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Preparation of high temperature water gas shift catalyst with coprecipitation method in microemulsion system

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ABSTRACT

In this paper nanocrystalline mesoporous iron-based high temperature water gas shift catalysts were prepared by coprecipitation method in water-in-oil (W/O) microemulsion. The prepared samples were characterized by using X-ray diffraction (XRD), N₂ adsorption (BET), temperature-programmed reduction (TPR), Fourier transform infrared spectroscopy (FTIR), transmission and scanning electron microscopies (TEM, SEM) techniques. The results revealed that the Fe₂O₃ possessed low specific surface area and catalytic activity in high temperature water gas shift reaction. The addition of copper to Fe₂O₃ favored the active phase formation and significantly decreased the reduction temperature of hematite to magnetite and consequently improved the catalytic activity of Fe₂O₃. The incorporation of chromium in hematite increased the surface area and catalytic activity of Fe₂O₃. The results also showed that the prepared Fe–Cr–Cu catalyst showed higher activity than the commercial catalyst. In addition, the effects of GHSV, steam/gas ratio, and calcination temperature were investigated on the catalytic performance of Fe–Cr–Cu catalyst.

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1. Introduction

The water gas shift (WGS) reaction can be employed for the production of pure hydrogen. Water gas shift reaction is a reversible and slightly exothermic chemical reaction and thermodynamically limited at high temperature. Water gas shift reaction is performed using two units. The first unit using Fe₂O₃/Cr₂O₃, known as high temperature shift (HTS) catalyst operates at high inlet temperature (370–400 °C). The second unit known as low temperature shift (LTS) operating at the lowest possible inlet temperature (200 °C), by using a CuO/ZnO/Al₂O₃ catalyst. With these two units, it is possible to achieve exit CO concentrations as low as 0.1–0.3%.

Typically, HTS catalysts contain 88–92 wt.% Fe₂O₃ and 8–12 wt.% Cr₂O₃ (Byron Smith et al., 2010). In addition, the activity of high temperature water gas shift catalysts can be improved by the addition of different promoters, e.g., copper, lead, cobalt, magnesium, zinc, etc. (Meshkani and Rezaei, 2014; Rhodes et al., 2002).

The role of chromia is mainly to stabilize the material, although recent studies have shown that it can also catalyze the reaction, but in a lower extent than iron oxide (Byron Smith et al., 2010). The commercial catalysts contain a small amount of copper as an activity and selectivity enhancer. The most conventional method for preparation of these catalysts is coprecipitation method. However, there are several methods

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for preparation of iron-oxide-based catalysts. These methods include hydrothermal synthesis (Sreeja and Joy, 2007; Daou et al., 2006), thermal decomposition (Simeonidis et al., 2007; Zhou et al., 2008), co-precipitation (Yu et al., 2006; Nedkov et al., 2006), sol–gel method (Hu et al., 2005), etc.

Among these preparation methods, the effective way to controlling the size and shape of nanoparticles is the use of microemulsion (Li et al., 2008; Zhang et al., 2008; Asim et al., 2008). Water-in-oil (W/O) microemulsion solutions are transparent, isotropic liquid media with nanosized water droplets dispersed in a continuous oil phase and stabilized by surfactant molecules at the water/oil interface. The surfactant-covered water pools act as microreactors for processing reactions and inhibit the aggregation of particles because the surfactants could adsorb on the particle surface when the particle size approaches to that of the water pool. As a result, the particles obtained in such a medium are generally very fine and monodispersed (Paul and Moulik, 1997; Chen and Wu, 2000; Vidal-Vidal et al., 2006). In this work, the iron based catalysts were prepared by coprecipitation method in microemulsion system for high temperature water gas shift reaction. In addition, the effect of calcination temperature, GHSV, steam/dry gas molar ratio was investigated on the catalytic performance of the selected catalyst.

2. Experimental

2.1. Starting materials

The starting materials were Triton X-100 ($C_{34}H_{62}O_{11}$, HLB = 13.5), cyclohexane (C_6H_{12}), 1-butanol, $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 4H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$ and NaOH. All chemicals were of analytical grade and used without further purification. Distilled deionized water was used for the preparation of all aqueous solutions.

2.2. Catalyst preparation

The catalysts were prepared by coprecipitation method in a water-in-oil microemulsion system with different Fe/Cr/Cu ratios. The prepared samples were (i) pure iron oxide, (ii) iron and chromium mixed oxide (Fe–Cr, Fe/Cr weight ratio = 10); (iii) iron and copper mixed oxide (Fe–Cu, Fe/Cu weight ratio = 40), and (iv) iron, chromium and copper mixed oxide (Fe–Cr–Cu, Fe/Cu weight ratio = 20 and Fe/Cr weight ratio = 10). In addition, the commercial catalyst with the composition of 88.8% Fe_2O_3 , 8.88% Cr_2O_3 and 2.32% CuO was used for better comparison.

To prepare the microemulsion, cyclohexane, Triton X-100 and n-butyl alcohol were used as the oil phase, surfactant, and cosurfactant, respectively. The desired amounts of these reagents were mixed under stirring to form a transparent solution. The molar ratio of the surfactant to cosurfactant was chosen as 1:1.6. After that aqueous solution of metal precursors was added to the solution containing surfactant and cosurfactant at room temperature and stirred for 3 h. The mole ratios of water to surfactant and water to oil phase were chosen as 20 and 1.6, respectively. Then an aqueous solution of NaOH was added to the prepared solution to adjust the pH value at 12. After precipitation, the prepared slurry was aged for 2 h at room temperature. The precipitate was filtered and washed with distilled water and ethanol. Finally, the prepared samples were dried at 80 °C for 12 h and calcined at 400 °C for 4 h.

2.3. Characterization

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-K α monochromatized radiation source and a Ni filter in the range $2\theta = 10^\circ$ – 80° equipped with a Cu-K α source, at 40 kV and 20 mA. The BET surface areas of the catalysts were determined via nitrogen adsorption at $-196^\circ C$ 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. Infrared spectra were recorded on a NEXus Fourier transform infrared (FTIR) spectrophotometer using KBr pellets containing 1 wt.% of the sample. 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 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 H_2 :Ar (10:90). The surface morphology of the catalysts was observed with scanning and transmission electron microscopies techniques (SEM, Vega@Tescan, and JEOL JEM-2100UHR).

2.4. Catalytic reaction

The catalytic reactions were performed in a tubular fixed bed flow reactor made of quartz (i.d. 8 mm) under atmospheric pressure. The total catalyst charged for each reaction was held constant (100 mg and with a particle size of 0.25–0.5 mm). A gaseous mixture of 15% CO , 75% 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 the gaseous mixture of 15% CO , 75% H_2 , 10% CO_2 and a water steam with H_2O /dry gas molar ratio of 0.6 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

Fig. 1a shows the pore size distributions of the prepared samples. As can be seen, pure iron oxide exhibited a very broad pore size distribution. The addition of Cu to pure iron oxide significantly affected the pore size distribution and shifted that to smaller sizes. This catalyst (Fe–Cu) showed a mesoporous structure with pore size centered at 14 nm. The addition of Cr to pure iron oxide catalyst (Fe–Cr) also led to a shift of the pore size distribution to smaller sizes and this catalyst exhibited a narrow single modal pore size distribution centered at 9 nm. Furthermore, the Fe–Cr–Cu catalyst exhibited the narrowest pore size distribution. For comparison, the pore size distribution of commercial catalyst was also presented in Fig. 1a. This catalyst also exhibited a very broad pore size distribution.

The nitrogen adsorption/desorption isotherms of the prepared catalysts and commercial sample are shown in

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