# Influence of Water Vapour on Low-temperature CO Oxidation over Au/Fe$_2$O$_3$ Catalyst

## Goran Šmit,[a,*] Károly Lázár,[b] and Menno W. J. Crajé[c]

[a]*Department of Chemistry, J. J. Strossmayer University of Osijek, Croatia*

[b]*Institute of Isotope and Surface Chemistry, P.O. Box 77, CRC H-1525, Budapest, Hungary*

[c]*Interfacultair Reactor Instituut, Delft University of Technology, Mekelweg 15, 2629 JB, Delft, The Netherlands*

Influence of water vapour on the activity of Au/Fe$_2$O$_3$ catalyst was tested in the reaction of low-temperature CO oxidation. Addition of water vapour had a positive influence in the temperature range from 303 K to 383 K. *In situ* DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) and FT-IR measurements in a vacuum showed the importance of water and –OH groups, as water-derived species, for the efficiency of the catalyst in low-temperature oxidation of CO.

## INTRODUCTION

In most cases, practical application of low-temperature ($T$ < 373 K) CO oxidation demands high activity of catalysts also in wet conditions. Different influences of water vapour or moisture on the activity of supported gold catalysts were observed: from the positive effect on Au/Fe$_2$O$_3$, Au/Co$_3$O$_4$, Au/NiO, Au/TiO$_2$, Au/Al$_2$O$_3$ and Au/Mg(OH)$_2$[1–4] to none or even negative one on Au/Fe(OH)$_3$, Au/Ti(OH)$_4$ and Au/TiO$_2$.[5,6] Explanations were very different for all these examples as well as for Au/Fe$_2$O$_3$. In one case, positive effect was caused by water, which prevented reduction of oxidized gold to less active metallic gold,[2] and in another case it was because of –OH groups which decreased gold agglomeration.[7] These conditions are achievable through different pre-treatments and/or reaction conditions. In this work, investigations were conducted by DRIFTS in the reaction conditions involving addition of water vapour to reaction gases and by FT-IR in vacuum with a wet catalyst.

## EXPERIMENTAL

### Catalyst Preparation

A sample of pure magnetite[8] was prepared by adding a stoichiometric mixture of Fe$^{II}$- (FeSO$_4$ · 7 H$_2$O, Kemika) and Fe$^{III}$-ions (FeCl$_3$ · 6 H$_2$O, Riedel-de Haën) at a ratio 1:2 into 0.7 M NH$_4$OH containing citric acid trisodium salt (Kemika). The mixture was vigorously stirred (1500 rotations per minute) at room temperature for 30 minutes (pH = 9.79, pH meter Mettler Toledo MP-220). Finally, the solid was separated and washed twice, dried at 323 K, ground and heated at 433 K for 4 hours.

* Author to whom correspondence should be addressed. (E-mail: gsmit@ffos.hr)

Thus prepared magnetite was immersed into a mixture of 0.05 M HAuCl$_4$ · 3 H$_2$O (Sigma) and 1 M NH$_4$OH (Kemika) with the gold loading of 2 % (*w*) and pH = 11.44. After 1 hour at room temperature, the solid was separated (pH = 11.30), washed and heated at 433 K for 4 hours.

### Characterization

[57]Fe Mössbauer spectrum was recorded at room temperature with a conventional KFKI spectrometer operated in a constant acceleration mode. The isomer shifts data were referred to metallic α-iron as a standard. The accuracy of positional parameters was ±0.03 mm s$^{-1}$ and the spectrum was decomposed to Lorentzian shape lines.

[197]Au Mössbauer experiment was performed with sources made by irradiation with thermal neutrons of Pt powder, enriched in [196]Pt to 97 %. Both source and absorber were cooled to temperature of 4.2 K (liquid helium). The spectrum was recorded using a high purity germanium detector in 1024 channels for a complete period of the sinus and then folded to 512 channels to remove the background. Calibration of the spectrum was done by recording a spectrum of SNP (sodium nitroprusside) using a [57]Co:Rh source and the velocity was reported relative to the centre of that spectrum.

### Catalytic Measurements

Catalytic activities were measured in a DRIFTS cell (Harrick) at atmospheric pressure using 0.08 g of catalyst. Composition of inlet gases ($\varphi$(CO) = 2 % in air) was manipulated with a computer controlled gas blender with 80 cm$^3$ min$^{-1}$ passing through the catalyst bed (space velocity, SV = 60 000 cm$^3$ g$_{(CAT.)}^{-1}$ h$^{-1}$). 2.7 % ($\varphi$) of water was injected with a syringe pump (Razel) and then evaporated by heating. Effluent gases were analyzed using a quadrupole mass spectrometer (QMS 311, Balzers). Before catalytic tests, the prepared catalyst was pre-treated by heating in a stream of air (80 cm$^3$ min$^{-1}$) for 2 hours at 673 K.

### In situ *DRIFTS*

*In situ* DRIFTS experiments were conducted at the same time as catalytic measurements using a Perkin-Elmer 1750 FT-IR fitted with an MCT detector. The DRIFTS cell was equipped with CaF$_2$ windows and a heating cartridge controlled by REX-P200. The spectra were recorded at different reaction temperatures by accumulating 200 scans and employing resolution of 4 cm$^{-1}$. (Label »start« in Figure 3 indicates a spectrum before introducing inlet gases.)

### FT-IR Measurements

FT-IR experiments were carried out in a quartz infrared cell containing CaF$_2$ windows and an external furnace section that was glass blown to a standard vacuum line (pressure of $1 \times 10^{-3}$ Pa). The catalyst sample was used as a 16 mm diameter self-supporting disc of 0.03 g by pressing (2 tons) the prepared powder between two polished steel dies. Prior to adsorption experiments, the sample was calcined *in situ* by

flowing air (100 cm$^3$ min$^{-1}$) for 2 hours at 673 K. After that, the cell was evacuated for 30 minutes with the disc at the same temperature before cooling to room temperature. Three spectra were obtained: before (label »start« in Figure 5) and after introducing a pulse of CO under the pressure of 1333 Pa and, finally, after evacuation of the cell for 10 minutes. For the measurement in wet conditions, the cell was saturated with water vapour (1333 Pa) and evacuated after 5 minutes before introducing CO. In general, 100 scans were recorded at 298 K using a Perkin-Elmer Model 1710 FT-IR spectrometer fitted with an MCT detector and operated at 4 cm$^{-1}$ resolution.

## RESULTS AND DISCUSSION

Figure 1 shows [57]Fe and [197]Au Mössbauer spectra of the tested catalyst, while Table I contains [57]Fe and [197]Au Mössbauer parameters and the chemical composition of the same sample. The [57]Fe spectrum is almost completely typical of haematite (there is a very small portion of a superparamagnetic component) while the isomer shift of –1.27 mm s$^{-1}$ in [197]Au Mössbauer spectrum confirms the presence of pure metallic gold in the sample.[9,10]
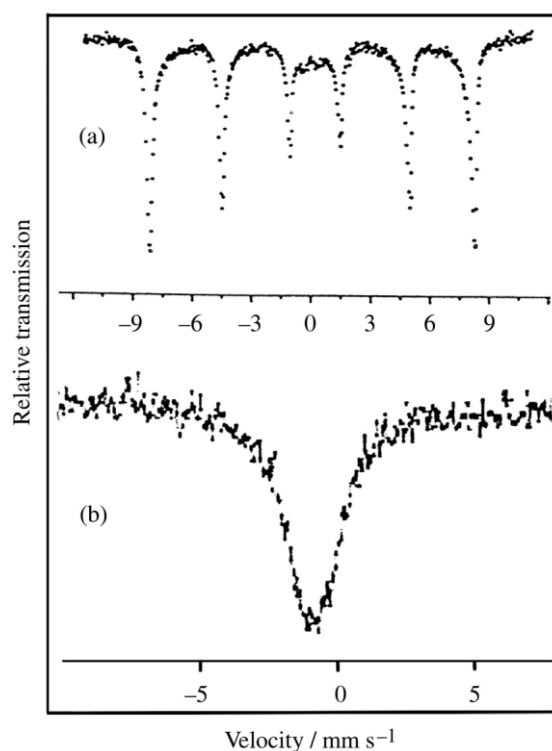


Figure 1. [57]Fe Mössbauer spectrum recorded at 300 K (a) and [197]Au Mössbauer spectrum recorded at 4.2 K (b) of Au/Fe$_2$O$_3$ catalyst.

Figure 2 represents Arrhenius plots for the rates of CO oxidation (*T* < 383 K) over Au/Fe$_2$O$_3$ in dry conditions and with addition of 2.7 % ($\varphi$) of water vapour in a mixture of reaction gases. It is obvious that the activity of

TABLE I. $^{57}$Fe and $^{197}$Au Mössbauer parameters of the Au/Fe$_2$O$_3$ sample[a]

| Mössbauer spectroscopy | Composition | $\dfrac{IS}{mm\ s^{-1}}$ | $\dfrac{QS}{mm\ s^{-1}}$ | $\dfrac{MHF}{T}$ | $\dfrac{LW}{mm\ s^{-1}}$ | $\dfrac{RI}{\%}$ |
|---|---|---|---|---|---|---|
| $^{57}$Fe | FeO (spm)[b] | 0.32 | 1.05 | – | 1.26 | 27[c] |
| | α-Fe$_2$O$_3$ | 0.37 | 0.22 | 50.9 | 0.29 | 54 |
| | ( )-Fe$_2$O$_3$ | 0.37 | 0.21 | 48.5 | 0.55 | 19 |
| $^{197}$Au | Au | −1.27 | – | – | 2.15 | – |

[a] IS: isomer shift, QS: quadruple splitting, MHF: magnetic hyperfine field, LW: line width (full width at half maximum), RI: relative intensity (spectral contribution).
[b] spm: superparamagnetic component.
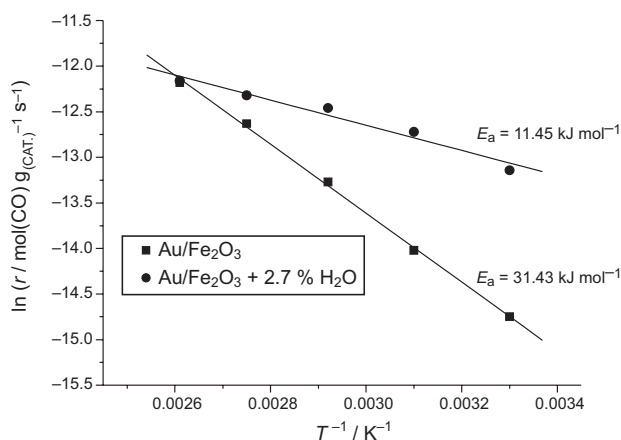[c] Sum of the doublet and the curved superparamagnetic background.



Figure 2. Arrhenius plots for the rates of CO oxidation over Au/Fe$_2$O$_3$ catalyst in dry conditions and with 2.7 % ($\varphi$) of water vapour added in the feedstream.



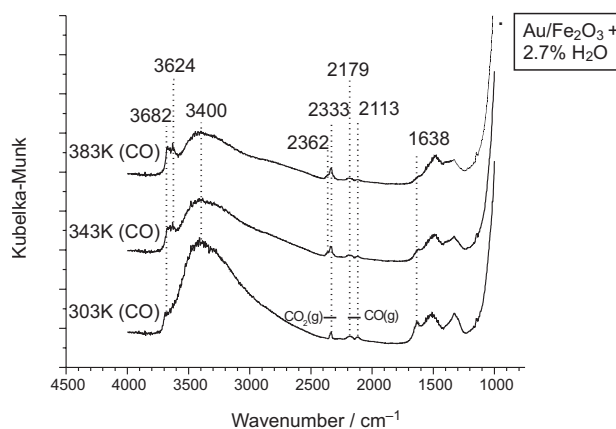Figure 4. *In situ* DRIFTS spectra of Au/Fe$_2$O$_3$ catalyst recorded at the indicated temperatures during CO oxidation with 2.7 % ($\varphi$) of water vapour added in the feedstream.
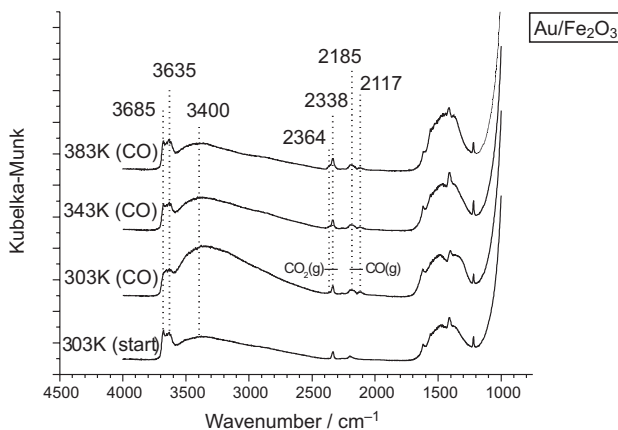


Figure 3. *In situ* DRIFTS spectra of Au/Fe$_2$O$_3$ catalyst recorded at the indicated temperatures during CO oxidation in dry conditions.

the sample was increased in wet conditions because the activation energy is approximately 20 kJ mol$^{-1}$ lower and the rates at 300 K are $2.00 \times 10^{-6}$ mol(CO) $g_{(CAT.)}^{-1}$ s$^{-1}$

with water vapour and $3.55 \times 10^{-7}$ mol(CO) $g_{(CAT.)}^{-1}$ s$^{-1}$ without it.

*In situ* DRIFTS spectra of Au/Fe$_2$O$_3$ during CO oxidation in dry conditions are shown in Figure 3. After inlet of a stream of reaction gases through the catalyst, there is a visible small decrease of bands at 3685 and 3635 cm$^{-1}$ corresponding to free or almost free –OH groups and –OH groups H bonded to water molecules, respectively.[11] The reason for this decrease is the formation of water at the beginning of the reaction (303 K), which is characterized by a very broad band at ≈3400 cm$^{-1}$ originating from stretching vibration of adsorbed water.[12] Increasing temperature of the catalyst led to less adsorbed water but more gaseous CO$_2$ determined by bands at 2364 and 2338 cm$^{-1}$.[13] Correspondingly, there is less gaseous CO indicated by bands 2185 and 2117 cm$^{-1}$,[14,15] but the presence of –OH groups is obvious all the time.

Figure 4 shows *in situ* DRIFTS spectra of the same catalyst in wet conditions. At the start of the reaction, a very broad band at ≈3400 cm$^{-1}$ is dominant. The presence of a band at 1638 cm$^{-1}$, from the bending vibration
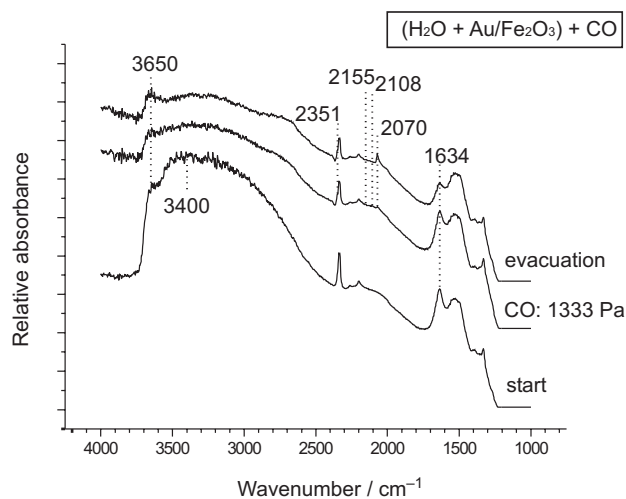
Figure 5. FT-IR spectra of wet Au/Fe$_2$O$_3$ catalyst recorded before and after adsorption of CO and after evacuation of the IR cell.

of adsorbed water,[12] at temperatures below 383 K proves the catalyst surface well saturated with water. After high consumption of water at the beginning of the reaction, the very broad band at $\approx$3400 cm$^{-1}$ can be observed even at a temperature of 383 K just like bands of –OH groups (3682 and 3624 cm$^{-1}$). The amount of CO$_2$ is larger compared to dry conditions and, consequently, the amount of CO is smaller, which is in agreement with the results of the catalytic activity test.

The importance of adsorbed water and –OH groups for low-temperature oxidation of CO is evident even in a vacuum (Figure 5). After introducing a pulse of CO into the wet sample, high consumption of adsorbed water ($\approx$3400 and 1634 cm$^{-1}$) and production of CO$_2$ (2351 cm$^{-1}$) occurred. Here, for the first time, very small bands at 2155, 2108 and a distinct one at 2070 cm$^{-1}$ are visible, which could be attributed to irreversibly adsorbed CO at different sites of metallic gold particles.[13–18] Namely, none of these bands appeared in the same experiment with a pure and dry support.[19] The band at 2155 cm$^{-1}$ may be due to adsorbed CO on gold-isolated sites[18] while bands from 2110–2101 cm$^{-1}$ are usually described as CO adsorbed on metallic gold.[16] Bands in a range from 2080–2060 cm$^{-1}$ on some other supported metals, like Pt, Ir and Cu, were explained by linearly bonded CO species (carbonyls) on metallic sites[14] and the same could be done in the case of the peak at 2070 cm$^{-1}$. In any case, because this band is absent in the DRIFTS spectra, and especially at the start of the reaction considering its distinction, it could be concluded that the main path in CO oxidation at low temperature is over the reaction between gaseous CO and –OH groups over formates as intermediates:[20]

$$CO + {-}OH \rightarrow HCOO_{(ad)} \qquad (1)$$

Thus formed, very reactive, formates (visible on the pure support[19] because the reaction is not very intensive) can be easily oxidized even in a vacuum and wet conditions by oxygen adsorbed on gold particles and from the support:[20]

$$2\ HCOO_{(ad)} + \tfrac{1}{2}\ O_2 \rightarrow 2\ CO_2 + H_2O \qquad (2)$$
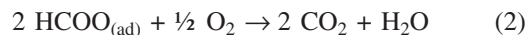
In that case, the gold particles would act as oxygen reservoirs,[21] and especially in the reaction conditions, because they do not adsorb CO molecules but the reaction is much more intense compared to the support without gold.[19]

Water formed in this reaction can easily dissociate and keep a constant amount of –OH groups on the oxide surface:[22]

$$M^{n+1}O^{2-} + H_2O \rightarrow HO^-M^{n+}\ {}^-OH \qquad (3)$$

This could be an explanation for higher activity of Au/Fe$_2$O$_3$ in CO oxidation below 383 K with addition of water. Rise of the reaction temperature increases the rate but decreases the amount of adsorbed water. Replenishment of water through the feedstream keeps the amount of –OH groups, over the reaction given by Eq. (3), needed for the development of reactive formates. These results, relating to activities, are very similar to the measurements over Au/TiO$_2$.[23]

## CONCLUSIONS

The obtained results point to the following conclusion: water adsorbed on the catalyst has a positive influence on the activity of Au/Fe$_2$O$_3$ during low-temperature CO oxidation. This means that the low-temperature CO oxidation involves water-derived species on the catalyst surface, mainly –OH groups. They react directly with CO and develop very active formates. Gold particles are reservoirs of oxygen, which easily oxidizes formates to carbon dioxide and water. In any case, further investigations are needed.

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# SAŽETAK

## Utjecaj vodene pare na niskotemperaturnu oksidaciju CO preko Au/Fe₂O₃ katalizatora

### Goran Šmit, Károly Lázár i Menno W. J. Crajé

Utjecaj vodene pare na aktivnost Au/Fe$_2$O$_3$ katalizatora ispitana je u reakciji niskotemperaturne oksidacije CO. Dodatak vodene pare imao je pozitivan utjecaj u temperaturnom intervalu od 303 do 383 K. *In situ* DRIFTS i FT-IR mjerenja u vakuumu potvrdila su važnost vode i –OH grupa, koje potječu od vode, za efikasnost katalizatora u niskotemperaturnoj oksidaciji CO.