



# Efficient bimetallic catalysts for hydrogen generation from diesel fuel<sup>☆</sup>

Praveen K. Cheekatamarla\*, Alan M. Lane

*Department of Chemical and Biological Engineering, Box 870203, The University of Alabama, Tuscaloosa, AL 35487, US*

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## Abstract

Fuel cell requires hydrogen as its fuel source for generating power. Hydrogen for use in auxiliary power units is produced in a fuel processor by the catalytic reforming of hydrocarbons. Diesel, jet fuel, gasoline, as well as natural gas, are potential fuels that all have existing infrastructure of manufacture and distribution, for hydrogen production for fuel cell applications. It is well known that essentially all hydrocarbon feeds contain sulfur at different concentrations. In addition to coking, sulfur poisoning is the main force for deactivation of pre-reforming and reforming catalysts. The objective of this paper is to develop, test and characterize efficient catalysts for hydrogen generation from diesel autothermal reforming. Bimetallic catalysts exhibited superior performance compared to the commercial catalyst and the monometallic counterparts. BET, TPD, TPR, and XPS were utilized for surface analysis of these formulations, which showed that the enhanced stability is due to a strong metal–metal and metal–support interaction in the catalyst.

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## 1. Introduction

Polymer electrolyte membrane (PEM) fuel cells show considerable promise for fuel-efficient vehicular applications and therefore a substantial amount of effort has recently been directed at their production and optimization [1]. The PEM fuel cell requires hydrogen as its fuel source. In order to avoid storing high-pressure hydrogen, the fuel can be generated in an onboard fuel processor [2 and 3]. For transportation applications, the primary focus is on reforming gasoline, because a production and distribution infra-

structure already exists [4,5]. For auxiliary power units, the focus is on reforming both gasoline (for automotive applications [6]) and diesel (for trucks and heavy-duty vehicles [7]). For portable power generation, the focus has been on reforming natural gas and liquefied petroleum gas.

The conversion of hydrocarbon fuels to H<sub>2</sub> can be carried out by several catalytic reaction processes, including steam reforming (SR), partial oxidation (POX), and autothermal reforming (ATR). ATR involves the reaction of oxygen, steam, and fuel to produce H<sub>2</sub> and CO<sub>2</sub>. In essence, this process can be viewed as a combination of POX and SR and has recently attracted considerable attention due to its higher energy efficiency than the above processes and also low investment process using a simple system design [8].

The design of ATR catalysts can be challenging, particularly for gasoline/diesel reforming due to the complex and ill-defined nature of the fuel. ATR catalysts have to be active for both steam reforming and partial oxidation, be resistant to high temperatures and tolerant against sulfur poison and

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\* Corresponding author. Tel.: +1 303 949 1629; fax: +1 509 335 4806.

*E-mail addresses:* [cheek004@bama.ua.edu](mailto:cheek004@bama.ua.edu) (P.K. Cheekatamarla), [alane@coe.eng.ua.edu](mailto:alane@coe.eng.ua.edu) (A.M. Lane).

coke formation, especially in the catalytic zone with inadequate oxygen concentration.

Catalyst formulations for ATR fuel processors depend on the fuel choice and operating temperature. For methanol, Cu-based formulations can be used [9]. For higher hydrocarbons the catalyst typically comprises of metals such as Pt, Rh, Ru and Ni deposited or incorporated into carefully engineered oxide supports such as ceria-containing oxides [10].

Current interest in bimetallic catalysts is increasing, in particular, because they show superior selectivity and resistance to poisoning as well as improved activity and stability. The main objective of the present work was to determine whether the autothermal reforming activity of Pt can be improved when a second metal is added to the substrate.

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. Ceria-based catalysts

The CeO<sub>2</sub> support material has a purity of 99.9%. The metal originates from a nitrate-based precursor material. Each catalyst was prepared by the incipient wetness method using distilled water as the solvent for the precursor materials. The catalysts were then dried in air at 110 °C overnight. Each catalyst was also calcined in air at 300–500 °C for 4 h. Bimetallic catalysts were prepared by depositing a metal first, drying, calcining and then depositing the second metal with subsequent drying and recalcination.

#### 2.1.2. Alumina-based catalysts

The support material is Al<sub>2</sub>O<sub>3</sub> (acidic, gamma). The active metal sites were obtained from nitrate precursors. The preparation technique adopted was incipient wetness method using distilled water as the solvent for the precursor materials. The catalyst was then dried in air at 110 °C overnight followed by calcination in air at 400 °C for 3 h. The catalyst was then reduced in a mixture of 5% H<sub>2</sub> and N<sub>2</sub> for 1 h at 350 °C. Bimetallic catalysts were prepared by depositing one metal first, drying (110 °C) and calcining (400 °C) and then depositing the other metal, with subsequent drying and calcination (400 °C). The catalyst was then reduced in a mixture of 5% H<sub>2</sub> and N<sub>2</sub> for 1 h at 350 °C.

### 2.2. Reactor system

All the experiments were performed in a  $\frac{3}{8}$ " adiabatic fixed-bed tubular (quartz) reactor. Liquid feed consisting of water and diesel was vaporized and mixed along with air in a pre-heater containing silicon carbide bed to enhance mixing. Calibrated HPLC pumps and unit mass flow controllers were used to control the flow rates. The gaseous mixture from the pre-heater was maintained at a temperature of 400 °C. The reactor with the catalyst bed was well insulated to achieve the adiabatic reaction conditions. The

hot product gas leaving the reactor was cooled down in a heat exchanger/condenser system to separate water and liquid hydrocarbons from the product gas. Pressures above 2 psig were not encountered. The dry product gas from the condenser was analyzed using a SRI gas chromatograph to monitor H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and O<sub>2</sub> concentrations. In each test, 2 g of fresh non-diluted commercial catalyst sample (pellets with an average size of 2 mm) was supported on a layer of quartz wool.

The experiments reported in this document were performed under the following conditions: steam/C ratio = 3, oxygen/C ratio = 0.5, Pre-heater/Reactor temperature = 400 °C, space velocity = 17000 hr<sup>-1</sup>. These conditions were chosen according to the experimental work done on synthetic diesel and JP8 fuel [11]. Oxygen was never observed in the effluent during any of the experiments at any of the temperatures tested. Condensate from the reactor was considered as unconverted/reformulated hydrocarbon. Hydrogen yield defined in the experiments is the ratio of molar hydrogen concentration in the product to the molar concentration of hydrogen in the reactants (diesel + water).

### 2.3. BET (surface area) and CO chemisorption (dispersion) measurements

BET surface area of the catalysts was analyzed by nitrogen adsorption–desorption technique. CO chemisorption at –80 °C was utilized to measure the dispersion of these catalysts using the pulse technique, this method is known to avoid to some extent the spillover phenomenon which affects accuracy of the data [12].

### 2.4. Temperature-programmed reduction (TPR) experiments

Temperature-programmed reduction was performed in a U-tube quartz reactor using a CHEMBET 3000 apparatus manufactured by Quantachrome, provided with thermal conductivity detector (TCD). Pellets (~ 0.4 gm) or fine powder (~ 0.25 gm) was used. To remove any water and CO<sub>2</sub> adsorbed on the surface, the catalysts were pre-heated to 250 °C for 2 h followed by purging and cooling in helium. Then a reducing gas mixture consisting of 5% H<sub>2</sub> in helium was passed through the catalyst and the temperature was ramped from 25 to 800 °C at a heating rate of 20 °C/min.

### 2.5. Temperature-programmed desorption (TPD) experiments

TPD of catalysts was carried out in the CHEMBET apparatus described above. In all the TPD experiments, the catalysts were preheated to 300 °C in helium for 1 h to remove residual H<sub>2</sub>O and CO<sub>2</sub>. After cooling down to room temperature in helium, the TPD data were acquired with a heating rate of 20 °C/min to 600 °C. The flow rate of the gas was typically 70 cm<sup>3</sup>/min.

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