



# Steam-CO<sub>2</sub> reforming of methane on Ni/γ-Al<sub>2</sub>O<sub>3</sub>-deposited metallic foam catalyst for GTL-FPSO process

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## ABSTRACT

The steam-CO<sub>2</sub> reforming (SCR) of methane on a Ni/γ-Al<sub>2</sub>O<sub>3</sub>-deposited metallic foam catalyst was assessed for the GTL-FPSO (gas to liquids-floating production, storage and offloading) process. The metallic foam catalyst was prepared by the wash-coating of a γ-Al<sub>2</sub>O<sub>3</sub> layer and the subsequent impregnation of a Ni catalyst. The prepared Ni/γ-Al<sub>2</sub>O<sub>3</sub>/Ni foam catalyst was characterized by scanning electron microscopy and X-ray diffraction. The SCR reaction on the Ni/γ-Al<sub>2</sub>O<sub>3</sub>/Ni foam catalyst was evaluated at different temperatures and space velocities. A uniform and robust catalyst layer was formed on the surface of the Ni foam. The metallic foam catalyst showed a higher CH<sub>4</sub> conversion than a pellet catalyst. The durability of the metallic foam catalyst was evaluated at a space velocity of 130,000 h<sup>-1</sup> for 50 h. The CH<sub>4</sub> conversion decreased by 10% compared to that after the reaction was initiated.

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## 1. Introduction

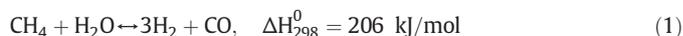
Gas to liquids (GTL) technology has been mainly developed to produce clean synthetic fuels and to transform gas into liquid for more convenient transportation. Natural gas, which is exhaust from an oil field and is not applicable economically due to the limited reserves, can be converted to synthetic liquid fuels using the GTL process [1]. GTL technology is being developed as a new business model by major oil companies because of its merits in terms of the exploitation of small-scale undeveloped gas resources and the alternative to oil depletion.

The GTL process consists of three parts: reforming, Fisher-Tropsch (FT) synthesis and upgrading process. The reforming process involves the conversion of CH<sub>4</sub> to a syngas composed of H<sub>2</sub> and CO. The FT reaction is a synthesis reaction to obtain a high hydrocarbon containing wax as the main species. Finally, a clean synthesis fuel, such as a diesel, kerosene, jet fuel, gasoline and naphtha, can be produced through an upgrading process. Recently, there has been increasing interest in clean synthetic fuel production from stranded gas fields and associated gas in oil fields on ships using GTL-FPSO (floating production, storage and offloading) process.

A reforming process is needed to produce the syngas from natural gas. The reforming process includes steam reforming [2], dry reforming [3], partial oxidation [4], and auto-thermal reforming [5]. Steam

reforming involves the conversion of CH<sub>4</sub> with H<sub>2</sub>O, which is abundant in the ocean, and might be suitable to GTL-FPSO applications. On the other hand, the steam reforming produces syngas with a H<sub>2</sub>/CO molar ratio of 3–4. Therefore, an additional process to adjust the H<sub>2</sub>/CO molar ratio is needed because the FT synthesis requires a H<sub>2</sub>/CO molar ratio of 2 [6]. Dry reforming utilizes CO<sub>2</sub>, which is a typical greenhouse gas, and might be suitable for GTL-FPSO applications because the natural gas in gas fields contains a large quantity of CO<sub>2</sub>. On the other hand, the reformat gas contains a high CO content. Therefore, dry forming does not meet the H<sub>2</sub>/CO molar ratio for FT synthesis. Partial oxidation is unsuitable for GTL-FPSO applications because it is difficult to control the hot spots and explosion danger caused by the high reforming temperature, even if it meets the H<sub>2</sub>/CO molar ratio for FT synthesis. Auto-thermal reforming, which is a combination of steam reforming and partial oxidation, can solve the drawbacks of partial oxidation. On the other hand, it requires an ASU (air separate unit), which is too bulky to equip it on a ship taking a severe space restriction.

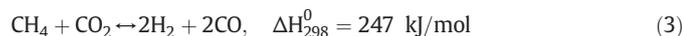
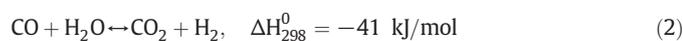
Steam-CO<sub>2</sub> reforming (SCR) is a combination of steam reforming and dry reforming. The H<sub>2</sub>/CO molar ratio of syngas for FT synthesis can be controlled by adjusting the steam to CO<sub>2</sub> molar ratio. Water and CO<sub>2</sub> can be obtained easily from submarine gas fields. Therefore, the SCR is the most suitable reforming process for GTL-FPSO applications. The CH<sub>4</sub> SCR reaction consists of three reactions: steam reforming (SR), water-gas shift (WGS) reaction, and CO<sub>2</sub> reforming, which is called dry reforming (DR) [7].



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The  $\text{CH}_4$  steam reforming produces  $\text{H}_2$  and  $\text{CO}$ , as expressed in Eq. (1).  $\text{CO}$  with  $\text{H}_2\text{O}$  is converted to  $\text{H}_2$  by a WGS reaction, as expressed in Eq. (2).  $\text{CO}_2$  is reacted with  $\text{CH}_4$ , as expressed in Eq. (3), to synthesis gas [8].

Noble metals, such as Pt, Pd, and Ru, are mostly used as catalysts for SCR but these metals are very expensive [9–11]. Recently, it was reported that non-noble metals, such as Co and Ni, also have high reactivity on the SCR reaction. The catalysts were coated on a support, which is normally formed into spherical and cylindrical shapes, to allow the catalysts to be packed into a reactor. Ceramic materials, such as alumina, ceria and zirconia, are mostly selected as the catalyst support [12]. As the reactor scale is increased, however, the catalyst support on the ceramics shows low catalytic activity due to its low thermal conductivity. A uniform temperature distribution through the catalyst bed is a very important factor for maximizing the performance of the SCR reactor [13].

In the present study, metallic foam was selected as a substrate of the catalyst support because of its high thermal conductivity. The catalyst support was coated as a thin layer on the metallic foam substrate. The catalytic activity of the metallic foam catalyst on the SCR was measured under a range of conditions, such as the temperature and space velocity. The metallic foam catalyst was compared with the existing  $\text{Al}_2\text{O}_3$ -pellet catalyst.

## 2. Experiments

### 2.1. Preparation of the metallic foam catalyst

The metallic foam catalyst is composed of Ni as an active site for the SCR reaction,  $\gamma\text{-Al}_2\text{O}_3$  layer as a support of the Ni sites, and the Ni foam

as a substrate for the  $\gamma\text{-Al}_2\text{O}_3$  support, as shown in Fig. 1.  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (SAMCHUN PURE CHEMICAL Co.) was used as a precursor of the Ni catalyst. The Ni foam (Pore Tech Co.) was selected as a substrate of the catalyst. Ni foam has a network structure with a porosity and density of 40 ppi (pore per inch) and  $0.339 \text{ g/cm}^3$ , respectively. The thermal conductivity of the Ni foam was  $\sim 90 \text{ W/m K}$ , which is 3.6 times higher than that of  $\text{Al}_2\text{O}_3$  ( $\sim 25 \text{ W/m K}$ ).

The catalyst could not be coated directly on the surface of the metallic foam. A thin layer of  $\gamma\text{-Al}_2\text{O}_3$  as the catalyst support was wash-coated on the Ni foam using a sol–gel method. After wash-coating, the precursor of the Ni catalyst was impregnated on the  $\gamma\text{-Al}_2\text{O}_3$  support. Consequently, the  $\text{Ni}/\gamma\text{-Al}_2\text{O}_3/\text{Ni}$  foam catalyst was obtained. The detailed procedure for catalyst preparation is as follows.

Aluminum isopropoxide (Alfa Aesar Co.) was dissolved in distilled water, and then polyvinyl alcohol (Alfa Aesar Co.) as a binding agent was added to the aqueous solution. The pH of the aqueous solution was controlled by adding  $\text{HNO}_3$  (JUNSEI) and the pH was maintained at 2.0. After drying for 2 h at room temperature, a transparent sol was prepared.  $3 \mu\text{m}$   $\text{Al}_2\text{O}_3$  powder (Alfa Aesar Co.) was added to the prepared sol in order to increase its viscosity and  $\text{Al}_2\text{O}_3$  content in the sol. After stirring for 1 h, the  $\text{Al}_2\text{O}_3$  sol for wash-coating was prepared.

The Ni foam was cut to the desired size and shape, as shown in Fig. 1(a). A piece of Ni foam was immersed into a 10%  $\text{HCl}$  solution (SK Chemicals Co.) to remove contaminants from the Ni foam surface. After rinsing in distilled water, the Ni foam was dried at a convection oven at  $120 \text{ }^\circ\text{C}$  for 1 h. The  $\text{Al}_2\text{O}_3$  sol was wash-coated on the prepared Ni foam using a dip-coating method. The wash-coating process was repeated to obtain the desired weight fraction. The wash-coated Ni foam was dried at  $100 \text{ }^\circ\text{C}$  for 12 h and pre-calcined at  $300 \text{ }^\circ\text{C}$  in air. Fig. 1(b) shows the prepared  $\gamma\text{-Al}_2\text{O}_3/\text{Ni}$  foam. The weight fraction of the  $\text{Al}_2\text{O}_3$  layer to the Ni foam was 19.59 wt.%.

Finally, the Ni catalyst was coated on the prepared  $\gamma\text{-Al}_2\text{O}_3/\text{Ni}$  foam using a wet-impregnation method. The precursor solution was prepared by dissolving  $\text{Ni}(\text{NO}_3)_2$  in distilled water. The  $\gamma\text{-Al}_2\text{O}_3/\text{Ni}$  foam

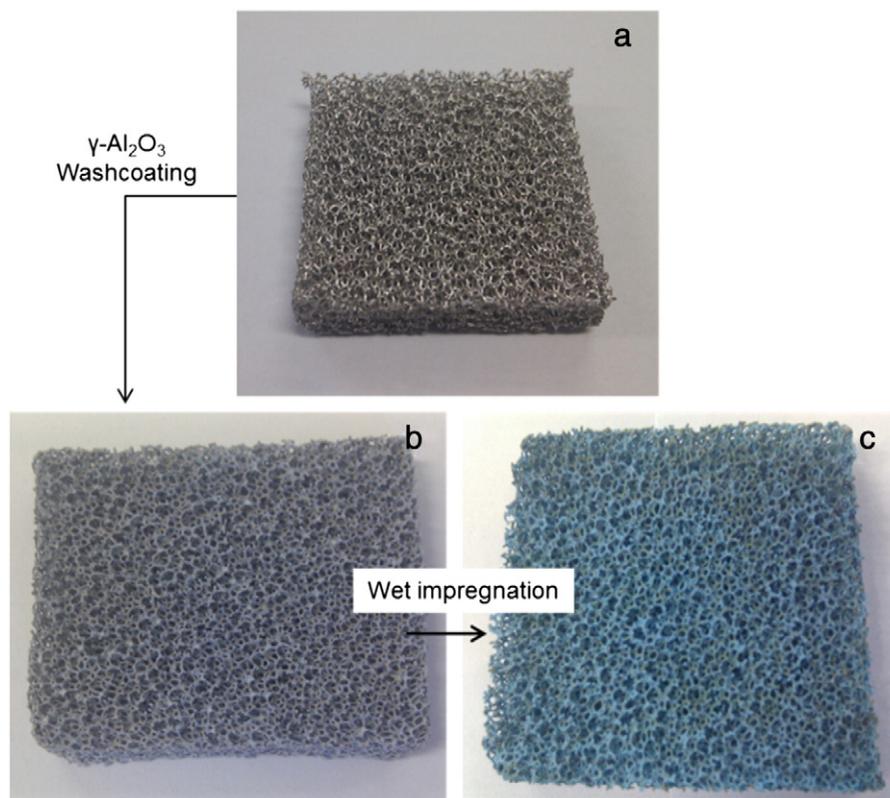


Fig. 1.  $\text{Ni}/\gamma\text{-Al}_2\text{O}_3/\text{Ni}$  foam catalyst; (a) bare Ni foam, (b)  $\gamma\text{-Al}_2\text{O}_3$ -supported Ni foam, and (c)  $\text{Ni}/\gamma\text{-Al}_2\text{O}_3/\text{Ni}$  foam.

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