Synergetic Effect of Bimetallic Au-Ru/TiO\textsubscript{2} Catalysts for CO and Methanol Complete Oxidation

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It is well known that gold nanoparticles supported on metal oxides are active in various reactions of environmental importance.\textsuperscript{1} Particularly, supported Au nanoparticles is well known as very efficient catalysts for CO oxidation at low temperature.\textsuperscript{3} 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 CO\textsubscript{2} and H\textsubscript{2}O, 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.\textsuperscript{2} Ruthenium-based catalysts have been studied in VOCs oxidation reaction, and in conjunction with gold, they exhibit an improvement in catalytic activity.\textsuperscript{3,4} Methanol is frequently employed as one of the model molecules for the total oxidation of VOCs; it has been investigated using gold catalysts supported on metal oxides.\textsuperscript{4}

To study the effect of the addition of Ru to Au/TiO\textsubscript{2} catalysts, three types of Au-Ru/TiO\textsubscript{2} 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/TiO\textsubscript{2} and 1.6 wt% Ru/TiO\textsubscript{2}. Depending on the preparation method and the activation temperature, i.e., the temperature at which the samples were in situ reduced under H\textsubscript{2} before the reaction, the Au-Ru/TiO\textsubscript{2} (1:1) catalysts exhibited catalytic activity, either close to Au/TiO\textsubscript{2} or close to Ru/TiO\textsubscript{2}, 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 H\textsubscript{2}, 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.\textsuperscript{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/TiO\textsubscript{2} catalysts and that they were oxidized at lower temperatures than the monometallic Ru and Au counterparts.\textsuperscript{4}

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References

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