A facile method for preparation of iron based catalysts for high temperature water gas shift reaction

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ABSTRACT

Nanocrystalline Fe_3O_4 based catalysts with theoretical particle size of 31–78 nm were synthesized by a facile direct pyrolysis method and employed in high temperature water gas shift reaction. XRD analysis showed that this method led to obtaining the catalysts directly in the active phase with chromium and copper incorporated into magnetite lattice. The results showed that the addition of chromium significantly increases the BET surface area of the pure iron oxide from 14.87 to 35.42 $m^2\,g^{-1}$. Among the catalysts evaluated, Fe–Cr–Cu catalyst revealed higher activity compared to commercial catalyst and showed high stability during 10 h time on stream.

1. Introduction

The water-gas shift (WGS) is one of the oldest heterogeneous catalytic reactions operating in industry: $CO + H_2O \leftrightarrow CO_2 + H_2$. In recent years, great attention has been focused on hydrogen generation from synthesis gas produced by coal gasification or fuel reforming to power fuel cells. WGS has been gaining renewed interest for preliminary CO clean up and additional hydrogen production from synthesis gas [1,2]. To obtain economically acceptable conversions, this reaction is generally carried out according to a two-step process, HTS (high temperature shift reaction, 350–450 °C) and LTS (low temperature shift reaction, 250–300 °C), over two main types of catalysts, Fe–Cr and Cu–Zn based, respectively.

The industrial HTS catalyst is mainly composed of iron oxide particles with the addition of promoters such as chromium and copper. These catalysts are often commercialized as hematite (α-Fe_2O_3) and are reduced in situ to produce magnetite (Fe_3O_4), which is found to be the active phase [3]. Under HTS conditions, pure magnetite catalyst rapidly sinters and loses its activity. The addition of chromia leads to a better resistance against sintering and as a consequence against the decrease of surface area, acting as a textural promoter [4]. Although the highest sintering resistance is obtained when chromia concentration is around 14 wt.% [5], the best compromise is achieved with concentration of 8–10 wt.%. At these lower values, there is an optimization of both the textural properties and intrinsic activity (activity per unit of surface area of the catalyst). This balance must be taking into consideration because Cr(III) replaces active Fe(III)/Fe(II) octahedral sites [5] and at higher concentration, there is a drawback concerning the loss of intrinsic activity [5]. Copper oxide has also been used as promoter for HTS catalysts, providing a final material with superior selectivity and catalytic performance than the pure mixed oxide Fe_2O_3/Cr_2O_3 [6,7]. It is important to note, however, that both promoters are necessary since only Fe_2O_3/CuO has smaller intrinsic activity than pure Fe_2O_3 [6,7].

These catalysts are often synthesized by a coprecipitation method as Fe_2O_3 which reduced to the active phase. The reduction process is highly exothermic and should be controlled to avoid the production of metallic iron, which may catalyze undesirable reactions. In industrial processes, large amounts of steam are used to inhibit metallic iron formation, but this implies high operational costs [4].

There are several methods to prepare these materials directly in the active phase such as oxidation–precipitation method [8], co-precipitation of Fe(II) and Fe(III) ions by a base, usually sodium hydroxide or aqueous ammonia [9], thermal decomposition of alkaline solution of Fe(III) chelate in the presence of hydrazine and by sonochemical decomposition of hydrolyzed Fe(II) salt followed by thermal treatment [10], etc.

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In general, these methods need complicated synthetic steps, high reaction temperature, surfactant, and template. Although the synthesis of Fe_3O_4 based materials has been well documented, the large-scale, low-cost, and template-free preparation of Fe_3O_4 based materials is still of great interest [11]. In general, ethylene glycol, as solvent, reducing agent, complexing and capping agents, was widely used during the synthesis of various nanoparticles of metals and metal oxide [12]. Chen et al. have developed an alternative strategy for the preparation of Fe_3O_4 nanosheets by direct pyrolysis of the EDTA ferric sodium salt and ferric nitrate-ethylene glycol gel [11]. During the synthesis, the reducing atmosphere which created from the decomposition of the ferric nitrate-ethylene glycol gel caused the partial reduction of Fe(III) to Fe(II) and resulted in the formation of Fe_3O_4 [11].

This paper describes for the first time the use of a facile pyrolysis method for the synthesis of Fe_3O_4 based catalysts for WGS reaction without adding any template and surfactant. The catalytic activity of prepared catalysts was investigated and the addition of chromium and copper promoters was studied.

2. Experimental

2.1. Fe₃O₄ based catalyst preparation

Four types of catalysts were prepared with different Fe/Cr/Cu ratios by a facile pyrolysis method. The prepared samples were (i) pure iron oxide, (ii) iron and chromium mixed oxide with weight ratio Fe/Cr = 10 (Fe–Cr); (iii) iron and copper mixed oxide with weight ratio Fe/Cu = 40 (Fe–Cu), and (iv) iron, chromium and copper mixed oxide with weight ratio Fe/Cu = 20 and Fe/Cr = 10 (Fe–Cr–Cu). The catalysts were prepared by the pyrolysis route. Firstly, appropriate amounts of ferric nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), 9H₂O), chromium (III) nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$) and copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) were dissolved in 25 ml ethylene glycol and under stirring at room temperature. After that, the prepared solution was heated at 100 °C to form a dry gel. Finally, the pyrolysis was performed at 400 °C for 10 h in air atmosphere with the heating rate of 10 °C/min.

2.2. Characterization

The crystalline structure of catalysts was determined by X-ray powder diffraction (XRD) using a X-ray diffractometer (PANalytical X'Pert-Pro) using a Cu Kα monochromatized radiation source and a Ni filter in the range $2\theta = 10$–$80°$ equipped with a Cu Kα source, at 40 kV and 20 mA. The BET surface areas of the catalysts were determined via nitrogen adsorption at −196 °C using an automated gas adsorption analyzer (Tristar 3020, Micromeritics). The pore size distribution was calculated from the desorption branch of the isotherm by the Barrett, Joyner and Halenda (BJH) method. Temperature-programmed reduction (TPR) was carried out using an automatic apparatus (Chemisorb 2750, Micromeritics) equipped with a thermal conductivity detector. Before the TPR experiment, the fresh sample (ca. 50 mg) was treated under an inert atmosphere at 300 °C for 3 h, and then subjected to a reduction treatment with a heating rate of 10 °C/min in a reducing gas flow (30 mL/min) containing a mixture of H₂:Ar (10:90). Infrared spectra were recorded on a NEXus Fourier transform infrared (FTIR) spectrophotometer using KBr pellets containing 1 wt.% of sample. Temperature programmed desorption behavior of CO_2, H_2O or CO species on the Fe–Cr–Cu catalyst surface was carried out on the same apparatus as H₂-TPR. Before the experiment, the catalyst was reduced at 350 °C under a reducing gas flow (30 mL/min) containing a mixture of H₂:Ar (10:90) for 2 h. After that the reduced Fe–Cr–Cu catalyst was saturated by the CO, H_2O or CO_2 molecular 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 min⁻¹ from room temperature to a needed temperature under He stream.

2.3. Catalytic reaction

The catalytic reaction test was performed in a tubular fixed bed flow reactor made of quartz (i.d. 8 mm) under atmospheric pressure. The thermocouple was inserted in bottom of the catalyst bed for monitoring the temperature. The total catalyst charged for each reaction was held constant (100 mg and with particle size of 0.25–0.5 mm). A gaseous mixture of 30% CO, 60% H₂, 10% CO_2 and a water steam with a H_2O/dry gas molar ratio of 0.6 were supplied to the catalyst bed. Prior to reaction, the catalysts were reduced using the same reactant gas mixture at a heating rate of 10 °C/min from room temperature to 400 °C and then maintained at 400 °C for 2 h.

The activity tests were carried out at different temperatures ranging from 300 °C to 500 °C in steps of 50 °C. Before each analysis, the effluent passed through a water-trap to remove the water from the product stream. The gas composition was analyzed by a HID YL-6100 gas chromatograph equipped with a carboxen1010 column.

3. Results and discussion

3.1. Structural properties of the prepared catalysts

The XRD patterns of prepared catalysts are displayed in Fig. 1. For pure iron oxide, hematite (Fe_2O_3) and magnetite (Fe_3O_4) are the crystalline phases detected, as evidenced by diffraction features located at Bragg angle (2θ) values of at 24.43, 33.46, 35.94, 41.15, 43.62, 49.77, 54.41, 57.75, 62.76, 64.28, 69.83, 72.25 and 76.15° for Fe_2O_3 and 30.51, 35.94, 43.62, 54.41, 57.75, 62.76, 72.25 and 76.15° for Fe_3O_4, respectively. Compared with the XRD pattern of pure iron oxide, it can be seen that by addition of copper to pure iron oxide, because of its undetectable level, no change in its pattern was noted.

In addition, it is obvious that by addition of chromium to pure iron oxide, no separate Cr-containing crystalline phases are observed on the prepared samples, suggesting that chromium could exist in a solid solution within the magnetite matrix and iron chromium oxide (Cr_2FeO_4) was presented in all diffraction peaks. XRD analysis was also performed to examine crystalline phases present in the commercial catalyst. As can be seen, hematite (Fe_2O_3) and magnetite (Fe_3O_4) crystalline phases were observed on this catalyst.

By addition of Cu to the Fe–Cr sample, copper iron oxide ($CuFe_2O_4$) phase was added to all diffraction peaks and separate crystalline phases of copper or chromium oxides were not detected in the XRD patterns. As above-mentioned, it is well known that two
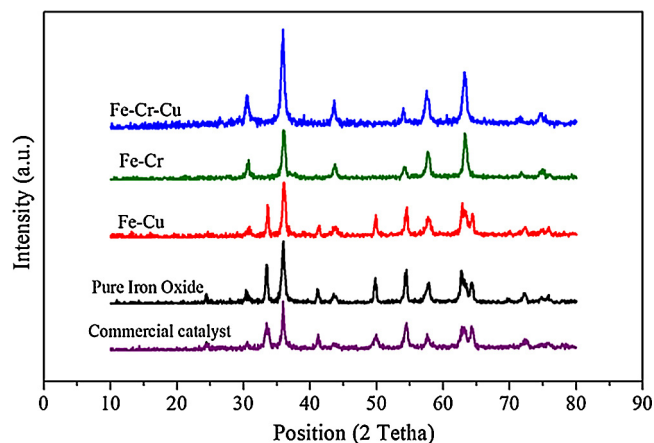

Fig. 1. XRD pattern of the prepared catalysts.