Catalytically active gold sites: nanoparticles, borderline sites, clusters, cations, anions? FTIR spectra analysis of ^{12}CO and of ^{12}CO - ^{13}CO isotopic mixtures

Floriana Vindigni, Maela Manzoli,
Anna Chiorino, Flora Boccuzzi*

Department of Chimica IFM and NIS Centre of Excellence, Università di Torino, via P. Giuria 7, 10125 Turin, Italy e-mail: flora.boccuzzi@unito.it

Abstract

The analysis of FTIR absorption spectra of CO and of ^{12}CO - ^{13}CO isotopic mixtures is reported for gold catalysts supported on a number of oxides. Relationships between the nanostructure and the CO adsorbing properties of the different gold catalysts are discussed. In particular, on titania supported gold, where particles of metallic nature are present, two kinds of surface sites do adsorb CO, the 6-coordinated corners and the 7-coordinated edges, while the terrace sites, 8 coordinated, are not able to adsorb even at 90 K. Moreover, the adsorbing sites are not isolated, but mutually interacting. On zirconia supported gold, the adsorbing sites, mutually interacting, are exposed at the surface of non metallic gold nanoclusters. Almost isolated and negatively charged gold adsorbing nanoclusters have been highlighted on the sample supported on reduced ceria, and, finally, isolated cationic sites on oxidized gold supported on a mixed ceria-titania oxide have been detected.

Keywords: gold, nanoparticles, nanoclusters, IR spectroscopy, ^{12}CO and ^{12}CO - ^{13}CO adsorption

1 Introduction

Gold catalysts are very active in the CO oxidation, in the PROX and in the WGS reaction, therefore they are good candidates for the catalytic production and purification of hydrogen for the fuel cell applications. Experimental and theoretical works suggest that for the PROX reaction the active sites for CO and oxygen activation may be uncoordinated sites of gold nanoparticles. As for the WGS reaction, a recent work on model samples [1] shows that water dissociates on oxygen vacancies of the oxide nanoparticles, in close contact with the gold sites. Moreover, the roles of cationic and anionic Au [2] are widely discussed in the last times. As for the real catalysts, it can be relevant to utilize methods able to test and distinguish the different gold sites exposed at the surface, i.e. step and corner sites on nanoparticles, cationic or anionic nanoclusters, borderline sites between the metal sites and the supports, because all of them can be significant for the different reactions. A detailed analysis of the FTIR spectra of adsorbed CO and of its isotopic mixtures may be very useful in order to have additional information on the nature, structure and on the oxidation state of the gold surface species. Sheppard and Nguyen elegantly demonstrated the correlation that exists between the bonding geometry of adsorbed carbon monoxide on the metals and the wavenumber of the C-O stretching vibrations [3]. They also drew attention to two other factors which can influence this wavenumber, the coexistence of surface atoms having different numbers of nearest neighbours, and the dipolar interaction between adsorbed molecules. These factors are of particular importance in spectra from supported catalysts since coordinatively unsaturated edge and defect sites represent a large proportion of all the available adsorption sites on small particles. Dipolar interactions lead to coverage-dependent values of the wavenumber, since the predominant effect is to couple the vibrations of individual molecules to produce collective oscillations having infrared active modes that exhibit vibrational frequencies higher than the isolated singleton molecule. In subsequent years, these factors have been extensively studied on single crystal substrates. In particular, investigations using stepped surfaces have allowed more controlled studies on the influence exercised by the coordination changing of the surface atom to which a CO molecule is bonded. It has been found that molecules at step sites do indeed exhibit different wavenumbers from those on terrace sites, but that the direction of the shift depends on the nature of the substrate. For example, on copper surfaces step sites give rise to bands $\approx 15\text{ cm}^{-1}$ higher than terrace sites do [4], while on platinum the step site bands are shifted by a similar amount, but in the opposite side [5]. This difference has been rationalised in terms of the relative balance of σ and π bonding of the two surfaces: on both metals, bonding at step sites is stronger than at terrace ones, but on platinum the increased bonding interaction is associated with increased back-donation of metal electrons

Table 1

Assignments of the FTIR absorption bands of CO on gold on different supports and in different experimental conditions

	Exp. cond.	corner sites of np ^a	step sites of np ^a	Neutral nanoclusters ^b	Anionic nanoclusters ^c	Cationic nanoclusters ^d	Refs.
Au/ZnO	90K, r.t.	2106-2118	2090-2110			2147	(7, 8)
Au/TiO ₂	90K, r.t.	2098-2118	2090-2110		1990-2050	2154	(8, 9, 10, 11)
Au/CeO ₂ , Au(La)CeO ₂ Au/doped CeO ₂	90K, r.t.	2100-2118			2020-2080	2130-2160	(12, 13, 14, 15)
Au/ThO ₂	90 K	2098	2087-2097				(16)
Au/Fe ₂ O ₃	r.t.	2100			1990-2050		(17)
Au/ZrO ₂	90K, r.t.	2100	2080-2090	2080-2090		2140	(18, 19)
Au/CeO ₂ -ZrO ₂ Au/CeO ₂ -TiO ₂	90 K, r.t.	2116-2125			2060-2080	2166	(20)

[a, b, c, d: see Figure 5]

into the molecule's $2\pi^*$ orbital, and hence a fall in wavenumber, whereas on copper and gold it is believed that the predominant change is a reduction in the occupancy of the σ orbital, with a concomitant shift to higher wavenumber (6). The observation of bands due to molecules on the two types of site is complicated by dipolar coupling interactions which tend to transfer intensity from low wavenumber bands to their higher wavenumber counterparts. In a number of cases, isotopic mixtures have been used to modify these interactions in order to clarify the vibrational spectra. Up to now, such kind of data are not yet available, nor for cationic and anionic species, nor for nanoclusters.

In this paper we will present a comparative study of ^{12}CO and ^{12}CO – ^{13}CO isotopic mixtures on some different gold catalysts supported on different oxides and mixed oxides differently pretreated. The absorption changes, both in position and shape, observed with the temperature and with the isotopic mixtures composition, will be examined and interpreted. The previous assignments to the adsorption on corner, step, borderline or nanocluster sites in gold nanostructured catalysts will be rediscussed on the basis of these additional data.

2 Experimental

The examined samples have been prepared by the deposition-precipitation method, as reported in the references quoted in Table I, that contains also additional experimental information. The samples that will be examined in detail in this paper have been differently pretreated, in particular Au/TiO₂, Au/CeO₂ and Au/ZrO₂ have been reduced in H₂ at 423 K, while Au/CeO₂-TiO₂, with a

Table 2

Properties of the examined samples

Sample	Au wt%	Surface area BET m ² /g	Au TEM size
Au/TiO ₂	1.51	55	3.8±0.8nm
Au/ZrO ₂	1.94	92	1.6±0.6nm
Au/CeO ₂	3.0	118	Bimodal >10nm and <1nm
Au/CeO ₂ -TiO ₂	3.0	98	≤ 2.0 nm

CeO₂/TiO₂ ratio = 50:50, has been calcined at 673 K. Further specific characterisation data (gold loading, BET surface area and TEM particle sizes) are reported in Table II.

FTIR spectra were taken on a Perkin-Elmer 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). From each spectrum, the background before the inlet of CO was subtracted.

3 Results and discussion

A summary of the main FTIR spectroscopic features determined by CO adsorption on gold sites, taken from the studies made in our laboratory in the last 15 years is shown in Table I. The assignments reported on top of the columns are

made, in many cases, looking at experiments at different temperatures, on differently pretreated samples and at different equilibrium pressures. Moreover, some new data, mainly ^{12}CO – ^{13}CO isotopic mixtures experiments, will be illustrated in the next sections. All these data are taken from spectra run in well controlled conditions, therefore, the positions of the ν_{CO} bands can be taken as evidence of a given oxidation state of supported gold, of the coordination of the gold and of the special structures containing gold sites, i.e. step sites, cationic nanoclusters and anionic nanoclusters, as reported in the references quoted in Table I. These assignments have been made looking at the band intensities by increasing or decreasing the CO equilibrium pressure and by decreasing the temperature, following the band behaviour by interaction with oxygen and looking at the FTIR literature data of CO adsorption on monocrystalline gold [21] or on model gold catalysts [22].

As for the frequency ranges of the bands summarized in the same Table, some overlaps for different species occur. However, the assignments are supported by the specific experimental conditions in which the spectra were run, for example, the assignment to negatively charged nanoclusters can be surely excluded when the CO interaction was performed on oxidized, unreduced samples. Moreover, additional experimental data, particularly the spectra produced by interaction with isotopic ^{12}CO – ^{13}CO mixtures can be very useful.

CO, when used as a probe, can relatively easily reduce gold cations, possibly leading to metallic gold: the problem can be overcome by studying the CO interactions at temperatures as low as 90 K. These experiments are significant, as in the last years the relevance of cationic gold as active sites for CO activation in the WGS reaction has been claimed [22]. The charge state of the gold nanoclusters, a controversial and widely discussed matter, is among the different factors that have been considered: for the discussion we will take into account the very recent theoretical considerations on the C–O vibrational shifts with the charge, made by Bagus and Pacchioni for CO adsorbed on neutral, cationic and anionic gold clusters [23].

3.1 Corner and step sites on metallic nanoparticles

On many gold supported catalysts [7–24] it has been observed that the absorption spectra of CO adsorbed on metallic gold nanoparticles produces a band at 2110 cm^{-1} , showing an asymmetric broadening from the low frequency side. As for an example, the IR absorption spectra produced by adsorption of 10 mbar of CO at room temperature (r.t.) on an Au/TiO₂ sample reduced at 423 K and their evolution by decreasing the pressure are shown in Figure 1a. By reducing the equilibrium pressure, the maximum of the absorption blue shifts up to 2117 cm^{-1} and the integrated intensity gradually decreases. However, the linewidth and the asymmetry from the low frequency side remain still present. Looking at the spectra produced by interaction with

1:1 ^{12}CO – ^{13}CO mixture at different equilibrium pressure on the Au/TiO₂ (Figure 1b), bands at 2096 cm^{-1} and at 2049 cm^{-1} are observed. The 2096 cm^{-1} component, related to the ^{12}CO absorption, is slightly red shifted compared with pure ^{12}CO and significantly stronger than the other one at 2049 cm^{-1} , related to the ^{13}CO absorption. Moreover, the band is also broader and more symmetric than the band of pure ^{12}CO shown in Figure 1a (FWHM = 22 cm^{-1} in the 1:1 ^{12}CO – ^{13}CO mixture in respect to FWHM = 12 cm^{-1} in pure ^{12}CO). These features are highlighted by the curvefits of the spectra taken in 10 mbar of ^{12}CO (Figure 1a, inset) and in 10 mbar of ^{12}CO – ^{13}CO (Figure 1b, inset) with two and four lorentzian bands, respectively.

Looking at the spectra shown in Figure 1, it appears clear that on the gold nanoparticles there are two kinds of adsorbing sites, mutually interacting. At high coverages and in pure ^{12}CO an intensity transfer from the low to the high frequency band occurs, while the coupling is reduced at lower coverages or in the isotopic mixtures. The spectroscopic features quite clearly indicate an high homogeneity of exposed and uncoordinated gold sites. The behaviour is

Figure 1

IR absorption spectra produced by adsorption of 10 mbar of ^{12}CO (section a) and of 1:1 ^{12}CO – ^{13}CO mixture (section b) at decreasing pressure on reduced Au/TiO₂. Inset: Curvefit of spectra taken in 10 mbar of ^{12}CO (section a, black line) and 10 mbar of 1:1 ^{12}CO – ^{13}CO mixture (section b, black line) on reduced Au/TiO₂.

definitely different from the inhomogeneous broadening usually observed on dispersed samples, characterized by structural and chemical heterogeneity in the adsorption sites, not vibrationally coupled. In that case, no shifts are observed by decreasing the coverage, nor intensity transfers from low frequency bands to the high frequency ones at high coverages in isotopic mixtures.

The spectra obtained with isotopic mixtures of different compositions [24] at the same total pressure, show that, by increasing the ^{13}CO content, the band at 2055 - 2049 cm^{-1} grows up and shifts towards high frequency, while at the same time the band at 2100 cm^{-1} shifts towards low frequencies. From these experiments an extrapolated frequency of 2095 cm^{-1} for the ^{12}CO vibrationally decoupled oscillators is obtained. By comparison with the frequency of the same absorption band extrapolated to zero coverage shown in Figure 1a, that is 2117 cm^{-1} , a chemical shift of -21 cm^{-1} is found. These results further show that lateral interactions produce significant effects on the observed spectra.

On the basis of these data, the two components can be assigned to CO adsorbed on two different kinds of uncoordinated sites, closely related, as step and corner sites

exposed on small nanoparticles. This assignment is a revision of the previously proposed one in the oldest papers [8-11], where the 2110-2117 cm^{-1} band was assigned to gold sites exposed on the metal particles and the 2090-2110 cm^{-1} one to gold sites exposed on the contact perimeter with the oxide. The revision is based mainly on the results of combined spectroscopic and volumetric measurements.

3.2 Neutral and negatively charged nanoclusters

Figure 2a and 2b show the behaviour of the CO absorption bands on Au/ZrO_2 reduced at 423 K, initially in contact with 4 mbar of ^{12}CO and ^{12}CO - ^{13}CO 1:1 mixture, respectively, at 90 K and heated up to r.t. in the same atmosphere. The increase of the temperature produces an effect similar to the reduction of the equilibrium pressure, i.e. a decrease of the surface coverage. In Figure 2a, a band centred at 2100 cm^{-1} is evident. The position of the band is similar to that observed on the Au/TiO_2 sample at the maximum coverage, but, in this case, the maximum does not shift by increasing the temperature (decreasing the coverage). The ^{12}CO - ^{13}CO 1:1 mixture interaction on the same sample produces two broader bands, at 2093 and 2046 cm^{-1} , that smoothly shift up by increasing the temperature. A shift of the ^{12}CO mode

Figure 2

IR absorption spectra produced by adsorption of 4 mbar of ^{12}CO (section a) and of 1:1 ^{12}CO - ^{13}CO mixture (section b) at increasing temperatures from 90 K up to r.t. on reduced Au/ZrO_2

Figure 3

IR absorption spectra produced by adsorption of 10 mbar of ^{12}CO (section a) and of 1:1 of ^{12}CO - ^{13}CO mixture (section b) at decreasing pressure on reduced Au/CeO_2

from 2100 cm^{-1} in pure ^{12}CO to 2093 cm^{-1} in the mixture, its intensity higher than that of the ^{13}CO band (2046 cm^{-1}) at the lowest temperatures, becoming more similar by temperature increase, all these features indicate that also on this sample the adsorbed CO are mutually interacting.

Figure 3a and 3b show the behaviour of the CO absorption bands on Au/CeO₂ reduced at 423 K, initially in contact with 10 mbar of ^{12}CO and ^{12}CO – ^{13}CO 1:1 mixture, respectively, at r.t.. The shape, the position of the bands and their evolution by decreasing the gas phase pressure are remarkably different from those reported in Figure 1 and in Figure 2 for the Au/TiO₂ and Au/ZrO₂ samples. On Au/CeO₂ at the maximum ^{12}CO coverage (Figure 3a) a quite broad and significantly red shifted band appears at 2069 cm^{-1} ; while in the isotopic mixture experiment (Figure 3b) the maximum of the band related to ^{12}CO is not shifted at all and two broad absorptions, at 2069 and 2033 cm^{-1} , are evident. By decreasing the pressure, the intensity of both these bands decreases, without changes in their relative intensity.

The spectroscopic features reported in this section suggest that the adsorbing gold sites for the Au/ZrO₂ sample can be gold nanoclusters and, as for the Au/CeO₂, negatively charged nanoclusters, stabilized by the interaction with surface defects as oxygen vacancies and Ce^{x+}.

3.3 Cationic gold sites

Figure 4 shows the FTIR spectra produced by the adsorption of 15 mbar CO at r.t. and at decreasing coverages at the same temperature on Au/CeO₂–TiO₂ (section a, orange curve) and those produced by the interaction with a ^{12}CO – ^{13}CO mixture (section b, orange curve), being the sample previously oxidized at 673 K. Besides the usual bands related to CO on the support and on partially oxidized metallic gold at 2205, 2185 and 2118 cm^{-1} , a broad absorption band at 2166 cm^{-1} is observed in the section a. This band is almost completely irreversible to the outgassing at r.t., giving an evidence of a strong bond (blue curve in Figure 4a).

The spectra of the 1:1 ^{12}CO – ^{13}CO isotopic mixture are shown in section b: In this case, additional bands are detected: a component at 2135 cm^{-1} , quickly depleted by decreasing the CO pressure, assigned to ^{13}CO on Ti⁴⁺ sites (behavior with the pressure similar to that shown by the component at 2185 cm^{-1} , assigned to ^{12}CO on Ti⁴⁺ sites); two components at 2112 cm^{-1} , that is superimposed to an irreversible band, and at 2066 cm^{-1} , that can be assigned respectively to ^{12}CO and ^{13}CO adsorbed on very small gold particles partially oxidized. Finally two bands at 2160 and 2111 cm^{-1} almost completely irreversible to the outgassing and assigned to ^{12}CO and ^{13}CO adsorbed on cationic gold. The small frequency shift respect to the band at 2166 cm^{-1} (section a) and the absence of any intensity difference indicates that the cationic sites are isolated and stabilized on the mixed oxide surface. It is well known that the most stable gold carbonyls are those of the Au⁺ cations. The theoretical work of Bagus and Pacchioni [23] pointed out that the modifications in the CO

Figure 4

IR absorption spectra produced by adsorption of 10 mbar of ^{12}CO (section a) and of 1:1 mixture of ^{12}CO – ^{13}CO (section b) at decreasing pressure on oxidized Au/CeO₂–TiO₂

stretching frequency as a function of the oxidation state of gold are basically determined by two terms, i) the purely electrostatic change in field-dipole interaction (Stark effect); ii) the change in back donation which varies linearly with the net cluster charge. Interestingly, we already observed a band in a similar position showing quite similar features in the same experimental conditions after CO adsorption on gold catalysts supported on ceria modified by the insertion of lanthanum [14]. It can be supposed that the stabilising effect on Au⁺ obtained by the La doping is the same result by mixing the two oxides.

Conclusions

A deep understanding of the relationship between the nanostructure and the physical and chemical properties of gold catalysts has been attained by the analysis of FTIR absorption spectra of CO isotopic mixtures. Looking also at the previously illustrated data, at the microstructural characterizations reported in the quoted papers, at the quantitative CO chemisorption results [25, 26, 19], and at the

spectroscopic features summarized in Table I, it can be concluded that:

- Two kinds of mutually interacting sites, (corner and edge sites), are the adsorption sites of CO on the gold metallic particles, with sizes of 3-4 nm.
- Sites, mutually interacting, exposed at the surface of neutral, non metallic nanoclusters are the adsorbing gold sites on highly dispersed gold on unreducible oxides, as zirconia, previously shown ($d = 1.6$ nm).
- Almost isolated and negatively charged are the gold adsorbing sites exposed on reducible oxides, as the reduced ceria previously shown.
- Cationic and isolated gold sites, irreversibly adsorbing CO up to 373 K, are stable on doped ceria or on mixed oxides containing ceria, as oxidized $\text{Au/CeO}_2\text{-TiO}_2$, previously shown.

These four different surface structures are shown schematically in Figure 5.

Figure 5

Scheme of the different CO adsorbing gold sites

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About the authors

Floriana Vindigni has taken her PhD in the Department of Chimica IFM at the Università di Torino in the field of Physical Chemistry. The research work is focused on the characterisation, by spectroscopic methods of nanostructured solid materials for catalytic application. Particularly her interest is devoted to the study of gold catalysts supported on different oxides for the hydrogen production and purification.

Maela Manzoli is a Research Technician in the Department of Chimica IFM and in the NIS Centre of Excellence at the Università di Torino. She has experience in the spectroscopic characterisation of metal nanoparticles supported on oxidic systems for catalytic application. In addition, she developed her skills in the characterisation of nanostructured materials by high resolution electron microscopy.

Anna Chiorino is Associate Professor of Physical Chemistry at the Università di Torino. She does research in the Department of Chimica IFM and in the NIS Centre of Excellence on surface properties and surface reactivity of nanostructured solid materials for catalytic application, mainly by spectroscopic methods, FTIR in particular, together with surface texture characterizations and with gas phase analysis.

Flora Boccuzzi is full Professor of Physical Chemistry at the Università di Torino. She does research in the Department of Chimica IFM and in the NIS Centre of Excellence. She works in the fields of Solid State Chemistry and Catalysis. Recently her scientific interest has been focused on the relationships between the surface structure and reactivity of gold supported on different oxides by the combined use of different techniques, in collaboration with different national and international institutions and universities.

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