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Oxygen-enhanced WGS over ceria-supported Au–Co_3O_4 bimetallic catalysts

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HIGHLIGHTS

- Au–Co_3O_4/CeO_2 catalyst performance in WGS enhances by O_2 addition.
- Gold addition increases OSC in the range 120–250 °C.
- Catalysts show better performance when cobalt is added by IWI compared to DP.

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ABSTRACT

Aiming at enhancing CO conversion in Water Gas Shift (WGS) for fuel cell application, a small amount of oxygen was added to reactor feed stream in Oxygen-enhanced WGS reaction (OWGS) over monometallic Co_3O_4 and bimetallic Au–Co_3O_4 catalysts, both supported on ceria and prepared by different methods. Both CO conversion and H_2 yield were found to increase by the oxygen addition. Ceria-supported Co_3O_4 monometallic catalysts were prepared by incipient wetness impregnation and deposition precipitation methods (both with 10 wt.% of Co loading). Au incorporation was added by deposition precipitation method (1 wt.% of Au loading). The as prepared catalysts were characterized by a sort of different techniques in order to correlate their activity with the physicochemical properties. The accumulation of carbonates and H_2O during reactions on the tested catalyst is revealed by O_2-TPO. The results indicated a high dispersion of gold independent of the preparation method of Au–Co bimetallic catalysts. Gold incorporation at Co_3O_4/CeO_2 catalysts was observed to increase the capacity to release lattice oxygen from the catalysts to oxidize CO at low temperatures than pure Co_3O_4/CeO_2. OSC cycles demonstrated that gold-containing catalysts increase the CO_2 formation at 120 and 250 °C. Higher CO conversion is achieves in OWGS than in WGS, independent of the gold presence. Au–Co_3O_4/CeO_2 show strong synergetic promoting effect in OWGS.

1. Introduction

Proton exchange membranes (PEM) fuel cells have attracted much attention as a potential power source of electric vehicles due to their low operation temperature, excellent energy efficiency and null emissions of air pollutants [1]. Hydrogen is the preferred fuel for fuel cells, however there are still many problems related to the issue of hydrogen distribution and storage. One of the alternatives is to produce energy on board from any hydrocarbons by means of consecutive multistep catalytic processes in the called Fuel Processor Unit (FPU) [2]. Depending of on the type of reforming, operation conditions and employed fuel, the reformer exit stream contains 3–10 vol.% of CO, and is further converted to CO_2 (with additional formation of H_2) via the double step Water Gas Shift reaction (WGS) (reaction (1)) which is a preferable method for CO removal due to a lower calorific value than the oxidation [3]. Further CO removal is required in order to achieve PEM fuel cell requirements (namely <50 ppm CO) for which purpose CO-PROX (reactions (2) and (3)) is the most suitable method. Combining WGS and CO-PROX reactions in a single stage process, called Oxygen-enhanced assisted-Water Gas Shift (OWGS), will decrease the total volume for the FPU which is optimal beneficial for automotive applications.

Some works pointed that the gas phase oxygen promotes the WGS reaction [4–6] by facilitating the dissociative adsorption of water [7–9]. OWGS reaction involves many simultaneous reactions (reactions (1)–(3)) being reaction (1) the only that produces H_2, while reaction (3) causes loss of H_2. Addition of small amounts of O_2 enhances CO removal from reformed fuels without consuming significant amounts of H_2 [10].

$$CO + H_2O \leftrightarrows CO_2 + H_2 \quad \Delta H^\circ = -41.1 \text{ kJ mol}^{-1} \tag{1}$$

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$$CO + 1/2O_2 \rightarrow CO_2 \quad \Delta H^\circ = -283\ kJ\ mol^{-1} \qquad (2)$$

$$H_2 + 1/2O_2 \rightarrow H_2O \quad \Delta H^\circ = -242\ kJ\ mol^{-1} \qquad (3)$$

Cu–ZnO–Al_2O_3 are the typical catalyst employed for low temperature (LT) WGS in stationary hydrogen plants, but these catalysts are not suitable for on board fuel cell applications due to their large volume occupying in the FPU and their pyrophoric nature that requires careful pre-conditioning and periodic regeneration. For automotive applications the objective is to find suitable catalysts to OWGS reaction. There are several reports describing the use of noble metals for CO oxidation and WGS; however, due the high cost of noble metals, considerable attention has been paid to various transition metal oxides and mixed metal oxides [11]. Ceria supported metal oxide such as Co_3O_4 or bimetal Pd–Fe, Pd–Mo, Cu–Pd, Cu–Au, Co_3O_4–Au [3,12–15] have been identified as promising catalysts for both WGS and CO-PROX, due to the enhanced redox properties associated to the metal-ceria interaction. In both reactions, ceria contributes to the reaction by facilitating redox process, providing activated oxygen to oxidize the CO adsorbed on the metal; subsequently, Ce^{+3} is reoxidized by water or oxygen H_2O or O_2 [16–19]. Also the promoter metal species interacting with the support plays an active role in the reaction. Cobalt oxide (Co_3O_4) is very attractive promoter for the preparation of oxidation catalysts because of the presence of mobile oxygen in the resulting oxide Co_3O_4 [20,21]. The high activity of Co_3O_4 on CO oxidation is likely related to the relative weak Co–O bond which facilitates an easy release of lattice oxygen [22].

It was experimentally proven that higher CO conversions are obtained in a single OWGS step than in consecutive WGS + CO-PROX [4–6]. In previous work [14] we studied Au–CuO/Ceria catalysts and found that sample prepared by DP showed the best performance. The aim of this work is to check the proficiency of cobalt oxide as alternative of copper oxide, in both the activity and hydrogen-yield in OWGS reaction. For such an objective we explore the effect of the preparation of cobalt on ceria catalysts method as well as the promotion of addition of small amount of gold for their use in OWGS reaction.

2. Experimental

2.1. Catalysts preparation

Commercial high surface ceria (Rhodia, $S_{BET} = 227\ m^2/g$) has been used as a support, previously stabilized at 900 °C. Monometallic cobalt/ceria catalysts were prepared by incipient wetness impregnation (IWI) and deposition precipitation method (DP) from aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$, with a nominal cobalt loading of 10 wt.%, then dried at 110 °C overnight and calcined in air at 500 °C for 5 h. The as-prepared samples were labelled as CoCe-IWI and CoCe–DP, respectively.

For the preparation of bimetallic Au–Co_3O_4/CeO_2 catalysts, gold was deposited on previously prepared Co/Ceria substrates (CoCe–DP and CoCe–IWI) by deposition precipitation method (DP) from aqueous solution of $HAuCl_4{\cdot}3H_2O$ with nominal gold loading of 1 wt.%. The samples were dried overnight at 110 °C in air and finally calcined at 350 °C for 3 h.

2.2. Characterization of catalysts

Specific surface area and pore size distribution of the samples were determined by N_2 adsorption–desorption isotherms at 78 K (MicromeriticsTristar 3000). Actual gold and cobalt content were evaluated by atomic absorption spectroscopy (Perkin Elmer AAnalyst 800). The phase identification was carried out by XRD (Philips PW1710 diffractometer) using a finely grounded powder sample with Cu Kα radiation in continuous scan mode (2θ = 10–50°). PANalyticalX'pert High Score specific software was used for data interpretation, and the phases present in the samples were identified by comparing with the JCPDS Power Diffraction File (PDF) database. Crystallite sizes for the detected phases were estimated by means of Scherrer equation.

Raman measurements were carried in powder form out using a Renishaw In via Raman spectrometer, joined to a Leica DMLM microscope using 532 nm ion-argon laser. For each spectrum, 30 s were employed and 10 scans were accumulated in the spectral window from 150 to 1500 cm^{-1}.

The redox capacity of the samples was investigated by multiple techniques as H_2-TPR, CO-TPD and OSC. Before H_2-TPR experiments, the CoCe samples (ca. 0.3 g) were heated in 5% O_2/He flow from room temperature up to 600 °C (400 °C in the case of AuCoCe samples) up to 400 °C and then cooled to −20 °C in He flow. H_2-TPR profiles were recorded during the heating stage of the sample from −20 to 400 °C in 5% H_2/Ar flow, with a heating ramp of 10 °C/min. Hydrogen consumption was continuously monitorized by TCD detector.

The catalysts ability to adsorb CO was analyzed by temperature-programmed desorption (CO-TPD). 5% CO/He flow was passed through the catalyst bed at 0 °C during 30 min, then purged in He flow for 2 min. Finally, the sample was heated in He flow from 0 to 400 °C with heating ramp of 20 °C/min meanwhile the exhaust gas was continuously monitorized by QMS (MKS Cirrus 300) coupled to NDIR selective detector for CO (Siemens Ultramat 23). QMS signals for CO (m/z = 28), and CO_2 (m/z = 44) were followed.

O_2-TPD was carried out in order to elucidate the active species for oxygen adsorption. The samples were pre-treated in He at 300 °C for 1 h, then the oxygen adsorption was proceeded with 5% O_2/He at 200 °C for 0.5 h. After cooling to room temperature, the O_2-TPD measurement was performed, the sample was heated in He flow (30 mL/min) from room temperature to 900 °C with heating ramp of 20 °C/min.

The catalyst ability to store and release oxygen in dynamic operation (OSC, defined as the CO_2 formed during a CO step pulse after oxidation in O_2) were carried out immediately after the CO-TPD and measured at 120 and 250 °C, which are taken as a representative temperatures for CO-PROX and LTWGS reactions, respectively, with the following procedure: 5% CO/He, 9 min→He, 6 min→ 5% O_2/He, 9 min→ He, 6 min, with a total flow of 100 mL/min in all steps. Also QMS was used for continuous monitoring of reactor exhaust. H_2-TPR, CO-TPD, O_2-TPD, O_2-TPO and OSC measurements were carried out in the same experimental equipment (MicromeriticsAutochem 2910).

O_2-TPO was performed to detect the possible formation of carbonates species during the reaction test. The samples used after OWGS reaction were purged in a He flow at 200 °C for 1 h and were cooled to room temperature prior to the analysis. A flow of 5% O_2/He (30 mL/min) was then switched into the system, and the sample was heated up to 500 °C with heating ramp of 10 °C/min. The amount of O_2, CO, CO_2, H_2 and H_2O in the exhaust gas was continuously monitorized by QMS (MKS Cirrus 300).

2.3. Activity measurement

Catalysts activity in WGS and OWGS reaction were evaluated in a down-flow plug flow reactor (Microactivity-Reference, P&ID) at atmospheric pressure. About 0.1 g of catalyst (0.16–0.25 mm diameter) was loaded and diluted with about 0.5 g alumina to reach a total volume of 1 mL in order to dissipate the heat released in the reaction. For all the activity experiments, a total flow rate of 200 mL/min ($GHSV = 12{,}000\ h^{-1}$, $WSV = 1.83\ NL\ min^{-1} g^{-1}$) was fed into the reactor. The composition of feed gas (in vol.%) for WGS reaction was $CO/H_2O/H_2/CO_2$ = 4/9.4/37.9/3 balanced to He.