

## Abstract

The global energy consumption is estimated to reach around  $262 \times 10^{12}$  kWh/year by 2050 for 9 billion people. It is a challenge to meet global energy requirement via clean fuel (hydrogen) and by reducing/utilizing the CO<sub>2</sub> emissions. Designing of efficient and stable catalysts could control the process economics, providing higher yields of H<sub>2</sub> at low temperatures along with low CO<sub>2</sub> emissions. Based on the current scenario of continuing fossil fuel utilization, researchers are developing technologies that can produce H<sub>2</sub> efficiently from fossil fuels such as methane, diesel, glycerol and hydrocarbons. Developing efficient catalysts is a means of improving the process efficiency. Though the thermo-catalytic route can be beneficial for effective H<sub>2</sub> generation, the purification steps (preferential CO oxidation, water-gas shift (WGS)) for H<sub>2</sub> increases the CO<sub>2</sub> concentration. On the other hand, H<sub>2</sub> generation methods such as photocatalytic water splitting and electrochemical methods are attractive with no CO<sub>2</sub> emissions, but these methods have low efficiencies and scalability that leaves the catalytic route of hydrogen generation to meet global energy requirement as the only viable option.

It is important to understand the nature of the catalyst and its salient properties to design suitable catalysts for energy applications. In this thesis, we have addressed several factors such as strong metal support interaction (SMSI), morphology, oxygen storage capacity (OSC) and nature of the catalyst surface to improve the catalytic activity. The behavior of reactant molecules should be understood on the catalyst surface for developing the reaction mechanisms to determine its kinetics. To address the reactants behavior on catalyst surface, we have carried out reactions such as CO oxidation, preferential CO oxidation, water-gas shift (WGS) under reformat feed, catalytic hydrogen combustion, dry reforming of methane, autothermal reforming of methane and methane combustion. The

structure of the thesis indicates the systematic approach of catalyst design by improving the salient properties to design thermally stable coke resistant catalysts.

This thesis contains 7 chapters. **Chapter 1** reviews the industrial approach for hydrogen generation, role of catalysts in each step of purification steps, brief review of other approaches for hydrogen generation and their limitations. **Chapter 2** focuses on the synthesis of noble metal substituted titania catalysts for reforming of methane. Various reforming reactions such as partial oxidation, CO<sub>2</sub> dry reforming and autothermal reforming of methane have been discussed. The mechanistic and kinetic aspects of reforming reactions are discussed elaborately. Further, the effective properties such as redox nature of the catalyst, SMSI, surface nature and OSC on the reaction mechanism and the stability were addressed.

**Chapter 3** emphasizes on the synthesis of other reducible catalysts such as cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) and copper substituted cobalt oxide. These catalysts were subjected to low temperature reactions such as CO oxidation and preferential CO oxidation (PrOX) under H<sub>2</sub> rich conditions. The redox nature and high OSC properties improved the catalytic activity and allowed reactions to occur below 170°C. Further, the role of intermediate species such as carbonates, carboxyl and formate groups in the reaction mechanism for CO oxidation under H<sub>2</sub> rich conditions have been investigated to develop the rate expression and kinetics.

**Chapter 4** focuses on the development of Pt and Pd substituted Co<sub>3</sub>O<sub>4</sub> – ZrO<sub>2</sub> (CZ) catalysts using PEG – assisted sonochemical synthesis. Our objective is to design thermally stable catalysts and understand the behavior of the reactants on the catalyst surfaces. Hydrogen and oxygen activation are crucial steps in the mechanisms for hydrogen combustion, water-gas shift and reforming reactions and that can be achieved by modifying supports with suitable noble metals. The effect of oxygen vacancies in the reaction mechanism was found to be insignificant with Pt and Pd substituted CZ supports. This study

is key for extending our work to design thermally stable catalysts for WGS and high temperature methane combustion reactions.

**Chapter 5** deals with the important industrial H<sub>2</sub> upgradation step of low temperature WGS under reformat feed conditions using noble metal (Pt, Pd and Ru) substituted CZ catalysts. The objective of WGS is to upgrade H<sub>2</sub> in the product stream by reacting CO with steam. However, low temperature WGS is a challenging reaction under reformat feed conditions. The reformat feed contains CO, CO<sub>2</sub> and H<sub>2</sub> in different concentrations and these can block the active sites of the catalyst and become favorable for side reactions such as methanation. In this study, the catalysts were modified by redesigning catalyst with potassium promoter. Thus the stable catalyst system was designed by eliminating the undesirable methanation reaction. Further, this chapter focuses on the mechanism of WGS on noble metal substituted CZ catalysts below 300°C. The role of promoter in the reaction mechanism and possible surface intermediates have been discussed in detail. This study gives insights of the behavior of reactant molecules on the catalyst surface, which further allowed us to design the catalysts for high temperature reactions such as methane combustion.

**Chapter 6** focuses on catalytic activity of composite catalysts for high temperature methane combustion reaction. The low cost transition metal substituted (Ni, Cu and Fe) CZ composites have been developed for methane combustion. Due to its oxygen storage capacity over a wide range of temperature, these catalysts were found to be stable at a temperature of 600°C without noticeable sintering. The spectroscopic studies gave an insight of possible reaction mechanism over the synthesized catalysts. **Chapter 7** summarizes the major conclusions drawn from each chapter and highlights the further outlook of the work.