Gold nanoparticles supported on Al$_2$O$_3$, SiO$_2$, TiO$_2$ and CeO$_2$ as catalysts for the WGS reaction.

Alberto Sandoval$^1$, Antonio Gómez-Cortés$^2$, Rodolfo Zanella$^1$, José M. Saniger$^1$, Gabriela Díaz$^1$

$^1$CCADET, Universidad Nacional Autónoma de México (UNAM), A. P. 70-186, México D. F. 04510, México $^2$Instituto de Física, UNAM, A. P. 20-364 México D. F. 01000 México. diaz@fisica.unam.mx, zanella@ccadet.unam.mx

**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 (4), epoxidation of C$_x$H$_y$ (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$_2$O$_3$) 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$_2$O$_3$ 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 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$_2$O 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$_2$O$_3$ and SiO$_2$ and varied as follows for reaction temperatures below 200°C TiO$_2$>CeO$_2$>>Al$_2$O$_3$>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 200°C after 24h on stream showed practically no deactivation of the Au/TiO$_2$, Au/CeO$_2$ and Au/Al$_2$O$_3$ catalysts. CO and CO$_2$H$_2$O 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 °C) CO adsorption is evidenced on Au when supported on TiO$_2$, CeO$_2$ and Al$_2$O$_3$. 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.

**Acknowledgements**

To L. Rendon of LCMIF for HRTEM images.

**References**