Catalysis Letters 47 (1997) 273–276

FT-IR study of Au / Fe_2O_3 catalysts for CO oxidation at low temperature

S. Minicò [a], S. Scirè [b], C. Crisafulli [b], A.M. Visco [a] and S. Galvagno [a]

[a] *Dipartimento di Chimica Industriale, Università di Messina, Salita Sperone 31,*
I-98166 Messina, Italy
[b] *Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6,*
I-95125 Catania, Italy

Received 7 May 1997; accepted 17 July 1997

Coprecipitated Au / Fe_2O_3 catalysts used for low-temperature catalytic oxidation of carbon monoxide have been studied by FT-IR spectroscopy of adsorbed CO. The FT-IR results have shown that after preparation and exposure to a CO / O_2 mixture gold is present on the surface mainly as Au^{1+} and Au^0 species. It has been found that in the CO oxidation Au^{1+} is more active and less stable than Au^0.

Keywords: CO oxidation, gold, FT-IR spectroscopy

1. Introduction

CO oxidation at room temperature is obtaining growing attention due to some important practical applications, such as CO and O_2 recombination in close-cycle CO_2 lasers and CO abatement in air purification systems [1,2].

Gold is generally considered a poor catalyst due to its chemical inertness. However, more recently it has been reported that metallic gold highly dispersed on metal oxides can present a remarkable activity towards low-temperature CO oxidation [3–8]. Among the systems investigated, Au / Fe_2O_3 has been found to be one of the most active. However, a comparison of the literature data shows that the catalytic activity is strongly affected by the preparation method and the pretreatment conditions used [3–5,9].

Haruta et al. have suggested that the active species is made of small metallic gold particles [3,4], whereas more recently some authors [9,10] have proposed that unreduced gold species, stabilized by an interaction with the support, are more active than Au^0.

In this paper we report an FT-IR study of CO adsorbed on coprecipitated Au / Fe_2O_3 samples in order to identify the active species responsible for CO oxidation.

2. Experimental

Au / Fe_2O_3 catalysts were prepared by coprecipitation from $HAuCl_4$ (Fluka) and $Fe(NO_3)_3 \cdot 9H_2O$ (Fluka). An aqueous mixture of the precursors was poured at 7.5 ml / min rate into an aqueous solution of Na_2CO_3 (1 M and pH = 11.9) under vigorous stirring (500 rpm); the precipitation temperature was maintained at 75°C.

The coprecipitated samples obtained were kept digesting for about 24 h, washed several times with hot water, then dried under vacuum at 80°C for three days and finally ground before use. A detailed Mössbauer investigation has shown that under these conditions iron is obtained as hematite and/or ferrihydrite [11]. Moreover, the X-ray analysis has shown that all samples reported in this paper are amorphous.

The Au content in the catalysts used in this work, measured by a spectrophotometric method at $\lambda = 400$ nm, is: sample AF560 = 5.6 wt% Au, sample AF626 = 6.26 wt% Au, sample AF968 = 9.68 wt% Au.

Catalytic activity tests were performed in a continuous-flow fixed-bed microreactor filled with catalyst (100–200 mesh) diluted with an inert glass powder. Ultra-high purity (99.99%) mixtures of CO / He (10 vol% of CO), O_2 / He / Ne (10 vol%) of O_2 and 2 vol% of Ne), as well as pure He were used as reactants. Ne was used as an internal standard. Before the catalytic tests the samples were pretreated by flowing a O_2 / He / Ne stream at room temperature for 30 min and subsequently a He stream for 30 min. The reaction mixture (3.3 vol% of CO and 1.6 vol% of O_2 diluted with He) was then admitted on the catalyst.

The effluent gases were analyzed by a gas chromatograph using a packed column of Carboxen 1000 (Supelco) and a thermal conductivity detector.

For IR studies the powdered samples were compressed (using a pressure of 15×10^3 bar) into thin self-supporting discs of about 25 mg cm^{-2} and 0.1 mm thick. The disc was placed in an IR cell which allows thermal treatments in vacuum or in a controlled atmosphere. In the cell all the samples were evacuated at room temperature for three hours before the admission of the adsorbate (CO or CO/O_2 mixture).

The FT-IR spectra were recorded with a Perkin-Elmer system 2000 FT-IR spectrophotometer with a resolution of 2 cm^{-1} equipped with a MCT detector. Data are reported as difference spectra obtained by subtracting the spectrum of the sample before the admission of the adsorbate and are normalized to the same amount of catalyst per cm^2.

3. Results and discussion

Figure 1 shows the FT-IR spectra, recorded at increasing exposure time, after admission of 16 mbar of a mixture of CO and O_2 (CO/O_2 = 0.5) on the AF626 sample. The spectrum (a) (recorded after 10 min) exhibits an intense band at 2159 cm^{-1} and a shoulder at about 2138 cm^{-1}. The high-frequency band (HF) at 2159 cm^{-1} can be attributed to CO adsorbed on Au^{1+} species. This is in agreement with Qiu et al. [12] who assigned this band, observed on a Au/ZSM5 sample, to CO adsorbed on Au^{1+} located on the external surface of the zeolite. A band at 2162 cm^{-1} has been also reported [13,14] in the case of Au(I)COCl complexes in CH_2Cl_2 solution. A band at 2154 cm^{-1} has been observed by Boccuzzi et al. [15] on Au/TiO_2 and attributed to CO adsorbed on isolated and to some extent positivized gold sites.

The shoulder observed at 2138 cm^{-1} can be assigned to CO adsorbed on gold metal atoms directly bonded to adsorbed oxygen [16].

In the range 2000–2200 cm^{-1} no bands of adsorbed CO were observed on the Fe_2O_3 support. Spectra b–d of figure 1, recorded at different exposure times, show that the intensity of the HF band (2159 cm^{-1}) decreases continuously as a function of time, whereas the intensity of the 2138 cm^{-1} band correspondingly increases. One hour after admission of the CO/O_2 mixture (spectrum d) the two bands present a comparable intensity. This behaviour indicates that the Au^{1+} species is progressively reduced when the CO/O_2 mixture remains in contact with the catalyst. The appearance (upper right window of figure 1) of a band at about 2340 cm^{-1}, which progressively increases as a function of time, indicates the formation of CO_2.

Previous investigations carried out on Au/Fe_2O_3 samples obtained by a preparation procedure similar to that used in this work and treated at low temperature (< 100°C) have shown that gold is present as metallic gold and Au(III) compounds [4,17]. The ratio Au^0/Au(III) is dependent on subtle variations in the preparation method. The absence in our spectra of a band of CO adsorbed on Au^{3+} is likely related to the instability of these species which are readily reduced in the presence of CO even at room temperature. The reductive carbonylation of anhydrous $AuCl_3$ to Au(CO)Cl in thionyl chloride has been reported by Belli Dell'Amico et al. [18].

In figure 2 are reported the FT-IR spectra recorded on the AF626 sample at different CO/O_2 ratios. The CO/O_2 ratio was changed by introducing pulses of CO and recording the spectrum after 10 min. It is possible to observe that increasing the CO/O_2 ratio the band at

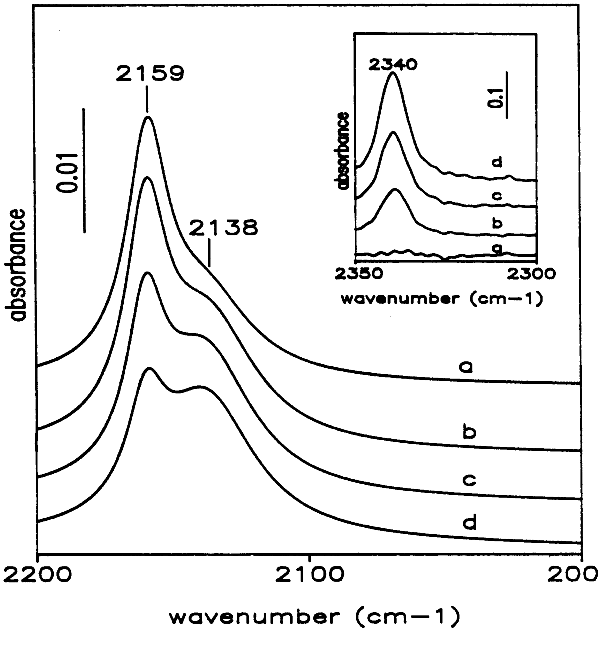

Figure 1. FT-IR spectra recorded 10 min (a), 20 min (b), 30 min (c) and 1 h (d) after admission of 16 mbar of CO/O_2 (CO/O_2 = 0.5) on the AF626 sample.

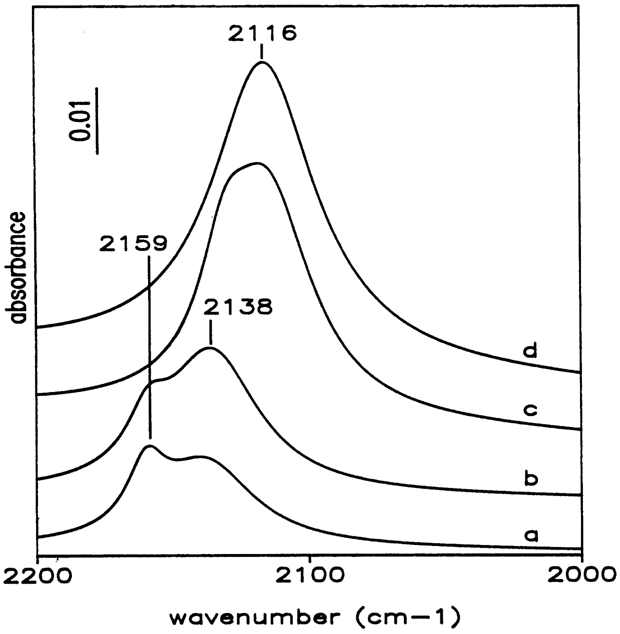

Figure 2. Influence of addition of CO pulses on the FT-IR spectra recorded on the AF626 sample. (a) CO/O_2 = 0.5, spectrum "d" of figure 1; (b) after addition of 7 mbar of CO; (c) after addition of 14 mbar of CO; (d) after addition of 21 mbar of CO.

2159 cm^{-1} gradually decreases in intensity whereas the 2138 cm^{-1} band becomes more intense and then shifts at lower frequency down to 2116 cm^{-1}. According to literature data [4,7,19] the band at 2116 cm^{-1} can be attributed to CO adsorbed on reduced gold metal particles (Au^0). The behaviour shown in figure 2 suggests that a CO/O_2 ratio higher than the stoichiometric one, leads at first to a progressive reduction of the Au^{1+} (gold oxide/hydroxide species) to metallic gold (disappearance of the band at 2159 cm^{-1}) and then to the consumption of the oxygen atoms chemisorbed on the metallic gold. When all the oxygen has been consumed only the band of CO adsorbed on metallic gold is observed. It is noteworthy that evacuation at room temperature (or treatment in oxygen up to 300°C) of the sample used to record spectrum d of figure 2 and subsequent readmission of the CO/O_2 mixture causes the re-appearance of the band at 2138 cm^{-1}, whereas the 2159 cm^{-1} band is no more detected. This indicates that the reduction of Au is an irreversible process.

The contact of CO (20 mbar) with a fresh AF626 sample, in the absence of O_2, produces already after few minutes only the band at 2116 cm^{-1}. In this case, just recording the spectrum immediately (a few seconds) after the admission of CO it is possible to observe the band at 2138 cm^{-1} with a shoulder at 2159 cm^{-1}.

On the other gold samples studied in this work (AF560 and AF968) the FT-IR spectra recorded after admission of the CO/O_2 mixture show the presence of the same bands as observed on the AF626 sample. However, the stability of the band at 2159 cm^{-1} was found to depend on the catalyst sample investigated. In figures 3 and 4 are reported the spectra recorded on all the Au/Fe_2O_3 samples after 10 min (figure 3) and after 1 h (figure 4) from admission of the CO/O_2 mixture. It can be noted that the ratio between the intensity of the 2159 cm^{-1} and the 2138 cm^{-1} bands is in the order AF626 > AF560 > AF968. This suggests that the stability of the oxidized Au^{1+} species in the coprecipitated Au/Fe_2O_3 samples follows the same order.

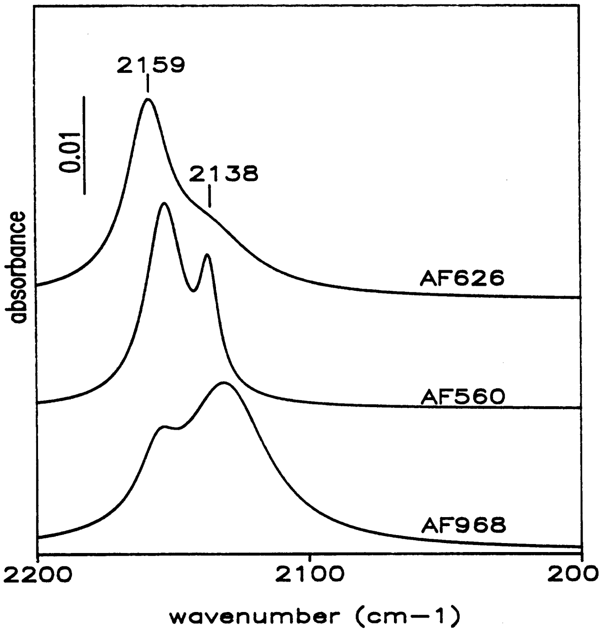

Figure 3. FT-IR spectra of the Au/Fe_2O_3 samples recorded after 10 min exposure to 16 mbar of CO/O_2 (CO/O_2 = 0.5).

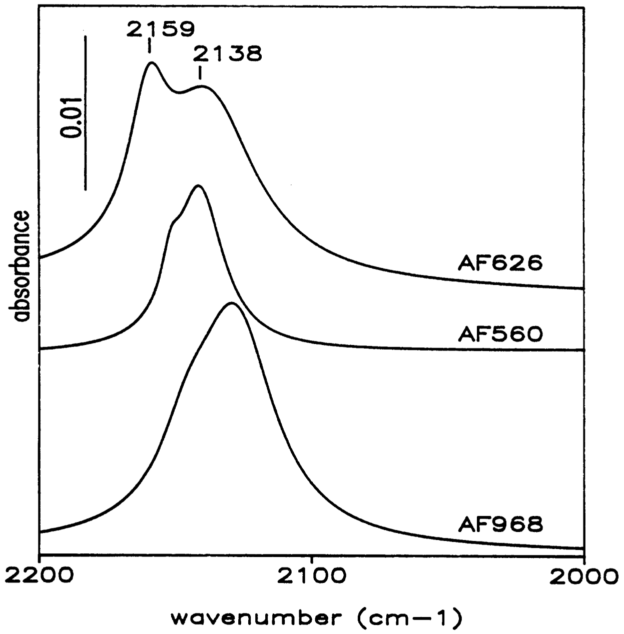

Figure 4. FT-IR spectra of the Au/Fe_2O_3 samples recorded after 1 h exposure to 16 mbar of CO/O_2 (CO/O_2 = 0.5).

Figure 5 shows the catalytic activity towards the oxidation of CO of the investigated Au/Fe_2O_3 samples. The rate of reaction, measured at 20°C as a function of time of stream (CO/O_2 = 2), is expressed as rate of CO_2

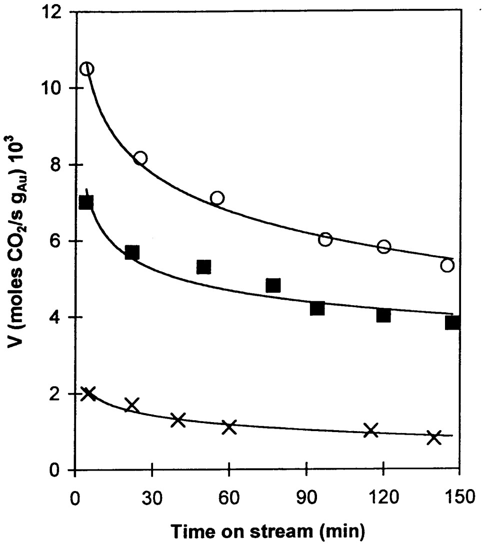

Figure 5. Rate of CO_2 production, V, in CO oxidation at 20°C (CO/O_2 = 2) as a function of time on stream. (○) AF626 sample; (■) AF560 sample; (×) AF968 sample.

formation per second and per gram of gold. It is possible to observe that the AF626 sample exhibits the highest initial catalytic activity. It can be also noted that the activity of all samples decreases with time on stream. The sample with the highest amount of gold (AF968) is the least active among the three samples investigated.

A comparison of the catalytic activity data with the FT-IR results seems to suggest that the unreduced gold species (Au^{1+}) formed just after exposure to CO are more active than metallic gold. On the AF626 sample, which presents the highest initial activity, FT-IR spectra have in fact revealed the highest percentage of Au^{1+} species.

A further confirmation of this hypothesis comes from the deactivation behaviour of our samples. As observed in figure 5 the activity of all samples decreases with time on stream with a concomitant decrease of the band at 2159 cm^{-1} assigned to Au^{1+}. The deactivation appears to be irreversible. It is not possible, in fact, to restore the initial activity of the catalysts. Analogously FT-IR results have shown that Au^{1+} species tend to be irreversibly reduced to a more stable Au^0 species.

4. Conclusions

On the basis of the catalytic activity results and the FT-IR data reported in this work the following conclusions can be drawn:

(a) Au/Fe$_2$O$_3$ catalysts prepared by coprecipitation present a high activity towards CO oxidation at low temperature.

(b) Exposure of the catalysts to a CO/O$_2$ mixture leads to the formation of Au^{1+} and Au^0 species.

(c) Au^{1+} species are more active towards the CO oxidation than Au^0. However, Au^{1+} is not stable and tends to be irreversibly reduced to Au^0 during the reaction, accounting for the irreversible deactivation observed.

(d) In order to prepare active and stable gold catalysts for CO oxidation the stabilization of Au^{1+} species on the support should be required.

Acknowledgement

This work has been carried out with the financial support of CNR and MURST.

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