Gold nanoparticles supported on Al_2O_3, SiO_2, TiO_2 and CeO_2 as catalysts for the WGS reaction.

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Introduction

An emerging application for the WGS reaction is the production of hydrogen for proton exchange membrane (PEM) fuel cells. This reaction is important because it removes CO, a poison to the fuel cell electrocatalysts, which is produced during the steam reforming and/or partial oxidation reactions. Moreover WGS reaction is one of the key steps involved in the automobile exhaust processes, converting CO and water to hydrogen and CO_2 and including the produced hydrogen as a very effective reductant for NO_x removal (1, 2). Presently great attention is paid to gold-containing catalysts because of their high catalytic activity at low temperatures in a series of important reactions, such as oxidation of CO and H_2 (3), reduction of NO_x (4), epoxidation of C_3H_6 (5), selective CO oxidation in hydrogen rich stream (6) and combustion of methane (7). In this work we compare the catalytic behavior of gold supported on reducible (TiO_2 and CeO_2) and non-reducible (SiO_2 and Al_2O_3) oxides for the WGS reaction in order to determine the role of the support on the catalytic activity and stability of the gold particles.

Materials and Methods

The preparation of gold nanoparticles was done using liquid phase methods, DP Urea in the case of TiO_2, CeO_2 and Al_2O_3 and cationic adsorption of $[Au(en)_2]Cl_3$ on SiO_2. Gold loading was fixed at 4 and 8 wt.%. Samples were activated by calcination in air in the range 200-400 °C. The catalysts were characterized by HRTEM, TPR and DRIFT. The WGS reaction was studied in the temperature range of 50-400°C in a flow reactor at atmospheric pressure. Prior to the catalytic run the catalyst was purged in He before admittance of the reactant gas mixture which composition was 5% CO in He saturated with H_2O vapor (10%). The space velocity was 9,000 h^{-1}. At each reaction temperature reaction was allowed to stabilize before collecting any data. The exit gases were analyzed by online GC (TCD) using a Carboxen 1000 packed column.

Results and Discussion

TPR experiments showed an enhanced reduction of Au/CeO_2 that was evidenced by a high H/Au ratio, Figure 1. The Au/TiO_2 presented the lowest reduction temperature. Figure 2 shows the temperature dependence of the WGS activity for catalysts calcined at 300°C. This calcination temperature produced the more active catalysts with an initial average gold particle size of ca. 2-3 nm for all samples. The activity of gold nanoparticles on the reducible supports was much higher than the one observed on Al_2O_3 and SiO_2 and varied as follows for reaction temperatures below 200°C $TiO_2>CeO_2>>Al_2O_3>>>SiO_2$. The bare CeO_2 presented at this temperature about 6% CO conversion. At reaction temperatures above 200 °C, the $4Au/CeO_2$ catalyst is more active compared to the $4Au/TiO_2$ one, Figure 2. Deactivation runs at 200ºC after 24h on stream showed practically no deactivation of the Au/TiO_2, Au/CeO_2 and Au/Al_2O_3 catalysts. CO and CO/H_2O adsorption was followed by DRIFT. Under reaction conditions absorption bands related to stable formate species which are present mostly on the bare CeO_2 support. Intensity of these bands decreases when Au is present on the support. After activation of the catalyst (calcined in air at 300 ºC) CO adsorption is evidenced on Au when supported on TiO_2, CeO_2 and Al_2O_3. Fast conversion of formate species in Au/TiO_2 and Au/CeO_2 takes place. This explains the higher activity displayed by these catalysts.

Significance

Contribution to the understanding of support effects on the WGS activity of gold nanoparticles.
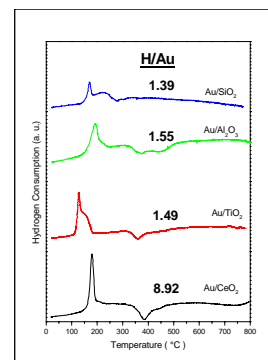

Figure 1. TPR profiles of Au supported catalysts. Hydrogen consumption corresponds to peaks below 350 °C.
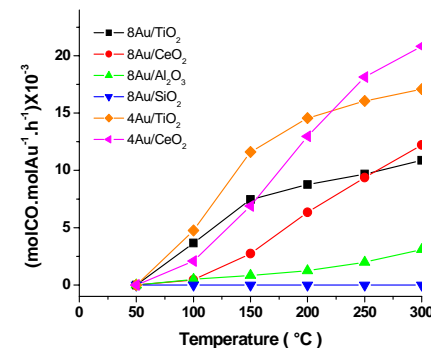
Figure 2. Catalytic activity in the WGS as a function of reaction temperature. XAu/Support where X is the nominal Au loading.

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