Nanomaterials for Fuel Processing Applications

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ABSTRACT

A NanoSpray Combustion™ process has been used to synthesize a variety of nano-sized materials for use as catalysts to generate hydrogen from heavy hydrocarbon fuels via steam reformation. The hydrogen generation capability of these catalysts has been demonstrated with ultra-low-sulfur-diesel (ULSD) and Jet A. Initial hydrogen conversion efficiencies of up to 80% have been achieved with some catalysts that have logged over 140 hours of operation. Due to the high surface areas associated with these nano-sized catalysts, hydrogen generation could even be carried out at a temperature of 600C, significantly lower than what is typically used in convention hydrocarbon steam reformers. While our current studies utilize low-sulfur fuels, we are also researching approaches to desulfurize fuel prior to reformation. Nanomaterials and processes for desulfurization will also be discussed.

Keywords: hydrogen generation, steam reformation, desulfurization, nanomaterials, catalyst

1 INTRODUCTION

While some strategic energy initiatives may call for the speedy replacement of petroleum-based fuels with alternative fuels and energy sources, it is unreasonable to expect that this will happen in the near-term. In the foreseeable future, it is more realistic to expect cleaner fossil fuel technologies to be developed alongside alternative fuel and energy technologies, such as biofuels, wind and photovoltaic. To this end, nGimat has used its proprietary NanoSpray Combustion™ process for developing nanomaterials that have wide-ranging applications for generating cleaner burning petroleum fuels. These materials include nano-sorbents that can be used for adsorptive desulfurization of high-sulfur containing fuels and nano-catalysts for generating hydrogen gas from petroleum-based fuels. The latter could be used in reforming systems for on-board generation of hydrogen in fuel cells. In one version of the materials developed for these applications, the active sorbent and/or catalyst sites are distributed on the surface of a variety of nano-sized support structures like Zirconia or Ceria. The high oxygen ion conductivity in the support structures is known to enhance the catalytic activity of metals such as Nickel. [1] This paper will discuss recent advances made at our company in optimizing these materials for each of these important areas.

2 SYNTHESIS & CHARACTERIZATION OF NANOMATERIALS

Figure 1 shows the schematic of the NanoSpray Combustion ™ process. Precursors for the catalyst are mixed into a solution and pumped into a sub-micron capable atomizer, called the Nanomiser™, mixed with combustion gases and then combusted in a flame. The resulting vapors condense into nanopowders that are collected in a powder collection or dispersion system. This process is similar to Combustion Chemical Vapor Deposition but higher solution concentrations are used. [2] Although simple, the procedure calls for precise control of process parameters and also careful tailoring of precursor composition and stoichiometry. In addition to catalysts, this process has also been utilized to obtain a variety of other materials for energy applications, including battery & supercapacitor electrodes, fuel cell electrolytes and membrane-electrode assemblies (MEA).

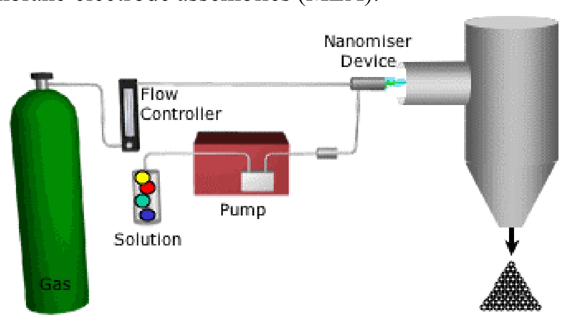

Figure 1: Schematic of NanoSpray Combustion system for synthesizing catalyst & sorbent nanomaterials.

For the hydrogen generation application, we have mainly focused on base metals with stable oxides, and in this paper we will present some of the Nickel (Ni) based nanomaterial catalysts. Figure 2 shows transmission electron micrographs (TEM) and the corresponding electron diffraction pattern for one such catalyst system which is mainly composed of Ni supported on a Yttrium stabilized Zirconia (YSZ) matrix. Based on the TEM results, the average particle size in this material is well

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under 100 nm. This material, which we refer to as NiO-YSZ, is in its oxidized state as synthesized and can be converted to Ni-YSZ, by reducing with hydrogen gas. X-ray Diffraction (XRD) patterns (not shown) confirmed the crystalline structure of the as synthesized NiO-YSZ to be a combination of NiO and YSZ. X-ray fluorescence (XRF) spectroscopy was used to confirm that the final composition of the catalyst was consistent with the initial pre-cursor composition used for synthesis.

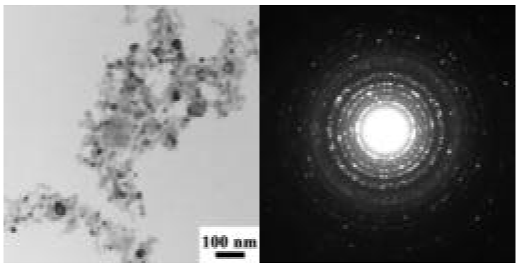

Figure 2: Transmission electron micrographs and their corresponding electron diffraction patterns for NiO-YSZ.

3 HYDROGEN GENERATION BY STEAM REFORMATION

There are several methods available to generate hydrogen from hydrocarbon fuels, including autothermal reformation, partial oxidation and steam reformation. [3] The NiO-YSZ nanomaterials synthesized in our labs were tested in a bench-top steam reformation system that typically utilized 20-30g of catalyst packed into a stationary bed reactor. Fuel and steam were fed into the reformer in a steam to carbon mole ratio of around 2.5. The gases produced during the steam reformation were detected using a thermal conductivity detector on a Gas Chromatography (GC) set-up. Condensates, usually water, were also collected to track mass balance. Ultra-low sulfur diesel (ULSD) from a commercial source was used as the representative heavy fuel and reformation was performed at 600C. Figure 3 shows a typical result from the GC demonstrating that 70-80% of the gas stream is composed of hydrogen. Other gases in the stream include methane (CH_4) and carbon dioxide (CO_2). Very little if any carbon monoxide (CO) is formed. We are currently investigating ways to minimize CH_4 in the stream.

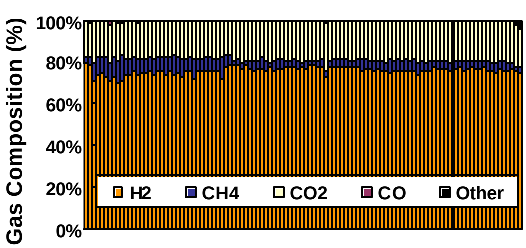

Figure 3: Composition of gas stream produced by a steam reformer using Ni-YSZ & ULSD fuel over 140 hours.

Initial values for hydrogen conversion efficiency exceeded 80%. The catalyst continued to operate well for almost 140 hours with the efficiency gradually dropping to 50%.

4 DESULFURIZATION MATERIALS

The high surface area that is characteristic of nanomaterials also enables adsorption of sulfur-containing species. This adsorption can be achieved at relatively low temperatures, ~150C, compared to 350-400C used in industrial desulfurization processes. By choosing the appropriate nanopowders, it will also be possible to regenerate (reuse) the adsorbents over several cycles, thereby making desulfurization a cost effective solution for markets where it was previously considered cost prohibitive. nGimat sorbent materials have demonstrated the capability to significantly reduce the sulfur content in model fuels from 300ppm to <15ppm. In this paper we will provide an insight into our approach to optimizing sulfur adsorption capacity and regeneration cycle life. We will also discuss feasibility analysis of using sulfur-adsorbing nanomaterials in desulfurization systems designed for the military and commercial sectors.

5 SUMMARY

Nickel-based catalysts for steam reformation were produced using a NanoSpray Combustion process. The catalysts were able to generate hydrogen from ultra-low sulfur diesel with initial efficiencies of around 80% at temperatures as low as 600C. Work is in progress to minimize undesired gases like methane that make up a small amount of the rest of the gas stream. Nanomaterials are also being developed for desulfurization in order to provide on-board sulfur removal capability for the fuel used in the reformer.

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