PREFERENTIAL OXIDATION OF CO IN PRESENCE OF H₂
BEHAVIOR OF PtSn/γ-Al₂O₃ CATALYSTS MODIFIED BY K OR Ba

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Abstract — The behavior of catalysts based on Pt/γ-Al₂O₃ is analyzed in the CO oxidation reaction. Experiments were performed in the temperature range between 50°C and 250°C with a feed H₂ rich, and a concentration of 1% CO and 0.6% O₂. Catalysts studied were: monometallic Pt/γ-Al₂O₃, bimetallic PtSn/γ-Al₂O₃ with a ratio Sn/Pt=1.6 at/at and two catalysts prepared by modification of the last one with K or Ba. The catalyst that showed maximum activity and selectivity levels is the PtSnK/γ-Al₂O₃. The tin addition increases the activity which allows the reaction to occur at lower temperatures due to the decrease in the CO-Pt interaction. The addition of K or Ba produces a subsequent improvement with respect to the CO oxidation temperature, which leads to a selectivity increase. The selectivity of the CO oxidation passes through a maximum value as a function of the temperature. This maximum is explained by the importance acquired by the reverse of water gas shift reaction at temperatures near 200°C.

Keywords — Preferential Oxidation, Hydrogen purification, PtSn/γ-Al₂O₃.

1. INTRODUCTION

The requirements imposed worldwide demand the search of technological alternatives, although the control of gaseous emissions from conventional thermal machines has experienced some advances. One of these alternatives is the use of fuel cells fed by hydrogen, that allow to optimize the use of the more scarce energetic resources since they are capable to transform the energy from chemical to mechanical one with an efficiency quite higher than the one of the conventional thermal machines. For example, in the case of internal combustion engines of mobile sources, the fuel cells are able to almost duplicate their efficiency with null or minimum emissions of pollutants.

The hydrogen is a fuel with difficulties for its distribution as well as for its storage, consequently the challenge is to generate it in situ (on board) or in a service station, from the reforming or partial oxidation of natural gas, hydrocarbons, methanol or ethanol. In all cases the formation of carbon oxides (CO and CO₂) is unavoidable. The carbon monoxide must be eliminated because in concentrations higher than 20 ppm it leads to the deactivation of the electrodes of the fuel cells type PEM (Polymer Electrolyte Membrane) used for these systems (Manasip and Gulari, 2002).

The need that the generated hydrogen must be an ultra pure product forces to technological solutions such as membrane reactors or catalytic processes for purification. In the case of membrane reactors, that allow the selective passage of hydrogen, one of the difficulties to defeat with actual technologies is the necessity to operate with a high pressure difference on both sides of the membranes (Irusta et al., 2005). In catalytic purification processes part of the carbon monoxide can be eliminated via water gas shift reaction (WGSR), up to levels between 500 and 1000 ppm fixed by thermodynamics. The CO remainder can be eliminated by methanization or by selective oxidation (Preferential oxidation, PROX), in which the conversion of hydrogen must be minimized. The methanization is easily performable in presence of catalysts based on Ni (Takenaka et al., 2004; Schubert et al., 2004; Farrauto, 2005); however, they present as a problem the need to reach high temperature levels for an effective elimination (>250°C); on the other hand the use of Ni in mobile applications is considered a potential health hazard.

Since investigations about the development of catalysts with higher tolerance to the CO presence continue, the PROX appears as the most adequate way to feed ultra pure hydrogen to the fuel cells. In this case different catalytic systems have been studied and they can be classified in three groups:

(i) Catalysts based on supported Au; they present a very high activity at low temperatures (Margitfalvi et al., 2004; Trimm, 2005). These systems are strongly dependent on the preparation method and in general they present deactivation problems and penalization of the selectivity by hydrogen oxidation at temperatures higher than 80°C (Recupero et al., 2004). Evidences about resistance to poisoning and to sintering through experiments at prolonged times seem necessary for these systems.

(ii) Catalysts based on supported Cu were also studied with good results for the activity, although problems inherent to Cu with respect to the stability and to the control of its oxidation state seem not to be defeated (Recupero et al., 2004; Shiau et al., 2006; de Souza et al., 2006).

(iii) Catalysts based on noble metals (Pt, Ru, Rh, Pd) have demonstrated to be active in the oxidation of CO to CO₂ even at low temperatures (Roberts et al., 2003;