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Platinum-Silica Aerogel Nanocomposite via Supercritical Impregnation: Effect of Silica Surface Properties

Satoshi Yoda, Yoshihiro Takebayashi, Tsutomu Sugeta, Katsuto Otake
Research Institute for green technology, National Institute of Advanced Industrial Science and Technology
1-1-1 Higashi, Tsukuba, Ibaraki, 305-8565, Japan
Fax: 81-29-861-4567, e-mail: s-yoda@aist.go.jp

Supercritical CO_2($scCO_2$) is an useful fluid for preparation of nanocomposite by impregnation of reactant into substance, because of its low viscosity, high diffusivity and weak interaction to the reactant. For preparation of inorganic composites, toxic expensive metal components such as fluorinated complexes, or additional organic co-solvents have been used to surmount low solubility of metal compound to $scCO_2$. In this work, we demonstrated the preparation of platinum(Pt)-silica aerogel nanocomposite without using such complexes or co-solvents. The composite was prepared using $scCO_2$ drying of silica alcogel followed by impregnation of Pt (II) acetylacetonate immediately, because the silica aerogel surface was expected to have large number of silanol group and high surface roughness at the stage. The Pt-silica composite aerogels successfully prepared with sufficient Pt content (0.58-1.59 wt %). Control of surface properties of silica by changing aging time or by surface modification using silane coupling reagent were found to be effective to increase Pt loading and to improve Pt particle distribution.

Key words: supercritical carbon dioxide, silica aerogel, platinum nanoparticles, impregnation

1. INTRODUCTION

Supercritical carbon dioxide ($scCO_2$) has been paid a significant attention as alternative to organic solvents. $ScCO_2$ have the property of non-polar organic solvent such as hexane and it is non-toxic, non-flammable, and environmentally sustainable solvent. Operation of $scCO_2$ can be performed under mild condition, since critical condition of CO_2 is 304 K and 7.3 MPa. For these reasons, applications of $scCO_2$ as a solvent for chemical process have been studied in many fields.

$ScCO_2$ also have an aptitude for impregnating solvent on preparation of composite materials because of its extremely low viscosity and high diffusivity. Vanishing of liquid-vapor interface under supercritical condition is also effective to make distribution of impregnating reagents homogeneously. The interactions of $scCO_2$ molecules with reactants are weaker than that of conventional organic solvents, and interaction between impregnating substances and pore surfaces are less inhibited. Additionally, the impregnating process doesn't require the solvent vaporizing process, because $scCO_2$ can be easily removed by depressurization.

Noble metal particle-dispersed material is applicable to catalysts, optical materials, sensors and hydrogen separation systems. Impregnation method has advantage on control of their porous structure and dispersion of metal particles independently. Fabrication of such materials using supercritical impregnation method had been successfully performed for polymer film-metal composite using $scCO_2$-soluble metal complexes [1-5]. Recently Morley et. al. reported the impregnation of silver complexes into silica aerogel for preparation of silver-silica complex [6]. In these work, metal complexes including fluoroacetylacetonate (Facac) or cyclooctadecyl(COD) ligands were used because of their higher solubility in $scCO_2$ than normal metal complexes. However, the use of these harmful and expensive compounds may ruin the environmental-sustainable aspect of $scCO_2$ process. Use of co-solvent is an alternative way for increasing the solubility of metal complex, but it may also spoil the advantage of this process as dry and solvent free systems. It should be clarified whether such harmful complex and co-solvent is really necessary for the supercritical impregnation method.

In this work, we demonstrated preparation of platinum(Pt)-silica aerogel composite by the supercritical impregnation method without using co-solvent and highly toxic components. We selected Pt(II) acetylacetonate $(Pt(II)acac)_2$ as an impregnating agent, having lower solubility than Pt complex including COD or Facac ligands. Our concept to overcome the lower solubility of the complex is to use high reactivity of silica aerogel surface at the state of immediately after supercritical drying. This method had already applied to the preparation of silica-titania aerogels [7]. To enhance the Pt loadings, we also attempted two different methods to control the silica surface properties. One is shortening aging time of silica alcogels to increase surface silanol groups and surface roughness. Another was hydrophobitization of silica surface by silane coupling agent for increasing affinity to hydrophobic $scCO_2$. Effect of these surface modifications on Pt loadings and dispersions were investigated.

2. EXPERIMENTAL

Silica alcogels (30 mm diameter and 10 mm thickness) were prepared by mixing tetramethoxysilane (TMOS), water, methanol and ammonia catalyst as described elsewhere[8]. Two different aging conditions were tested, namely, 333 K for 2 days followed by solvent exchange for 1day (notified using "A" in sample marking, hereafter) and 30min at room temperature followed by solvent exchange for 1 hour ("NA" sample). Solvent exchange was performed using excess amount of fresh methanol with changing the solvent repeatedly during the process time.

Pt(II)acac$_2$ (Aldrich, 97%) was used without further purification. Pt(II)(acac)$_2$ reacts with surface silanol group of silica aerogel (or surface adsorbed water) and is immobilized. The solubility of Pt(II)(acac)$_2$ in scCO$_2$ is ca. $3.0\text{x}10^{-5}$ mol per (CO$_2$ mol) at 20 MPa, 353 K., which is almost one-tenth of Pt(COD)(CH$_3$)$_2$ used in ref [1]. Evaluation of the solubility of such compounds in scCO$_2$ is under investigation.

Figure 1 shows the schematic apparatus of this work. Pt(II)(acac)$_2$ was mixed with glass beads and packed in the saturator(h) under dry nitrogen atmosphere.

The samples using scCO$_2$ drying and impregnation ("C" sample) were prepared by following procedures. Three pieces of alcogels were placed in a 50 cm^3 of high-pressure vessel(i) with additional methanol for preventing dry up. The vessel(i) was pressurized by CO$_2$ to 20 MPa and heated to 353 K. CO$_2$ was then flowed in the reactor(i) with maintaining the pressure at 20 MPa using backpressure regulator (JASCO, SCF-BPR) until methanol was completely extracted. After that, the saturator(h) was connected to the flow line and Pt(II)(acac)$_2$-saturated scCO$_2$ was introduced into the vessel(i) for impregnation and flowed for 6 hours. After finishing the impregnation process, the reactor was washed by fresh scCO$_2$ and then depressurized at a rate of 0.1 MPa$\cdot$ min^{-1} to atmospheric pressure. Finally, the aerogels were removed from the vessel and calcinated at 773K for 2 hours in air to decompose Pt(II)(acac)$_2$ and organic remains.

Samples by impregnation of Pt(II)(acac)$_2$ dissolved in tetrahydroflane(THF) were prepared for comparison ("T" sample). In this case, THF was used instead of methanol for solvent exchange of alcogels. Impregnation was performed using pure THF in this case. The impregnation was performed by immersing alcogels in excess amount of 0.005 moldm^{-3} Pt(II)(acac)$_2$ /THF solution for 24 hours before supercritical process. The impregnated alcogel was rinsed by THF and then set into the reactor with additional THF. The pressurization, extraction of THF, depressurization and calcinations were performed like sample "C" series.

Hydrophobitization of silica surface ("HP" sample) was performed between drying(extraction of solvent) and impregnation by flowing hexametylenedisilazane (HMDS) dissolved in scCO$_2$. HMDS react with surface silanol groups and inactivated them by following reaction.

$$\equiv\text{Si-OH} \quad + 1/2 \quad (\text{CH}_3)_3\text{-Si-NH-Si-(CH}_3)_3$$
$$\rightarrow \ \equiv\text{Si-O-C(CH}_3)_3 + 1/2\ \text{NH}_3 \qquad (1)$$

The HDMS was diluted with methanol and pumped from solvent pump(e). Total flowing amount of HMDS was calculated to be equivalent to the quantity which end-caps 50% of silanol groups. The silanol group number of the gel was estimated from specific surface area of the corresponding silica aerogel without Pt impregnation using surface silanol density of 2.4/nm^{-2}[7]. After finishing the HMDS treatment, the gel was washed with pure fresh scCO$_2$ for 30 minutes before impregnation.

Pt content was determined using X-ray fluorescence analyzer (SEIKO SEA2010). BET specific surface area was determined by nitrogen adsorption using Coulter SA3100 analyzer (Beckmann-Coulter Co. Ltd.) after evacuating the sample for 24 hours at 423 K. Mesopore size distribution was determined by BJH method. Microstructures were observed by transmission electron microscopy (TEM) (JEOL TEM2010F). Metal dispersions, specific surface area of Pt, average Pt crystal size were analyzed from the volumetric CO adsorption analysis using BELSOAP18 adsorption-desorption analyzer (Nippon Bell. Co. Ltd.)[12].

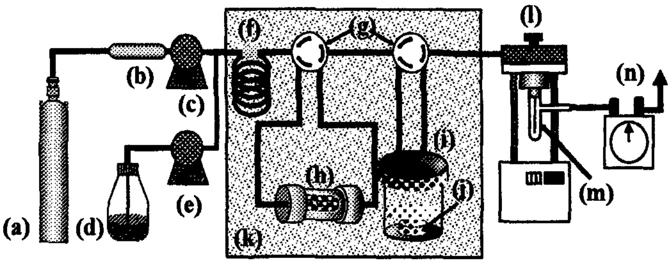

Fig.1 Apparatus for this work. (a)CO$_2$ cylinder, (b)Gas dehydration column,(c)CO$_2$ pump, (d)HMDS solution, (e)Solvent pump, (f)Preheat coil ,(g)6-port valve (h) Saturator for Pt(II)(acac)$_2$,(i)High pressure vessel for alcogel (j)Alcogel, (k)Constant temperature oven (l)Backpressure regulator, (m)Receiver for excess Pt(II)(acac)2, (n)Integrating gas flow meter.

Table I Preparation condition and bulk properties of Pt silica aerogel nanocomposites

Sample mark	Aging condition of alcogel	Impregnation method	Surface hydrophobitization	Linear shrinkage %	Apparent density gcm^{-3}	Specific surface area m^{2}g^{-1}
AC	333K, 2days	scCO$_2$, flow	×	8.8	0.16	1062
ACHP	333K, 2days	scCO$_2$, flow	○	9.7	0.17	1018
NAC	r.t. 1hr	scCO$_2$, flow	×	16.9	0.23	953
NACHP	r.t. 1hr	scCO$_2$, flow	○	18.1	0.24	1145
AT	333K, 2days	THF, batch	×	8.0	0.13	822

3. RESULTS AND DISCUSSION

Monolithic Pt-silica aerogel composites were successfully prepared for all runs. Table I summarizes the preparation condition, bulk properties and porous structures. Sample names indicate the preparation procedure, e.g., NACHP means prepared from non-aged alcogels using $scCO_2$ drying/impregnation and hydrophobitization of the surface. All samples showed large specific surface area around 1000 $m^2 g^{-1}$ and peak pore size of 15-17nm. The NAC and NACHP sample showed larger shrinkage and higher density than others, probably because of their poor development of networking. Since their mesoporosity and specific surface area were not influenced so much, the large shrinkage would affect macroporosity of these gels.

Figure 2 shows the appearance of the prepared Pt silica aerogels. The sample showed dark brown to black colors of Pt particles. NAC, ACHP and NACHP were opaque, indicating high loading of Pt. The Pt particle distribution was not completely homogeneous, but it reached to the center of the gel for all samples. For example the central part of the AC gel (about 10mm diameter and 5mm thickness) contained 0.57% of Pt, whereas that of the outside part was 1.12wt%.

Table II summarizes experimental results for Pt content and Pt particle dispersion. AC samples showed much larger Pt content than TA samples. Direct comparison of these results is difficult, however, it may be said that the supercritical drying/impregnation method is effective to obtain high Pt loading with short impregnation time. Judging from the result in table II, dispersion of Pt particle was considered to be pretty bad for AC.

ACHP, NAC and NACHP samples contained larger amount of Pt than AC. Improvement of Pt dispersion was observed on ACHP and NAC samples. Silica aerogel prepared with short aging time of alcogel was known to have bimodal mesoporosity, indicating large roughness of the silica network and surface [11]. It would affect the increase of Pt dispersion. Hydrophobitizaiton of silica surface will be effective to increase the affinity of $Pt(II)(acac)_2$-dissolved $scCO_2$, and diffusion of the $scCO_2$ solution would be extended to smaller structure of silica aerogels. Hydrophobitization could inactivate certain amount of silanol groups, but it would be covered by improvement of the diffusion in this case.

NACHP sample shows similar tendency to ACHP and NAC, but Pt distribution was worse than that of them. Hydrophobitization would be insufficient for this

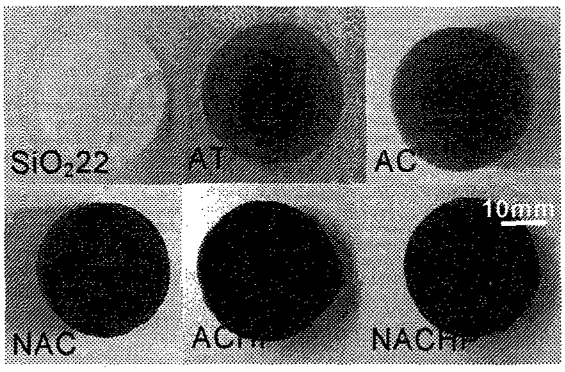

Fig. 2 Appearance of Pt-SiO_2 aerogel prepared by different impregnation conditions.

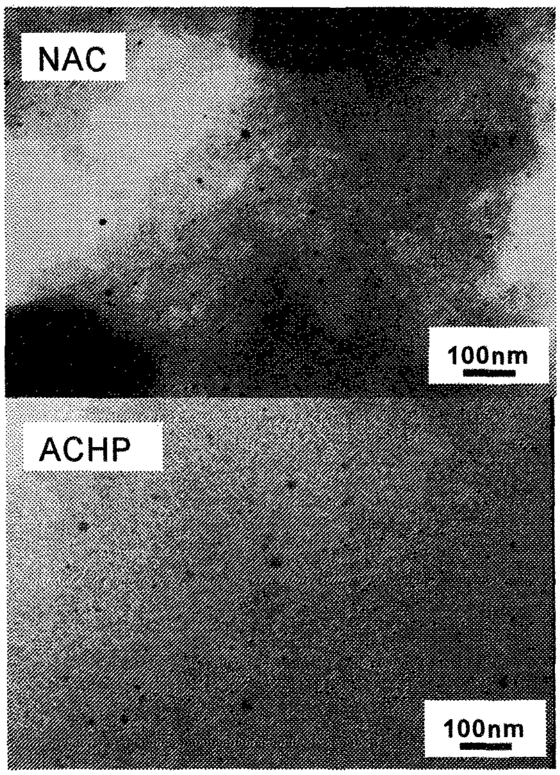

Fig. 3 TEM Photographs of NAC and ACHP samples.

Table II Pt content and dispersion properties of Pt-silica aerogel

Sample mark	Pt content wt%	Metal dispersion %	Metal specific surface area m^2g^{-1}	Average crystal size nm
AC	0.58	1.70	4.2	67
ACHP	1.21	26.6	65.6	4.3
NAC	1.59	18.9	46.7	6.0
NACHP	0.96	5.97	14.3	19
AT	0.20	15.9	39.3	7.1

case since the silanol group would be much larger than ACHP. Reproducibility of surface structures of "NA" samples during impregnation should also be considered.

Figure 3 shows TEM photographs of NAC and ACHP samples. As indicated from CO adsorption analysis, Pt particles with a diameter under 10 nm were observed dispersing in the silica matrix.

4. CONCLUSIONS

Pt-silica aerogel nanocomposite was successfully prepared by supercritical impregnation method. Pt loading was higher than liquid impregnation with a short treatment time. The Pt content of those composite was ranged from 0.58 to 1.59wt% and was considered to be sufficient for general use as catalyst. Shortening the aging time of the alcogel was effective to increase Pt loading probably because of higher content of silanol groups and larger surface roughness than aged alcogel. Hydrophobitization of silica surfaces also increased the Pt loading and dispersion of Pt particles were extended. Hydrophobicity of the matrix surface would be necessary for fabrication of highly dispersed structure by $scCO_2$ impregnation technique. At the optimized conditions, Pt nano-particles were observed dispersing in the silica matrix.

Inorganic synthesis using $scCO_2$ will be a potential method, especially for fine particle-dispersed porous materials. Our study would be an example that special metal compounds having CO_2-philic structures, such as fluoroalkyl group or COD ligands, are not necessary for the synthesis of inorganic composite materials using $scCO_2$.

ACNOLEDGEMENT

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