Studies on Ceria Nanofiber Catalysts in Water Gas Shift Reaction

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Doctor of Philosophy

By

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CHAPTER 5

SUMMARY AND CONCLUSIONS:

Synthesis and characterization of CeO_2 and CuO/CeO_2 composite nanofibers were carried out and their activity for water gas shift reaction was studied. Composite CuO/CeO_2 nanofibers containing 10, 20, 30, 40, 50 and 60 mol. % Cu as well as pure ceria were successfully prepared using sol-gel and electrospinning technique from solutions containing polyvinyl pyrrolidone (PVP), cerium nitrate hexahydrate and copper acetate monohydrate after calcination at 500ºC temperature for 3hrs. 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. Both fibers were well-distributed and remarkably straight over several micrometers of length and had uniform and smooth surface. It was found that the viscosity of the casting solution was the most important factor affecting the fiber morphology and diameter.

The average diameter of the pure ceria nanofibers was found to be more than that of Cu loaded ceria. This could be attributed to the reduction in gel solution viscosity due to the addition of copper acetate monohydrate. It was also observed that the average diameter of the nanofibers decreased by about 20-30% after calcination. The EDX analysis confirmed the Cu mole percentages used in CuO/CeO_2 composites. Furthermore, it was found that the copper mole percentage (on copper-cerium basis) in the nanofibers varied only slightly during calcination. The nanofibers exhibited characteristic peaks (CeO_2 at 2θ values of 28.83° and CuO at 2θ values of 47.45°) of a fluorite-like cubic phase. The average crystallite size of calcined CeO_2 and CuO/CeO_2 nanofibers varied from 8 to 14 nm.

The catalytic activity of all nanofibers were evaluated for the water gas shift reaction in the temperature range of 150-400^{o}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 295^0C. But with 60% copper it decreased to 76.5% at the 295^0C. 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 295^0C, whereas the pure ceria nanofiber gave the lowest CO conversion of 68% at the same temperature. The activities were found to be in the order of: -50% CuO/CeO_2 >60% CuO/CeO_2>40% CuO/CeO_2 > 30% CuO/CeO_2 > 20% CuO/CeO_2 > 10% CuO/ CeO_2> CeO_2, respectively. Hydrogen yield and selectivity were maximum at 50% Cu content: 44% and 99%, respectively and stability also give maximum at 50% Cu content and Weight hourly space velocity of 3816 h^{-1}.

The order of reaction was found to be one and the activation energy and frequency factor were found to be 55KJ/mol and $6.03x10^9$ sec^{-1}, respectively. The kinetics of water gas shift reaction over CeO_2 nanofiber and composite CuO/CeO_2 nanofiber catalysts in the temperature range 298-373K represents the following rate expression: Rate = $6.03 * 10^9 exp (-55kJ/RT)(C_{CO})$ mol $gcat^{-1}s^{-1}$. Overall,the findings of the study revealed that the ceria nanofiber catalyst (having equimolar CuO/CeO_2) has significantly higher surface area and activity at lower energy consumption (at temperature around 295^oC) which will help in effective WGS reaction.

Suggestions for Future Work:

It would be interesting and useful to investigate the effects of following parameters:

- Effect of calcinations temperature on synthesized nanofibers.
- Effect of variation in composition of polymer on the properties of nanofibers.
- Synthesis of nanocopmosites using different structure of these nanoparticles (like round, oval, rod, flower like) in order to evaluate the effect of catalyst morphology, if any.
- Comparative study of the catalytic activity of nanofibers with various nanoparticles.
- Vander LH model used for the kinetic study of catalytic water gas shift reaction.