Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

Synergetic effect of bimetallic Au-Ru/TiO$_2$ catalysts for complete oxidation of methanol

Lina A. Calzada[a], Sebastian E. Collins[b], Chang W. Han[c], Volkan Ortalan[c], Rodolfo Zanella[a,*]

[a] Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, Circuito Exterior S/N, Ciudad Universitaria, C.P. 04510 Mexico City, Mexico
[b] Instituto de Desarrollo Tecnológico para la Industria Química (INTEC) – Universidad Nacional del Litoral and CONICET, Güemes 3450, C.P. 3000 Santa Fe, Argentina
[c] School of Materials Engineering, Purdue University, West Lafayette, IN, USA

ARTICLE INFO

ABSTRACT

Bimetallic Ru-Au/TiO$_2$ catalysts prepared by deposition-precipitation with urea method were tested for the first time in the total oxidation of methanol. Different Ru:Au atomic ratios were used (1:1–0.25:1). The catalytic activity results showed a synergetic effect at low temperature (RT–50 °C), mainly for the 1:1 and 0.75:1 atomic ratio. HAADF-STEM and STEM-EDS characterization confirmed the interaction between Ru and Au. TPR, UV–vis spectra, XPS and DRIFTS-CO results also confirm this interaction. FTIR spectra, recorded following the oxidation of methanol as a function of the reaction temperature, showed that formates are the main reaction intermediates in the oxidation of methanol, which are formed from RT on bimetallic Ru-Au catalysts and are oxidized at lower temperatures compared to their monometallic Ru and Au counterparts.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Volatile organic compounds (VOCs), which are characterized by high vapor pressure and low water solubility, are precursors of ozone and photochemical smog. They are emitted from outdoor sources, such as transport and industrial processes as well as from indoor sources, such as household products. The most efficient and low-cost method for their abatement is the catalytic combustion to CO$_2$ and H$_2$O, preferentially at low temperatures [1,2].

Methanol is frequently employed as a model molecule for the total oxidation of VOCs; it has been investigated using gold catalysts supported on metal oxides because gold is known to be catalytically active in oxidation reactions when it is well dispersed on reducible metal oxides. The most remarkable reaction is CO oxidation at temperatures lower than ambient [3–6], although it has also been studied in VOCs oxidation using different molecules probes as propene, benzene, hexane, ethanol, toluene and acetone [7–11]. Particularly, gold catalysts supported on metal oxides such as Fe$_2$O$_3$ [12,13], CeO$_2$ [14,15], MCM-41 (modified by V and Nb)

[16], ZnO [17] and TiO$_2$ [18] have been investigated for the oxidation of methanol. Au/Fe$_2$O$_3$ has shown higher catalytic activity and, in some cases, better performance than Pt and Pd catalysts for this reaction [12,13].

A few studies have been focused on explaining the reaction mechanism of the total oxidation [15,17] and decomposition of methanol [19,20] on Au supported catalysts, indicating that methoxy and formate species are the principal reaction intermediates. The reaction between methanol and surface OH groups producing methoxy species adsorbed on the support with elimination of water is generally agreed. This methoxy species are then transformed into formates and also oxidized totally to CO$_2$. The last step is the oxidation of formates to CO$_2$, although it has been reported that formates can also act as a catalyst poison [17]. The activation of oxygen has been proposed to be performed in the periphery of the Au particle with the support [19,20], and sometimes the support can deliver some oxygen from the lattice, as in the case of TiO$_2$, CeO$_2$ and Fe$_2$O$_3$ [12,14]. Scirè et al. [12,14] proposed that highly dispersed small gold particles are able to weaken the Ce—O and Fe—O bonds adjacent to the Au atom, increasing like this the mobility of the lattice oxygen, also called metal-assisted Mars-Van Krevelen mechanism.

Bimetallic catalyst systems have been employed to improve the activity, selectivity and stability, compared to their monometallic counterparts. It is known that the physical and chemical properties of bimetallic particles are different from those of the monometallic ones, including changes in their optical and electronic properties, which are tunable with composition and particle size. The final composition of these catalysts depends strongly on the method of synthesis, interaction between metals, atmosphere and temperature of activation, among others. The addition of the second component may induce significant changes in activity and selectivity, attributing the enhancement of the catalytic properties to ensemble or ligand effects [21].

It has been reported that, despite their immiscibility in bulk state [22,23], Au and Ru can interact in supported catalysts, showing an enhancement of their catalytic properties in the oxidation of methanol [24,25], glycerol [23] and CO in a mixture of $CO/NH_3/O_2$ [26], compared to their monometallic counterparts. Particularly, the bimetallic $Au-Ru/Fe_2O_3$ catalyst [24] exhibited a higher hydrogen production in the partial oxidation of methanol, compared to the monometallic Ru and Au catalysts. The increase in activity was attributed to the strong metal–metal and metal-support interaction in the catalyst. Sreethawong et al. [25] studied Au-Ru catalysts supported on Al_2O_3 and SiO_2 observing that the interactions between Au and Ru was beneficial for the total oxidation of methanol because of the creation of different types of adsorption/desorption sites that modify the mechanism of methanol decomposition.

The aims of this work were to evaluate, for the first time, the effect of ruthenium in bimetallic Ru-Au catalysts supported on TiO_2 in the total oxidation of methanol as a function of the Ru:Au atomic ratio and to try to elucidate the nature of the interaction between gold and ruthenium. To obtain information about the reaction mechanism, FTIR spectra were recorded following the oxidation of methanol as a function of the reaction temperature.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Preparation of monometallic samples

Titania Degussa P25 was used as support ($45\,m^2\,g^{-1}$, nonporous, 70% anatase and 30% rutile, purity >99.5%). Commercial $HAuCl_4 \cdot 3H_2O$ (Sigma) and $RuCl_3 \cdot 3H_2O$ (Pressure Chemical) were employed as gold and ruthenium precursors. Prior to preparation, TiO_2 was dried in air at $100\,°C$ for at least 24 h. The nominal metal loadings in the monometallic catalysts were 3 wt.% for gold and 1.56 wt.% for Ru, which is equivalent to 0.4 at.% for each sample.

The preparation of the Au/TiO_2 sample was performed by deposition-precipitation with urea (DPU) in the absence of light, according to the previously reported procedure [27,28]. In this preparation, the $HAuCl_4$ (4.2×10^{-3} M) and urea (0.42 M) were dissolved in 37 mL of distilled water.. Then, 1 g of titania was added to this solution. The suspension was heated at $80\,°C$ and kept constant for 16 h under vigorous stirring. Afterwards, the suspension was centrifuged, washed with water and centrifuged again four times. The solid recovered was dried under vacuum for 2 h at $80\,°C$. The monometallic Ru/TiO_2 sample was prepared following the same method, 1 g of titania was added to an aqueous solution (37 mL) containing $RuCl_3$ (4.2×10^{-3} M) and urea (0.42 M). The suspension was stirred vigorously and kept at $80\,°C$ for 2 h, then it was centrifuged and washed four times with water, as in the case of the Au/TiO_2 sample. The solid recovered in both samples was dried under vacuum for 2 h at $80\,°C$ and stored at room temperature in a desiccator under vacuum, away from light in order to prevent any alteration [29].

2.1.2. Preparation of bimetallic samples

In bimetallic samples, the nominal gold loading was kept constant (3 wt.%), whereas for ruthenium was chosen to synthesize Ru-Au catalysts with different Ru:Au atomic ratios: 1:1, 0.75:1, 0.5:1 and 0.25:1. A sequential deposition method was used to prepare these catalysts. Gold was first deposited on TiO_2, according to the DPU method described above. After being dried at $80\,°C$ for 2 h, ruthenium was also deposited by DPU as previously described. The same procedure of washing and drying as above was employed. The samples were identified as Ru-Au followed by the nominal Ru:Au atomic ratio, e.g., Ru-Au 0.75-1.

2.2. Characterization techniques

The elemental analysis of Au and Ru in the dried samples was performed by X-ray fluorescence (XRF) using a XEPOS HE (AMETEK) spectrometer. The Au and Ru weight loadings were expressed in grams of each metal per gram of sample.

After *ex situ* thermal treatment under the same conditions as those used for the oxidation reaction of methanol, the samples were examined by transmission electron microscopy in a Jeol-2010 FasTem analytical microscope equipped with a high-angle annular dark-field (HAADF) detector. The average size of particles and the histograms of particle sizes were obtained from the measurement of 300–500 particles. The size limit for the detection of the metal particles on TiO_2 was about 0.6 nm. The average particle diameter d_s was calculated with the formula: $\Sigma n_i d_i / \Sigma n_i$, where n_i is the number of particles of diameter d_i. The standard deviation was calculated with the formula: $[\Sigma(d_i - d_s)^2 / \Sigma n_i]^{1/2}$. High resolution Z-contrast scanning transmission electron microscopy (STEM) imaging and STEM energy dispersive X-ray spectroscopy (EDS) analysis were performed using a probe aberration-corrected JEOL ARM200CF equipped with an Oxford X-Max100TLE windowless detector. The microscope was operated at 200 kV. The probe current and convergent semiangle were 79 pA and 15 mrad, respectively. The collection angle of the HAADF detector was 68–280 mrad. The STEM-EDS maps, linescan profiles and compositions were collected using the Oxford Aztec software. The quantification of the compositions of bimetallic nanoparticles was performed by the Cliff-Lorimer method [30] using the Aztec software.

Diffuse reflectance UV–vis spectra of the catalysts were obtained using a CARY 5000 spectrophotometer equipped with a Praying Mantis and a high temperature reaction chamber (Harrick). The spectra were recorded from 300 to 800 nm during the activation thermal treatment under hydrogen. In each experiment, approximately 30 mg of dried sample was packed in the sample holder and pretreated *in situ* under hydrogen flow ($30\,mL\,min^{-1}$ and $5\,°C\,min^{-1}$) up to $300\,°C$, followed by a 60-min plateau. A spectrum of Teflon (from Aldrich) was used as reference.

The hydrogen temperature programmed reduction (H_2-TPR) analysis of the dried catalysts was performed in a RIG-150 unit under a flow of 10% H_2/Ar mixture ($50\,mL\,min^{-1}$) employing a heating rate of $10\,°C\,min^{-1}$ from room temperature to $600\,°C$. H_2O produced during the reduction process was trapped before the TCD detector.

CO adsorption was followed by DRIFT spectroscopy to characterize the metallic surface. The experiments were carried out in a Nicolet 670FT-IR spectrophotometer equipped with a Praying Mantis and a low/high temperature reaction chamber (Harrick). In each experiment, approximately 40 mg of dried sample was packed in the sample holder and pretreated *in situ* under hydrogen flow ($40\,mL\,min^{-1}$, heating rate $5\,°C\,min^{-1}$) up to $300\,°C$ followed by a plateau of 1 h. After thermal treatment, the sample was cooled down to room temperature under the same gas flow and then purged with N_2 before the introduction of 5% CO in N_2 ($40\,mL\,min^{-1}$). A spectrum recorded under N_2 was used as refer-