



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

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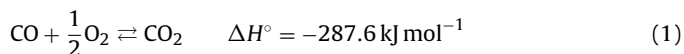
ABSTRACT

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 O₂ and CO compete in the adsorption on the same type of active sites. It is noteworthy that the addition of La₂O₃ modifies the reaction mechanism. In this case, CO is not only adsorbed on the Pt active sites but also on La₂O₃, 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 CO₂. CO oxidation with surface hydroxyl groups was activated producing simultaneously CO₂ and H₂.

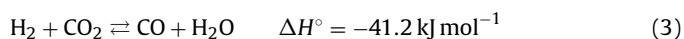
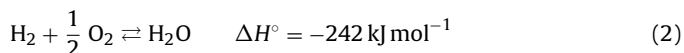
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1. Introduction

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 CO₂ in hydrogen presence, without H₂ consumption.



It is necessary to optimize operation conditions such as temperature, O₂/CO ratio and catalyst mass/stream flow ratio, in order to minimize the H₂ 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 H₂ 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-Fe₂O₃, TiO₂, CoO_x, NiO_x, Mg(OH)₂, CeO₂, SnO₂, MnO_x, γ-Al₂O₃ 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 CeO₂, Al₂O₃, SiO₂, SiO₂–Al₂O₃, La₂O₃, MgO, CeO₂, Ce_xZr_(1-x)O₂, TiO₂, 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, O₂ and an inert gas (N₂ or He) using a O₂/CO ratio between 1 and 20/1. Some studies of H₂ addition (5–75%) were reported, being CO₂ and H₂O 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, O₂, H₂ and an inert gas, with an O₂/CO ratio range between 1/1 and 10/1 and a H₂ concentration of 40–50%, without CO₂ addition. Finally, type three catalysts are operated in a wide temperature range (80–300 °C) and they are fed with 1% CO, 1–4% O₂, 30–70% H₂, 10–20% CO₂ and 10–20% H₂O.

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 CO₂ or H₂O presence. Many efforts have been made to improve the activity and selectiv-

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ity of Pt catalyst used in COPROX process. For example, dopants and promoters have been added to Pt/Al₂O₃ catalysts [11,12], in order to minimize the adsorption of CO on Pt, which blocks the O₂ adsorption sites (oxygen adsorption is the rate-determining step), making CO oxidation difficult. CO oxidation rate seems to decrease with the increase on the strength of CO–Pt interaction.

The goal of this work is to study the influence of the addition of support modifiers on the activity and selectivity of platinum supported on alumina-based catalysts. The effect on acidity, reducibility and the CO adsorption mechanism was also determined.

2. Experimental

2.1. Catalysts preparation

Four platinum-based catalysts were prepared by impregnation in dissolution method. They were supported on alumina (PtAc) and alumina with 20 wt.% SiO₂ (PtSiA), 50 wt.% MgO (PtMgA) and 3 wt.% La₂O₃ (PtLaA), H₂ PtCl₆·6H₂O (Degussa) was the precursor salt used for the active phase. The nominal platinum concentration was 1 wt%. After drying in air (110 °C, 12 h), the catalysts were calcined in air at 500 °C for 2 h.

2.2. Characterization

Specific surface area (*S*_{BET}) was measured by N₂ adsorption at 77 K in a *Micromeritics Asap 2010* apparatus. Prior to measurement, the sample was out-gassed at 140 °C during 24 h on a *Vacprep 061 Lb Micromeritics* equipment.

XRD patterns were obtained on powder samples in a diffractometer *Seifert XRD 3000P* at 2θ range 2–100°, using Cu Kα radiation (λ = 1.540598 Å), removing Kα radiation by a nickel filter, with a 0.05° s⁻¹ scanning and a accumulation time of 2 s. Crystalline phases were identified comparing the patterns obtained with Joint Committee on Powder Diffraction Standards 1971 data base.

The acidity and the acid strength of the support sites were determined by temperature programmed NH₃ desorption, performed in a *Micromeritics Asap 2010*. Samples were out-gassed in a *Vacprep 061 Lb Micromeritics* apparatus.

Temperature programmed reduction (TPR) tests were performed with 10% H₂–90% N₂ (50 cm³ min⁻¹) in the temperature range of 25–700 °C. Tests were performed in a micro-activity equipment, *PID Eng&Tech* being hydrogen consumption analyzed by an *Agilent 6890N* chromatograph equipped with TCD and FID detectors.

Metal dispersion (*D*_M) defined as metal particles present on the surface of the catalyst vs. total amount of metal contained in the catalyst, was determined from H₂ dynamic chemisorption measurements carried out in a *Pulse Chemisorb 2700 Micromeritics* apparatus. Samples were reduced under pure H₂ and they were further out-gassed under argon flow. It is well-known the mechanism of hydrogen adsorption on Pt sites. Considering a dissociative adsorption, the adsorption stoichiometry considered to calculate platinum dispersion was H_{ad}:Pt_s = 1:1. Therefore, the exposed platinum surface was calculated from the hydrogen consumption taking into consideration that physisorption on the metal and the support are negligible.

CO chemisorption isotherms were obtained in a volumetric apparatus at 25 °C up to 180 Torr. CO TPD (temperature programmed desorption) experiments were performed to obtain information about surface active sites distribution. A 0.15 mg powder catalyst sample was placed in an adsorption reactor and was submitted to a reduction pre-treatment. TPD experiments were carried out by increasing temperature rate of 10 °C min⁻¹ from room temperature up to 500 °C and maintaining at 500 °C for 10 min. Composition of desorbed gases was measured by a mass spectrometer *Pfeiffer Vacuum GMBH D 35614* connected to a vacuum volumetric apparatus.

2.3. Activity tests

Catalytic tests were carried out in a *Microactivity Reference PID Eng&Tech* equipment. The catalytic bed was formed by a catalyst sample and an inert diluter (SiC) in a 1:4 weight ratio. Prior to the catalytic measurement, the catalysts were reduced *in situ* with pure H₂ flow of 100 cm³ min⁻¹ for 1 h at 500 °C. Catalytic samples were submitted to a temperature scan from 25 to 255 °C. The reaction mixture composition was 41% H₂, 1% CO and 1% O₂ (N₂ balance) being the W/F ratio 0.09 g_{cat} s cm⁻³. Oxygen concentration fed was twice the stoichiometric (λ = 2, λ = 2[O₂]/[CO]).

W/F ratio (4) is defined as the catalyst mass (*W*_{cat}) divided by the gas flow fed (*F*_T):

$$\frac{W}{F} (\text{g}_{\text{cat}} \text{ s cm}^{-3}) = \frac{W_{\text{cat}}}{F_T} \quad (4)$$

Catalytic activity denoted as *X*_{CO} is defined in the following equation:

$$X_{\text{CO}}(\%) = \left(\frac{([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}})}{[\text{CO}]_{\text{in}}} \right) \cdot 100 \quad (5)$$

where [CO]_{in}: mol of CO in reactor input, [CO]_{out}: mol of CO in reactor output.

Selectivity to CO₂, defined as the oxygen converted to produce CO₂ vs. oxygen converted to produce H₂O, was calculated using an oxygen mass atom-gram balance in each chromatograph analysis (Eq. (6)):

$$S_{\text{CO}_2}(\%) = \left(\frac{2 [\text{CO}_2]}{2 [\text{CO}_2] + [\text{H}_2\text{O}]} \right) \cdot 100 \quad (6)$$

The product reaction analysis was performed with an on-line *Agilent 6890N* chromatograph, equipped with TCD and FID detectors.

3. Results and discussion

3.1. Characterization

Texture parameters for each support and catalyst considered, calculated from isotherms, are compiled in Table 1. The support with SiO₂ (SiA) showed the highest surface area (390 m² g⁻¹), followed by LaA and MgA (supports with La₂O₃ and MgO, respectively) (148 and 140 m² g⁻¹, respectively), and finally by alumina (Ac) (93 m² g⁻¹). After the impregnation of Pt, surface area decreased, especially for PtSiA catalyst. A decrease in pore diameter and an increase in pore volume are also observed in PtAc. However, in

Table 1
Textural features of supports and catalysts: BET surface area (*S*_{BET}), pore diameter (*d*_{pore}), pore volume (*V*_{pore}).

Support	<i>S</i> _{BET} (m ² g ⁻¹)	<i>d</i> _{pore} (nm)	<i>V</i> _{pore} (cm ³ g ⁻¹)	Catalyst	<i>S</i> _{BET} (m ² g ⁻¹)	<i>d</i> _{pore} (nm)	<i>V</i> _{pore} (cm ³ g ⁻¹)
Ac	93.2	48.6	0.285	PtAc	92.3	22.3	0.710
MgA	140.6	10.4	0.505	PtMgA	130.8	8.8	0.231
SiA	390.3	6.8	0.772	PtSiA	351.6	6.1	0.756
LaA	148.2	10.4	0.505	PtLaA	141.2	10.3	0.496

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