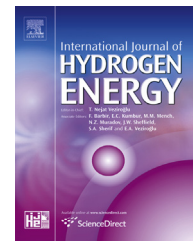




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# Hydrogen production by high temperature water gas shift reaction over highly active and stable chromium free Fe–Al–Ni catalysts

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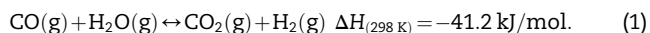
## ABSTRACT

High temperature water gas shift reaction is carried out over nanocrystalline chromium free Fe<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub>–NiO catalysts with and without alkaline earth promoters. Mesoporous catalysts are prepared by coprecipitation method. The prepared catalysts are characterized using N<sub>2</sub> adsorption (BET), temperature-programmed reduction (TPR) and desorption (TPD), X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The results indicate that alkaline earth promoters improve the catalytic activity and suppress the progress of methanation reaction, which is related to the increment of amount in weakly basic sites through promoter addition. Furthermore, it is found that the Fe<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub>–NiO catalyst promoted by Ba exhibits the highest catalytic activity and the lowest methanation among the prepared catalysts and the commercial chromium containing one. In addition, the effect of Ba content on the CO conversion is investigated and the results indicate that the catalyst with 3 wt.% Ba possesses high activity and stability without any decrease in CO conversion during 50 h time on stream.

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## Introduction

Due to the increasing environmentally friendly energy concerns, H<sub>2</sub> attracts significant research interest because it is a clean energy carrier [1,2]. The water-gas shift (WGS) reaction is an exothermic reaction and important process for hydrogen production, particularly in ammonia synthesis plant, where CO is reacted with water to give H<sub>2</sub> and CO<sub>2</sub> (Eq. (1)) [3]:



Because of thermodynamic and kinetic aspects, water gas shift (WGS) reaction in commercial plants was performed in two stages. The first stage at high temperature (HTS, at temperature ranged 350–500 °C) using iron based catalysts and the second stage at low temperatures (LTS, at temperature ranged 190–250 °C) using CuO–ZnO–Al<sub>2</sub>O<sub>3</sub> catalyst [4]. The conventional high temperature water gas shift (HTS) catalyst is Fe<sub>2</sub>O<sub>3</sub>–Cr<sub>2</sub>O<sub>3</sub>–CuO, in which chromium is a structural promoter, avoiding the sintering of the active phase of catalyst (Fe<sub>3</sub>O<sub>4</sub>) during the reaction [5,6]. In this catalyst, CuO

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(2–4 wt.%) was also used as a promoter, which can create additional active sites and improve the catalytic activity of water gas shift catalyst [7]. However, it is well known that the commercial high temperature water gas shift catalyst with 8–14 wt.%  $\text{Cr}_2\text{O}_3$  generally contain about 2 wt.%  $\text{Cr}^{6+}$  compound, which is highly toxic to humans and environment [8–10]. Thus, the removal of chromium from the catalyst composition has received much attention in recent years.

Reddy et al. [11] was studied different types of metal-modified ferrites codoped with Cu (Ce, Ni, Co, Mn, and Zn) in order to prepare Cr-free Fe-based WGS catalysts. In addition, the effects of  $\text{ThO}_2$ ,  $\text{MnO}_2$ ,  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  on the catalytic performance of iron based water gas shift catalyst were investigated and the results revealed that  $\text{Al}_2\text{O}_3$  could improve the catalyst stability in high temperature water gas shift reaction [12–14]. Jeong et al. compared the catalytic activity of Fe–Al–Cu and Fe–Al–Ni catalysts using simulated waste-derived synthesis gas and found that Fe–Al–Cu has higher activity than Fe–Al–Ni catalyst [15].

Zhang et al. [16] investigated the effect of Cu loading on the structural and catalytic properties of the Cr-free Fe–Al–Cu catalysts. Although the synthesized catalysts exhibited high activity but the results also showed that at higher Cu contents, the loss in catalytic activity with time-on-stream may be an issue. It is known that the melting point of nickel (1455 °C) is higher than copper (1085 °C) and also it is active in water gas shift reaction. Based on these properties, it seems that the nickel promoted iron based catalysts can exhibit higher stability in this reaction compared to high content copper promoted iron based catalysts [17]. But the main drawback is the production of a small amount of  $\text{CH}_4$  produced by methanation reaction [17]. Production of methane should be avoided from the economical point of view, since it consumes hydrogen and lowers the efficiency and productivity of the hydrogen production process. It is known that the addition of alkali and alkaline earth metals can suppress the methanation activity. Hwang et al. [18] used potassium as promoter for Ni catalysts for HTS reaction and found that potassium promoted Ni catalyst is more active and selective for the WGS reaction than the unmodified Ni catalyst. The effect of Cs addition on the catalytic performance of Fe–Ni catalysts was also investigated by Lee et al. [19]. They found that the Cs/Ni/Fe catalysts with 3.9–6.0 wt.% Cs exhibited high CO conversion and low methane formation due to increasing the amount of weakly basic sites in promoted catalyst. In this paper, we prepared promoted chromium free  $\text{Fe}_2\text{O}_3$ – $\text{Al}_2\text{O}_3$ –NiO catalysts with alkaline earth promoters (Ba, Ca, Sr and Mg) and the effect of promoter addition on the HTS and methanation activity was investigated.

## Experimental

### Materials

The starting materials were  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NaOH}$ . All chemicals were of analytical grade and used without further purification. Distilled deionized water was used for the preparation of all aqueous solutions.

### Catalyst preparation

The conventional coprecipitation method was employed for preparation of catalysts. The details of preparation method were reported in our earlier work [20]. Depending on the catalyst composition the desired amounts of metal salt precursors were dissolved in distilled water. After that an aqueous solution of  $\text{NaOH}$  (1 M) was added dropwise at room temperature to the prepared solution containing metal salt precursors under rapid stirring by careful pH adjustment to 10. After precipitation, the slurry was refluxed at 60 °C for 5 h under vigorous stirring. Then the suspension was cooled to room temperature, filtered and washed several times with deionized water for an effective removal of ions. The washed filter cake was dried at 90 °C for 24 h and calcined at 400 °C for 4 h in air atmosphere with the heating rate of 5 °C/min.

### Characterization

The X-ray powder diffraction was used to study the crystalline structure of the prepared catalysts using a X-ray diffractometer (PANalytical X'Pert-Pro). The specific surface area was determined by the BET method using  $\text{N}_2$  adsorption at –196 °C by an automated gas adsorption analyzer (Tristar 3020, Micromeritics). The Barrett, Joyner and Halenda (BJH) method was employed to determine the pore size distribution from the desorption branch of the isotherm. The reduction behavior of the prepared catalysts was investigated by temperature-programmed reduction (TPR) technique using an automatic apparatus (Chemisorb 2750, Micromeritics) equipped with a thermal conductivity detector. Before the TPR experiment, the calcined sample (ca. 50 mg) was degassed under  $\text{N}_2$  atmosphere at 250 °C for 2 h. After that the pre-treated catalyst was subjected to a reduction treatment with a heating rate of 10 °C/min in a reducing gas flow (20 mL/min) containing a mixture of  $\text{H}_2$ :Ar (10:90).

Temperature programmed desorption behavior of  $\text{CO}_2$  and  $\text{CO}$  was carried out on the same apparatus as mentioned for  $\text{H}_2$ -TPR. Before the experiment, the catalyst was reduced at 400 °C under a reducing gas flow (30 mL/min) containing a mixture of  $\text{H}_2$ :Ar (10:90) for 2 h. After that the reduced catalyst was saturated by the  $\text{CO}$  or  $\text{CO}_2$  at room temperature for 1 h and then the saturated sample was purged with He at room temperature for 30 min. TPD was carried out with a ramp of 10 °C  $\text{min}^{-1}$  from room temperature to a needed temperature under He stream. The surface morphology of the catalysts was observed with scanning electron microscopy technique (SEM, Vega@Tescan).

### Catalytic reaction

The high temperature water gas shift reaction tests were evaluated using 0.3 g powder (0.1 g catalyst + 0.2 g  $\alpha$ -alumina as diluent) in a tubular fixed bed flow reactor made of quartz (ID 8 mm × 500 mm long) under atmospheric pressure. The catalyst bed temperature was measured by a thermocouple inserted in bottom of the catalyst bed. The catalyst weight in each reaction was held constant (100 mg and with particle size of 0.25–0.5 mm). The feed composition was a gaseous mixture of 30%  $\text{CO}$ , 60%  $\text{H}_2$ , 10%  $\text{CO}_2$  and a water steam with desired

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