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FABRICATION OF COPPER-CERIA NANOFIBER BY ELECTROSPINNING TECHNIQUE FOR APPLICATION IN WATER GAS SHIFT REACTION

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ABSTRACT

CeO_2 and 10 mol. % Cu/CeO_2 composite nanofibers were prepared by Electrospinning method. Copper acetate monohydrate and cerium nitrate hexahydrate were used as the inorganic precursors and the electrospinning was carried out at 12kV DC by maintaining tip to collector distance of 10 cm. The synthesized nanofibers were characterized by SEM analysis and the average diameters of pure ceria and 10 mol. % Cu/CeO_2 nanofibers were found to be 130 nm and 124 nm (both before calcination), respectively. After calcination for 3 hours, the fiber diameters were reduced by around 20-40% due to the removal of organic compounds present in the nanofiber mats. The crystal structure of the nanofibers was determined by X-ray diffraction (XRD), and the average crystalline sizes of CeO_2 and 10 mol. % Cu/CeO_2 were calculated to be 13 nm and 10 nm, respectively. The WGSR was carried out in the temperature range of 150-400°C; pure CeO_2 and 10 mol. % Cu/CeO_2 nanofibers exhibited CO conversion efficiencies of around 57% and 59%, respectively.

Keywords: Ceria, Electrospinning Hydrogen, Nanofibers, Water Gas Shift Reaction.

I. INTRODUCTION

Hydrogen has attracted the attention of researchers worldwide due to its applicability as a clean fuel source. Hydrogen fuel burns cleanly and gives water as the only by-product. Moreover, it can be stored and transported easily [1]. Hence, it can be effectively utilized to minimize the evolution of various harmful gases. Hydrogen can be produced by steam reforming of methane and by gasification of coals, heavy oils and petroleum coke [2]. However, steam reforming is the most widely method at present [3]. This method involves reacting methane and steam to produce H_2 and CO. The undesirable CO can be removed by implementing another crucial technique known as the Water Gas Shift Reaction (WGSR). The reaction is favoured thermodynamically at lower temperatures and kinetically at higher temperatures, but is not affected by changes in pressure [4]. The reaction is facilitated by using suitable catalysts having the desirable properties. There are certain common characteristics of catalysts used for Water Gas Shift Reaction such as available oxygen vacancies, activity for the dissociation of water, and low CO adsorption strength [5].

Presently, ceria-based Water Gas Shift (WGS) catalysts are being extensively investigated because of their elevated oxygen transport capacity and the ability to easily switch between reduced and oxidized states [6].

Synthesizing ceria-based catalysts in the form of one-dimensional nanomaterials has the capacity to produce even more enhanced WGS catalysts. Nanofibers of ceria-based WGS catalysts may be fabricated by using Electrospinning technique [7-11]. Electrospinning is a low cost and simple technique to produce nanofibers in an efficient fashion [12-14]. In this technique, the spinning parameters and calcination conditions determine the formation of one-dimensional structures [15-17].

The aim of the present work is to study the synthesis of pure ceria (CeO_2) and Cu /CeO_2 composite nanofibers having 10 mol. % Cu (copper-ceria basis) by the electrospinning technique for possible use as catalysts in the Water Gas Shift Reaction. Pure ceria and Cu/CeO_2 composite nanofibers were synthesized by using Cerium nitrate hexahydrate and Copper acetate monohydrate as inorganic precursors.

II. EXPERIMENTAL

2.1. Preparation of the spinning solution

Cerium nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$) and cupric acetate monohydrate ($Cu(CH_3COO)_2.H_2O$) precursors were used as received. Polyvinyl pyrrolidone (PVP) was used as the guiding polymer. Ethanol and de-ionized water were selected as the solvent and co-solvent, respectively. Glacial acetic acid was employed as the reducing agent.

Two different solutions were prepared - pure ceria and 10 mol. % Cu. For a typical synthesis, 12 mL of spinning solution was prepared. Ethanol and de-ionized water were taken in different vials in a 2:1 ratio. The 10% w/v PVP was added to the vial containing ethanol and was magnetically stirred. Thereafter, 0.434 g of $Ce(NO_3)_3.6H_2O$ and 0.022 g (10 mol% Cu) of $Cu(CH_3COO)_2.H_2O$ were added to the vial containing water. The contents of both the vials were mixed together and acetic acid was added drop-wise (2-3 drops) to the final solution. The mixed solution was then magnetically stirred for 3 hours at room temperature to form a homogeneous solution. For preparing casting solution for pure ceria nanofibers, above procedure was followed but no $Cu(CH_3COO)_2.H_2O$ was added.

2.2 Preparation of electrospun nanofiber

The electrospinning setup consists of a high voltage power supply, syringe pump, metallic needle and a conductive collector plate. The details of the set have been described elsewhere [9]. The precursor solution was filled in a 6 ml plastic syringe equipped with a stainless steel flat-tip needle (21 gauge). The syringe arrangement was configured vertically and attached to a syringe pump. The flow rate from the syringe was set at 1 ml/hr. The metallic collector plate was covered with aluminium foil and kept directly under the needle tip to collect the nanofibers. The distance between the syringe tip and the collector plate was maintained at 10 cm. An AC-to-DC converter was used to generate a high DC voltage of about 12 kV between the needle tip and the collector. The experiment was carried out in air and at room temperature. Proper care was taken to avoid the formation of droplets at the needle tip and their fall from it on to the collector plate. The needle tip was cleaned from time to time to prevent clogging. The electrospun nanofibers were finally collected and calcined in air at 500^0C for 3 hours to obtain Cu/CeO_2 nanofibers, cooled and subjected to morphological characterization.

2.3 Catalytic reaction

The experimental setup consisted of four sections: feeding, reactor, product cooling and separation unit. The carbon monoxide and nitrogen are fed from cylinders using flow measuring device; mercury safety device and water vapour generating sparger. Reaction system is consisted of a compact bench scale tubular reactor, a tubular furnace and a micro processor based temperature controller. The products are sent to the cooling section and ultimately to gas liquid separating systems.

The reactor was a quartz tube reactor in which 50 mg of the catalyst was packed over the glass wool. The reaction experiments were carried out at atmospheric pressure and in the temperature range of 150-360^{0}C. A J-type thermocouple was inserted into the centre of the catalyst bed to monitor the reaction temperature. The feed was consisted of a mixture of 1.5 ml/min. of CO and 58.5 N_2 ml/min. The mixed gas was divided into two parts primary and secondary. The secondary part of the gas mixture was bubbled through a fine epidermis needle in water sparser burette to generate and feed water vapour at a controlled rate of 0.15 mL/h (as liquid). The primary gas and the secondary gas with water vapour mixed before entering into the reactor. To maintain the constant rate of water evaporation, the level of water in the sparser burette was maintained by filling it after vaporization of 1mL of liquid water. The catalyst bed temperature was maintained at desired temperature with the help of a microprocessor temperature controller. The temperature was varied from 150 to 400^{o}C and the reactor effluent was analyzed by an on-line gas chromatograph (NUCON-5765).

The flow rates of nitrogen and CO was measured with the help of digital flow meters. Nitrogen and CO were fed from compressed gas cylinders. The reactants mixture (CO, N_2, water vapour) were sent to the reactor where reaction was take place. A thermocouple was used to measure the temperature of catalyst bed. The reaction products from the bottom of the reactor were sent to a condenser and gas-liquid separating assembly kept in an ice-bath to remove water from the mixture before gas-chromatographic analysis. The gaseous products from the separator were sent for analysis by an online Gas Chromatograph. A porapack Q column, methanizer and FID were used to analyze CO and CO_2. H_2 was analyzed using molecular sieve column and TCD. For complete analysis of CO, CO_2 and H_2 each experiment was performed twice under the same operating conditions due the availability of single gas chromatograph.

III. RESULTS AND DISCUSSION

3.1. Scanning Electron Microscopy Analysis (SEM)

The morphologies of the electrospun nanofibers were analyzed with the help of a scanning electron microscope. The SEM analysis confirmed the formation of cylindrical nanofibers of varying diameters. Fig.1 shows the images of pure ceria electrospun nanofibers (a) before and (b) after calcination. Fig.2 shows the images of 10 mol. %Cu/CeO_2 electrospun nanofibers (a) before and (b) after calcination. Pure ceria nanofibers had an average diameter of about 130 nm (Fig.1a), whereas the average diameter of the nanofibers containing 10 mol. % Cu was found to be approximately 124 nm (Fig.2a). After calcination, the average diameters got reduced to about 20-40 % of the initial values. Post calcination, the diameter of the 10 mol. % Cu/CeO_2 nanofibers was found to be 87 nm (Fig.2b). The diameter of pure ceria nanofibers was reduced to 98 nm (Fig.1b). The reduction in diameter takes place due to the loss of PVP and other organic compounds during calcination.

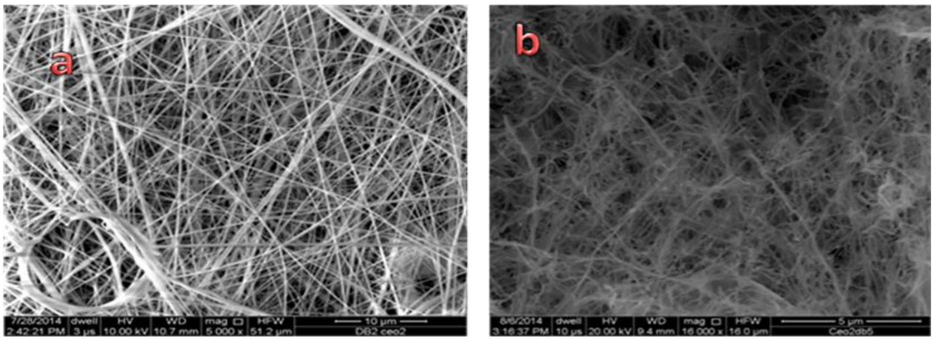

Fig. 1. SEM images of pure ceria electrospun nanofibers (a) before calcination and (b) after calcination.

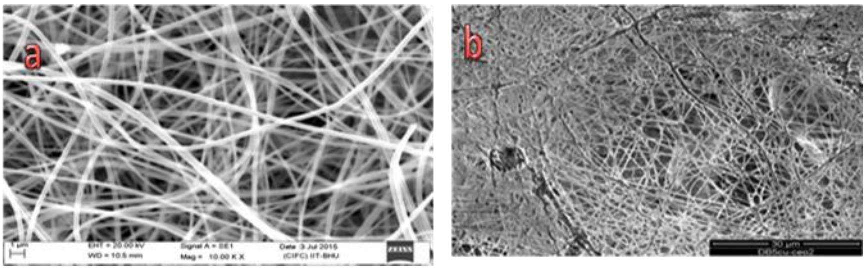

Fig. 2. SEM images of 10 mol. % Cu/CeO_2 electrospun nanofibers (a) before calcination and (b) after calcination.

3.2 Energy Dispersive X-Ray Spectroscopy (EDX) Analysis

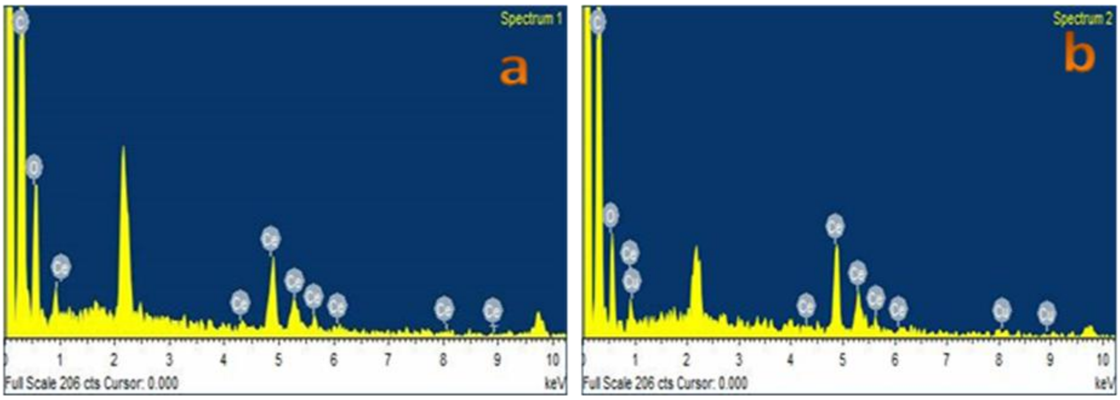

Fig. 3. EDX of nanofibers containing a) pure $CeO_2$and b)10 mol. % Cu/CeO_2

The atomic compositions of the synthesized nanofibers were estimated using an Energy Dispersive X-Ray Spectroscopy system (EDX; X-ACT 51-ADD0048, OXFORD INSTRUMENTS). **Fig. 3a** and **b** show the EDAX finger-print of the synthesized nanofibers (pure CeO_2 and 10 mol % Cu/CeO_2, respectively) prior to calcinations. **Fig. 3a and b** gives an overall atomic composition of nanofibers prepared with 0 and 10% Cu. From Fig. 3a it is seen that the synthesized nanofibers do not contain any copper. Similarly, from Fig. 3b it is seen that atomic composition of Cu and Ce is 0.24% Cu and 1.63% Ce, which translates into a copper-cerium (Cu/[Cu + Ce]) mole fraction ratio of roughly 0.128 (~ 0.1). These results confirm uniform distribution of Cu in casting solutions.

3.3 X-Ray Diffraction Analysis

XRD data was recorded by 18KW rotating anode based powder diffractometer (Rigaku, Japan) fitted with a curved crystal monochromatic in the diffracted beam operating at 40KV and 150MA. Powder XRD data were collected in the two-theta range 20-80^0 at a scan rate of 2 degree/minute and scan step of 0.02 degree. The diffraction patterns have been indexed by comparison with the JCPDS files. The XRD patterns of the CeO_2 and 10 mol. % Cu/CeO_2 nanofibers are presented in Fig.4. The graph exhibits characteristic peaks of a fluorite-like cubic phase. The most intense reflections of CeO_2 at 2θ values of 46.83° are clearly visible and average crystalline size of CeO_2 (13 nm) and 10 mol. % Cu/CeO_2 (10 nm) were calculated by Debye Scherer formula.

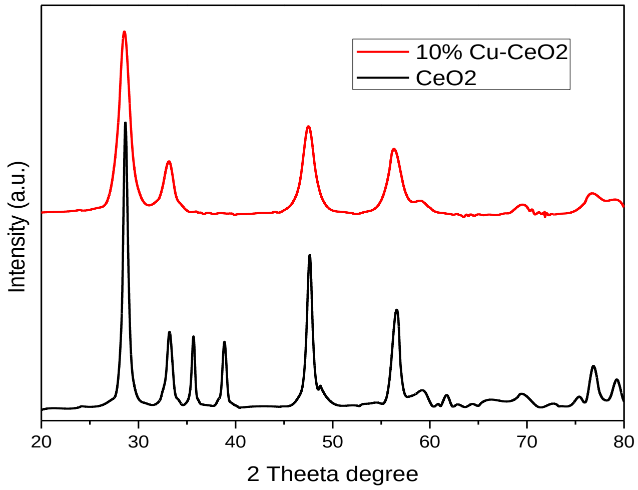

Fig.4. XRD of CeO_2 & 10 mol. % Cu/CeO_2 nanofiber calcined at 500°C, 3hrs.

3.4 Fourier Transforms Infrared Spectroscopy

The functional group analysis of the prepared nanofibers was carried out by a FTIR spectrometer. Nanofibers mixed in KBr pellets were scanned in the range 400-1400 cm^{-1} for 16 times and spectrum was recorded. The FTIR spectra of CeO_2 and 10 mol. % Cu/CeO_2 nanomaterials are presented in Fig. 5.

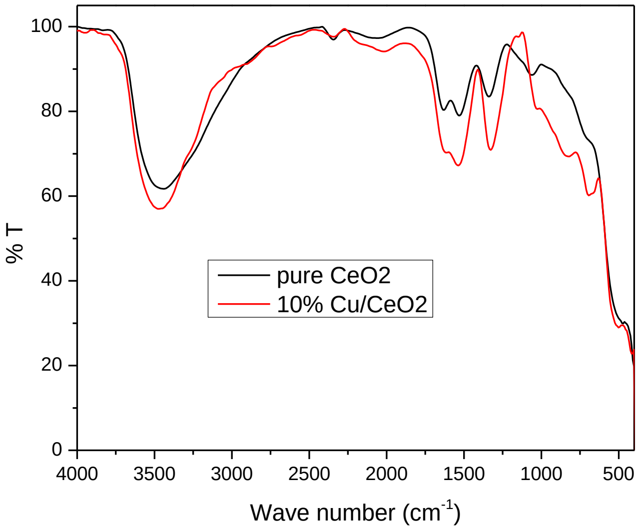

Fig.5. FTIR spectra of CeO_2 & 10 mol. % Cu/CeO_2 nanofiber calcined at 500°C, 3hrs.

The broad band (3700 to 3000 cm^{-1}) was present due to the stretching vibration of hydroxyl (OH) group of chemisorbed water. The disappearance of peak (900-1630 cm^{-1}) after calcination of CeO_2 at 500°C indicates removal of most of the organic materials present in the sample. The significant enhancements in the absorption band (500-1060 cm^{-1}) represent formation of CeO_2 nanofiber.

3.5 Activity of catalysts for water gas shift reaction

The water gas shift reaction runs in the temperature range of 150-360^{o}C. The catalysts used CeO_2 and Cu/CeO_2 nanofiber. The experimental procedure and product analysis are already discussed in experimental section. In general, the conversion of CO increases with increasing temperature in the beginning and then decreases at higher temperature showing maxima for all the catalysts. At lower temperature there is a large difference in the experimental conversion and corresponding equilibrium conversion but at higher temperature the conversion reaches near the equilibrium conversion. These differences are due to fact that at lower temperature rate of reaction is low and the residence time is far below the time required for equilibrium conversion also because being exothermic reaction equilibrium conversion is high at lower temperature.

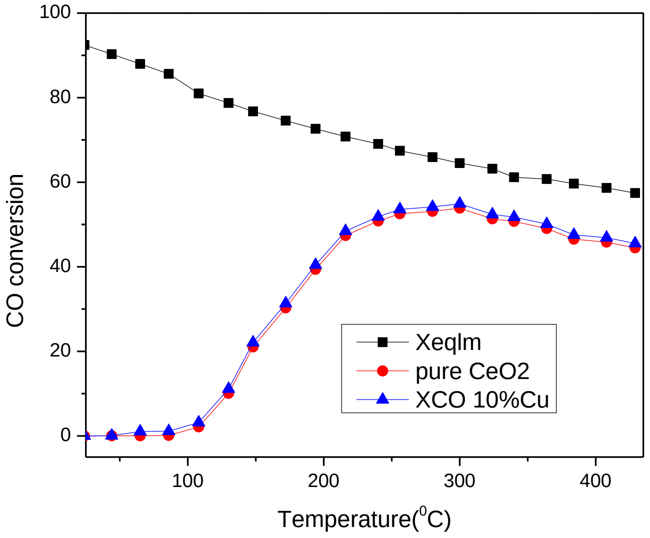

Fig .5: Stability of CeO_2 and 10 mol. % Cu/CeO_2 catalysts during WGSR runs in 150-400 $^{\circ}$C, feed gas flow rate: 1.5 ml/min. CO, 58.50 ml/min N_2 and water vapors.

IV. CONCLUSIONS

The electrospun nanofibers of pure CeO_2 and 10 mol. % Cu/CeO_2 were successfully fabricated using electrospinning technique. The average diameters of the synthesized nanofibers (after calcination) were found to be in the range between 80 to 100 nm. The nanofibers exhibited characteristic peaks of a fluorite-like cubic phase in the XRD analysis. The average crystalline sizes of calcined pure CeO_2 and 10 mol. % Cu/CeO_2 nanofibers were calculated to be 13 nm and 10 nm (from Debye Scherer formula), respectively. The WGSR was carried out in the temperature range of 150-400°C; pure CeO_2 and 10 mol. % Cu/CeO_2 nanofibers exhibited CO conversion efficiencies of around 57% and 59%, respectively.

V. ACKNOWLEDGEMENT

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