Ultra-thin porous silica coated silver–platinum alloy nano-particle as a new catalyst precursor†

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Templated sol–gel encapsulation of surfactant-stabilised micelles containing metal precursor(s) with ultra-thin porous silica coating allows solvent extraction of organic based stabiliser from the composites in colloidal state hence a new method of preparing supported alloy catalysts using the inorganic silica-stabilised nano-sized, homogenously mixed, silver–platinum (Ag–Pt) colloidal particles is reported.

Synthesis of nano-sized mono-/bi-metallic particles of well-defined size, geometry, structure and composition as catalysts prior to their deposition on supports is of a tremendous interest because the unusual high activity/selectivity for many reaction(s) associated with small particles. Nano-sized alloys of various compositions have been the recent focus in particular with regards to their interesting tuneable catalytic properties.[1] The employment of micelles or reversed micelles stabilised by organic stabilizers in water/oil microemulsion for the template catalyst synthesis therein are well documented.[2] However, the organic stabilizers always passivate nano-particle surface, isolate metal particles from desirable metal–support interaction or/and affect the crystallographic matching between metal and support for stable adhesion.[3] Their removal (*i.e.* calcinations, vaporization, solvent extraction) could induce particle agglomerization[4] and phase segregation[5] in the case of alloy particles. Reports have therefore been found using inorganic stabilisers such as phosphonium chloride[6] or bulk sol–gel oxide matrices[7] to replace the organic appendages; however, such techniques are rather specialized with a large and broad distribution of monometallic particles.

Here, we present a novel but generic method for the synthesis of new precursors for *metal alloy catalyst* preparation by developing an inorganic stabiliser, the use of ultra-thin silica coating. Detailed descriptions of the new catalysts and uses will be presented.[8] Typically, Silica-gel@5%Pt and Silica-gel@5%(Ag–Pt) nano-composites were prepared as follows: 6.0743 g cetyltrimethylammonium bromide, CTAB (this surfactant concentration is well above the critical micelle concentration needed) was added to dry toluene (150 ml) under vigorous stirring. Then an aqueous solution of Pt precursor salt, $(NH_4)_2PtCl_4$, (0.0958 g in 4.347 ml DI water) was added dropwise to the suspension of CTAB in toluene and was stirred overnight to create aqueous reversed micelles. In the case of Ag–Pt, aqueous solutions of two metal precursors, $(NH_4)_2PtCl_4$ and $AgNO_3$ were added separately. The Ag/Pt atomic ratio was set at 2 (0.0915 g $(NH_4)_2PtCl_4$ and 0.0827 g $AgNO_3$ in a total of 4.20 ml H_2O). 0.66 ml 5 M NaOH solution was added afterwards and stirred for 2 h and the reduction of the metal salts was accomplished, at ambient temperature, by dropwise addition of excess 98% hydrazine monohydrate (Aldrich) (0.5 ml). The pink coloured slurry was generally changed to black but with no precipitation observed. This clearly implied that the reduction process does not significantly interfere with the stability of the microemulsion. Finally, 6.9346 g of tetraethyl orthosilicate, TEOS, was added dropwise into the black slurry and the reaction mixture was allowed to age for 6 days at ambient conditions under a constant stirring. Formation of the silica-gel coating at the interface (water/toluene) of the micelle carrying the metal nano-particle was expected to achieve since the NaOH previously added, is known to catalyse hydrolysis/condensation of the TEOS (nucleophilic substitution) to form a sol–gel coating. The nano-composites were then centrifuged and filtered. It was noted that the filtrate was colourless indicating the composites were mostly retained in the residue. The residue was then washed with excess toluene followed by hot ethanol. In order to extract all the trapped surfactant molecules from the nano-composites the solid material was exhaustively washed in refluxing ethanol overnight. This procedures for centrifugation, washed and reflux with ethanol were then repeated. The final resulting nano-composites were found dispersed in the ethanol as *meta-stable* colloids despite the absence of organic surfactant molecules, see Fig. 1 (stable against precipitation for weeks). This indicates that the surface –OH on the silica sol–gel coating could stabilize the small particles against precipitation in the polar ethanol solution. Thermogravimetric analysis (TGA) was used to investigate the levels of organic moieties present in the centrifuged powder samples by recording their weight changes upon their temperature ramping in air. Comparing the Silica-gel@5%Pt samples before and after the surfactant extraction, the ethanol treatments showed less than 1% drop instead of a weight loss of ~22% (exothermic peak) at around 220–280 °C hence surfactant molecules were readily extracted despite the presence of the sol–gel coatings (akin to extraction of surfactant from MCM-41). It is particularly noted that sol–gel coating techniques[9] primarily on monometallic particles though have been explored, our ultra-thin porous silica overlayers could allow the effective removal of organic stabilisers while maintaining them in colloid state.

Our typical TEM micrographs (Fig. 2a) show the dense (dark) spherically shaped metallic clusters of uniform size (~4–5 nm) each of which are clearly found enclosed by an extremely thin (light) sol–gel porous silica-rich coating of *ca.* 2.50 nm. Fig. 2b shows a HR-TEM micrograph of the Ag–Pt core where a lattice spacing of 2.30 ± 0.02 Å is clearly visible. One key point is to determine whether the application of the silica-gel coating induces phase segregation of the alloy particles (expand the technique to prepare coated nano-alloys). A detailed EDX analysis of the Silica-gel@5%(Ag–Pt) sample has been performed using a nano-probe of a spot size of *ca.* 27.5 nm (<5 nano-composites) to map 5 areas randomly. The result
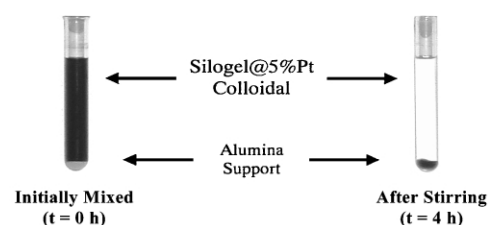

Fig. 1 Impregnation of nano-composites onto γ-alumina.

clearly shows the ~ 1:1%wt composition (2:1 Ag to Pt atomic ratio) with no evidence of any phase segregation (~ 5wt% metal alloy with the rest being the SiO_2). The porous nature as typical of sol–gel silica of the coated nano-composites is reflected from the large BET N_2 surface area obtained (193.85 m^{2}g^{-1}). The XRD analysis of the Silica-gel@5%(Ag–Pt) powder shows a very broad peak at 38.80° (2θ) with the d-spacing of 2.32 ± 0.01Å. This value perfectly matches with the fringe separation observed by HRTEM in Fig. 2b. However, this does not resemble the Pt (111) of 39.85° obtained over the Silica-gel@5%Pt or the Ag(111) of 38.10° but with a clearly good agreement with the reported $Ag_{0.67}Pt_{0.33}$ (111) alloy.[1] Lattice constants of our new silica gel encapsulated Pt and Ag–Pt alloy particles calculated from the {111} lattice spacings (all with F.C.C. structure) are depicted in Table 1 along with the reported values for bulk metals and for uncoated colloids prepared *via* a specific bimetallic complex route.[7] It is noted that the lattice constants of our silica coated Pt and the bimetallic Pt–Ag agreed within the error with the reported values of the corresponding pure Pt and $Ag_{0.67}Pt_{0.33}$. The lattice constant of our coated bimetallic nano-particles also agreed with the value calculated based on the assumption of Vegard's law *i.e.*, the additivity of lattice constants for bimetallic alloy. It should be noted that the lattice spacings of our silica coated mono-metallic and bime-tallic nano-particles (and also the uncoated colloids) are somewhat (*ca.* 1%) smaller than those of bulk metals. This is presumably due to lattice contractions with decreasing particle size as reported for Cu and Ni clusters by EXAFS measurements.[8] Based on the XRD analysis, the average particle size of the silica coated Pt (Silica-gel@5%Pt) and the coated $Ag_{0.67}Pt_{0.33}$ (Silica-gel@5%Ag–Pt) were determined to be 4.8 nm and 5.3 nm, respectively. An optical plasmon absorption peak at 330 nm† was observed over the coated alloy but not with the pure Pt.

The dispersion of the silica-coated nano-composites onto a high surface area activated-acidic-γ-alumina by mixing and drying them has been investigated. It was found that a maximum of 186 mg of nano-composites can be adsorbed on 1 g of activated-γ-alumina (BET N_2 surface area of 133.63 m^{2}g^{-1}). This value was derived from the change of the UV-vis spectra using excess Silica-gel@5%Pt colloidal solution (0.0013 g ml^{-1}). The uptake value is high (~ 20% wt%) though it is still below the theoretical monolayer coverage (assuming the close packing of composites on the surface). Fig. 1 shows clearly the change of black colloidal Silica-gel@5%Pt to a
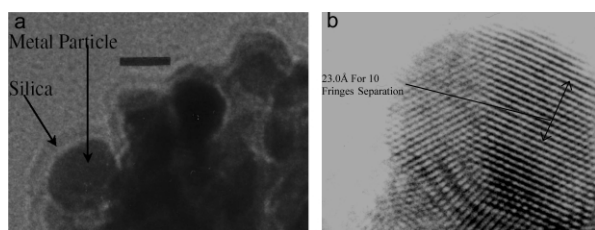
Thermal treatment, 1 h/K	Pt/SiO$_2$ (2%Pt)	Silica-gel@ Pt/Al$_2$O$_3$ (2% Pt)
573	1^b	1^c
873	0.459	0.905
1073	0.011	0.660
1123	0.005	0.661

^{a} 60 ml min^{-1} with 0.8 mol% toluene in H_2 over 10 mg catalyst (plug flow). ^{b} Rate of MCH production 42.2 mmol g-cat^{-1}h^{-1}. ^{c} Rate of MCH production 56.6 mmol g-cat^{-1}h^{-1}.

colourless solution and the white alumina to gray when excess alumina powder was used. FTIR spectra† show clearly the disappearance of Si–O(H) groups stretching bands at ~ 980 cm^{-1} associated with a progressive shift of the Si–O asymmetric stretching band to lower wavenumbers on increasing the alumina content. Since substitution of Al amongst the Si–O network is known to progressively attenuate the stretching wavenumber (due to Si–O(Al))[11] this observation clearly suggests the formation of Si–O–Al linkage from the dehydroxylation (gelation) reaction of the Si–OH and Al–OH leading to a firm anchoring of the nano-composites. Metal/alloy on silica commonly shows a higher hydrogenation activity[12] and resistance to poisons (*i.e.* sulfur) than on other supports. However, weak metal–silica interactions and the fragile nature of silica render practical difficulties of these catalysts. Typically, toluene hydrogenation (Table 2, methyl–cyclohexane, MCH was exclusively formed) over Pt metal using silica support (by incipient wetness) was compared with its silica encapsulation on γ-alumina at 373 K at steady state (5 h). The supported composite shows a higher activity than Pt/SiO$_2$ (2.6 nm) despite the larger metal size. This agrees with the observation that sol–gel catalysts with metal embedded in silica matrix showed stronger metal–support interaction giving a higher activity than impregnation catalysts due to the existence of M$^{\delta+}$ species.[13] Notice that the new supported catalyst shows a much higher thermal resistance with a larger retention of residue activity fraction. There was no apparent change in metal size (deactivation is attributed to some pore blockage due to dehydroxylation) but a severe metal sintering (> 50 nm metal particles) was observed over the Pt/SiO$_2$ by the TEM. Such a high thermal stability of thin SiO$_2$ protected metal catalysts on mechanically more stable γ-alumina rendering the new catalysts superior.

Fig. 2 (a) TEM micrograph showing the silica coated Pt nano-composites (scale bar = 5 nm); (b) A direct HRTEM imaging of the Ag–Pt core showing the Ag–Pt {111} spacing of 2.30 ± 0.02 Å.

Table 1 Lattice Constants, a, of Silica-gel@5%Pt and 5% Silica-gel@($Ag_{0.67}Pt_{0.33}$) from the XRD as compared to the literature values

Material	a/Å	Referenced data	a/Å
Silica-gel@5%Pt	3.91 ± 0.01	Bulk Pt[10]	3.92
		Colloid Pt[1]	3.91
n.d.	n.d.	Bulk Ag[10]	4.09
		Colloid Ag[1]	4.04
Silica-gel@5%(Ag–Pt)	4.02± 0.01	Bulk $Ag_{0.67}Pt_{0.33}$[1]	4.03
		Colloid $Ag_{0.67}Pt_{0.33}$[1]	4.00

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