Abstract

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Title: Hydrogen Generation from Hydrous Hydrazine Decomposition over Solution Combustion Synthesized Nickel-based Catalysts
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Hydrous hydrazine ($N_2H_4 \cdot H_2O$) is a promising hydrogen carrier for convenient storage and transportation owing to its high hydrogen content (8.0 wt%), low material cost and stable liquid state at ambient temperature. Particularly, generation of only nitrogen as byproduct, in addition to hydrogen, thus obviating the need for on-board collection system for recycling, ability to generate hydrogen at moderate temperatures (20-80 °C) which correspond to the operating temperature of a proton exchange membrane fuel cell (PEMFC), and easy recharging using current infrastructure of liquid fuels make hydrous hydrazine a promising hydrogen source for fuel cell electric vehicles (FCEVs). Since hydrogen can be generated from catalytic hydrazine decomposition, the development of active, selective and cost-effective catalysts, which enhance the complete decomposition ($N_2H_4 \rightarrow N_2+2H_2$) and simultaneously suppress the incomplete decomposition ($3N_2H_4 \rightarrow 4NH_3+N_2$), remains a significant challenge.

In this dissertation, CeO_2 powders and various Ni-based catalysts for hydrous hydrazine decomposition were prepared using solution combustion synthesis (SCS) technique and investigated. SCS is a widely employed technique to synthesize nanoscale materials such as oxides, metals, alloys and sulfides, owing to its simplicity, low cost of precursors, energy- and time-efficiency. In addition, product properties can be effectively tailored by adjusting various synthesis parameters which affect the combustion process.

The first and second parts of this work (Chapters 2 and 3) are devoted to investigating the correlation between the synthesis parameters, combustion characteristics and properties of the resulting powder. A series of CeO_2, which is a widely used material for various catalytic applications and a promising catalyst support for hydrous hydrazine decomposition, and Ni/CeO_2 nanopowders as model catalysts for the target reaction were synthesized using conventional SCS technique. This demonstrated that crystallite size, surface property and concentration of defects in CeO_2 structure which strongly influence the catalytic performance, can be effectively controlled by varying the synthesis parameters such as metal precursor (oxidizer) type, reducing agent (fuel), fuel-to-oxidizer ratio and amount of gas generating agent. The tailored CeO_2 powder exhibited small CeO_2 crystallite size (7.9 nm) and high surface area (88 m^2/g), which is the highest value among all prior reported SCS-derived CeO_2 powders. The Ni/CeO_2 catalysts synthesized with 6 wt% Ni loading, hydrous hydrazine fuel and fuel-to-oxidizer ratio of 2 showed 100% selectivity for hydrogen generation and the highest activity (34.0 h^{-1} at 50 ºC) among all prior reported catalysts containing Ni alone for hydrous hydrazine decomposition. This superior performance of

the Ni/CeO_2 catalyst is attributed to small Ni particle size, large pore size and moderate defect concentration.

As the next step, SCS technique was used to develop more efficient and cost-effective catalysts for hydrous hydrazine decomposition. In the third part (Chapter 4), noble-metal-free $NiCu/CeO_2$ catalysts were synthesized and investigated. The characterization results indicated that the addition of Cu to Ni/CeO_2 exhibits a synergistic effect to generate significant amounts of defects in the CeO_2 structure which promotes catalytic activity. The 13 wt% $Ni_{0.5}Cu_{0.5}/CeO_2$ catalysts showed 100% H_2 selectivity and 5.4-fold higher activity (112 h^{-1} at 50 ºC) as compared to the 13 wt% Ni/CeO_2 (20.7 h^{-1}). This performance is also superior to that of most reported non-noble metal catalysts and is even comparable to several noble metal-based catalysts. In the fourth part (Chapter 5), low Pt loading $NiPt/CeO_2$ catalysts were studied. The modified SCS technique was developed and applied to prepare $NiPt/CeO_2$ catalysts, that overcomes the typical problem of conventional SCS which leads to deficiency of Pt at catalyst surface due to the diffusion of Pt into bulk CeO_2. The $Ni_{0.6}Pt_{0.4}/CeO_2$ catalysts with 1 wt% Pt loading exhibited high activity (1017 h^{-1} at 50 ºC) along with 100% H_2 selectivity owing to the optimum composition of NiPt alloy, high metal dispersion and a large amount of CeO_2 defects. Its activity is higher than most of the reported NiPt-based catalysts which typically contain high Pt loading (3.6-42 wt%).

Next, the intrinsic kinetics of hydrous hydrazine decomposition over the $NiPt/CeO_2$ catalysts, which are necessary for efficient design and optimization of the hydrous hydrazine-based hydrogen generator system, were investigated (Chapter 6). From the experimental data obtained at different reaction temperatures, the intrinsic kinetic model based on the Langmuir-Hinshelwood mechanism was established. The developed model provides good predictions with the experimental data, especially over a wide range of initial reactant concentration, describing well the variation of reaction order from low to high reactant concentration.

Finally, the conclusions of the dissertation and recommendations for future work are summarized in Chapter 7.