

Available online at www.sciencedirect.com

ScienceDirect

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

High temperature water gas shift reaction over promoted iron based catalysts prepared by pyrolysis method

Fereshteh Meshkani ^a, Mehran Rezaei ^{a,b,*}

^a Catalyst and Advanced Materials Research Laboratory, Chemical Engineering Department, Faculty of Engineering, University of Kashan, Kashan, Iran

^b Institute of Nanoscience and Nanotechnology, University of Kashan, Kashan, Iran

ARTICLE INFO

Article history:

Received 3 May 2014

Received in revised form

20 July 2014

Accepted 27 July 2014

Available online 28 August 2014

Keywords:

Pyrolysis

Fe₃O₄

Nanocrystalline

Promoter

Water–gas shift

ABSTRACT

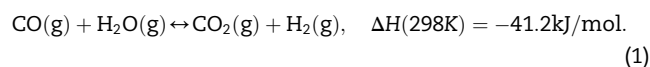
In this work the effects of different promoters (Cr, Al, Mn, Ce, Ni, Co and Cu) on the structural and catalytic properties of Nanocrystalline iron based catalysts for high temperature water gas shift reaction were investigated. The catalysts were prepared in active phase (Fe₃O₄) via a facile direct synthesis route without any additive and characterized using X-ray diffraction (XRD), N₂ adsorption (BET), temperature-programmed reduction (TPR), transmission and scanning electron microscopies (TEM, SEM) techniques. The obtained results indicated that synergic effect of Mn and Ni promoters can lead to obtain a Cr-free catalyst with high activity. In addition, the effect of Ni content on the structural and catalytic properties of the Fe–Mn–Ni catalysts was investigated. It was found that Fe–Mn–Ni catalyst with Fe/Mn = 10 and Fe/Ni = 5 weight ratios showed the highest catalytic activity among the prepared catalysts and possessed a stable catalytic performance without any decrease during 10 h time on stream. Moreover, the effect of GHSV and steam/gas ratio on the catalytic performance of this catalyst was investigated.

Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

In the process of hydrogen production and carbon monoxide removal from syngas, water gas shift reaction is a crucial unit reaction in many processes such as ammonia production, fuel cell or other processes, which need maximum H₂ with high purity or CO acts as a poison for their catalyst [1,2]. This reversible and exothermic reaction converts CO to CO₂ in the presence of steam (Eq. (1)) and economically takes place in two

stages. 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/Al₂O₃ or precious metal-based catalysts [3].



The active phase of the HTS catalyst is magnetite (Fe₃O₄), which rapidly sinters and its activity decreases due to decreasing the surface area. Hence chromium oxide is used as

* Corresponding author. Institute of Nanoscience and Nanotechnology, University of Kashan, Kashan, Iran. Tel.: +98 31 55912469; fax: +98 31 55511121.

E-mail addresses: meshkani.fereshteh@yahoo.com (F. Meshkani), rezaei@kashanu.ac.ir, rezaei.mehran@gmail.com (M. Rezaei).
<http://dx.doi.org/10.1016/j.ijhydene.2014.07.176>

0360-3199/Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

a stabilizer to enhance sintering resistance by replacing active Fe(III)/Fe(II) octahedral sites [4,5]. But these catalysts have some problems when used in commercial plants because fresh and spent catalysts usually contain 1–2 wt. % of Cr⁶⁺, which classified as a toxic hazardous substance and is banned by environmental regulations [6]. Therefore many attempts have been done for developing of the Cr-free iron based catalysts. An interesting feature of magnetite is the possibility to replace iron by other metals while maintaining the spinel structure. The physico-chemical properties of the ferrites are strongly dependent on the site, nature and amount of metal incorporated in the structure [7,8]. For example, substitution of Fe²⁺ or Fe³⁺ by fixed valence cations such as Mg⁺² [9], Zn⁺² [10], Al⁺³ [11] improves the stability of the ferrites. It has also been observed that transition metals such as Ni, Cu [11] or Mn [12] and Co [13], in the spinel lattice can strongly modify the redox properties of the ferrites and also influence their stability. Various kinds of metal-modified ferrites codoped with Cu such as Ce, Ni, Co, Mn, and Zn, to replace Cr₂O₃ in order to achieve Cr-free Fe-based WGS catalysts were studied [14]. Liang et al. [15] investigated the influence of substituting metals such as Ti, V, Cr, Mn, Co and Ni on the thermal stability of magnetite and they found that except V, the other studied ions show a positive effect in the thermal stability of magnetite. Liu et al. studied an Al/Ce-promoted Fe catalyst (Fe/Al/Ce), which exhibited a comparable catalytic activity to commercial Fe/Cr catalyst [16]. Ozkan et al. prepared Fe/Al/Cu catalysts and proved that Al played a role similar to that of Cr, inhibiting the thermal growth of the magnetite phase and stabilizing the phase against further reduction to FeO and Fe [17].

Lee et al. prepared Ni/Fe catalysts by conventional co-precipitation method and found that Ni can be referred to a functional promoter but undesirable methane byproduct produced during the reaction and they could overcome the problem by using cesium as promoter [2].

In other hand, as mentioned before active phase of HTS catalyst is Fe₃O₄ whereas many synthesis route lead to prepare catalyst in Fe₂O₃ phase, which should be transformed to the Fe₃O₄ through pre-reduction with reaction gas [2]. 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 [18]. Hence it is very worthwhile to find a method, which could prepare HTS catalysts directly in active. There are several methods to prepare HTS catalysts directly in the active phase such as oxidation–precipitation method [19], co-precipitation of Fe(II) and Fe(III) ions [20], 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 [21], etc. In general, these methods need complicated synthetic steps, high reaction temperature, surfactant, and template. Although the synthesis of Fe₃O₄ based materials has been well documented, the large-scale, low-cost, and template-free preparation of Fe₃O₄ based materials is still of great interest [22]. One of these methods is pyrolysis using ethylene glycol as solvent, reducing, complexing and capping agents [18–23]. In this method, during the synthesis, the

reducing atmosphere created in calcination process 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 Fe₃O₄ [22].

The objective of this work is considering these couple of issues by preparing Cr-free catalysts directly in active phase via simple, low cost pyrolysis method. In fact the effects of different promoters on the structural properties and catalytic activity of the iron based catalysts were investigated and the long term stability and the effects of GHSV and steam/gas ratio on the activity performance of the catalyst with the highest activity were studied.

Experimental

Materials

The starting materials were Fe(NO₃)₃·9H₂O, Cr(NO₃)₃·9H₂O, Cu(NO₃)₂·3H₂O, Ce(NO₃)₃·6H₂O, Al(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O, Mn(NO₃)₂·4H₂O, and Ni(NO₃)₂·6H₂O as Fe, Cr, Cu, Ce, Al, Co, Mn and Ni precursors, respectively. Ethylene glycol was used as solvent, reducing, complexing and capping agent. All chemicals were used as received without further purification.

Catalyst preparation

Promoted iron based catalysts were prepared with different Fe/metal weight ratios by a simple pyrolysis method. The details of preparation conditions were described in our earlier work [5]. In summary, firstly, appropriate amounts of metal nitrate salts were dissolved under stirring in 25 mL ethylene glycol at room temperature. After that, the solution was heated at 100 °C to form a dry gel. Finally, the pyrolysis was performed at 400 °C with a heating rate of 10 °C/min under air atmosphere for 10 h.

Characterization

X-ray powder diffraction (XRD) patterns were recorded on a X-ray diffractometer (PANalyticalX'Pert-Pro) with a Cu-K α monochromatized radiation source and a Ni filter in a scanning range 2 θ = 10–80° for determination of the crystalline phases of the prepared samples. The specific surface areas (BET) of the samples were determined by nitrogen adsorption by an automated gas adsorption analyzer (Tristar 3020, Micromeritics). The pore size distribution was also conducted by the N₂ desorption branch of the isotherm by the Barrett, Joyner and Halenda (BJH) method. Temperature programmed reduction (TPR) analysis was used for evaluating the reduction properties of catalysts with Micromeritics chemisorb 2750 instrument. In the TPR measurement, 50 mg catalyst was subjected to a heat treatment (10 °C/min) in a gas flow (20 mL/min) containing a mixture of H₂:Ar (10:90). Before the TPR experiment, the fresh sample was degassed at 300 °C for 3 h under an inert atmosphere. The surface morphology of the catalysts was observed with scanning and transmission electron microscopies techniques (SEM, Vega@Tescan and JEOL JEM-2100UHR).

Download English Version:

<https://daneshyari.com/en/article/1280970>

Download Persian Version:

<https://daneshyari.com/article/1280970>

[Daneshyari.com](https://daneshyari.com)