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# Enhancing hydrogen production by dry reforming process with strontium promoter

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## ABSTRACT

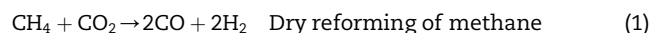
Hydrogen is an ideal energy carrier and can play a very important role in the energy system. The present study investigated the enhancement of hydrogen production from catalytic dry reforming process. Two catalysts namely Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> promoted with different amounts of strontium were used to explore selectivity and yield of hydrogen production. Spent and fresh catalysts were characterized using techniques such as BET, XRD, H<sub>2</sub>-TPR, CO<sub>2</sub>-TPD, TGA and O<sub>2</sub>-TPO. The catalyst activity and characterization results displayed stability improvement due to addition of Sr promoter. The least coke formations i.e. 3.8 wt% and 5.1 wt% were obtained using 0.75 wt% Sr doped in Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 0.5 wt% Sr doped in Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts respectively. Time on stream tests of promoted catalysts for about six hours at 700 °C showed stable hydrogen selectivity. Moreover, the hydrogen selectivity was significantly improved by the addition of Sr in Ni and Co based catalysts. For instance the hydrogen selectivity increased from 45.9% to 47.8% for Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and from 48% to 50.9% for Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst by the addition of 0.75 wt% Sr in Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 0.5 wt% Sr in Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst respectively.

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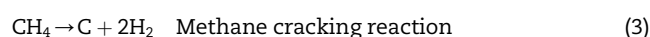
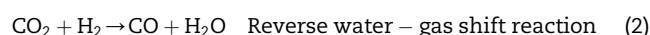
## 1. Introduction

The depletion of worldwide petroleum reserves and stringent environmental regulations to mitigate CO<sub>2</sub> emissions has stimulated research towards hydrogen production. Hydrogen is clean and sustainable energy source. The use of hydrogen has considerable advantage in decreasing the greenhouse gases, improving the security of energy supply and enhancing the economic competitiveness, potential fuel for transport sector [1–3]. Hydrogen is produced using traditional processes such as natural gas reforming, coal gasification or water electrolysis [4–8]. The methane reforming of carbon dioxide is an efficient hydrogen-producing method but requires optimization of the process technique. The

process is very useful to application with oilfield gas containing large amounts of CO<sub>2</sub> gas that can be converted to synthesis gas without the requirement of CO<sub>2</sub> separation. However, because of the rapid catalyst deactivation the process has not largely been implemented in the industry. The deactivation is due to carbon deposition and the sintering of both support and active metal [9,10]. The main reaction of the reforming process is:

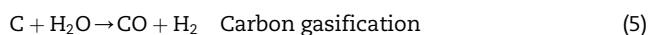
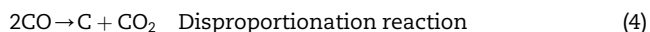


While side reactions include the following:



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It is well known that the performance of supported catalysts could be improved by selection of proper promoting materials. Supported transition metals especially Ni, Ru, Rh, Pd, Ir, and Pt have considerable activity for reforming reactions. But supported nickel is preferred and more frequently used for industrial reforming processes because of its high availability and lower cost [11,12]. However, the Ni-based catalysts are readily deactivated by the deposition of carbon on the active centers. Noble metal-based catalysts, like palladium, rhodium, and platinum are used to reduce the deactivation [13–15]. On the other hand, supported cobalt catalyst shows considerable activity for dry reforming of methane process [16]. Even though the catalytic performance, such as activity is neither superior to nickel nor to the noble metal catalyst, study on the supported cobalt catalysts demonstrate good stability against temperature changes and that cobalt catalyst is a potential alternative among non-noble metal catalysts with a small amount of carbon deposition and better catalytic performance [17]. Various promoters have been tested with metal-based catalysts in an attempt to decrease carbon deposition and prolong the life of the catalyst [18–20]. Yue et al. investigated the promotional effect of Ca on the catalytic property of Pd/Ce–Zr/Al<sub>2</sub>O<sub>3</sub> catalyst towards methane combustion. They found that addition of Ca to Pd/Ce–Zr/Al<sub>2</sub>O<sub>3</sub> increased extremely both low-temperature activity and high temperature thermal stability [21]. Fatish et al. investigated the reforming of methane by Zr and Ce promoters and found that Zr enhanced the gasification of formed carbon [22]. The study of SanJose'-Alonso et al. revealed that the addition strontium as promoter could prevent the catalyst from carbon deposition [23]. Alternatively, Chang-lin et al. studied the effect of strontium promoter on the catalytic performance of Co/Al<sub>2</sub>O<sub>3</sub> catalyst for partial oxidation of methane to synthesis gas and found that it greatly enhanced the catalyst activity and stability [24]. In this paper, the selectivity and yield performances of hydrogen production from methane reforming with carbon dioxide were studied. Strontium promoted nickel and cobalt catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were used for the reforming reactions.

## 2. Experimental

### 2.1. Catalysts development

Nickel, cobalt and strontium nitrate salt precursors: [(Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), (Co (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and Sr (NO<sub>3</sub>)<sub>2</sub>] and high surface area alumina support of 230 m<sup>2</sup>/g BET were wet impregnated to prepare promoted Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (SA-6175) and Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (SA-6175) catalysts with different loadings of Sr (0.0–1.5 wt%). The catalysts were dried for 13 h at 110 °C and calcined at 600 °C for 5 h. The specific surface area was measured using an automated gas sorption analyzer (Micromeritics Tristar II 3020) via N<sub>2</sub> adsorption in liquid N<sub>2</sub>. The sample was degassed in vacuum for at least 3 h at 300 °C before analysis. BET method was used to determine specific surface

area of samples. EXSTAR SII TG/DTA 7300 (Thermo-gravimetric/Differential) analyzer was used to measure thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of coke deposited on used catalyst in air atmosphere up to 800 °C at a heating rate 10 °C/min. The deposited amount of carbon was determined from the weight loss.

### 2.2. Catalytic activity study

Catalytic activity was monitored in a fixed-bed continuous-flow reactor. Fig. 1 displays experimental setup which comprises three sections: gases delivery, catalytic reactor and products analysis. The reforming of methane was carried out using 0.6 g of catalyst in a 9.4 mm i.d. and 48 cm long stainless steel-tube at atmospheric pressure. A thermocouple placed in the center of the catalyst bed was used to measure the reaction temperature. Before the reaction, the catalyst was reduced at 550 °C using hydrogen flow rate of 40 ml/min for 2 h. Then N<sub>2</sub> gas was used to cool the reactor to the desired temperature. Volume ratio of feed gases, methane/carbon dioxide/Nitrogen was set to 17/17/2. The total flow rate was 36 ml/min with a space velocity of 3600 ml/h·g<sub>cat</sub>. Reaction temperatures of 500, 600 and 700 °C were employed. Online gas chromatography (Varian Star 3400) equipped with a thermal conductivity detector was used for analysis of effluents. After the reaction, again nitrogen gas was introduced to replace the reactant gases at the reaction temperature. Then the reactor was cooled to room temperature and subsequently the cooled catalyst was taken for characterization. The reported results present an average of duplicate or triplicate of experimental runs. These runs were done with good reproducibility. In this work, % selectivity and % yield were calculated according to the following formulae:

$$\% \text{Selectivity of H}_2 : S_{\text{H}_2} = \frac{\text{moles of hydrogen produced}}{\text{Total moles of product}} \times 100$$

$$\% \text{Yield of H}_2 : Y_{\text{H}_2} = \frac{\text{moles of hydrogen produced}}{2 \times \text{moles of CH}_4 \text{ in feed}} \times 100$$

### 2.3. Catalyst characterization

#### 2.3.1. Textural measurements

In the BET surface area measurement, about 0.3 g sample was tested for each run. All the runs were done with 40 points (20 adsorption, 20 desorption).

#### 2.3.2. X-ray diffraction

Rigaku (Miniflex) diffractometer with a Cu K $\alpha$  radiation operated at 40 kV and 40 mA was used to perform X-ray diffraction (XRD) studies of catalysts. The analyses were carried out from 10° to 85° with a step size of 0.020°/min. The divergence slit was set at 1° and the anti-scatter slit was set at 0.5°. The ceramic tube with Cu K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ) was set up to operate at a voltage of 40 kV and 30 mA current. Jade diffraction software was used to identify the diffraction peaks.

2.3.3. Temperature programmed characterization of catalysts  
Chemisorption apparatus (Micromeritics Auto Chem II apparatus) was used to measure Temperature programmed

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