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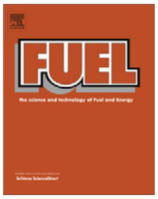

High pressure Water Gas Shift performance over a commercial non-sulfide CoMo catalyst using industrial coal-derived syngas

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ABSTRACT

High pressure Water Gas Shift performance over a commercial non-sulfide CoMo catalyst was studied in a bench scale set-up, using an industrial coal-derived syngas feed. CO conversion showed an important dependence on both reaction temperature and space velocity but remained almost constant with increasing H_2O_v/CO molar ratios. Hydrogen selectivity showed the same trend although it was enhanced with increasing H_2O_v/CO molar ratios. The effect of the activation method on CO conversion was also studied. Despite non-sulfide CoMo catalysts have been widely considered as non-active for WGS reaction, a surprisingly high CO conversion comparable to that attained by the sulfide one, was displayed by this catalyst in the range of conditions studied. However, non-sulfide CoMo catalyst still resulted in lower conversion values if compared with pre-sulfide one.

1. Introduction

Extensive studies on the coal gasification as an element of clean coal technologies are carried out recently, especially in coal dependent countries (i.e., Spain). Hydrogen production from coal-gasification in an Integrated Gasification Combined Cycle (IGCC) plant has attracted attention recently [1,2], since it is an important feedstock for being used in ammonia synthesis and hydrocarbon processing. In fact, there has been an increasing interest in using hydrogen as a future fuel for use in gas turbines and fuel-cells for power generation in both stationary and transport applications, leading to a demand for large-scale central hydrogen production facilities [3,4].

The Water–Gas Shift (WGS) reaction is an important step in the processing of coal-derived syngas, since it is commonly required for adjusting the CO/H_2 ratio needed for synfuel production (e.g. Fischer–Tropsch process). However, even when coal gasification is a viable technology to produce hydrogen; there are still some technological challenges to overcome before this technology becomes feasible for commercialization (catalyst stability, operating limits or resistance to impurities).

Although the WGS reaction could be catalyzed by many materials [5–8]; at a commercial scale, it is basically carried out by using $Fe–Cr_2O_3$ and Cu–ZnO [9–12]. These catalysts are potentially applied for industrial natural gas-derived syngases. However, in the case of coal-derived syngases, where the CO concentration is relatively high and the total amount of sulfur compounds can be significant, sulfur-resistant CoMo based catalysts, similar to those used for hydrodesulfuration, are required [12,13–17].

Moreover, although the WGS reaction is customarily used in industry, the reaction has not been explored at the conditions envisioned in a gasification process. However, high temperature and pressure were found to provide a unique scenario to increase the hydrogen yield. In this sense, the effects of operating conditions and catalyst pretreatment on the high pressure WGS reaction were previously investigated [18]. A bench scale set-up, using a commercial CoMo catalyst, and an industrial coal-derived syngas feed (from IGCC-ELCOGAS plant, Puertollano, Spain) were considered. Sulfur pretreated commercial CoMo catalyst was found to provide the best catalytic results according to literature [19,20]. However, catalytic performance over the non-sulfide CoMo catalyst was surprisingly high if compared to that obtained before [21]. Therefore, in this work the effects of operating conditions on the high pressure WGS reaction over the non-sulfide CoMo (oxidized) catalyst were studied.

2. Experimental

2.1. Bench scale set-up description

The facility, which is fully automated and computerized, consisted of three physically separated parts: (gas and liquid) feed mixing and supply system, reaction system and product analysis system (Fig. 1).

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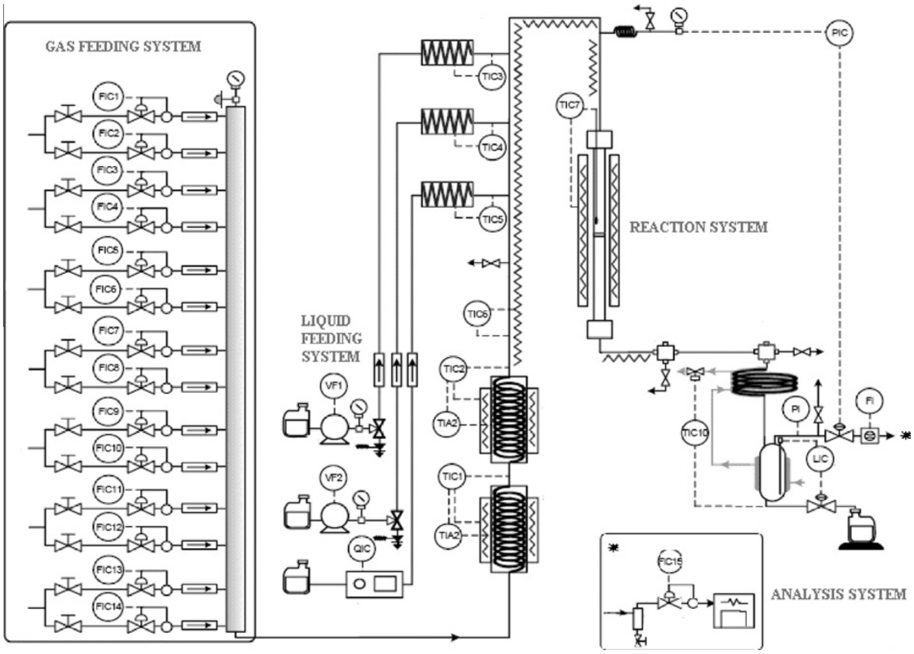

Fig. 1. Simplified process diagram of the bench scale set up for WGS reaction.

N_2, H_2, CO and CO_2 (high purity supplied by PRAXAIR), were fed to the plant as the main gases, whereas H_2S (PRAXAIR) was introduced into it as the sulfide agent for the catalyst pretreatment. Each of these gases could be fed through two separate lines that had the same elements but different flow rates.

The water supply system consisted of a liquid dosing pump (Damovo) and a vaporizer, which achieved complete vaporization of the liquid driven by the pump before entering the reactor. The bench scale set-up included an Inconel fixed bed reactor (17.7 mm ID and 1000 mm length) for WGS experiments.

The gaseous effluent was connected to the input of a gas chromatograph by means of a Peltier cell. The analysis system consisted of a gas microchromatograph (CP-4900 Micro-GC VARIAN) with two analysis columns (Molsieve 5A for H_2, N_2, CH_4 and CO and Pora Pack Q column for CO_2, ethane and propane) using Ar and He as carrier gases, respectively.

The liquid effluent, after crossing a level control valve, was placed in a polyethylene tank positioned on a balance of 6 kg capacity.

2.2. Catalyst

A commercial high temperature CoMo WGS catalyst was performed in this work. A pretreatment (activation) step was required since the catalyst was not in the active phase. In order to determine activation conditions, TPR measurements were carried out with an Autochem HP 2950 analyzer as reported elsewhere [18].

2.3. Activity test

Water Gas Shift reaction was performed under 19 bars in agreement to ELCOGAS industrial gasification process. Table 1 shows the composition of the dry feed gas (v/v %) established by the ELCOGAS IGCC plant. Non-sulfide CoMo catalyst was filled in the bench scale Inconel reactor between layers of SiC, commonly used as inert material. Prior to the reaction test, the catalyst was reduced with pure H_2 at atmospheric and 550 °C for 12 h. In order to compare with the sulfide CoMo catalyst, an independent experiment was run with a certain amount of $(H_2S/N_2)/H_2$ 90/10 v/v % at 210 °C. After pretreatment, the catalyst was flushed with N_2 at 350 °C until pressure rise up to 19 bars. Catalytic activity was studied setting both reaction temperature and gas hourly space velocity (GHSV) ranges on 350–500 °C and 2757–39,404 h^{-1}, respectively. Once operating conditions remained stable, steam was added to the preheated feed gas upstream of the reactor. Three different H_2O/CO molar ratios ranging from 2.4 to 4.7 were used. Effluent gas composition was analyzed online at 15 min intervals. A reaction time of 2.5 h was allowed for steady state to be achieved. Hydrogen selectivity was calculated using the following equation:

Table 1
Dry feed gas composition.

Dry feed gas composition (v/v %)	
CO	60.4
H_2	21.9
N_2	17.7 (internal standard)

$$\text{Hydrogen selectivity}\ (\%) = CO_2\ \text{selectivity}\ (\%) - 3CH_4\ \text{selectivity}\ (\%) \tag{1}$$

since no other side-reactions were observed. Table 2 resumes the detailed experimental conditions used in this work. The catalyst will be referred to as follows: CoMo–H_2 corresponds to a CoMo commercial catalyst reduced with pure H_2 whereas CoMo–94H_2S corresponds to a CoMo commercial catalyst activated with 94 ppm of S (contained in H_2S) as the sulfide agent.

Moreover, a comparison between calculated (from flow measurement) and measured (from GC analyses) mole fraction values of different components of the gas mixture was made showing an excellent agreement. The set of experiments was carried out at conditions that provided CO conversion lower than that of equilibrium.

3. Results and discussion

TPR profile of the commercial catalyst is depicted in Fig. 2. It can be seen three maxima of hydrogen consumption. The first one