

Role of metallic and cationic gold species supported on nanosized Ce-Zr-Al-O mixed oxides in CO oxidation

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Introduction

While gold has been demonstrated to be chemically most inactive among noble metals due to its electronic configuration [1], matrix-trapped finely dispersed gold species are known to be highly reactive for CO oxidation even at low temperature [2], particular those supported on nano crystalline ceria [3,4]. The present paper is devoted to study of CO oxidation over gold species supported on nanosized ceria stabilized in alumina as pure oxide or as that doped with Zr.

Materials and Methods

The supports based on nano crystalline pure alumina, pure ceria, alumina doped by ceria (10 and 30%), alumina doped with CeZrO₂ (10 and 30%) have been prepared by sol gel technique described elsewhere [5] using organic precursors. Gold (3wt.%) catalysts were prepared by DP technique.

FTIR spectrometer Nexus-760 with *in situ* cell from Harrick was used for DRIFT analysis of CO adsorbed at low temperature. Catalytic activity test and transient kinetic analysis were performed in a laboratory made flow micro reactor with gas mixture 1%CO+0.5%O₂+He (80 ml/min) and in-line mass spectroscopic analysis (HPR 20, Hiden). Residence time was about 13 (g_{CAT}×h×mol CO⁻¹). UHP grade gases and catalyst samples with granular diameter within 0.2-0.5 mm were used for experiments.

Results and Discussion

Gold species supported on supports as alumina, pure ceria and massive CeZrO₂ are characterized by relatively low activity in CO oxidation at room temperature (about 0.05 mol CO/mol Au per s) in comparison with mixed oxides prepared by organic sol gel (about 0.2 mol CO/mol Au per s).

The type of sample activation affects strongly on the interaction of sample and reaction mixture during the first seconds of contact. So, over prerduced samples the consumption of CO does not occur during first 10 seconds while the gas phase oxygen is consumed completely. CO consumption starts only after adsorption of about 0.8 μmol of atomic oxygen.

According to FTIR CO at low temperatures there are only Au⁰ species on alumina or alumina doped with Ce-Zr-O mixed oxides after reduction of samples *in situ* (Fig.1). Adsorption of the

trace amounts of oxygen on ceria vacancies located near gold species deals to the formation of positively charged Au⁺ with subsequent huge increase of CO₂ formation rate (Fig.1).

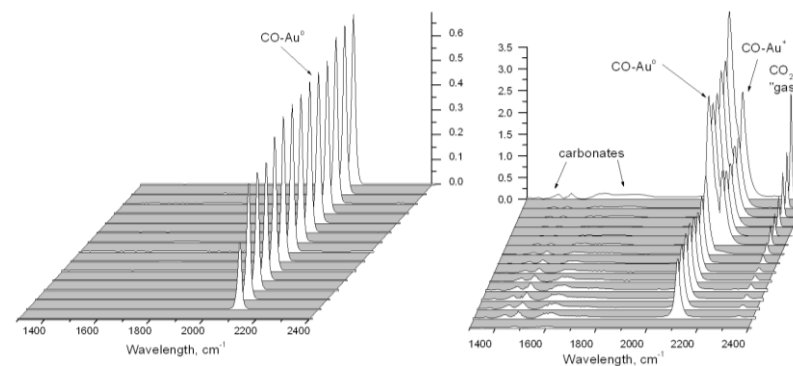


Figure 1. FTIR of CO adsorption vs time at -40°C on Au-Al-O (left) and on Au-Ce-Zr-Al-O (right). Catalysts were reduced *in situ* in hydrogen flow at 350°C.

So, metal gold species are less active in CO oxidation than oxidized ones according to our direct measurement using transient techniques and FTIR of CO adsorption at low temperatures. This result is in good agreement with mechanisms proposed by several authors speculatively on the role of cationic gold species in CO oxidation.

Significance

It was shown first by direct measurements the higher activity in CO oxidation of oxidized gold species in comparison with reduced ones.

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