Synthesis of Phase Controlled Nickel Sulfide Nanostructures and their Catalytic Applications

（課程博士・様式７）（Doctoral qualification by coursework,Form 7）

学 位 論 文 要 旨

Abstract of Doctoral Thesis

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論文題目：
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論文要旨：
Abstract：

Wastewater pollution has always been a major problem throughout the world. The availability of suitable water used for drinking, agriculture, farming etc. has been decreased through the years. 4-nitrophenol is one of the artificially created pollutants through industries such as, leather, pharmaceutical, paint colorings. It is one of the hazardous and toxic pollutants, which is known to cause adverse health effects in living organisms. The decay time for these chemicals in air and water takes long time and it is easily soluble in water. Out of many methods, catalytic reduction is one of the easy way to reduce the 4-nitrophenol to environmental friendly 4-aminophenol.

In the growing trends of advanced nanostructured materials, nickel sulfide is one of the important materials in the metal sulfide family because of the variety in its phases and diversity in applications. It is an abundant and cheap material, therefore nickel sulfide is a good candidate for catalytic reduction application. There are several reports exist on synthesis of nickel sulfide nanostructures by controlling the concentration, pH, growth period, temperature and surfactants. However synthesis of well-defined growth processes and the parameters affecting its phase and morphology has never been investigated for the synthesis of nickel sulfide nanomaterials. Specifically, structural and morphological changes and its effects on catalytic applications has not been studied yet.

The objective of the thesis is to investigate (1) the role of source concentration on the formation of hierarchical nickel sulfide nanostructures by hydrothermal method, (2) the effect of organic ligand for the phase control by hydrothermal and temperature assisted hot injection method, (3) synthesis of phase dependent nickel sulfide by temperature controlled injection method, (4) the effect of addition of graphene on nickel sulfide phase formation and (5) the reaction rate and catalytic activity of 4-nitrophenol reduction with the synthesized nickel sulfide nanomaterials.

Monodispersed hierarchical architectures of nickel sulfide nanomaterials were

synthesized by hydrothermal method using ethylynediaminetetraaceticacid (EDTA) as a capping agent. The molar concentration of the source material such as nickel nitrate and thiourea was varied as 0.5, 0.75 and 1.0 M. The role of EDTA was investigated by varying its concentrations for the phase and morphological behavior. The number of phases was restricted for the interaction of EDTA with nickel source. Concentration of 1:2 nickel to sulfur ratio yielded a highly monodispersed hierarchical structures of Ni_3S_4 and $Ni_{17}S_{18}$ phases. To study the phase formation of hierarchical structures, whole precursor concentrations were varied by keeping the constant growth temperature and period. Catalytic reduction of 4-nitrophenol was carried out with the fabricated nickel sulfide nanostructures and good catalytic activity was achieved by the sheet composed and ball-like architecture of $Ni_{17}S_{18}$ and Ni_3S_4 phases.

Highly structure controlled nickel sulfide nanoparticles with an average size of less than 20 nm were prepared using oleylamine as a solvent by temperature assisted hot injection method. The complexity on the formation of single phase nickel sulfide was overcome by forming the sulfur-amine mixture for the controlled reaction. The effect of concentration ratio such as 1:1, 1:2, 3:4 and 3:2 was studied for the formation of highly uniform nanoparticles of NiS, NiS_2, Ni_3S_4 and Ni_7S_6 phases. The NiS phase exhibited high reaction rate as 8.95×10^{-3} s^{-1} for the reduction of 4-nitrophenol to 4-aminophenol. The stability of the NiS phase was investigated and there was no phase change observed even after its catalytic reduction and the repeated reaction rate was well matched with the initial experiments.

Reduced graphene oxide (rGO) functionalized nickel sulfide nanoparticles with uniform phase control were prepared using mixed solvent such as, oleylamine, octadecine, oleic acid by hot injection method. The reduction of graphene oxide was confirmed in the presence of oleylamine by XRD and TEM analysis. Single solvent as oleylamine experiments for rGO/nickel sulfide hybrid structures had less control on nickel sulfide phases. The excess of sulfur source concentration was required to achieve a single phase nickel sulfide nanoparticles on rGO supports. The multi solvents experiments resulted the better phase control of nickel sulfide on rGO sheets over the single solvent method. The particle dispersion on rGO nanosheets was uniform with the sizes less than 20 nm for all the nickel sulfide phases. The higher surface of rGO/nickel sulfide hybrid was utilized for the catalytic reaction because of its higher adsorption sites, which increases the contact between the 4-nitrophenol and nickel sulfide. The catalytic activity was enhanced for the rGO/NiS phase with the best reaction rate of 16.3×10^{-3} s^{-1}.

The above results clearly confirmed that source concentration and capping agent played an important role on the formation of phase controlled nickel sulfide nanostructures. NiS and rGO/NiS had enhanced catalytic activity. The phase dependent catalytic activity of nickel sulfide was investigated for the first time.