silica has been one of the main catalyst supports. The main topic of research into materials is uniformity of the shape, pore volume and the specific surface area [1, 2]. Among particles with all kinds of morphology, monodispersed silica spheres are very promising because of many applications in the area of catalysis and absorbents. The porous silica was synthesized and classified as mesoporous silica or submicroporous silica according to the diameter of the pore.

Silica sphere has been synthesized by various methods, such as using cationic surfactant under acidic condition, using nonionic surfactant as a template under static and acidic con-

dition, by addition of CTBA as co-surfactant or using the two step synthesis by pH adjustment and addition of small amount of fluoride as catalyst [3].

It has become possible to synthesize silica by the sol-gel method. The synthesis of monodispersed mesoporous silica spheres by modifying the Stöber procedure [4], with the further addition of the surfactant template, such as and alkyl amine. The synthesis has been extended to control the diameter and pore size of particle. However, the methods for preparation mesoporous silica spheres with uniform particle size and good dispersibility are still required.

Cobalt supported on silica has been subject of many studies. During the past 10 years,

cobalt based catalysts appear as the most popular system for Fischer-Tropsch and carbon oxide hydrogenation [5]. Many researches were investigated the metallic/bimetic support and promoter effect to the activity and selectivity of hydrocarbon formation. However, the effect of physical and chemical properties of support on the performance of Co catalysts in Fischer-Tropsch and carbon oxide synthesis still remains unclear [6].

The present work describes the synthesis of silica spheres with silica source of tetraethylsiloxane (TEOS) and n-dodecyltrimethyl ammonium bromide ($C_{12}TMABr$) as a surfactant template in a sol-gel method in alkali aqueous solution. The morphology and size of particle were controlled with the ethylene glycol co-solvent weight ratio of variation in the range of 0.10 to 0.50. The silica spheres were used as catalyst support of Co/SiO_2 and prepared by the incipient wetness technique. The silica sphere support and catalyst were characterization by X-ray diffraction (XRD), scanning electron microscopes (SEM), nitrogen physisorption (BET surface areas), CO chemisorptions isotherm. The activity and selectivity of catalyst were tested for the CO_2 hydrogenation when amounts of hydrocarbon product are generated.

EXPERIMENTAL

Material synthesis

Silica spheres (SiO_2) were prepared by the sol-gel method. $C_{12}TMABr$ (>99%), TEOS (>99%) and cobalt (II) nitrate hexahydrate (98%) were purchased from Aldrich. Sodium hydroxide solution (1 M) and ethylene glycol were purchased from Merck. All gas in the reaction test was supplied by Thai Industrial Gas Co., Ltd.

In a typical synthesis procedure, 2.08 g of $C_{12}TMABr$ and 3.74 ml of 1 M sodium hydroxide solution were dissolved in 500 g of ethylene glycol/water (25/75=w/w) solution (weight

ratio 0.25). Then, 3.12 g of TEOS was added to the solution. The composition of the reaction mixture was $1SiO_2:0.45C_{12}TMABr:0.25NaOH:133ethylene\ glycol:1392H_2O$. Then, stirred continuously at 293 K for 8 h. The white particles were filtered and washed with distilled water at least three times, and then dried the particles at 383 K for 48 h. The particles obtained were calcined in air at 823 K for 6 h. The silica spheres were also synthesized with different diameters by changing the weight ratio of ethylene glycol co-solvent in the range of 0.10 to 0.50 in the same sol-gel method.

The Co/SiO_2 catalysts were prepared by the incipient wetness impregnation with calcined SiO_2 and aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$. The Co loading was set to 20 wt.%. Then, dried at 383 K for 48 h overnight and calcined at 823 K for 5 h in air.

Characterization

Powder X-ray diffraction measurements were carried out with SIEMENS D-500 X-ray diffractometer using $Cu-K\alpha$ radiation. The scan range was $20\sim 80^\circ$ with 0.04° step at the room temperature. Scanning electron microscopy (SEM) was obtained using JSM-5800VL (JEOL). The average particle diameter was calculated from the diameter of 50 particles observed in a SEM picture. BET surface areas were measured by nitrogen physisorption using a Micromeritics Chemisorb ASAP2620 automatic system at 77 K. The specific surface area was estimated by the BET method. The pore diameter and the pore volume were calculated from desorption branches using the Barrett-Joyner-Halenda (BJH) method. CO chemisorptions isotherms were measured at 303 K. The reactor was loaded with 0.5-1.0 g of catalyst using Micromeritics pulse 2750. Analyst of the catalysts was reduced in H_2 at 623 K for 3 h.

The activity test

The activity and selectivity of catalyst were tested in CO_2 hydrogenation. The stainless

steel fixed bed reactor (i.d. 10 mm) was used with 0.8-1.2 g of catalyst loading into the reactor and operated in an up flow mode with the bed help between quartz wool plugs. After the catalyst was reduced in H₂ at 623 K for 3 h under flow rate of 50 ml min⁻¹, the temperature was decreased to the reaction temperature at 493 K and H₂ gas was purged with high purify argon at the flow rate of 8.8 ml min⁻¹. The CO₂/H₂ (8.8%CO₂) reactant was passed through the reactor at the flow rate 21.3 ml min⁻¹ to

combine the argon gas. The reaction products were analyzed by gas chromatography (Shimatzu GC14B) with a VZ10 column and flame ionization detector (FID). The remainder reactant and carbon monoxide intermediate was detected by gas chromatography (Shimatzu GC8B) with a Molecular sieve 5A column and thermal conductivity detector (TCD). The reaction was analyzed not less than 6 h for the steady-state reaction.

Table 1. Properties of representative spherical silica

| Sample | Weight ratio of Ethylene glycol | Average particle diameter [μm] | Standard deviation [%] | Specific surface area [m^2/g] | Mean pore diameter [nm] | Pore volume [cm^3/g] |
|--------|---------------------------------|---|------------------------|---|-------------------------|--|
| S1 | 0.10 | 0.58 | 21 | 1335 | 2.24 | 0.54 |
| S2 | 0.15 | 0.68 | 9 | 1153 | 2.45 | 0.56 |
| S3 | 0.20 | 0.74 | 5 | 1125 | 2.53 | 0.46 |
| S4 | 0.25 | 1.04 | 5 | 1105 | 2.56 | 0.46 |
| S5 | 0.30 | 1.16 | 28 | 1075 | 2.54 | 0.52 |
| S6 | 0.40 | 1.33 | 30 | 1085 | 2.38 | 0.56 |
| S7 | 0.50 | 1.64 | 35 | 1092 | 2.45 | 0.40 |

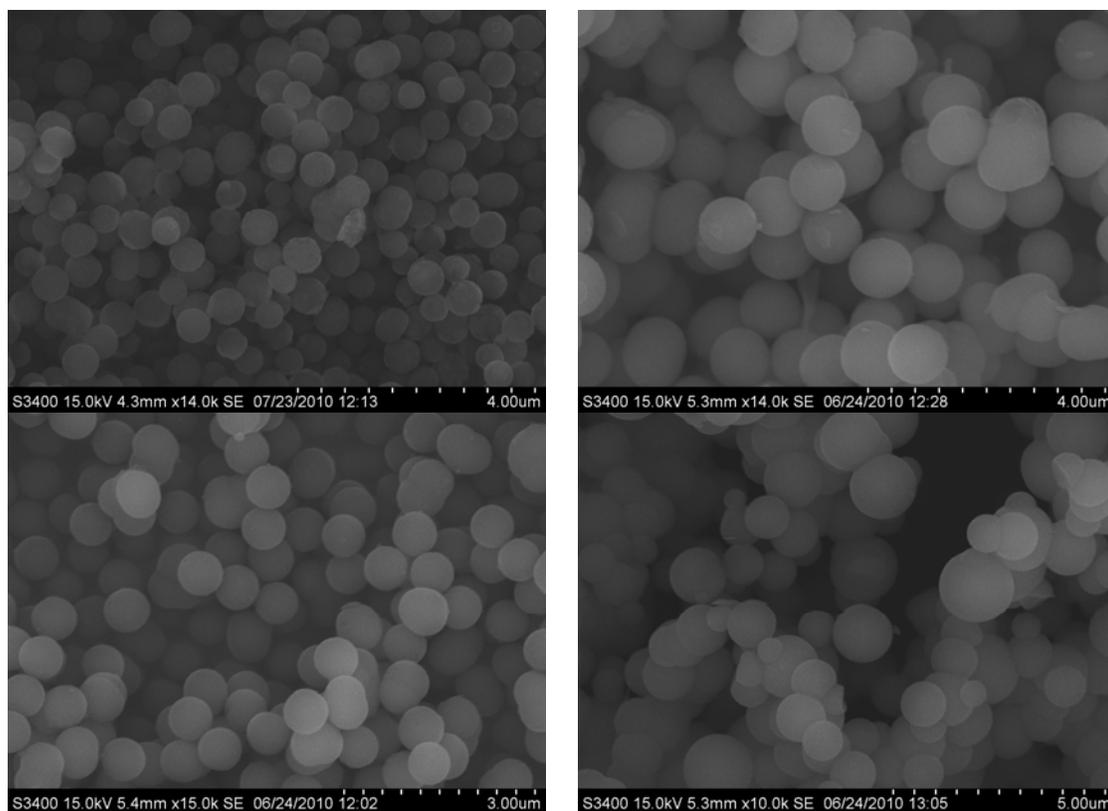


Figure 1. SEM images of various samples, the name of which are denoted in Table 1.

RESULTS AND DISCUSSION

Silica spheres with sol-gel method

The SEM images of the representative sample are shown in Fig 1. The sample exhibited good spherical morphology in all co-solvent ratios. The synthetic results of the silica spheres as the variation of co-solvent ratio are listed in Table 1. The higher weight ratio of the co-solvent was changed to the size control of particle. The average particle decreased when the co-solvent weight ratio was reduced. However, the size distribution uniformity was poor with the co-solvent out of range 0.15 to 0.30. All of silica spheres have high specific surface area ranging from 1000 to 1300 m²/g. The pore size and pore volume of the silica spheres prepared using different weight ratio of co-solvent were similar in the narrow range. When the weight ratio of co-solvent was reduced until 0.1, the silica sphere led to increase the surface area, but the mean pore diameter was lower than other sample. However, the weight ratio of ethylene glycol hardly affected on the uniform and structure of silica sphere.

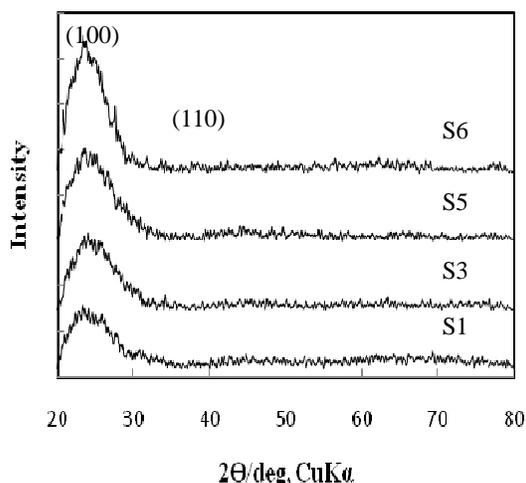


Figure 2. XRD Patterns of Spherical Silica

The small angle X-ray diffraction patterns of the sample exhibited one single board at (100) plane in all particles. Respectively, the boarded peak was small shifted to the higher angle and

higher order peaks when the diameter of particle was changed to the larger one. The representative XRD patterns are depicted in Fig.2

Cobalt-based silica sphere (Co/SiO₂)

The impregnation and calcination procedures were applied for catalyst preparation in the same Co loading. The catalyst was maintained the spherical morphology and constant particle size nearly as the support particle. The specific surface area of catalyst was reduced about 25 percentage of the support surface area as same as the pore volume, but the mean pore diameter of catalyst was not deviated value. The SEM picture was confirmed the shape and diameter of the catalyst in the Fig.3. The homogeneity and dispersibility of catalyst was obtained by SEM-EDS in the Fig 4. The dispersibility of catalyst on spherical silica is good and smoothness.

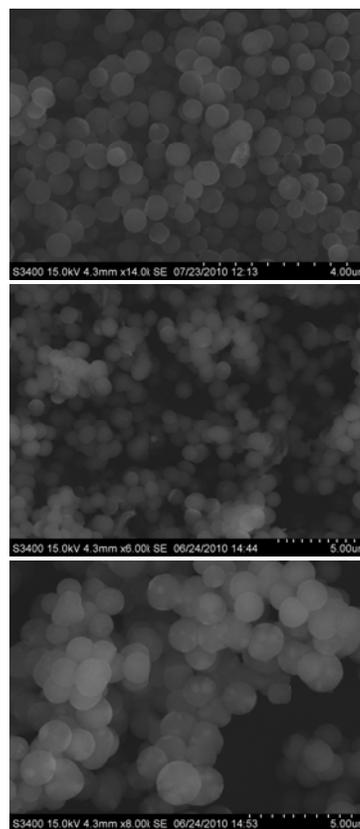


Figure 3. SEM images of various catalysts sample, the name of which are donated in Table 2.

Table 2. The CO Chemisorption of CO/SiO₂

| Catalyst | Loading on support | CO Chemisorp (μmole CO/g catalyst) | Active site (molecules/g catalyst) | Dispersion (%) | CO Chemisorp/BET Surface Area (mole CO/m ²) |
|----------|--------------------|------------------------------------|------------------------------------|----------------|---|
| C1 | S1 | 29.38 | 1.77E+19 | 0.87 | 0.0298 |
| C2 | S2 | 26.07 | 1.57E+19 | 0.77 | 0.0265 |
| C3 | S3 | 26.89 | 1.62E+19 | 0.79 | 0.0276 |
| C4 | S4 | 26.63 | 1.60E+19 | 0.74 | 0.0284 |
| C5 | S5 | 26.06 | 1.57E+19 | 0.77 | 0.0261 |
| C6 | S6 | 26.48 | 1.59E+19 | 0.78 | 0.0265 |
| C7 | S7 | 26.21 | 1.58E+19 | 0.78 | 0.0271 |

Table 3. Conversion and selectivity of Co/SiO₂ catalyst in CO₂ hydrogenation

| Catalyst | CO ₂ Conversion (%) | | Rate of reaction (mol CO ₂ /(g cat. h)) | CH ₄ Selectivity (%) | CO Selectivity (%) |
|----------|--------------------------------|--------------|--|---------------------------------|--------------------|
| | Initial | Steady state | | | |
| C1 | 9.50 | 9.11 | 4.13E-2 | 64.20 | 35.80 |
| C2 | 10.40 | 10.42 | 5.58E-2 | 78.05 | 21.95 |
| C3 | 22.79 | 17.60 | 9.75E-2 | 87.25 | 12.75 |
| C4 | 24.51 | 23.53 | 14.27E-2 | 90.84 | 9.16 |
| C5 | 26.86 | 20.00 | 12.21E-2 | 91.73 | 8.27 |
| C6 | 21.63 | 21.50 | 12.73E-2 | 87.27 | 12.73 |
| C7 | 20.39 | 21.07 | 12.46E-2 | 90.20 | 9.80 |

The cobalt catalyst was a crystalline, evaluated by XRD. The characteristic sharp peak of cobalt was appeared in XRD patterns. The cobalt crystallite size of catalyst C1 was the largest and decreased crystallinity due to the lower surface area. The representative XRD patterns are depicted in Fig.5

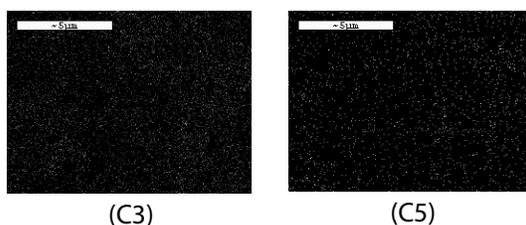
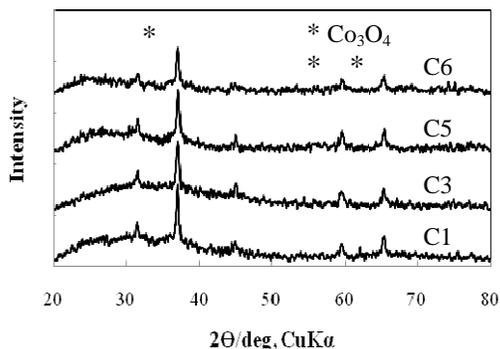
**Figure 4.** SEM-EDS images of catalysts C3 and C5

Table 2 summarizes the CO chemisorption result of catalyst. All samples exhibited high active sites. The chemisorptions results show the similar μmole of CO that can be absorbed per gram catalyst. The catalyst C1 was represented the different performance in the chemisorptions and dispersion percentage from other samples because it had larger specific surface area.

**Figure 5.** XRD patterns of Co/SiO₂

The activity test

The conversion and selectivity of cobalt-based silica sphere catalyst in CO₂ hydrogenation are shown in the Table 3. The initial state was tested around 5 min after started reaction and the steady-state was determined the average result within 3 to 6 h after started reaction. The primary major product in CO₂ hydrogenation of Co/SiO₂ catalyst is methane and small ethane is a secondary product of reaction. The carbon monoxide intermediate was generated from the reverse water-gas

shift reaction (RWGS) used to calculate the rate of reaction and selectivity. Based on results, the catalyst has nearly CO₂ conversion between initial and steady state and the conversion was larger when the particle of support increased to diameter of 1.0 μm . The rate of reaction and selectivity exhibited the result as same as the conversion. However, the catalyst C1 has the highest active site, but it conducted poor conversion, selectivity and rate of reaction. The particle size distribution and uniform shape affected on the reaction. The CO selectivity is inverse value. The intermediate was generated from RWGS, but not to be used in the hydrogenation. The catalyst number C4 and upper exhibited good results in the activity test, perhaps due to a very small particle was pressed in the reactor against the adsorption and increased pressure in the reactor.

Furthermore, catalyst C1 and C2 having a small particle size and broad size distribution will be investigated more in the near future.

CONCLUSION

In summary, the sol-gel method was successfully used to synthesize the spherical silica from TEOS and C₁₂TMABr as a surfactant template. The particle has a good shape and morphology. The particle diameter was controlled by changing the weight ratio of ethylene glycol co-solvent. The uniformity of particle diameter has a high standard deviation, when the weight ratio outside the range of 0.15 to 0.30. The 20 wt% loading of cobalt catalysts on different spherical silica exhibits nearly similar characteristics. However, the smaller particle of catalyst has a larger surface area and active site, but poor activity. Moreover, the control of the physical and morphology of support has effect on the performance of Co catalysts in CO₂ hydrogenation.

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REFERENCES

- L.M. Yang, Y.J. Wang, Y.W. Sun, G.S. Luo, and Y.Y. Dai: *J. Colloid Interface Sci.*, **299** (2006) 823.
- Y. Yamada, K. Yano: *Micropor. Mesopor. Mater.* **93** (2006) 190.
- Z. Zhang, L.Yang, Y.Wang, G. Luo, and Y. Dai: *Micropor. Mesopor. Mater.* **115** (2006) 447.
- W. Stöber, A. Fink: *J. Colloid Interface Sci.*, **26** (1968) 62.
- Y. Borodko, G.A. Somorjai: *Appl. Cat. A* **186** (1999) 355.
- H. Li, J. Li, H. Ni, and D. Song: *Catalysis letters* **110** (2006) 71