

# Use of iron pentacarbonyl as a novel probe for the characterization of gold supported on silica

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## Abstract

Iron pentacarbonyl has been used as a novel probe molecule in investigations of the surface state of gold Au/SiO<sub>2</sub> solids prepared by means of sol–gel procedures. The use of in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) reveals that there is a strong interaction between Fe(CO)<sub>5</sub> and the Au centers. The adsorption of Fe(CO)<sub>5</sub> on a reduced Au/SiO<sub>2</sub> sample is characterized by IR absorption bands at 2013 and 2032 cm<sup>-1</sup>. With an oxidized sample, two additional bands at 2026 and 2040 cm<sup>-1</sup> are seen, attributed to the between Fe(CO)<sub>5</sub> and oxidic gold sites. The results of density functional theory (DFT) calculations support the assignments of the IR absorption bands.

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## 1. Introduction

Gold is attracting increasing attention as a catalyst in many reactions [1–3], particularly since the successful preparation of very small supported gold clusters by Haruta et al. [4]. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has been used to investigate the properties of gold species on surfaces [5,6], and has value in assisting with the understanding of catalytic processes [7–9] and in identifying surface species present on metal catalysts [9,10]. Sometimes the adsorption of carbon monoxide on gold is relatively weak and DRIFTS signals due to adsorbed CO can be insufficiently intense for practical application of the method. This is true of some silica sup-

ported gold samples. Yet the Au/SiO<sub>2</sub> system is of special interest in that it promises to provide a base case situation for studying the effects that addition of promoter elements exert on the chemisorptive and catalytic properties of gold. In environmental catalysis, the conversion of carbon monoxide features strongly, for example in the total oxidation of CO from partial combustion of hydrocarbons [11], or in the water gas shift reaction, which shows promise for hydrogen clean-up in fuel cell applications [11]. We have now found that the surface chemistry of gold supported on silica can be revealed using DRIFTS by using iron pentacarbonyl as an IR active probe in those situations where IR data cannot readily be obtained using CO. The IR absorption bands associated with Fe(CO)<sub>5</sub> adsorbed on gold silica samples are far more intense than those attributable to adsorbed CO [12]. Moreover, we have found that the positions of such bands are sensitive to the degree of oxidation of the gold present at

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the surface. In this contribution,  $\text{Fe}(\text{CO})_5$  is used as a molecular probe of supported gold species and, in addition, density functional theory (DFT) calculations were used to support the assignment of observed IR absorption bands.

## 2. Experimental

The  $\text{Au}/\text{SiO}_2$  samples were synthesized by means of a sol–gel method with tetraethoxysilicon (TEOS) and chloroauric acid ( $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ ) providing the source of silica and gold, respectively. Briefly, the chloroauric acid solution was mixed with ethanol and the TEOS added dropwise to this solution with vigorous stirring (TEOS:ethanol:water mole ratio = 1:3.8:0.5). The mixture was stirred for a further 24 h at room temperature and then aged for a further 24 h. The resulting gel was dried in air at  $110^\circ\text{C}$  for 24 h. The samples contained 5 mass% Au. Gold-free silica samples were prepared in an analogous manner with omission of the chloroauric acid.

Diffuse reflectance spectra were recorded using a Nicolet Impact 420 IR spectrometer equipped with a diffuse reflectance unit and a reaction cell, at a spectral resolution of  $4\text{ cm}^{-1}$  using a total of 1024

scans per spectrum. Samples were pretreated in situ at  $300^\circ\text{C}$  in either hydrogen or oxygen for 2 h. The pretreatment gas was then replaced by nitrogen and the sample cooled to room temperature. The background spectrum of the sample was recorded prior to adsorption studies which were carried out by injecting a known aliquot of  $\text{Fe}(\text{CO})_5$  into the nitrogen gas in the cell. Spectra were recorded after a period of about 10 min had elapsed and the pressure of nitrogen subsequently adjusted in the range 200–400 kPa.

## 3. Results and discussion

Fig. 1 depicts spectra resulting from the adsorption of  $\text{Fe}(\text{CO})_5$  at room temperature on  $\text{Au}/\text{SiO}_2$ , pretreated in  $\text{H}_2$ . The figure shows the evolution of the spectral features due to adsorbed  $\text{Fe}(\text{CO})_5$ . Two bands at 2032 and 2013  $\text{cm}^{-1}$  were observed for this reduced sample. No bands were observed in the case of using a gold-free silica sample and so the bands observed are attributed to adsorption of  $\text{Fe}(\text{CO})_5$  on gold sites. The bands associated with  $\text{Fe}(\text{CO})_5$  adsorbed on gold exhibit a large blue shift in comparison with bands due to free  $\text{Fe}(\text{CO})_5$  which lie at 1992 and 2018  $\text{cm}^{-1}$ . There

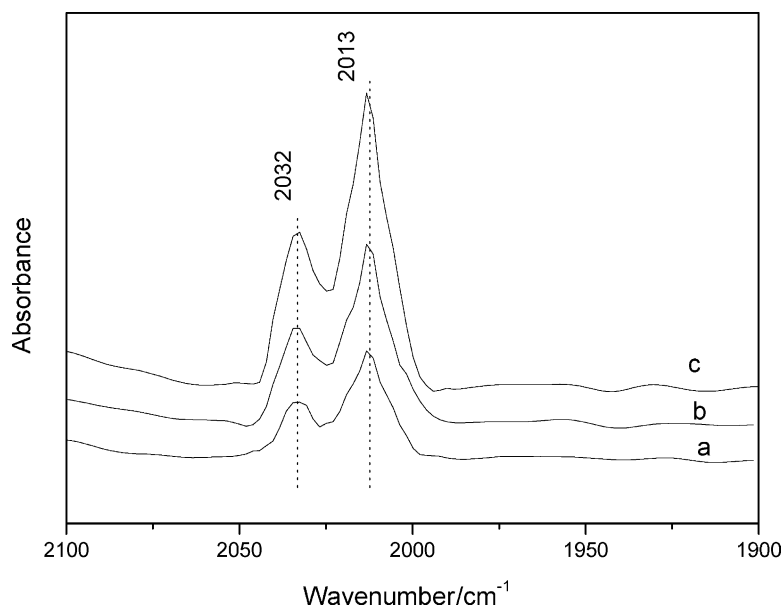


Fig. 1. Room-temperature IR spectra after adsorption of  $\text{Fe}(\text{CO})_5$  on reduced  $\text{Au}/\text{SiO}_2$  sample at (a) 200 kPa, (b) 300 kPa and (c) 400 kPa.

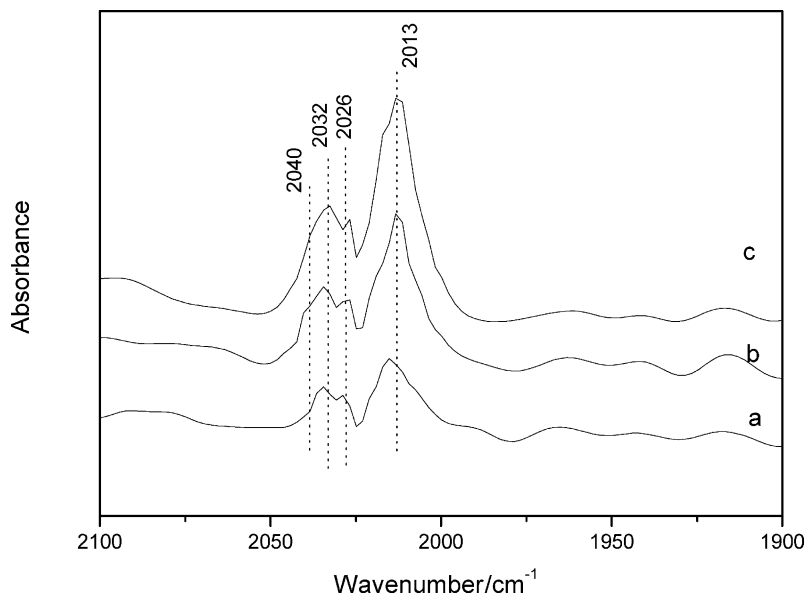


Fig. 2. Room-temperature IR spectra after adsorption of  $\text{Fe}(\text{CO})_5$  on oxidized  $\text{Au}/\text{SiO}_2$  sample at (a) 200 kPa, (b) 300 kPa and (c) 400 kPa.

is therefore a strong interaction between  $\text{Fe}(\text{CO})_5$  and surface gold. The DRIFTS spectra of  $\text{Fe}(\text{CO})_5$  adsorbed on oxidized  $\text{Au}/\text{SiO}_2$  are depicted in Fig. 2 which reveals four intense bands at 2013, 2026, 2032 and  $2040\text{ cm}^{-1}$ . According to our XRD data small crystallites of gold are present in  $\text{Au}/\text{SiO}_2$  samples, even after drying at  $110^\circ\text{C}$ . The bands at 2013 and  $2032\text{ cm}^{-1}$  are assigned to  $\text{Fe}(\text{CO})_5$  adsorbed on  $\text{Au}^0$  sites; those at 2026 and  $2040\text{ cm}^{-1}$  were not found on the reduced sample (Fig. 1) and are assigned to  $\text{Au}^{\delta+}$  sites.

In order to support the IR assignments for  $\text{Fe}(\text{CO})_5$  interacting with Au a DFT study was performed, with calculations being carried out at the B3LYP level with LanL2DZ basis sets by Gaussian 98 [13]. The point group  $\text{C}_{4v}$  was used throughout and the results are listed in Table 1.

The results of IR absorption band frequencies show that IR peaks for  $\text{Fe}(\text{CO})_5$  at  $1973\text{ cm}^{-1}$  (E) and  $1986\text{ cm}^{-1}$  (A1), close to those observed experimentally. When an Au atom was attached to the Fe atom, the length of the CxOx bond (the bond which is collinear with the Au–Fe bond) was shortened slightly from 117.3 to 117.0 pm. The IR vibrational mode A1 that is associated with the CxOx group does

not change in position. However, the bond lengths of the CpOp groups (those which do not have C–O bonds lying collinear with the Au–Fe bond) were shortened from 117.4 to 116.9 pm and this results in a blue shift of the frequency of the E mode vibration of  $27\text{ cm}^{-1}$ . Therefore, there are still two IR active vibrational modes in the Au– $\text{Fe}(\text{CO})_5$  unit but the frequencies are expected at 1987 and  $2000\text{ cm}^{-1}$ , i.e. blue shifted with respect to the bands seen for free  $\text{Fe}(\text{CO})_5$ . This finding agrees with our experimental observations. When an  $\text{Au}^+$  ion is used instead of the  $\text{Au}^0$  atom, calculations suggest that the Au– $\text{Fe}(\text{CO})_5$  interaction is significantly stronger. The lengths of all CO bonds were shortened to 115.8–115.9 pm, similar to the bond length of free CO, which is 115.6 pm at this level of calculation. This shortening of the CO bonds gives rise to a further blue shift of the IR active bands associated with the  $\text{Fe}(\text{CO})_5$  unit. The frequency of the E vibrational mode is shifted to  $2072\text{ cm}^{-1}$  and that of the A1 vibrational mode to  $2083\text{ cm}^{-1}$ , i.e. a blue shift of almost  $100\text{ cm}^{-1}$  with respect to the situation found with free  $\text{Fe}(\text{CO})_5$ . Such calculations show that a positive charge on the Au center may be expected to lead to such blue shifts and the model is qualitatively consistent with our IR

Table 1  
Optimized structure and frequencies analysis of Au-coordinated Fe(CO)<sub>5</sub>

	Fe(CO) <sub>5</sub>		Au–Fe(CO) <sub>5</sub>		Au <sup>+</sup> –Fe(CO) <sub>5</sub>	
Bond length (pm)						
Fe–Au	–		279.4		253.4	
Fe–Cx <sup>a</sup>	180.3		185.7		183.8	
Cx–Ox <sup>a</sup>	117.3		117.0		115.8	
Fe–Cp <sup>b</sup>	181.2		184.2		186.0	
Cp–Op <sup>b</sup>	117.4		116.9		115.9	
Total atomic charge						
Au	–		–0.20		0.36	
Fe	–0.01		–0.84		–1.14	
Cx	0.15		0.26		0.32	
Ox	–0.13		–0.12		–0.02	
Cp	0.13		0.33		0.40	
Op	–0.11		–0.10		–0.03	
	Frequency	IR intensity	Frequency	IR intensity	Frequency	IR intensity
Frequencies analysis (cm <sup>–1</sup> )						
E: Cp–Op	1973	1476	2000	1124	2072	837
B2: Cp–Op	1978	0	2003	0	2079	0
A1: Cx–Ox	1986	916	1987	549	2083	266
A1: Cx–Ox	2067	1	2059	145	2120	319

<sup>a</sup> Cx, Ox: the C and O atoms of the CO group collinear with the Au–Fe bond.

<sup>b</sup> Cp, Op: other C and O atoms.

data on adsorbed Fe(CO)<sub>5</sub>. In the oxidized Au/SiO<sub>2</sub> solids, the gold might exist in the form of surface gold oxide or at least in the form of Au surrounding by oxide ions. The presence of these oxide ions might weaken the interaction between the ionic gold and the Fe(CO)<sub>5</sub> relative to the situation expected for Fe(CO)<sub>5</sub> interacting with a naked Au<sup>+</sup> ion, consistent with the ca. 8 cm<sup>–1</sup> blue shift seen when comparing spectra for reduced and oxidized gold/SiO<sub>2</sub> samples.

In summary, Fe(CO)<sub>5</sub> is a useful novel molecular probe for studying supported gold systems, and may also find use in other situations where CO adsorption is too weak or where the concentration of adsorbing centers is too low to permit direct observation of IR bands due to adsorbed CO alone. It might be of value to extend the method to other metal carbonyls capable of rendering adsorption sites visible by means of infrared spectroscopy. We acknowledge that the method will be more useful once the detailed mode of interaction between such metal carbonyls and gold surfaces is better understood. Attempts at arriving at an improved understanding are now receiving our attention.

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