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NHC-Based Submicroplatforms for Anchoring Transition Metals

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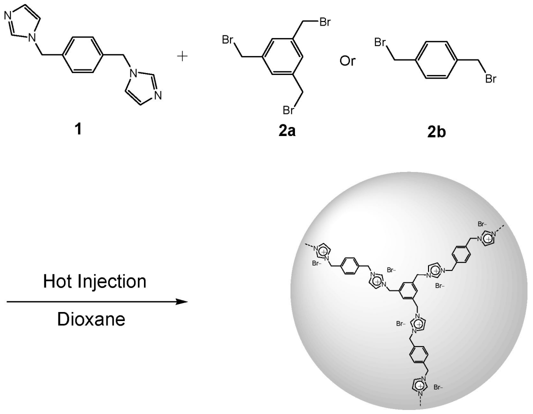
N-heterocyclic carbene (NHC) ligands have created new opportunities in organometallic chemistry.[1] Their coordination abilities to a variety of transition metals have stimulated the competitive synthesis of a number of novel organometallic compounds.[2] In particular, NHC ligands have made a significant impact in the area of transition metal catalysis.[3] As has been well-established, these ligands exhibit unique electron donor ability, as compared with the already well-developed phosphine ligands.[4] Recently, for industrial applications, the development of heterogeneous catalysts with NHC ligands has become a subject of increased interest and several heterogeneous catalytic systems based on insoluble/soluble polymer have been developed.[5]

In the past two decades, advances in nanotechnology have shown that size effects can result in the generation of new physically and chemically versatile properties. One major benefit of nanotechnology in heterogeneous catalysis may be an enhancement of catalytic activity, as a consequence of increased surface area.[6] Another such benefit involves an enhancement of dispersion ability in reaction media, as the result of the reduced size of heterogeneous solid supports. For example, carbon nanotube-based nanosupports showed superior efficiency in the catalytic hydrogenation of palladium metal because of superior dispersion of insoluble catalysts throughout the reaction media.[7]

Our research group and others have paid attention to the preparation of functional nanospheres using the predesigned building blocks for catalytic applications.[8] Recently, we presented the formation of spherical nanocatalysts through a hapticity change of organometallic building blocks.[8a] Ding group has shown the facile synthesis of asymmetric-heterogeneous catalysts via coordination of functional ligands to transition metals.[8b] Xu group presented the preparation of coordination polymer gels containing palladium, which evidenced the excellent catalytic activities in the oxidation of benzyl alcohol to benzaldehyde.[8c] In these examples, the functional units were formed concomitantly in the construction process of materials, which enable the synthetic strategies to be very efficient. In this work, we describe the preparation of new submicroplatforms for the potential development of NHC-based heterogeneous catalysts by anchoring the diverse transition-metal complexes.

Scheme 1. Synthesis of Submicroplatforms



As has been well-documented, the NHC coordination mode can be generated via the abstraction of protons from disubstituted imidazolium salts.[9] One of the simplest methods for the preparation of these salts involves the reaction of monosubstituted neutral imidazole derivatives with alkyl or aryl halides.[10] Scheme 1 depicts our synthetic approach to submicroplatform preparation.

We designed a precipitation-induced size control strategy. In order to induce the insoluble networks, we prepared diimidazole derivatives (**1**) and di- or tribromomethyl benzene building blocks (**2a**, **2b**). We postulated that the continuous connection of two building blocks would generate multicharged networks, which may have low solubility in relatively less polar solvents. This will induce precipitation, by which the sizes of the formed particles can be controlled. Using the connector **2a**, which has three arms, polymeric networks of enhanced density can be generated via cross-linking. Also, it is noteworthy that infinite networks can be formed with concomitant formation of the disubstituted imidazolium salts in materials. Compared to dendrimer-based materials,[11] the building blocks used are quite simpler. We expected that insoluble particles might be

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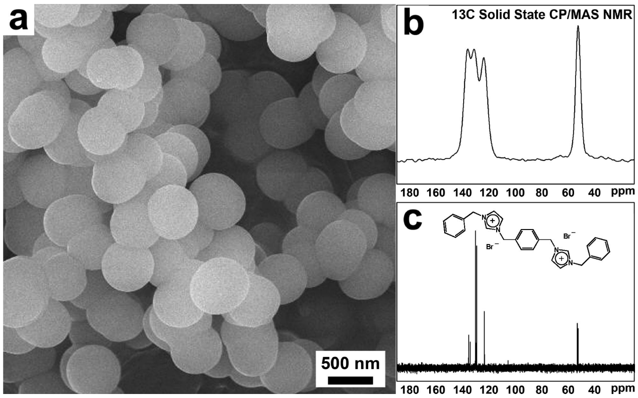


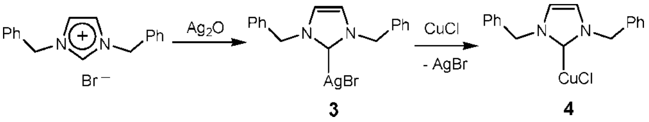
Figure 1. Typical SEM image (a) of the synthesized submicroplatforms; solid-phase $^{13}C-CP/MAS$ NMR spectrum (b) of the synthesized submicroplatforms, and normal ^{13}C NMR spectrum (c) of model compound.

utilized as functional nanosupports for anchoring diverse transtion metals.

In typical synthesis, **1** (0.21 mmol) and **2a** (0.14 mmol) were dissolved in 2 and 1 mL of 1,4-dioxane, respectively (**1**/**2a** = 3/2). Solution **1** was heated to 100 °C. Solution **2a** was injected rapidly into solution **1**, which resulted in the formation of white precipitates. After 1 h, the precipitates were collected via centrifugation, washed several times with 1,4-dioxane and dried under a vacuum. The white powder was analyzed with scanning emission microscopy (SEM). As the solvent volume increased, the size of submicrospheres was decreased. (see Figures S1 and S2 in the Supporting Information).When the dioxane volume was increased to 20 mL, spheres of the minimum size (580 nm) were generated. The use of 40 mL of dioxane exerted no significant influence on the resultant sphere size. Interestingly, when building block **2b** was used rather than **2a**, the formed powder in 1,4-dioxane evidenced relatively large size and amorphous morphology (see Figure S3 in the Supporting Information), which demonstrates the importance of cross-linking in the formation of spherical particles.

Figure 1a shows a representative SEM image of the 580 nm sized submicrospheres produced using 20 mL of dioxane (see Figure S2 in the Supporting Information for the size distribution diagram) To gain information regarding the inner structures of the spheres, we conducted a solid NMR experiment. For easy interpretation of ^{13}C NMR spectrum of submicrospheres, the model compound shown in Figure 1c was prepared by the reaction of **1** with benzyl bromide and fully characterized. In comparison with the ^{13}C NMR spectrum of the model compound, the spectrum of the submicrospheres in Figure 1b clearly confirms that the sphere was formed as the result of the connection of building blocks **1** and **2a**. Elementary analysis results revealed that the measured compositions of carbon (48.0%) and nitrogen (10.8%) were quite close to the expected values (C, 50.4; N, 11.8%).[12] In an effort to remove the possible free N coordination site of the terminal neutral imidazole group, the spheres were dispersed in hexane, after which excess benzylbromide was added, followed by 6 h of refluxing.

Scheme 2. Model Transmetalation Reaction for Synthesis of NHC-Copper Compound



Recently, extensive studies have been done on NHC-based copper and palladium catalysis.[13] Thus, as a model reaction, the complexation of copper and palladium to submicrospheres was then performed by two well-established methods. First, the transmetalation technique (also referred to as the silver base method)[14] was utilized to incorporate copper(I). As has been well-known, silver oxide is one of the most common metal bases, which can be used as a metalation agent for the imidazolium salts. There were several reports on the synthesis of NHC-copper compounds via transmetalation between NHC-silver compounds and copper halides.[15] As shown in Scheme 2, the model transmetalation reaction was performed using the model compound, 1,3-dibenzylimidazolium salt. The mixture of 1,3-dibenzylimidazolium salt (0.20 g, 0.61 mmol) and silver oxide was heated for 12 h in methylene chloride. ^1H NMR spectrum of the resultant product (**1**) revealed the disappearance of one proton peak in imidazole ring, which implies the coordination of silver. The mixture of compound **3** and CuCl was then heated for 12 h in methylene chloride to form silver bromide and compound **4** (0.19 g, 0.54 mmol).

For complexation of copper to submicrospheres, silver bromide was initially introduced to NHC ligands via the reaction of submicrospheres with silver oxide in methylene chloride for 12 h (Figure 2)[14] After washing, the resultant submicrospheres were analyzed with an elemental mapping experiment, using energy-dispersive X-ray spectroscopy (EDS) of HR-TEM.

As shown in images a and b in Figure 2, the silver was detected homogeneously in the submicrospheres (NHC-Ag). As expected, the X-ray photoelectron spectroscopy (XPS) showed evidence of the existence of Ag(I).[16a] NHC-Ag submicrospheres were reacted with copper chloride for 12 h in methylene chloride or acetonitrile. As shown in images c and d in Figure 2, copper was detected homogeneously in the submicrospheres in HRTEM-EDS mapping experiment (NHC-Cu). The SEM-EDS mapping experiment revealed that homogeneous distribution of copper in a wide region of

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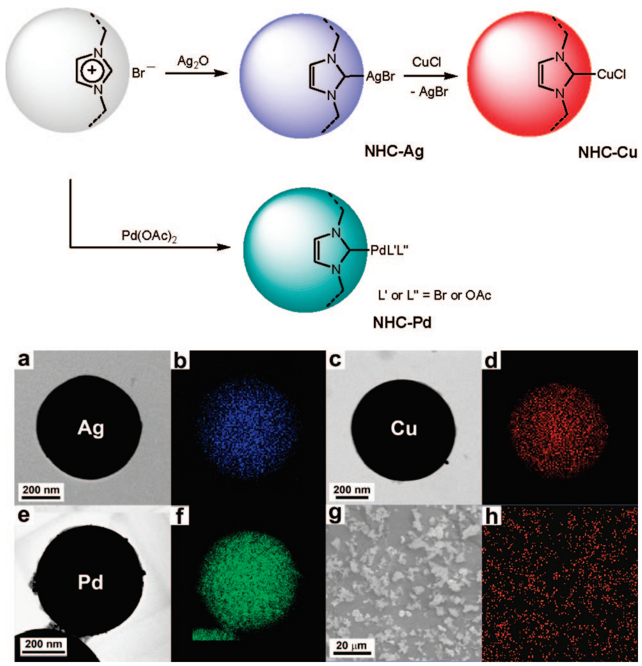

Figure 2. Complexation of submicrospheres with transition metals and typical TEM images and their elementary mapped images of NHC-Ag (a, b), NHC-Cu (c, d), and NHC-Pd (e, f); green, blue, and red colors reveal palladium, silver, and copper distributions, respectively; typical SEM image and its Cu-mapped image (g, h) of NHC-Cu.

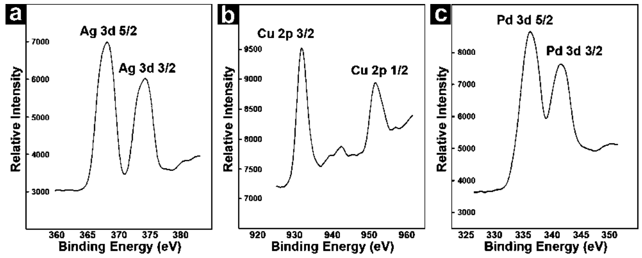

Figure 3. XPS spectra of Ag, Pd, and Cu in NHC-Ag (a), NHC-Cu (b) and NHC-Pd (c), respectively.

sample (images g and h in Figure 2). It should be noted that the samples prepared via direct complexation of copper chloride (without- use of silver) showed no detectable copper on submicrospheres in EDS. The XPS peaks at 932.1 and 952.0 eV of NHC-Cu corroborate the presence of Cu(I) species.[16b] (Figure 3b) Interestingly, the silver EDS mapping experiment of NHC-Cu gave some information about the transmetalation process (see Figure S4 in the Supporting Information). The EDS intensity of silver located close to surface became very weak. In contrast, that of core silver remains significantly. Additionally, several islands containing silver were found inside the sphere. These observations imply that the transmetalation occurred from the surface and the silver aggregates might be generated by replacement of coordinated silver bromide with copper chloride to form the islands (Figure S4 in the Supporting Information).

Second, it has been reported that certain metal sources can react directly with imidazolium salts to generate NHC−metal complexes through a concerted process of the deprotonation and subsequent metalation.[17] For example, $Pd(OAc)_2$ can be employed in the formation of NHC complexes without base in tetrahydrofuran, 1,4-dioxane, dimethylformamide, or dimethylsulfoxide.[17] The synthesis of NHC-Pd compound using 1,3-dibenzylimidazolium and palladium acetate was reported recently.[17] Thus, for preparation of submicrospheres containing Pd, the submicrospheres were treated with palladium acetate in THF, dioxane, or DMSO under heating. According to the EDS mapping experiment shown in images e and f in Figure 2 and the XPS spectrum[16c] in Figure 3c, we found that palladium was loaded successfully onto the submicroplatforms. (NHC-Pd) We believe that research into these submicroplatforms can be extended for the potential development of more diverse NHC-based heterogeneous catalysts.

In conclusion, NHC-based submicroplatforms were prepared and described in this work. The copper and palladium could be incorporated into submicrospheres by either transmetalation or direct complexation with the submicrospheres. Because of the nanosize effect, they are expected to evidence superior dispersion capability to the conventional solid supports.

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Supporting Information Available: Details of experimental procedures and additional SEM and TEM images (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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