



## Design studies for monolithic high temperature shift catalysts: Effect of operational parameters



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### ABSTRACT

In this study, the performance of a commercial high temperature shift (HTS) catalyst has been investigated. The catalyst was a wash-coated ceramic monolith type and used to adjust the H<sub>2</sub>/CO ratio in a simulated syngas stream. In the experiments, the effects of inlet gas composition, gas hourly space velocity, inlet steam to CO ratio and reaction temperature have been investigated. The results showed that all these parameters have considerable influence on the design of HTS reactor. Precious metal based monolith catalysts enable working under high space velocities and thus reduce the volume of HTS reactor. Specifically defined selectivity, as ratio of the total amount of CO<sub>2</sub> and H<sub>2</sub> to the amount of CO<sub>2</sub> formed during the process, seems to be a good measure of possible unwanted side reactions that might occur. It was found that the selectivity ratio should be ideally about two for HTS process, minimizing the formation of side reactions. Selectivity values below 2.0 indicate the presence of unbalanced H<sub>2</sub> which is incompatible with WGS reaction stoichiometry. Results showed that steam is an effective parameter in determining the probability of side reactions, especially the reactions leading to the catalyst deactivation through coke deposition. Another point is that coking tendency of the catalyst is more severe at lower operating temperatures. The formation of methane, an unwanted by-product, was seen to be favored by lower gas hourly space velocities, possibly via the reaction with H<sub>2</sub>. The formation of methane results in hydrogen consumption to some extent and consequently alters the product composition. The optimum operating conditions of the wash-coated monolith type HTS catalyst studied were found to be as follows: Temperature = ~375–400 °C, GHSV = ~50,000 h<sup>-1</sup> and the inlet steam to CO ratio = ~2.0.

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### 1. Introduction

Syngas, a mixture of carbon monoxide, carbon dioxide and hydrogen, is used extensively in the industrial applications. Production of many of the commodities such as hydrogen, methanol, ammonia, dimethyl ether, synthetic diesel, synthetic methane and conventional processes such as petroleum refining, reduction of oxide ores all requires syngas. The origin of syngas may be any of hydrocarbon feedstock such as coal, natural gas, LPG and other alternative hydrocarbon sources (biomass, waste tires etc.). H<sub>2</sub>/CO ratio of syngas has crucial importance and should be adjusted according to the requirements of industrial processes. For example, a H<sub>2</sub>/CO ratio of 2 is a prerequisite for high temperature Fischer–Tropsch reaction and methanol synthesis, while pure hydrogen is needed for ammonia plants and fuel cells. CO is a poisonous gas and its concentration is required to be lower than

1 ppmv for proton exchange membrane type fuel cell while it is desired as a better reductant than H<sub>2</sub>, for the reduction of iron, [1–9].

Elimination of carbon monoxide by converting it into dioxide form is also critical in gas separation applications. While CO<sub>2</sub> can be easily removed from the products of the reactions by absorption in amine solutions, CO has to be removed either by liquefaction or copper liquor scrubbing [1]. Adsorption isotherms of CO and H<sub>2</sub> on adsorbents are more similar than those of CO<sub>2</sub> and H<sub>2</sub>. The similarity of adsorption isotherms results in poor hydrogen yield of adsorption based gas separation processes such as pressure swing adsorption in relation to the case of CO<sub>2</sub>–H<sub>2</sub> mixture [10–12]. Therefore, for an effective carbon capture and storage, the gas stream has to be shifted to CO<sub>2</sub> from CO. CO<sub>2</sub> can more easily be separated from the gas mixtures either by absorption based scrubbing or by membrane processes in relation to CO. For this reason, conversion of CO to CO<sub>2</sub> is mandatory in order to attain CO<sub>2</sub> purity higher than 90% [13] in the effluent stream.

Water gas shift (WGS) is a catalytic reaction. In the reaction, CO is oxidized with steam to shift into CO<sub>2</sub> and H<sub>2</sub>. It is a moderately exothermic reversible reaction. There are four general types of water gas shift catalysts: iron oxide (350–450 °C), copper–zinc oxide (190–250 °C),

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cobalt and molybdenum sulfides (sour gas shift) and copper–zinc catalysts modified by iron oxide (275–350 °C) [14,15].

In response to the need of fuel cell applications, alternative noble metal-based reforming and WGS catalysts are under intense development worldwide. The use of these catalysts wash-coated on monolith provides various advantages such as reducing catalyst bed volume due to high space velocities, high catalytic activity and eliminating the self-heating issue [16–25].

In the present study, the operational window of the high temperature WGS reaction has been driven in order to reach a better design of gas conditioning unit for gasification plants. Although design constraints have been quite definite and operational borders are widely available in the literature for HTS catalysts, in this study a specific precious metal based monolithic catalyst was studied. The effects of the inlet gas composition, the gas hourly space velocity, the inlet steam to CO ratio and the reaction temperature on the activity of the catalyst were investigated in order to determine the optimum operation conditions for mobile applications and semi-pilot scale gasification plants.

## 2. Experimental

### 2.1. Material and methods

A commercial ceramic monolith catalyst coated with finely divided platinum group metals (including platinum, palladium and rhodium) on mixed metal oxides (including zirconium) support was tested in the experiments. The catalyst has a diameter of 13 mm and a cell density of 600 cpsi.

Catalyst performance tests were carried out by using an experimental set-up schematically shown in Fig. 1. It essentially consists of a fixed bed reactor, equipment for feeding, measuring/adjusting the flow rate of gases and steam, analyzing the compositions of gases, cooling of effluent gases, measuring and controlling temperature. The reactor is a

310 grade stainless steel tube of 15.55 mm i.d. and 500 mm in length and is externally heated by an electrical furnace equipped with a programmable temperature control assembly. The monolith catalyst was positioned at the center of the reactor and supported by a porous quartz disk. The temperature measurements were carried out with three K-type thermocouples (TC) which are positioned along the reactor tube as seen in Fig. 1. The first TC was inserted just before the monolith, the second one was located on the outer surface of the monolith and the last TC was positioned just after the monolith. All TCs were connected to a multi channel digital read-out to monitor the temperature values. Simulating gas mixtures were prepared from pure gases. Gases from gas cylinders, passed through purifiers, were measured via digital mass flow controllers and introduced into a common gas line leading to the bottom of the reactor. Steam was supplied by a controlled evaporator–mixer (CEM) equipment which could supply vapor at desired and constant flow rates. Gas lines leading to the reactor were heated and insulated to prevent vapor condensation. In order to remove vapor, gases from the reactor were cooled in a chiller before they are sent to the gas analysis unit. A gas chromatography (Agilent 6890) with two thermal conductivity detectors (TCD) was used to measure permanent gases, namely H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>. H<sub>2</sub> was detected by a TCD with a HP-PLOT Q column, while other gases were analyzed by using a second TCD under helium atmosphere. CO<sub>2</sub> has been separated from CO, N<sub>2</sub> and CH<sub>4</sub> with a six-way valve and analyzed separately via another HP-PLOT Q column. The separated gas mixture of CO, N<sub>2</sub> and CH<sub>4</sub> was detected on the same TCD by using HP-PLOT/Molsieve column. Gas chromatograph was calibrated by using the standard gas samples of known compositions prior of each run.

In a typical performance test, 8.62 g catalyst with a diameter of 13 mm was loaded into the reactor in monolith form. A ceramic material was used to blanket the outer surface of the catalyst for tightness. Then it was inserted into the center of the reactor tube so that the gas flows completely through the cells of the monolith catalyst.

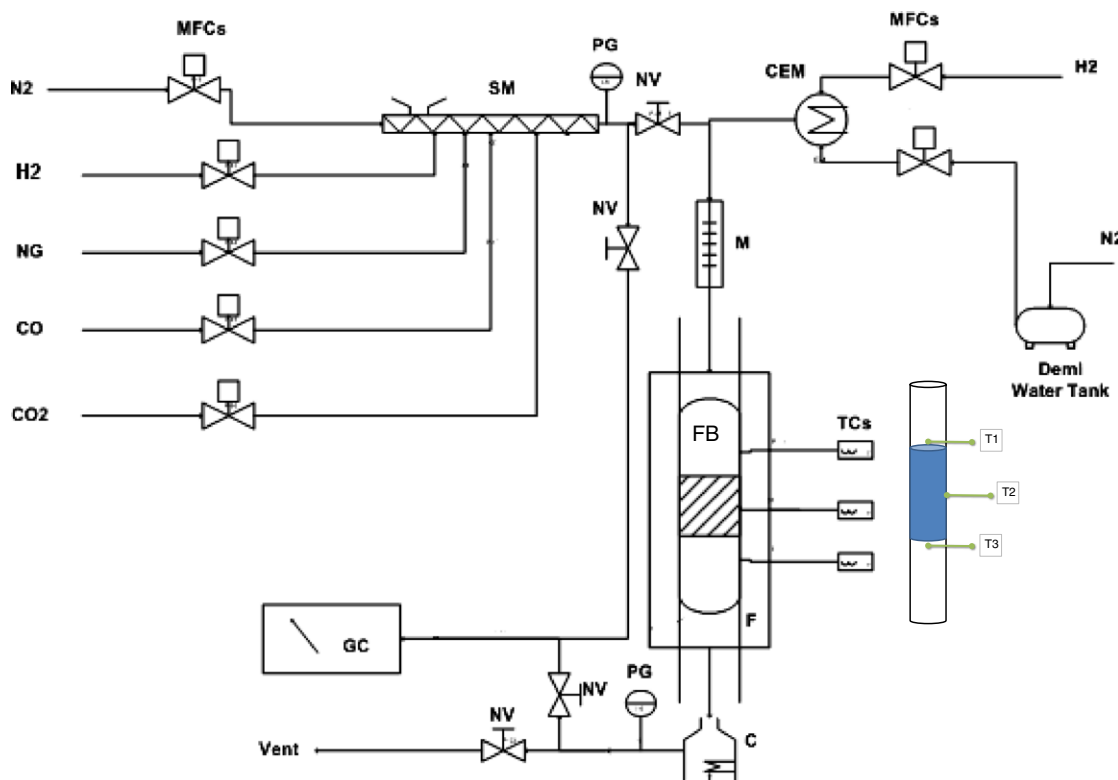


Fig. 1. Schematic representation of the test system. F: furnace, FB: fixed bed reactor, GC: gas chromatograph for permanent gas analysis, MFC: mass flow control valves, CEM: controlled evaporator and mixer, M: mixing manifold, NV: needle valve, SM: static mixer, PG: pressure gauge, TC: thermocouple, NG: natural gas, C: condenser.

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