

Research note

# Quantitative determination of gold active sites by chemisorption and by infrared measurements of adsorbed CO

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## Abstract

Quantitative measurements of CO chemisorption in the range 140–180 K, supported by FTIR data on adsorbed CO, were performed on Au/TiO<sub>2</sub>, Au/Fe<sub>2</sub>O<sub>3</sub>, and Au/CeO<sub>2</sub> catalysts. On the first two samples, which had similar particle size distributions, an average Au/CO chemisorption stoichiometry of about 3, referred to step-edge Au atoms, was found. On Au/CeO<sub>2</sub>, where very small clusters and quite large particles are present, the CO-chemisorbed volume was much higher than expected, due to the prevailing contribution of very small Au clusters. On the same sample, a change in the IR absorption coefficient was observed and was reasonably explained.

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## 1. Introduction

The catalytic properties of finely dispersed gold particles have attracted much attention of late [1]. Bulk gold itself is an inert material, and the reason for small gold particle activity is still a matter of debate. It has been shown that the gold's catalytic activity depends critically on the preparation method, the support type, and the pretreatment procedure. The most popular explanation for the variability of the catalytic properties of gold catalysts focuses on the size of the gold particles and on the amount of low-coordinated gold sites. Other factors have also been considered in the recent literature, including the metal–support interface, charge transfer from the support, and metal cationic sites [1]. In an Au/TiO<sub>2</sub> model system, Goodman [1] showed that active Au spread on titania nucleating on reduced Ti defects, forming bilayer structures and electron-

rich gold sites. However, the real catalysts are less well-defined than the model ones discussed in Goodman's work: therefore, well-defined and widely accessible characterization methods are needed to improve our understanding of the origin of the different activities observed for different samples and to enable us to discriminate between conflicting explanations. As already mentioned, the most popular explanation for the variability of the catalytic properties of gold catalysts is the amount of low-coordinated gold sites. The concentration of low-coordinated sites is usually related to the size of gold metallic particles, which in most work is determined by transmission electron microscopy (TEM). When performed accurately, TEM provides a particle size distribution from which a mean size can be derived, but because very small metallic particles (< 1 nm) are barely detectable, the method is not ideally applicable for samples with highly dispersed gold. In these cases, other techniques, such as EXAFS and XANES, can be used to obtain information on the coordination number of gold. But these alternative measurement techniques are not yet in wide use and thus cannot be proposed as routine tests.

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Easier, faster, and less expensive than TEM, chemisorption is a widely used technique, especially in industrial laboratories, for measuring metal particle size in supported catalysts. But despite the increasing attention given to gold-based catalysts over the past 15 years, characterization of supported gold by chemisorption methods has not been as widely investigated as common applications of H<sub>2</sub>, O<sub>2</sub>, CO, and N<sub>2</sub>O chemisorption for characterizing other metals have been. In fact, gold surfaces do not readily chemisorb many molecules. Only few papers have reported O<sub>2</sub> and CO chemisorption on supported gold [2–4]. Recently, the static oxygen adsorption and hydrogen pulse titration of O<sub>2</sub> chemisorbed on Au/Al<sub>2</sub>O<sub>3</sub> have been reported [5] to determine surface area and average particle size, although at an unusual temperature (323–473 K). Margitfalvi et al. [6] attempted to measure CO chemisorption on supported gold catalysts using volumetric equipment. Due to the low sticking coefficient of CO on gold, these authors used an unusually high pressure for the chemisorption measurements. Apart from the long time required for the test, they were faced with problems of physical adsorption. Both inconveniences can be overcome by using the pulse-flow technique, provided that chemisorption is fast enough at the temperature of chemisorption.

In the present work, CO chemisorption by a pulse-flow technique and Fourier transform infrared measurements of adsorbed CO in well-defined and well-controlled conditions of temperature and pressure are proposed as widely accessible and reproducible methods that can be used in both academic and industrial laboratories to determine the concentration of gold active sites and to compare different samples.

## 2. Experimental

Reference catalysts 1.51 wt% Au/TiO<sub>2</sub> and 4.48 wt% Au/Fe<sub>2</sub>O<sub>3</sub>, provided by the World Gold Council, were examined. As reported in the catalyst data sheets of World Gold Council, these catalysts expose gold particles with mean diameter and standard deviation (as determined by TEM) of 3.8 ± 1.5 nm for Au/TiO<sub>2</sub> and of 3.7 ± 0.9 nm for Au/Fe<sub>2</sub>O<sub>3</sub>. Moreover, a 3.0 wt% Au/CeO<sub>2</sub> [7], prepared by deposition–precipitation of gold hydroxide, was studied. High-resolution TEM analysis and EDS measurements were obtained on this sample, and the presence of very small and highly dispersed ca. 1-cm clusters and ca. 10- to 25-nm particles was found (for more details, see the supplementary material).

The supports used as reference were TiO<sub>2</sub> (P-25 Degussa), CeO<sub>2</sub> prepared by precipitation at 333 K of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O with K<sub>2</sub>CO<sub>3</sub> at constant pH (pH = 9), and Fe<sub>2</sub>O<sub>3</sub> prepared by precipitation of Fe(NO<sub>3</sub>)<sub>3</sub> with Na<sub>2</sub>CO<sub>3</sub> at constant pH (pH = 8) at 333 K. After precipitation, the supports were washed, dried at 383 K for 18 h, and finally calcined at 673 K in air for 120 min.

Pulse chemisorption was done using inexpensive homemade equipment. In principle, the system was made of a U-shaped Pyrex reactor equipped with an oven controlled by a PID temperature programmer, mass flowmeters, a sampling valve, a Gow-Mac TCD detector, and a quadrupole mass detector. Before chemisorption, the following standard pretreatment pro-

cedure was applied: the sample (0.2 g) was reduced in H<sub>2</sub> flow (40 ml min<sup>-1</sup>) at 373 K for 60 min, cooled in H<sub>2</sub> 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<sup>-1</sup>) saturated with a proper amount of water. The sample was then cooled in He flow to the temperature chosen for CO chemisorption. Measurements were performed at different temperatures in the 140–180 K range. The chosen temperatures could be easily attained and maintained by simply adding liquid nitrogen to the suitable solvent in a Dewar flask, and thus no cryostatic equipment is required; the 142 K temperature can be attained by a *n*-pentane–liquid nitrogen cryogenic mixture.

FTIR spectra were obtained with a Perkin–Elmer 1760 spectrometer (with an MCT detector) with the samples in self-supporting pellets introduced in a cell allowing thermal treatment in controlled atmosphere and spectrum scanning at controlled temperatures from 120 K up to room temperature. The samples were examined after reduction in H<sub>2</sub> at 373 K, followed by hydration at 298 K. Band integration was carried out by “Curvefit” in Spectra Calc (Galactic Industries). The integrated areas obtained were normalized to the Au content of each sample.

## 3. Results and discussion

The CO pulse chemisorption and spectroscopic experiments were performed on mildly reduced and hydrated samples to avoid CO chemisorption on uncoordinated support ions. CO chemisorption was preliminary investigated in a wide temperature range (77–273 K), and the 140–180 K range was found to be suitable and proper. The results are reported in Table 1. For the two reference samples (Au/TiO<sub>2</sub> and Au/Fe<sub>2</sub>O<sub>3</sub>), the same value of 0.03 mol of CO per mol of total Au was found. On the other hand, measurements performed at lower temperature (i.e., 110 K) resulted in a larger value, whereas at higher temperature (over 190 K), a significant decrease in chemisorbed CO occurred. Preliminary runs carried out on the bare supports in the same experimental conditions showed the absence of CO chemisorption.

FTIR spectra of CO adsorbed on Au/TiO<sub>2</sub> and on Au/Fe<sub>2</sub>O<sub>3</sub> shown in Figs. 1a and 1b confirm that in the 140–180 K range, the chemisorption data are related only to chemisorption on gold. Moreover, in that temperature range, the integrated inten-

Table 1  
Chemisorption and FTIR data on Au/TiO<sub>2</sub>, Au/Fe<sub>2</sub>O<sub>3</sub> and Au/CeO<sub>2</sub> at different temperatures

Temperature (K)	Ratio (mol <sub>CO</sub> /mol <sub>Au</sub> )			Absorption coefficient of CO on Au <sup>0</sup> sites (×10 <sup>4</sup> ) <sup>a</sup>		
	Au/TiO <sub>2</sub>	Au/Fe <sub>2</sub> O <sub>3</sub>	Au/CeO <sub>2</sub>	Au/TiO <sub>2</sub>	Au/Fe <sub>2</sub> O <sub>3</sub>	Au/CeO <sub>2</sub>
142	0.033	0.029	0.081	2.76	2.95	1.33
157	0.033	0.028	0.074	2.66	2.86	1.32
179	0.033	0.028	0.079	2.38	2.57	1.32

<sup>a</sup> Ratio between the integrated area of the band of adsorbed CO per mol of Au<sup>0</sup> ( $I_{\text{int}}/\text{mol}_{\text{Au}}$ ) and the moles of chemisorbed CO per mol Au<sup>0</sup> ( $\text{mol}_{\text{CO}}/\text{mol}_{\text{Au}}$ ).

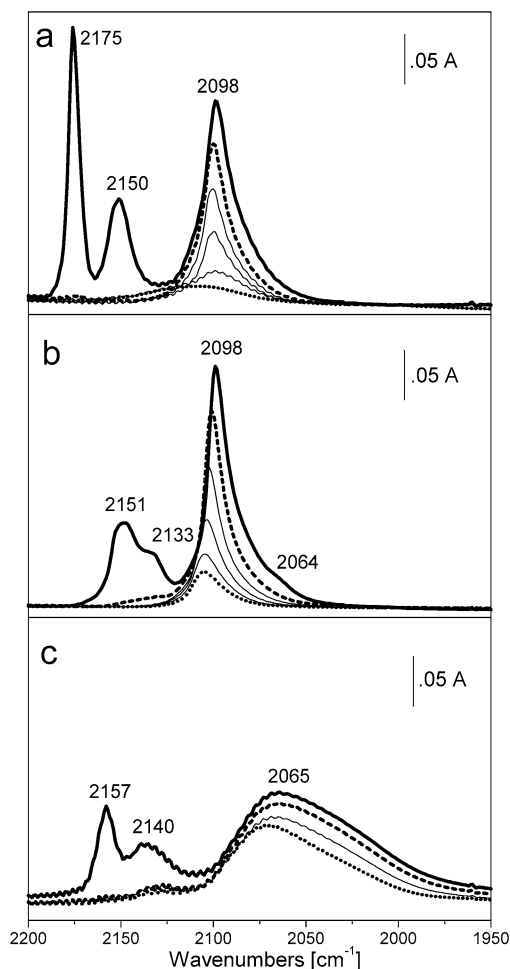


Fig. 1. FTIR spectra of CO adsorbed at 120 K (—), at 180 K (---), at increasing temperature (—) up to r.t. (···) collected on Au/TiO<sub>2</sub> (a), Au/Fe<sub>2</sub>O<sub>3</sub> (b) and Au/CeO<sub>2</sub> (c).

sities of the carbonylic band of CO on Au<sup>0</sup> referred to the moles of Au are very similar for both samples.

CO adsorption on Au/TiO<sub>2</sub> and on Au/Fe<sub>2</sub>O<sub>3</sub> at a lower temperature (120 K) produces the following changes in the FTIR spectra in both cases: a band at 2098 cm<sup>-1</sup> related to CO on Au<sup>0</sup> sites exposed at the surface of the metallic particles [9] and a band at about 2150 cm<sup>-1</sup> due to the interaction of CO and OH groups of the support (denoted by the bold curves in Figs. 1a and 1b). Moreover, at this temperature, residual bands at 2175 cm<sup>-1</sup> for Au/TiO<sub>2</sub> and at 2133 cm<sup>-1</sup> with a weak component at 2064 cm<sup>-1</sup> in the case of Au/Fe<sub>2</sub>O<sub>3</sub> are observed. These bands, which are completely absent at the temperature of the quantitative chemisorption measurements (see dashed curves) and are very weak compared with those reported in the quoted references on nonhydrated samples, have been assigned to CO on the cations of the supports [10,11]. In conclusion, the chemisorbed amount on the two reference catalysts in the 140–180 K range can be taken as a measure of the gold sites able to adsorb CO.

The CO chemisorbed volume per gram of gold is almost three times higher on the Au/CeO<sub>2</sub> sample than on the Au/TiO<sub>2</sub> and Au/Fe<sub>2</sub>O<sub>3</sub> samples. The integrated intensity of the FTIR

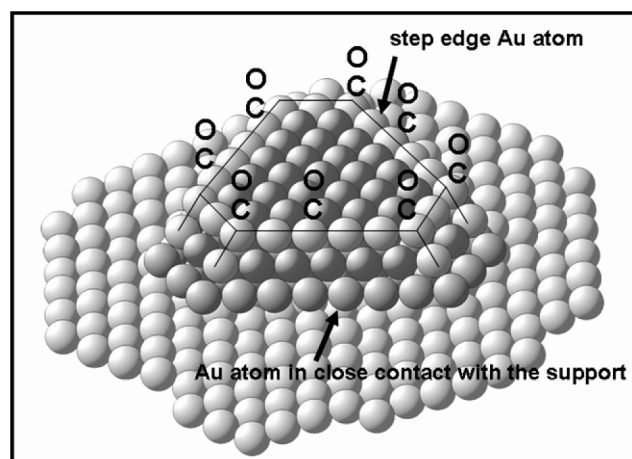


Fig. 2. Wulff-like model of a 3-layer thick Au particle with a mean diameter of 3.8 and 1 nm high.

band is also larger on the former sample than on the latter two samples, but only by a factor of ca. 1.3.

Considering the FTIR data reported in Fig. 1c, for this sample a broad absorption extending from 2100 to 1950 cm<sup>-1</sup>, with a maximum at 2055 cm<sup>-1</sup>, is produced by CO adsorption at 120 K (bold curve). These spectroscopic features are a clear indication that the adsorbing sites are different than those of the reference samples, assigned to CO coordinated with the step sites of the small Au particles. A negligible amount of these sites is expected on the big particles of Au/CeO<sub>2</sub>. The red shift of the band suggests an assignment to small clusters negatively charged as a result of electron transfer from the reduced support [12].

The ratio between the integrated area of the FTIR band of adsorbed CO and the mol of chemisorbed CO, both per mol of Au, was calculated for each sample at different temperatures. The results, including the values of the (molar) absorption coefficients, are given in Table 1. It appears that for gold on ceria, not only the shape and the maximum position of the band, but also the absorption coefficient, are modified.

### 3.1. Considerations for chemisorption stoichiometry

When gold nanoparticles are supported on reducible oxides, they have a flattened shape [13,14]. According to a Wulff-like model, three-layered [15] metal particles with a mean diameter of 3.8 nm and height of 1 nm are assumed in our case, based on TEM data (see Fig. 2). Consequently, as for the two reference samples Au/TiO<sub>2</sub> and Au/Fe<sub>2</sub>O<sub>3</sub>, some considerations about the stoichiometry of chemisorption can be drawn. The ratio between step-edge Au atoms and total Au atoms is estimated as 9.1%, neglecting those atoms in direct contact with the support. Because only the poorly coordinated Au atoms (step-edge atoms) are able to chemisorb CO [8], a mol<sub>CO</sub>/mol<sub>Au</sub> ratio of 0.28–0.31 per step-edge Au atom in the 140–180 K range can be calculated. Thus the chemisorption stoichiometry in such temperature range is approximately 3 Au step-edge atoms every CO. This value may appear rather high compared with the stoichiometries determined for other supported metals

but is in agreement with the recent literature on CO on gold. In fact, Goodman and coworkers, in a recent paper on IRAS studies of CO on the Au(110)-(1 × 2) surface, reported an estimated coverage of 30% at 170 K [16].

Now, in the case of Au/CeO<sub>2</sub>, we cannot refer to the mean particle size to discuss chemisorption stoichiometry, taking into account that this sample has exhibited both very small clusters and quite large particles [7]. The larger chemisorbed volume must be mainly related to the presence of the very small Au clusters, where almost all of the atoms are exposed at the surface, whereas the large particles make no contribution to chemisorption. On such small clusters, all of the surface gold atoms are probably able to chemisorb CO. Through mass spectrometry measurements on selected gold clusters in the gas phase, Wallace et al. [17] and Fielicke et al. [18] observed that in the small Au clusters containing up to 13 atoms, the saturation ratio between CO and Au is close to 1, a much higher value than that found for our reference catalysts (0.03). Looking at the peculiar spectroscopic features of the Au/CeO<sub>2</sub> sample, we can assume an Au/CO ratio of approximately 1:1 for this catalyst. The decreased absorption coefficient determined for this sample (see Table 1) may be correlated with the varying nature of the adsorbing sites (clusters vs. steps) and/or with CO overcrowding [19,20].

### 3.2. Final remarks

Using a pulse-flow system and after proper pretreatment, CO chemisorption at 140–180 K can be an effective method for quantitatively determining gold active sites, particularly for Au/TiO<sub>2</sub> and Au/Fe<sub>2</sub>O<sub>3</sub> samples. We are currently extending this study to other gold catalysts that show similar CO absorption bands, in terms of maximum wavenumber and shape, as those of the reference samples, along with well-defined particle size distributions, to test the further validity of the absorption coefficient presented herein.

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## Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi: 10.1016/j.jcat.2005.11.026.

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