



Short communication

## Investigation of activity losses of gold nanoparticles in the CO selective oxidation

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## ABSTRACT

Gold catalysts nanometrically dispersed over Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> are prepared and tested in selective CO oxidation. XRD, DRS, Raman and in situ DRIFTS techniques are used to investigate the main causes of activity loss after long period storage, evaluating the physical–chemical properties of the fresh catalyst and after 2 years storage. Storing in darkness is not efficient to maintain the catalytic activity. The gold particle sizes increase 13–54% depending on the support. The auto-reduction of cationic gold nanoparticles causes the decrease of CO chemisorption capacity and hence a drastically decrease in the activity.

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## 1. Introduction

It has been demonstrated that gold catalysts exhibit a high catalytic activity when deposited as nanoparticles on metal-oxide supports [1] and it is also well known that its catalytic activity is strongly dependent on the particle size and the metal-support interface [2]. The preparation method has strong influence on the catalyst performance, and only preparations that allow gold particles lower than 10 nm lead to active catalyst. The literature has already reported that gold catalysts lose activity during long storage periods that limits applications [3]. Storing Au/TiO<sub>2</sub> materials in refrigerator and vacuum effectively prevents sintering of particles and preserves the catalytic activity, but storage under these conditions may be inconvenient in several applications [4].

Gold catalysts have been used in the selective CO oxidation (SELOX) for purification of hydrogen-rich feed streams. Experimental and theoretical studies have been developed to elucidate the reaction mechanisms [5–9], optimization of reactors conditions [6], improvements on methods of catalyst preparation [10], new catalytic systems with a second metal as a promoter [11]. The crucial point of these catalysts is their storage, however, few reports have paid attention on this problem and almost all studied the Au/TiO<sub>2</sub> system.

Moreau and Bond [12] observed that the catalysts with low gold content (<0.2%) lost activity during the first 3 months storage. Daté et al. [13] also observed for a 1% Au/TiO<sub>2</sub> continuous loss of

activity. Boccuzzi et al. [14] observed that the storage time affected the gold particle sizes when treated at low temperature (<100 °C). Daté et al. [13] showed sintering after thermal treatment up to 400 °C. Zanella et al. [15] observed particle growth associated not only to the radiation of light, but also to the presence of water in the sample. Schumacher et al. [16] suggested the storage of catalysts in the shelter of light and in a freezer.

The main objective of this study is to investigate the main causes of activity losses after a long period storage of gold catalysts supported on Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and 10%ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> in the selective CO oxidation reaction, using different “in situ” characterization techniques.

## 2. Experimental

## 2.1. Preparation of catalysts

The preparation of gold catalysts supported on different materials has been already reported, as described elsewhere [17]. The following supports were used: Al<sub>2</sub>O<sub>3</sub> (232 m<sup>2</sup> g<sup>-1</sup>), ZrO<sub>2</sub> (43 m<sup>2</sup> g<sup>-1</sup>) and 10% ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (208 m<sup>2</sup> g<sup>-1</sup>).

Gold was added by deposition/precipitation [10,17]. Firstly, the support was suspended with deionized water under vigorous stirring and temperature rising up to 70 °C. In parallel, a solution of gold in deionized water was prepared, using HAuCl<sub>4</sub>·3H<sub>2</sub>O (Acros) as precursor, at pH 8.0 using a solution of 0.1 M NaOH. Subsequently, the aqueous solution of gold (15 g L<sup>-1</sup> of AuO) was added to the support suspension and kept under stirring for 2 h. After the addition of gold solution and during the time of stirring, the final pH was maintained at 8.0 by adjusting with 0.1 M NaOH. Then, the solid

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was filtered and washed with hot water. The resulting powder was dried at 90 °C overnight. Finally, the samples were calcined in flowing air (120 mL min<sup>-1</sup>) at 300 °C (10 °C min<sup>-1</sup>) for 3 h. These samples were codified as AuAl, AuZr and AuZrAl, for gold on alumina, zirconia and zirconia/alumina supports, respectively. The catalysts were stored putting in dim plastic bottles and covering completely with aluminum paper into a closed box for 2 years.

## 2.2. Characterization of catalysts

The crystalline phases were evaluated by X-ray diffraction (XRD) using the powder method. The diffraction patterns were recorded on a Rigaku DMax 2200 diffractometer with an Anton Paar XRK 900 reaction chamber. Reduction and oxidation were performed in situ under the same conditions used for the catalytic tests. The diffractograms were recorded in the range of  $2^\circ \leq 2\theta \leq 120^\circ$  with  $0.05^\circ$  and speed of  $0.15^\circ \text{ min}^{-1}$ .

Diffuse reflectance infrared Fourier transform spectroscopy of adsorbed CO (DRIFTS-CO) was carried out on a Nicolet spectrometer (Nexus 470 model) with a MCT detector and equipped with a diffuse reflectance chamber (Spectra-Tech) for high temperature treatment and ZnSe window. Priority, the samples were reduced at 250 °C (10 °C min<sup>-1</sup>) for 30 min, using the mixture 10% H<sub>2</sub>/He (30 mL min<sup>-1</sup>). After cooling to room temperature in He flow at 30 mL min<sup>-1</sup> the samples were analyzed by DRIFTS. The in situ treatment was carried out switching to the feed composition of CO + O<sub>2</sub> + H<sub>2</sub> (1:1:30–40 mL min<sup>-1</sup>) and analyzed before and after evacuation. Then, after desorptions between 25 and 100 °C new spectra were recorded for each step.

Diffusive reflectance spectroscopy (DRS) with a spectrophotometer Varian Cary 5 Vis-NIR was carried out at room temperature on samples without pre-treatment. The contribution of the support was subtracted from the catalyst spectra and results are expressed by the Schuster–Kubelka–Munk function.

Raman HR-UV 800 infinity microprobe (Jobin Yvon) equipped with CCD detector (–70 °C) and He–Ne laser supplying the excita-

tion line at 632 nm was used. The power was less than 10.7 mW at the sample. The gold standard was prepared by deposition of metallic gold and sputtering technique on a alumina wafer disc. The gold layer was 300 nm.

## 2.3. Catalytic activity

The CO selective oxidation (SELOX) was measured in a continuous fixed-bed U-shaped reactor, under atmospheric pressure. The sample (100 mg) was reduced with a mixture 10% H<sub>2</sub>/He (30 mL min<sup>-1</sup>) at 250 °C (10 °C min<sup>-1</sup>) for 30 min. The feed composition was 1% CO, 1% O<sub>2</sub>, 60% (vol%) H<sub>2</sub> in He at 100 mL min<sup>-1</sup>. The reaction was studied for different temperatures from 0 °C up to the maximum CO conversion temperature. Effluent gases were analyzed by gas chromatography (micro GC Varian 4900) equipped with a COx column. The catalysts were tested after preparation and after 2 years storage.

## 3. Results and discussion

The gold content was 2 wt.% and very close to the nominal value, which allows comparing catalyst properties. Moreover, chlorine content was very low, showing that it is an efficient preparation method, as reported in [17].

The storage time of any product is a basic property for its market. It is well known that gold catalysts suffer modifications with continuous exposition to light [13–15]. It was possible to observe visually little changes in the color of the catalysts. The AuAl catalyst was originally gray and AuZrAl with a light tone of rose became dark pink. The pink AuZr catalyst became violet. These modifications suggest the transformation of the cationic species into metallic gold [3].

Fig. 1 presents the catalytic performance of the catalysts recently prepared and after 2 years storage. The aged samples exhibited much lower activities than the fresh samples, and thus, structural modifications after long storage time. All catalysts lost activity,

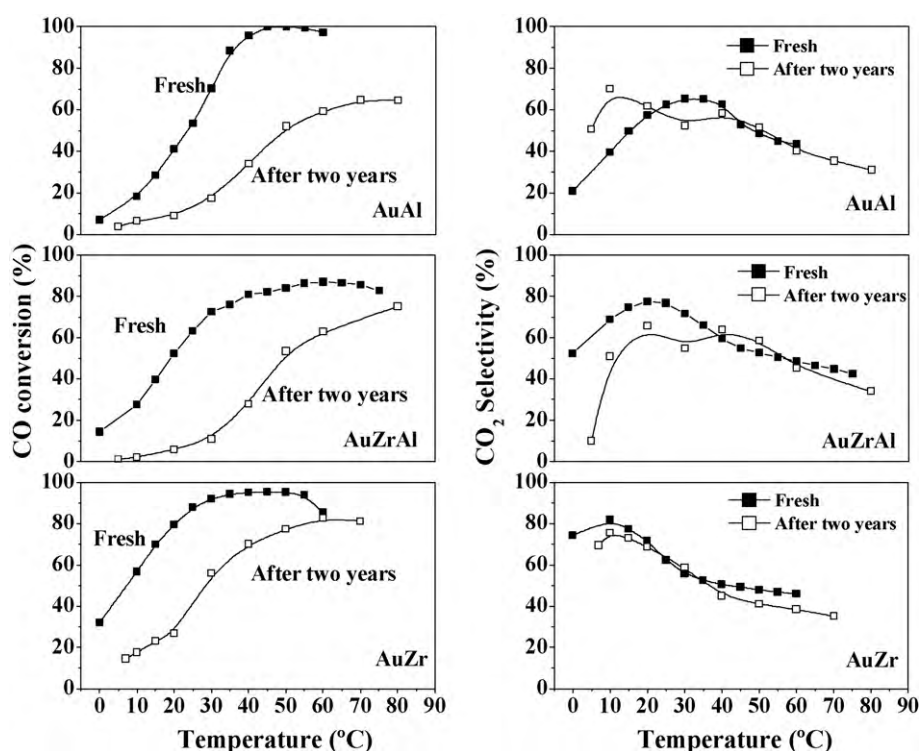


Fig. 1. Evaluation of storage time on selective CO oxidation for different catalysts in terms of CO conversion and O<sub>2</sub> conversion.

**Table 1**  
Effect of storage time in CO conversion and selectivity to CO<sub>2</sub>.

	AuAl		AuZr		AuZrAl	
	Fresh	Aged	Fresh	Aged	Fresh	Aged
T <sub>50%CO</sub> (°C)	23	48	8	28	18	47
Selectivity to CO <sub>2</sub> (%)	61	59	75	59	75	59
Activity loss <sup>a</sup> (%)	34.6		12.9		7.2	

<sup>a</sup> Difference between maximum value of conversion in fresh samples and after 2 years of storage.

decreasing the CO conversion. For comparison, Table 1 presents the temperature needed for 50% CO conversion and the corresponding selectivity to CO<sub>2</sub>. The AuZrAl catalyst exhibited the largest temperature difference (29 °C) for 50% CO conversion, followed by AuAl (25 °C). However, concerning the absolute loss of activity, the AuAl catalyst presented a decay of 34% and the AuZrAl catalyst only 7.2%. Daté et al. [13] noticed an increased activity for 1% Au/TiO<sub>2</sub> after the first days (up to 15 days) but then a continuous decay of activity. Moreuau and Bond [12] also reported for Au/TiO<sub>2</sub> catalysts with low gold contents (<0.2%) loss of activity after 3 months, around 34% for the catalyst stored in darkness and 77% for that exposed to light, which then remained constant for a period of 1 year.

Searching for possible causes these catalysts were analyzed by XRD, UV-vis, Raman and in situ DRIFT spectroscopy. The fresh catalysts were already characterized by XRD and TEM, as reported in a previous paper [17] and the average crystallite sizes are summarized in Table 2. Fig. 2 shows the diffractograms of AuAl and AuZr catalysts after 2-year storage. Using Rietveld's methodology and Scherrer's equation the average crystallite sizes were calculated. The average Au<sup>0</sup> crystallite sizes for AuAl and AuZr catalysts were 4.93 ± 0.05 and 5.93 ± 0.03 nm, respectively. When compared to the fresh samples (see Table 2), the gold crystallites increased 54% and 13% on AuAl and AuZr, respectively, suggesting sintering of gold crystallites, in accordance with the literature [18]. The AuAl catalyst presented the highest activity loss (34%).

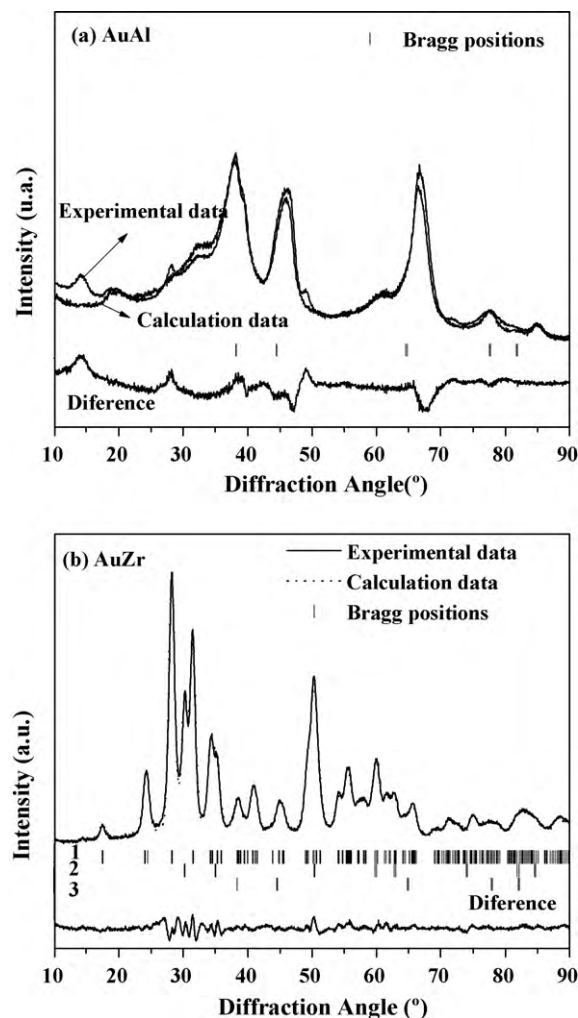
Bocuzzi et al. [14], studied the effect of storage time on gold particles sizes after treatment at low temperatures (<100 °C). Daté et al. [13] say that Au/TiO<sub>2</sub> catalysts sinter after heating at 400 °C and storing in darkness. Zanella et al. [15] observed a growth of gold particle sizes on Au/TiO<sub>2</sub> from 2 to 5 nm in a few weeks. These authors claim that not only light but also the presence of water influence growth of gold particles. Shumacher et al. [16] recommended storage in darkness and in the freezer. They observed that the samples thermally stabilized and stored in darkness suffered auto-reduction and sintering, while those samples stored in a shelter of light and in the freezer did not present significant changes of particle sizes, because the partial pressure of water was very low.

However, the loss of activity can also be attributed to structural modifications in the particles and weakening of gold/support interaction. DRS analyses were carried out to check possible modifications in the oxidation state of gold particles. Fig. 3 shows DRS results for all catalysts. The analysis was carried out with the catalyst and the respective support, and after subtraction of the spectra, the profile displays only the contribution of gold particles.

All catalysts exhibited great modifications in the spectrum after storage, indicating changes in the oxidation state of gold parti-

**Table 2**  
Average crystallite size of fresh samples.

Catalyst	Average crystallite size (nm)	Average crystallite size (nm), after storage (2 years)
AuAl	3.0 ± 0.5	4.93 ± 0.05
AuZr	5.1 ± 0.2	5.93 ± 0.03
AuZrAl	2.3 ± 0.4	3.30 ± 0.04



**Fig. 2.** XRD of AuAl (a) and AuZr (b) samples after 2 years storage. | Bragg positions: 1 monoclinic zirconia, 2 cubic zirconia and 3 metallic gold. For the AuAl graph only metallic gold was identified.

cles. The fresh AuAl catalyst showed absorption bands at 225 and 538 nm, while the spectrum of the sample after 2-year storage exhibited bands at 233, 271 and 538 nm. Also the fresh AuZr catalyst displayed two bands at 245 and 550 nm, while the aged sample presented peaks at 259 and 552 nm. Regarding the AuZrAl catalyst the same behavior was observed, displaying a band at 223 nm on the fresh catalyst and at 536 nm on the aged catalyst.

The adsorption bands of gold nanoparticles can be separated in three species [19]:

- (1) At 200–230 nm: attributed to the presence of Au<sup>3+</sup> or Au<sup>+</sup>;
- (2) At 230–270 nm: typical region for the charge transfer transitions of Au<sup>3+</sup> and Au<sup>+</sup> ions with ligands or for the absorption bands due to transition of electrons between molecular orbital of the few-atomic clusters (Au<sub>n</sub> with n < 10);
- (3) At 500–600 nm: attributed to a collective oscillation of conduction electrons in response to optical excitation, the plasmon band. This band of absorption is normally observed when the wavelength of the light exceeds the size of the metal particle [20].

The fresh AuAl catalyst presented a mixture of cationic (Au<sup>3+</sup> or Au<sup>+</sup>) and metallic particles, as observed from bands at 225 and 538 nm, respectively. With increasing storage time the plasmon

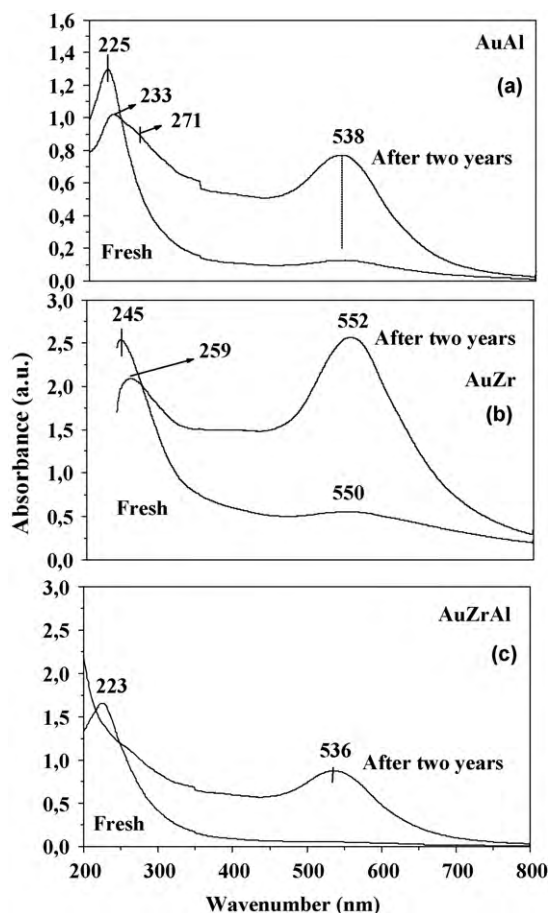


Fig. 3. DRS spectra of (a) AuAl, (b) AuZr and (c) AuZrAl samples recently prepared and after 2 years of storage.

band (538 nm) increased substantially, indicating the reduction of cationic particles. New bands at 233 and 271 nm are probably attributed to small gold clusters, as observed by XRD analysis. Photocatalysis on a semiconductor takes place by the absorption of one photon with equal or higher energy than a gap of the oxide, producing a couple of electrons–holes ( $e^-/h$ ). The couple  $e^-/h$  then acts like a donor or acceptor of electrons from its neighbors. When gold-based catalysts are excited by a beam of light, the electrons of the gap of the support reduce gold particles to metallic gold. The interaction of gold particles with the support, as well as the formation of particles from metallic gold, may change the metal/support interaction, taking place the migration of gold from the surface to the bulk catalyst [3].

The fresh AuZr catalyst displayed a small plasmon band at 550 nm and a charge transition band at 245 nm relative to  $Au^{3+}$  or  $Au^+$  as small clusters. After storage the spectra displayed a band at 259 nm, which is attributed to small gold clusters. The plasmon band became more intense with a small shift towards higher frequency (553 nm), which indicates the collection and growth of the gold particles, according to Tuzovskaya et al. [19].

The spectra of AuZrAl catalyst were similar to the AuAl catalyst. The fresh sample presented only a band at 223 nm, assigned to cationic gold. The aged sample showed a band at 536 nm, suggesting a complete reduction of gold particles. Lee et al. [4] studied the influence of light on gold particles of the  $Au/TiO_2$  catalyst, and noticed that after 5 months storage in the absence of light the particles suffered auto-reduction, displaying the plasmon band. This process was intensified after storing in light. Huang et al. [20] studied the effect of calcination temperature on the plasmon band of

gold catalysts supported on titania, which appeared at temperatures above 90 °C. Up to 190 °C no significant change was observed on the intensity of this band but only a slight shift towards higher wave numbers. However, during the reduction with hydrogen, Tuzovskaya et al. [19] observed the plasmon band at 50 °C, without any modification above 200 °C.

Raman spectroscopy was complemented to DRS results to check the formation of metallic gold at the surface after storage. Results of the AuAl and the standard sample are shown in Fig. 5. It evidences clearly metallic gold particles at band 126 and 185  $cm^{-1}$  and a band at 543  $cm^{-1}$ , after comparing with pure metallic gold sputtered over the same alumina support. The increasing intensity band 543  $cm^{-1}$  suggests a stronger interaction of gold nanoparticles with the support and therefore the enhanced mobility of electron transfer of the electronic structure of the metal and the support. According to literature [21] with increasing Au content this intensity band decreases and therefore the electron transfer to the support. On other hand, this intensity band can be shifted depending on the support. DRS and XRD results confirm that the effect of the support does not affect the structure of gold particles, but the presence of alumina on the AuZrAl catalyst impede the agglomeration of gold particles (Table 2). In addition, no ionic gold over this support was found after 2 years storage. It is a strong evidence of metallic gold formation.

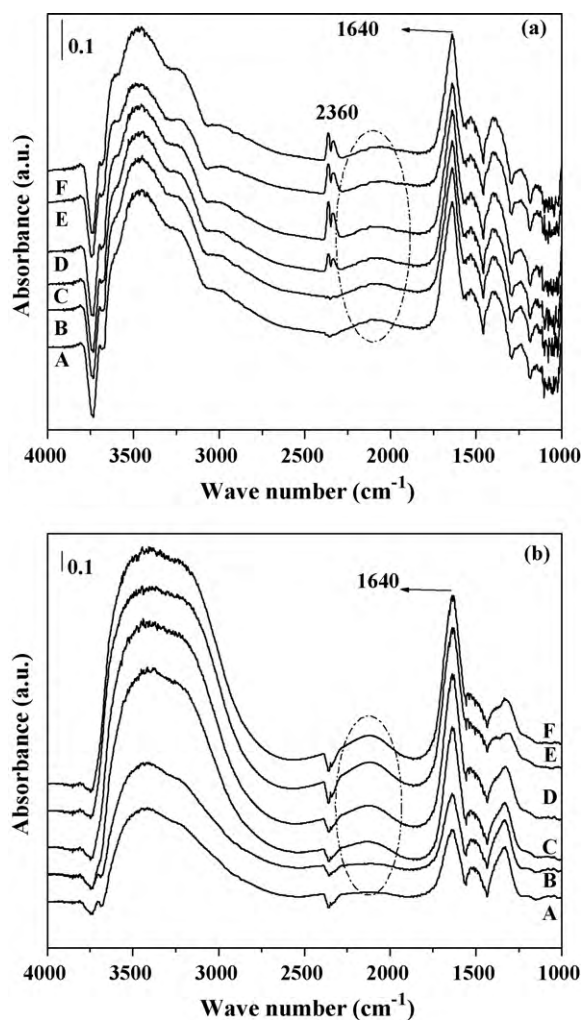


Fig. 4. In situ DRIFTS spectra of selective CO oxidation reaction for the aged samples: (a) AuAl and (b) AuZr. Reaction temperatures: (A) 35 °C, (B) 45 °C, (C) 55 °C, (D) 65 °C, (E) 80 °C, (F) 100 °C.

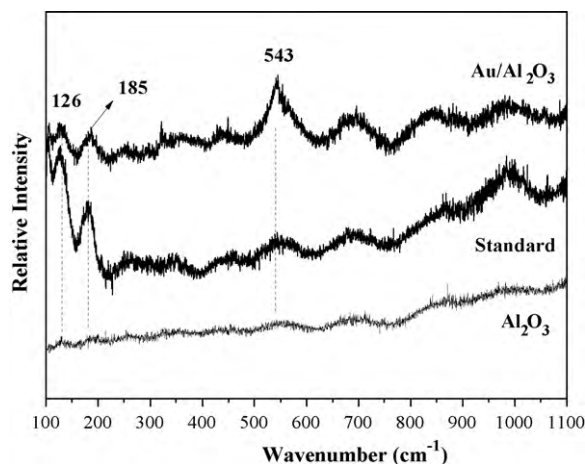


Fig. 5. Raman spectra of AuAl after 2 years storage.

In situ DRIFTS analysis of selective CO oxidation reaction was performed on AuAl and AuZr catalysts after 2-year storage and the results are displayed in Fig. 4. Both catalysts are very similar, and indicate the absence of the CO adsorption band on metallic gold ( $\sim 2100\text{ cm}^{-1}$ ) and on cationic gold ( $\sim 2170\text{ cm}^{-1}$ ), which is a strong evidence of loss of reactivity.

The  $\text{CO}_2$  selectivity as a function of temperature on fresh and aged samples (Fig. 1) and for 50% CO conversion showed less decreasing selectivity (Fig. 1).

It suggests that  $\text{CO}_2$  may react with the support forming carbonates, independent of the gold particles. These carbonate species in addition to the grown crystallites deactivated more severely the activity, as observed in Fig. 1.

This fact can be observed in DRIFTS analysis by the formation of water during the reaction through a broad band at  $2800\text{--}3600\text{ cm}^{-1}$ , which represents the vibration of OH groups of water molecules interacting with hydroxyl at the surface. Besides, the band at  $1640\text{ cm}^{-1}$  is typical of vibration of nondissociated water molecules [22]. With increasing reaction temperature the relative intensity of the band of water increases together with the appearance of a band at  $1800\text{--}2100\text{ cm}^{-1}$ . It is due to the substitution of CO weakly adsorbed for  $\text{H}_2$  molecules, increasing drastically the degree of coverage and consequently the formation of water. This spectrum also shows intense bands corresponding to carbonates or bicarbonates ( $1200\text{--}1630\text{ cm}^{-1}$ ). The AuAl sample displayed one band at  $2360\text{ cm}^{-1}$  which is assigned to  $\text{CO}_2$  formation, probably due to the decomposition of carbonates/bicarbonates.

#### 4. Conclusions

The effect of 2 years storage of gold nanoparticles on the selective CO oxidation reaction showed a drastically decay of the activity and selectivity caused by the increasing crystallite sizes, depending on the support. DRS results showed that gold particles suffer photo-reduction by transformation of cationic gold ( $\text{Au}^{3+}$  and  $\text{Au}^+$ ) into metallic  $\text{Au}^0$ . With increasing storage time there is a great increase of the plasmon band ( $538\text{ nm}$ ) indicating the reduction of cationic gold. Raman spectra showed metallic gold nanoparticles after storage and the influence of nanoparticles on the electronic structure of gold with the support. The in situ DRIFTS analyses showed a great loss of CO adsorption capacity after 2 years storage which is responsible for the decreasing catalytic activity. It also shows increased carbonate formation and changes in the superficial hydroxyl structure.

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