Renewable Energy 74 (2015) 588–598

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

Preparation of nanocrystalline metal (Cr, Al, Mn, Ce, Ni, Co and Cu) modified ferrite catalysts for the high temperature water gas shift reaction

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ARTICLE INFO

Article history:
Received 4 July 2014
Accepted 16 August 2014
Available online 16 September 2014

Keywords:
Cr-free catalyst
Fe_2O_3
Nanostructure
Promoter
Water-gas shift

ABSTRACT

Water gas shift reaction is an essential process of hydrogen production and carbon monoxide removal from syngas. Fe–Cr–Cu catalysts are typical industrial catalysts for high temperature water gas shift reaction but have environmental and safety concerns related to chromium content. In this work nanocrystalline metal (M)-modified ferrite catalysts (M = Cr, Al, Mn, Ce, Ni, Co and Cu) for replacement of chromium were prepared by coprecipitation method and the effects of promoters on the structural and catalytic properties of the iron based catalysts were studied. Prepared catalysts were characterized using X-ray diffraction (XRD), N_2 adsorption (BET), temperature-programmed reduction (TPR) and transmission electron microscopies (TEM) techniques. Temperature-programmed reduction measurements inferred that copper favors the active phase formation and significantly decreased the reduction temperature of hematite to magnetite. In addition, water gas shift activity results revealed that Fe–Al–Cu catalyst with Fe/Al = 10 and Fe/Cu = 5 weight ratios showed the highest catalytic activity among the prepared catalysts. Moreover, the effect of calcination temperature, GHSV and steam/gas ratio on the catalytic performance of this catalyst was investigated.

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1. Introduction

Nowadays, hydrogen is primarily produced from hydrocarbons or alcohols through reforming processes. Regardless the kind of reforming (steam reforming, partial oxidation, dry reforming or autothermal reforming), the reactor effluent typically contains mixtures of hydrogen, carbon monoxide, carbon dioxide and steam besides unreacted hydrocarbon [1–6]. The removal of carbon monoxide from this hydrogen-rich stream is essential for many processes since it can irreversibly poison most of metallic catalysts used in chemical and petrochemical processes [7,8]. The reaction is reversible and exothermic (Eq. (1)), favored by low temperatures and large amounts of steam. However, in order to obtain high conversions for economical purposes, the WGSR is usually performed in two stages in industrial processes [9]. The high-temperature shift (HTS) reaction conducted at 310–450 °C using Fe–Cr oxide catalyst, while the low temperature shift (LTS) reaction performed at 220–240 °C using $Cu/ZnO/Al_2O_3$ or precious metal-based catalysts [10].

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g), \quad \Delta H(298\,K) = -41.2\,kJ/mol. \tag{1}$$

For the high temperature catalyst, the active phase is magnetite (Fe_3O_4), which rapidly sinters at the range of reaction (300–500 °C). Therefore the chromium oxide is used to increase the thermal stability of the magnetite. It has been proposed that chromia forms a solid solution in Fe_3O_4 and that Cr^{3+} displaces equal amounts of Fe^{2+} and Fe^{3+} from the octahedral sites and the displaced Fe^{2+} were consequently located in the tetrahedral site [11,12]. Even though chromium oxide has been used as a stabilizer in industrial HTS catalysts, its replacement with more benign components is highly desirable due to environmental concerns related to chromium. Therefore, several studies have been carried out aiming to replace chromium by other dopants.

Araujo and Rangel [13] investigated the catalytic performance of Al-doped Fe-based catalyst with small amounts of copper ($Cu \approx 3$ wt.%) and showed similar catalytic activity compared to the

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http://dx.doi.org/10.1016/j.renene.2014.08.037
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commercial Fe–Cr–Cu catalyst. Rangle Costa et al. have found that Fe–Th–Cu to be promising for industrial applications compared with Fe–Cr–Cu catalyst [8]. Vanadium was another element incorporated into the iron oxide structure [14]. Liu et al. reported promising catalytic performance of Fe–Al–Ce catalysts for HT-WGS [15]. In this study, we investigated the potential textural promoters for Cr replacement and structural promoters for enhancing catalytic activity of Fe-based catalysts. In addition, the effect of GHSV and steam/gas ratio on the activity performance of the catalyst with the highest activity was studied.

2. Experimental

2.1. Catalyst preparation

The starting materials were $Fe(NO_3)_3$. $9H_2O$, $Cr(NO_3)_3$. $9H_2O$, $Cu(NO_3)_2$. $3H_2O$, $Ce(NO_3)_3$. $6H_2O$, $Al(NO_3)_3$. $9H_2O$, $Co(NO_3)_2$. $6H_2O$, $Mn(NO_3)_2$. $4H_2O$, and $Ni(NO_3)_2$. $6H_2O$ as Fe, Cr, Cu, Ce, Al, Co, Mn and Ni precursors, respectively and sodium hydroxide was used as precipitant. All chemicals were used as received without further purification. Initially, an aqueous solution of the metal nitrate hydrate precursors was prepared with appropriate ratios to yield desired metal weight ratio in the product. NaOH solution was added drop-wise to adjust the pH of the system to 10. After precipitation, the slurry was aged for 5 h under continuous stirring. Then the mixture was cooled to room temperature, filtered and washed with hot deionized water for an effective removal of ions. The final product was dried at 90 °C for 24 h and calcined at different temperatures for 4 h in air atmosphere with the heating rate of 5 °C/min.

2.2. Characterization

The specific surface area was evaluated by the BET method using N_2 adsorption at −196 °C (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 250 °C for 2 h, and then 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 H_2:Ar (10:90). The crystalline structure of catalysts was determined by X-ray powder diffraction (XRD) using an 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 surface morphology of the catalysts was observed with transmission electron microscopies techniques (JEOL JEM-2100UHR).

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% H_2, 10% CO_2 and a water steam with desired H_2O/dry gas molar ratio were supplied to the catalyst bed.

Prior to reaction, the catalysts were reduced using a gaseous mixture of 30% CO, 60% H_2, 10% CO_2 and a water steam with a H_2O/dry gas molar ratio of 0.6 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. Replacement of chromium

The XRD patterns of Fe promoted with various components are shown in Fig. 1. For pure iron oxide, the XRD pattern well correspond to the standard card of hematite (α-Fe_2O_3, ICDD# 079–0007). It is seen that Cr, Ce and Mn doped iron oxides were composed of α-Fe_2O_3 and no other phase besides hematite were observed. As can be seen, the doped samples with Cr, Ce and Mn possessed high crystallinity compared to Al-doped iron oxide. The Al-doped iron oxide showed a low degree of crystallinity. The lower peak intensities of Al-doped iron oxide sample are attributed to the formation of amorphous mixed oxide phases in this sample. The effect of alumina could be regarded as isolator, which prevents the severe sintering of FeOx phase during the post-treatment processes. For Cr-doped iron oxide, there is no driving force for the segregation of Cr to surface as the segregation energy is positive, due to the similar radii of Fe^{3+} and Cr^{3+} which can incorporate Cr^{3+} into the bulk lattice of hematite. The ionic radius of Mn^{3+} is slightly smaller than Fe^{3+} and the segregation energy is small. The most stable position of the dopant is in the bulk, similar to Cr^{3+}. Ce^{4+} is the largest cation and has the largest, negative segregation energy and can not stay in solution but will form a second phase.

The structural properties of doped iron oxides with various components are presented in Table 1. As can be seen, pure iron oxide exhibited a low specific surface area and pore volume. Addition of promoter significantly increased the surface area. It is seen that Mn and Al doped iron oxide samples showed higher surface area compared to Cr and Ce doped iron oxide samples. The lower surface area of these samples could be related to broader pore size distribution as shown in Fig. 2a. As can be seen in Fig. 2a, the Al-doped iron oxide showed the narrowest pore size distribution and consequently the highest surface area. The results in Table 1 revealed that Al-doped iron oxide has the lowest pore size and the Ce-doped iron oxide, which has the lowest surface area showed the largest pore size. These results are in agreement with pore size distribution results.

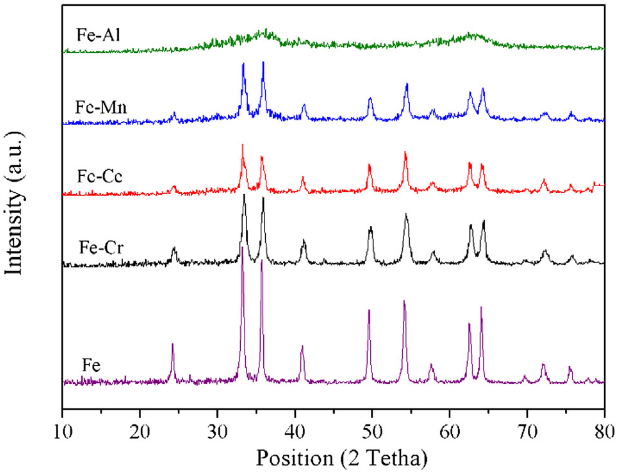

Fig. 1. XRD patterns of the Fe-promoted catalysts calcined at 400 °C.

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