Synopsis of the thesis entitled, “Synthesis of metal and metal oxide nanosponges for hydrogen storage and catalytic applications”, submitted by Sourav Ghosh (S. R. No. 9210-310-091-06492) under the supervision of Prof. Balaji R. Jagirdar, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, for the PhD degree in the Faculty of Science

Nanoporous metal represents a particular form of a metal, which combines the characteristics of metals, such as good thermal and electrical conductivity, catalytic activity with the materials properties characteristic of nanoporosity, which include high surface area, low density, large number of pores, etc. Nanoporous metals have applications in various fields such as catalysis, hydrogen storage, electrochemical sensing, membranes, SERS, and supercapacitors. The three dimensional porous structures offer high specific surface area and large pore volumes, which enhance substrate diffusion within the porous structures and provide a large number of surface active sites for catalytic applications. However, synthesis of nanoporous metal based on conventional approach (template assisted synthesis and dealloying) suffers from scalability issue, specific for few metals, additional synthetic steps etc. Challenges still remain in this field to fabricate three dimensional porous metals where pores are interconnected (bicontinuous). Recently, development of the synthesis of nanoporous metal got a thrust by the advent of the concept of assembly of nanoparticles in either an ex-situ or in an in-situ manner.

Objectives

1. Establish the synthetic strategy of metal nanosponge formation by capping agent dissolution method (ex-situ assembly)
2. Explore the catalytic activity of these metal nanosponges towards 4-nitrophenol reduction and alkene hydrogenation reactions
3. Elucidate the mechanism of formation of metal nanosponge in solution state (kinetic in-situ assembly of nanoparticles) using ammonia borane as a reducing agent in water under different conditions
4. Investigate the hydrogen storage properties and catalytic arene hydrogenation activities of metal nanosponges
5. Synthesis of bismuth oxide nanosponge using bismuth nanosponge as a template. Study of the photocatalytic dye degradation behavior using bismuth oxide nanosponge under visible light irradiation

**Significant results**

Synthesis of metal nanosponges was carried out using capping agent dissolution method wherein addition of water to M@BNH\(_x\) polymer gives metal nanosponges. The B-H bond of BNH\(_x\) polymer is unstable in the presence of water and gets hydrolyzed to give hydrogen gas bubbles which act as dynamic templates for the formation of metal nanosponges. The pristine nature of the surface of these metal nanosponges was elucidated by several analytical techniques. The catalytic activity of these metal nanosponges (Ag, Au, Pd, Pt, and Cu) was demonstrated using 4-nitrophenol reduction reaction in the presence of sodium borohydride as a reducing agent.

Iridium nanosponge was obtained by capping agent dissolution method from Ir@BNH\(_x\) polymer. Mesoporous high surface area iridium nanosponge was found to be an active catalyst for alkene hydrogenation reaction, whereas Ir@BNH\(_x\) polymer does not exhibit any catalytic activity under similar reaction conditions. The effects of temperature, solvent, substrate to catalyst ratio, and pressure on catalyst activity were established using styrene as a substrate. The thermal stability (up to 300 °C) and robustness over several cycles were demonstrated for the iridium nanosponge. Several alkenes (linear alkene, cycloalkane, and conjugated alkene) were successfully hydrogenated using iridium nanosponge at room temperature and 4 bar hydrogen pressure. Generality of the synthetic procedure was explored by using different iridium precursors which gave iridium nanosponges exhibiting similar catalytic activity.

Silver, gold, palladium, platinum, and copper nanosponges have been synthesized by chemical reduction method (*in-situ* kinetic assembly of nanoparticles) using ammonia borane as a reducing agent in water as a solvent. The effect of variables (metal salt to amine borane ratio, concentration of the reactants, solvent, temperature, and reducing agent) were thoroughly investigated using the silver system as a model. In the absence of a capping agent, metal salt reduction was carried out using amine borane which forms nanoparticles. In a high dielectric solvent, the colloidal particles attach together to form agglomerates. During the course of the reaction, hydrogen gas bubbles were generated which produce pores within the
agglomerates leading to the formation of three dimensional nanosponge structures. Finally, the hydrogen storage properties (pressure composition isotherm and sorption kinetics) of these metal nanosponges were investigated under different conditions. These metal nanosponges exhibit reasonable, reversible storage characteristics: Ag (3 wt%), Pd (5.5 wt%), Pt (6 wt%), and Cu (2.5 wt%).

Phase selective ruthenium nanospone was synthesized using chemical reduction method. It was found that amine borane as a reducing agent for certain ruthenium precursors results in the hcp phase of ruthenium whereas, reduction using sodium borohydride affords fcc phase of ruthenium. Hcp and fcc phases of ruthenium were established using electron and X-ray diffraction methods. Surface characterization technique showed the pristine nature of ruthenium nanospone. Both hcp and fcc ruthenium nanosponges were employed as catalysts for hydrogenation of benzene; it was found that hcp ruthenium is more active than fcc ruthenium for benzene hydrogenation to cyclohexane. Substrate to catalyst ratio, temperature, hydrogen pressure, and solvent effect were thoroughly investigated using benzene as a model substrate. It was found that hcp ruthenium nanospone is capable of hydrogenating a variety of alkyl substituted benzenes under ambient conditions. The catalyst was found to be active over several cycles without any loss in its activity. Phosphine was used as a catalyst poison and hot filtration test was performed separately to show the true heterogeneous nature of the active catalyst. Hydrogen storage experiments were performed to understand the interaction of hydrogen with different phases of ruthenium.

Bismuth nanospone was synthesized using chemical reduction method. Synthesis of different polymorphs of bismuth oxide nanosponges (tetragonal, monoclinic and body centered cubic) were carried out by calcination of bismuth nanospone at different temperature (300 °C, 500 °C, and 800 °C). The phase purity of bismuth oxide nanosponges were established using X-ray and electron diffraction method. It was found that surface area decreases with increasing the calcination temperature. Tetragonal bismuth oxide (300 °C annealed sample) nanospone shows the highest photocatalytic activity as compared to other polymorphs. Mechanistic investigation suggests that hole and hydroxyl radical are responsible for dye degradation. Recyclability study demonstrated the formation of bismuth oxycarbonate
which leads to a drop in catalytic activity. However, the tetragonal phase of bismuth oxide with high catalytic activity could be regenerated upon annealing at 300 °C for 3 h.