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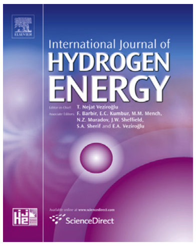

Synthesis of copper promoted high temperature water–gas shift catalysts by oxidation–precipitation

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ABSTRACT

Copper promoted high temperature water–gas shift catalysts were directly synthesized in the active phase (Fe_3O_4) through an oxidation–precipitation (oxiprecipitation) method, avoiding the usual reduction step used to activate the catalyst in the conventional method based on coprecipitation. They were characterized using X-ray diffraction, X-ray fluorescence, infrared spectroscopy, adsorption–desorption of N_2 at 77 K, transmission electron microscopy and temperature programmed reduction. Their catalytic activity was also studied. The results indicated that the materials obtained through this new synthesis method exhibited higher catalytic activity than the commercialized catalysts. Furthermore, the addition of copper improved the catalytic performance of oxiprecipitated Fe–Cr materials, increasing the reducibility of the sample and its stability under reaction conditions.

Introduction

The water gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) is an important step in the industrial manufacture of hydrogen. This reversible and slightly exothermic reaction is used to increase the hydrogen concentration of the syngas obtained in many processes for hydrogen production from fossil fuels and biomass. Additionally, the carbon monoxide concentration of the gas mixture is reduced to an appropriate value for fuel cell applications [1]. The equilibrium constant of water gas shift (WGS) reaction decreases as temperature increases. So, high carbon monoxide conversions are favoured at lower temperatures. However, higher temperatures are required to achieve adequate reaction rates. For this reason, two stages are used to take advantages from kinetics and thermodynamics. The first step is performed at high temperatures (320–450 °C) using catalysts based on Fe_3O_4–Cr_2O_3. In the second step a catalyst based on $Cu/ZnO/Al_2O_3$ is used, applying a temperature between 210 and 240 °C [2].

The active phase of the catalysts for the high temperature stage is magnetite (Fe_3O_4), but this iron oxide loses its activity because of the reduction of its surface area by thermal sintering in the operation conditions. For this reason, chromium

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oxide is added to magnetite as structural stabilizer [3]. Magnetite active phase forms an inverse spinel cubic structure with tetrahedral positions occupied by Fe^{3+} and the octahedral ones by equal amounts of Fe^{3+} and Fe^{2+}. The activity of magnetite in WGS reaction is related to the fast electron hopping between $Fe^{3+} \leftrightarrow Fe^{2+}$ redox couple [4]. There is still some controversy about the role of Cr_2O_3 in the stabilization of the active phase. Some researchers have proposed that Cr^{3+} ions are in solid solution within the Fe_3O_4 lattice [5–7]. On the other hand, several authors suggest that Cr_2O_3 appears as fine particles that physically block the sintering of magnetite [8].

Currently, the commercial catalysts for high temperature WGS reaction also contain small amounts of copper. This metal improves the intrinsic activity of the catalyst and this effect depends on its concentration [9]. Andreev et al. proposed that copper acts providing new active sites similar to those present in low temperature WGS catalysts [10]. Rhodes et al. determined that copper decreases the activation energy of the catalyst and suggested that this metal is incorporated into magnetite lattice, modifying the electronic properties of the solid [11]. Recently, Khan et al. studied the incorporation of different metals in ferrite catalysts indicating that Cu improves the catalytic performance of the catalysts because it produces an increase of the hydroxyl groups on the surface, due to its higher electronegativity [12].

High temperature WGS catalysts are usually prepared by the coprecipitation method, obtaining the iron phase as Fe_2O_3 that is not active in the WGS reaction [13,14]. Therefore, an additional reduction step is necessary to prepare the active phase, Fe_3O_4. This reduction process has to be controlled to avoid metallic iron formation by over-reduction that catalyzes side reactions and undesirable methane generation. In industrial processes, large amounts of steam are used to inhibit metallic iron formation, but this implies high operational costs. Therefore, the development of new synthesis methods to prepare high temperature WGS catalysts directly in the active phase would increase the process efficiency [7]. In a previous work we reported that oxidation-precipitation method is an interesting alternative to prepare Fe–Cr catalysts directly in the active phase [15]. The Fe–Cr material obtained by this method exhibited similar catalytic activity than that of the conventional commercial catalyst at temperatures over 400 °C, even though the latter contained copper in its formulation as an activity enhancer, while the former was just composed of Fe_2O_3–Cr_2O_3. This paper goes in depth in this research, studying the incorporation of copper by the oxidation-precipitation (oxiprecipitation) method.

Experimental

Catalysts preparation

Oxiprecipitation method was used to prepare FeCr and FeCrCu catalysts. Initially, an aqueous solution of the corresponding metals was prepared with a Fe/Cr ratio of 12.2 (wt.) and a Fe/Cu ratio of 32.6 (wt.). $FeCl_2$, $CrCl_3$, and $CuCl_2$ were the precursors used to prepare the catalysts. The solution was heated up to 70 °C, stirred at 300 r.p.m. and oxidized bubbling air into the system. NaOH solution (0.5 M) was added drop-wise adjusting pH to 7 until the end of reaction. The solids were filtered and washed out with water to remove ions and finally dried at 70 °C overnight.

Catalysts characterization

X-ray powder diffraction (XRD) patterns of the catalysts were obtained with a Philips X-Pert diffractometer using Cu Kα radiation. The data were recorded in the 2θ range from 10° to 70°. Average crystallite sizes were calculated by applying the Scherrer equation. X-ray fluorescence (XRF) spectrometer Philips MagiX was used to determine Fe/promoter ratios. Fourier transformed IR (FT-IR) spectra were recorded with a Varian 3100 FT-IR Excalibur Series spectrophotometer using the KBr (1-200 dilution) wafer technique. Transmission electron microscopy (TEM) micrographs were obtained with a Philips Tecnai-20 electron microscope operating at 200 kV and equipped with an energy dispersive X-ray (EDX) spectrometer. Temperature programmed reduction (TPR) was performed in a Micromeritics Autochem 2910 instrument. The sample (50 mg) was heated up from 323 K to 1173 K (heating rate 10 K/min) under a hydrogen–argon mixture (10% H_2) with a flow rate of 40 ml/min. BET surface areas of samples were calculated from N_2 adsorption–desorption isotherms at 77 K, that were measured on a Quantachrome Nova 4000 Series instrument. Carbon deposition on the catalysts during the reaction was measured in a LECO CHNS-932.

Catalytic activity test

The catalytic tests were carried out in a Microactivity Pro Unit. The gas mixture was fed into the system, controlling the flow with a Hi-Tech mass flow controller and was preheated before entering the reactor. The maximum operating gas flow rate was 4.5 N L/min and the facility could work up to 650 °C and 30 bar. Deionised water was fed to the system by a Gilson 307 piston pump and then vaporised and preheated in a hot box before mixing with the dry gas mixture and entering the reactor. To this purpose the whole experimental unit was housed in a forced air circulation oven which provided the desired temperature up to 190 °C. All the experiments were performed in a fixed-bed SS tubular micro reactor (ID 9 mm × 220 mm length) housed in a single zone electric furnace. The process temperature was measured directly in the catalyst bed which was supported inside the reactor by a porous plate. Inlet and outlet gas compositions were analysed on line by gas chromatography. The chromatograph was a 5890 Series II Hewlett–Packard, equipped with two packed 530 μm columns (6 Ft Porapak Q, 80/100 19001A-00 and a 6 Ft Molecular Sieve 5Å 60/80 19001A-MA2) connected in series and a thermal conductivity detector (TCD). Helium was used as the carrier gas with a flow rate of 20 ml/min.

The performance of the catalysts was tested under isothermal conditions (380 °C), 10 bar and $GHSV = 10{,}000\ h^{-1}$. All experiments were carried out using 1–1.4 g of catalyst adjusting the gas flow rate to obtain the desired gas space velocity. The composition of the fed gas used for the catalytic tests corresponded to a theoretical biomass pressurized oxygen-blown gasification process: 40% H_2, 44% CO and 15%