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journal homepage: www.elsevier.com/locate/apcataQuantitative determination of sites able to chemisorb CO on Au/ZrO₂ catalystsF. Menegazzo^{a,b}, F. Pinna^{a,b}, M. Signoretto^{a,b,*}, V. Trevisan^{a,b}, F. Boccuzzi^c, A. Chiorino^c, M. Manzoli^c^a Dipartimento di Chimica, Università Cà Foscari, Dorsoduro 2137, 30123 Venezia, Italy^b Consorzio INSTM-UdR, Venezia, Italy^c Dipartimento di Chimica IFM and NIS Centre of Excellence, Università di Torino, via P. Giuria 7, 10125 Torino, Italy

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ABSTRACT

Quantitative volumetric measurements of low temperature CO chemisorption on Au/ZrO₂ catalysts and Fourier transform infrared measurements of adsorbed CO in well defined and controlled conditions of temperature and pressure are here presented as widely accessible and reproducible methods for determining the concentration of gold sites able to chemisorb CO on Au/ZrO₂ catalysts. HRTEM analyses were also performed in order to support the validity of the measurements.

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1. Introduction

Gold supported on oxides or carbon, once considered catalytically inert, is now firmly established as an effective catalyst and the repertoire of reactions that it can catalyze is really wide. Gold catalysts already have done it out of the lab and into commercial use, and a very large number of papers was published regarding catalysis by gold. It has been shown that the nature and the structure of the support strongly influence the catalytic performances of gold-based samples, but exploration of catalytic activity and selectivity of Au nanoparticles on the basis of sizes was the main focus of most research in this field. Experimentally, the size of gold metallic particles is mainly detected by TEM. However TEM is an expensive method and, even if performed accurately, it is hardly applicable for highly dispersed samples, since the very small metallic particles (<1 nm) are detectable in an over-complicated way. A technique more widely diffuse both in academic and industrial laboratories, reproducible and fast, such as chemisorption test, should be very useful for these systems. Unfortunately, as well known, gold does not chemisorb many molecules easily, and in fact there are only few scientific works related to characterization of supported gold by chemisorption methods [1–5]. We have

recently shown [6] that CO chemisorption by a pulse flow technique and Fourier transform infrared measurements of adsorbed CO in well defined and controlled conditions of temperature and pressure can be taken as effective methods for the quantitative determination of the gold active sites on Au/TiO₂ and Au/Fe₂O₃, two reference catalysts provided by the World Gold Council, and on a Au/CeO₂ sample. In particular we have demonstrated that using a pulse flow system after a proper pretreatment, CO chemisorption at 140–180K can be taken as a widely accessible and reproducible technique for determining the concentration of gold active sites and for comparing different samples. The goal of the present work is to extend that study to zirconia supported gold catalysts in order to test further the validity of the method already presented. We choose zirconia because it is of particular interest in a large field of applications, since it possesses desirable properties such as tuneable surface acidity/basicity (controlled by the addition of different dopants), redox properties and tuneable porosity and surface area. Recently, it has been found that zirconia is a very efficient support for gold-based catalyst for the low-temperature water gas-shift (WGS) reaction [7–9]. Moreover, Au/ZrO₂ materials are of significant interest as catalysts for CO oxidation [10], butadiene hydrogenation [11], epoxidation of styrene [12]. We present here a detailed investigation of a series of Au/ZrO₂ samples with different metal content and various particle sizes, deeply characterized by a number of techniques, in order to improve, through a systematic study, the possibility of the quantitative determination of gold sites able to activate CO.

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2. Experimental

2.1. Catalyst preparation

The support was prepared by precipitation from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Fluka) at constant pH (pH 8.6), aged under reflux conditions for 20 h [13,14], washed free from chloride (AgNO_3 test) and dried at 383 K overnight. Then the prepared $\text{Zr}(\text{OH})_4$ was sulfated with $(\text{NH}_4)_2\text{SO}_4$ (Merck) by incipient wetness impregnation (2.5 wt% $\text{SO}_4^{2-}/\text{ZrO}_2$) and finally heated (90 K/h) up to 923 K in flowing air (30 mL/min STP) and kept at this temperature for 6 h, followed by slow cooling to room temperature [8]. Gold was deposited on the calcined support by deposition precipitation (hereafter denoted as dp) with both constant and variable pH, using either a Na_2CO_3 aqueous solution (1 M) (Riedel-de Haen) [(c) samples] or a NaOH aqueous solution (0.5 M) (Riedel-de Haen) [(n) samples]. A proper amount of HAuCl_4 aqueous solutions was used in order to give different nominal Au contents. In this way, five different samples supported on sulfated zirconia were prepared (see Table 1). After filtration, the catalysts were finally dried at 310 K for 15 h. Another sample was prepared exactly in the same way of the 1Au(c) catalyst but without adding the HAuCl_4 aqueous solution (denoted as blank(c)).

2.2. Methods

Surface area and pore size distribution were obtained from N_2 adsorption/desorption isotherm at 77 K (using a Micromeritics ASAP 2000 Analyser). Calcined support (400 mg) was pre-treated at 300 °C for 2 h under vacuum. Surface area was calculated from the N_2 adsorption isotherm by the BET equation, and the pore size distribution was determined by the BJH method also applied on the adsorption branch [15]. Total pore volume was taken at $p/p_0 = 0.99$.

The amount of sulfate was determined by ion chromatography (IEC) after dissolution of the materials [16]. Sulfate concentration was calculated as the average of two independent sample analyses, and each analysis included two chromatographic determinations.

Actual metal loading was determined by atomic absorption spectroscopy after microwave disgregation of the samples (100 mg).

HRTEM analysis was performed on all catalysts using a JEOL 3010 EX electron microscope (300 kV) equipped with a side entry stage and a LaB_6 filament. The powdered samples were ultrasonically dispersed in isopropyl alcohol and the obtained suspension was deposited on a copper grid, coated with a porous carbon film. The mean particle diameters and size distribution measurements were performed by counting a statistically significant number either for the zirconia supports or for the gold.

FTIR spectra were taken on a PerkinElmer 1760 spectrometer (equipped with a MCT detector) with the samples in self-supporting pellets introduced in a cell allowing thermal treatments in controlled atmospheres and spectrum scanning at controlled temperatures (from 120 to 300 K). The pretreatment of the samples was: (i) reduction in H_2 at 423 K; (ii) hydration at r.t.. Band integration was carried out by “Curvefit”, in Spectra Calc

(Galactic Industries Co.). The obtained integrated areas were normalized to the Au content of each sample.

CO pulse chemisorption measurements were performed at 157 K. Preliminary tests were carried out at different temperatures in the 140–180 K range [6]. An inexpensive home made equipment was used for pulse chemisorption. In principle the system was made of a U-shaped Pyrex reactor equipped with an oven controlled by a PID temperature programmer, mass flowmeters, sampling valve, a Gow-Mac TCD detector and a quadrupole mass detector. Before chemisorption the following standard pretreatment procedure was applied: the sample (200 mg) was reduced in H_2 flow (40 ml min^{-1}) at 423 K for 30 min, cooled in H_2 to ambient temperature, purged in He flow and finally hydrated at ambient temperature. The hydration treatment was performed by contacting the sample with a He flow (10 ml min^{-1}) saturated with water (2.7 mmol(H_2O) m^{-2}). The sample was then cooled in He flow to the temperature chosen for CO chemisorption. Such temperature could be easily attained and maintained by simply adding liquid nitrogen to the suitable solvent in a Dewar flask, and therefore no cryostatic equipment was required. (i.e. the temperature of 157 K can be attained by an ethanol–liquid nitrogen cryogenic mixture). For standard measurements the following operating conditions are recommended: CO content in pulses (5 vol%), helium flow rate (30 ml min^{-1}), pulse size (0.4–0.7 ml), time interval between pulses (4 min).

3. Results and discussion

Sulfated zirconia [17] has been the object of extensive research, due to its characteristics: sulfates cause modifications of the acid properties and affect surface features: they retard crystallization, stabilize the tetragonal phase, improve the surface area and the pore size. These properties make sulfated zirconia interesting both as catalyst and as catalyst support. In the present work we have used sulfated zirconia as support and we have characterized it by N_2 physisorption and sulfur content measurements. The N_2 physisorption analysis shows a type IV isotherm with hysteresis loop typical of mesoporous materials. Such calcined support presents a surface area of about 80 m^2/g and mean pore size around 11 nm, according to previous papers [18].

Sulfate loading on the support before calcination is 2.5 wt%, while after calcination is 2.1 wt%. On the contrary, tests of the sulfates carried out on the samples after deposition of gold, show that final catalysts do not contain sulfates anymore. This is not unexpected, since the methodology of gold deposition–precipitation on the support is carried out at a basic pH (pH 8.6), leading to the disappearance of sulfates from the catalysts [16,19]. For this reason we refer to catalysts object of this work as Au/ZrO₂ samples. Gold contents of each catalyst are reported in Table 1, since they are a critical parameter in the volumetric CO chemisorption determinations.

HRTEM measurements were performed on all prepared catalysts. As for the support, which is the same for all samples, crystalline zirconia nanoparticles, with globular–elongated shape and an average size of about 11 nm, have been observed. No gold

Table 1
CO chemisorption data (at 157 K) and FTIR spectroscopic features of the absorption bands.

Sample	Preparation method	Au (wt%)	$\text{mL}_{\text{CO(STP)}}/\text{g}_{\text{Au}}$	$\text{mol}_{\text{CO}}/\text{mol}_{\text{Au}}$	$I_{\text{int}}/\text{mol}_{\text{Au}} (\times 10^3)^a$	Absorption coefficient $\text{cm}^{-1} \text{mol}^{-1} (\times 10^4)$
0.5Au(c)	dp ^a with Na_2CO_3	0.43	8.0	0.07	0.5	–
1Au(c)	dp ^b with Na_2CO_3	0.8	19.3	0.17	2.64	1.55
0.5Au(n)	dp ^b with NaOH	0.47	15.2	0.13	2.0	1.54
1Au(n)	dp ^b with NaOH	1.0	21.7	0.19	2.84	1.49
3Au(n)	dp ^b with NaOH	1.94	34.2	0.30	5.54	1.85

^a Variable pH.

^b Constant pH.

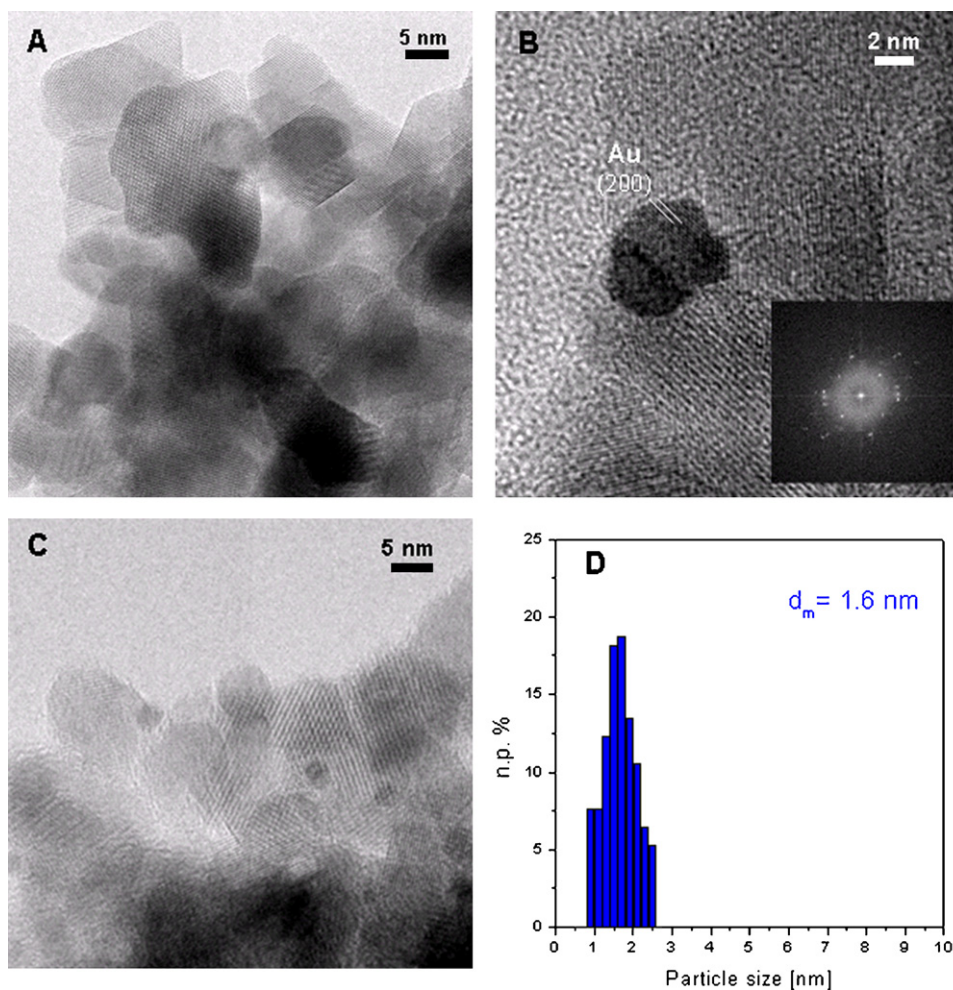


Fig. 1. HRTEM images of 0.5Au(n) (Section A) original magnification $\times 300k$, 0.5Au(c) (Section B) original magnification $\times 600k$, 3Au(n) (Section C). Original magnifications: $\times 300k$, $\times 600k$ and $\times 400k$, respectively. Size distribution and mean diameter of 3Au(n) (Section D).

particles were detected on 0.5Au(n), 1Au(c) and 1Au(n), indicating a very high metal dispersion on these catalysts (see Fig. 1, Section A, where the HRTEM image of 0.5Au(n) is reported as example). On the contrary, some Au particles agglomerate with size ranging between 5 and 15 nm, were observed on the 0.5Au(c) sample (Fig. 1B). Their composition and morphology have also been confirmed by the Fourier transformed of the image (see inset). Looking at different electron micrographs, the 3Au(n) sample shows several gold nanoparticles, i.e. particles whose size ranges between 1 and 10 nm, as the one reported in Fig. 1, Section C. The gold average size is 1.6 nm and the particle size distribution (obtained by counting 171 particles) is quite narrow and symmetric and it is reported in figure (Fig. 1D).

FTIR spectra of adsorbed CO were collected in the 120–180 K temperature range on the samples previously reduced in hydrogen at 423 K and hydrated at r.t. in order to reproduce the same experimental conditions adopted to perform CO chemisorption measurements, as it will be illustrated in detail later on. Section A of Fig. 2 shows the FTIR spectra, normalized to the gold content of each pellet, of CO adsorbed at 157 K on the 0.5Au(n) (bold curve), 0.5Au(c) (dashed curve) and 1Au(n) (fine curve) samples in the carbonylic region. CO adsorption on these samples produced a symmetric and quite broad band in the frequency range typical of CO adsorbed on Au⁰, but with shape quite different from that found on other Au/ZrO₂ samples previously studied by some of us [20,21], where metal particles, with mean size equal to 4.1 nm, were detected by HRTEM. Particularly, the integrated area of the band

related to CO on 0.5Au(n) is 4 times larger than the one related to 0.5Au(c) (see Table 1). HRTEM measurements indicate a different gold dispersion on the two samples. On the 0.5Au(c) a fraction of gold is present as metallic particle agglomerates, unable to adsorb CO, hence the total adsorbing sites are less abundant. Moreover, these absorption bands are thermally stable in the 120–180 K range and did not show any frequency shift by increasing the temperature, as reported in Section B of Fig. 2 for the 1Au(c) sample taken as example. This behaviour is clearly different from what observed in the same experimental conditions on Au/TiO₂ and Au/Fe₂O₃ reference catalysts provided by the World Gold Council [6], whose mean gold particle size were 3.8 and 3.7 nm, respectively. Taking into account all these features, it can be proposed that gold nanoclusters, with size below 1 nm, are present on 0.5Au(n), 1Au(n), 1Au(c) and that a fraction of the gold on the 0.5Au(c) sample is in this form. Moreover, a red shift between the band related to 0.5Au(n) (Section A, bold curve) and that of 1Au(n) (Section A, fine curve) is observed.

Fig. 2, Section C shows the FTIR spectra, normalized to the gold content of each pellet, of CO adsorbed at 157 K on the reduced (fine curve) and reduced and subsequently hydrated (bold curve) 3Au(n) sample in the carbonylic region. Besides the weak absorption detected at 2170 cm⁻¹, due to CO interacting with the cations of the support, the band related to the stretching of gold carbonyls shows different intensity, shape and maximum position respect to the previously examined samples. It appears as the overlap of two different absorption bands, a broad one, related to

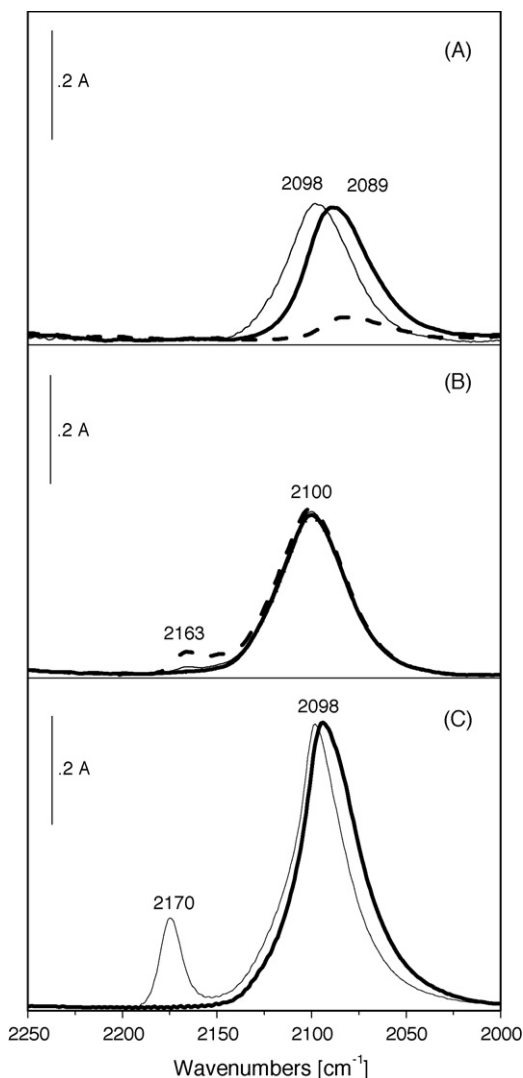


Fig. 2. Section A: FTIR spectra of CO adsorbed at 157 K on 0.5Au(n) (bold curve), on 0.5Au(c) (dashed curve) and on 1Au(n) (fine curve). Section B: FTIR spectra of CO adsorbed at 120 K (dashed curve), at 142 K (fine curve), at 157 K (bold curve) and at 179 K (dotted curve) on 1Au(c). Section C: FTIR spectra of CO adsorbed at 157 K on reduced (fine curve) and reduced + hydrated (bold curve) 3Au(n). All spectra were reported in the carbonylic region and normalized to the gold content of each pellet.

CO adsorbed on gold nanoclusters and a narrower one, due to CO on nanoparticles. The HRTEM analysis confirmed the presence of the nanoparticles.

Moreover, the comparison between the spectra of Section C well demonstrates that the CO chemisorption quantitative measurements on hydrated samples at 157 K are effectively relative only to the adsorption on gold sites. [6].

Finally, the possible formation of formates or other non-carbonylic species on the zirconia support was tested on the different samples, looking at the mid-IR region spectra and no bands have been detected.

As already mentioned, volumetric measurements of CO chemisorption were performed on mildly reduced catalysts and after saturation of the surface with water, in order to avoid CO chemisorption on uncoordinated support ions [6]. In the present work we have chosen to perform pulse flow CO chemisorption measurements at the temperature of 157 K. Values obtained performing chemisorption measurements at a lower temperature (140 K) are lightly higher and present broad peaks, indicating that under these experimental conditions part of CO chemisorbs on

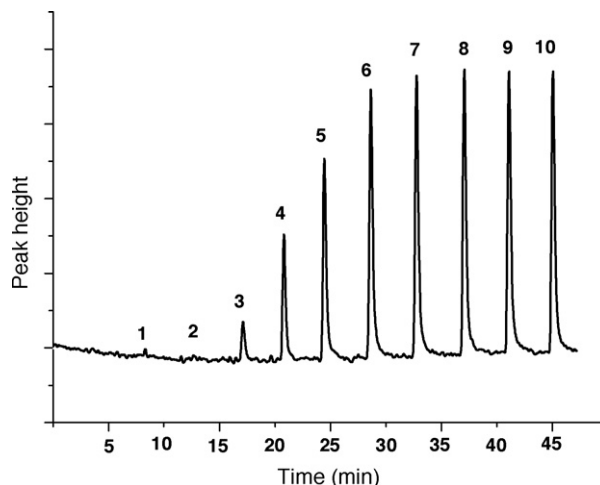


Fig. 3. Typical experimental plot of CO uptake vs time of measure. (3Au(n) sample).

support ions. On the contrary, measurements carried on at higher temperature (180 K) are, under the experimental error, identical to the ones obtained at 157 K. However, since the latter is a temperature which is easier to attain, we suggest to use it for the routine analyses.

For sake of clarity a typical experimental plot of gas uptake vs time of measure is reported in Fig. 3.

Preliminary runs carried out on the bare support, the blank sample (c), in the same experimental conditions (meaning at 157 K after a reducing + hydrating pretreatment) have shown the absence of CO chemisorption on uncoordinated support ions. On the contrary, as a proof of the reliability of the selected experimental conditions, measurements on the same blank sample (c) at 157 K but without performing the hydrating pretreatment, have shown that a fraction of CO (13%) has been chemisorbed on the support.

The results obtained by pulse flow CO chemisorption on Au/ZrO₂ catalysts are reported in Table 1, together with the integrated intensities of the FTIR absorption band of CO adsorbed on gold sites at the same temperature on reduced + hydrated samples and the related absorption coefficients. First of all we would like to stress that chemisorption, if performed under proper conditions, is not only an easy, fast and economic technique, but it is also very reproducible and so reliable. In fact we have estimated an experimental error in the mol_{CO}/mol_{Au} ratio of ±0.01, ascertained that the main error of the methodology is the quantitative determination of the real gold content. Looking at chemisorption data on the five different samples prepared, reported in Table 1, we can make the following observation: measurements performed on samples that both HRTEM and FTIR have indicated as highly dispersed give a very large chemisorption value, while in the sample 0.5Au(c), in which HRTEM analysis has revealed the presence of bigger gold particles, a significant decrease of chemisorbed CO occurs, as well as the integrated area of the FTIR CO band, indicating that the total adsorbing sites are less abundant. Moreover, from Table 1, it is evident that Au/ZrO₂ catalysts show different mol_{CO}/mol_{Au} ratio, (from 0.07 to 0.30 mol_{CO}/mol_{Au}), but all of them are higher than that one previously found for the Au/TiO₂ and Au/Fe₂O₃, reference samples provided by the World Gold Council [6]. On 3Au(n) catalyst, for example, the CO chemisorbed volume per gram of gold is even ten times higher than in the case of Au/TiO₂, in which a particle size distribution centered on 3.8 nm was found [6]. The integrated area of the FTIR band of adsorbed CO per mole of Au has been calculated for each sample at the chemisorption temperature (157 K). Fig. 4 reports the plot of CO chemisorbed amounts vs integrated peak intensities. A quite good linear relationship is

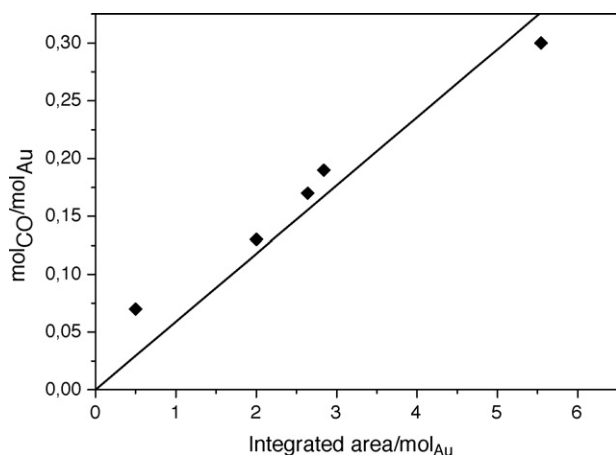


Fig. 4. CO chemisorbed amounts vs. integrated peak intensities.

observed, even if a deviation is detectable at the ends of the plot. In particular the deviation of the sample with the highest Au content can be due to a contribution of the nanoparticles. The absorption coefficients have been also obtained, except for 0.5Au(c), whose absorption band is too weak (see Table 1). FTIR spectra show that the high amounts of chemisorbed CO on 0.5Au(n), 1Au(n) and 1Au(c) are completely and definitely due to the chemisorption as carbonylic species on Au nanoclusters, not detectable by HRTEM, where almost all the atoms are exposed at the surface. Moreover, the obtained values of their absorption coefficients are almost equal (Table 1), confirming the presence of the same Au adsorbing sites on these samples. The value is different for 3Au(n), particularly it is the highest one. We previously found that gold adsorbing sites exposed at the surface of the nanoparticles have an absorption coefficient close to $3 \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1}$, as a consequence of the metallic nature of these sites, as reported for Au/TiO₂ and Au/Fe₂O₃ samples [6]. Hence, the value of the absorption coefficient ($1.85 \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1}$), obtained for 3Au(n), can be explained considering the extra contribution of the Au nanoparticles, also present on this sample and detected by HRTEM.

4. Conclusions

In summary, this work demonstrates that CO chemisorption performed by a pulse flow system at 157 K on prehydrated samples can be taken as a method for the quantitative determination of the gold sites also on Au/ZrO₂ catalysts, where gold particles cannot be detected by TEM.

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