Research article

Water gas shift catalysts for hydrogen production from biomass steam gasification

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A B S T R A C T

Iron/ceria based catalysts were developed for high temperature Water Gas Shift (WGS) reaction in order to increase hydrogen content in the syngas at the outlet of a steam biomass gasifier working at atmospheric pressure. Alumina foam was used as support to deposit ceria and iron phase to prepare catalysts. The use of ceramic foams with different porosities (30 ppi and 45 ppi) assured a very low pressure drop in the process. The optimal conditions for WGS were determined in line with conditions occurring after gasification. The activity of the 45 ppi catalyst in the WGS reaction at 450 °C (CO conversion = 50%) can be reached by the 30 ppi catalyst by adjusting the gas hourly space velocity. The amount of carbon deposition observed on the catalyst, under the gas mixture representative of the syngas at the gasifier outlet, can be limited by the addition of steam (S/C ratio ≥ 2). These conditions also led to less stable carbon. Characterizations on the spent catalyst indicated the in-situ activation of the catalyst with no over-reduction of iron oxide. The stabilization of the catalytic activity could be related to the stabilization of both the particle size and carbon deposition. The carbon formation rate (decreasing exponential curve) stabilization could be associated to the beginning of a steady state, the carbon remaining on the catalyst being at the lowest stable form.

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1. Introduction

Biomass is known to be a major potential resource to produce renewable energy. Thermal conversion processes (combustion, pyrolysis, liquefaction, gasification) can lead to the direct production of energy such as electricity and heating or to the production of bio-oils and syngas which can be converted into electricity, chemical products or fuels [1–4].

To obtain a continuous process for pure hydrogen production from biomass, a circulating bubbling fluidized bed gasifier was developed (European Collaborative Project: UNIQUE gasifier for Hydrogen production "UNIfHY" [5]) using steam as the oxidative agent to increase H_2 content in the produced syngas [1,4]. A Water Gas Shift (WGS) unit working at the outlet of the gasifier is needed to optimize the H_2 production before a Pressure Swing Adsorption (PSA) system.

Typically, the WGS reaction is performed in two steps: a high temperature step (HT, 300–500 °C) with an iron based catalyst as α-Fe_2O_3 which can be reduced in the Fe_3O_4 active phase and a low temperature step (LT, 200–300 °C) with a copper based catalyst as CuO crystallites which can be reduced in the Cu^0 active phase [6–10]. One of the most important difficulties encountered with HT catalysts is the thermal sintering of iron particles [11] which leads to a loss of catalytic activity.

Cr_2O_3 is generally used as a promoter to increase catalyst stability. However, the toxicity of chromium oxide has led researchers to turn towards other less toxic oxides such as Ce, Ca, La, Al, Cu or Zr oxides [7–14].

Another difficulty met by the WGS catalysts is the pressure drop induced by the use of a fixed bed reactor. The development of a WGS catalyst supported on ceramic foam [15] permits the limiting of the pressure drop in the WGS reactor and to operate at atmospheric pressure in the biomass gasifier.

The very low specific surface area of the alumina ceramic foams can be improved by the use of a ceria washcoat to increase the further dispersion of iron oxide particles and its better anchorage [15]. The thermal sintering of the catalytic phase is then limited by increasing the stability of the catalyst [16–18]. Ceria can also limit carbon formation during catalytic tests and help to maintain the catalyst in partially oxidized active form (Fe_3O_4) because of the high oxygen mobility of ceria structure [17–21].

The aim of this study is to validate the efficiency of some iron/ceria/foam catalysts previously developed [15] for high temperature Water Gas Shift reaction and which would be used in the conditions (temperature, gas flow rate, gas composition) of the gasifier outlet. The influence of operating parameters such as S/C ratio and time on stream was evaluated on the catalysts efficiency and stability during high temperature Water Gas Shift and related to the particles sintering and the coke formation on iron catalysts supported on foam with various porosities.

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2. Material and methods

2.1. Catalyst preparation

Alumina ceramic cylinder foams (20 mm outer diameter and 20 mm length), provided by Pall Filtersystems GmbH, were used as support to deposit iron phase to prepare Water Gas Shift catalysts. Two different porosities were studied: 45 and 30 pores per inch (ppi).

Preparation of the WGS catalysts was performed in two steps. First, the foam was washcoated with a wet impregnation of a cerium nitrate aqueous solution (1.7 mol L^{-1}), dried (100 °C for 52 h) and calcined (3 °C/min, 400 °C for 4 h). Second, the washcoated foam was impregnated (same method) by an iron nitrate aqueous solution (2.1 mol L^{-1}) then dried (100 °C for 52 h) and calcined in the same conditions (3 °C/min, 400 °C for 4 h).

2.2. Characterization techniques

X-ray diffraction patterns were acquired with a Brucker AXS-D8 Advanced using CuK radiation (λ = 1.5406 Å) to identify the crystalline phases (step = 0.06°, time per step = 2 s) in a 2θ range of 20°–70°. The diffraction spectra have been indexed by comparison with the JCPDS files (Joint Committee on Powder Diffraction Standards). The washcoat and catalyst particle sizes were determined by Debye – Scherrer equation from the width at half-height (FWMH) of the more intense and better deconvoluted ray of each.

The surface area of washcoated and catalytic foams (BET) was obtained by means of nitrogen adsorption at 77 K using a Micromeritics ASAP 2420 instrument. Before the taking of each measurement, the samples were degassed overnight under vacuum, at 250 °C.

The temperature programmed reduction (TPR) was performed with a Micromeritics Autochem II Chemisorption Analyzer on 150 to 500 mg of sample under $10\%H_2$/Ar with a total gas flow of 50 mL·min^{-1}. The temperature was increased from room temperature to 900 °C at a rate of 15 °C·min^{-1} and the hydrogen consumption of the samples was followed by a thermal conductivity detector (TCD) until returning to the baseline.

The temperature programmed oxidation (TPO) was performed on 150 to 500 mg of sample under $1\%O_2$/He with a total gas flow of 5 mL·min^{-1}. The temperature was increased from room temperature to 950 °C at a rate of 15 °C·min^{-1} by using a Micromeritics Autochem II Chemisorption Analyzer coupled with a mass spectrometer (Quadrupole Pfeiffer Omnistar, Ion Current 44) to follow CO_2 production and deduce the amount of carbon formed on the catalyst during the reactivity tests.

2.3. Reactivity tests

The catalysts were tested in high temperature Water Gas Shift reaction (450 °C). The inlet gas mixture was controlled by mass flowmeters. Steam was produced by the injection of water in a vaporization room (100 °C) then carried to the reactor by the flow of gas mixture. The catalytic foams were tested in a quartz tubular reactor (i.d. of 2 cm) equipped with two pressure taps for the pressure drop measurement. The latter was performed with a PD-41× (KELLER instrument, 0–30 mbar) at 25 °C under 450 mL·min^{-1} of air to evaluate whether the foam pores filling could be penalizing for further application. The reactor was placed in a furnace controlled by a thermocouple. At the reactor outlet, water was trapped by condensation in an ice bath.

Gaseous products were analyzed on-line by a micro-gas chromatograph (Hewlett Packard Quad Series, Micro GC Model G2891 A, SRA instruments) equipped with a TCD and two different columns permitting the N_2 + CO, CH_4 and CO_2 separation on a PoraPLOT U column and the H_2, N_2, CH_4 and CO separation on a molecular sieve MS5A column.

The reactivity tests were performed at 450 °C by using a fresh catalyst for each test under a gas mixture corresponding to that obtained at the gasifier outlet (dry composition: 47% H_2, 27% CO, 19% CO_2, 2% CH_4 and 5% N_2). Steam was added to this mixture in order to obtain an S/C ratio in the range between 0.65 and 3. The gas hourly space velocity then changed from 7200 h^{-1} to 11,250 h^{-1} due to steam addition.

The total flow rate varied from 80 NmL·min^{-1} to 410 NmL·min^{-1} to study the effect of the gas hourly space velocity (GHSV) which was chosen in accordance with the conditions of the biomass gasification (from 1800 to 9500 h^{-1}).

The catalysts reactivity in Water Gas Shift reaction are given in terms of CO conversion which was calculated as the fraction of CO consumed to CO in the inlet feed (Eq. (1)).

$$\%CO_{conv} = \frac{CO_{in}\text{-}CO_{out}}{CO_{in}} \tag{1}$$

where the CO_{in} and CO_{out} are the CO moles in the inlet and outlet gas, respectively.

The comparison of H_2 content at the reactor outlet (calculated in the dry gaseous mixture) and H_2 content at the reactor inlet (47%) also permitted the evaluating of the catalytic reactivity in Water Gas Shift reaction. The values of CO conversion and H_2 content were always compared to the thermodynamic values calculated under the same conditions (Prosim software).

The carbon balance (CB) was determined by the following equation (Eq. (2)).

$$CB = \frac{CH_{4out} + CO_{2out} + CO_{out}}{CH_{4in} + CO_{2in} + CO_{in}} * 100 \tag{2}$$

where the $CH_{4\ out}$ and $CO_{2\ out}$ are the CH_4 and CO_2 moles in the outlet gas, respectively, and the $CH_{4\ in}$ and $CO_{2\ in}$ are the CH_4 and CO_2 moles in the inlet gas, respectively. No other carbonaceous product was detected.

3. Results and discussion

3.1. Catalyst characterization

The catalysts studied are presented in Table 1. The optimal ceria and iron contents were chosen after characterizations [14] for the two foam porosities, respectively.

These catalysts were characterized by X-ray diffraction, BET surface area and temperature programmed reduction before reactivity tests.

3.1.1. X-ray diffraction

X-ray diffraction patterns of catalytic foams show the presence of corundum syn-Al_2O_3 (JCPDS: 10-0173), ceria CeO_2 (JCPDS: 65-5923) and hematite α-Fe_2O_3 (JCPDS: 33-0664). X-ray diffraction was also used to determine ceria and hematite particle sizes (Table 2).

The size of ceria particles is within an average of 9 nm and the size of hematite particles is between 22 and 29 nm. The porosity of the foam (45 ppi or 30 ppi) and the increase in ceria content from 4.8 to 7.4 wt.% have no influence on ceria particle size and a slight influence on hematite particle size.

Table 1
Catalysts composition and BET surface area of washcoated foams and catalytic foams.

Foam porosity (ppi)	Washcoated foams		Catalytic foams	
	wt% CeO_2	BET surface area (m²·g^{-1})	wt% Fe	BET surface area (m²·g^{-1})
45	4.8	4.8	5.7	7.9
30	7.4	8.4	5.5	8.0