PREFACE

Human beings have been using fossil fuels for meeting their energy needs since long. Reducing availability of these non-renewable energy sources due to increasing consumption and resultant adverse effects on the environment has led the researchers across the world to focus on renewable and cleaner energy alternatives. Hydrogen is one such promising option which can serve as a renewable and cleaner alternative to conventional fossil fuels. Water-gas shift (WGS) reaction is currently widely employed to produce hydrogen from fossil carbonaceous as well as renewable biomass feed-stocks. WGS reaction involves reaction between CO and water (steam) over a suitable catalyst to enrich the gaseous mixture with H_2 and convert CO to CO_2 that can be easily removed from hydrogen. Traditionally, iron-chromium (Fe-Cr) and copper-zinc (Cu-Zn) catalysts have been used to facilitate the reaction at high and low temperatures, respectively. But over the years, WGS reaction catalyst technology has advanced dramatically and the catalysts has been suitably modified to assist the reaction even in the medium temperature range and achieve higher CO conversion. Most of the current research is focused on ceria (CeO_2) based WGS catalysts because of their unique favorable properties. Furthermore, there have been an ever-increasing number of recent studies which deal with fabricating nano-structured catalysts for WGS reaction because of the advantages offered by nano-materials over their conventional bulk counter parts.

In present study composite CuO/CeO_2nanofibers containing 10, 20, 30, 40, 50 and 60 mol. % Cu as well as pure ceria were successfully prepared using sol-gel and electro-spinning technique from solutions containing polyvinylpyrrolidone (PVP), cerium nitrate hexahydrateand copper acetate monohydrate. The electrospinning was carried out at 12kV DC by maintaining the tip to collector distance as 10 cm. The green nanofibers thus obtained were calcined at 500°C for three hours. The morphology of the synthesized nanofibers (both green and calcined) was determined by SEM analysis and their elemental composition was verified using XPS, EDX spectroscopyand other characterization for functional groups (FTIR), thermal stability (TGA). The average diameter of the green composite fibers was found to be in the range of 98-130 nm, while that of the calcined ones was in the range of 78-98 nm. The crystal structure of nanofibers was determined by X-ray diffraction (XRD) which showed the peaks of CeO_2 appearing at 2   of 28.83° and those for CuO at 47.45°. The average crystallite size of CeO_2 and CuO/CeO_2, calculated by Debye-Scherer formula, were found to be 14nm for CeO_2 and 9-12nm for CuO/CeO_2 composites of different copper loadings. The activity of the catalysts was tested for WGS reaction in a fixed-bed continuous flow reactor in medium temperature condition (150-400°C). The reactant gas, 2.5 vol. % of CO and 50.0 vol. % of H_2O (N_2 balance), was fed into the glass reactor. The total flow rate was 60ml/min and 50 mg of the catalyst was taken. The effluents were analyzed for CO and CO_2 contents by on-line gas chromatography (NUCON-5765).The catalytic activity of all nanofibers were evaluated for the water gas shift reaction in the temperature range of 150-400°C. A comparative study of the catalytic activity of CeO_2 and composite CuO/CeO_2 nanofibers was carried out. By changing the concentration of copper from zero to 50% the CO conversion increased from 68 to 78% at the temperature 295^{0}C. But with 60% copper it decreased to 76.5% at the 295^{0}C. Thus it was seen that the equimolar copper-ceria nanofiber (50% Cu) exhibited the best catalytic activity giving the maximum CO conversion of 78% at 295^{0}C, whereas the pure ceria nanofiber gave the lowest CO conversion of 68% at the same temperature. Hydrogen yield and selectivity were maximum at 50% Cu content: 44% and 99%, respectively and stability also give maximum at 50% Cu content.

The results obtained are discussed and presented in this thesis. The subject matter contained in the thesis has been arranged in six different chapters including references.

General introduction about the energy scenario; sources and methods of hydrogen production such as steam reforming of alcohol, methane, auto thermal reformingand application water gas shift reaction and its industrial uses are given in **Chapter 1.**

Chapter 2 presents a critical review of the available literature on the water gas shift reaction and provides a detailed description of the process along with a comprehensive and critical assessment of the efficacy of various catalysts that have been traditionally used to facilitate the reaction. Furthermore, it also gives an idea about how the WGS catalysts have evolved in terms of their structure and performance over the years and provides a futuristic picture of the research required in this area.

Experimental details the synthesis and characterization of nanocomposite fibers and suitable for use as catalyst are incorporated in **Chapter 3**. Details of the procedures usedfor preparation, characterization and use of copper oxide/cerium oxide (CuO/CeO_2) nanofibers as catalyst are also elaborated.

Chapter 4 presents and discusses the results of experiments on the characterization of various catalysts in terms their morphology, chemical composition, surface area, structure, thermal stability and catalytic activity. Details of the results of characterization and catalytic activity of all prepared catalyst are presented and discussed in various sections of this chapter.

Chapter 5 summarizes the important conclusions of the present study and also makes some useful recommendations for further work in this area.