

Synergetic Effect of Bimetallic Au-Ru/TiO₂ Catalysts for CO and Methanol Complete Oxidation

L. Calzada¹, S. Collins², L. Delannoy³, C. Louis³, Ch W. Han⁴, V. Ortalan⁴, R. Zanella^{1*}

(1) *Centro de Ciencias Aplicadas y Desarrollo Tecnológico, UNAM, Cd. Mx., Mexico*

(2) *Instituto de Desarrollo Tecnológico para la Industria Química, UNL, Santa Fe, Argentina*

(3) *Laboratoire de Réactivité de Surface, CNRS-Sorbonne Université, Paris, France*

(4) *School of Materials Engineering, Purdue University, West Lafayette, IN, USA.*

It is well known that gold nanoparticles supported on metal oxides are active in various reactions of environmental importance.¹ Particularly, supported Au nanoparticles is well known as very efficient catalysts for CO oxidation at low temperature.¹ It is also possible to perform the oxidation of some volatile organic compounds (VOCs) such as light hydrocarbons and alcohols at room temperature. The most efficient and low-cost method for their abatement is the catalytic combustion to CO₂ and H₂O, preferentially at low temperatures. On the other hand, the preparation of bimetallic catalysts has been proposed as an alternative to improve the activity, stability and/or selectivity of gold catalysts. In this way, the addition of a second metal could modify the physicochemical and electronic properties of the first metal.² Ruthenium-based catalysts have been studied in VOCs oxidation reaction, and in conjunction with gold, they exhibit an improvement in catalytic activity.^{3,4}

Methanol is frequently employed as one of the model molecule for the total oxidation of VOCs; it has been investigated using gold catalysts supported on metal oxides.⁴

To study the effect of the addition of Ru to Au/TiO₂ catalysts, three types of Au-Ru/TiO₂ catalysts were prepared using methods involving deposition-precipitation with urea, with 3 wt% Au and 1.6 wt% Ru, i.e., with a 1:1 atomic ratio:

- co-deposition-precipitation,
- sequential deposition-precipitation with gold deposited first, then ruthenium,
- sequential deposition-precipitation with ruthenium deposited first, then gold.

They were tested in the reaction of CO oxidation performed at increasing temperature, from RT to 300 °C, and compared to monometallic 3 wt% Au/TiO₂ and 1.6 wt% Ru/TiO₂. Depending on the preparation method and the activation temperature, i.e., the temperature at which the samples were *in situ* reduced under H₂ before the reaction, the Au-Ru/TiO₂ (1:1) catalysts exhibited catalytic activity, either close to Au/TiO₂ or close to Ru/TiO₂, i.e., high or poor activity at low temperature, respectively. The most active catalyst was the one prepared by sequential deposition-precipitation with gold deposited first, then ruthenium, and HAADF and microEDS analysis showed that Ru core-Au shell type particles were formed. In contrast, for the poorly active catalysts, gold was in the core and Ru in the shell. For the most active sample, the Au:Ru atomic ratio was varied (1:1, 1:0.75, 1:0.5 and 1:0.25). The catalyst with the 1:0.75 atomic ratio exhibited the highest catalytic activity showing a synergetic effect due to the addition of ruthenium.

These catalysts (sequential deposition-precipitation (gold first then ruthenium)), thermally treated at 300 °C in H₂, were also tested in the total oxidation of methanol. The catalytic activity showed a synergetic effect at room temperature mainly for the 1:1 and 0.75:1 atomic ratio.⁵ TPR, UV-Vis spectra, XPS and DRIFTS-CO results also confirm the interaction between Ru and Au. Operando FTIR spectroscopy, performed during the oxidation of methanol as a function of the reaction temperature, showed that formates were the main reaction intermediates of the reaction, that they were already formed at RT on bimetallic Au-Ru/TiO₂ catalysts and that they were oxidized at lower temperatures than the monometallic Ru and Au counterparts.⁴

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References

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Corresponding author email: rodolfo.zanella@ccadet.unam.mx