Low temperature CO oxidation and long-term stability of Au/In$_2$O$_3$-TiO$_2$ catalysts

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Introduction

Gold catalysts have increasingly attracted the attention of researchers due to their potential applications to the environmental pollution abatement. The most remarkable application of supported gold has been obtained in the CO oxidation at sub-ambient temperature [1]. One of the most important limitations in the use of gold catalysts is that they deactivate during the catalytic test, showing low resistance to sintering [2]. In this way, the support plays a major role for the stability of the gold particles that depends on both its structure and the specific interaction occurring between the gold particles and it. Under the reaction conditions, the long-term stability during the CO oxidation is also a key feature, since the activity progressively decreases with time. In this case, the deactivation of gold supported catalysts is produced by the adsorption of CO on either the gold particles or on the support, forming carbonates that block the active sites co-participating in the catalytic reaction [3]. Additionally, the agglomeration of the small Au particles giving larger but less active particles [3] produces, in this case, an irreversible and more important deactivation. Many studies have been done in order to stabilize the supported gold nanoparticles. It has been suggested that the use of binary mixed oxides as gold supports could be a good solution for the stabilization of gold nanoparticles [4]. The gold particles can be anchored to the support, which stabilizes them and prevents their sintering [5, 6].

Materials and Methods

TiO$_2$ and In$_2$O$_3$-TiO$_2$ with 1, 6 and 12 wt % of In loading supports were prepared by the sol-gel method. The Au supported nanoparticles were obtained from the DP–Urea process [7, 8] The catalysts were characterized by X-ray diffraction, nitrogen physical adsorption (BET method), DRIFTS CO adsorption experiments, H$_2$-TPR, and high-angle annular dark-field scanning transmission electron microscopy (HAADF). The CO + O$_2$ reaction was studied in a flow reactor at atmospheric pressure in the temperature range between 0 and 300 °C. For the stability tests the reaction temperature was 10 °C. The reactant gas mixture was 1% vol. CO and 1% vol. O$_2$ balanced N$_2$ (total flux: 100 mL/min).

Results and Discussion

In$_2$O$_3$-TiO$_2$ supports prepared by the sol-gel method allow the formation of solids with high specific surface areas (Table 1). Using the urea deposition precipitation method the gold particle sizes on the supports fall into the 2.4-3.6 nm particle size range (Table 1). The gold particle size decreased with the In content. A diminution in the anatase crystallite size with In doping is observed (Table1). When In atoms are incorporated into the anatase crystalline structure the number of structural defects increases. A very high activity for the oxidation of CO at sub-ambient temperature reaction (0°C) was found on the gold supported on the In$_2$O$_3$-

TiO$_2$ mixed catalysts (Fig. 1a). DRIFTS experiments (Fig. 1b) showed that the high activity on the In$_2$O$_3$-TiO$_2$ catalysts can be related to a higher concentration of low coordinated sites in the gold particles. It will be show that the Au/In-TiO$_2$ catalysts are more stable under reaction conditions than the parent Au/TiO$_2$ catalyst. This is apparently due to a stronger anchoring of the gold particles over the well dispersed indium oxide on the In$_2$O$_3$-TiO$_2$ mixed oxides or over the structural defects of the support caused by the doping of the anatase with In, that can serve as particle pinning centers of gold crystallites, hindering its diffusion on the surface of support.

Table 1. Characterization of the sol-gel Au/In$_2$-O$_3$-TiO$_2$ catalysts.

Catalyst	Au loading wt %[*]	In loading wt %	BET Area (m^2/g)	Anatase crystallite size (nm)	Gold particle size (nm)
Au/TiO$_2$	2.1	---	66	24	3.6
Au/In-TiO$_2$(1-99)	2.2	1.0	170	12	3.1
Au/In-TiO$_2$(6-94)	2.0	6.7	122	11	2.4
Au/In-TiO$_2$(12-88)	2.3	12.3	174	9	2.4

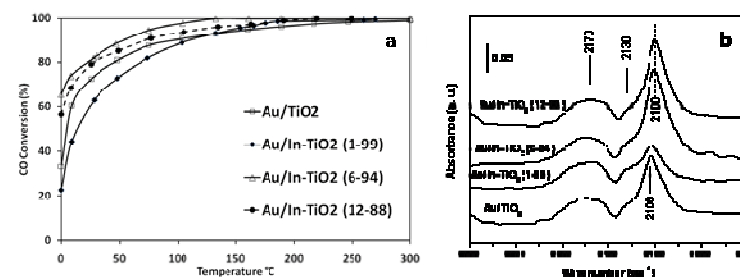[*]Theoretical gold loading of 2 wt %.

Figure 1. a) CO oxidation on the Au/In-TiO$_2$ catalysts, b)DRIFT spectra of adsorbed CO on the Au/TiO$_2$ and Au/In-TiO$_2$ catalysts

Significance

This paper is a contribution to the development of stable and active Au-based catalysts.

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