

Development and study of self-sustained electrochemical promotion catalysts for hydrocarbon reforming

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We proposed a novel concept for catalyst design that utilizes a long-distance coupling between selective anode and cathode phases to enable an electrochemical promotion effect on the active phases. The concept is schematically illustrated in Fig. 1. The SSEP catalysts consist of four main components: **selective anodic catalysts**, **selective cathodic catalysts**, **O²⁻ ions conductor**, and **electronic conductor**. Unlike the normal electrochemical promotion devices with separated anode and cathode, the catalysts contain tiny anodes and cathodes in the form of fine particles, typically 20 nm-0.5 μm. Because of the difference of the electrochemical potentials of the selective cathode and anode, the oxygen ion species (O₂⁻, O₂²⁻, O⁻, O²⁻, in general, O^{δ-}) that are produced at the cathode will be driven to the anode through the oxygen ion conductor and participate in the oxidation of the hydrocarbon while the electrons produced from the oxidation reaction are driven to the cathode through the electronic conductor and participate in the reduction of oxygen. Thus, the electrochemical promotion does not need an external power supply or it is self-sustained.

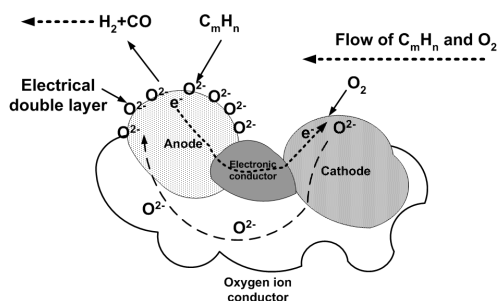


Fig. 1 Schematic showing electrochemically promoted partial oxidative reforming of hydrocarbon fuel, C_mH_n.

We synthesized three types of SSEP catalysts based on respectively yttria-stabilized zirconia (YSZ), gadolinium-doped ceria (GDC), and yttrium-doped ceria (YDC) oxygen ion conductors. As shown in Figs. 2 and 3. The SSEP catalysts based on YSZ give the best performance: the zero noble metal SSEP catalysts yield more than 90% conversion and 90% hydrogen sensitivity at temperatures of 450-650°C for methane and heavy hydrocarbon reforming. The conversion and sensitivity are two orders of magnitude greater than those of a commercial Pt based catalyst and Ni based catalysts at temperatures of 350-550°C under same pressure and flow rate. We prove that the high performance of the SSEP catalysts is primarily due to the coupling of the anode and cathode nano-phases. This is convinced by the modelling and simulation results (Figs. 4 and 5). The multiscale modelling method incorporates a reactive fluid dynamic model and nano-scale electrochemical model in a self-consistent way and successfully describes the major characteristics of hydrocarbon reforming over SSEP catalysts. The results, findings, and understandings obtained from this research suggest that the utilization of the long-distance coupling in the SSEP catalysts may give rise to dramatic advancements in many other areas of catalysis including conversion of CO₂ into fuel, reduction of NO_x emission, and photo-catalysis.

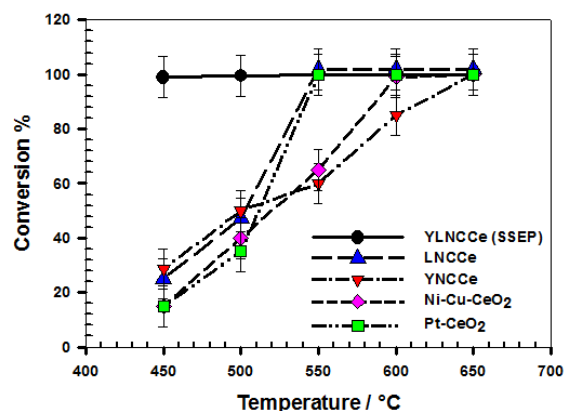


Fig. 2 Conversion of n-pentadecane in POXR experiments as a function of temperature and type of catalyst. YLNCCe is the only SSEP catalyst whereas others are Ni and Pt based catalysts.

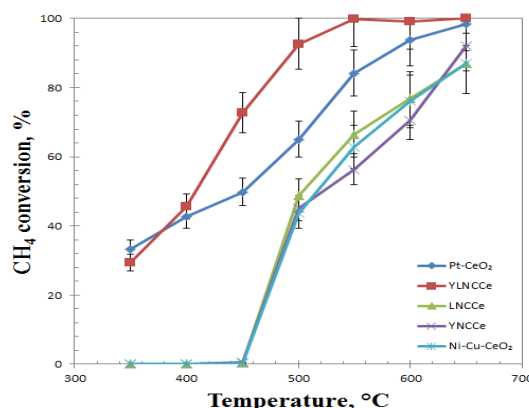


Fig. 3 CH₄ conversion over the Pt-CeO₂, YLNCCe, LNCCe, YNCCe and Ni-Cu-CeO₂ catalysts. YLNCCe is the only SSEP catalyst whereas others are Ni and Pt based catalysts.

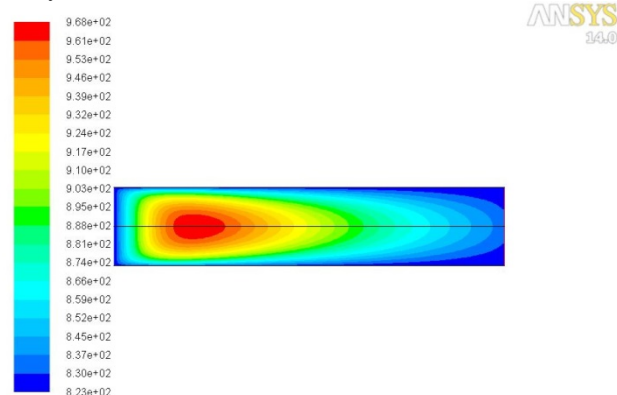


Fig. 4 – The temperature profile along the catalyst bed predicted by the CFD modeling.

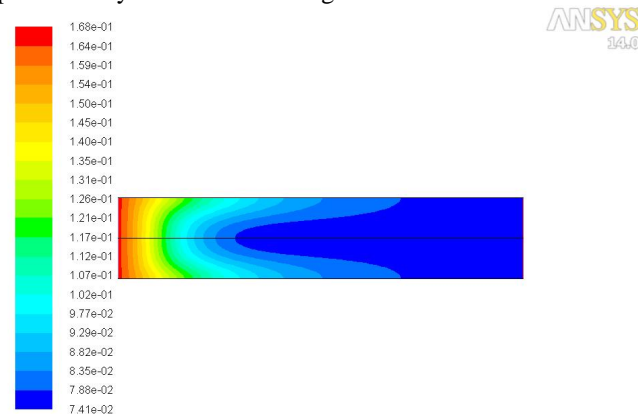


Fig. 5 – Mass fraction of CH₄ over the Ni-Cu-CeO₂ catalyst bed (550 °C, CH₄:O₂=2).