

## Steam reforming of *n*-hexadecane using a Pd/ZrO<sub>2</sub> catalyst: Kinetics of catalyst deactivation

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Received 14 March 2007; accepted 14 March 2007

Available online 1 May 2007

### Abstract

A systematic study of catalyst deactivation is required for the development of a coke resistant and sulfur tolerant catalyst for diesel fuel reforming systems to be used in conjunction with the solid oxide fuel cell (SOFC). In the present study, the performance of a Pd–ZrO<sub>2</sub> catalyst coated on a metal foil at various steam to carbon ratios (S/C), temperatures (*T*) and sulfur content (S) of the fuel were investigated for the steam reforming of *n*-hexadecane using a tubular reactor. Here *n*-hexadecane is used as the surrogate for diesel fuel. A decrease in time dependent hydrogen yield indicated catalyst deactivation, with the effects of reaction conditions on the rate of deactivation determined through a statistically designed experiment. A first-order kinetic model, with first-order deactivation rate, was used to obtain best fit values for the reaction rate constant (*k*<sub>0</sub>) and the deactivation rate constant (*k*<sub>d</sub>) as a function of S/C, temperature and sulfur loading. Palladium-catalyzed steam reforming of *n*-hexadecane was adequately modeled using first-order kinetics, the reaction rate was enhanced by increased temperatures and S/C ratios, but was decreased by the presence of sulfur. Catalyst deactivation was more rapid in the presence of sulfur, at low S/C ratios, and at lower temperatures.

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**Keywords:** Methane steam reforming; Natural gas; Hydrogen; Catalytic reforming; Metal foil catalyst

### 1. Introduction

An anticipated hydrogen economy has provided a unique opportunity to investigate available technologies for the production of hydrogen. Different types of fuel cells are being used to convert chemical energy to electrical energy among which solid oxide fuel cells (SOFC) have shown very good potentials to be utilized as an auxiliary power unit (APU) in trucks and recreational vehicles [1]. Use of onboard-generated hydrogen in vehicles has certain advantages over conventional fuels including higher efficiency, lower weight, compact design (e.g. SOFC-APU unit), reduced greenhouse emission, improved air quality, and less dependence on petroleum resources [2,3]. Because SOFCs can tolerate relatively high concentrations of CO in the feed gas, the production of hydrogen from on-board fuel in combination with a SOFC provides a viable APU technology.

For example, an overall 33% increase in the average idling engine efficiency has been reported in case of SOFC-APU unit in trucks [4]. However, one limitation to adopting SOFCs as a mainstream energy provider is the lack of an available and practical hydrogen source. Current fuel distribution systems are based on hydrocarbon fuels, such as liquid petroleum and natural gas, not hydrogen. Therefore, widespread use of fuel cells will require development of a hydrogen distribution infrastructure or an efficient process to produce adequate amounts of hydrogen from hydrocarbon fuels such as natural gas, gasoline and diesel fuel.

There are a number of conventional technologies available to produce hydrogen, such as steam reforming, partial oxidation, and auto-thermal reforming of hydrocarbons, as well as ammonia cracking and direct electrolysis of water [5]. Commercial processes used to produce large quantities of hydrogen in petroleum refining processes are based upon steam reforming of natural gas. Since reforming is an endothermic process, external energy input is required for the reaction to take place.

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In the alternative partial oxidation process, the fuel is partially oxidized to produce hydrogen and carbon monoxide. This is an overall exothermic process; therefore, no external energy input is required. But the efficiency of this process is relatively low because of high coke formation on the catalyst surface in a continuous operation which leads to deactivation of the catalyst over time [6]. The auto-thermal reforming process combines the advantages of steam reforming and partial oxidation; however, the proper mixture of steam, fuel and air is required to achieve higher efficiency [7]. Ammonia cracking is a simple method to produce hydrogen but separation of hydrogen from nitrogen is not cost effective. Direct electrolysis of water could be an environmentally friendly process, except that a large amount of energy is required to split water into hydrogen and oxygen. While the energy required for electrolysis can be provided through solar or wind energy, making water electrolysis an environmentally attractive alternative to other hydrogen generation processes, current technologies would rely on electricity from the grid, and thus overall reliance depends on coal and other fossil resources. Under present scenarios, steam reforming remains one of the most economical alternatives because of the higher yield and concentration of hydrogen in the effluent gas [6,8,9].

Although steam reforming is an attractive technology for hydrogen production, catalyst deactivation due to coke formation and sulfur poisoning while reforming of diesel or jet fuel are the main challenges. As conventional Ni/Cu/Zn catalysts are deactivated [10,11] in long time operation, the steam reforming reaction becomes less efficient because byproducts such as alkanes and alkenes are preferentially formed, thereby reducing the hydrogen yield. Regeneration of the catalyst would be required to recover the desired activity and productivity. Moreover, steam reforming is usually carried out at high temperatures which sometimes leads to loss in surface area of support due to sintering [11–13].

Deactivation of the catalyst due to coke formation and sulfur poisoning are very complex processes that are not well understood [14]. Many attempts have been made to understand the mechanism of these reactions [15,16]. A detailed systematic study of catalyst deactivation and its mechanism is required before coke resistant and sulfur tolerant catalysts can be designed.

Noble metal catalysts have better stability and activity than conventional catalysts at higher temperatures [17,18] and can be used for steam reforming of hydrocarbon fuels. Because carbon monoxide is one of the products of steam reforming and platinum catalyst undergoes deactivation in the presence of CO [15,19], platinum-based catalysts are not appropriate. However, palladium appears to be a reasonable alternative as it is a well-known oxidation catalyst that is mostly stable in the CO environment and has good activity towards hydrogen generation [20], although it deactivates in the presence of coke [21]. Zirconia is a highly stable support even at high temperature. Therefore, we chose a Pd/ZrO<sub>2</sub> catalyst as a base metal catalyst for testing. *N*-hexadecane was used as surrogate for the diesel fuel and thiophene was used as a dopant for sulfur tolerance studies.

The purpose of this research was to evaluate the rates of catalyst deactivation during steam reforming and use these results to identify a set of reaction conditions that provided highest hydrogen yield and greatest catalyst stability in the presence of sulfur under the operating conditions. The data were analyzed assuming first-order reaction kinetics and first-order deactivation of the catalyst.

## 2. Experimental setup

Reactions were conducted in a continuous flow, packed bed, stainless steel reactor (1.7 cm ID) as shown in Fig. 1. Separate feeds for *n*-hexadecane and water were introduced into the pre-heater, which was maintained at 600 °C. A trace amount of nitrogen (50 ml/min) was also introduced separately into the pre-heater. Nitrogen served as an analytical standard to facilitate product analysis. After entering the pre-heater, feed streams were mixed and introduced into the reactor as a single feed. The reactor was maintained at atmospheric pressure and the catalyst was tested at different reaction temperatures (600–900 °C) and various steam to *n*-hexadecane feed flow rates (S/C=3–6), while maintaining a gas hourly space velocity (GHSV) of 22,000 h<sup>-1</sup> (at reaction conditions). Product gases were separated into permanent gases and condensable (liquid products) using a condenser operating with house cooling water.

The Pd–zirconia catalyst was spray coated on the rectangular corrugated metal foil (91.44 cm × 2.54 cm, Fig. 2a) and used as prepared by Catacel corporation [22]. A strip of 15 cm in length and 2.5 cm in width was cut and wound to make a 1.7 cm × 2.5 cm button (Fig. 2b) which was then inserted into the reactor and supported by glass wool.

The gas stream was sent to an online Shimadzu 2010 gas chromatograph (GC) equipped with a mega-bore splitless

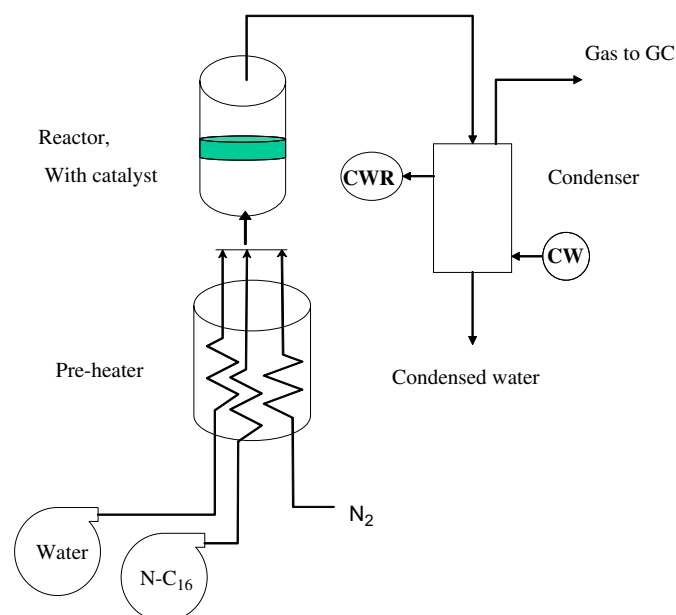


Fig. 1. Schematic diagram of the laboratory reforming reactor.

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