



## Platinum supported catalysts for carbon monoxide preferential oxidation: Study of support influence

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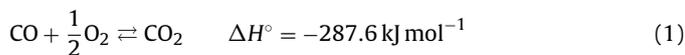
### ABSTRACT

The aim of this work is to study the influence of the addition of different oxides to an alumina support, on surface acidity and platinum reducibility in platinum-based catalysts, as well as their effect on the activity and selectivity in CO preferential oxidation, in presence of hydrogen. A correlation between surface acidity and acid strength of surface sites and metal reducibility was obtained, being Pt-support interaction a function of the acid sites concentration under a particular temperature range. In platinum supported on alumina catalysts, CO oxidation follows a Langmuir–Hinshelwood mechanism, where O<sub>2</sub> and CO compete in the adsorption on the same type of active sites. It is noteworthy that the addition of La<sub>2</sub>O<sub>3</sub> modifies the reaction mechanism. In this case, CO is not only adsorbed on the Pt active sites but also on La<sub>2</sub>O<sub>3</sub>, forming bridge bonded carbonates which leads to high reactivity at low temperatures. An increase on temperature produces CO desorption from Pt surface sites and favours oxygen adsorption producing CO<sub>2</sub>. CO oxidation with surface hydroxyl groups was activated producing simultaneously CO<sub>2</sub> and H<sub>2</sub>.

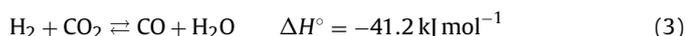
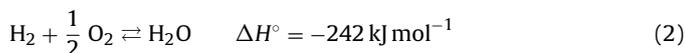
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### 1. Introduction

In the transition to hydrogen economy, the development of processes that produce hydrogen from fossil fuels has a remarkable worldwide interest. In these processes hydrogen is usually obtained by steam reforming or partial oxidation in combination with the water gas shift reaction. The resulting gases contain about 1% of CO, which needs a further reaction stage in order to obtain a CO free stream. The aim of carbon monoxide preferential oxidation, denoted as COPROX (1), is to diminish CO concentration at ppm levels by means of selective oxidation with oxygen, producing CO<sub>2</sub> in hydrogen presence, without H<sub>2</sub> consumption.



It is necessary to optimize operation conditions such as temperature, O<sub>2</sub>/CO ratio and catalyst mass/stream flow ratio, in order to minimize the H<sub>2</sub> oxidation (2) or the reverse water gas shift reaction (3) which could take place simultaneously or consecutively, decreasing consequently hydrogen production efficiency.



Catalysts used for COPROX processes in presence of H<sub>2</sub> reported in the literature can be classified in three types [1,2]: (1) gold catalysts supported on one or two of the following oxides: α-Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CoO<sub>x</sub>, NiO<sub>x</sub>, Mg(OH)<sub>2</sub>, CeO<sub>2</sub>, SnO<sub>2</sub>, MnO<sub>x</sub>, γ-Al<sub>2</sub>O<sub>3</sub> and ZnO; (2) catalysts based on metal oxides, such as Cu, Ce, Mn, Co and Ni alone or combined with others [3,4]; (3) noble metal catalysts (Pt, Ir, Pd, Ru or Rh) supported on CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, MgO, CeO<sub>2</sub>, Ce<sub>x</sub>Zr<sub>(1-x)</sub>O<sub>2</sub>, TiO<sub>2</sub>, mordenite and active carbon [5,6].

The articles found in literature related to gold catalysts show results where catalysts usually operate in the temperature range 50–100 °C, they are fed with CO, O<sub>2</sub> and an inert gas (N<sub>2</sub> or He) using a O<sub>2</sub>/CO ratio between 1 and 20/1. Some studies of H<sub>2</sub> addition (5–75%) were reported, being CO<sub>2</sub> and H<sub>2</sub>O addition found less frequently [7]. At low temperatures, highly dispersed gold particles over an oxide support showed high activity and selectivity. However, the catalyst activity strongly depended on the preparation method [8–10].

In the case of type two catalysts, catalyst are operated at temperatures between 80 and 160 °C, they are fed with CO, O<sub>2</sub>, H<sub>2</sub> and an inert gas, with an O<sub>2</sub>/CO ratio range between 1/1 and 10/1 and a H<sub>2</sub> concentration of 40–50%, without CO<sub>2</sub> addition. Finally, type three catalysts are operated in a wide temperature range (80–300 °C) and they are fed with 1% CO, 1–4% O<sub>2</sub>, 30–70% H<sub>2</sub>, 10–20% CO<sub>2</sub> and 10–20% H<sub>2</sub>O.

Platinum supported catalysts are solid candidates to be used in a fuel processor, due to their ability to operate at high temperatures and their high resistance to deactivation by CO<sub>2</sub> or H<sub>2</sub>O presence. Many efforts have been made to improve the activity and selectiv-

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