



# Preparation of Au/TiO<sub>2</sub> Catalyst by a Liquid-Phase Reduction Method for Preferential Oxidation of Carbon Monoxide in a Hydrogen Rich-Stream (CO-PROX reaction)

Julian M. de Souza Pereira<sup>a</sup>, Ligia Ciotti<sup>a</sup>, Jorge Moreira Vaz<sup>a</sup>, Estevam Vitorio Spinacé<sup>a\*</sup>

<sup>a</sup>Instituto de Pesquisas Energéticas e Nucleares IPEN-CNEN/SP, Centro de Células a Combustível e Hidrogênio - CCCH, Av. Professor Lineu Prestes 2242, 05508-000, São Paulo, SP, Brazil

Received: August 23, 2017; Revised: October 31, 2017; Accepted: November 19, 2017

Au nanoparticles supported on TiO<sub>2</sub> were prepared by a liquid-phase reduction method using HAuCl<sub>4</sub>.3H<sub>2</sub>O as the Au precursor, TiO<sub>2</sub> as the support, a solution of ethylene glycol/water as solvent and reducing agent and sodium citrate as reducing agent and stabilizer. The Au/TiO<sub>2</sub> catalysts were prepared using different routes and characterized by Energy-dispersive X-ray spectroscopy, X-ray diffraction and Transmission Electron Microscopy and tested for preferential oxidation of carbon monoxide in hydrogen-rich stream (CO-PROX reaction). The way that the Au precursor, the TiO<sub>2</sub> support and the sodium citrate is added to the ethylene glycol/water solution strongly influences the Au nanoparticle sizes and the catalytic activity of the obtained materials.

**Keywords:** Au nanoparticles, TiO<sub>2</sub>, hydrogen, carbon monoxide, CO-PROX reaction.

## 1. Introduction

The chemical industry produces millions of tons of hydrogen in the world through the steam reforming process of hydrocarbons (methane, coal) and the water-gas shift reaction resulting in a hydrogen-rich gas mixture (reformate gas) containing 15-20% of CO<sub>2</sub>, 10% of H<sub>2</sub>O and about 1% vol (10.000 ppm) of carbon monoxide (CO). Currently most of this hydrogen produced in the world is used in the manufacture of ammonia for use in fertilizers<sup>1</sup> and lately, there is also a great interest in the use of hydrogen in low temperature fuel cells<sup>2</sup>. On the other hand, the catalysts used in the ammonia production process and in the low temperature fuel cells are very sensitive to CO contamination and, therefore, the hydrogen from these processes must be purified (below 10 ppm CO). The main methods currently used to remove CO from the hydrogen-rich gas mixture are pressure swing adsorption which requires high investment in infrastructure and the CO methanation process which causes significant losses of the hydrogen produced by non-selective methanation of CO<sub>2</sub> present in the reformate gas<sup>1</sup>. The preferential oxidation of CO with oxygen in hydrogen-rich gas mixtures (CO-PROX reaction) has been considered a very promising process, as it can drastically reduce energy and hydrogen losses. However, the main challenge in this process is the developments of catalysts that achieves a high CO conversions and CO<sub>2</sub> selectivities and not convert H<sub>2</sub> to H<sub>2</sub>O<sup>1,3</sup>.

The preparation of Au nanoparticles supported in TiO<sub>2</sub> (Au/TiO<sub>2</sub> catalysts) have been described by different methods<sup>4</sup> and it is well known that the particle size of Au nanoparticles enormously affects the catalytic activity of supported Au

catalysts in many reactions<sup>5</sup>. Studies have been shown that Au/TiO<sub>2</sub> catalysts is one of the most active and selective catalysts for CO-PROX reaction at low temperatures (< 100°C) and that the activity of these catalysts is quite dependent on the method of preparation, which influences the Au particle size and structure<sup>6-10</sup>.

We studied the preparation of Pt nanoparticles supported on carbon (Pt/C electrocatalysts for fuel cells) by a liquid-phase reduction method, called alcohol-reduction process, using ethylene glycol as reducing agent<sup>11,12</sup>. In this methodology, the Pt precursor (H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O) is dissolved in an ethylene glycol/water solution and the carbon support is added. The resulting mixture is heated and refluxed and the obtained solid (Pt/C) is filtered and washed with water. The procedure is really quite simple and allows to obtain Pt/C electrocatalysts with high Pt content (20 wt%) and small Pt particle sizes in the range of 2 - 5 nm homogeneously dispersed on the carbon support<sup>11,12</sup>. Grass et al<sup>13</sup> showed in the preparation of Rh nanoparticles using ethylene glycol as solvent and reducing agent that the addition of sodium citrate as stabilizer led to smaller nanoparticle sizes.

In this study, we prepared Au/TiO<sub>2</sub> catalysts by a liquid-phase reduction method using HAuCl<sub>4</sub>.3H<sub>2</sub>O as the Au precursor, TiO<sub>2</sub> as the support, a solution of ethylene glycol/water as solvent and reducing agent and sodium citrate as reducing agent and stabilizer.

## 2. Experimental

### 2.1 Preparation of Au/TiO<sub>2</sub> catalysts

The Au/TiO<sub>2</sub> catalysts (1wt% of Au) were prepared using different conditions:

\* e-mail: [espinace@ipen.br](mailto:espinace@ipen.br)

- **Route A** - A solution of tetrachloroauric(III) acid ( $\text{H}_2\text{AuCl}_4 \cdot 3\text{H}_2\text{O}$ ) was dissolved in ethylene glycol/water solution (3/1, v/v). The titanium oxide ( $\text{TiO}_2$  P25 - Degussa) was added and the resulting mixture was immersed in a heated oil bath and was refluxed for 2h (at about  $160^\circ\text{C}$ ). After this period, the solid was filtered, washed with water and dried at  $80^\circ\text{C}$  for 2 h.

- **Route B** -  $\text{TiO}_2$  support was dispersed in the ethylene glycol/water solution and the resulting mixture was immersed in a heated oil bath and after reached  $160^\circ\text{C}$ , a solution of tetrachloroauric(III) acid in 5 mL of water was quickly added.

- **Route C** - similar route B, except that a solution of tetrachloroauric(III) acid and sodium citrate (Au:citrate molar ratio of 1:10) in 5 mL of water was quickly added.

- **Route D** - A solution of tetrachloroauric(III) acid and sodium citrate (Au:citrate molar ratio of 1:10) was added to ethylene glycol/water solution under reflux (at about  $160^\circ\text{C}$ ), where a red color solution forms immediately and after that  $\text{TiO}_2$  support was added under the resulting mixture remains under reflux for 2 h.

## 2.2 Characterization of Au/TiO<sub>2</sub> catalysts

The chemical composition of the catalysts was determined in a Philips Scanning Microscope, model XL30 with electron beam of 20 keV equipped with EDAX microanalyzer model DX-4. Data were collected at random points of the sample and the final result corresponds to an average of these points.

The X-ray diffractograms were obtained in a Rigaku diffractometer, model Miniflex II, with a Cu K $\alpha$  radiation source ( $\lambda = 1.54 \text{ \AA}$ ), with scanning at  $2\theta$  from  $20^\circ$  to  $90^\circ$  with 0.05 step and 2 s count.

The micrographs were obtained in an Electronic Transmission Electron Microscope (MET) brand JEOL model JEM-2100 (200 kV). For the analysis, a suspension of each catalyst in 2-propanol was prepared, where it was homogenized in an ultrasound system. Subsequently, an aliquot of the sample was deposited on a copper grid (0.3 cm in diameter) with a carbon film. On average, 8 micrographs were taken for each sample, so that the data collection allowed the construction of histograms that represented the size distribution of the nanoparticles.

## 2.3 Catalytic tests

The catalysts prepared were evaluated in a fixed bed reactor in the temperature range of 25 to  $225^\circ\text{C}$ . A gas mixture containing 1% v CO and 99% v  $\text{H}_2$  was mixed with the oxygen gas (3% v) to achieve volumetric  $\text{O}_2/\text{CO}$  ratio of 3. A total flow of this gas mixture of  $50\text{mL min}^{-1}$  was used and the mass of the catalyst in the catalytic bed was 100mg (space velocity =  $30.000 \text{ mL} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ ). No catalyst pretreatment process was applied before all the catalytic tests. The products obtained were analyzed by gas

chromatography (GC) and quantified using calibration curves. The CO conversion,  $\text{O}_2$  consumed and  $\text{CO}_2$  selectivity were calculated as follows:

$$\text{CO conversion} = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100$$

$$\text{O}_2 \text{ consumed} = \frac{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}}{[\text{O}_2]_{\text{in}}} \times 100$$

$$\text{CO}_2 \text{ selectivity} = \frac{0.5 * [\text{CO}_2]_{\text{out}}}{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}} \times 100$$

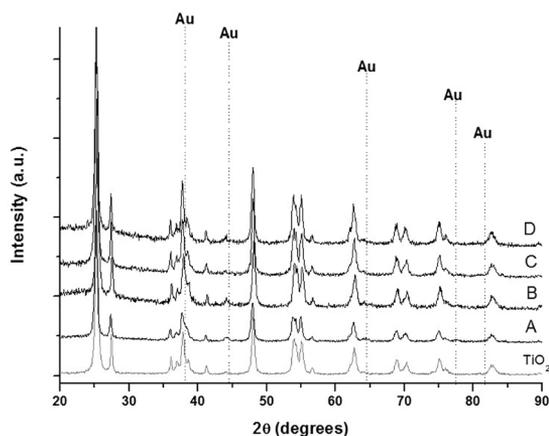
## 3. Results and Discussion

The EDX analysis of Au/TiO<sub>2</sub> catalysts obtained by routes A-D (Table 1) showed for all samples that the contents of Au and TiO<sub>2</sub> (wt%) are very similar to the nominal values indicating that the Au precursor was reduced and deposited on TiO<sub>2</sub> support.

**Table 1.** EDX analysis of Au/TiO<sub>2</sub> catalysts (1wt% Au and 99wt% TiO<sub>2</sub>).

Route	Au (wt%)	TiO <sub>2</sub> (wt%)
A	1.0	99.0
B	1.2	98.8
C	1.1	98.9
D	1.1	98.9

X-ray diffractograms of TiO<sub>2</sub> support and Au/TiO<sub>2</sub> (A-D) catalysts are shown in Figure 1.



**Figure 1.** X-ray diffractograms of the TiO<sub>2</sub> support and Au/TiO<sub>2</sub> catalysts.

The diffractogram of TiO<sub>2</sub> support (P25 Degussa) present a bicrystalline structure comprising of 75% of anatase (peaks at  $2\theta = 25.3^\circ, 37.7^\circ, 47.9^\circ, 53.8^\circ$  and  $62.5^\circ$ ) and 25% of rutile (peaks at  $2\theta = 27.4^\circ, 36.1^\circ$  and  $54.4^\circ$ ) phases and it has a surface area of  $52 \text{ m}^2 \text{ g}^{-1}$  and 21 nm of particle size<sup>14,15</sup>. The peaks of face-centered cubic (fcc) phase of Au nanoparticles

are observed at  $2\theta = 38.2^\circ, 44.5^\circ, 64.5^\circ, 77.5^\circ$  and  $81.7^\circ$ <sup>10</sup>; however, no distinct Au(fcc) peaks were observed on the diffractogram of Au/TiO<sub>2</sub> catalysts because the crystallite sizes were too small to be detected and/or due to the small amount of Au (1 wt%) present in the samples. This could reflect in a broad and/or low-intensity of Au peaks that in the presence of well-defined and high intensity crystalline peaks of anatase and rutile phases difficult the identification.

The transmission electron micrographs and histograms of the Au/TiO<sub>2</sub> (A-D) catalysts are shown in Figure 2.

The micrograph of Au/TiO<sub>2</sub> prepared by route A (Fig. 2 a) showed that it contains Au nanoparticles as large as 200 nm. Pt and Pt-based nanoparticles supported on carbon prepared by an alcohol-reduction process<sup>11,12</sup> resulted in samples containing Pt nanoparticles in the range of 2-5 nm highly dispersed on the carbon support, even if for 20wt% of Pt loading. Therefore, the preparation of Au/TiO<sub>2</sub> catalyst by this process by means of route A showed not be adequate to obtain Au nanoparticles with sizes in the range of 2-10

nm even with 1wt% of Au loading. It has been shown that the particle sizes of Au strongly affect the catalytic activity of supported Au catalysts for CO oxidation and CO-PROX reaction and the catalysts have high activities when the Au nanoparticles sizes were in the range of 2-10 nm<sup>6,10,16</sup>. Thus, modifications were done in the methodology to reduce the Au nanoparticle sizes. By route B, the TiO<sub>2</sub> support was dispersed in ethylene glycol/water solution and the resulting mixture was heated at about 160 °C under reflux. After reached the temperature, a water solution containing the Au precursor was quickly added. The micrograph (Fig. 2b) showed that Au nanoparticles decreased from about 200 nm to 22 nm. In this case, the addition of the Au precursor at higher reaction temperature (route B) influenced on the reduction rates of Au precursor probably increasing the reduction kinetics and nuclei formation and decreasing the Au nanoparticle sizes; however, the obtained Au nanoparticles sizes were not in the expected range. It was shown that the preparation of Rh nanoparticles using ethylene glycol as a reducing agent led

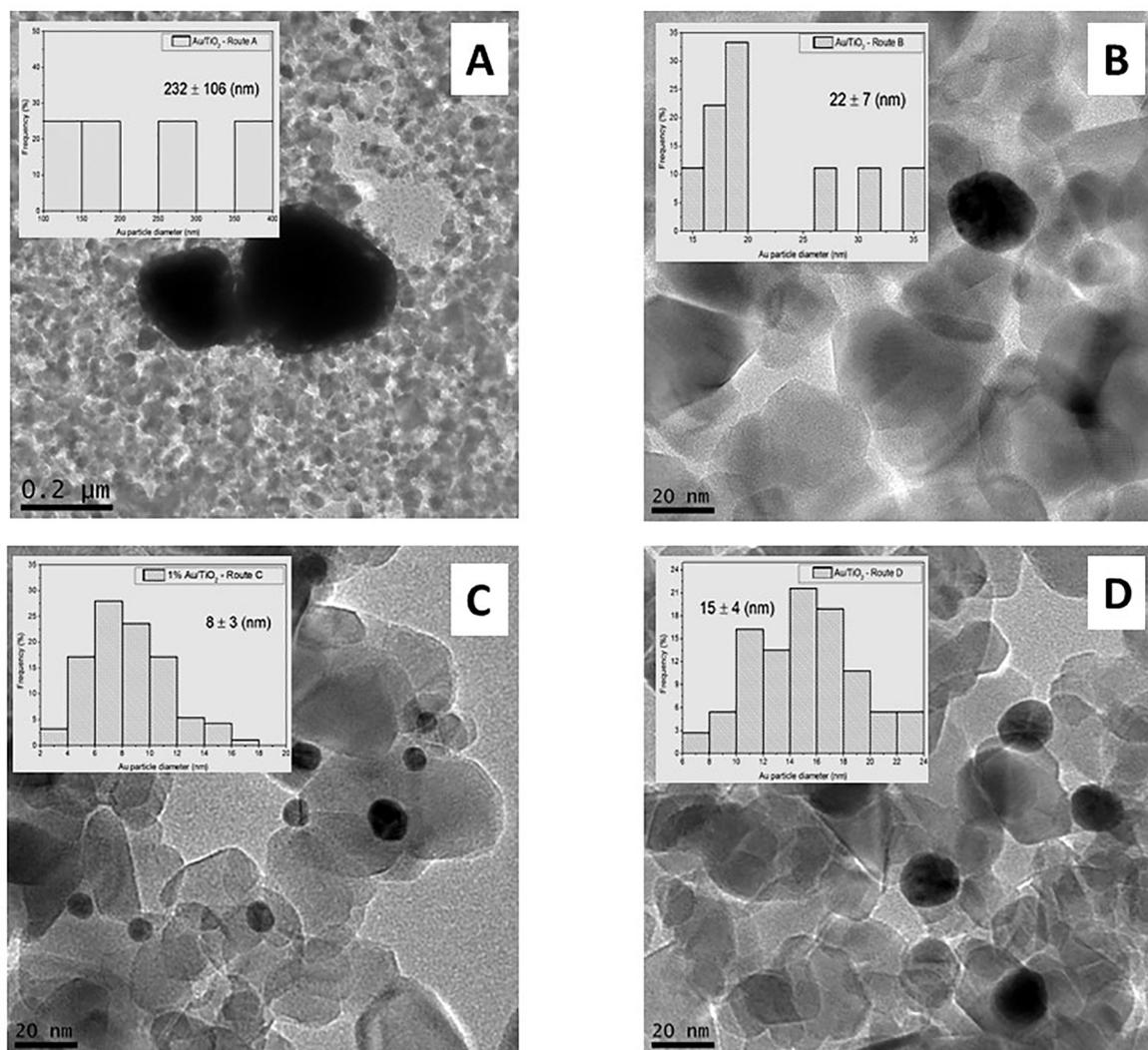


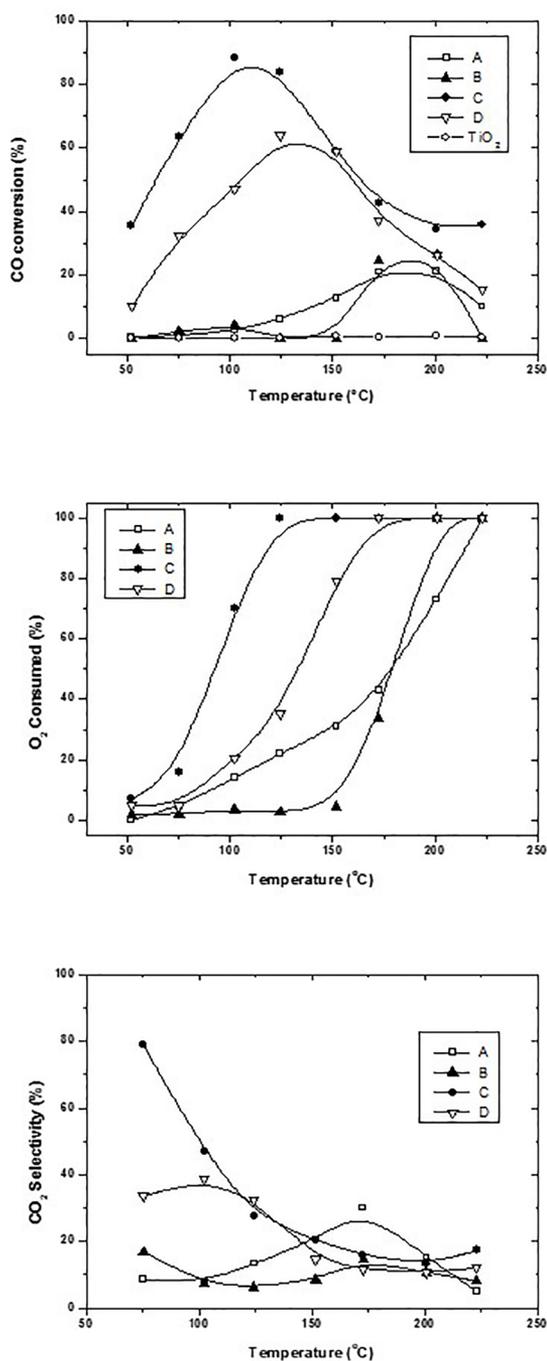
Figure 2. Transmission electron micrographs and histograms of Au/TiO<sub>2</sub> catalysts.

to smaller nanoparticle sizes with the addition of sodium citrate as stabilizer<sup>13</sup>. Sodium citrate has also been described as stabilizing and reducing agent in the preparation of Au nanoparticles<sup>17</sup>. By route C, a solution containing the Au precursor and sodium citrate was quickly added to TiO<sub>2</sub> support dispersed in ethylene glycol/water solution under reflux. The micrograph of the resulting Au/TiO<sub>2</sub> catalyst (Fig. 2c) showed a significant decrease of the Au nanoparticles sizes to  $8 \pm 3$  nm and a more uniform distribution on the support. A new route D was also performed where the Au precursor/sodium citrate solution was added to ethylene glycol/water solution under reflux (at about 160°C). In this case, the addition of Au/citrate solution to the reaction medium immediately resulted in a clear red color solution suggesting that Au nanoparticles were formed and stabilized. After this, the TiO<sub>2</sub> support was added to this solution. The micrograph of this sample (Fig. 2d) showed Au nanoparticles sizes in the range of  $15 \pm 4$  nm. Comparing the catalysts obtained by route C and D, the addition of the Au/citrate solution seems to be more adequate in the presence of the TiO<sub>2</sub> support (route C) to obtain Au nanoparticles with smaller sizes.

The CO conversion, O<sub>2</sub> consumed and CO<sub>2</sub> selectivity of the catalytic tests of TiO<sub>2</sub> support and Au/TiO<sub>2</sub> catalysts (A-D) in CO-PROX reaction are shown in Figure 3.

The TiO<sub>2</sub> support did not present catalytic activity in the whole studied temperature range. Au/TiO<sub>2</sub> (A) catalyst showed a low CO conversion of 22% only at 200°C with a low CO<sub>2</sub> selectivity of around 20%. The O<sub>2</sub> consumed increased with the increase of temperature being all consumed at 200°C. Similar results were also observed for Au/TiO<sub>2</sub> (B) catalyst. Thus, Au/TiO<sub>2</sub> (A) and (B) catalysts presented low activities and selectivities for CO-PROX reaction when compared to the results described in the literature<sup>6-10,14,18</sup>, which may be related to the size of the Au nanoparticles present in these catalyst (> 20 nm). Au/TiO<sub>2</sub> (D) catalyst showed a CO conversion of 64% and a CO<sub>2</sub> selectivity of 32% at 125°C, which could be due the particle sizes of about 15 nm. As expected, Au/TiO<sub>2</sub> (C) catalyst showed a significant improvement of the catalytic activity comparing samples obtained by routes A, B and D reaching a CO conversion of 88% and CO<sub>2</sub> selectivity of 47% at 100°C. This improvement of CO conversion and CO<sub>2</sub> selectivity could be related to a decrease of Au nanoparticles sizes (8 nm) observed for this catalyst. Similar results are described in the literature for Au/ZrO<sub>2</sub> catalyst obtained by oxidation of AuZr alloy. This material had Au nanoparticles size of 7 nm and 92% of CO conversion and 55% of CO<sub>2</sub> selectivity at 100°C<sup>19,20</sup>. A review of Au catalyst for CO-PROX reaction<sup>20</sup> described for Au/ZrO<sub>2</sub> and Au/TiO<sub>2</sub> catalyst with Au nanoparticles sizes of 5 nm a CO conversion of 100% at temperatures in the range of 40-60°C.

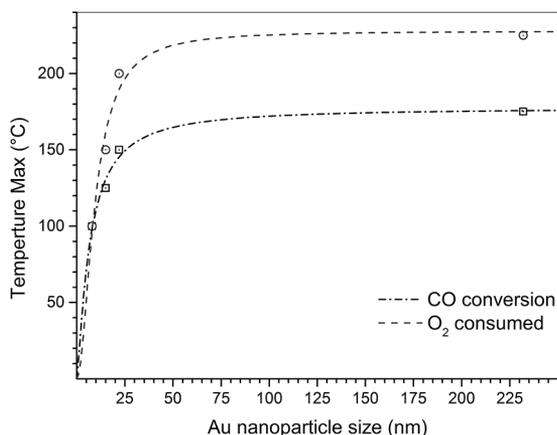
The maximum values of CO conversion and O<sub>2</sub> consumed were plotted as a function of the temperature that they were



**Figure 3.** CO conversion, O<sub>2</sub> consumed and CO<sub>2</sub> selectivity in function of temperature of Au/TiO<sub>2</sub> catalysts.

obtained and of the Au nanoparticles sizes for Au/TiO<sub>2</sub> catalysts (Fig. 4).

It was known that the Au nanoparticles sizes strongly affect the catalytic activity of supported Au catalysts in many reactions including CO oxidation<sup>5,21</sup> and CO-PROX reactions<sup>20,22</sup> so that the smaller particles produce higher activities. As seen in Fig 4, it could be observed that the maximum CO conversion and O<sub>2</sub> consumed occurred at lower



**Figure 4.** Maximum values of CO conversion and O<sub>2</sub> consumed in function of temperature and Au nanoparticles sizes for Au/TiO<sub>2</sub> catalyst.

temperatures for Au/TiO<sub>2</sub> catalysts having Au nanoparticles with smaller sizes. Studies have shown that Au-based catalysts with particle sizes in the range of 2-4 nm can exhibit high CO conversions at temperatures in the range of 20-50 °C<sup>20</sup>.

## 4. Conclusions

The way that the Au precursor, the TiO<sub>2</sub> support and the sodium citrate is added to the ethylene glycol/water strongly influences the Au nanoparticles sizes of the obtained Au/TiO<sub>2</sub> catalysts. The values of CO conversion, CO<sub>2</sub> selectivity and O<sub>2</sub> consumed were also greatly influenced by the size of Au nanoparticles, so that the values increase as the sizes decrease. Also, the increase of these values occurs at lower temperatures with decreasing particle size. The influence of some synthesis parameters, such as the use of different Au precursors, the Au:citrate molar ratio, the pH of the reaction medium and the use of higher boiling alcohols (glycerol, diethylene glycol) as solvent could be investigated in order to further reduce the size of Au nanoparticles.

## 5. Acknowledgments

CNPq (Proc. n° 443046/2014-0 and 304869/2016-3), FAPESP (Proc. n° 2014/09087-4) and FAPESP-Shell (Proc. n° 2014/50279-4) are grateful for the financial support. Centro de Ciência e Tecnologia dos Materiais (CCTM) - IPEN-CNEN/SP is acknowledged for TEM measurements.

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