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# Production of hydrogen by catalytic methane decomposition over alumina supported mono-, bi- and tri-metallic catalysts

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## ABSTRACT

Hydrogen, an environmentally benign source of energy, has significantly attracted the attention of researchers in recent decades. This article discusses hydrogen production by methane decomposition over alumina supported iron-nickel-cobalt based mono-, bi- and tri-metallic catalysts. The catalysts were prepared by using wet-impregnation strategy. The fresh catalysts were characterized using different techniques such as BET, H<sub>2</sub>-TPR, and XRD. Likewise, a morphological study of selected spent catalyst was complemented by employing TEM as well as TPO. The catalytic activity results revealed that bimetallic catalysts consisting of 30 wt.% Fe and 15 wt.% Co exhibited excellent performance among all the tested catalysts. In addition, the results of sensitivity analysis revealed that an activation span of 90 min, GHSV of 5000 mL/h g<sub>cat</sub> at 700 °C as a reaction temperature were found to be the optimum process conditions. Significantly, it can be seen that in an extended run of 1400 min involving 12 regeneration cycles, high methane conversion (>55%) can be maintained.

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## Introduction

The search for alternative and sustainable source of energy has intensified over the decades [1] due to the depletion of fossil fuels along with the related environmental pollution [2]. The fossil fuels generate greenhouse gases such as CO<sub>2</sub> and CH<sub>4</sub> that cause global warming [3,4]. To reduce the influence of greenhouse gases and to find other source of energy, many methods have been examined [5,6], in which the greenhouse

gases are used as feed stock for steam reforming, partial oxidation and dry reforming [7–10], etc., to produce syn-gas or hydrogen. Today hydrogen is primarily produced from fossil fuels, one extremely attractive route for the future is catalytic methane decomposition (CMD) [11–14]. The CMD is typified by the generation of clean hydrogen and valuable carbon as per Equation (1). In addition, the associated carbon oxides formed with conventional reforming of methane are eliminated in the CMD process [15–18]. Despite these benefits, the CMD process

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is still limited to laboratory scale studies. The development of a process depends upon the availability of a suitable catalyst system. A lot of efforts have been made in the past to achieve this goal and several metal catalysts [19,20], diverse supports including various carbon based catalysts have been investigated extensively [21,22]. Transitional metals such as Ni, Co and Fe are the most studied catalysts for the CMD reaction due to economic reasons [23,24]. Nevertheless, the overall performance of the catalysts for CMD depends on all the catalysts components (metals, supports and promoters, etc.) [25]. It has been reported that Fe based catalysts are very efficient for CMD process [26,27] and their combination with other active metals such as Co and Ni lead to some promising catalysts [28].



In this submission preparation, characterization and catalytic performance of Fe/Al<sub>2</sub>O<sub>3</sub>, Co-Fe/Al<sub>2</sub>O<sub>3</sub>, Ni-Fe/Al<sub>2</sub>O<sub>3</sub> catalysts with different amounts of Co and Ni loading for the catalytic decomposition of methane to pure hydrogen and carbon nanomaterials, is reported. The effect of Ni, Co, and Ni,

$$\text{Relative Carbon Yield (\%)} = \frac{\text{Weight of deposited carbon on the catalyst}}{\text{weight of metal content (Fe) in the catalyst}} \times 100\% \quad (4)$$

Co on Fe/Al<sub>2</sub>O<sub>3</sub>, reaction temperature, F/W, activation time and regeneration cycles on catalyst performance are discussed.

## Experimental

### Catalyst preparation

Alumina supported Ni, Co and Fe based catalysts used in this study were prepared by incipient wet-impregnation method. All chemicals used were analytical grade. In a typical wet-impregnation method, the required amount of metal precursors i.e., [Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O], [Ni(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O] or [Co(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O] were dissolved in double-distilled water, followed by contacting with γ-Al<sub>2</sub>O<sub>3</sub> under constant stirring at 80 °C for 3 h, dried at 120 °C for 12 h and calcined 450 °C in air for 3 h. The Fe loading was maintained at 30 wt.%. Ni and Co loadings were varied on purpose. The catalysts are denoted as XCo-

YNi-30Fe/Al catalysts, where X and Y indicate the weight loadings of Co and Ni. All tested catalysts and their compositions are presented in Table 1.

### Catalyst testing

CMD experiments were performed in a fixed bed reactor (ID 10 mm). Prior to CDM reaction, the catalysts (0.3 g) were *in-situ* reduced under H<sub>2</sub> flow (40 ml/min) at 500 °C for 100 min followed by flushing with N<sub>2</sub> for 20 min. Then the reactor was programmed up to the desired reaction temperature 700 °C under N<sub>2</sub>. The products were analyzed by using an online GC (Alpha MOS PR 2100) equipped with a sampling valve and two thermal conductivity detectors for analyzing lighter and heavier gases. CH<sub>4</sub> conversion, H<sub>2</sub> and carbon yields were calculated using the following Equations (2)–(4).

$$\text{CH}_4 \text{ Conversion (\%)} = \frac{\text{CH}_{4\text{in}} - \text{CH}_{4\text{out}}}{\text{CH}_{4\text{in}}} \times 100 \quad (2)$$

$$\text{H}_2 \text{ Yield (\%)} = \frac{\text{H}_{2(\text{out})}}{2 \times \text{CH}_{4(\text{converted})}} \times 100\% \quad (3)$$

### Catalyst characterization

The specific surface areas, pore volumes and PSD of the catalysts were determined from N<sub>2</sub> adsorption-desorption data at –196 °C by using Micromeritics Tristar II 3020. For each analysis, 0.3 g of catalyst was degassed at 250 °C for 3 h to rid the catalyst surface from moisture and other adsorbed gases.

The temperature programmed reduction (TPR) measurements were performed on a Micromeritics Auto Chem II apparatus. Catalyst samples (~70 mg) were pretreated with high purity Argon at 150 °C for 30 min, followed by cooling down to room temperature and then heated in a furnace up to 800 °C (10 °C min<sup>-1</sup>, under 10 vol.% H<sub>2</sub>/Ar mixture). The signal of H<sub>2</sub> consumption was monitored by TCD.

Powdery X-ray diffraction (XRD) analyses of the fresh and used catalysts were carried out using a Rigaku (Miniflex) diffractometer with a Cu Kα radiation operated at 40 kV and 40 mA. The scanning step and range of 2θ for analysis were 0.02° and 20–80°.

Transmission electron microscopy (TEM) measurements of spent catalysts were performed with a JEOL JEM-1400 TEM operated at 120 kV accelerating voltage for in-depth analysis of the morphology of the nano-structured deposited carbon.

The coke deposition on the surface of the spent catalysts during 3-h reaction time was analyzed by thermo-gravimetric analysis (TGA) in air using EXSTAR SII TG/DTA 7300 (Thermo-gravimetric/Differential) analyzer. The used catalysts were heated in air from room temperature to 800 °C at a heating rate of 20 °C min<sup>-1</sup>.

**Table 1 – Catalysts with their composition.**

Catalysts	Composition
30Fe-Al	30% Fe/Al <sub>2</sub> O <sub>3</sub>
30Fe-15Ni-Al	30% Fe-15%Ni/Al <sub>2</sub> O <sub>3</sub>
30Fe-5Ni-10Co-Al	30%Fe-5%Ni-10%Co/Al <sub>2</sub> O <sub>3</sub>
30Fe-7.5Ni-7.5Co-Al	30% Fe-7.5%Ni-7.5%Co/Al <sub>2</sub> O <sub>3</sub>
30Fe-10Ni-5Co-Al	30% Fe-10%Ni-5%Co/Al <sub>2</sub> O <sub>3</sub>
30Fe-15Co-Al	30% Fe-15%Co/Al <sub>2</sub> O <sub>3</sub>

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