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Au/TiO_2 catalysts prepared by borohydride reduction for preferential CO oxidation at near-ambient temperature

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Abstract: Au nanoparticles were prepared in solution using $HAuCl_4.3H_2O$ as Au precursor, sodium citrate as stabilizing agent and sodium borohydride as reducing agent. The influence of synthesis parameters such as BH_4:Au and Citrate:Au ratios were studied. In a further step, the stabilized Au nanoparticles were supported on TiO_2 with different Au loadings (wt%). The resulting Au/TiO_2 catalysts were characterized by Energy-dispersive X-ray spectroscopy, X-ray diffraction and Transmission Electron Microscopy and tested for the preferential oxidation of carbon monoxide in hydrogen-rich stream. Au nanoparticles stabilized in solution were obtained with sizes in the range of 3-4 nm. After supported on TiO_2, the Au nanoparticles size did not change and the Au/TiO_2 catalysts exhibited excellent performance and stability in the temperature range of 20 - 50 °C.

Keywords: Au nanoparticles, TiO_2, hydrogen, carbon monoxide, preferential oxidation.

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1 Introduction

Preferential oxidation of carbon monoxide in hydrogen-rich stream (CO-PROX reaction) has attracted attention because it could reduce the hydrogen and energy loss when compared to the main methods actually employed like pressure swing adsorption, which requires large capital investments and low flow rates. Moreover, CO methanation causes significant losses of the produced hydrogen. However, the main challenge is to achieve high CO conversion and CO_2 selectivity in the presence of hydrogen [1, 2].

Au nanoparticles supported on TiO_2 (Au/TiO_2 catalyst) have been considered as one of the most active catalyst at temperatures lower than 100 °C for CO-PROX reaction and studies have shown that the procedure used to prepare Au/TiO_2 catalysts has a significant influence on the catalytic performance as a result of Au nanoparticles size that should be smaller than 5 nm and Au-TiO_2 interactions [1, 3]. A typical goal for CO-PROX reaction, which arises from the requirements for Proton Exchange Membrane Fuel Cell (PEMFC) is to reduce the CO concentration of about 50 ppm with a CO_2 selectivity of at least 50% [2]. Also, the CO conversion at near-ambient temperature could be particularly important for PEMFC applications in transportation [4]. Au/TiO_2 catalysts have been prepared by different methodologies but only few catalysts showed maximum CO conversions in the temperature range of 20-50°C [5]. Recently, we used a simple and easy strategy to prepare Au/TiO_2 catalysts where Au nanoparticles were first prepared in solution using citrate as stabilizing agent and sodium borohydride as reducing agent and in a further step the pre-formed Au nanoparticles with sizes in the range of 3-4 nm were supported on TiO_2. The resulting Au/TiO_2 catalysts (1 wt% Au) showed good catalytic performance for CO-PROX reaction and a CO conversion reached 99.5% and CO_2 selectivity was maintained at

around 45% at 45ºC even using a volumetric O_2/CO ratio of 2 (l = 4) and 97 vol. % of hydrogen in the gas stream [5].

In this study, we investigated synthesis parameters of Au nanoparticles preparation such as BH_4^-:Au and Citrate:Au molar ratios and the Au loading (wt%) of Au/TiO_2 catalysts on the performance for CO-PROX reaction.

2 Experimental

2.1 Preparation of stabilized Au nanoparticles solution

Stabilized Au nanoparticles were prepared in solution using $HAuCl_4.3H_2O$ as Au precursor, sodium citrate as stabilizing agent and sodium borohydride as reducing agent. An aqueous solution of the Au precursor (3,95 x 10^{-4} mol L^{-1}) was used and different BH_4^-:Au molar ratios and Citrate:Au molar ratios were investigated. The UV-Vis spectra of Au nanoparticles solutions were obtained using a Varian UV-Vis spectrometer model Cary 50 from 350 to 700 nm and Au nanoparticles sizes were determined by the procedure described by Haiss et al [6].

2.2 Preparation of Au/TiO_2 catalysts

An appropriate amount of TiO_2 support (Degussa P25) was added to the stabilized Au nanoparticles solutions and the resulting mixtures were kept under stirring for 24 h. After this period, the solid materials (Au/TiO_2) were separated by centrifugation, washed with water and dried at 80 ºC for 2 h.

2.3 Characterization of Au/TiO_2 catalysts

The chemical composition of Au/TiO_2 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 4 random points of the sample and the final result corresponds to an average of these points.

The X-ray diffractograms of Au/TiO_2 catalysts were obtained in a Rigaku diffractometer, model Miniflex II, with a Cu Kα radiation source (λ = 1.54 Å), with scanning at 2θ from 20 ° to 90 ° with 0.05 step and 2 s count.

The micrographs of Au/TiO_2 catalysts were obtained in an Electronic Transmission Electron Microscope (TEM) brand JEOL model JEM-2100 and (TEM-FEG) JEM-2100F (200 kV). A suspension of Au/TiO_2 catalyst in 2-propanol was homogenized in an ultrasound system and an aliquot was deposited on a copper grid with a carbon film. The histograms were constructed by measuring the diameter of the Au nanoparticles from micrographs.

2.4 Catalytic Tests

The as-prepared Au/TiO_2 catalyst was evaluated in a fixed bed reactor in the temperature range of 25 to 120°C. The inlet gas was fed at a flow rate of 25 mL min^{-1} with the following composition (vol. %): 1% CO, 2% O_2 and 97% H_2. The mass of the catalyst in the catalytic bed was 100mg (space velocity = 15.000 mL . g_{cat}^{-1}. h^{-1}). No catalyst pretreatment process was applied before the catalytic test. The products obtained were analyzed by gas chromatography (GC) and quantified using calibration curves. The CO conversion, CO_2 selectivity and turnover frequency (TF) were calculated as follows:

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

$$CO_2 \text{ selectivity} = 100 \times (0.5 * [CO_2]_{out}) / ([O_2]_{in} - [O_2]_{out})$$

Turnover frequencies (TOF) are expressed as the number of moles of CO converted per mol of Au per second.

The Arrhenius activation energy (E_a) was calculated from the slope of the log of the rate (mmol of CO converted) plotted against 1/T using the data obtained in the first cycle of catalytic tests.

3 Results and Discussion

Initially in the preparation of the stabilized Au nanoparticles solutions a BH_4/Au molar ratio of 3 and 4 were chosen [7] and the citrate/Au molar ratio was varied from 0.3 to 10 as shown in Fig.1.

Using a BH_4/Au molar ratio of 3 and a citrate/Au molar ratio of 0.3 the Au nanoparticles were obtained with a big size of 37 nm; however a sharp decrease of the Au nanoparticles size to 4.4 nm was observed increasing the citrate/Au molar ratio only to 0.6. In the region of Citrate/Au molar ratio from 1.5 to 4.5 the average Au nanoparticles sizes practically does not vary (sizes between 3.3 and 3.5 nm) and after this, the Au nanoparticles sizes increase again reaching values of 3.9, 4.5 and 7.4 nm with the increase of citrate/Au molar ratio to 6, 8 and 10, respectively. Increasing a BH_4/Au molar ratio to 4 the Au nanoparticles sizes practically did not change (about 3.2

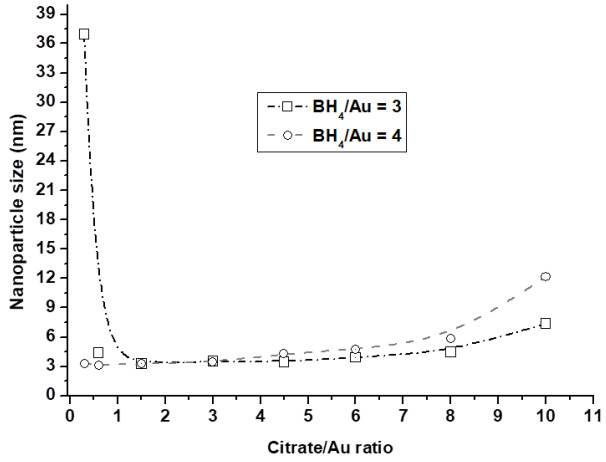

Figure 1: Au nanoparticle sizes in function of citrate/Au ratio (BH_4/Au molar ratios of 3 and 4)

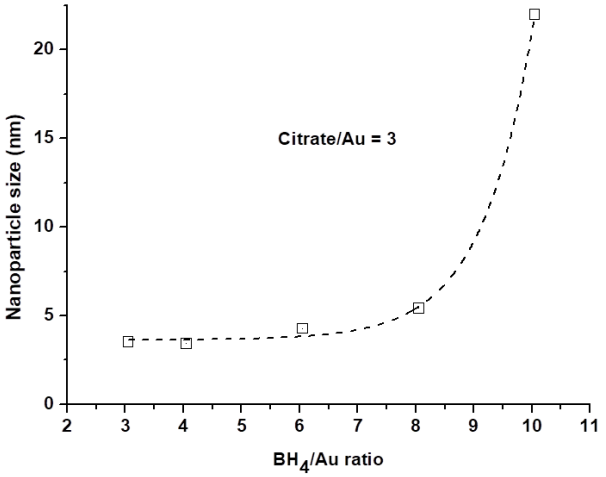

Figure 2: Au nanoparticle sizes in function of BH_4/Au molar ratios (citrate/Au molar ratio of 3)

nm) when citrate/Au molar ratio varied from 0.3 to 3. After this, the nanoparticles sizes increase to 4.3, 4.7, 5.8 and 12.2 nm with the increase of citrate/Au molar ratio to 4.5, 6, 8 and 10 nm, respectively. Thus, in the next step (Fig. 2) the citrate/Au molar ratio was fixed to 3 and the BH_4/Au molar ratio was varied from 3 to 10 [7]. By varying the BH_4/Au molar ratio from 3 to 6 the Au nanoparticles sizes remains in the range of 3 to 4 nm. Increasing the BH_4/Au molar ratio to 8 the Au nanoparticles sizes increased again (5.4 nm) reaching the size of 22 nm for the molar ratio of 10.

It could be seen that Au nanoparticles with smaller sizes were obtained using BH_4^-/Au molar ratios between 3 and 6 and citrate/Au molar ratios between 1.5 and 3; in this manner, Au/TiO_2 catalysts with different Au loadings (wt%) were prepared using stabilized Au nanoparticles solutions synthesized in these ranges of values (Table 1).

The EDX analysis of Au/TiO_2 catalysts with different Au loadings (wt%) showed that Au and TiO_2 loadings were very similar to the nominal values indicating that all Au nanoparticles present in the solutions were deposited on TiO_2 support independently of the Au loading. The transmission electron micrographs and histograms of the Au/TiO_2 catalysts (Fig. 3) showed a good distribution of Au nanoparticles on TiO_2 support with average nanoparticles sizes in the range of 3-4 nm for the different Au loadings. These values were very similar to the ones observed for stabilized Au nanoparticles solutions (Fig. 1 and 2) showing that after supporting Au nanoparticles on the surface of TiO_2 the nanoparticles sizes did not change. In this manner, this methodology has the advantage of allowing the preparation of Au/TiO_2 catalysts with different Au loadings and similar Au nanoparticle sizes.

The X-ray diffractograms of Au/TiO_2 with different Au loadings (Fig. 4) showed only the well-defined and high intensity crystalline peaks of anatase (2θ = 25.3°, 37.7°, 47.9°, 53.8° and 62.5°) and rutile (at 2θ = 27.4°, 36.1° and 54.4°) phases [8] present in the TiO_2 support (P25 Degussa). The peaks of face-centered cubic (fcc) phase of Au nanoparticles at 2θ = 38.2°, 44.5°, 64.5°, 77.5° and 81.7° [9] were not observed in all diffractograms due to its small sizes resulting in broad and low-intensity peaks that were too small to detect [8].

For the catalytic tests of Au/TiO_2 catalysts (first reaction cycle) no previous treatments were done in the catalysts before the reactions. In the first reaction cycle it was observed for all catalysts an increase of CO conversion with the increase of temperature until 120 °C; however CO conversions in the range of 20–50 °C were below 20% increasing to about 80% at 120 °C. On the other hand, CO_2 selectivity values decrease strongly above 50 °C while the O_2 consumption increase sharply above this temperature favoring the undesired reaction of hydrogen oxidation with formation of water [5]. After the end of this first reaction cycle the catalysts were cooled to room temperature and a new catalytic cycle was started (second reaction cycle). Interestingly, in the second reaction cycle (Table 2) the catalysts begin to show good CO conversions and CO_2 selectivity at near room temperature (in the range of 20–50°C). On the other hand, in the second reaction cycle, when the temperature was increased above 50 °C the hydrogen oxidation becomes predominant.

From Table 2 it could be seen that the best values of maximum CO conversions and CO_2 selectivity were observed for catalysts containing 0.5 and 1 wt% of Au loading at 45 °C, while for catalyst containing 2 wt%

Table 1: Au/TiO_2 catalysts prepared from stabilized Au nanoparticles synthesized from different BH_4/Au and Citrate/Au molar ratios

Sample	% Au (nominal)	BH_4^-/Au (molar ratio)	Citrate/Au (molar/ratio)	% Au (EDX)	Au particle size –TEM (nm)
Au0.5 - 4/1.5	0.5	4	1.5	0.61	--
Au0.5 – 4/3	0.5	4	3	0.51	--
Au0.5 – 6/3	0.5	6	3	0.48	3.6
Au1 - 4/1.5	1.0	4	1.5	1.04	3.5
Au1 – 4/3	1.0	4	3	1.04	--
Au1 – 6/3	1.0	6	3	1.02	4.2
Au2 - 4/1.5	2.0	4	1.5	2.08	--
Au2 – 4/3	2.0	4	3	--	--
Au2 – 6/3	2.0	6	3	1.93	3.8

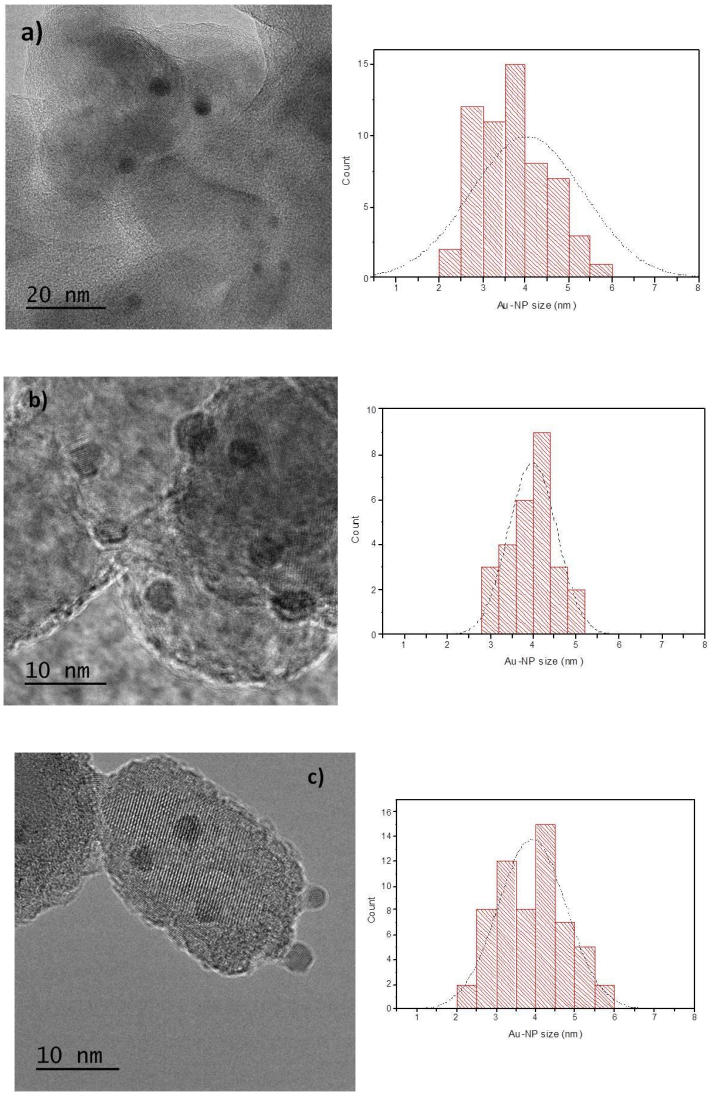

Figure 3: Transmission electron micrographs of **a)** Au0.5 – 6/3, **b)** Au1 – 6/3 and **c)** Au2 – 6/3

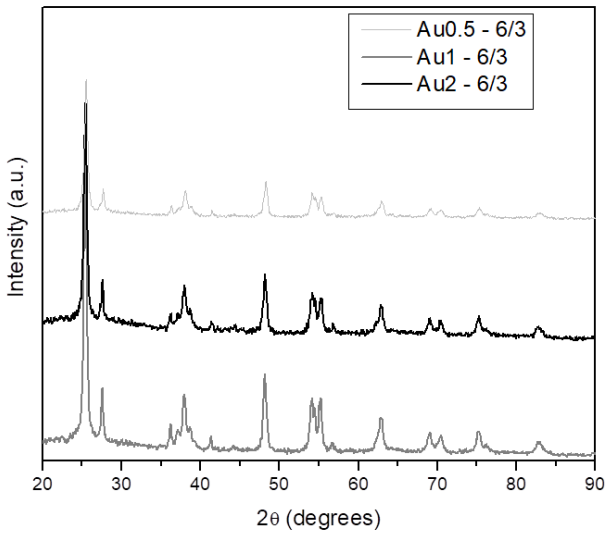

Figure 4: X-ray diffractograms of Au/TiO_2 catalysts with different Au loadings (BH_4/Au molar ratio of 6 and citrate/Au molar ratio of 3)

Table 2: Catalytic Tests (second reaction cycle) of Au/TiO_2 catalyts for CO-PROX reaction (100 mg catalyst, flow rate 25 mL min^{-1}, feed composition 1%CO, 2% O_2 and 97% H_2, space velocity 15,000 mL g_{cat}^{-1} h^{-1})

	20 °C		45 °C	
Sample	**CO conversion (%)**	**CO_2 Selectivity (%)**	**CO conversion (%)**	**CO_2 Selectivity (%)**
Au0.5 - 4/1.5	44.5	84	96.8	35
Au0.5 – 4/3	59.4	98	93.8	53
Au0.5 – 6/3	48.4	93	**97.5**	**40**
Au1 - 4/1.5	14.5	52	49.8	26
Au1 – 4/3	89.3	46	100.0	26
Au1 – 6/3	76.7	44	**99.4**	**42**
Au2 - 4/1.5	99.6	40	96.5	24
Au2 – 4/3	99.8	55	100.0	23
Au2 – 6/3	**99.9**	**62**	99.8	17

of Au loading this has already occurred at 20 °C. In all these cases, these values were observed for the catalysts prepared from the Au solutions using BH_4^-/Au and citrate/Au molar ratios of 6 and 3, respectively. In Figure 5 it is shown a CO conversion and CO_2 selectivity in function of Au loading (wt%) for Au/TiO_2 catalysts prepared with BH_4^-/Au and citrate/Au molar ratios of 6 and 3, respectively. At 20 °C (Fig. 5a) it was observed an increase of CO conversion from 48% until almost 100% with the increase of Au loading from 0.5 to 2 wt%, while CO_2 selectivity decrease from 93% to about 50%. At 45°C (Fig. 5 b) practically all CO conversion occurred from 0.5 to 2 wt%; however, the CO_2 selectivity value of about 40% for the samples with 0.5 and 1 wt% decreases drastically to 18% for sample with 2 wt%. From these results, it could be concluded that catalysts with 0.5 and 1 wt% of Au loading are more adequate to operate at 45°C and with 2 wt% to operate at 20°C.

The long-term stability test results for Au/TiO_2 catalysts with different Au loadings are shown in Fig. 6. For Au/TiO_2 catalysts with 0.5 and 1 wt% of Au loading the tests were performed at 45°C and for the material with 2wt% at 20°C. In all cases the CO conversion and CO_2 selectivity values were similar to ones described in Table 2 and these values remained stable throughout the period evaluated showing the stability of the catalysts under the applied reaction conditions.

The turnover frequency in function of Au loading is shown in Figure 7.

At 20°C the TF values decrease proportionally to the increase of Au loading and TF values of 0.22, 0.12 and 0.06 s^{-1} were observed for samples with 0.5, 1.0 and 2.0 wt%, respectively, showing similar specific activities per gram of Au. At 45°C a decrease of the TF values was observed when compared to the values obtained at 20°C. For catalyst with 2 wt% of Au loading it could be seen that practically all CO (Table 2) was converted at 20°C and 45°C and the TF values become equal at both temperatures showing that the CO conversion is controlled by the space velocity in these conditions and the reaction is under mass transport control [10].

The activation energy was calculated from data of first reaction cycle and the obtained values were 45, 32 and 31 kJ mol^{-1} for catalysts with 0.5, 1 and 2 wt% of Au loading, respectively, showing to be independently of Au loading. These similar values of activation energy and specific activity (TF values) are in accordance with our method of preparation give similar Au nanoparticles sizes for different Au loadings [10].

Klyushin et al [11] prepared Au nanoparticles on transition-metal oxides by two different methods: precipitation (co-precipatation and deposition-precipitation) and photoinduced decomposition of an intermediate gold-azido complex and only samples prepared by the precipitation method showed significant CO conversions at low temperature. It was suggested that a mechanism of Au activation by means of a strong metal-support interaction and that this interaction is more important than the size reduction of the Au nanoparticles. For Au/TiO_2 catalysts prepared by precipitation an activation energy of 28 kJ mol^{-1} was observed for CO

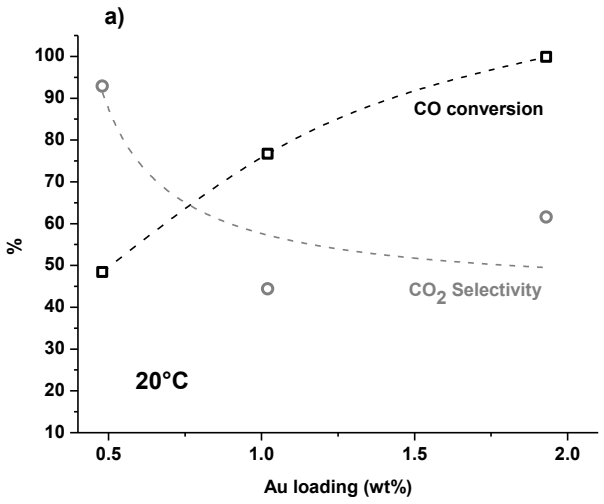

Figure 5: CO conversion and CO_2 selectivity in function of Au loading **a)** 20°C and **b)** 45°C for Au/TiO_2 catalysts 6/3 (100 mg catalyst, flow rate 25 mL min^{-1}, feed composition 1%CO, 2% O_2 and 97% H_2, space velocity 15,000 mL g_{cat}^{-1} h^{-1})

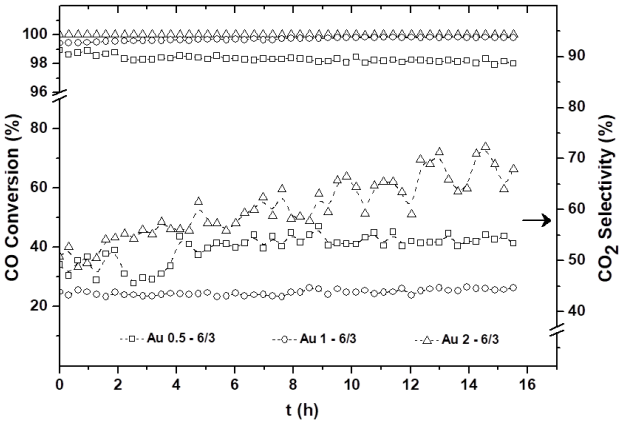

Figure 6: CO conversion and CO_2 selectivity in function of time for Au0.5 – 6/3 and Au1 – 6/3 catalysts at 45°C and Au2 – 6/3 catalyst at 20°C (100 mg catalyst, flow rate 25 mL min^{-1}, feed composition 1% CO, 2% O_2 and 97% H_2, space velocity 15,000 mL g_{cat}^{-1} h^{-1})

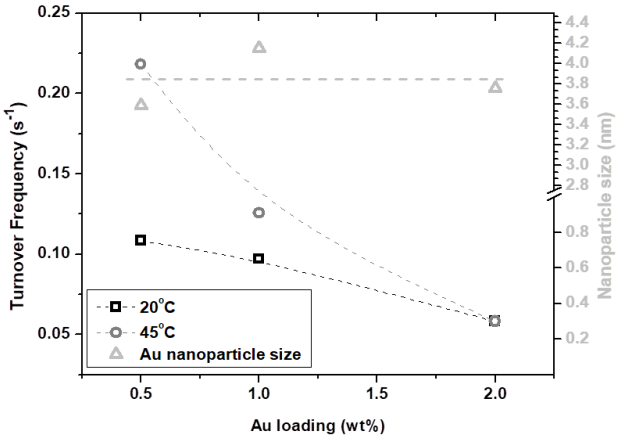

Figure 7: Turnover frequency in function of Au loading at 20°C and 45°C (100 mg catalyst, flow rate 25 mL min^{-1}, feed composition 1% CO, 2% O_2 and 97% H_2, space velocity 15,000 mL g_{cat}^{-1} h^{-1})

oxidation that is very similar to the values obtained for our Au/TiO_2 catalysts for CO-PROX reaction. Recently, Klyushin et al [12] showed that CO oxidation occurs via reaction with lattice O from TiO_2 support and that the nature of Au-oxide bond (strong metal support interaction) is a key factor for Au activation.

4 Conclusions

Au/TiO_2 catalysts could be prepared by a facile methodology with different Au loadings and similar nanoparticles sizes. The catalysts showed to be very active (CO conversion > 99%), selective (CO_2 selectivity around 50%) and stable for CO-PROX reaction in the range of 20°C to 50°C. This activity at low temperatures for CO-PROX reaction could be due an optimal interaction between the Au nanoparticles and the TiO_2 support resulting from the method of preparation.

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