Immobilized Metal Nanoparticles Containing Ionic Liquids on SBA-15: Preparation and Application in Catalysis

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Abstract:
Various metal Nanoparticles (AuNPs, PdNPs, CuNPs, and RuNPs) were prepared by the reduction of Immobilized metal ions containing ionic liquids on SBA-15 using NaBH\textsubscript{4}. The effects of different metal NPs with average sizes of 2-5 nm on the catalytic performance of \textit{p}-nitrophenol reduction and other organic reaction such as Suzuki-Miyaura coupling reaction, have been studied. In addition, PdNPs containing different alkyl-chain length ionic liquids on SBA15 were prepared in order to study its effects on the NPs size as well as catalytic performance. All materials before (MCl\textsubscript{me}-Im@SBA-15) and after reduction (MNP\textsubscript{me}-Im@SBA-15) were characterized by XRD, TEM, FTIR, XPS and EXAFS.

Keywords: Metal nanoparticles, SBA-15, Ionic liquid, \textit{p}-nitrophenol, coupling reaction.

1. Introduction
Metal nanoparticles have attracted tremendous attention as reflected by the large number of publications especially in the field of catalysis as heterogeneous catalysts. Most of the syntheses procedures of these metal nanoparticles are based on wet methods by using soluble metallic precursors loaded on solid supports. The use of stabilizing agents such as polymers, surfactants and ionic liquids are very efficient for controlling the particle size and morphology of NPs. The use of SBA-15 as a suitable solid support offers many advantages such as high surface area, large pore size, and uniform pore size distribution. In this study, we demonstrate the synthetic procedure of metal NPs on SBA-15 in the presence of immobilized ionic liquids using NaBH\textsubscript{4} as a reducing agent.

2. Experimental
Immobilized metal ion-containing ionic liquid, MCl\textsubscript{me}-Im@SBA-15 was prepared according to the procedure reported by our group\textsuperscript{1}, using 1-methyl-3-(3-trimethoxysilylpropyl)-imidazolium chloride or 1-butyl-3-(3-trimethoxysilylpropyl)-imidazolium chloride as ionic liquid, and metal chlorides (AuCl, PdCl\textsubscript{2}, CuCl\textsubscript{2} and RuCl\textsubscript{3}) as metal precursors. In a typical synthesis, SBA-15 was reacted with ionic liquids in dehydrated toluene by refluxing at 111 °C for 48 h under N\textsubscript{2} atmosphere. The dried solid then was reacted with metal chloride in acetonitrile at 82 °C for 24 h. the chemical reduction was performed using 10 ml of 100 mM NaBH\textsubscript{4} solution at fixed feed rate under N\textsubscript{2} flow at room temperature (20 °C). The fully dried resulting powder then was denoted as MNP(size)\textsubscript{me}-Im@SBA-15.

\[ \text{Scheme 1. Preparation steps for MNP\textsubscript{me}-Im@SBA-15.} \]
3. Results and discussion

The morphology and nanoparticle size distribution of all the synthesized materials were observed by TEM. The average size of metal NPs determined by TEM was found in the range of 2-4 nm. AuNPs with the average size of 2.0 nm were obtained at a fixed feed rate of 0.2 ml/min (AuNP(2.0 nm)_me-Im@SBA-15). Nanoparticles size of PdNPs containing different ionic liquids, 1-methyl-3-(3-trimethoxysilyl-propyl)-imidazolium chloride and 1-buthyl-3-(3-tri-methoxysilylpropyl)-imidazolium chloride, were found to be 2.4 nm and 3.4 nm respectively (PdNP(2.4 nm)_me-Im@SBA-15 and PdNP(3.4 nm)_me-Im@SBA-15). On the other hand, CuNPs with average size of 2.9 nm were obtained at 1.6 ml/min feed rate (CuNP(2.9 nm)_me-Im@SBA-15). The transformation of metal ions into metal and/or metal oxide NPs were confirmed from XPS spectra. Chloride anions were replaced by OH- as the counter anion of imidazolium cations surrounding metal NPs. FTIR analysis suggested that the bonding strength between ionic liquids and surface siliceous SBA-15 is very strong.

The catalytic performances of all prepared catalysts were expressed by its rate constant $k$ in the reduction of $p$-nitrophenol. The reaction was performed using NaBH$_4$ as the hydrogen donor with the molar ratio of $p$-nitrophenol:NaBH$_4$ in the mixture was fixed 1:50. The $k$ values for AuNP(2.0 nm), CuNP(2.9 nm), RuNPs, PdNP(2.4 nm) on me-Im@SBA-15, and PdNP(3.4 nm)_bu-Im@SBA-15 were 13.4 $\times 10^{-3}$ s$^{-1}$, 1.6 $\times 10^{-3}$ s$^{-1}$, 4.9 $\times 10^{-3}$ s$^{-1}$, 47.4 $\times 10^{-3}$ s$^{-1}$, and 15.7$\times 10^{-3}$ s$^{-1}$, respectively. These MNPs catalysts were reusable up to four consecutive recycle processes by very simple procedures. In addition, these catalysts are also being investigated for coupling reactions, such as Suzuki-Miyaura coupling reaction between aryl halides and phenylboronic acid. This ongoing work studies the catalytic activity of MNPs especially in aqueous media in the presence of base.

4. Conclusions

In summary, various metal nanoparticles (Au, Cu, Ru and Pd) were successfully synthesized from immobilized metal chloride containing ionic liquids on mesoporous SBA-15. All the prepared catalysts were active for $p$-nitrophenol reduction and reusable up to four recycle processes. The order of rate constants for fresh catalyst in the reduction of $p$-nitrophenol is Pdme > Pdbu > Au > Ru > Cu.

References