Performance of a sulfur-resistant commercial WGS catalyst employing industrial coal-derived syngas feed

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ABSTRACT

Catalyst pretreatment and reaction conditions (reaction temperature, H_2O/CO molar ratio and space velocity) for the Water Gas Shift reaction were studied in a bench scale set-up, using a commercial catalyst and an industrial coal-derived syngas feed. Catalytic activity showed an important dependence on reaction temperature and space velocity although it remained almost constant with varying H_2O/CO molar ratio. The effect of reduction with H_2 or sulfide activation with H_2S or carbonyl sulfide (COS) was also studied, giving good catalytic results for 94 ppm S provided by either H_2S or COS as sulfide agents. Selectivity to hydrogen was close to 100% in all catalytic reaction tests.

1. Introduction

The water–gas shift (WGS) reaction has become well known since first reported in 1888. It became one of the most important industrial catalytic reactions in 1915, when the first coal-based ammonia synthesis plant was put into operation [1,2]. The WGS reaction is an important step in the processing of coal-derived syngas, both as a precursor to fuel gas decarburization and for adjusting the CO/H_2 ratio for downstream synfuel production. The reaction is mildly exothermic and thermodynamically limited at high temperatures:

$$CO\ (g) + H_2O\ (g) \leftrightarrows CO_2\ (g) + H_2\ (g),\ \Delta H\ (298\ K) = -41.2\ kJ/mol \quad (1)$$
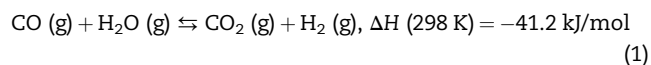
Coal is now being recognized as the most abundant fossil fuel, with 216 [3] to over 500 years global recoverable reserves [4] at current usage rates. Moreover, coal is also a much delocalized resource and it has lower cost among the different fossil fuels.

Conventional electric power plants are based on coal combustion. Due to the high rate of greenhouse gas emissions associated with current stationary electricity production, alternative technologies are being sought to reduce the environmental impact associated with coal utilization (Clean Coal Technologies, CCT). Integrated Gasification Combined Cycle (IGCC) plants are an example of this technology due to the production of negligible amounts of NO_x and SO_2 [5,6]. Much research has been done on IGCC processes, with 5 prototype plants in operation worldwide – 2 in Europe (one of them ELCOGAS in Puertollano, Spain) – with efficiencies close to 50% [7].

Future energy systems must provide a secure, more sustainable, environmentally friendly and acceptable energy supply. In this context, hydrogen has been proposed for decades as a promising energy carrier for a future low carbon energy economy. Hydrogen production from coal-gasification is a technology that has increasingly attracted attention in recent years. However, there are few reports related with hydrogen

production at high pressure using industrial-gasified derived syngas from these power generation systems [8,9]. One of the most important operation units in the next generation IGCC plants is the conversion of CO from coal-derived syngas to H_2 and CO_2 (with subsequent CO_2 capture) using the catalytic water–gas shift (WGS) reaction.

WGS reaction can be catalyzed by many materials but only two classes of catalysts are used almost exclusively in industry: iron oxide-based (Fe–Cr_2O_3 at ∼500 °C) and copper oxide-based (Cu–ZnO at ∼200 °C) catalysts [10–13]. These catalysts work extremely well in industrial application for natural gas-derived syngases where the CO concentrations are in the range 5–10%. However, in the case of coal-derived syngases where CO concentration is relatively high (40–60%), a considerably higher degree of shifting is required [14]. Moreover, the total amount of sulfur compounds (generally H_2S and carbonyl sulfide (COS)) can be significant depending upon the sulfur content present in the feed coal. In this sense, as both types are highly sensitive toward sulfur contamination of the feed, a new class of CoMo sulfur-resistant WGS based catalysts, similar to those already applied in the HDS process, were proposed [2,13,15–17]. Besides the noble metals, only a limited number of elements have been used for sulfide catalyst such as Mo and W as the primary species in composing active sulfide catalyst and Fe, Ni or Co as the indispensable promoters.

WGS reaction over Co–Mo catalysts has been extensively studied at laboratory conditions; however there are few papers [18] where industrial feed and bench scale set-up are used.

In this work, the effects of operating conditions on the high pressure WGS reaction as well as the catalyst pretreatment were investigated. A bench scale set-up, using a sulfur-resistant commercial catalyst and an industrial coal-derived syngas feed (from IGCC-ELCOGAS plant, Puertollano, Spain), were considered.

2. Experimental

2.1. Bench scale set-up description

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

N_2, H_2, CO and CO_2 (high purity supplied by PRAXAIR), were fed to the plant as the main gases, and H_2S and COS (1.5 ppmv and 12 ppmv, respectively from PRAXAIR) as sulfide agents 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.

Fig. 1 shows a schematic diagram of the experimental bench scale plant for WGS reaction.

2.2. Catalyst

The catalyst studied in this work was a high temperature industrial WGS catalyst, which consisted of a mixture of cobalt and molybdenum oxides. The catalyst was not in the active phase, so it did require a pretreatment (activation) step.

TPR measurement of the catalyst was carried out with an Autochem HP 2950 analyzer. After loading, the sample was out-gassed by heating at 10 °C min^{-1} in an argon flow up to 200 °C and kept constant at this temperature for 30 min. Next, it was cooled to room temperature and stabilized under an argon/hydrogen flow (≥99.9990% purity, 83/17 volumetric ratio). The temperature and detector signal were then continuously recorded while heating at 5 °C min^{-1} up to 1000 °C. The liquid formed during the reduction process were retained by a cooling trap placed between the sample and the detector. TPR profiles were reproducible, being standard deviations of the maxima temperature peak ±2%.

2.3. Activity test

Water Gas Shift reaction was performed under 19 bar, which is an operating pressure representative of the pressurized gasification industrial process. Table 1 shows the composition of the dry feed gas (v/v %) established by the ELCOGAS IGCC plant. CoMo catalyst was packed in the bench scale Inconel reactor between layers of inert material (SiC). Prior to the reaction test, the catalyst was pretreated at atmospheric pressure by two different methods: (a) reduced with pure H_2 at 550 °C for 12 h; (b) activated with a certain concentration of (H_2S/N_2)/H_2 90/10 v/v % or (COS/N_2)/H_2 90/10 v/v % at 210 °C. After pretreatment, the catalyst was flushed with N_2 at 350 °C and getting pressure rise up to 19 bar. Catalytic activity has been studied in the temperature range of 350–500 °C. Gas hourly space velocity (GHSV) was set on 7877–2757 h^{-1} by adjusting feed gas flow rate to provide the desired value. The lowest space velocity value that could be attained with our experimental facility was 2757 h^{-1}. Once operating conditions remained stable, water vapour was added to the preheated feed gas upstream of the reactor. Three different H_2O/CO molar ratios 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:

$$\text{Hydrogen selectivity (\%)} = CO_2 \text{ selectivity (\%)} - 3 \times (CH_4 \text{ selectivity) (\%)} \qquad (2)$$

Table 2 outlines the detailed experimental conditions used in this work. The catalyst will be referred to as CoMo followed by the activation treatment. For instance, CoMo–42H_2S corresponds to a CoMo commercial catalyst activated with 42 ppm of S (contained in either COS or H_2S) as the sulfide