

Effect of process variables on Pt/CeO₂ catalyst behaviour for the PROX reaction

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Abstract

A Pt/CeO₂ catalyst has been evaluated for CO oxidation, both in the absence of H₂ and in H₂-rich feedstreams. The catalyst shows high activity and selectivity at temperatures as low as 80 °C, what makes it a viable catalyst for the selective depletion of CO in the temperature range at which PEMFC operate. The effect of: oxygen excess during operation (λ), the presence of either CO₂ (5%), H₂O (5%) or both in the feedstream, and the spatial time, on catalyst activity and selectivity has been evaluated.

A λ value of at least 2.25 was required for achieving total CO conversion, which occurs in the temperature range of 80–100 °C, being the selectivity practically stable at 44%. The presence of CO₂ slight activates the catalyst, while steam inhibits catalyst activity. Water gas shift reaction contribution to CO oxidation was checked to be negligible in the 25–200 °C range.

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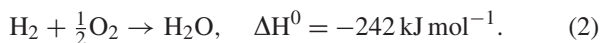
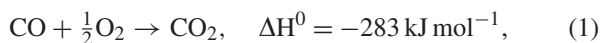
Keywords: Cerium oxide; Pt; CO oxidation; Selective CO oxidation; Catalyst yield

1. Introduction

Hydrogen is a fuel for the proton exchange membrane fuel cells (PEMFC). For transport and residential applications, hydrogen could be produced by means of fuel reforming, which should be followed by water gas shift reaction (WGSR) in order to remove CO [1,2]. CO content in the outlet to the WGSR, amounting to 0.5–1%, is too high to be directly fed to a PEMFC stack, because platinum-based electrodes irreversibly deactivate with CO content above 10 ppm [3]. Therefore, an additional stage is needed in order to reduce CO content down to acceptable values. Different methods can be chosen for

CO removal: (a) methanation, which consumes H₂ with the subsequent loss of fuel efficiency [4–6]; (b) selective H₂-diffusion through membranes, which requires high temperature and pressure gradients [7,8]; and (c) preferential CO oxidation (PROX) [9–12].

PROX is a simple, efficient method for removing low levels of CO from H₂-rich gas streams. The method consists of the addition of oxygen to the fuel processor effluent in order to preferentially oxidise CO than H₂. The main reactions occurring in such system are:



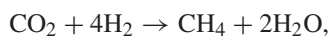
Due to the gas composition, WGSR and methanation reactions (of both CO and CO₂) could also take place:



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$$\Delta H^0 = -165 \text{ kJ mol}^{-1}. \quad (5)$$

While WGS is beneficial in its forward sense, methanation reactions are always detrimental and should be avoided.

An effective PROX catalyst should show: high activity for CO oxidation, oxidising CO much easier than hydrogen (high selectivity), an operation temperature between two ranges—170–230 °C, which is the outlet temperature for low temperature WGS, and 80–100 °C, which is the operation temperature for PEMFC, wide operation window—in order to avoid precise temperature controls, effective operation at high GHSV values, and resistance to deactivation by carbon dioxide and water present in the feedstream.

Theoretically, the amount of oxygen necessary for complete CO oxidation is half the molar amount of CO in the feedstream, according to Eq. (1). However, an excess of oxygen is needed due to the simultaneous oxidation of H₂. This excess of oxygen is characterised by process parameter λ , which is defined as

$$\lambda = 2 \times \frac{P_{\text{O}_2,0}}{P_{\text{CO},0}}. \quad (6)$$

Selectivity is defined as the ratio between oxygen involved in CO oxidation and total reacted oxygen (for oxidising CO and H₂). Thus, selectivity is inversely proportional to oxygen excess. Thus, the ideal catalyst should be active even at low λ values, in order to maintain selectivity at acceptable values.

Traditional catalysts for PROX reaction include a noble metal (Pt, Pd, Ru) supported on alumina [10–16]. Oxidation of CO on these catalysts is a multi-step process obeying single-site competitive Langmuir–Hinshelwood mechanism between CO and O₂, which compete for noble metal surface. These catalysts are characterised by operating at high temperatures (about 170 °C) and needing a high λ value (about 3) for complete depletion of CO, with the corresponding loss of selectivity (typically 34%). However, they are resistant to deactivation by water [12], although slightly inhibited by CO₂ [17].

The key for improving the CO oxidation rate is to allow for a non-competitive dual-site mechanism for CO and O₂. New catalyst formulations are being developed towards supplying these catalysts with an additional site for oxygen adsorption, which will enhance the reaction rate, by addition of a promoter [18,19]. An example of this development is the addition of Fe as a promoter for

Pt catalysts [19–23]. Pt metal serves as the site for CO adsorption, whereas Fe oxide promoter dissociates the O₂ molecule, resulting in a non-competitive, dual-site mechanism. Son et al. [24] reported the promotional effect of CeO₂ addition to Pt/Al₂O₃ catalyst, enhancing the CO conversion as well as selectivity at low temperatures. Yan et al. [25] promote the Pt/Al₂O₂ catalyst with Co.

Base-oxide supported Au has also been studied. The results have shown that these catalysts are very active for the PROX reaction, especially if they are deposited onto iron-oxide support [26–30]. Extremely fine deposited gold particles are very active at low temperatures (as low as 80 °C) and have similar selectivity than platinum. However, they are very sensitive to the presence of CO₂ and steam. Mixed CuO–Cerium have been also reported as powerful catalysts for PROX reaction [17,31], as well as zeolite-based [32] and bimetallic catalysts of Pt–Sn [33,34].

Ceria-based supports are also being studied for PROX reaction. Ceria presents very high oxygen storage capacity (OSC) [35,36], which is very helpful for oxidation on reductive environments, with the cyclic incorporation/removal of structural oxygen. Wootsch et al. [37] studied a series of Pt/Ce_xZr_{1-x}O₂ catalysts and found they are very active in the 80–100 °C range. Roh et al. [38] have also studied the Pt/Ce–ZrO₂ catalyst series and found they are very active even at 60 °C, with 78% conversion and 96% selectivity in stoichiometric oxygen, the most active support being the one with 80% ceria and 20% zirconia.

In this work, a Pt/CeO₂ catalyst has been tested for CO oxidation both in H₂-free and H₂-rich environments. The effect of CO₂ and H₂O on CO oxidation behaviour has been studied, and activity and selectivity towards CO oxidation have been calculated. Also, the effect of spatial time on catalyst activity and selectivity has been studied.

2. Experimental

2.1. Catalyst preparation and characterisation

A Pt/CeO₂ catalyst was prepared by impregnation. The actual platinum content was evaluated by ICP. The support, a high surface ceria, supplied by Rhodia, was previously calcined in air at 500 °C for 4 h. Pt was deposited by impregnation from aqueous solution of chloride-free platinum salt—tetraamminplatinum(II) nitrate. After impregnation, the sample was dried overnight at 110 °C, and then calcined in air at 400 °C for 5 h. Catalyst particle size in the range 0.16–0.25 mm

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