One-Step Synthesis of AuCu/TiO₂ Catalysts for CO Preferential Oxidation

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Au/TiO₂ (1wt% Au), Cu/TiO₂ (1wt% Cu) and AuCu/TiO₂ (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 H₂-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 TiO₂ phase; no peaks of metallic Au and Cu species or oxides phases were observed. TPR and high-resolution TEM analysis showed that AuCu/TiO₂ 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 TiO₂ surface. The AuCu/TiO₂ 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 CO₂ selectivity of 47% was obtained for Au₅₅Cu₄₅/TiO₂ catalyst at 100°C.

Keywords: AuCu/TiO₂ 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. 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.

Au nanoparticles supported on TiO₂ (Au/TiO₂ catalyst) showed good CO conversions and CO₂ selectivity for CO-PROX reaction in the range of 20 to 100°C; however, the procedure used to prepare Au/TiO₂ 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-TiO₂ interactions. Sangeetha et al. prepared Au nanoparticles supported on CuO-TiO₂ (x from 1 and 10 wt%), where the support was prepared by impregnation of Cu(NO₃)₂ in TiO₂ (Degussa P25) and treating at 350°C. The deposition of Au nanoparticles was carried out by the deposition-precipitation method obtaining nanoparticle sizes of about 2.5 nm. The resulting Au/CuO-TiO₂ catalysts were more active than the Au/TiO₂ catalyst with CO conversions close to 100% and CO₂ selectivity values of 60 to 80% in the temperature range of 50 °C to 100 °C. Duh et al. also prepared a series of Au/CuO-TiO₂ 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 in Au/TiO₂ catalyst enhanced the activity significantly for CO oxidation at low temperature, which was attributed to the interactions among Au, CuO and TiO₂. Recently, Qi et al. prepared nanosized CuO and Cu₂O 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 Cu₂O materials. It was concluded that CuO not Cu₂O 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/TiO₂, Cu/TiO₂ and AuCu/ 
TiO₂ catalysts in one-step synthesis by co-reducing the 
Au³⁺ and Cu²⁺ ions with sodium borohydride in the presence 
of the TiO₂ support. The catalysts were characterized and 
tested for CO-PROX reaction.

2. Experimental

2.1 Synthesis of Au/TiO₂ catalyst (1.0 wt% Au)

A suspension containing 346.5 mg of TiO₂ (P25 Evonik) 
and 45 mL of deionized water was prepared. Then 6.12 x 
10⁻⁴ L of tetraethylammonium iodide (H₂AuCl₄) 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 NaBH₄ 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/TiO₂ catalyst (1.0 wt% Cu)

The procedure was similar to that described above, but 
using 5.50 x 10⁻⁴ L of Cu(NO₃)₂ solution (1 x 10⁻¹ mol L⁻¹).

2.3 Synthesis of AuCu/TiO₂ catalyst with different 
mass ratios

The procedure was similar to that described above but using 
H₂AuCl₄ solution (2.88 x 10⁻² mol L⁻¹) and Cu(NO₃)₂ solution 
(1 x 10⁻¹ mol L⁻¹) in the desired proportions and 5.14 x 10⁻⁴ L 
of NaBH₄ 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 
= 1.5418 Å) 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 H₂ consumption 
was measured using a thermal conductivity detector (TCD). 
Initially the catalyst was treated in a flow of N₂ (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 H₂/N₂ at a 
flow rate of 30 mL min⁻¹ and heated to 750°C at 10°C 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 O₂ and 98 mol% of 
H₂ (O₂/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 CO₂) detectors. To evaluate the 
performance of each catalyst, CO conversion and CO₂ 
selectivity were calculated according to the Equations 1 and 2:

\[
\text{CO conversion} = \frac{[\text{CO}]_{i} - [\text{CO}]_{f}}{[\text{CO}]_{i}} \times 100 
\]

\[
\text{CO₂ selectivity} = \frac{0.5 \times [\text{CO}]_{f} \times 100}{[\text{O₂}]_{i} - [\text{O₂}]_{f}} 
\]

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 TiO₂ support as the mother liquor 
was slightly colored after centrifugation.

The X-ray diffractograms of the TiO₂ support and Au/ 
TiO₂, Cu/TiO₂ and Au₀.₅Cu₀.₅/TiO₂ catalysts are shown in 
Figure 1.

For all catalysts it was observed the diffraction peaks of 
the support TiO₂, 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).

| Catalyst composition (wt%) | Au (wt%) EDS | Cu (wt%) EDS | d (nm) TEM |
|----------------------------|--------------|--------------|-----------|
| Auₓ/TiO₂                   | 0.99         | --           | 4.9 ± 1.2 |
| Cuₓ/TiO₂                   | --           | 0.35         | --        |
| Auₓ⁻⁴Cu₉⁺/TiO₂             | 0.10         | 0.45         | 3.5 ± 0.7 |
| Auₓ⁻³Cu₉⁺/TiO₂             | 0.31         | 0.29         | 3.6 ± 0.9 |
| Auₓ⁻²Cu₉⁺/TiO₂             | 0.73         | 0.25         | 2.9 ± 0.7 |
| Auₓ⁻¹Cu₉⁺/TiO₂             | 0.87         | 0.21         | 3.9 ± 1.0 |
| Auₓ⁻⁰₉Cu₉⁻¹/ TiO₂           | 0.96         | 0.06         | 4.6 ± 0.9 |
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(211) (110), (101), (211) and 20% of rutile phase with 2θ: 27.4°, 36.1° and 54.4° corresponding to the planes (110), (101), (211)\(^6\). 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: 43.24°; 50.35°; 73.96° for Cu (#PDF 4-784) and 38.17°; 44.37°; 64.55° for Au (#PDF 4-836)\(^7\) nor the presence of copper oxide phases such as CuO or Cu₂O\(^1\). 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 TiO₂ support make their identification difficult\(^1\)

The transmission electron micrographs of Cu/TiO₂, Au/TiO₂ and AuCu/TiO₂ catalysts are shown in Figure 2.

For Cu/TiO₂ 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\(_{0.50}\)/TiO₂ 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 TiO₂ 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 TiO₂ surface.

The temperature programmed reduction (TPR) profiles of TiO₂ support and Au/TiO₂, Cu/TiO₂ and Au\(_{0.50}\)/Cu\(_{0.50}\)/TiO₂ catalysts are shown in Figure 4.

The H₂-TPR profile of the TiO₂-P25 support showed no reduction peaks in the studied temperature range as already reported in the literature for temperatures from ambient to 800 °C\(^2\). The H₂-TPR profile of Cu/TiO₂ catalysts showed an intense peak at about 150 °C attributed to the reduction of CuO to Cu(0)\(^2\) 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\(^2\). It was also observed on H₂-TPR profile of Cu/TiO₂ catalyst a peak at about 575 °C. Ramirez and Gutiérrez-Alejandre\(^2\) observed a peak at about 570 °C in the TPR profile of pure anatase TiO₂ support. Kang et al.\(^2\) reported for CuO supported on pure anatase TiO₂ 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 TiO₂ phase only one peak at around 120 °C was observed. Zhang et al.\(^2\) described that no peaks were observed between 25 and 500 °C in the TPR profile of an anatase TiO₂ support; on the other hand, the TPR profile of the Pt/TiO₂ catalyst showed two peaks at 80 and 360 °C that were

![Figure 1. X-ray diffractograms of the TiO₂ 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)](image)

![Figure 2. Transmission electron micrographs and histograms of a) Cu/TiO₂, b) Au/TiO₂, c) Au\(_{0.50}\)/Cu\(_{0.50}\)/TiO₂ and d) Au\(_{0.75}\)/Cu\(_{0.25}\)/TiO₂ catalysts](image)
attributed to the reduction of PtOx to metallic Pt and to the reduction of the surface capping oxygen of TiO2, 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 TiO2 P-25 support that is favored by the interaction with Cu species. The H2-TPR profile of Au/TiO2 catalyst did not shown reduction peaks below 100 °C suggesting that Au was predominantly found in the metallic form. Taking into account that pre-treated (reduced) Au catalyst do not shown any peak of reduction. However, it was observed a very small and broad peak at about 225 °C that could be related to ionic Au-species interacting with TiO2 phases. For Au0.50Cu0.50/TiO2 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 TiO2 phases. In the region of temperature between 350 and 450 °C two small peaks are observed for Au0.50Cu0.50/TiO2 catalyst, which could be a result of the interaction of Au and Cu species with TiO2 support and a peak at about 575 °C resulting from reduction of TiO2 support. Thus, it could be inferred from these results that AuCu/TiO2 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 H2-TPR and microscopy it could be inferred that Au and CuOx species interact with each other and with TiO2 support.

The catalytic performances of the Cu/TiO2, Au/TiO2 and Au0.50Cu0.50/TiO2 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/TiO2 catalyst showed low CO conversions (below 20%) until 100 °C increasing to 75% at 150 °C. The CO2 selectivity showed a maximum value of 70% at around 120 °C. Au/TiO2 catalyst showed a maximum CO conversion of 55% at 75 °C; however, CO2 selectivity values were very low (around 20%) in all range of temperature. For all AuCu/TiO2 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 Au0.50Cu0.50/TiO2 catalyst (Figure 5a).
and, after that, these values began to decrease (92.0% for \(\text{Au}_{0.50}\text{Cu}_{0.50}/\text{TiO}_2\) catalyst) as the amount of Au was increased further. Conversely, \(\text{CO}_2\) selectivity values increased with the increase of Cu content and the values varied between 35% and 55% at 100 °C. The \(\text{CO}_2\) selectivity value for \(\text{Au}_{0.50}\text{Cu}_{0.50}/\text{TiO}_2\) catalyst was 47% (Figure 5b) reaching a maximum value of 55% for \(\text{Au}_{0.25}\text{Cu}_{0.75}/\text{TiO}_2\) catalyst and after that decreased to 50% for \(\text{Au}_{0.10}\text{Cu}_{0.90}/\text{TiO}_2\) catalyst. Thus, \(\text{AuCu}/\text{TiO}_2\) catalysts showed to be more active for CO-PROX reaction than \(\text{Au}/\text{TiO}_2\) and \(\text{Cu}/\text{TiO}_2\) catalysts in the temperature range of 20 °C to 100 °C, as already observed for CO-PROX reaction and for CO-oxidation at low temperature. 

Figure 6 shows the CO conversion as a function of Au content (wt%) and nanoparticle sizes for \(\text{AuCu}/\text{TiO}_2\) catalysts prepared with different contents of Au and Cu. It could be seen that there is a relationship between Au content and nanoparticle sizes where the maximum CO conversion was observed for the sample \(\text{Au}_{0.50}\text{Cu}_{0.50}/\text{TiO}_2\) 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 \(\text{Au}_{0.50}\text{Cu}_{0.50}/\text{TiO}_2\) catalyst is shown in Figure 7 showing CO conversions above 90% and \(\text{CO}_2\) 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. in long test time using as catalyst \(\text{AuCuO}_x/\text{TiO}_2\) (1wt% of Au and a \(\text{CuO}_x/\text{TiO}_2\) ratio of 4.8:95.2) at 80 °C for 49 h. A maximum CO conversion of 95% with a \(\text{CO}_2\) selectivity of about 65% was obtained using a gas composition of 1.33% \(\text{CO}\), 1.33% \(\text{O}_2\), 65.33% \(\text{H}_2\), and 32.01% \(\text{He}\) and a space velocity of 30000 mL g\(^{-1}\) h\(^{-1}\).

Sangeetha et al. also observed an increase of maximum CO conversion and \(\text{CO}_2\) selectivity for CO-PROX reaction comparing \(\text{Au}/\text{TiO}_2\) and \(\text{AuCuO}_x/\text{TiO}_2\) catalysts and attributed this increase due to the presence of Au(0) and \(\text{CuO}_x\) species, where \(\text{CuO}_x/\text{TiO}_2\) was proposed to be a supplier or storage of oxygen. Wang et al. 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 CuOx supported on Au nanoparticles) resulting in interfacial sites between them. FTIR studies of CO adsorption showed that CO adsorbed on Au(0) while CuOx species were responsible for providing active oxygen in the same way as reducible oxides do. Recently it was shown that CuO not CuOx 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. 

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 CuOx species are in good interaction with each other and with TiO\(_2\) support.

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