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One-Step Synthesis of AuCu/TiO_2 Catalysts for CO Preferential Oxidation

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Au/TiO_2 (1wt% Au), Cu/TiO_2 (1wt% Cu) and $AuCu/TiO_2$ (1wt% AuCu) catalysts with different Au:Cu mass ratios were prepared in one-step synthesis using sodium borohydride as reducing agent. The resulting catalysts were characterized by X-ray diffraction (XRD), X-ray Dispersive Energy (EDX), Transmission Electron Microscopy (TEM) and Temperature Programmed Reduction (TPR) and tested for the preferential oxidation of carbon monoxide (CO-PROX reaction) in H_2-rich gases. EDS analysis showed that the Au contents are close to the nominal values whereas for Cu these values are always lower. X-ray diffractograms showed only the peaks of TiO_2 phase; no peaks of metallic Au and Cu species or oxides phases were observed. TPR and high-resolution TEM analysis showed that $AuCu/TiO_2$ catalysts exhibited most of Au in the metallic form with particles sizes in the range of 3-5 nm and that Cu was found in the form of oxide in close contact with the Au nanoparticles and well spread over the TiO_2 surface. The $AuCu/TiO_2$ catalysts exhibited good performance in the range of 75-100 °C and presented a better catalytic activity when compared to the monometallic ones. A maximum CO conversion of 98.4% with a CO_2 selectivity of 47% was obtained for $Au_{0.50}Cu_{0.50}/TiO_2$ catalyst at 100°C.

Keywords: *$AuCu/TiO_2$ catalyst, carbon monoxide, preferential oxidation, hydrogen.*

1. Introduction

Hydrogen gas is produced predominantly by combining the methane steam reforming and the gas-water shift reactions resulting in a hydrogen-rich mixture containing about 1% of carbon monoxide (10.000 ppm of CO). This CO level is not sufficiently low for application of hydrogen in Proton Exchange Membrane Fuel Cell (PEMFC) and in ammonia synthesis because CO poison the catalysts used in these processes[1-5]. Therefore, the purification of the hydrogen-rich mixture is necessary and one process that has been considered very promising is the preferential oxidation of CO in hydrogen-rich mixtures (CO-PROX reaction), because it can dramatically reduce energy and hydrogen losses when compared to the processes currently used in the industry such as CO methanation and pressure swing adsorption (PSA). However, the catalysts for CO-PROX reaction should be active and especially highly selective, as it should selectively oxidize CO and avoid hydrogen oxidation[1-5].

Au nanoparticles supported on TiO_2 (Au/TiO_2 catalyst) showed good CO conversions and CO_2 selectivity for CO-PROX reaction in the range of 20 to 100°C; however, the procedure used to prepare Au/TiO_2 catalysts has a significant influence on the catalytic performance, which is a result of Au nanoparticles sizes (should be smaller than 5 nm) and Au-TiO_2 interactions[6-12]. Sangeetha et al.[13] prepared Au nanoparticles supported on CuO_x-TiO_2 (*x* from 1 and 10 wt%), where the support was prepared by impregnation of $Cu(NO_3)_2$ in TiO_2 (Degussa P25) and treating at 350ºC. The deposition of Au nanoparticles was carried out by the deposition-precipitation method obtaining nanoparticle sizes of about of 2.5 nm. The resulting Au/CuO_x-TiO_2 catalysts were more active than the Au/TiO_2 catalyst with CO conversions close to 100% and CO_2 selectivity values of 60 to 80% in the temperature range of 50 °C to 100 °C. Duh et al.[14] also prepared a series of Au/CuO_x-TiO_2 catalysts with various Cu/Ti ratios by incipient-wetness impregnation and Au was supported by deposition-precipitation. It was observed that the addition of CuO_x in Au/TiO_2 catalyst enhanced the activity significantly for CO oxidation at low temperature, which was attributed to the interactions among Au, CuO_x and TiO_2. Recently, Qi et al.[15] prepared nanosized CuO and Cu_2O materials and followed by the deposition of Au nanoparticles. The catalytic activities of the resulting AuCu catalysts for CO-PROX showed a significant enhancement when compared to CuO and Cu_2O materials. It was concluded that CuO not Cu_2O species play a critical role for the CO oxidation and that the cooperative effect between CuO and Au nanoparticles enhanced the activity of Au/CuO catalyst when a strong interaction between them occurred.

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In this work we prepare Au/TiO_2, Cu/TiO_2 and $AuCu/TiO_2$ catalysts in one-step synthesis by co-reducing the Au^{+3} and Cu^{+2} ions with sodium borohydride in the presence of the TiO_2 support. The catalysts were characterized and tested for CO-PROX reaction.

2. Experimental

2.1 Synthesis of Au/TiO_2 catalyst (1.0 wt% Au)

A suspension containing 346.5 mg of TiO_2 (P25 Evonik) and 45 mL of deionized water was prepared. Then 6.12 x 10^{-4} L of tetrachlorouric acid ($HAuCl_4$) solution (2.88 x 10^{-2} mol L^{-1}) was added and stirred for homogenization for about 10 min. After this, 2.02 x 10^{-4} L of $NaBH_4$ solution (2.643 x 10^{-1} mol L^{-1}) was added and the resulting mixture remained under stirring for 24h. Then, the solid was then separated by centrifugation, washed with excess water and dried at 70 °C.

2.2 Synthesis of Cu/TiO_2 catalyst (1.0 wt% Cu)

The procedure was similar to that described above, but using 5.50 x 10^{-4} L of $Cu(NO_3)_2$ solution (1 x 10^{-1} mol L^{-1}).

2.3 Synthesis of $AuCu/TiO_2$ catalyst with different mass ratios

The procedure was similar to that described above but using $HAuCl_4$ solution (2.88 x 10^{-2} mol L^{-1}) and $Cu(NO_3)_2$ solution (1 x 10^{-1} mol L^{-1}) in the desired proportions and 5.14 x 10^{-4} L of $NaBH_4$ solution (2.643 x 10^{-1} mol L^{-1}). The pH of the synthesis solutions were in the range of 4.5 and 5.

2.4 Characterizations

The semi-quantitative chemical analysis of the catalysts were performed by Energy-dispersive X-ray spectroscopy (EDS) on a Philips Scanning Microscope model XL30 with 20 kV electron beam equipped with an EDAX model DX-4 micro analyzer.

Transmission electron microscopy (TEM) was performed on a JEOL Transmission Electron Microscope, model JEM-2100 (200 kV). The particle size distributions were obtained by measuring de diameter of more than 100 nanoparticles from the micrographs.

X-ray diffraction (XRD) was performed on a Rigaku Multiflex diffractometer using Cu Kα radiation source (λ = 1.5418Å) with 2θ scan between 20º and 90º, with 0.06º step and time per step of 4s.

Temperature Programmed Reduction (TPR) experiments were performed on Quantachrome ChemBET Pulsar using 50 mg of catalyst in a U-shaped quartz cell and H_2 consumption was measured using a thermal conductivity detector (TCD). Initially the catalyst was treated in a flow of N_2 (50 mL min^{-1}) at 200 °C for 1 h and after cooling to room temperature the catalyst was exposed to gas containing 10% vol H_2/N_2 at a flow rate of 30 mL $min^{-1}$and heated to 750ºC at 10ºC min^{-1}.

2.5 Catalytic tests

The catalytic tests were performed in a fixed bed reactor (U-tube) using 100 mg of catalysts in the temperature range between 25 °C to 150 °C using a gas composition containing 1 mol% of CO, 1mol% of O_2 and 98 mol% of H_2 (O_2/CO volumetric ratio of 1, λ =2) and a flow rate of 25 mL min^{-1} (spatial velocity of 15000 mL $gcat^{-1}$ h^{-1}). The reaction products and unconverted reagents were quantified using a Gas Chromatograph Agilent HP 7890A with TCD and FID (methanation of CO and CO_2) detectors. To evaluate the performance of each catalyst, CO conversion and CO_2 selectivity were calculated according to the Equations 1 and 2:

$$\text{CO conversion}: \frac{([CO_i] - [CO_f])\times 100}{[CO_i]} \quad (1)$$

$$CO_2\text{selectivity}: \frac{0.5\times[CO_{2\,f}]\times 100}{([O_{2\,i}] - [O_{2\,f}])} \quad (2)$$

3. Results and Discussion

The semi-quantitative EDS analyses of the catalysts are shown in Table 1.

In a general manner, it was observed that the amounts of Au and Cu determined by EDS increase with the increase of the nominal values; however, the values determined for Au are close to the nominal values, while for Cu these values are always smaller than the nominal ones. This could be explained by the EDS analysis having been performed in a semi-quantitative way and/or or that not all Cu species were deposited on the TiO_2 support as the mother liquor was slightly colored after centrifugation.

The X-ray diffractograms of the TiO_2 support and Au/TiO_2, Cu/TiO_2 and $Au_{0.50}Cu_{0.50}/TiO_2$ catalysts are shown in Figure 1.

For all catalysts it was observed the diffraction peaks of the support TiO_2 P25, which has about 80% of anatase phase with 2θ: 25.36º, 37.89º, 48.14º, 54.03º, 55.18º corresponding to the planes (101) , (004), (200), (105),

Table 1. Chemical composition and average particle sizes of the catalysts.

Catalyst composition (wt%)	Au (wt%) EDS	Cu (wt%) EDS	d (nm) TEM
$Au_{1.0}/TiO_2$	0.99	--	4.9 ± 1.2
$Cu_{1.0}/TiO_2$	--	0.35	--
$Au_{1.0}Cu_{0.90}/TiO_2$	0.10	0.45	3.5 ± 0.7
$Au_{0.25}Cu_{0.75}/TiO_2$	0.31	0.29	3.6 ± 0.9
$Au_{0.50}Cu_{0.50}/TiO_2$	0.73	0.25	2.9 ± 0.7
$Au_{0.75}Cu_{0.25}/TiO_2$	0.87	0.21	3.9 ± 1.0
$Au_{0.9}Cu_{0.1}/TiO_2$	0.96	0.06	4.6 ± 0.9

(211) (110), (101), (211) and 20% of rutile phase with 2θ: 27.4º, 36.1º and 54.4º corresponding to the planes (110), (101), (211)[6,16]. However, it was not observed the presence of Cu^0 and Au^0 having a face-centered cubic structure (fcc) where the diffracting planes are (111), (200), (220) which correspond to 2θ: 43.24º; 50.35 °; 73.96 ° for Cu (#PDF 4-784) and 38.17 °; 44.37 °; 64.55 ° for Au (#PDF 4-836)[17] nor the presence of copper oxide phases such as CuO or Cu_2O[18]. This could be due to the low content of these metals or to the average diameter of the crystallites (< 5 nm) resulting in low intensity and broad peaks that in the presence of well-defined and high intensity crystalline peaks of TiO_2 support make their identification difficult[19].

The transmission electron micrographs of Cu/TiO_2, Au/TiO_2 and AuCu/TiO_2 catalysts are shown in Figure 2.

For Cu/TiO_2 catalyst (Figure 2a) it was not observed in the TEM micrographs the presence of black dots while for catalysts having Au (Figure 2b-d) they were observed having average sizes in the range of 3-5 nm (see Table 1). Figure 3 shows a high-angle annular dark-field scanning transmission electron microscopy (HAADF/STEM) image, EDS mapping and line-scan of $Au_{0.50}Cu_{0.50}/TiO_2$ catalyst.

HAADF/STEM image showed bright dots of small sizes (average 3 nm) what is coming from the differences between metals and support element atomic numbers contributing to a high contrast in the image showing that metal nanoparticles are dispersed on TiO_2 support. The EDS mapping and line scan confirmed that Au is exclusively located in the position of bright dots while Cu is also located at these positions in close contact with Au and distributed over the TiO_2 surface.

The temperature programmed reduction (TPR) profiles of TiO_2 support and Au/TiO_2, Cu/TiO_2 and $Au_{0.50}Cu_{0.50}/TiO_2$ catalysts are shown in Figure 4.

The H_2-TPR profile of the TiO_2-P25 support showed no reduction peaks in the studied temperature range as already reported in the literature for temperatures from ambient to 800 °C[20]. The H_2-TPR profile of Cu/TiO_2 catalysts showed an intense peak at about 150 °C attributed to the reduction of CuO to Cu(0)[20-23] and a small peak at about 375°C that could be ascribed to the reduction of CuO nanoparticles having little or no interaction with the support[23,24]. It was also observed on H_2-TPR profile of Cu/TiO_2 catalyst a peak at about 575 °C. Ramírez and Gutiérrez-Alejandre[25] observed a peak at about 570 °C in the TPR profile of pure anatase TiO_2 support. Kang et al.[22] reported for CuO supported on pure anatase TiO_2 phase two peaks at 140 and 470 °C that were attributed to reduction of Cu^{+2} to Cu^0 and to the reduction of anatase phase, respectively; however, for CuO supported on pure rutile TiO_2 phase only one peak at around 120 °C was observed. Zhang et al.[26] described that no peaks were observed between 25 and 500 °C in the TPR profile of an anatase TiO_2 support; on the other hand, the TPR profile of the Pt/TiO_2 catalyst showed two peaks at 80 and 360 °C that were

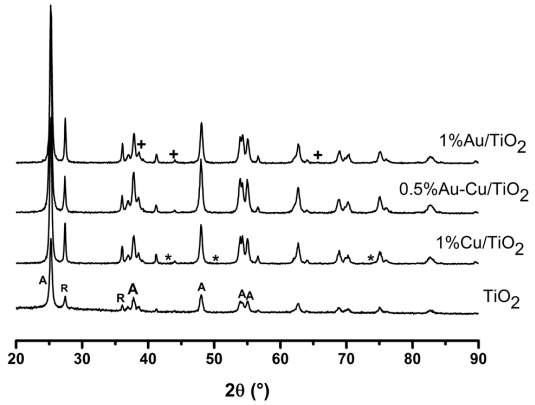

Figure 1. X-ray diffractograms of the TiO_2 support and the catalysts (A = peaks of Anatase phase, R = peaks of Rutile phase, * peaks position of Cu (fcc) phase and + peaks position of Au (fcc) phase)

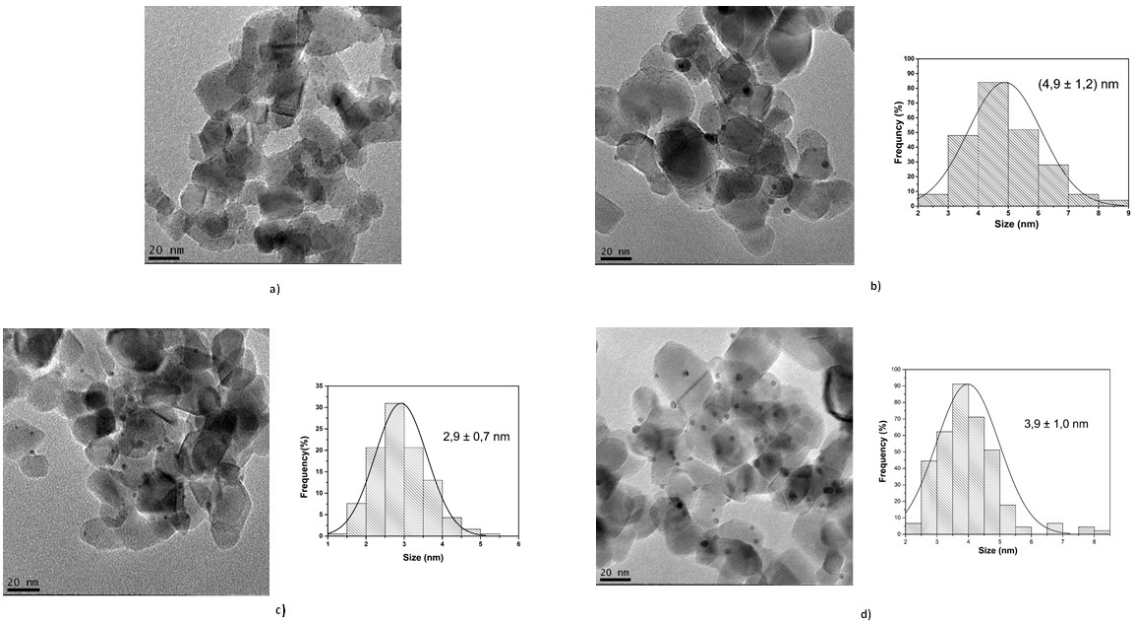

Figure 2. Transmission electron micrographs and histograms of **a)** Cu/TiO_2, **b)** Au/TiO_2, **c)** $Au_{0.50}Cu_{0.50}/TiO_2$ and **d)** $Au_{0.75}Cu_{0.25}/TiO_2$ catalysts

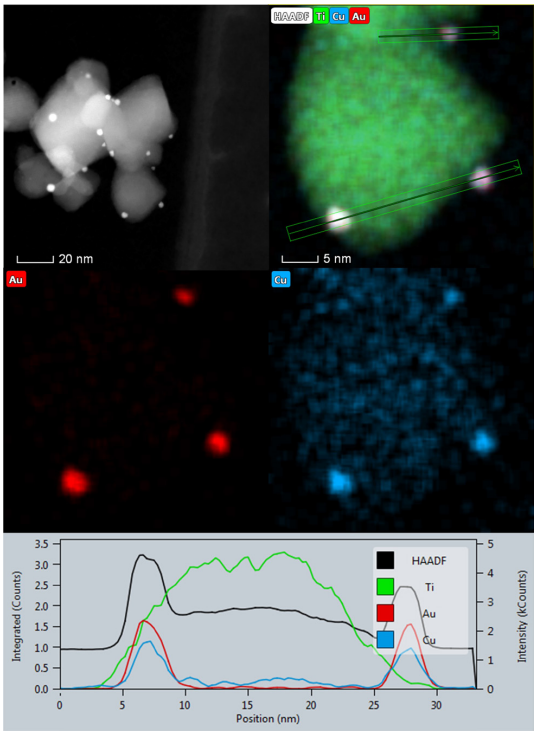

Figure 3. High-angle annular dark-field scanning transmission electron microscopy (HAADF/STEM) image, EDS mapping and line-scan of $Au_{0.50}Cu_{0.50}/TiO_2$ catalyst

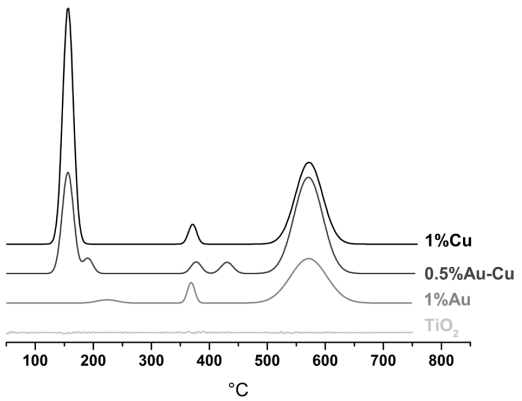

Figure 4. H_2-TPR profiles of TiO_2 support and the catalysts

attributed to the reduction of PtO_x to metallic Pt and to the reduction of the surface capping oxygen of TiO_2, respectively. Thus, the peak observed at 575 °C in the TPR profile may result from the reduction of the surface oxygen of anatase phase of TiO_2 P-25 support that is favored by the interaction with Cu species. The H_2-TPR profile of Au/TiO_2 catalyst did not shown reduction peaks below 100 °C suggesting that Au was predominantly found in the metallic form[27] taking into account that pre-treated (reduced) Au catalyst do not shown any peak of reduction[28]. However, it was observed a very small and broad peak at about 225 °C that could be related to ionic Au-species interacting with TiO_2 phase[27,28]. For $Au_{0.50}Cu_{0.50}/TiO_2$ catalyst it was observed a peak at about 150 °C attributed to the reduction of CuO to Cu(0) and a small and broad peak at about 180 °C that could be due to ionic Au-species interacting with CuO and TiO_2 phases. In the region of temperature between 350 and 450 °C two small peaks are observed for $Au_{0.50}Cu_{0.50}/TiO_2$ catalyst, which could be a result of the interaction of Au and Cu species with TiO_2 support and a peak at about 575 °C resulting from reduction of TiO_2 support. Thus, it could be inferred from these results that $AuCu/TiO_2$ catalysts prepared by this methodology exhibit most of the Au in metallic form while most of the Cu is in oxide form (CuO). In fact, by analyzing the results of H_2-TPR and microscopy it could be inferred that Au and CuO_x species interact with each other and with TiO_2 support.

The catalytic performances of the Cu/TiO_2, Au/TiO_2 and $Au_{0.50}Cu_{0.50}/TiO_2$ catalysts were studied in the temperature range of 20 °C to 150 °C (Figure 5). No previous treatments were done in these samples before catalytic tests and the results shown correspond to the second cycle of the catalytic reactions.

Cu/TiO_2 catalyst showed low CO conversions (below 20%) until 100 °C increasing to 75% at 150 °C. The CO_2 selectivity showed a maximum value of 70% at around 120 °C. Au/TiO_2 catalyst showed a maximum CO conversion of 55% at 75 °C; however, CO_2 selectivity values were very low (around 20%) in all range of temperature. For all $AuCu/TiO_2$ catalysts prepared with different contents of Au and Cu the maximum CO conversions occurred at 100 °C. In addition, the CO conversion values increased with the increase of Au content reaching a maximum value of 98.4% for $Au_{0.50}Cu_{0.50}/TiO_2$ catalyst (Figure 5a)

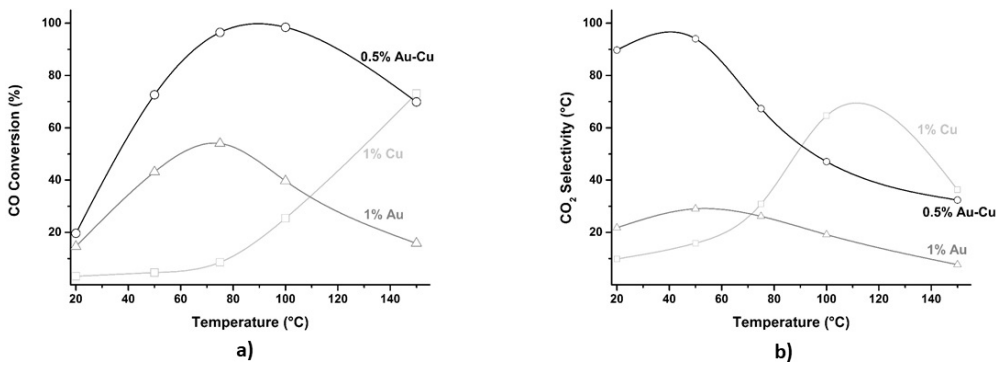

Figure 5. (a) CO conversion and **(b)** CO_2 selectivity in function of the temperature for Cu/TiO_2, Au/TiO_2 and $Au_{0.50}Cu_{0.50}/TiO_2$ (1.0% CO, 1.0% O_2, 98.0% H_2 and a space velocity of 15000 mL g_{cat}^{-1} h^{-1})

and, after that, these values began to decrease (92.0% for $Au_{0.75}Cu_{0.25}/TiO_2$ catalyst) as the amount of Au was increased further. Conversely, CO_2 selectivity values increased with the increase of Cu content and the values varied between 35% and 55% at 100 °C. The CO_2 selectivity value for $Au_{0.50}Cu_{0.50}/TiO_2$ catalyst was 47% (Figure 5b) reaching a maximum value of 55% for $Au_{0.25}Cu_{0.75}/TiO_2$ catalyst and after that decreased to 50% for $Au_{0.10}Cu_{0.90}/TiO_2$ catalyst. Thus, AuCu/TiO_2 catalysts showed to be more active for CO-PROX reaction than Au/TiO_2 and Cu/TiO_2 catalysts in the temperature range of 20 °C to 100 °C, as already observed for CO-PROX reaction[13] and for CO-oxidation at low temperature[14].

Figure 6 shows the CO conversion as a function of Au content (wt%) and nanoparticle sizes for AuCu/TiO_2 catalysts prepared with different contents of Au and Cu. It could be seen that there is a relationship between Au content and nanoparticles sizes where the maximum CO conversion was observed for the sample $Au_{0.50}Cu_{0.50}/TiO_2$ with similar quantities of Au and Cu and that`s where a smaller size of the Au nanoparticles was observed.

The long-term stability test results for $Au_{0.50}Cu_{0.50}/TiO_2$ catalyst is shown in Figure 7 showing CO conversions above 90%

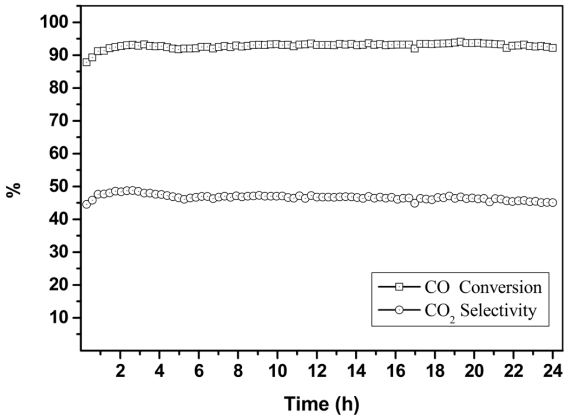

Figure 6. CO conversion at 100 °C in the function of Au content (wt%) and nanoparticle sizes for AuCu/TiO_2 catalysts with different Au and Cu content (1.0% CO, 1.0% O_2, 98.0% H_2, 100 °C and a space velocity of 15000 mL g_{cat}^{-1} h^{-1})

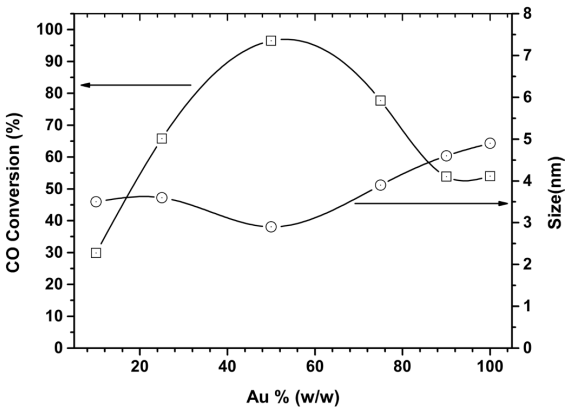

Figure 7. CO conversion and CO_2 selectivity in function of time for $Au_{0.50}Cu_{0.50}/TiO_2$ catalyst at 100 °C (1% of CO, 1% of O_2 and 98% of H_2, spatial velocity of 15000 mL g_{cat}^{-1} h^{-1})

and CO_2 selectivity values in the range of 45-50%, which remained stable throughout the period evaluated showing the stability of the catalysts under the applied reaction conditions. Similar results were observed by Sangeetha et al.[13] in long test time using as catalyst Au/CuO_x-TiO_2 (1wt% of Au and a CuO_x:TiO_2 ratio of 4.8:95.2) at 80 °C for 49 h. A maximum CO conversion of 95% with a CO_2 selectivity of about 65% was obtained using a gas composition of 1.33% CO, 1.33% O_2, 65.33% H_2, and 32.01% He and a space velocity of 30000 mL g_{cat}^{-1} h^{-1}.

Sangeetha et al.[13] also observed an increase of maximum CO conversion and CO_2 selectivity for CO-PROX reaction comparing Au/TiO_2 and Au/CuO_x-TiO_2 catalysts and attributed this increase due to the presence of Au(0) and CuO_x species, where CuO_x-TiO_2 was proposed to be a supplier or storage of oxygen. Wang et al.[29] studied the synergistic effects of different Au bimetallic alloy catalysts in low temperature CO oxidation and observed for AuCu alloy catalyst that a phase segregation occurs during CO oxidation forming a Au@CuOx hybrid structure (nano or even sub-nano CuO_x supported on Au nanoparticles) resulting in interfacial sites between them. FTIR studies of CO adsorption showed that CO adsorbed on Au(0) while CuO_x species were responsible for providing active oxygen in the same way as reducible oxides do. Recently it was shown that CuO not Cu_2O species played a more critical role for CO oxidation at low temperature and that CuO and Au(0) species enhanced the activity of Au/CuO catalyst only if a strong interaction occurs between them[15].

4. Conclusions

Active, selective and stable AuCu/TiO_2 catalysts was prepared by a simple one-step methodology for CO-PROX reaction. The AuCu/TiO_2 catalysts exhibited good activities and selective in the range of 75-100 °C and presented a better catalytic activity when compared to the monometallic ones. The analyses showed that Au is predominantly found in its metallic form while Cu in its oxide form and that Au(0) and CuO_x species are in good interaction with each other and with TiO_2 support.

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