Structural changes in Au/TiO_2 during VOC oxidation

Faviola Altuzar, Sergio A. Gómez* and Gustavo A. Fuentes
Department of Process Engineering, Universidad A. Metropolitana – Iztapalapa, A.P. 55-534, 09340 Mexico, D.F. (Mexico)
*sgomez@xanum.uam.mx

Introduction

Gold catalysts are an interesting alternative for the oxidation of VOCs [1], but to be feasible in practice it is necessary to solve some of the existing discrepancies concerning the active sites and reaction mechanism. Of particular interest to us are the variations in activity of Au/TiO_2 catalysts during the oxidation of CH_4 and C_2H_4. In this study we show that those variations are caused by significant structural modifications that occur in Au/TiO_2 catalysts during reaction.

Materials and Methods

Au/TiO_2 catalysts having 0-2.7 Au wt. % were prepared by the deposition precipitation method. CH_4 and C_2H_4 oxidation reactions were performed at 24000 h^{-1} in a mixture containing 0.4-1% O_2, 0-24% CO_2, and N_2. We followed the activity using programmed temperature reaction cycles. The light-off temperature was close to 300°C in the case of C_2H_4 and to 450°C for CH_4. Catalyst characterization was done by XRD, diffuse reflectance in the UV-Vis region, CO-FTIR, Raman and XANES.

Results and Discussion

As expected, catalysts having high-Au content had a lower light-off temperature. In all cases the light-off temperature increased with the number of reaction cycles. The different analytical techniques helped us determine that used catalysts suffered significant structural modifications both of the Au nanoparticle size and location, as well as of the support. These changes were temperature dependent.

By XRD, we determined a large change in the rutile to anatase ratio (R/A) as a result of the high temperatures reached during reaction, but it was a function of the Au content. Blank experiments with pure TiO_2 showed that R/A reached a value of 12. When Au was present, that ratio was in the 3.6 – 0.7 range, depending on the Au content, as is shown in Table 1. It is clear that the presence of Au moieties inhibited the phase transition in TiO_2.

Diffuse reflectance spectra in the UV-Vis region of all catalysts showed the presence of a gold surface plasmon, see Figure 1. The position of the maximum and the area under the curve were linked to the occurrence Au° nanoparticles of different sizes. There were changes during reaction indicative of Au sintering and of the phase transition from anatase to rutile of TiO_2. We found that the Au plasmon (λ_{SP}) red-shifted as the number of reaction cycles increased, typically from 545 to 600 nm. The changes depended also on the amount of rutile phase present in the support. As Au nanoparticles sinter, a fraction of nanoparticles was found to be located on rutile. Independent experiments suggest that the nanoparticles located on rutile were less active than the nanoparticles on anatase. Also, the band gap energy of TiO_2 decreased when gold was present. There is a report of lower band gap as a Au/TiO_2 sample was calcined from room temperature to 700°C [2], but there is no indication of Au content. Our results show that the higher the gold content the lower the band gap energy of TiO_2, stressing the close interrelation between Au moieties and TiO_2.

Table 1. Rutile to Anatase ratio in fresh and used catalysts

	Gold wt. %				
	0	**0.14**	**0.24**	**0.97**	**2.73**
	R/A				
Fresh Catalysts	0.26	0.35	0.25	0.35	0.28
Used catalysts	12	3.6	1.1	0.9	0.7

Significance

In this work we establish for the first time the close relationship between the changes in Au nanoparticles and support modifications with the catalytic activity of Au/TiO_2 during the oxidation of CH_4 and C_2H_4. It is apparent that the electronic structure of the material, determined through an analysis of the Au surface plasmon and of the band gap energy of TiO_2, suffers large variations, too, and that they are dependent on the Au loading. We present a global structural model that permits further understanding of this type of catalysts.

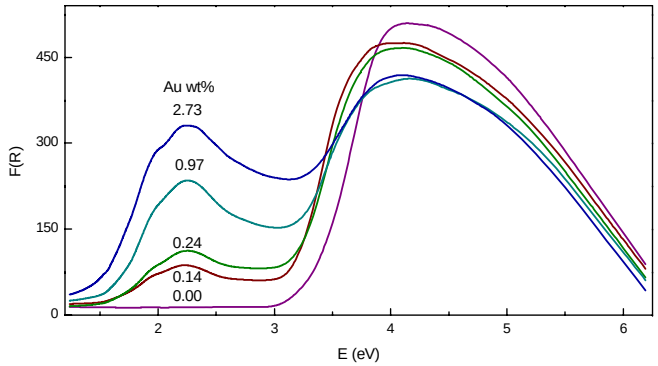

Figure 1. UV-Vis diffuse reflectance spectra of Au/TiO_2 having 0 – 2.75 Au wt. %.

References

1. Bond, G.C., Louis, C., Thompson, D.T. in "Catalysis by Gold", Catalytic Science Series, (Hutchings G.,Series Editor) Vol 6, Ch 1, Imperial College Press., 2006.
2. Debelia, M.A., Raphulu, M.C, Mokoena, E., Avalos, M., Petranovskii, V., Coville, N.J., and Scurrell, M.S., *Mat. Sci. Eng. A* 396, 70 (2005).