



AuCu/TiO₂ Catalysts prepared using electron beam irradiation for the preferential oxidation of carbon monoxide in hydrogen-rich mixtures

Alencar^a C. S. L., Paiva^a A. R. N., Silva^a L. G. A., Somessari^a E. S. R., Vaz^a J. M.,
Spinacé^a E. V.

^a*Instituto de Pesquisas Energéticas e Nucleares - IPEN/CNEN – SP
Av. Professor Lineu Prestes, 2242 – Cidade Universitária
05508-000 São Paulo, SP - Brazil*

cslalencar@usp.br

ABSTRACT

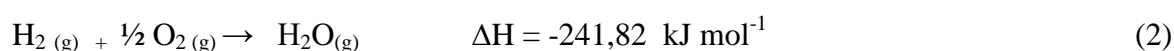
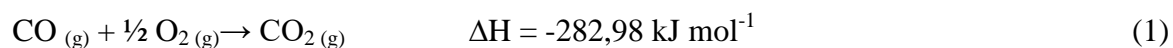
The major part of the world production of hydrogen (H₂) is originated from a combination of methane steam reforming and water-gas shift reaction resulting in an H₂-rich mixture known as reformat gas, which contains about 1% vol (10,000 ppm) of carbon monoxide (CO). The preferential oxidation reaction of CO in H₂-rich mixtures (CO-PROX) has been considered a very promising process for H₂ purification, reducing CO for values below 50 ppm allowing its use in PEMFC Fuel Cells. Au nanoparticles supported on TiO₂ (Au/TiO₂) catalysts have been shown good activity and selectivity for CO-PROX reaction in the temperature range between 20-80 °C; however, the catalytic activity strongly depends on the preparation method. Also, the addition of Cu to the Au/TiO₂ catalyst could increase the activity and selectivity for CO-PROX reaction. In this work, AuCu/TiO₂ catalysts with composition 0.5%Au0.5%Cu/TiO₂ were prepared in a single step using electron beam irradiation, where the Au³⁺ and Cu²⁺ ions were dissolved in water/2-propanol solution, the TiO₂ support was dispersed and the obtained mixture was irradiated under stirring at room temperature using different dose rates (8 – 64 kGy s⁻¹) and total doses (144 – 576 kGy). The catalysts were characterized by energy dispersive X-ray analysis, X-ray diffraction transmission electron microscopy, temperature-programmed reduction and tested for CO-PROX reaction. The best result was obtained with a catalyst prepared with a dose rate of 64 kGy s⁻¹ and a total dose of 576 kGy showed a CO conversion of 45% and a CO₂ selectivity of 30% at 150 °C.

Keywords: hydrogen, catalyst, CO-PROX.

1. INTRODUCTION

Hydrogen gas is mainly produced by methane steam reforming and water-gas-shift processes representing 48% of world production [1]. After these processes, it was obtained an H₂-rich mixture with about 1% vol of carbon monoxide (10,000 ppm) [2]. The most part of the hydrogen production (about 50%) is used in the ammonia synthesis and more recently there is a great interest for use hydrogen as combustible in proton exchange membrane fuel cell (PEMFC) [3,4]. However, the catalysts used in the ammonia synthesis reaction and in PEMFC devices are very sensitive to CO and H₂ must be purified to reduce the CO concentration at low ppm level (below 50 ppm) [5]. The main industrial processes currently used to remove CO from hydrogen-rich mixtures are pressure swing adsorption, which requires high investment in infrastructure and is a non-continuous process and CO methanation that causes significant losses of the hydrogen produced and energy [6].

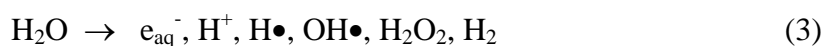
The preferential oxidation CO in hydrogen-rich mixtures (CO-PROX) has been considered very promising because it could reduce hydrogen and energy loss [6,7]. The CO-PROX reaction involves the oxidation of CO on a suitable catalyst using molecular oxygen forming CO₂ (Eq. 1) and avoiding the oxidation of H₂ to H₂O, which would compromise the efficiency of the process (Eq. 2).



Among the catalysts used for the CO-PROX reaction, the Au/TiO₂ (Au nanoparticles supported on TiO₂) catalysts have been shown good activity and selectivity for CO-PROX reaction at low temperatures (in the range of 20 °C to 100 °C). The performances of these catalysts are very dependent on the preparation methodology, which has been attributed to catalysts having Au nanoparticles smaller than 5 nm and strong metal-support interaction [8]. Studies have also shown that the addition of Cu to Au catalysts can improve the activity of these materials for CO conversion and especially for an increase of CO₂ selectivity [9-11]. Mozer et al [10] prepared bimetallic Au-Cu

catalysts supported on Al₂O₃ by the precipitation-deposition method and observed that the addition of Cu improved the CO₂ selectivity. Sangeetha et al [11] prepared Au nanoparticles supported on TiO₂ and CuO_x-TiO₂ by the deposition-precipitation method. The Au/CuO_x-TiO₂ catalysts were more active than the Au/TiO₂ catalyst showing CO conversions close to 100% and CO₂ selectivity between 60% and 80% in the temperature range of 50 °C to 100 °C. Kugai et al [12] prepared Pt and PtCu bimetallic catalyst supported on CeO₂ using electron beam irradiation for CO-PROX reaction and observed that Pt-Cu showed activity in low temperatures compared to monometallic Pt catalyst while keeping high CO₂ selectivity.

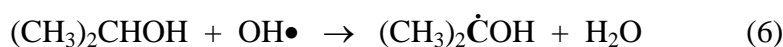
In this work, AuCu/TiO₂ catalysts were prepared in a single step by simultaneous reduction of Au(III) and Cu(II) ions in the presence of the TiO₂ support using the water/2-propanol solution as reaction medium. The resulting mixtures were submitted to the electron beam, which causes the ionization and excitation of water forming the species showed in Equation 3 [13].

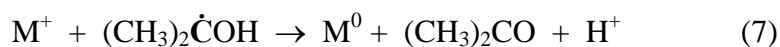


The solvated electrons, e_{aq}^- , and H[•] atoms are strong reducing agents and reduce metal ions down to the zero-valent state (Equations 4 and 5).



Similarly, multivalent ions, like Au (III) and Cu(II), are reduced by multistep reactions. On the other hand, OH[•] radicals could oxidize the ions or the atoms into a higher oxidation state and thus to counterbalance the reduction reactions (4) and (5). Thus, an OH[•] radical scavenger is added to the solution, in this case, 2-propanol, which reacts with these radicals leading to the formation of radicals exhibiting reducing power that is able to reduce metal ions (Equations 6 and 7) [13].





In this manner, the atoms produced by the reduction of metals ions progressively coalesce leading to the formation of metal nanoparticles.

The dose rate and total dose were varied and the obtained AuCu/TiO₂ catalysts were tested for CO-PROX reaction.

2. MATERIALS AND METHODS

2.1 Preparation of catalysts

Au/TiO₂ catalysts (0.5% mass of Au and Cu) were prepared by electron beam irradiation using different dose rates (kGy s⁻¹) and total doses (kGy) as described in Table 1. The irradiation source is an electron beam accelerator JOB 188 (Dynamitron®) energy 1.5 MeV beam current 25 mA, scan 60 to 120 cm, beam power 37.5 kW, located at the Centro de Tecnologia das Radiações (CTR-IPEN/CNEN).

Table 1: Values of dose rate and total dose used to prepare AuCu/TiO₂ catalysts.

Catalyst	Dose rate (kGy s ⁻¹)	Total dose (kGy)
a	8	144
b	8	288
c	8	576
d	16	576
e	32	576
f	64	576

Initially, 346.5 mg of TiO₂ (P25 Degussa 99.7% of purity) was added in a beaker containing 50 mL of isopropyl alcohol (99.7% purity)/water solution (50/50, v/v). After this, 3.08 x 10⁻⁴ L of HAuCl₄ solution (99.9% of purity) (2.88 x 10⁻² mol L⁻¹) and 2.75 x 10⁻⁴ L Cu(NO₃)₂ (99,1% of

purity) solution ($1 \times 10^{-1} \text{ mol L}^{-1}$) were added. The beaker was taken to the electron beam and the mixture was stirred for the entire irradiation period. After irradiation, the obtained materials were separated by centrifugation in Hettich® Universal 320/320R centrifuge, washed with water and dried in an oven Orion® 515 Fanem, at 75 °C for 2 hours.

2.2 Characterization

The chemical composition of the catalysts was determined by X-ray dispersive energy (EDX) using a JEOL analytical scanning microscope, model JSM-6010LA with a 20 kV electron beam equipped with a multi-channel analyzer (spectrum analyzer) localized in Centro de células a combustível e hidrogênio (CCCH). The X-ray diffraction (XRD) analysis was performed on a Multiflex Rigaku diffractometer, Cu K α radiation source ($\lambda = 1.5418 \text{ \AA}$) with a 2θ scan at 20° to 90°, with 0.06° step and 4 seconds count, localized in Centro de ciência de tecnologia de materias (CCTM). The particle size distribution of the samples was obtained by transmission electron microscopy (TEM) using a JEOL transmission electron microscope model JEM-2100 (200 kV), localized in CCTM. The analysis of temperature programmed reduction (TPR) was performed on ChemBET Pulsar TPR/TPD equipment localized in CCCH, with the addition of 50 mg of catalyst in a quartz reactor, and the feed gas composition was 10% vol H₂/N₂ with 30 mL min⁻¹ of flow rate, the gas was heated to 750 °C with a ramp of 10 °C min⁻¹. H₂ consumption was measured by a thermal conductivity detector (TCD).

2.3 Catalytic Activity

The catalytic activity was tested in a fixed reactor in the temperature range of 20 °C to 150 °C. The inlet gas was fed at the flow rate of 25 mL min⁻¹ with the following composition (vol%): 1% CO, 1% O₂ and 98% H₂. The mass of the catalyst in the catalytic bed was 100 mg (space velocity = 15,000 mL g_{cat}⁻¹ h⁻¹). The products were analyzed by gas chromatography.

The products obtained were analyzed by gas chromatography (GC) and quantified using calibration curves. The CO conversion and CO₂ selectivity were calculated as follows (Equations 8 and 9):

$$\text{CO conversion} = 100 \times ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}) / [\text{CO}]_{\text{in}} \quad (8)$$

$$\text{CO}_2 \text{ selectivity} = 100 \times (0.5 * [\text{CO}_2]_{\text{out}}) / ([\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}) \quad (9)$$

3. RESULTS AND DISCUSSION

3.1. Energy dispersive X-ray (EDX)

The EDX analyses of AuCu/TiO₂ catalysts are shown in Table 2. It could be seen for catalysts prepared with a dose rate of 8 kGy s⁻¹ that the amount of Au deposited on the TiO₂ support increased with the increase of total dose; however, not all Au has been deposited on the support. On the other hand, Cu deposition is practically not observed for these dose and total dose rates. Increasing the dose rate from 16 to 64 kGy s⁻¹ and keeping the total dose constant in 576 kGy it was observed that all Au deposited on the support and the deposition of Cu on the support was observed. Even so, only half of the amount Cu was deposited.

Table 2: Elemental chemical analysis and average particle size of AuCu/TiO₂ catalysts.

Dose rate (kGy s ⁻¹)	Total Dose (kGy)	Experimental (wt%)			
		Au	Cu	TiO ₂	Size (nm)
8	144	0.31	n.d*	99.69	11.9 ± 3.3
8	288	0.32	n.d*	99.68	8.4 ± 5.1
8	576	0.41	0.002	99.59	7.3 ± 2.3
16	576	0.59	0.15	99.26	8.2 ± 3.4
32	576	0.56	0.2	99.24	7.4 ± 3.0

64	576	0.66	0.25	99.09	8.8 ± 2.1
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**n.d. – not detected*

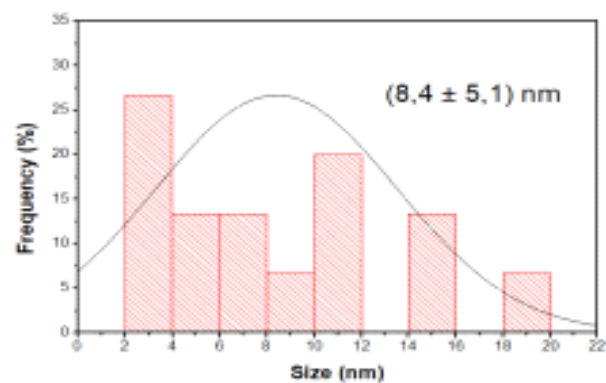
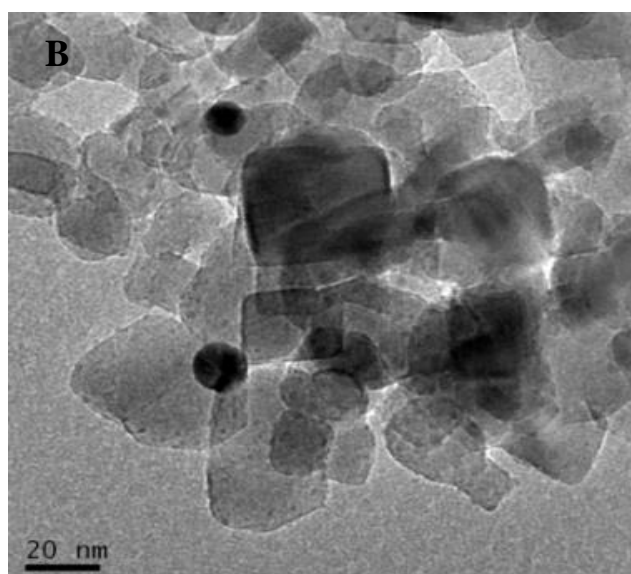
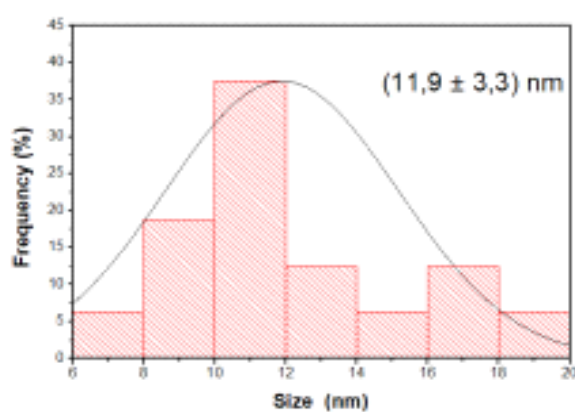
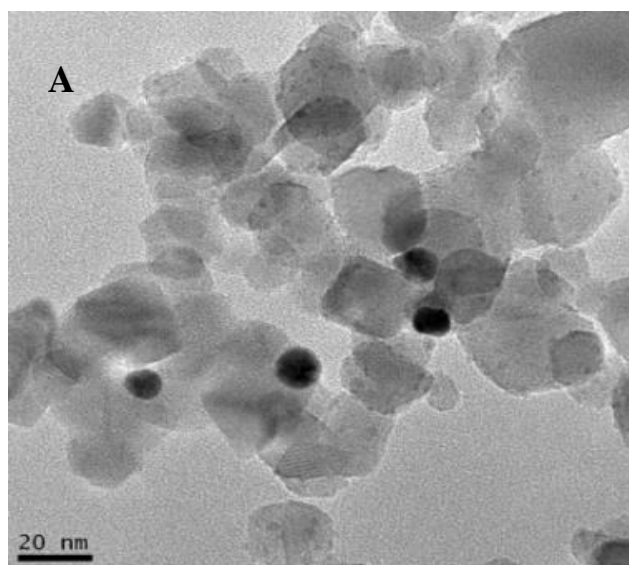
3.2. Transmission electron microscopy (TEM)

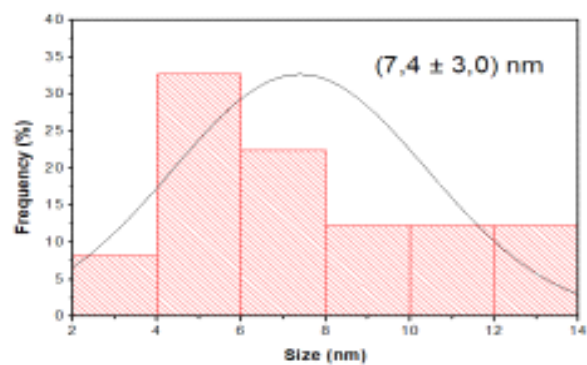
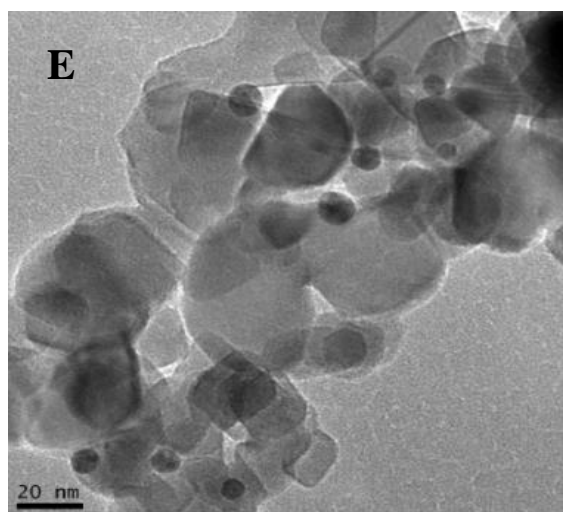
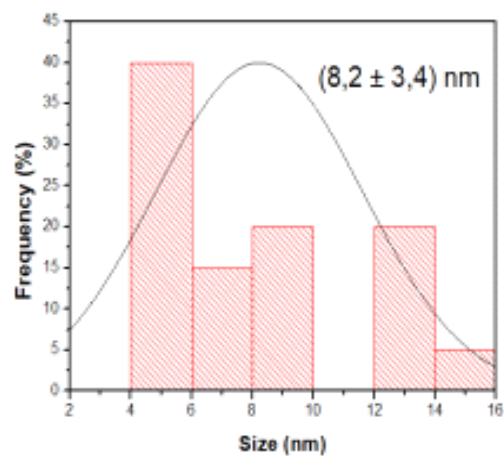
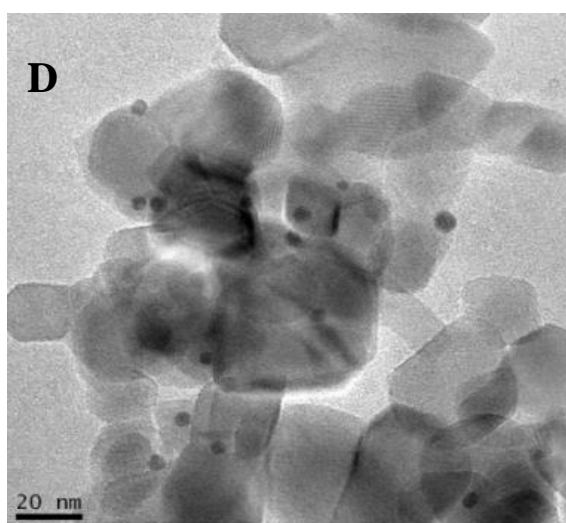
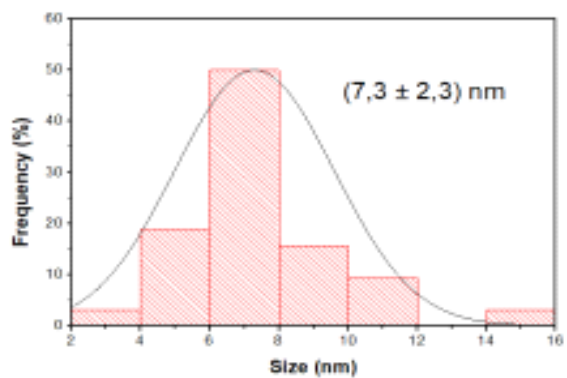
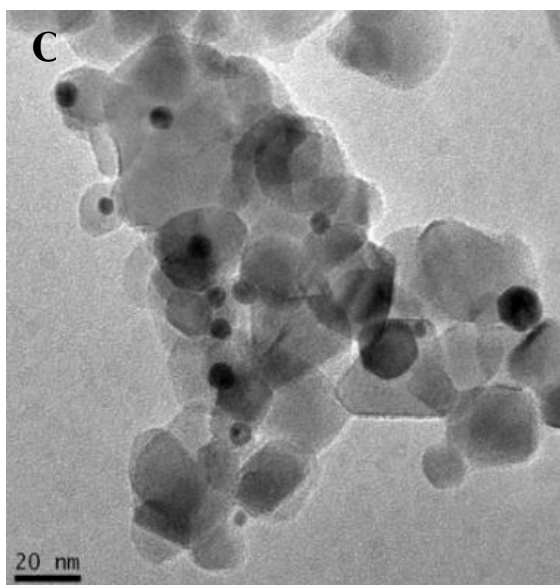
The transmission electron micrographs and the histograms of AuCu/TiO₂ catalysts are shown in Figures 1a-1h. It was observed for catalysts with a dose rate of 8 kGy s⁻¹ and different total doses a decrease of the mean nanoparticle sizes from 12 to 7 nm with the increase of total dose from 144 to 576 kGy. Keeping the total dose constant (576 kGy) and increasing the dose rate from 8 to 64 kGy s⁻¹ there is practically no change in mean nanoparticle sizes.

3.3. X-ray diffraction (XRD)

The X-ray diffractograms of the AuCu/TiO₂ catalysts (Figure 2) showed only the well-defined and high intensity crystalline peaks related to the tetragonal structure of TiO₂ P25 (Degussa), which has 75% anatase phase with peaks at 2θ: 25.36°, 37.89°, 48.14°, 54.03°, 55.18° corresponding to planes (101) (211), (200), (105), (211) (110), (101), (211) and 25% rutile with peaks at 2θ: 27.4°, 36.1° and 54.4° corresponding to the planes (110), (101), (211). The Cu and Au metals have a cubic face-centered (CFC) structure and the diffraction planes are (111), (200) and (220) corresponding respectively to 2θ at 38.17°; 44.37°; 64.55° for Au (#PDF 4-836) and 2θ at 43.24°; 50.35° and 73.96° for Cu (#PDF 4-784). In the diffractograms, it was not observed the peaks of Au and Cu CFC structure due to the low quantities and/or its small nanoparticle sizes (< 10 nm) resulting in broad and low-intensity peaks that are difficult to identify in the presence of well defined crystalline peaks and high-intensity TiO₂ support [14].

Figure 1: Micrographs obtained by TEM and histograms of the mean particle size distribution of the catalysts AuCu/TiO₂ with respective dose rates (kGy s⁻¹) and total dose (kGy): (a) 8 e 144 (b) 8 e 288 (c) 8 e 576 (d) 16 e 576 (e) 32 e 576 (f) 64 e 576.





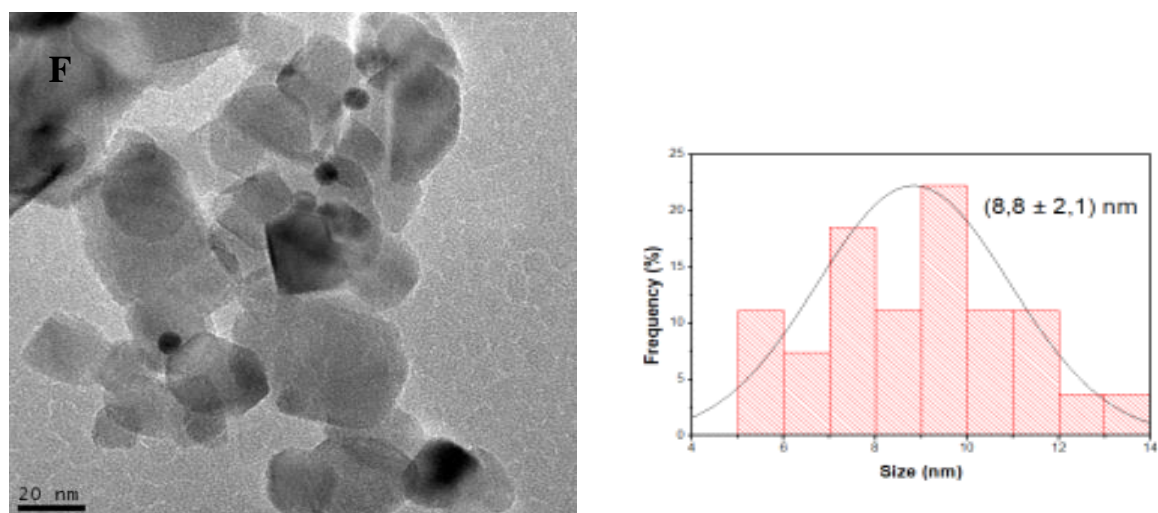
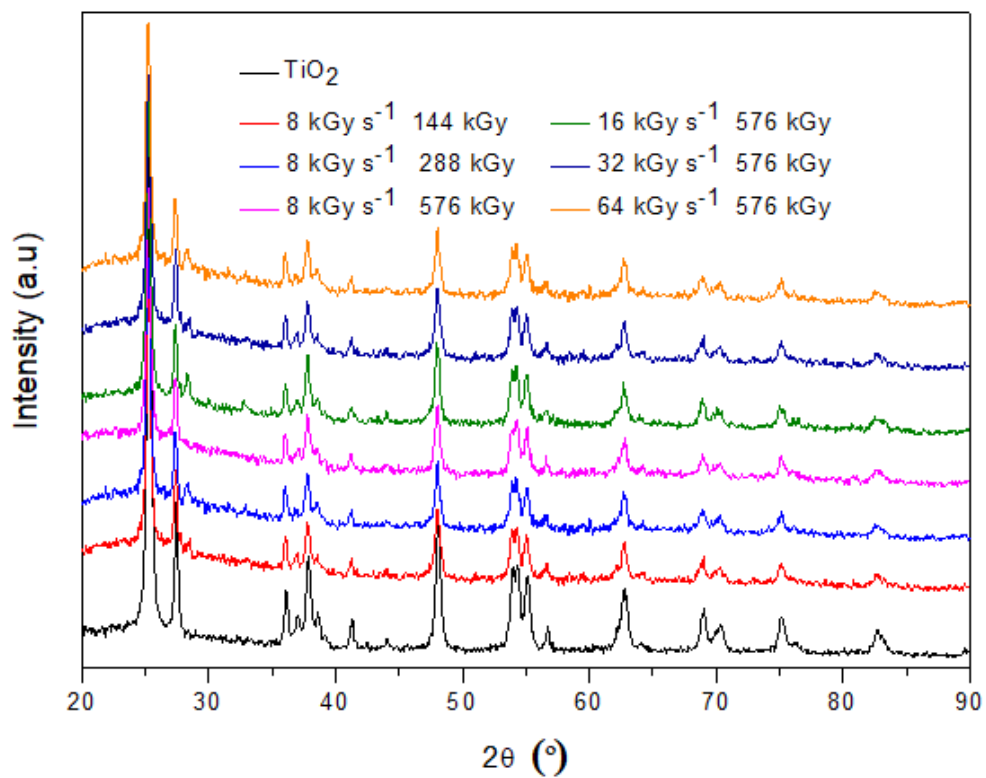


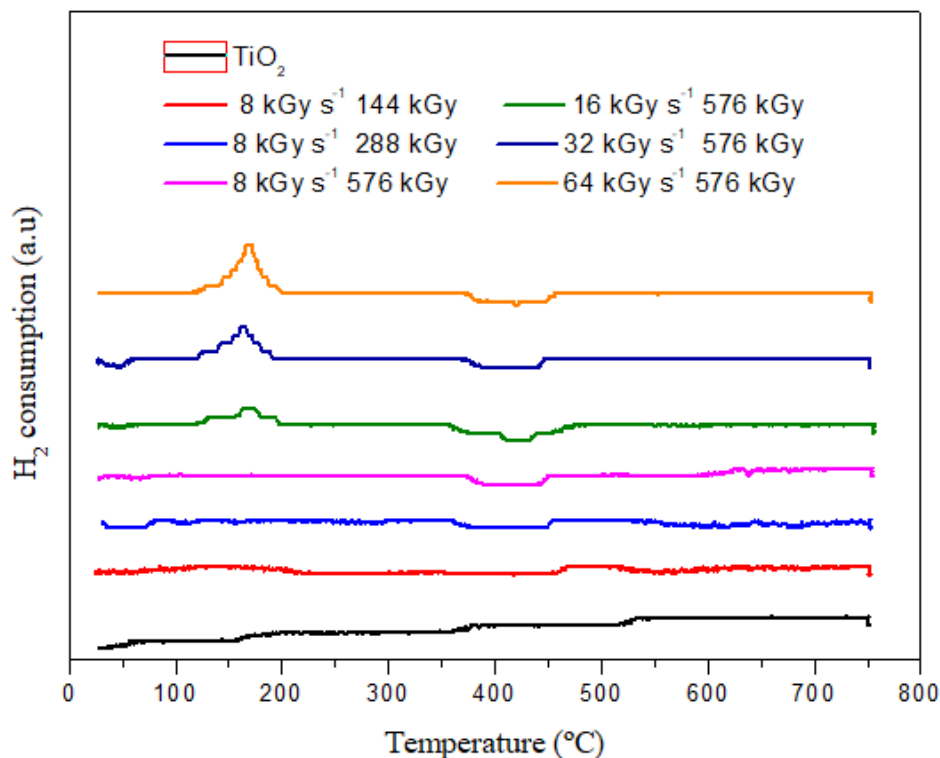
Figure 2: X-ray diffractograms for the TiO_2 support and AuCu/TiO_2 catalysts prepared with different dose rates and total doses.



3.4. Temperature-programmed reduction (TPR)

The results of temperature programmed reduction of AuCu/TiO₂ catalysts are shown in Figure 3. The TiO₂ support (P25 Degussa) practically does not exhibit reduction peaks from ambient temperature to 800 °C, as already described in the literature [15]. For the materials prepared with a dose rate of 8 kGy s⁻¹ and increasing the total dose from 144 to 576 kGy it was observed a profile very similar to that of the TiO₂ support, where no reduction peaks were observed. The EDX analysis of these materials showed only the presence of Au suggesting that Au was present as Au metallic (Au⁰) in these samples while Cu must not be undergoing reduction and deposition on the TiO₂ support. In the experiments where the total dose was kept constant and the dose rates were increased from 8 to 64 kGy s⁻¹, the presence of a peak around 170 °C was observed for all samples and their intensities increased with the increase of the dose rate.

For these samples, EDX analysis (Table 2) showed that the amount of Cu increased with the increase of the dose rate. According to the literature, these peaks correspond to CuO reduction in Cu⁰ [16,17]; in this manner, it could be inferred that in these samples Au deposited as Au⁰ while Cu could be deposited as CuO or deposited as Cu⁰ and undergoes subsequent oxidation to CuO when exposed to air. Also, the use of higher total doses may lead to the reduction/deposition of all Cu ions on TiO₂ support.

Figure 3: Programmed temperature reduction for TiO_2 support and AuCu/TiO_2 catalysts.

3.5. Catalytic tests

The results of CO conversion and CO_2 selectivity of the AuCu/TiO_2 catalysts are shown in Figure 4 and 5. It was observed for all catalysts low CO conversions ($< 10\%$) until $80\text{ }^\circ\text{C}$. Above this temperature, a clear distinction of performance between them was observed. For catalysts prepared using 8 kGy s^{-1} of dose rate, an increase of CO conversion was observed with the increase of the radiation absorbed dose. For catalysts with total dose of 576 kGy an increase of CO conversion was observed with the increase of dose rate. These results showed that both the dose rate and total dose affects the performance of the catalysts and should be investigated in more details. The best CO conversions of about 45% were observed for the catalysts prepared with dose rates of 32 and 64 kGy s^{-1} and total dose of 576 kGy . Regarding to CO_2 selectivity, at temperatures lower than $100\text{ }^\circ\text{C}$ such a trend is not observed; however, above $100\text{ }^\circ\text{C}$ the CO_2 selectivity values showed

a profile similar to that observed for CO conversion, where catalysts prepared with dose rates of 32 and 64 kGy s⁻¹ and dose of 576 kGy showed the best values (40-50%) in the temperature range of 100-150 °C.

Figure 4: CO Conversion of AuCu/TiO₂ catalysts in the function of the temperature.

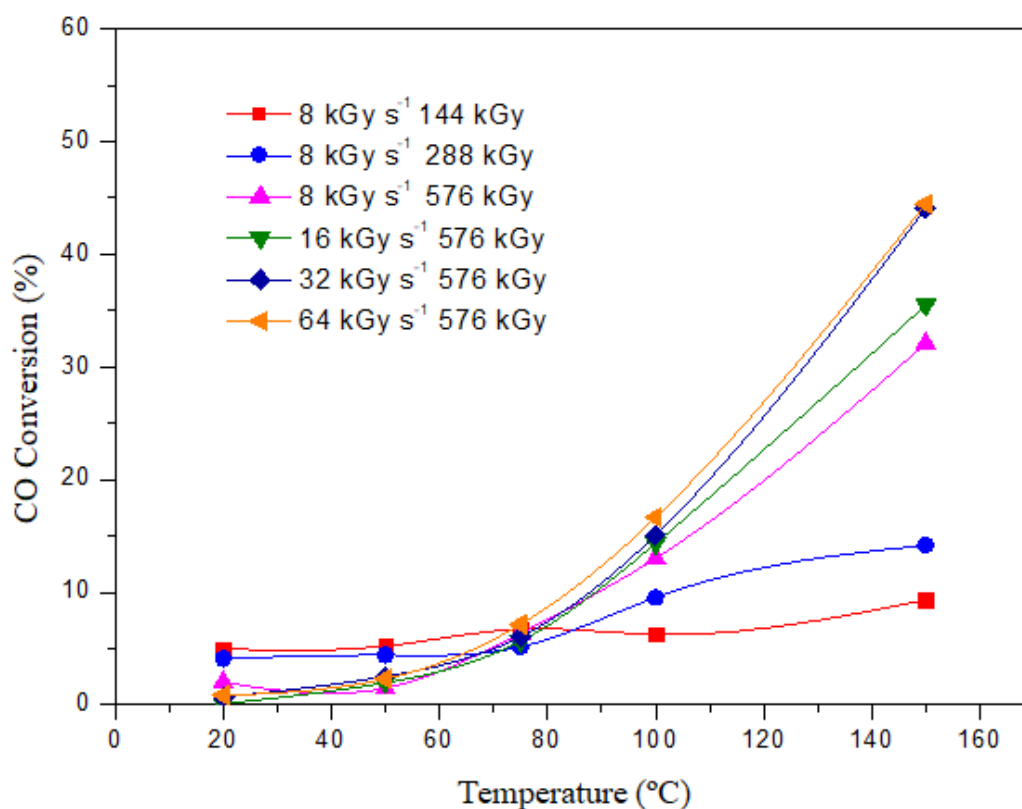
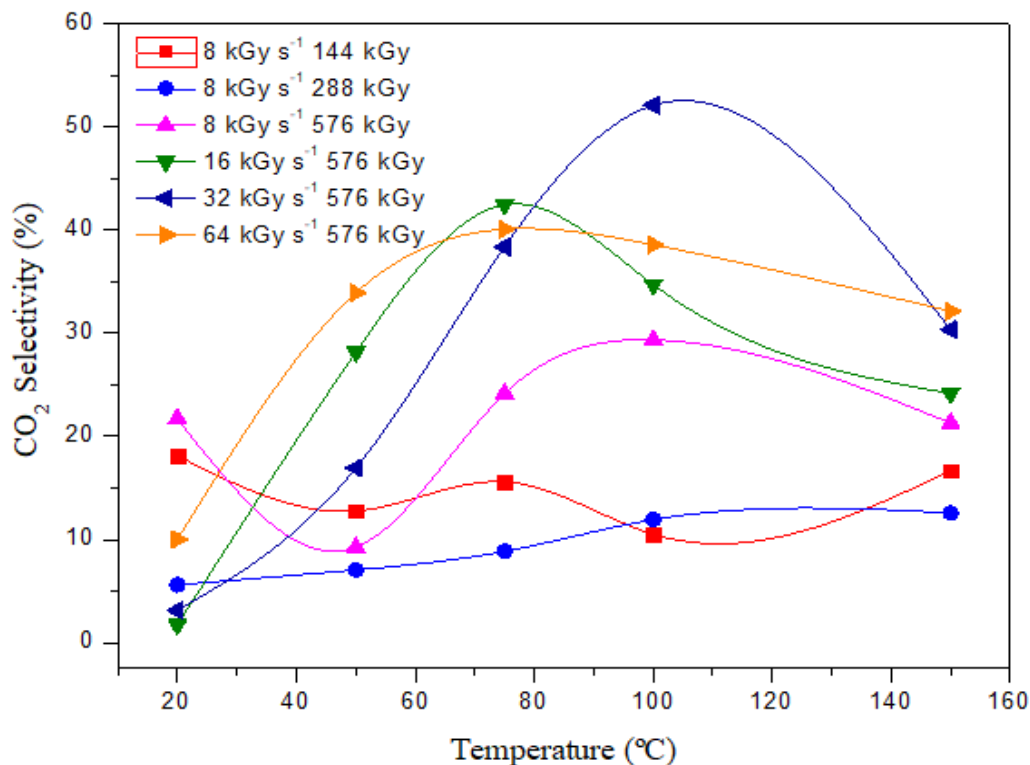


Figure 5: CO_2 Selectivity of AuCu/TiO₂ catalysts in the function of the temperature.

4. CONCLUSION

AuCu/TiO₂ catalysts could be prepared in a single step using electron beam irradiation. The dose rate (kGy s⁻¹) and radiation absorbed dose showed a strong influence on the amounts of Au and Cu that are deposited on TiO₂ support and on nanoparticles sizes, which consequently affect the catalytic activity of the resulting materials. Further studies have been performed to improve the catalytic activity.

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FAPESP/Shell Proc. No 2017/11937-4 (CINE), FAPESP Proc. 2014/09087-4 and 2018/04802-8 and to CNPq Proc. No. 304869/2016-3 for financial support. Centro de Ciência e Tecnologia dos Materiais (CCTM) – IPEN-CNEN/SP (JEOL JEM-2100F) for the use of TEM facilities and are greatly acknowledged and Centro de Tecnologia das Radiações (CTR) - IPEN-CNEN/SP for electron beam irradiation.

REFERENCES

- [1] VERAS, T.S.; MOZER, T.S.; SANTOS, D.C.R.M.; CÉSAR, A.S. “Hydrogen: Trends, production, and characterization of the main process worldwide”. **Int. J. Hydrog. Energy**, 42, 2018–2033, 2017.
- [2] NIKOLAIDIS, P.; POULLIKKAS, A. “A comparative overview of hydrogen production processes”. **Renewable and Sustainable Energy Reviews**, 67, 597-611, 2017.
- [3] CHAUBEY, R.; SAHU, S.; JAMES, O.O.; MAITY, S. “A review on the development of industrial processes and emerging techniques for the production of hydrogen from renewable and sustainable sources”. **Renewable and Sustainable Energy Reviews**, 23, 443–462, 2013.
- [4] WENDT, H.; GÖTZ, M.; LINARDI, M. “Tecnologia de células a combustível”. **Quim Nova**, 23, 538-546, 2000.
- [5] SHABANI, B.; HAFTANANIAN, M.; KHAMANI, S.; RAMIAR, A.; RANJAR, A.A. “Poisoning of proton exchange membrane fuel cells by contaminants and impurities: Review of mechanisms, effects and mitigation strategies”. **Journal of Power Sources**, 427, 21-48, 2019.
- [6] MISHRA, A.; PRASAD, R. “A Review on Preferential Oxidation of Carbon Monoxide in Hydrogen-Rich Gases”. **Bulletin of Chemical Reaction Engineering & Catalysis**, 6, 1–14, 2011.
- [7] SAAVEDRA, J.; WHITTAKER, T.; CHEN, Z.; PURSELL, C.J.; RIOUX, R.M.; CHANDLER, B.D. “Controlling activity and selectivity using water in the Au-catalysed preferential oxidation of CO in H₂”. **Nature Chemistry**, 8, 584-589, 2016.
- [8] HARUTA, M.; DATÉ, M. “Advances in the catalysis of Au nanoparticles”. **Applied Catalysis A: General**, 222, 427–437, 2001.

- [9] WANG, A.; LIU, X.Y.; MOU, C-Y.; ZHANG, T. “Understanding the synergistic effects of gold bimetallic catalysts”. **Journal of Catalysis**, 308, 258–271, 2013.
- [10] MOZER, T.S.; DZIUBA, D.A.; VIEIRA, C.T.P.; PASSOS, F.B. “The effect of copper on the selective carbon monoxide oxidation over alumina-supported gold catalysts”. **Journal of Power Sources**, 187, 209–215, 2009.
- [11] SANGEETHA, P.; ZHAO, B.; CHEN, Y. “Au/CuO_x-TiO₂ catalysts for preferential oxidation of CO in hydrogen stream”. **Ind. Eng. Chem**, 49, 2096-2102, 2010.
- [12] KUGAI, J.; MORIYA, T.; SEINO, S.; NAKAGAWA, T.; OHKUBO, Y.; NITANI, H.; MIZUKOSHI, Y.; YAMAMOTO, T.A. “Effect of support for Pt Cu bimetallic catalysts synthesized by electron beam irradiation method on preferential CO oxidation”. **Applied Catalysis B: Environmental**, 126, 306– 314, 2012.
- [13] BELLONI, J.; MOSTAFAVI, M.; REMITA, H.; MARIGNIER, J-L.; DELCOURT, M-O. “Radiation-induced synthesis of mono and multi-metallic clusters and nanocolloids”. **New J. Chem**, 22, 1239-1255, 1998.
- [14] YANG, Y-F.; SANGEETHA, P.; CHEN, Y-W. “Au/TiO₂ catalysts prepared by the photo-deposition method for selective CO oxidation in H₂ stream”. **International Journal of Hydrogen Energy**, 34, 8912–8920, 2009.
- [15] LI, J.; LU, G.; WU, G.; MAO, D.; GUO, Y.; WANG, Y.; GUO, Y. “Effect of TiO₂ crystal structure on the catalytic performance of Co₃O₄/TiO₂ catalyst for low-temperature CO oxidation”. **Catal. Sci. Technol**, 4, 1268–1275, 2014.
- [16] LI, K.; WANG, Y.; WANG, S.; ZHU, B.; ZHANG, S.; HUANG, W.; WU, S. “A comparative study of CuO/TiO₂-SnO₂, CuO/TiO₂ and CuO/SnO₂ catalysts for low-temperature CO oxidation”. **Journal of Natural Gas Chemistry**, 18, 449–452, 2009.
- [17] XIAOYUAN, J.; GUANGLIE, L.; RENXIAN, Z.; JIANXIN, M.; YUA, C.; XIAOMING, Z. “Studies of pore structure, temperature-programmed reduction performance, and microstructure of CuO/CeO₂ catalysts”. **Appl. Surf. Sci**, 173, 208-220, 2001.