



Preferential CO oxidation in hydrogen-rich stream over an electrochemically promoted Pt catalyst

A. de Lucas-Consuegra^{a,b,*}, A. Princivalle^b, A. Caravaca^a, F. Dorado^a, C. Guizard^b, J.L. Valverde^a, P. Vernoux^b

^aDepartamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Avenida Camilo José Cela 12, 13005 Ciudad Real, Spain

^bLaboratoire de Synthèse et Fonctionnalisation des Céramiques, UMR 3080 CNRS/SAINT-GOBAIN CREE, 550 Avenue Alphonse Jauffret, BP. 224, 84306 Cavailon Cedex, France

ARTICLE INFO

Article history:

Received 14 September 2009

Received in revised form 20 November 2009

Accepted 30 November 2009

Available online 4 December 2009

Keywords:

Electrochemical promotion

NEMCA effect

PROX

Preferential oxidation

Selective CO oxidation

ABSTRACT

We have conducted a study on the preferential CO oxidation in hydrogen-rich stream (PROX) coupling catalysis and electrochemistry, i.e., by using an electrochemical catalyst (Pt/K- β -Al₂O₃). It was shown that PROX activity and selectivity of a Pt catalyst can be strongly enhanced by electrochemical pumping of potassium ions from the solid electrolyte support. The observed promotional effect was attributed to a decrease in the CO and H₂ chemisorption and to an increase in the O₂ chemisorption which led to a relative increase in the CO oxidation reaction vs. the H₂ oxidation. The electrochemical promotion allowed decreasing the operating temperature window of the Pt catalyst and attenuating the inhibiting effect of H₂ on both catalytic activity and selectivity. In addition some of the catalytic results were supported by in situ electrochemical characterization techniques such as cyclic voltammetry and open circuit potential measurements. Finally a very interesting permanent NEMCA effect was shown. It demonstrated the high stability of the formed promoting species and the potential for a further development of NEMCA effect in PROX real configurations.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) has come to be regarded as one of the most promising candidates for utilizing hydrogen to produce heat and electricity, especially for electric vehicles, residential co-generation systems and portable power supplies for small devices [1]. Especially when the PEMFC feed stream is produced by reforming of methanol and hydrocarbons, the gas always contains some amount of CO as an impurity, which is a poison for the fuel cell anode catalyst. Therefore, the hydrogen production process must be equipped with a CO removal system. Several methods for the CO removal have been studied and recently revised by Park et al. [2]: selective H₂-diffusion through membranes, CO methanation and selective CO oxidation, also known as preferential CO oxidation (PROX) reaction. Among these methods, the PROX process has been considered as the most promising and cost effective one. It consists of the addition of oxygen to a fuel processor effluent in order to preferentially oxidize CO rather than H₂ [3]. Different catalyst systems have been

explored for the PROX reaction [2], including metal oxides, supported gold catalyst and novel metal supported catalysts such as Pt, Ru, Rh and Ir. Platinum supported catalysts are candidates to be used in a fuel processor, due to their ability to operate at high temperatures, their stability for long term operation and their high resistance to deactivation by CO₂ or H₂O [4,5]. In real configurations, the PROX unit should be typically placed and therefore operated between the low temperature shift reactor (\approx 200 °C) and the PEMFC (\approx 80 °C). However, the PROX activity of Pt based catalyst is usually limited to temperatures close to 200 °C [6]. Until now, several efforts have been made to improve this low temperature Pt PROX activity (attributed to the inability of Pt to activate O₂ [7]), e.g., using different kinds of supports [8], pre-treatment methods [9] and the presence of a second metal [10]. Recent studies [11–16] report that the introduction of alkalis (and especially potassium [16]) is effective for improving the activity and the selectivity of supported noble metal catalyst.

In this work, we propose the use of solid electrolytes as electro-active catalyst supports as a novel approach to improve the catalytic properties of Pt for the PROX reaction through the concept of electrochemical promotion. This phenomenon also known as NEMCA (Non-Faradaic Electrochemical Modification of Catalytic Activity) effect is based on the improvement of the catalytic properties of a heterogeneous catalyst by the electrochemical pumping of promoter ions from the solid electrolyte support

* Corresponding author at: Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Avenida Camilo José Cela 12, 13005 Ciudad Real, Spain. Tel.: +34 926 95300; fax: +34 926 295437.

E-mail address: Antonio.Lconsuegra@uclm.es (A. de Lucas-Consuegra).

[17–20]. Until now, this phenomenon has been demonstrated in more than 80 catalytic systems with several important technological possibilities, particularly in industrial product selectivity and in exhaust gas treatment [21,22]. However, to our knowledge, there are no previous studies on the direct application of the NEMCA effect for the PROX reaction. Only some recent approaches studying the water gas shift reaction have come from the group of Vayenas [23–25]. In these studies (carried out in a PEMFC configuration [23–25], under CO, CO₂, H₂, O₂ and H₂O) the authors found a moderate increase in the CO removal efficiency using a proton conducting nafion membrane.

Based on the previous mentioned studies about chemical promotion on conventionally dispersed catalyst [11–16], in this work Pt was selected as the catalyst and K-βAl₂O₃ as the solid electrolyte. The system was investigated under different reaction temperatures (below 200 °C) and under different compositions (H₂/O₂ ratio). The catalytic experiments were supported by different *in situ* characterization techniques (open circuit potential measurements and cyclic voltammetry), which provided useful information on the competitive chemisorption of the reactants under different conditions.

2. Experimental

2.1. Preparation of the tubular electrochemical catalyst

In this study, a tubular reactor design has been used in view of a potential practical application (Fig. 1). It consisted of a tubular K-βAl₂O₃ tube (supplied by Ionotec) with one end closed (outer diameter 30 mm, thickness 2 mm, length 100 mm). The catalyst-working electrode (Pt) and the counter electrodes (Au) were symmetrically placed in the outer and inner part of the tube, respectively, by using Pt and Au pastes (both of them supplied by Metalor) annealed at 800 °C for 2 h. Both electrodes were placed from the beginning of the end close side of the tube, with a total geometrical Pt catalyst-working electrode area of 35 cm² and a final Pt metal loading of approximately 1 mg/cm². The tubular electrochemical catalyst was inserted in a pirex-glass tube of 100 mm of length and 33 mm of diameter. The working electrode (W) was exposed to the reactive mixture whereas the counter electrode (C) was under reference air. It should be mentioned that due to the absence of reference electrode in the present configuration we could not measure the Pt working electrode variation. Therefore no direct link between the applied potential (V_{WC}) and the Pt catalyst work function could be established on the

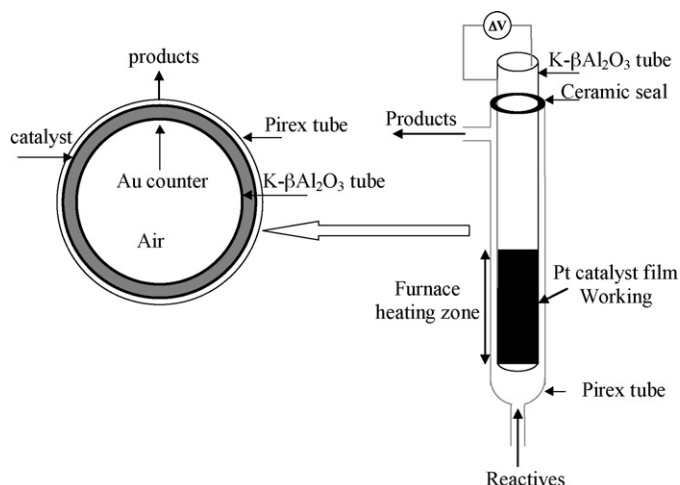


Fig. 1. Schematic drawing of the electrochemical reactor with Pt/K-βAl₂O₃ tube.

present configuration. This reactor design allowed having a suitable contact between the reactants and the Pt catalyst-working electrode film. Both electrodes were connected to a potentiostat-galvanostat Voltalab PGZ 402 (Radiometer Analytical).

2.2. Catalytic activity measurements

The reaction gases were mixtures of CO (1% in He), O₂ (1% in He), H₂ (40% in He) and pure He, supplied by Air Liquide. The gas composition was controlled by mass flow controllers (Brooks) and it was as follows: 0.4% CO, 0.2% O₂ (which corresponds to the stoichiometric ratio), 0–16% H₂, He balance and an overall flow rate of 15 L h⁻¹. Reactant and product gases were analyzed by a micro-gas chromatograph (Agilent). The micro-chromatograph was composed of two modules, each one equipped with a thermal conductivity micro-detector (TCD). The first module enables the separation of O₂ and CO by using a molecular sieve while the second module allowed separating CO₂ and H₂O by using a poraplot column. The catalytic activity of the system was evaluated on the basis of the following equations:

$$\text{CO conversion (\%)} = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100 \quad (1)$$

$$\text{O}_2 \text{ conversion (\%)} = \frac{[\text{O}]_{\text{in}} - [\text{O}]_{\text{out}}}{[\text{O}]_{\text{in}}} \times 100 \quad (2)$$

$$\text{CO}_2 \text{ selectivity (\%)} = 0.5 \times \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}} \times 100 \quad (3)$$

CO₂ selectivity was referred to oxygen conversion in order to take into account the simultaneous formation of water by H₂ oxidation.

During the catalytic experiments CO₂ was the only observed oxidation product and no CH₄ was detected under the explored reaction conditions. During the catalytic activity measurements an initial potential of +2 V was always applied in order to clean the Pt surface from promoter ions and define a reference state (unpromoted conditions). On the other hand, a decrease in the applied potential or current to negative values implies that potassium ions were electrochemically transferred to the Pt catalyst film (electro-promoted conditions).

2.3. In situ characterization measurements

The possibility of using solid electrolytes as catalyst supports in solid electrolyte cells allows using solid state electrochemistry techniques for *in situ* monitoring surface activities of the reactant species [18]. Thus, open circuit potential measurements have been carried out under reaction conditions in order to get information about the competitive chemisorption between the reactants.

Cyclic voltammetry was also performed with the potentiostat-galvanostat under different gas compositions and were recorded at a sweep rate of 20 mV/s. Before each cyclic voltammetry an initial potential of +2 V was always applied to define a reference state.

3. Results and discussion

3.1. Potentiostatic and galvanostatic transient experiments

The catalytic behaviour of the tubular Pt/K-βAl₂O₃/Au electrochemical catalyst for the PROX reaction (CO/O₂/H₂: 0.4%/0.2%/16%) was firstly investigated by a potentiostatic experiment carried out at 195 °C. Fig. 2 shows the steady state variation of the CO and O₂ conversion as well as the CO₂ selectivity under steady state conditions vs. the applied catalyst potential (V_{WC}). It can be observed that starting from a positive catalyst potential of +2 V

Download English Version:

<https://daneshyari.com/en/article/47695>

Download Persian Version:

<https://daneshyari.com/article/47695>

[Daneshyari.com](https://daneshyari.com)