Steam reforming of *n*-hexadecane over noble metal-modified Ni-based catalysts

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Abstract

Steam reforming of *n*-hexadecane, a main constituent of diesel, over noble metal-modified Ni-based hydrotalcite catalyst was carried out in a temperature range of 700–950 °C, at an atmospheric pressure with space velocity of 10,000–100,000 h^{-1} and feed molar ratio of $H_2O/C = 3.0$. The catalysts were prepared by a co-precipitation and dipping methods. The noble metal-modified Ni-based hydrotalcite catalyst displayed higher resistance for the sintering of active metal than the Ni-based hydrotalcite catalyst prepared by the conventional method. It was found that the Rh-modified Ni-based catalysts showed high resistance to the formation of carbon compared to Ni-based catalysts. The results suggest that Rh-modified Ni-based catalyst can be applied for the steam reforming (SR) reaction of diesel.
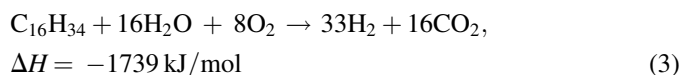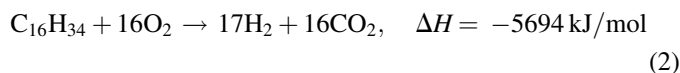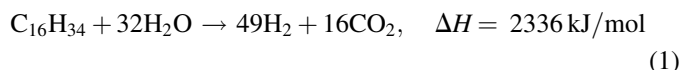© 2008 Elsevier B.V. All rights reserved.

Keywords: Steam reforming; *n*-Hexadecane; Ni-based catalyst; Noble metal-modified Ni-based catalyst; Hydrotalcite; Carbon formation

1. Introduction

Hydrogen is the fuel for fuel cell and can be prepared by the reforming of hydrocarbons such as methane, methanol, ethanol, liquefied petroleum gas (LPG), gasoline, kerosene, diesel and other oil derivatives [1,2]. Among the above hydrocarbon fuels, liquid fuels can be used as the energy carriers in many applications, especially, residential power generation (RPG) systems in remote areas and the auxiliary power units (APU) based on solid oxide fuel cell (SOFC) systems. Especially, diesel is an attractive fuel for the production of hydrogen by reforming because of its high gravimetric and volumetric hydrogen density and a well-established delivery infrastructure. The advantages of using liquid hydrocarbons for portable and stationary fuel processors compete some major challenges, as discussed in a recent review [3].

The technologies to reforming of hydrocarbons are steam reforming (SR), partial oxidation (POX) and autothermal reforming (ATR). These three reforming reactions for hexadecane ($C_{16}H_{34}$) as a surrogate of diesel are shown by the following chemical reactions, using an assumption of CO_2 formation for all the carbon involved [4–8]:

$$C_{16}H_{34} + 32H_2O \rightarrow 49H_2 + 16CO_2, \quad \Delta H = 2336 \, \text{kJ/mol} \tag{1}$$

$$C_{16}H_{34} + 16O_2 \rightarrow 17H_2 + 16CO_2, \quad \Delta H = -5694 \, \text{kJ/mol} \tag{2}$$

$$C_{16}H_{34} + 16H_2O + 8O_2 \rightarrow 33H_2 + 16CO_2,$$
$$\Delta H = -1739 \, \text{kJ/mol} \tag{3}$$

The steam reforming process, which produces high H_2 concentration of around 70% in the crude reformate gas, has widely been used to produce hydrogen from various hydrocarbons. The main products from the steam reforming of hydrocarbons are hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2), however, the formation of ethane, ethylene and methane is usually observed due to the decomposition of hydrocarbon and methanation reactions.

The main problems associated with the reforming of diesel are related to catalyst degradation during the reaction due to the harsh operating conditions (high temperatures and high H_2O/C

ratios) necessary to obtain high hydrogen yields. The reasons of such degradation include poisoning of the catalysts by sulfur, thermal sintering and extensive carbon formation due to the low H/C ratio and the high molecular weight of the molecules present in diesel fuel. Generally, the compositions of reforming catalyst typically comprise of transition metals (Ni, Co, Fe, etc.) or noble metals (Pt, Pd, Ru, Rh, etc.) deposited or incorporated into carefully engineered supports such as thermally stabilized alumina, doped alumina with promoters to accelerate carbon vaporization [9], mixed metal oxides [10]. In the study for catalysts affording steam reforming of diesel, hydrotalcite precursors are promising candidates. It was reported that the anionic clay-based hydrotalcite-like compounds have been researched [11] as the catalyst of various reactions such as hydrogenation, polymerization and reforming, or the antiacid, antipeptin and stabilizer in the medicinal chemistry. The hydrotalcites or hydrotalcite-like compounds after calcinations have the following properties: high-surface area, basic properties, formation of homogeneous mixtures of oxides with very small crystal size, "memory effect", which allows the reconstruction of the original hydrotalcite structure under mild conditions when contacting the product of the thermal treatment with water solutions containing various anions [11]. Takehira and coworkers reported [12–21] that the Ni-loaded catalyst prepared from Mg–Al hydrotalcite-like anionic clay has shown high and stable activity for CO_2 reforming, steam reforming and autothermal reforming of CH_4. Moon et al. reported [22,24] that the Ni-loaded catalyst prepared from Mg–Al hydrotalcite-like anionic clay has shown high and stable activity for steam reforming of LPG. The reforming of diesel over Ni-loaded hydrotalcite-like catalyst has not been reported, yet.

In this work, steam reforming of n-hexadecane (n-$C_{16}H_{34}$), the main component of diesel, was executed in a fixed bed reactor to evaluate the effect of Rh metal added in Ni-based hydrotalcite-like catalysts for restraining sintering of Ni metal.

2. Experimental

2.1. Catalyst preparation

Nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$], aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$], magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$] and rhodium(III) chloride ($RhCl_3 \cdot H_2O$, Rh 38.5–45.55%) with the purity of about 98–99% (Aldrich and Alfa Aesar) were used for the preparation of catalysts without additional purification. The distilled and deionized water was used throughout the whole experiment. The Ni/MgAl oxide catalysts using modified hydrotalcite were prepared by the co-precipitation method reported by Takehira et al. [19] with minor modification. An aqueous solution of the nitrate of Al(III) was added slowly with vigorous stirring into an aqueous solution of sodium carbonate. After disappearing the white powder, an aqueous solution of the nitrates of Mg(II) and Ni(II) was orderly added. The atomic ratio of Ni/Mg was kept at 1.0/2.5. Upon adjusting the pH of this solution to 10 with an aqueous solution of sodium hydroxide, fine greenish slurry was precipitated. The solution

was aged at 60 °C for 8 h and then cooled to room temperature. The precipitate was filtered, washed with distilled water until free from hydroxide ion. Then the precipitate was dried at 60 °C for 12 h in air. The Mg(Ni)–Al(O) hydrotalcite-like precursors obtained were calcined in air at 850 °C for 5 h by increasing the temperature at a rate of 5 °C/min to form the precursor of Ni/MgAl.

Rh loading has been done by adopting "memory effect" as follows: the powder of Ni/MgAl was dipped in an aqueous solution of Rh(III) chloride, stirred for 2 h at room temperature, dried at 110 °C for 5 h and finally calcined at 850 °C for 5 h to form the precursor of Rh–Ni/MgAl(O) catalysts.

2.2. Characterization of catalysts

The chemical composition of the calcined catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a PerkinElmer optima 3300 DV device. Specific surface area of the prepared catalyst was determined by physisorption analyzer (Quantachrome Co., Autosorb-1C). The active metal surface area was measured by chemisorption of CO with a sorption analyzer (Micromeritics Co., Autochem II). Temperature-programmed reduction (TPR) of catalyst was performed using a 5-vol.% H_2/Ar as a reducing gas at a heating rate of 10 °C/min with a sorption analyzer (Micromeritics Co., Autochem II). The X-ray diffraction (XRD) patterns of the catalyst were obtained using Shimazdu XRD-6000 with a Cu Kα radiation at 40 kV and 30 mA.

2.3. Steam reforming of n-hexadecane

Fig. 1 shows the schematic diagram for steam reforming of n-hexadecane. The steam reforming of n-hexadecane was performed in a fixed bed reactor system. Both preheater (14-mm o.d. and 0.25-m length) and steam reforming reactor (14-mm o.d. and 0.25-m length) were made of an Inconel 6600 tube. The Ni-based catalyst was reduced at 800 °C for 3 h in the hydrogen atmosphere prior to the reaction. The flow rates of n-hexadecane and water feeds were controlled by liquid flow controller (LFC) at 7 bar with nitrogen. The feeds were vaporized at 300 °C and preheated at 500 °C before being passed through the catalyst bed in the reactor. The unreacted H_2O was removed by a cold trap and then a gas effluent was analyzed by the on-line gas chromatographs (HP 6890 Series II, TCD and FID) equipped with carbosphere-packed column and DB-2887 capillary column connected to 10-port injector. The qualitative analysis of out gas was measured by GC/MS (HP 5890 Series/MS detector) equipped with HP-1 capillary column. All runs were carried out at a temperature range of 700–950 °C, at an atmospheric pressure with a space velocity of 10,000–100,000 h^{-1} and feed molar ratio of H_2O/C = 3.0.

3. Results and discussion

Blank test for the SR of n-hexadecane was carried out at 900–950 °C with steam for checking repercussions of thermal cracking of n-hexadecane before the catalytic reaction was