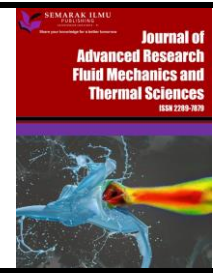




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Producing the Methane Conversion by Steam Methane Reforming Over SiO₂-NiO Catalyst

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ABSTRACT

Methane is the main compound of natural gas and is today used in various industrial processes and also as energy source in gas turbines or natural gas fuelled vehicles. Methane is considered a substantially more potent greenhouse gas than CO₂. This study presents an approach for the catalyst of SiO₂-NiO foam in steam methane reforming. The 35 wt.% composition of Silica (SiO₂) that produced from Rice Husk Ash (RHA) was used in this study by using slurry technique to produce of SiO₂-NiO foam at 950°C and 1250°C of sintering temperatures. The morphologies of SiO₂-NiO foams were observed by using the Scanning Electron Microscopy (SEM) to identify the pore size as a catalyst filter. The pore size of SiO₂-NiO foam were found in the range 13µm to 43µm. SiO₂-NiO catalyst were characterized by temperature programmed reduction (TPR). The TPR result showed present of SiO₂-NiO was successfully activated at the 320°C at 30 minutes. Meanwhile, in the temperature range of 500°C–600°C, the catalyst was shown to be particularly active and stable. The high methane conversion 42% was produced at the reaction temperature of 600°C.

1. Introduction

Ceramic foams are typically porous materials with porosity ranging from 70% to 90%. The increased interest in ceramic foams with controlled porosity levels is primarily due to their unique three-dimensional skeletal structure, high surface area, low density, high thermal stability, low thermal conductivity, and impressive chemical resistance, all of which are impossible to achieve in their dense counterparts. Polymeric foam is a well-known method for processing ceramic foams, resulting in a totally open pore structure [1].

Ceramic foams have been used as catalyst supports in the areas of ammonia oxidation, catalytic combustion, partial oxidation, steam reforming and exhaust catalysis. More works have since appeared on foam-supported catalysts for methane or propane combustions. Small-scale steam

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reforming of methane from biogas could provide a source of hydrogen for applications such as electricity generation via fuel cells. The efficiency of the reforming process is dependent on an active catalyst, so the current work aimed to create a highly active methane reforming catalyst that is resistant to deactivation [2].

Steam reforming, partial oxidation, dry reforming, and auto-thermal reforming are some of the reforming processes [3,4]. Steam Methane Reforming (SMR) is the oldest and most practical method of converting CH₄ to H among the reforming processes. Therefore, Malaysia's National Determined Contribution by 2030 is to reduce its carbon intensity against Gross Domestic Product (GDP) by 45 percent compared to 2005 levels in order to reduce Green House gas (GHG) emissions [5]. The National Green Technology that pertains to Energy, Environment, Economy, and Social Sustainability is included in Malaysia's Green Technology Master Plan (2017-2030), which includes policies and action plans to achieve a low-carbon, resource-efficient economy. SMR is a highly endothermic process that necessitates a reliable heat source. It is normally described as the result of the reforming (Eq. (1)) and the Water Gas Shift (WGS) reactions (Eq. (2)).



Accordingly, The SMR process is carried out in industrial furnaces and is supported by burning a portion of natural gas; as a result, high temperature operation has cost limitations, such as the costly tubular reformer and high energy consumption. Catalytic steam reforming of methane involves the reaction of methane with steam over a catalyst at elevated temperatures at the range of 400°C–900°C [6].

Steam methane reforming (SMR) can be catalysed by several metal catalysts. For instance, cobalt, platinum, palladium, iridium, ruthenium, rhodium and nickel have all been cited as usable for this purpose [7]. Rh is one of the most preferred components in terms of catalytic activity, syngas selectivity, and coking resistance, but researchers have produced an incredibly short contact time reaction using Rh impregnated foam catalyst and obtained extremely high syngas selectivity [8]. Even in the light of this, as one of the relatively lower-activity metals, nickel has become the industry standard catalytic metal used in steam methane reforming because of its relatively low cost, wide availability and sufficient catalytic activity, all combining to make it the most cost-efficient choice [3,9,10].

Nickel (Ni) has been found as a new metal that has catalytic properties for oxygen evolution, as well as much effort has been to developing Ni-based catalysts in alkaline solution, such as oxides, hydroxides, sulphides, and nitrides [11]. Ni has comparable activities to noble-metal catalysts, and increasing the activity catalyst by increasing the loading amount of Ni is reasonable in terms of cost [12]. Per catalyst volume. Although Ni is inferior to noble metals in regards to the resistance to carbon deposition and catalyst oxidation, the high resistance to coke formation and catalyst oxidation can be realised by the addition of minimal amounts of noble metals [13]. The active nickel is metal that has been finely dispersed over a porous alumina usually silica-based carrier [14].

Rice Husk Ash is an agricultural waste material that are produced approximately 150 million tons annually [15-17]. Approximately 20 kg of rice husks could be produced from 100 kg of rice [18]. Silica-based materials have attracted considerable attention because of their high surface area (>200 m²g⁻¹), ordered pore distribution, narrow pore size, high thermal stability and natural regeneration and reusability in comparison with several soils and soil components. Due to these properties, they are ideal base materials as catalysts, catalyst supports and adsorbents, and as a template for other

materials. Silica is appealing as a catalyst support because it has good structural stability, is chemically inert, and is stable even at high temperatures [2]. Furthermore, a combination of SiO₂ with NiO is a promising solution as a catalyst in the steam methane reforming industry [19]. Ni/SiO₂ catalyst synthesized by the ammonia method to obtain 60% conversion of methane (at 700°C).

This study focuses on the fabrication of Silica as derived from RHA with the addition of nickel oxide as a catalyst in the steam methane reforming process. The prepared catalyst has good catalytic activity for methane reforming. SiO₂-NiO foam were prepared by slurry method to produce the high porosity and open pore structure. The goal of this paper is to demonstrate the efficacy of silica-nickel particles as a catalyst for methane reforming processes.

2. Methodology

To prepare SiO₂-NiO catalyst, SiO₂, NiO and PVA powder (as binder) were mixed in an appropriate proportion and the mixture was then transformed into beaker. The NiO composition used in the study of 5 weight percentage in fabrication of green body of SiO₂-NiO foam. Polyurethane (PU) polymeric sponge in cylindrical shape of 125mm x 260mm was applied as the template slurry. The dipped PU foams with SiO₂-NiO slurry were dried in the drying oven at 110°C for 24 hours. The SiO₂-NiO foams were sintered at 1250°C with ramp rate of 2°C/min.

Scanning electron microscopy (SEM) was performed to observe the micro-structural surface morphology of the sample using Hitachi instrument, respectively, with an acceleration voltage of 20 kV.

Temperature programmed reduction (TPR) profiles were recorded on a Micromeritic AutoChem II instrument equipped with a thermal conductivity detector (TCD). Prior to reaction tests, the catalysts were reduced in Hydrogen with the condition of 1000ml/min at 700°C for 90 minutes. The experimental setup is shown in Figure 1. SMR reaction was carried out in a micro reactor whereby the coated substrate plate is inserted into a few slots inside a micro reactor with a channel depth of 200 µm at atmospheric pressure. The reaction temperature was measured by a K-type thermocouple inserted directly at the output stream of micro reactor. Saturated steam was produced by steam generator and injected into the mixer with high pressure pump. The mixing composition of saturated steam and methane directly flows into micro reactor.

The catalytic reactions were conducted at 500, 550 and 600°C with steam to carbon ratio (S: C) of 3:1 for 5 hours. Typically, the S: C 3:1 is chosen to avoid carbon coking build up at lower S: C and at higher S: C to minimize impact of low Hydrogen separation. Meanwhile 5 hours is at most operating reaction time for new catalyst characterization properties. The effluents from the micro reactor were collected by using Tedlar sampling bag and been analyzed with a gas chromatograph of Perkin Elmer Clarus 500 and equipped with a TCD detector.

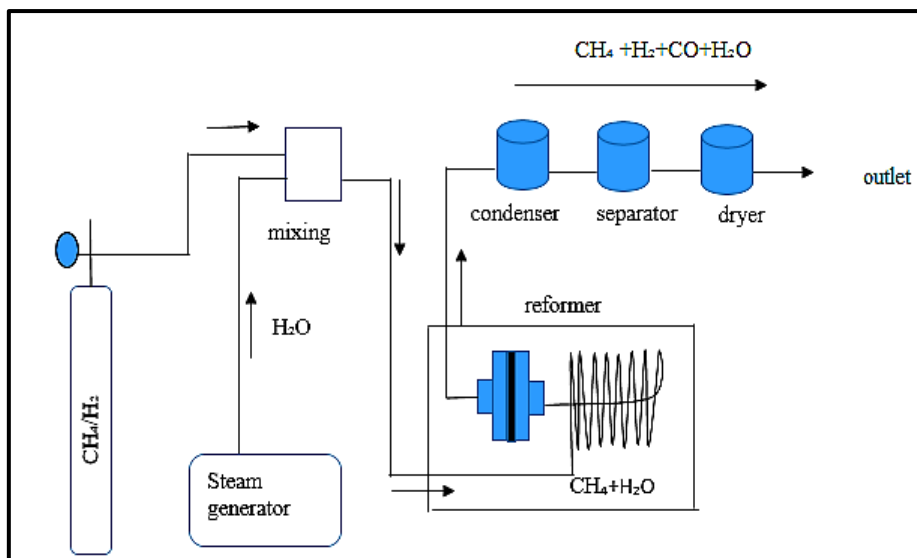


Fig. 1. Process flow diagram for steam methane reforming

3. Results

3.1 Morphology of SiO₂-NiO Foam

The morphology of SiO₂-NiO foam as observed by Scanning Emission Microscopy (SEM). The range of pore size of the SiO₂-NiO foam was in the range of 13μm to 43μm as Figure 2. The SiO₂-NiO foams also consist of the open, closed pores and interconnect of the strut [20,21]. The finding pore size of SiO₂-NiO foam were probably as catalyst as the having “large” (>10nm) and “small” (<10nm) sizes. The gradually form of pores were dense and cause of decreasing pore size [22]. Furthermore, the grains rearrangement was reduced the pore size of SiO₂-NiO foam as increasing of sintering temperatures. However, because the pore size for catalyst is in the range of 10nm to 10μm, the lower pore size (13μm) will still be employed as a steam methane reforming catalyst.

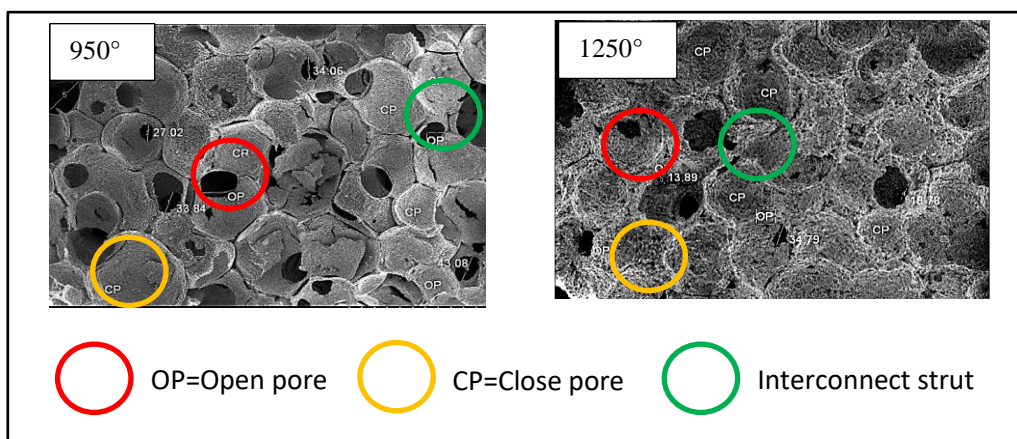


Fig. 2. Morphology of SiO₂-NiO foam

3.2 SiO₂-NiO Catalyst Activations

By activating the catalyst through reduction process, the active metal catalyst was able to form. The catalyst was activated by flowing H₂ gas through the catalyst solid in the micro reactor. The reducibility of the catalyst was determined by performing Temperature Programming Reduction (TPR).

The TPD results obtained from foam catalysts were related to the pore size of the catalysts. Larger pore size diameter of the catalyst results in larger material size and lower material dispersion.

The results in Figure 3 were obtained from the sample 5% Nickel loading calcination at 700°C which used in SMR. The peaks and area shown in the results indicating H₂ consumption. Thermal Conductivity Detector (TCD) concentration of the TPR depending on the Nickel weight percent. The highest peak indicating the most suitable temperature and time for reducing process to become NiO Catalyst active metal catalyst. Referring to Figure 3 the highest peak located at 320°C and timed at 30 minutes. The highest peak indicated the most suitable temperature and time for reducing NiO to Ni. The narrow peak indicates that the solid has a good dispersion with a good homogeneity of the active phase NiO over the support [23].

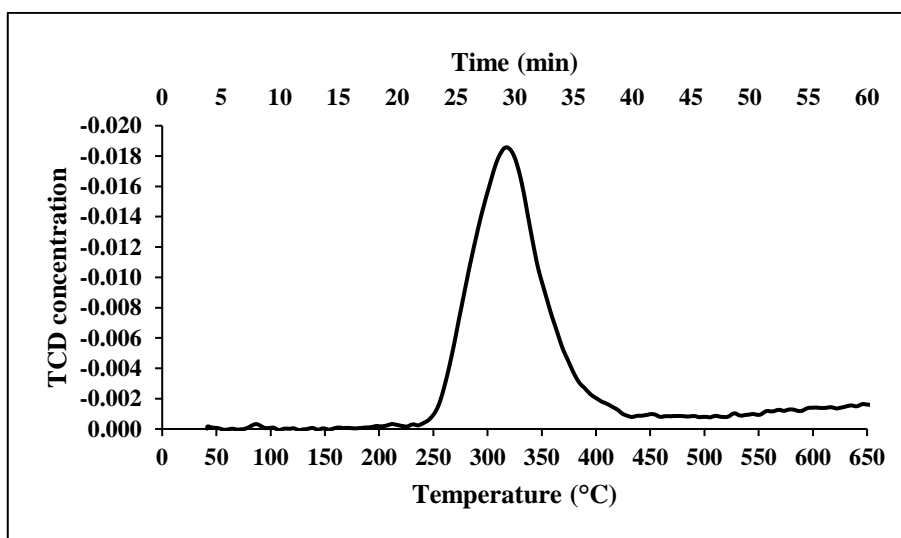


Fig. 3. TPR result for Nickel Oxide Calcined at 700°C

3.3 Effect of Reaction Temperature on Methane Conversion

The reaction temperatures in this study are in the range 500°C to 600°C. It was observed that methane was successfully converted at all chosen reaction temperatures (500°C, 550°C and 600°C). The minimum of reaction temperature in this study are 500°C because the amount of H₂O vapor does not significantly influence CH₄ conversion below 500°C. The rate of the conversion of methane (CH₄) was found to be between 34.72% and 42.60%. The presented rate of conversion CH₄ at low temperatures is due to agent foaming presented in silica which K₂O cause the ash to remain sticky at a much lower temperature and reacts with silica in the ash to produce eutectic mixes with low melting points ranging from 500°C to 600°C. The catalytic activity for react temperature on methane conversion as shown in Figure 4.

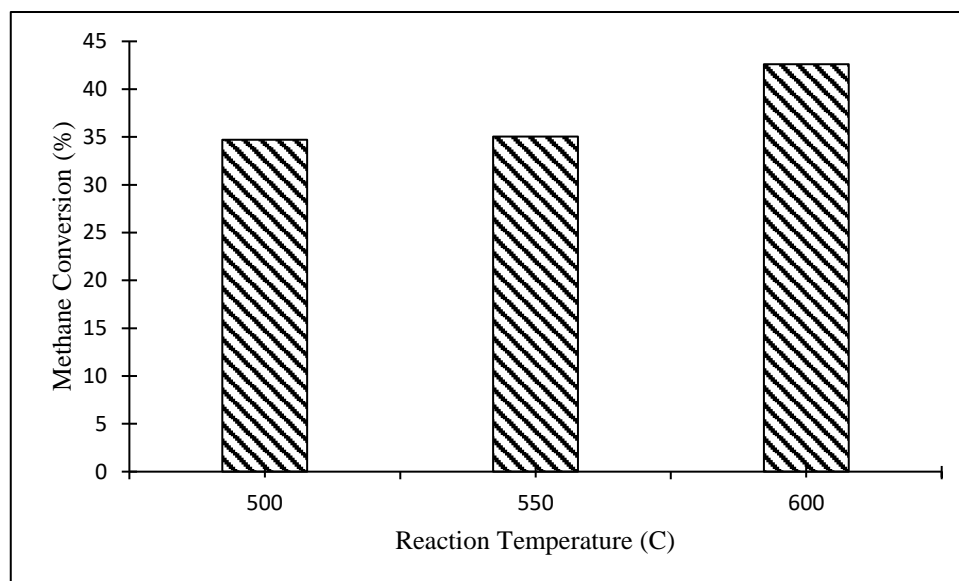


Fig. 4. CH₄ conversion by SiO₂-NiO catalyst at 180 min reaction hour

4. Conclusions

The SiO₂-NiO foam were successfully fabricated via replication sponge method at different sintering 950°C to 1250°C. Morphology of SiO₂-NiO foam for catalyst through SEM micrographs showed the formation pore size in the range 13µm to 43µm with the open pore, closed pore and interconnect strut of foam. The catalyst of SiO₂-NiO has been successfully trial run in a micro reactor with a few findings. The operating capability condition for methane conversion using SiO₂ as derived from RHA and Nickel had been discovered at 500°C to 600°C. Therefore, this constant stage is the optimal operating capability condition with 600°C reaction temperature yield the maximum output with the higher conversion 42.60% of methane. For future work, the reaction interval should be decreased to a smaller scale in order to establish the most effective reaction settings.

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