Short communication

Investigation of activity losses of gold nanoparticles in the CO selective oxidation

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ARTICLE INFO

ABSTRACT

Gold catalysts nanometrically dispersed over Al_2O_3, ZrO_2 and ZrO_2/Al_2O_3 are prepared and tested in selective CO oxidation. XRD, DRS, Raman and in situ DRIFTS techniques are used to investigate the main causes of activity loss after long period storage, evaluating the physical–chemical properties of the fresh catalyst and after 2 years storage. Storing in darkness is not efficient to maintain the catalytic activity. The gold particle sizes increase 13–54% depending on the support. The auto-reduction of cationic gold nanoparticles causes the decrease of CO chemisorption capacity and hence a drastically decrease in the activity.

1. Introduction

It has been demonstrated that gold catalysts exhibit a high catalytic activity when deposited as nanoparticles on metal-oxide supports [1] and it is also well known that its catalytic activity is strongly dependent on the particle size and the metal-support interface [2]. The preparation method has strong influence on the catalyst performance, and only preparations that allow gold particles lower than 10 nm lead to active catalyst. The literature has already reported that gold catalysts loose activity during long storage periods that limits applications [3]. Storing Au/TiO_2 materials in refrigerator and vacuum effectively prevents sintering of particles and preserves the catalytic activity, but storage under these conditions may be inconvenient in several applications [4].

Gold catalysts have been used in the selective CO oxidation (SELOX) for purification of hydrogen-rich feed streams. Experimental and theoretical studies have been developed to elucidate the reaction mechanisms [5–9], optimization of reactors conditions [6], improvements on methods of catalyst preparation [10], new catalytic systems with a second metal as a promoter [11]. The crucial point of these catalysts is their storage, however, few reports have paid attention on this problem and almost all studied the Au/TiO_2 system.

Moreuau and Bond [12] observed that the catalysts with low gold content (<0.2%) lost activity during the first 3 months storage. Daté et al. [13] also observed for a 1% Au/TiO_2 continuous loss of

activity. Boccuzzi et al. [14] observed that the storage time affected the gold particle sizes when treated at low temperature (<100 °C). Daté et al. [13] showed sintering after thermal treatment up to 400 °C. Zanella et al. [15] observed particle growth associated not only to the radiation of light, but also to the presence of water in the sample. Schumacher et al. [16] suggested the storage of catalysts in the shelter of light and in a freezer.

The main objective of this study is to investigate the main causes of activity losses after a long period storage of gold catalysts supported on Al_2O_3, ZrO_2 and $10\%ZrO_2/Al_2O_3$ in the selective CO oxidation reaction, using different "in situ" characterization techniques.

2. Experimental

2.1. Preparation of catalysts

The preparation of gold catalysts supported on different materials has been already reported, as described elsewhere [17]. The following supports were used: Al_2O_3 (232 $m^2 g^{-1}$), ZrO_2 (43 $m^2 g^{-1}$) and 10% ZrO_2/Al_2O_3 (208 $m^2 g^{-1}$).

Gold was added by deposition/precipitation [10,17]. Firstly, the support was suspended with deionized water under vigorous stirring and temperature rising up to 70 °C. In parallel, a solution of gold in deionized water was prepared, using $HAuCl_4 \cdot 3H_2O$ (Acros) as precursor, at pH 8.0 using a solution of 0.1 M NaOH. Subsequently, the aqueous solution of gold (15 g L^{-1} of AuO) was added to the support suspension and kept under stirring for 2 h. After the addition of gold solution and during the time of stirring, the final pH was maintained at 8.0 by adjusting with 0.1 M NaOH. Then, the solid