Selective CO Oxidation on Pt/Nb_2O_5 Catalysts for Fuel Cell Application

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Introduction

Fuel cells are an attractive alternative to the internal combustion engine because of their high efficiency and low emissions. The PEM (polymer electrolyte membrane) fuel cell is the primary candidate for using in vehicles due to its low temperature of operation and fast startup. Hydrogen is the best fuel for the PEM fuel cell and it can be produced onboard from a liquid fuel such as methanol or gasoline.

On the industrial scale, the production of hydrogen occurs in four steps: 1) hydrogen is produced by steam reforming of a liquid hydrocarbon [1] (fuel + $H_2O \rightarrow CO + H_2$); 2) the water-gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) eliminates most of the CO, producing more hydrogen; 3) any remaining CO is reduced to ppm levels by selective catalytic oxidation. Performing these operations in the small space of a car remains an engineering challenge. PEM fuel cells run at low temperatures (about 80ºC for optimum performance) and therefore the CO removal should be operated at similar temperatures. Finally, a typical CO concentration of 0.5 to 1% is obtained after the water-gas shift unit, but the performance of the fuel cell anode is decreased by as little as 10 ppm CO [2]. This paper was focused on the selective CO oxidation reaction in H_2-CO_2 containing streams using standard Pt/Al_2O_3 catalysts as well as Pt/Nb_2O_5 and Pt-Sn/Nb_2O_5 samples.

Experimental

The catalysts were prepared by incipient wetness using Al_2O_3 (200 m^2/g) and Nb_2O_5 (65 m^2/g) as supports. Pt was added from a H_2PtCl_6 solution while Sn was added from a $SnCl_2$ aqueous solution for the Al_2O_3 supported catalyst and from a $SnCl_4$ aqueous solution for the Nb_2O_5 supported catalyst. The samples were dried overnight and then calcined at 773 K for 2h. Platinum and tin contents were close to 1%. The samples were characterized by TPR (Temperature Programmed Reduction) and chemisorption of H_2 and CO at room temperature.

Results and Discussion

Pt/Al_2O_3 is a well-known oxidation catalyst and tin addition has been described as an important promoter in CO oxidation [3,4]. While CO oxidation is extensively described in literature, selective oxidation of CO in hydrogen is not nearly as well studied [5,6].

Samples were reduced before its use in the catalytic tests. Two different temperatures were employed: 573 and 773 K. The catalytic tests was performed from 373 to 573 K with a heating rate of 5K/min, in a stream of 18% CO_2, 1% CO and

0.5% O_2, H_2 balance. There was a complete conversion of oxygen bellow 523 K for all catalysts. The sequence of more active samples based on lower temperature for complete O_2 uptake, for samples reduced at 573 K, was: Pt-Sn/Nb_2O_5 (413 K), Pt/Nb_2O_5 (423 K), Pt-Sn/Al_2O_3 (453 K) and Pt/Al_2O_3 (503 K). Pt-Sn/Nb_2O_5 was also the most selective catalyst for CO oxidation (71%) while Pt/Nb_2O_5 and Pt-Sn/Al_2O_3 yielded 60% and Pt/Al_2O_3 only 50%. The use of higher reduction temperatures, for the samples Pt-Sn/Nb_2O_5 and Pt/Nb_2O_5, leaded to a decrease in the temperature needed to achieve complete consumption of oxygen, 391 and 398 K, respectively. Although they became more active, its selectivity to CO decreased to 50%. Under similar reaction conditions, Manasilp et al. [5] reported selectivities close to 50% for Pt/Al_2O_3 catalysts.

All the tests were performed under CO_2 concentration close to the typical gas streams produced from reformers and water-gas shift reactors. CO_2 is known to reduce the activity of selective CO oxidation due to three main factors: a) Reverse water-gas shift reaction; b) Increasing the carbonate concentration on surface can block the mobile oxygen close to the active sites; c) CO_2 can be dissociated on platinum and support [7] even increasing the amount of CO to be oxidized. On the other hand, water vapor in the feed increases the activity of Pt/Al_2O_3 catalysts dramatically [5]. Thus, we are working in conservative unfavorable conditions with no significant changes in the selectivity.

The activity and selectivity of the Pt/Nb_2O_5 and Pt-Sn/Nb_2O_5 catalysts for CO oxidation under H_2/CO_2 atmosphere may be explained in terms of inhibition of H_2 dissociation on Pt-Sn and Pt/NbO_x systems. Both bimetallic and SMSI interactions remain important under temperature between 100 and 200°C. The preferential CO-Pt interaction was confirmed by chemisorption measurements (CO/H_2 molar ratios were significantly higher than 2) and the inhibition of hydrogen dissociative adsorption is probably due to ensemble or ligand effects [8].

References

1. M.A. Peña, J.P. Gomes and J.L.G. Fierro, *Appl. Catal. A* 144 (1996) 7
2. H. Igarashi, T. Fujino and M. Watanabe*, J. Electroanal. Chem*. 391 (1995) 119.
3. A. Cohn, US Patent 3,216,783.
4. J. L. Margitfalvi, I. Borbáth, K. Lázár, E. Tfirst, A. Szegedi, M. Hegedüs and S. Göbölös, *J. Catal.* 203 (2001) 94.
5. A. Manasilp and E. Gulari, *Appl. Cat. B* 37 (2002) 17.
6. O. Korotkikh and R. Farrauto, *Cat. Today* 62 (2000) 249.
7. M. M. V. M. Souza, D. A. G. Aranda and M. Schmal, J. Catal. 204 (2001) 498.
8. D. A. G. Aranda, F. B. Passos and M. Schmal, *Cat. Today* 55 (2000) 25.