The Effect of Cationic Gold on the Electronic Structure of Iron in Fe$_2$O$_3$-Supported Gold Nanoparticles

Sergio A. Jimenez-Lam,[1] Gustavo A. Fuentes,[2] Sergio A. Gómez,[2] Brent E. Handy,[3] María G. Cárdenas-Galindo,[3] Javier Guzman,[4] and Juan.C. Fierro-Gonzalez[1]*

[1]*Department of Chemical Engineering, Instituto Tecnológico de Celaya, Celaya, Guanajuato (Mexico)*

[2]*Department of Process Engineering, Universidad A. Metropolitana – Iztapalapa, A.P. 55-534, 09340 Mexico, D.F., (Mexico)*

[3]*Facultad de Ciencias Químicas, Universidad A. de San Luis Potosí, San Luis Potosí, SLP, (Mexico)*

[4]*Center for Environmentally Beneficial Catalysis, Lawrence, Kansas, 66047 (USA)*
*jcfierro@iqcelaya.itc.mx

Introduction

Finely dispersed gold on metal oxides is catalytically active for many reactions. It has been observed that when gold is dispersed on semiconductive metal oxides (e.g., Fe$_2$O$_3$, TiO$_2$, NiO, etc.) it is more active for CO oxidation catalysis than when it is supported on insulating metal oxides (e.g., MgO, Al$_2$O$_3$, SiO$_2$, etc.). However, the origin of these differences in the catalytic activity of supported gold remains uncertain. There is evidence from various spectroscopic techniques of the presence of cationic gold in some Fe$_2$O$_3$-supported gold catalysts during CO oxidation, and it has been proposed that such species play a role in the catalysis [1]. It has also been proposed that the presence of cationic gold affects the reducibility of various supports [2-4], as evidenced by temperature-programmed reduction (TPR) experiments. However, the consumption of H$_2$ in TPR experiments may not always be ascribed exclusively to redox processes, as some TPR peaks might be the result of the reaction of H$_2$ with various surface species.

We used dispersive X-ray absorption spectroscopy to characterize Fe$_2$O$_3$-supported gold nanoparticles in the presence of reductive atmospheres to follow changes in real time of the electronic structures of both iron and gold. The samples were also characterized by TPR. Our results emphasize the importance of using complementary techniques to investigate the electronic structure of metals in supported metal catalysts.

Materials and Methods

Fe$_2$O$_3$-supported gold samples were prepared by coprecipitation, using HAuCl$_4$ as the gold precursor. X-ray absorption near edge structure (XANES) spectra characterizing the samples were recorded at the X-ray beamlines D04-B and D06-B at the Brazilian Synchrotron Light Laboratory. Spectra were recorded at the Au-L$_{III}$ and Fe-K edges in separate experiments as the samples were treated in flowing H$_2$ or He at increasing temperatures. TPR experiments were done at the same conditions as those used at the synchrotron.

Results and Discussion

TPR results characterizing the Au/Fe$_2$O$_3$ samples show consumption of H$_2$ at temperatures between 351 and 468 K. These results suggest the reduction of Au^{III} to Au^0 and the partial reduction of Fe^{III} species to Fe$_3$O$_4$. Dispersive XANES spectra recorded at the Fe K edge as a Fe$_2$O$_3$-supported gold sample was treated in flowing H$_2$ at increasing temperatures (Figure 1) show changes at approximately the same temperature as that at which TPR showed the onset of H$_2$ consumption by the same sample. These results confirm that the consumption of H$_2$ by the sample during TPR experiments is related to changes in the electronic structure of the Fe. In contrast, Au-L$_{III}$ edge XANES spectra characterizing the initially prepared samples show that they contained cationic gold, which was not reduced when the sample was treated in flowing He at 373 K. These results suggest that the partial reduction of iron occurs at temperatures that are lower than those at which the cationic gold is reduced.
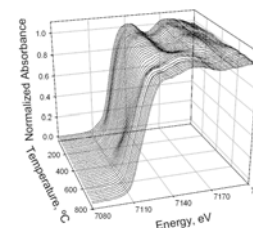

Figure 1. Fe-K edge dispersive XANES spectra characterizing a sample of Au/Fe$_2$O$_3$ containing 2 wt% Au as it was treated at increasing temperature in flowing H$_2$.

Dispersive XANES spectra characterizing the bare Fe$_2$O$_3$ support as it was treated in flowing H$_2$ at increasing temperatures show changes in the spectra at temperatures significantly higher than those observed for the Au/Fe$_2$O$_3$ samples. Thus, the data demonstrate that the presence of cationic gold has an influence on the electronic structure of the iron in the support.

Significance

Our results indicate that the presence of small amounts of cationic gold affects the electronic structure of the Fe$_2$O$_3$ in Au/Fe$_2$O$_3$ samples. Because there is evidence of cationic gold in some Fe$_2$O$_3$-supported gold catalysts during CO oxidation, our results are relevant, suggesting that the interaction between the gold and the support might stabilize catalytically active species for CO oxidation.

Acknowledgments

References

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