SELECTIVE PRODUCTION OF HYDROGEN BY OXIDATIVE STEAM REFORMING OF METHANOL OVER ZnO, CeO_2 AND ZrO_2 PROMOTED Cu/Al_2O_3 CATALYSTS

by

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DEDICATED

TO

MY FAMILY

CERTIFICATE

This is to certify that the thesis entitled, **"SELECTIVE PRODUCTION OF HYDROGEN BY OXIDATIVE STEAM REFORMING OF METHANOL OVER ZnO, CeO_2 AND ZrO_2 PROMOTED Cu/Al_2O_3 CATALYSTS"** being submitted by **Mr. Patel Sanjay S.** to the Indian Institute of Technology, Delhi for the award of Doctor of Philosophy is a record of bonafide research work carried out by him under my guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology Delhi.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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(Sanjay Patel)

ABSTRACT

Hydrogen is expected to play an important role in future energy systems. Hydrogen production from methanol has received considerable attention during recent years. Hydrogen produced from methanol by steam reforming or oxidative steam reforming can be used for various applications like electricity generation using fuel cell for stationary and mobile applications, hydrogen combustion engines etc. In the present investigation an attempt has been made to develop the multi-component copper based catalysts (Cu/ZnO/Al_2O_3, Cu/ZnO/CeO_2/Al_2O_3, Cu/CeO_2/Al_2O_3 and Cu/ZnO/ZrO_2/Al_2O_3) for the steam reforming of methanol (SRM) and oxidative steam reforming of methanol (OSRM) for high methanol conversion, improved hydrogen selectivity, suppression of CO formation; and reduced catalyst deactivation. The catalysts were prepared by wet impregnation and co-precipitation methods. All These catalysts were characterized for their surface area, pore volume and pore size distribution. X-ray diffraction (XRD), scanning electron microscopy (SEM), temperature programmed reduction (TPR); temperature programmed oxidation (TPO), CO pulse chemisorption, temperature programmed desorption (NH_3-TPD) and Thermogravimatric/differential thermal analysis (TG/DTA) techniques were also used for the characterization of fresh and used catalysts.

The performance of catalysts was evaluated in a packed bed reactor over a wide range of operating conditions. Results suggested that the Cu/ZnO/CeO_2/Al_2O_3 catalysts enhanced the catalytic activity significantly. A definite amount of CeO_2 and ZnO is necessary for higher hydrogen yield with low carbon monoxide formation. Cu/ZnO/CeO_2/Al_2O_3 (Cu/Zn/Ce/Al:30/20/10/40) catalyst prepared by co-precipitation method gave the maximum methanol conversion, hydrogen production and CO formation minimization with greater stability. Doping of ZrO_2 over Cu/ZnO/Al_2O_3

catalysts also improved the catalyst performance however CO formation was high. The effect of run-time on the catalyst activity showed that $Cu/ZnO/CeO_2/Al_2O_3$ catalysts are more stable compared to $Cu/ZnO/Al_2O_3$ catalysts. The results of the various characterization techniques were used to relate the observed catalytic activity and stability to the catalyst property. The enhanced activity of ceria based catalysts is due to higher dispersion and surface area of copper with easy reducibility of CuO to Cu. For the ceria based catalysts CO formation was also low due to oxygen storage-release capacity of ceria. Effect of catalyst preparation parameters were studied for the $Cu/ZnO/CeO_2/Al_2O_3$ catalysts prepared by co-precipitation method in which it was observed that the catalyst performance and physicochemical properties were affected by the precipitation pH, precipitation temperature, ageing time and calcination temperature.

Kinetic study was carried out for the steam reforming and oxidative steam reforming of methanol at following operating conditions: contact-time (W/F) 3-15 kg_{cat} s mol^{-1}, temperature 473-573 K, pressure 1 atm with steam to methanol (S/M) molar ratio 1-1.8 for SRM, and steam/methanol/oxygen (S/M/O) = 1-1.8/1/0-0.5 for OSRM. Methanol conversion and hydrogen production rate increased with the contact-time and temperature. The hydrogen selectivity decreased where as selectivity of carbon monoxide increased with increasing contact-time and temperature. Investigations revealed that the CO formation takes place as a secondary product via reverse water-gas shift reaction. The mechanistic kinetic model using Langmuir–Hinshelwood approach has been developed for the steam reforming of methanol process considering methanol reforming and reverse water gas-shift reactions. Five intrinsic kinetic models were proposed based on two reaction mechanisms. For the oxidative steam reforming of methanol three kinetic models were derived considering partial oxidation, methanol

reforming and reverse water-gas shift reactions. The parameters were estimated by nonlinear least square regression for which correlation among the parameters was minimized by temperature centering of Arrhenius and van't Hoff equations. The rigorous parameter estimation and model discrimination was carried out in order to obtain the appropriate kinetic model. A good agreement was obtained between the experimental and model predicated results. The activation energy values for reforming reaction and for reverse water-gas shift reaction were 87.7 and 74.2 kJ mol^{-1} respectively for the SRM process. For OSRM, the values of activation energy for partial oxidation, reforming reaction and for reverse water-gas shift reaction were 81.6, 89.2 and 75.4 kJ mol^{-1} respectively.

Detailed deactivation study was also done for SRM and OSRM reactions over copper based catalysts. The amount of carbon deposited onto the catalysts was determined using TG/DTA. The used catalysts were also characterized by temperature programmed oxidation (TPO), XRD and X-ray photoelectron microscopy (XPS). The simultaneous oxidative steam reforming of methanol and preferential oxidation of CO was performed in order to reduce the CO formation. By using a mixture of 0.5%Pt/Al_2O_3 and $Cu/ZnO/CeO_2/Al_2O_3$ (Cu/Zn/Ce/Al:30/20/10/40) catalysts, the CO formation was further reduced to a low level.

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