Efficient Bimetallic Catalysts for the Hydrogen Production from Diesel fuel

Praveen K. Cheekatamarla and Alan M. Lane

Department of Chemical Engineering, The University of Alabama, Tuscaloosa, AL-35487

Introduction

Autothermal reforming involves the reaction of oxygen, steam, and fuel to produce H₂ and CO₂. 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 [1]. The ATR is a stand-alone process in which the entire hydrocarbon conversion is carried out in one reactor aided by partial oxidation. The ATR process is generally defined by an idealized equation written as:

\[ C_2H_6O_2 + (n/2)O_2 + (x - n/2)pH_2O = (n/2)CO_2 + (n/2)xH_2 + (3.76x - x/2)N_2 \]

where, \( x \) is the oxygen-to-fuel molar ratio. When \( x = 0 \) equation reduces to the endothermic steam reforming; when \( x = n-p/2 \) equation is the combustion reaction.

ATR has several advantages over SR and POX: (1) less complicated reactor design and lower reactor weights, because less thermal integration (i.e. heat exchange between incoming reactants and the hot products) is required; (2) a wider choice of materials of construction; and (3) lower fuel consumption during startup because, for a given reactor mass, the energy required to heat a reformer is directly proportional to its operating temperature.

In the past, various fuels have been investigated for H₂ generation by reforming technologies for fuel cell systems. Suitable fuels involved gaseous HCs such as methane, propane etc. [2] and liquid HCs such as alcohols [3], gasoline [4, #2 diesel [5]].

For heavy fuels such as JP-8 or kerosene, autothermal reforming conditions were achieved by using a reformer including a POX zone and a separate SR zone. The operating conditions were maintained such that oxygen (air) was preheated to 450°C, and the temperature of POX chamber and SR chamber maintained at 1375°C and 925°C respectively [6]. It is also reported that in the autothermal reforming of the diesel feed, the thermodynamic equilibrium can be achieved at a Water/C of 1.25 and an oxygen/C ratio of 1 at an operating temperature of 700°C [7].

Although considerable work was done on heavy hydrocarbons, there haven’t been any studies related to synthetic diesel fuel and the performance of adiabatic reactors for autothermally reforming the fuel.

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 robust at high temperature and resistant to sulfur and coke formation, especially in the catalytic zone that runs oxygen limited.

Full conversion of all hydrocarbon components is desired; low levels of non-methane hydrocarbons, such as aromatics and olefins can undergo transformations, particularly hydrogenation on the downstream WGS catalyst, thus consuming hydrogen and decreasing the overall efficiency of the fuel processor.

Catalyst formulations for ATR fuel processors depend on the fuel choice and operating temperature. For methanol, Cu-based formulations can be used. 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.

The objective of this investigation was to synthesize and test stable and efficient autothermal reforming catalysts for hydrogen production in auxiliary power units.

Experimental

All the experiments were performed in a 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 and heat transfer. 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 adiabatic reaction conditions. Thermocouples were placed along the catalytic bed to read the temperature profile inside the reactor as the reactions occur over the catalytic surface and the corresponding product composition was measured by sampling at different positions. 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. The pressure was always less than 2 psig. The dry product gas from the condenser was analyzed using a SRI gas chromatograph to monitor H₂, CO, CO₂, CH₄ and O₂ concentrations.

In each test, 2 g of fresh non-diluted catalyst sample (pellets with an average size of 2 mm) was supported on a layer of quartz wool. The catalysts tested for the ATR activity were prepared by impregnation and co-impregnation techniques.

The experiments reported in this document were performed under the following conditions: Steam/C ratio = 1-3, oxygen/C ratio = 0.5-2, pre-heater and reactor inlet temperature = 400°C, Space Velocity = 17000 hr⁻¹.

Results and Discussion

The role of defect chemistry and the surface oxygen vacancies in determining the catalytic behavior of metal supported mixed oxide systems is well known. The focus was on the autothermal reforming activity of some catalysts, as well as, the effect and role of both the metal and the dopant on the catalytic properties. The experimental work involved developing, testing and characterizing: (a) single metal catalysts supported on reducible or non-reducible support; (b) bimetallic catalysts dispersed on various supports. Reactor studies involved the reforming of synthetic diesel fuel. Catalysts were prepared by impregnation, incipient wetness method and coprecipitation. Metal loadings generally range from 1-2% in the case of noble metals and 5-10% for non-noble metals.

Alumina supported catalysts

The main objective of the present work was to determine whether the autothermal reforming activity of Pt can be improved when a second noble metal (Pd) is added to the alumina substrate. This carrier was selected because of its non-reducible nature, as a part of fundamental study to better understand the performance of autothermal reforming catalysts: metals and metal oxides.

Three model samples were prepared to study the ATR activity of synthetic diesel fuel: Pt, Pd and Pt-Pd catalysts supported on alumina. Two different bimetallic samples were prepared by changing the order of impregnation: Pt(I)-Pd(II); Pd(I)-Pt(II).

The autothermal reforming activity response of alumina supported Pt and/or Pd catalysts is shown in Fig. 1. Before carrying out the activity tests, all the samples were reduced at 350°C in a 5%H₂/N₂ mixture. Samples loaded with Pt or Pd yielded about 50%
hydrogen compared to 45% from bare alumina. The most interesting results are obtained from the mixed metal bimetallic catalysts, the Pt-Pd samples. Each bimetallic sample shows high activity yielding ~60% hydrogen compared to 50% from their monometallic counterparts. The order of impregnation does not seem to have any impact on the performance of these catalysts as noted in the figure. The ATR activity on the Pt, Pd and Pt-Pd catalysts confirms a positive effect of Pt and Pd in the bimetallic sample, because the level of activity of this system was higher than on either of the monometallic components.

![Figure 1](image1)

**Figure 1.** Performance of alumina supported Pd and/or Pt catalysts

This higher intrinsic activity of these catalysts is probably due to the Pt-Pd interaction in the system. Temperature programmed reduction studies and XPS analysis confirmed the expected phenomenon.

TPR profiles of monometallic (Pd and Pt) and the bimetallic (Pt followed by Pd) samples are shown in Fig. 2. TPR pattern of alumina carrier is not shown because of its non-reducible nature.

The TPR profile (Fig. 2) of the Pd sample shows a negative peak at 75°C followed by a positive peak at 110°C. The former can be assigned to desorption of hydrogen from the decomposition of a bulk palladium hydride formed through H-diffusion in to the Pd-crystallites [214], while the latter is attributed to the Pd oxide species. In contrast, the TPR profile of the Pt sample shows a broad reduction profile extending from 50°C to 450°C. All platinum is reduced to Pt metal below 450°C. Two reduction peaks one at about 100°C and the other at 250°C were observed for Pt/Al₂O₃. The broadening suggests the presence of several Pt species. These reduction peaks are slightly lower than the reported reduction temperature [8] probably due to differences in Pt loading, alumina type, calcination temperature and ramp rates during the TPR.

The TPR profile of the bimetallic Pt-Pd catalyst is not simply the sum of the monometallic Pt and Pd samples. The bimetallic reduction profile exhibits peaks typical of PtO reduction (100°C) and PdO (110°C) in addition to the Pd hydride decomposition peak at 75°C, although both are much more intense than in the monometallic samples. Since the metal content is about the same in these catalysts, the increase in H₂ consumption associated with the metal oxide species seems to depend on the presence of second metal. In addition, the broader second peak centered at 400°C, detected in the Pt-Pd sample indicates the reduction of Pd species together with the co-impregnated Pt, probably due to some kind of interaction between the metals. Similar interactions in Pt-Pd systems were reported in TPR studies performed by Noronha et al. [9]. These interactions between the metals leading to the formation of an active phase seem to be a probable reason behind the activity enhancement.

![Figure 2](image2)

**Figure 2: TPR Profiles of alumina supported catalysts**

The XPS analysis performed over these samples verify the above conclusions. The high resolution XPS spectra of the Pt 4d and the Pd 3d binding energy regions obtained from the Pt/Al₂O₃, Pd/Al₂O₃ and Pt/Pd/Al₂O₃ samples are shown in Fig. 4-48a. Note a slight shift in the Pd 3d5/2 peak (~0.5 eV to higher binding energy) of the Pt-Pd/Al₂O₃ catalyst with respect to that of the Pt/Al₂O₃ catalyst. The shift in the Pd 3d5/2 peak may be due to the formation of stabilized Pd species due to a strong metal-metal interaction between Pd and Pt in the bimetallic sample.

![Figure 3](image3)

**Figure 3: XPS analysis of alumina supported catalysts**

**Ceria Supported Catalysts.**

Two different metals viz. Pt, Ni were chosen for their ATR activity. The ceria supported catalysts include monometallic components and their combinations with Pt (Pt-Ni). Two different bimetallic samples were also prepared by changing the order of impregnation on ceria substrate. It can be noted from Fig. 4 that these metals improved the ATR activity of ceria support. Similar to the
results observed over the alumina supported catalysts discussed in the above section, the selectivity to produce hydrogen from diesel fuel was highest for the bimetallic samples compared to their monometallic counterparts. The impregnation order clearly had an effect on the activity in case of the Pt-Ni bimetallic catalysts as observed in Fig. 4. Also these catalysts exhibited stable performance showing almost complete resistance to sulfur poisoning. A long-term experiment was carried out over these catalysts (Pt, and Pt-Ni). It is clear from Fig. 5 that the bimetallic sample shows stable catalytic activity even in presence of heavy sulfur content due to the JP8 fuel in the ATR tests conducted. The reason for this higher intrinsic activity and stability is underway.

Figure 4: ATR activity of Ceria supported Pt and/or Ni catalysts

Figure 5: ATR activity (Sulfur resistance) Pt-Ni catalyst

Conclusions

Autothermal reforming of synthetic diesel fuel was investigated for potential applications in auxiliary power units. Experimental results suggest that the presence of a second metal improves the performance of the ATR activity of Pt based catalysts supported on ceria and alumina. Higher intrinsic activity of these samples is possibly due to the interaction between these metals as suggested by TPR and XPS results.

References

(2) Ayabe S.; Omoto H.; Utaka, R.; Eguchi K.; Applied Catalysis A: General 2002, 6352, 1