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Could an efficient WGS catalyst be useful in the CO-PrOx reaction?

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ABSTRACT

This work presents an evaluation of a high performance series of water gas shift (WGS) catalysts in the preferential CO oxidation reaction (PrOx) in order to examine the applicability of the same catalyst for both processes as a first step for coupling both reactions in a single process. Gold based catalysts are applied in an extensive study of the CO-PrOx reaction parameters, such as λ, WHSV, CO concentration and $[H_2O]/[CO_2]$ ratio in order to obtain the best activity/selectivity balance. CO and H_2 oxidation reactions were treated separately in order to establish the degree of CO/H_2 oxidation competition. Additionally the catalysts behavior in the CO-PrOx parallel reactions such a WGS and RWGS have been also carried out to analyze their effect on product composition.

1. Introduction

The hydrogen-fueled polymer electrolyte membrane fuel cell (PEMFC) is considered a very promising candidate to directly convert chemical into electrical energy [1]. PEMFCs appear to be a viable technology for small-scale electricity production as required for electric vehicles and residential power generators due to their advantageous features, such as low-operating temperature (80–200 °C), sustained operation at high current density, low weight, and compactness, potential for low cost, fast start-up and suitability for intermittent operation [2]. These small-scale units depend on processing a hydrocarbon fuel for producing a H_2-rich product that fuels PEMFCs. Fuel processors convert liquid hydrocarbons, the volumetric energy content of which is much larger than that of bottled hydrogen, into an almost CO-free H_2-rich product through the coupling of several catalytic reactions, such as reforming, usually steam reforming, WGS, PrOx and/or methanation ones [3–6]. The water gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) is a critical step in fuel processors for preliminary CO clean-up and additional hydrogen generation prior to the CO preferential oxidation or methanation step [4–7]. WGS units are placed downstream of the reformer to lower the CO content and improve the H_2 yield. However, WGS is an equilibrium-limited reaction and CO concentrations below 10 ppm (requisite for the PEMFC anode) cannot be reached even with high H_2O/CO ratios at reaction temperatures above 200 °C [8]. Therefore, an additional CO removal process is always required.

Preferential CO oxidation of the pre-cleaned reformate stream (PrOx) with air is one of the most effective methods for CO abatement from the reformate stream prior to its introduction in the PEM cell [9]. High CO oxidation activities coupled with low hydrogen ones (at the desired oxidation temperature) are essential requirements for the PrOx catalysts [10,11].

In recent years, there has been great interest in the CO oxidation reaction over gold-based catalysts [12–14]. Despite bulk metallic gold being a very poor catalyst in this reaction, supported gold nanoparticles are able to eliminate CO even at sub-ambient temperatures [15,16]. Nanogold catalysts are promising candidates for the PrOx reaction for two main reasons: (i) they show extraordinarily high activity in the low temperature range, which is appropriate for fuel cell applications, (ii) the rate of CO oxidation exceeds that of hydrogen oxidation in the relevant temperature range [17,18]. In addition to high activity and selectivity, a suitable PrOx catalyst must also tolerate high amounts of CO_2 and H_2O present in the reformate stream [19]. Generally, the presence of both CO_2 and H_2O diminishes CO conversion, especially at low temperatures [20,21]. An excellent WGS catalyst withstands high amount of H_2O. The ability of a catalyst to admit large ranges of CO_2 concentrations in both WGS and PrOx, generally depends on its composition, specifically on the support nature, with acid supports more

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resistant to deactivation. It was recently reported by Tabakova et al. [2] that an $Au/CeO_2–Fe_2O_3$ system can successfully tolerate CO_2 and H_2O allowing good performance in the PrOx reaction. For the WGS reaction an efficient catalyst based on a similar system, $Au/CeO_2–FeO_x/Al_2O_3$ was also reported [22].

Following the concept of process intensification, it would be interesting to design a reactor where both reactions (PrOx and WGS) are successfully carried out in a single catalytic wall reactor by careful control of the temperature profile of the reactor and the reactant insertion zones, this way doing away with one reactor on the overall CO clean-up process (Scheme 1). The development of such an advanced reactor may reduce cost and system volume allowing the adaptation of this type of fuel processor to smaller devices for portable applications. Considering the experimental conditions in which WGS and PrOx take place, i.e. space velocity, temperature window, equilibrium limitations etc., coupling these reactions in a single reactor is a great challenge. Nevertheless, as a first step toward process intensification, the preparation of one efficient catalyst for both processes is required.

Considering the promising features of gold based systems for these reactions, the aim of this work is to study the possibilities of use of a gold-based WGS catalyst in the PrOx reaction with the idea of facilitating the possible future coupling of these reactions in a single reactor.

2. Experimental

2.1. Catalyst preparation

The supports were prepared by impregnation of $Ce(NO_3)_3·6H_2O$ and $Fe(NO_3)_3·9H_2O$ (Aldrich) on γ-alumina powder (Sasol) in order to obtain a cerium-iron mixed oxide dispersed on alumina. The precursor amounts were calculated in such a way so that the final loading of CeO_2, FeO_x or $CeO_2–FeO_x$ solid solution were 15 wt.% of the final solid. In order to ensure the production of a $FeO_x–CeO_2$ solid solution, the FeO_x content was always maintained below 3 wt.% [22]. Gold (2 wt.% nominal) was deposited by the direct anionic exchange method, assisted by NH_3, as described elsewhere [23].

In the adopted nomenclature, oxygen is omitted for simplification and the FeO_x contents are expressed as the theoretical catalyst loading. For example, the Au/CeFe0.5/Al solid contains 2 wt.% Au loading over a CeFe mixed oxide in which the FeO_x content is 0.5 wt.% and CeO_2 loading is approximately 14.5 wt.%, deposited on Al_2O_3 support.

2.2. Catalytic activity and selectivity

2.2.1. Preferential CO oxidation

PrOx reaction was carried out at atmospheric pressure on a cylindrical fixed bed quartz reactor (9 mm inner diameter) at 60,000 $cm^3\,g_{cat}^{-1}\,h^{-1}$. For each test, 100 mg of catalyst sieved between 100–200 μm were loaded in the reactor. To minimize, as far as possible, the thermal effects due to the oxidation reaction, the samples were diluted in quartz. The feed flow rate was 100 $cm^3\,min^{-1}$ containing 1% CO, 1.5% O_2, 50% H_2 and He as a balance. To study the effect of H_2O and CO_2 on catalyst activity and selectivity, 10% of each compound was added in the feed. Prior to catalytic measurements, the samples were treated under a 100 $cm^3\,min^{-1}$ flow of 21% O_2 in He, at 300 °C for 1 h. The influence of the λ parameter ($\lambda = 2[O_2]/[CO]$) was studied varying λ from 1 to 4 conserving 1% of CO in all the cases. The influence of space velocity was studied by varying the WHSV between 12,000 and 120,000 $cm^3\,g_{cat}^{-1}\,h^{-1}$. Water was added to the dry gas stream via a HPLC pump (Gilson 307). Product and reactant analyses were carried out by a gas chromatograph (ShimadzuGC-14B) equipped with a TCD detector.

The CO conversion was calculated according to Eq. (1) where CO_{in} is the CO concentration in the inlet and CO_{out} is the one at the outlet:

$$CO\,conversion\,(\%) = \frac{CO_{in} - CO_{out}}{CO_{in}} \times 100 \qquad (1)$$

The O_2 selectivity towards CO_2 formation was calculated with Eq. (2). O_{2in} corresponds to oxygen in the inlet and O_{2out} to the one at the outlet.

$$O_2selectivity\,(\%) = \frac{(CO_{in} - CO_{out}) \times 100}{2 \times (O_{2in} - O_{2out})} \qquad (2)$$

2.2.2. CO and H_2 oxidation

CO and hydrogen oxidation were carried out at atmospheric pressure in a stainless steel fixed bed reactor (9 mm inner diameter) at 30,000, 60,000 and 120,000 $cm^3\,g_{cat}^{-1}\,h^{-1}$. The composition of the CO oxidation stream was 1% CO, 1.5% O_2 and N_2 as balance, while for H_2 oxidation the reactant stream was 1.5% O_2, 50% H_2 balanced in N_2. The catalyst (100 mg, $100 < \phi < 200$ μm) was diluted with crushed glass particles in the same particle size range forming a bed of about 5 mm in length. Products and reactants were analyzed by on-line gas chromatography (Agilent® 6890) equipped with a HP PLOT Q and HP-5 columns and a TCD detector. Prior to catalytic measurements, the samples were treated under a 100 $cm^3\,min^{-1}$ flow of 21% O_2 in N_2, at 300 °C for 1 h.

2.2.3. Water gas shift and reverse water gas shift reactions

The study of the water gas shift reaction was carried out at atmospheric pressure in a stainless steel fixed bed reactor (7.5 mm inner diameter) at 60,000 $cm^3\,g_{cat}^{-1}\,h^{-1}$. A 100 $cm^3\,min^{-1}$ reaction mixture composed of 1% CO, 10% H_2O and N_2 as balance was flowed over 100 mg of catalyst. For the reverse water gas shift, the reaction flow was composed of 10% CO_2, 50% H_2 and N_2 as balance and the same space velocity was used. Products and reactants were analyzed by on-line URAS 2G CO, CO_2 gas analyzers (ABB A02020)

2.2.4. CO/H_2 and $CO/O_2/CO_2/CO$ pulses

For pulse experiments 100 mg of catalyst was loaded into a U-shaped quartz reactor. The samples were first activated in an O_2/He flow (50 $cm^3\,min^{-1}$) at 300 °C during 1 h. After cooling and stabilizing the temperature, 10 O_2 pulses followed by 10 H_2 pulses (1 cm^3 each) were sent in order to reproduce as far as possible the PrOx reaction conditions. After that, CO–H_2 pulses were alternatively introduced in the reactor every 2 min. The gas composition at the exit of the reactor was analyzed by a mass spectrometer PFEIFFER Vacuum Prisma Plus controlled by the program Quadera®.

To study the inhibitory effect of CO_2, a series of $CO/O_2/CO_2/CO$ pulses were also studied. The sample was pretreated at 300 °C as explained above. Afterwards, the sample was cooled and the temperature was fixed at 150 °C. $CO/O_2/CO_2/CO$ pulses (1 cm^3 each) were sent and the gas composition at the exit of the reactor was analyzed with the same mass spectrometer.

3. Results and discussion

3.1. Effect of iron in the PrOx reaction

Full details of characterization and preparation of the studied catalysts have been given elsewhere [22]. Although, they are not subject of this study they will be further used for correlating the results obtained in the present work with the catalyst properties. Nevertheless, it is worth to briefly summarize the main