SYNTHESIS OF THERMALLY STABLE METAL-OXIDE HYBRID NANOCATALYST WITH ENCAPSULATION OF Pt and Ru NANOPARTICLES

A. Satyanarayana Reddy[1], Hu Young Jeong[1], Kamran Qadir[1], Jung Yeul Yun[2], Osamu Terasaki[1], Jeong Young Park[1], *

[1]*Graduate School of EEWS (WCU), and Nanocentury KI, KAIST, Daejeon, 305-701, Republic of Korea*
[2]*Functional Materials Division, Korea Institute of Materials Science (KIMS), Chang-won, 641-823, Republic of Korea*

* Email: jeongypark@kaist.ac.kr

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1 Introduction

There has been significant progress recently in the synthesis of nanocatalysts of tunable particle size, shape and composition [1-3]. The advantages of nanoparticles in catalyzing chemical reactions have long been recognized. Catalytic studies of metal nanoparticles have shown that dispersion on an oxide or other support yields higher activity and selectivity [4]. However, thermal and chemical stability are crucial for nanoparticle use in industrial reactions. Organic capping agents, which are widely used in colloidal chemistry to stabilize nanoparticles at mild conditions, decompose at temperatures above 300–400°C, leaving the uncapped nanoparticles unprotected against sintering and deactivation [4]. To overcome sintering effects, various designs for high-temperature stable nanocatalysts have been reported [5-12] and developed, including alloying metal nanoparticles to increase the melting point, encapsulation of metals, core-shell models, loading of metals into the pores of mesoporous structures, and rare earth metal oxide supports, despite any disadvantages. Core-shell structures form a barrier layer, usually mesoporous oxides on the metal nanoparticle to prevent them from coming into contact with each other [6,7,10], and surface protected etching for encapsulation of the supported metal nanoparticles [10]. Mesoporoous silica can be formed by the removal of long-chain hydrocarbon-based capping molecules used on nanoparticles, silica precursor-containing long hydrocarbon chains, or etching of the silica layer [7,11,12]. However, it is challenging to form an oxide layer on smaller nanoparticles (<2 nm) and to achieve high dispersion of the metal in core-shell models to attain maximum catalytic performance. To overcome lengthy synthesis steps and to get a high dispersion of metal,

a facile synthesis of high-temperature stable hybrid nanocatalysts by coating ultra-thin titania on silica supported Pt nanoparticles has been developed [10]. This approach involves the design of a metal-oxide hybrid nanocatalyst, including coating an ultra-thin active-titania layer on supported nanoparticles, which prevents sintering and provides high thermal stability while maximizing the metal-oxide interface for higher catalytic activity. In addition, our hybrid nanocatalyst can be characterized by surface sensitive techniques, as the nanoparticles are covered by an ultra-thin oxide (few nanometers) that exposes metals on the surface.

In this paper, we present the synthesis of ultra-thin titania-coated supported-Pt and Ru hybrid nanocatalysts. It is highly desirable to explore the feasibility of our design to transform various important metal nanoparticles (Pt, Ru, Rh, PtNi etc.) into high-temperature stable catalysts. Herein, we focus on Pt- and Ru Ru-based nanocatalysts, and investigate their relative thermal stability and surface analysis by XPS. This structural investigation could be helpful for the rational design of heterogeneous catalysts that have high thermal and chemical stability.

2 Experimental details

2.1 Synthesis of Silica Supported Pt or Ru Nanoparticles

All the reagents used in this study were purchased from Sigma-Aldrich, Korea and used without further purification. Silica nanospheres of 25-30 nm were synthesized using a modified Stöber method [13]. The silica nanospheres were functionalized with an amine group by refluxing aminopropyl triehoxysilane (APTES, 50 μL) in isopropanol at 80°C for 2 h. Functionalized silica

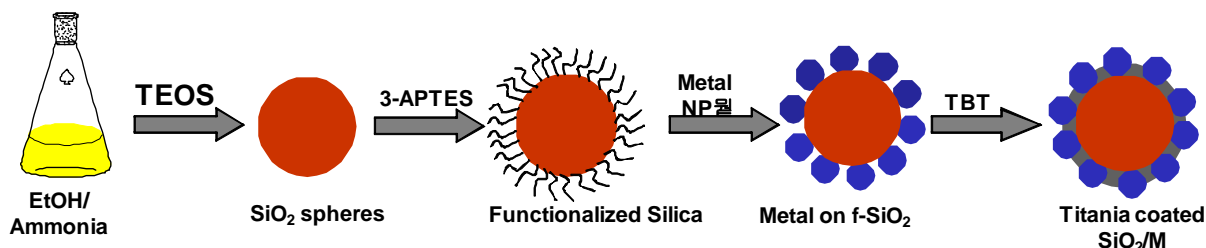# SYNTHESIS OF THERMALLY STABLE METAL-OXIDE HYBRID NANOCATALYST WITH ENCAPSULATION OF Pt and Ru NANOPARTICLES

Figure 1. Schematic representation of the synthesis of the SiO_2/M@TiO_2 (M =Pt or Ru) nanocatalyst. (a) Silica nanospheres were synthesized using the Stöber method and used as the core particles. (b) The silica nanospheres were functionalized with 3-minopropyl triethoxy silane, (c) Pt or Ru nanoparticles synthesized in a separate reaction were immobilized on the f-SiO_2, then (d) an ultrathin layer of titania was coated on SiO_2/M by hydrolyzing titanium butoxide.

nanoparticles were reacted with excess citrate-capped Pt nanoparticles, which were synthesized by the Turkevich method [13,14] in a separate reaction. The SiO_2/Pt colloids were centrifuged and dispersed in ethanol (3 mL) for further characterization. PVP-capped ruthenium nanoparticles were prepared by the polyol method in ethylene glycol, as reported [15].

2.2 Titania Coating on Silica-supported Pt or Ru Nanoparticles

Titania coating on SiO_2/Pt colloidal nanoparticles was carried out by hydrolyzing titanium-butoxide (TBT, Ti-(OBu)$_4$, 97%) in absolute ethanol [16]. In a typical synthesis, 1.5 mL of SiO_2/Pt (0.36g, on the basis of SiO_2) solution was added to the titania sol (volume ratio TBT/EtOH, 1/9) and subjected to ultrasonic treatment (10 min) followed by incubation at RT for 16 h. The mixture was centrifuged to remove excess titania sol and washed with ethanol. The separated hybrid colloidal spheres were condensed with ethanol/water (1:1) under magnetic stirring for 2 h. The titania coating process was repeated two times. Finally, the hybrid nanostructures were dispersed in ethanol for further characterization.

2.3 Characterization

The morphologies of the hybrid catalysts were characterized by transmission electron microscopy (TEM, Tecnai G2 F20) and energy dispersive X-ray spectroscopy (EDS) fitted to the TEM. Angular dark-field scanning transmission electron microscopy (ADF-STEM) images and EDS line mapping were obtained on a Hitachi HD-2300A. Drop-casting samples on Si wafer were used for XPS (Sigma Probe, Thermo VG Scientific) and TEM analysis for thermal stability.

3 Results and Discussion

3.1 Synthesis of Hybrid Nanocatalysts

Figure 1 illustrates various steps involved in the synthesis of the hybrid nanocatalyst. The average size of the silica nanoparticles is 25-30 nm and nearly monodispersed. Pt nanoparticles capped with citrate and Ru nanoparticles capped with poly(vinyl pyrrolidine, avg. MW- 55,000) with an average size of 2-3 nm were used. The Pt or Ru nanoparticles were immobilized on the amine-functionalized silica, followed by coating with titania. The amine-functionalized silica (f-SiO_2) is used because they are reported to have a positive ξ-potential resulting from the hydroxylation of APTES [17]. The capping molecules of the metal nanoparticles exchange with the amine group on the silica during the deposition. Finally, an ultra-thin titania layer was coated on the SiO_2/Pt colloids.

3.2 Transition Electron Microscopy

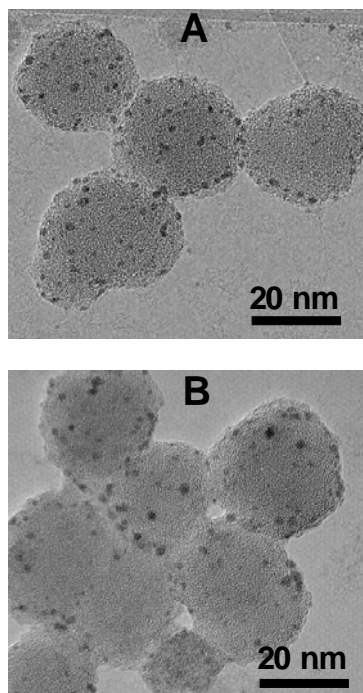# SYNTHESIS OF THERMALLY STABLE METAL OXIDE HYBRID NANOCATALYST FOR ENCAPSULATION OF Pt and Ru NANOPARTICLES

Figure 2. TEM images of (A) SiO_2/Pt and (B) SiO_2/Pt/TiO_2 .

Figure 3. TEM images of (C) SiO_2/Ru and (D) SiO_2/Ru/TiO_2.

Figure 2 shows TEM images of SiO_2/Pt (A) before and (B) after titania coating. The TEM image in Fig. 2(A) of Pt on silica shows a uniform dispersion of Pt nanoparticles. The average diameter of the silica and Pt nanoparticles were measured to be 25 ± 2.2 nm and $\sim 2.5 \pm 0.5$ nm, respectively. The Pt nanoparticles appear as dark dots spread uniformly on the silica spheres without aggregation. The uniform dispersion of the Pt on silica is due to the amine groups on the functionalized silica that bind to the citrate-capped Pt NPs. Functionalization of silica helps the metal nanoparticles to remain on the surface. After titania coating, SiO_2/Pt does not show considerable change in the morphology (Fig. 2B).

Figs. 3(A) and 3(B) show TEM images of SiO_2/Ru nanoparticles before and after titania coating, respectively. It can be seen that the uniformity of the metal nanoparticles remains unaltered after titania coating, except some decrease in the brightness of the metal nanoparticles, indicating that the initial structure of the SiO_2/M (M = metal) was preserved. The SiO_2/M@TiO_2 sample is amorphous, as there were no X-ray diffraction (XRD) peaks observed for silica or titania. After

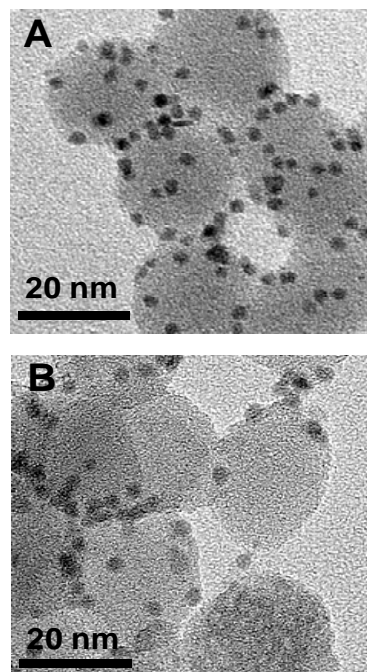titania coating, the metal nanoparticles are trapped in an ultra-thin layer of titania. However, some of the metal nanoparticle could be covered by the titania layer as the metal nanoparticles show a decrease in darkness (Figs. 2B and 3B). The energy dispersive spectrum (not shown here) showed corresponding peaks for Ti, indicating the presence of titania over the entire silica sphere. The formation of the titania layer was further investigated by ADF-STEM images of the hybrid structures.

3.3. ADF-STEM images and EDS line mapping of hybrid metal-oxide nanostructure.

To investigate the presence of a thin layer of titania on the SiO_2/M as well as uniformity of the coating, ADF images and EDS line mapping for constituent elements were verified. Figures 4(A and B) show ADF-STEM images of SiO_2/Pt/TiO_2 and SiO_2/Ru@TiO_2, respectively, with corresponding EDS line mapping spectra in Figs. 4(C and D). The ADF images expose constituent elements of different atomic number based on image contrast (Z-contrast). A clear, uniform contrast layer on the SiO_2/M spheres after titania coating indicates hybrid nanoparticles are coated with an active oxide layer. The corresponding EDS line mapping profile shows

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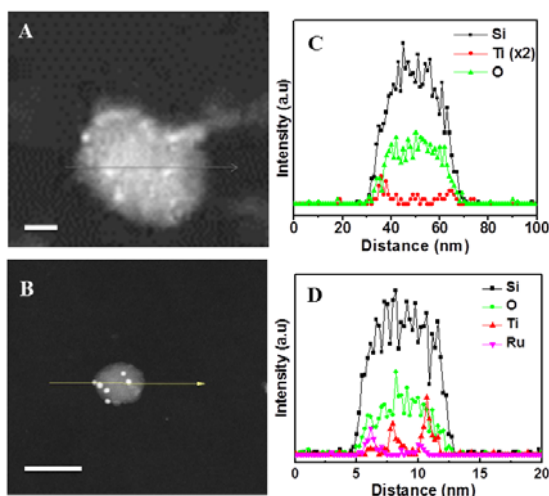signals for Si, Ti, O and Ru, confirming the presence

Figure 4. ADF-STEM images of (A) SiO_2/Pt/TiO_2 and (B) SiO_2/Ru@TiO_2 nanoparticles and corresponding EDS line spectra (C and D) to prove the existence of ultra-thin TiO_2 layer. The bars represent 10 nm (a) and (b) 8 nm.

of a titania layer on the SiO_2/M spheres. There is an increase in the intensity of the EDS peak of Ti at the edges of the spherical hybrid structure, which further corroborates the uniform titania coating over the hybrid spheres. Formation of the titania appears thicker and less uniform on SiO_2/Ru as the intensity of the Ti peak is higher compared to SiO_2/Pt. In these hybrid structures, the ultra-thin titania layer was calculated to be 3 and 4 nm for SiO_2/Pt/SiO_2 and SiO_2/Ru/TiO_2, respectively, from EDS line mapping data. Formation of a titania 2D layer on the silica/M spheres appears to be promising for the design of nanocatalysts to prevent sintering of the metal nanoparticles at high temperatures.

3.3. Thermal stability and chemical composition of SiO_2/M/TiO_2

Figure 5 shows TEM images of hybrid structures after heating at 600 ^{o}C in air. Figures 5A and 5B show the effect of heating on the morphology of SiO_2/Pt after heating and before and after titania coating. It can be seen that sintering of the Pt nanoparticles is evident without the titania layer on the supported Pt, while the titania-coated sample has no noticeable Pt sintering. Hence, the role of the titania thin layer is apparent to provide
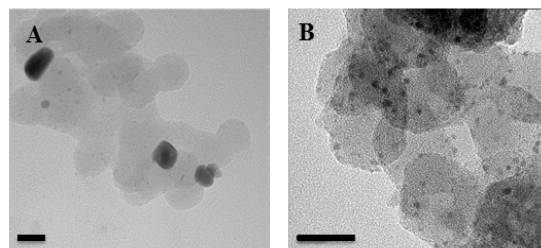

Figure 5. TEM images of SiO_2/Pt or Ru before and after heating at 600 ^{o}C in air/1 hr. (A) SiO2/Pt (B) SiO_2/Pt/TiO_2. The scale bars represent 20 nm.

thermal stability, preserving the initial morphology and metal dispersion of the hybrid structure. Furthermore, these hybrid structures with titania coating remained amorphous even after heating, as there was no X-ray diffraction (XRD) peaks observed for silica or titania. The amorphous nature of the hybrid system could be due to a large volume of porous/amorphous silica and a high dispersion of metal NPs in the hybrid system. It is evident from the TEM results that the SiO_2/M/TiO_2 hybrid structure exhibited remarkable thermal stability up to 600 ^{o}C in air. Characterization of nanostructured materials with highly dispersed smaller metal nanoparticles on a porous matrix is a challenge due to the very small length scales (pores on oxide supports and active metals) of these systems and their complex overlapping morphologies. The design of novel metal-oxide hybrid nanocatalysts offers high metal loading (52.6% for SiO_2/Pt/TiO_2) as determined by CO chemisorption and thermal stability (600 ^{o}C).

Figure 6 shows the XPS spectra of hybrid nanostructures. It can be observed that the ultra-thin titania on the supported metal nanoparticles shows peaks corresponding to the metal and titania. There are two peaks for O1s with binding energy at 532.4 and 529.8 eV (Fig. 6A), which can be attributed to SiO_2 and TiO_2, respectively [18]. Similarly, SiO_2/Ru/TiO_2 also showed two peaks for O1s (at 532 and 529.4 eV, Fig. 6C indicating the surface of the hybrid structure is covered with a titania layer. Both the samples showed peaks corresponding to Ti^{4+} at 458.8 eV (not shown here). Both Ti_{2p} and O_{1s} peaks indicate the presence of titanium oxide as TiO_2 [18,19]. Figs. 6B and 6D show peaks for Pt and Ru metals, respectively. Nanoparticles exhibit metallic Pt (main peak, 71 eV) or Ru (main peak, 279.8 eV), as well as their oxides (Pt^{2+} = 72.0 and

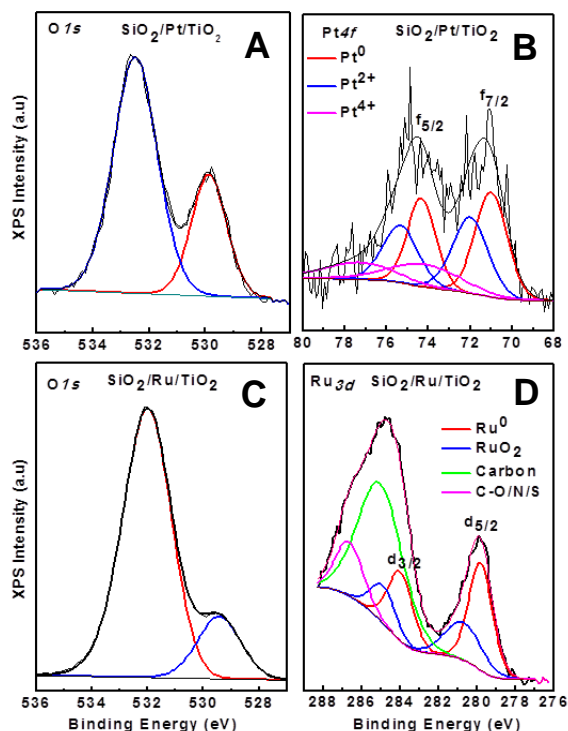# SYNTHESIS OF THERMALLY STABLE METAL OXIDE HYBRID NANOCATALYST FOR ENCAPSULATION OF Pt and Ru NANOPARTICLES

Figure 6. X-ray photoelectron spectra of $SiO_2/Pt/TiO_2$ and $SiO_2/Ru/TiO_2$ hybrid structures after drying at room temperature.

Pt^{4+}=74.2 eV; Ru^{4+}= 280.8 eV) and the source of oxygen could be the water used during the synthesis process. The Ru3d peaks overlap with C1s, deconvoluted spectra show carbon peaks which may be due to adsorbed carbon oxides and organic capping molecules. It is to be noted that our design of thermally stable nanocatalysts allows surface characterization of metal nanoparticles that is otherwise not possible, due to the ultra-thin layer of titania. This is a significant advantage of our design over other high-temperature stable nanocatalysts [7,10,13].

The major challenge associated with nanocatalysts is a lack of stability under realistic process conditions. Hence, rational design of high-temperature stable nanocatalysts rather than trial and error is more sought after. In this process, we have chosen to modify metal-support interfaces of the nanostructure so as to achieve the additional advantage of maximizing the strong metal-support interaction (SMSI) effects [20-22] apart from thermal stability. Our novel design addresses various key issues required for higher catalytic performance

in addition to thermal stability. Silica, a well-known support with high surface area and thermal stability, was used for the hybrid structure. The support oxide (25-30 nm), and metal nanoparticles (2-3 nm) are chosen so as to obtain higher metal dispersion, increasing the surface-to-volume ratio, while decreasing the size of the metal nanoparticles, which could increase their specific catalytic activity. In addition, the metal oxide, titania, as an active support material, is used to exploit possible synergic effects of metal-oxide interfaces for catalysis. Furthermore, the facile synthesis process avoids various laborious steps, making our design more attractive and can be easily extended to other metals and metal oxides.

4. Conclusions

We demonstrated the novel design of a hybrid catalyst with stabilization of Pt and Ru nanoparticles, while exposing the metal nanoparticles to the surface. High metal dispersion, ultra-thin titania and surface characterization are significant advantages of this design over other models. The ultra-thin-layer of titania could prevent sintering of metal nanoparticles up to 600 °C. The metal-oxide interfaces (Pt-titania or Ru-titania) can be exploited for catalytic reactions, where metal-oxide interfaces are crucial for higher catalytic activity and selectivity even at high reaction temperatures.

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