

Short communication

Selective CO oxidation in the presence of H₂ over Pt and Pt-Sn catalysts supported on niobia

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Received 5 August 2005; received in revised form 28 September 2005; accepted 29 September 2005

Available online 17 November 2005

Abstract

An essential requirement for the proton exchange membrane fuel cell (PEMFC) is to deliver clean H₂ to the anode electrode, the kinetics of which are greatly hindered by traces of CO present from the upstream hydrocarbon reforming and water–gas shift processes. The removal of CO from hydrogen-rich stream to a PEMFC tolerant level, by selective oxidation (SELOX) of CO, has been studied over 1%Pt/Al₂O₃, 1%Pt-1%Sn/Al₂O₃, 1%Pt/Nb₂O₅ and 1%Pt-1%Sn/Nb₂O₅ catalysts. The Nb₂O₅-supported catalysts presented higher activity in SELOX reaction at low temperatures, but with lower CO selectivity. The results were explained in terms of platinum modification by the presence of niobia (SMSI effect) and tin (bimetallic effect).

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Keywords: Selective oxidation; Carbon monoxide; Platinum; Tin; Niobia

1. Introduction

The selective oxidation of CO in a H₂-rich atmosphere (SELOX) has long been of considerable technical interest for purification of hydrogen feed gas, e.g., for H₂ supply in ammonia synthesis. Over the last years, the SELOX process has attracted new interest due to its application in fuel cell technologies. The most promising fuel cell technology for transport applications appears to be the proton exchange membrane fuel cell (PEMFC) fueled by hydrogen. In order to avoid storing high pressure hydrogen on a vehicle, it has been proposed that hydrogen for PEMFC can be produced in an onboard fuel processor [1].

The production of hydrogen in onboard reformers actually occurs in three catalytic processes in series: (i) autothermal reforming of a hydrocarbon or alcohol for producing synthesis gas (fuel + O₂ + H₂O → CO_x + H₂); (ii) water–gas shift (WGS) reaction (CO + H₂O → CO₂ + H₂), which maximizes H₂ yield and lowers the CO concentration; (iii) selective oxidation of

CO in the H₂-rich reformat in order to reduce CO concentration to less than 10 ppm [2]. CO impurities contained in the reformer gas (60–65% H₂, 10–15% H₂O, 1–2% CO, balance CO₂) are known to poison commonly used anode catalysts (Pt, PtRu) and decrease the efficiency of the fuel cell to an unacceptable level [3,4].

As with many catalytic processes, in selective oxidation of CO the challenges are activity and selectivity. The selectivity is crucial considering the competing H₂ oxidation that may lead to a decrease in the overall fuel cell efficiency. Besides oxidation of both CO and H₂, methanation and WGS reactions can also take place simultaneously. In addition, the reaction temperature must be kept between 200 °C, which is the operation temperature of the shift reactor, and 80 °C, the operation temperature of PEMFC. As a result, a CO oxidation catalyst having high activity and selectivity between 80 and 200 °C is necessary to maintain a stable operation of Pt-anode.

Supported noble metal catalysts, such as Pt, Ru and Rh, have been effective for the SELOX reaction [5–9]. For low temperatures, highly dispersed gold on an oxide support showed high activity and selectivity [10,11]. However, the activity of gold catalysts is strongly dependent on the preparation

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method and deactivation is more rapid upon long-term operation [12,13]. Supported platinum had a high conversion of CO at high temperatures (150–250 °C) but the activity decreased at low temperatures (<100 °C). Therefore, with enhanced low-temperature activity, supported Pt could be a practical SELOX catalyst satisfying start-up conditions in a transport fuel cell.

The lower temperature activity and selectivity could be improved adding promoters (Fe, Ce, Co) [2,14,15], sol-gel preparation [16], water pretreatment [17,18], forming alloys with Sn [19,20] or using reducible oxides as supports (CeO₂, ZrO₂, TiO₂) [21–23].

In the present study, the Pt and Pt-Sn catalysts supported over alumina and niobia were tested in total (H₂-free streams) and selective (H₂-rich streams) oxidation of CO. The activity and selectivity of these catalysts, as well as the long-term stability, were investigated in the low temperature range (70–180 °C) in order to determine the most promising catalyst for fuel cell applications.

2. Experimental

2.1. Preparation of catalysts

A commercial γ -Al₂O₃ from Degussa (BET area: 200 m² g⁻¹) and Nb₂O₅ (BET area: 65 m² g⁻¹), obtained by calcination of niobic acid (CBMM) in air at 500 °C for 2 h, were used as supports. Pt was added from a H₂PtCl₆ (Sigma) solution by incipient wetness impregnation of the supports, while Sn was added from a SnCl₂ (Sigma) aqueous solution for the Al₂O₃ supported catalyst and from a SnCl₄ (Sigma) aqueous solution for the Nb₂O₅ supported catalyst. The samples were dried overnight in an oven and then calcined in air at 500 °C for 2 h. Platinum and tin contents were close to 1 wt.%.

These samples have already been characterized by temperature programmed reduction (TPR), H₂ and CO chemisorption [24–26] and temperature programmed desorption (TPD) of CO [27].

2.2. Catalytic tests

The reactions were carried out in a fixed-bed flow-type pyrex reactor loaded with 140 mg of catalyst, under atmospheric pressure. The catalysts were dried in situ with flowing nitrogen at 150 °C before reduction with 10% H₂/N₂ for 1 h at 300 or 500 °C. After reduction, the catalyst was purged with nitrogen for 30 min at the same temperature. The total feed flow rate was held constant at 80 cm³ min⁻¹, with flowing He. The activity tests were performed with molar ratio O₂/CO = 1, at different temperatures, ranging from 70 to 230 °C, in steps of 10 °C that were kept for 30 min at each temperature. The deactivation test was performed at temperature of 100% of O₂ conversion in selective oxidation of CO.

The reaction products were analyzed by on-line gas chromatograph (CHROMPACK CP9001), equipped with a Hayesep D column and a thermal conductivity detector.

The conversions of CO and O₂ and the selectivity of CO were defined as follows:

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

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

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

2.3. Carbon deposition measurements

The amount of coke formed over the catalysts after deactivation tests was examined by thermogravimetric analysis (TGA), using a RIGAKU thermoanalyzer (model TAS 100). The samples were pretreated at 150 °C under flowing nitrogen and then heated at a rate of 10 °C min⁻¹ to 800 °C in a flow of 15% O₂/N₂ (50 cm³ min⁻¹).

3. Results and discussion

3.1. Total oxidation of CO

Fig. 1 presents CO conversion as a function of temperature for total oxidation of CO (H₂-free stream). Measurements at each temperature were taken after 30 min to allow the reaction to stabilize. Niobia supported catalysts showed higher activities than alumina catalysts, with 100% of CO conversion at lower temperatures. For Pt-Sn/Nb₂O₅, the increase in the temperature of reduction increased the catalytic activity: at 160 °C, CO conversion was 76% for the catalyst reduced at 300 °C and 100% after reduction at 500 °C. The effect of tin was less pronounced for alumina catalysts. These catalysts presented only moderate activity: CO conversion of 100% was only obtained at 220 °C for Pt-Sn/Al₂O₃ and 230 °C for Pt/Al₂O₃.

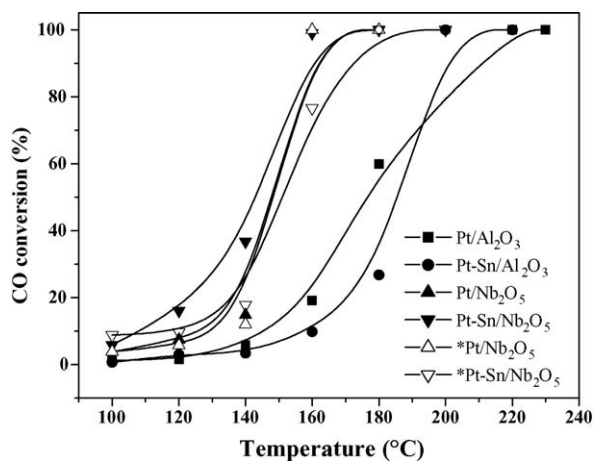


Fig. 1. Catalytic activities in terms of CO conversion as a function of temperature for total CO oxidation. Catalysts marked with '*' were reduced at 300 °C, otherwise the reduction temperature was 500 °C. Reaction conditions: 140 mg of catalyst and 80 mL min⁻¹ of 5% CO/5% O₂/He.

The niobia supported catalysts presented higher activities at low temperatures than alumina based catalysts and this difference can be related to a change in reaction mechanism over reducible supports. For alumina supported catalysts only the metallic surface is involved in CO oxidation: both CO and O₂ adsorb on the platinum crystallite and react together [28,29]. For reducible oxides, CO adsorbed on the platinum surface reacts with oxygen atoms which are first dissociatively adsorbed on support surface and then spilled over the Pt particle. This bifunctional mechanism involving CO adsorption on Pt surface and oxygen activated on the support has already been reported for CeO₂ and ZrO₂ supported Pt catalysts [22,28–30]. Niobia is also a well-known reducible oxide, with high oxygen storage capacity [24,25,31,32].

In relation to the effect of tin, the bimetallic interaction by Pt–Sn alloy formation can be ruled out under oxidative conditions due to the easy oxidation of this alloy even in the contact with very low O₂ concentration [26]. Thus, the slight decrease of the activity of niobia catalysts in the presence of Sn should only be related to a geometric effect of tin, decreasing the number of Pt–Pt neighbors and covering active sites on Pt–support interface.

3.2. Selective oxidation of CO

A feasible catalyst for low temperature CO oxidation in H₂-rich streams means the catalyst has both high activity and high selectivity to CO₂ production; the H₂ oxidation must be minimized, as well as, methanation and water–gas shift reactions. In our study, selectivity is a critical parameter since O₂ is in excess (O₂/CO = 1) in relation to stoichiometry of CO oxidation (O₂/CO = 0.5).

The comparison of catalyst activities for CO selective oxidation is displayed in Fig. 2A and B, in terms of O₂ and CO conversions, respectively. CO₂ and H₂O were the only reaction products; CH₄ formation was not observed. Niobia supported catalysts attained 100% of O₂ conversion at much lower temperatures than alumina catalysts (90 °C for Pt/Nb₂O₅ and 105 °C for Pt–Sn/Nb₂O₅, against 140 °C for Pt/Al₂O₃ and Pt–Sn/Al₂O₃). However, alumina catalysts showed higher CO conversions: 100% at 140 °C for Pt/Al₂O₃ and 82% for Pt–Sn/Al₂O₃, against 52% at 90 °C for Pt/Nb₂O₅ and 36% at 105 °C for Pt–Sn/Nb₂O₅. The higher CO conversions of alumina catalysts are reflected in their higher selectivities, especially at temperatures above 100 °C, as can be seen in Fig. 3.

For all catalysts there was a shift in the ignition temperature of CO oxidation toward lower values, in the presence of H₂, showing that H₂ enhances CO oxidation, as already observed in other studies [5,19,33].

Manasilp and Gulari [16] verified a similar behavior for Pt/Al₂O₃ catalyst prepared by sol–gel technique: the maximum CO conversion (80%) was obtained at 170 °C, with 1%CO, 1%O₂ and 60%H₂ in feed stream. The selectivity of the catalyst stayed essentially constant at 50% up to 170 °C.

To explain the lower CO conversion on niobia catalysts and the decrease of selectivity with temperature, it is essential to understand the mechanistic model involving CO and H₂ adsorp-

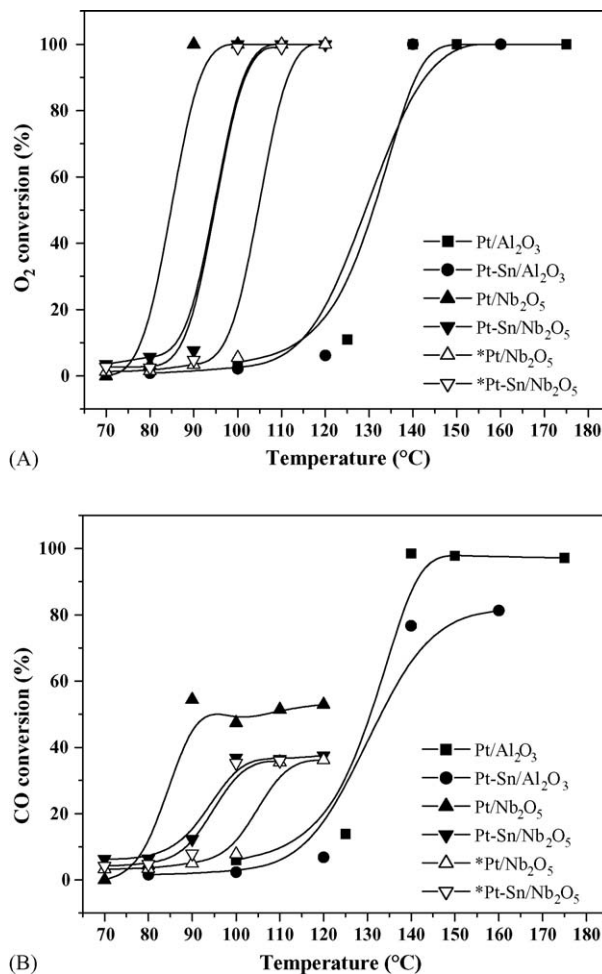


Fig. 2. Catalytic activities in terms of O₂ conversion (A) and CO conversion (B) as a function of temperature for selective CO oxidation. Catalysts marked with “*” were reduced at 300 °C, otherwise the reduction temperature was 500 °C. Reaction conditions: 140 mg of catalyst and 80 mL min⁻¹ of 12% H₂/5% CO/5% O₂/He.

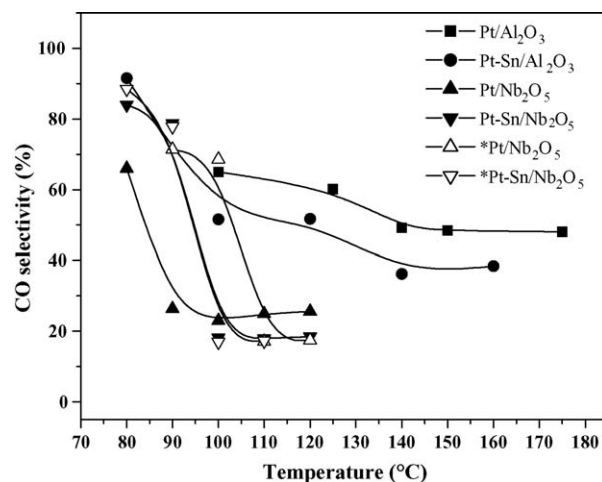


Fig. 3. Catalytic selectivities as a function of temperature for selective CO oxidation. Catalysts marked with “*” were reduced at 300 °C, otherwise the reduction temperature was 500 °C.

tion sites. At low temperatures (and high CO coverages) hydrogen adsorption and oxidation are practically inhibited, since limited by CO desorption (the heat of CO adsorption on Pt is higher than the value for H₂ [34]). With increasing temperature, the CO coverage decreases, leading to a decline in selectivity due to increasing H₂ oxidation rate. According to Aranda and Schmal [27], CO desorption on the niobia surface is easier than on alumina support, starting at much lower temperatures. The easier CO desorption could be responsible for lower CO conversion on niobia catalysts and lower selectivities, since H₂ adsorption is favored by the release of active sites from CO desorption. Thus, this model assumes a competitive CO and H₂ oxidation on Pt particles.

The activity of niobia catalysts at lower temperatures can be related to the strong metal–support interaction (SMSI) effect under reductive conditions. For Pt/Nb₂O₅ catalyst, the reduction at high temperatures caused an increase in CO conversion, but a decrease in CO selectivity. As the SMSI state is enhanced at high reduction temperatures, new active sites are created at the metal/support interface, increasing both CO and H₂ conversions.

The negative effect of tin on CO conversion for alumina and niobia supported catalysts can also be explained by the promotion of CO desorption from the metallic surface (verified by TPD of CO [27]). Moreover, bimetallic effect with Pt–Sn alloy formation decreases the CO oxidation activity in H₂-rich streams due to its H₂ adsorption capacity, according to Özkara and Aksoylu [20]. The activity of the Pt–Sn/Nb₂O₅ is practically independent of the reduction temperature, since the presence of tin led to a partial suppression of SMSI state due to bimetallic effect [24].

3.3. Deactivation tests

Deactivation tests were performed under the same conditions of selective CO oxidation, at temperatures on which O₂ conversion reached 100%. Comparison of catalyst stabilities is shown in Fig. 4. All catalysts presented good stabilities up to 24 h on stream, in different levels of conversion. It is also noteworthy that

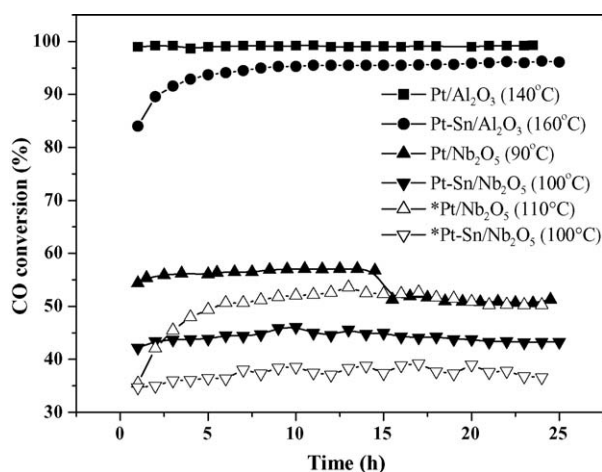


Fig. 4. Deactivation test in terms of CO conversion as a function of time on stream (temperatures are in parentheses). Catalysts marked with '*' were reduced at 300 °C, otherwise the reduction temperature was 500 °C. Reaction conditions: 140 mg of catalyst and 80 mL min⁻¹ of 12% H₂/5% CO/5% O₂/He.

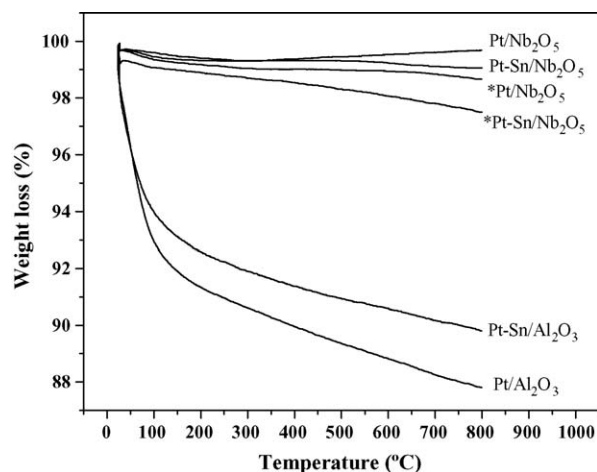


Fig. 5. TGA of Pt catalysts after deactivation tests. Conditions: 15% O₂/N₂, 10 °C min⁻¹ and feed flow rate = 50 cm³ min⁻¹.

some catalysts (Pt–Sn/Al₂O₃ and Pt/Nb₂O₅ reduced at 300 °C) presented an activation in the first 5 h on stream, which can be related to a superficial reconstruction under reaction conditions.

Pt/Nb₂O₅ catalyst reduced at 500 °C presented higher initial activity than the catalyst reduced at 300 °C, but the conversions become similar after 15 h on stream (although at different temperatures). Thus, the influence of reduction temperature is more pronounced in initial activity.

In order to verify the deposition of inactive carbon over these catalysts, thermogravimetric analysis was performed in an oxygen-containing atmosphere (Fig. 5). The weight loss of alumina supported catalysts at low temperatures (<100 °C) is related to a partial dehydroxylation of alumina support and not to coke oxidation, since the bare support showed a similar profile. Thus, all catalysts are resistant toward coke formation and presented good stabilities under reaction conditions.

4. Conclusions

Niobia supported Pt catalysts showed higher activities than alumina catalysts for total and selective CO oxidation. For total CO oxidation, Pt/Nb₂O₅ showed 100% of CO conversion at 160 °C, while for Pt/Al₂O₃ this temperature was 230 °C. As niobia is a reducible support, with interfacial active sites formed on the Pt/support perimeter, CO oxidation may proceed by a bifunctional mechanism: CO adsorbed on Pt particles and oxygen activated on the support.

For selective CO oxidation, although niobia catalysts are active at lower temperatures, CO conversions are lower than those of alumina catalysts (52% for Pt/Nb₂O₅ and 100% for Pt/Al₂O₃). The easier CO desorption on the niobia catalysts could be responsible for their lower selectivities, since H₂ adsorption and oxidation require the release of active sites from CO (a competitive mechanism between CO and H₂ oxidation on Pt sites). The increase in the temperature of reduction increased the CO conversion for Pt/Nb₂O₅ catalyst due to the enhancement of the SMSI effect.

The addition of tin has a negative effect on activity of both alumina and niobia supported catalyst, increasing the temperature

of O₂ total conversion and decreasing CO maximum conversion. The bimetallic interaction with Pt–Sn alloy formation decreases the CO oxidation activity and partially suppresses the SMSI state on niobia catalysts.

Although CO complete oxidation was not obtained on niobia catalysts under H₂-rich streams, these systems have a potential application in fuel processors due to their low temperature activity (~90 °C) and high stability toward coke formation. Lower CO exit concentrations could be achieved by performing the reaction at several stages. The effect of CO₂ and H₂O in the feed stream has to be evaluated in order to optimize these catalysts for realistic fuel cell applications.

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