

# A comparative study of CO adsorption and oxidation on Au/Fe<sub>2</sub>O<sub>3</sub> catalysts by FT-IR and in situ DRIFTS spectroscopies

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## Abstract

Influences of different iron oxides, used as gold supports, on CO oxidation were tested by FT-IR spectroscopy during adsorption of CO in a vacuum and by DRIFTS spectroscopy in the reaction conditions. The two techniques yielded different results but their recombination led to very valuable and interesting conclusions. The investigation showed that the adsorption and oxidation are independent of chemical composition and structure of the supports, but that they depend only on presence of surface –OH groups. Also, no correlation was observed between the catalysts with –OH groups, which showed almost equal high activity, and the gold particles less than 5 nm. Namely, the particles with 1.5 nm did not adsorb CO at all, while particles with 4 nm showed three suitable sites for CO adsorption (2172, 2115 and 2071 cm<sup>-1</sup>). The catalyst without –OH groups had significantly less activity despite the fact that it is almost identical in chemical composition and structure to one of the active catalyst.

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**Keywords:** Gold catalysts; CO adsorption and oxidation; Maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>); Haematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>); –OH groups

## 1. Introduction

Since the great Haruta's discovery of high gold activity for CO oxidation when it is dispersed at suitable support [1], there have been a lot of attempts to explain that phenomenon. As a result of that work, a great number of propositions for mechanism of CO oxidation over such catalysts were published. Analysis of the results ascribed different roles and influences to gold and its oxidation states but the same was with supports and their chemical or structural composition. While Haruta, Bollinger and Vannice [2,3] think that only metallic gold is responsible for the high activity, Park and groups of Galvagno and Hao published articles in which the significant activity of those catalysts was explained by oxidized or partially oxidized gold particles [4–6]. But, Galvagno's group also reported on a study in which no correlation was found between activity and gold, but there was a correlation only with chemical composition of support, i.e. with amount of ferrihydrite [7]. On the other hand, Haruta [2] concluded that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> do not have any influ-

ence as supports. Considering iron oxides as supports, there are also different opinions about influence of magnetite (Fe<sub>3</sub>O<sub>4</sub>), maghemite or haematite [6,8–10]. A few tries [11–13] to compile previous published results and mechanisms did not result in accepted generalizations. In addition to the different conditions during the experiments, the main problem could be the fact that some mechanisms were published after FT-IR studies in a vacuum [2,14–16] where there are completely different conditions in comparison to the conditions during the reaction. Investigations by DRIFTS in situ [17–19] offered significantly different results. In the present study, the influence of different iron oxides with supported pure metallic gold on CO adsorption and oxidation in a vacuum and in the reaction conditions was investigated. On the basis of the results, mechanisms of CO oxidation over these catalysts were suggested.

## 2. Experimental

### 2.1. Catalyst preparation

A starting material was magnetite [20] prepared by adding a stoichiometric mixture of Fe(II)–(FeSO<sub>4</sub>·7H<sub>2</sub>O, Kemika) and

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Fe(III)-ions ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , Riedel-de Haën) at a ratio 1:2 into 0.7 M  $\text{NH}_4\text{OH}$  containing citric acid trisodium salt (Kemika). After vigorously stirring (1500 rotations per minute) for 30 min at room temperature and pH 9.79 (pH meter Mettler Toledo MP-220), the solid was separated and washed twice, dried at 323 K, ground and heated at 433 K for 4 h.

So prepared magnetite was immersed into a mixture of 0.05 M  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (Sigma) and 1 M  $\text{NH}_4\text{OH}$  (Kemika) with the gold loading of 2 wt% (pH 11.44). After 1 h at room temperature, the solid was separated (pH 11.30), washed and heated at 433 K for 4 h.

It was the original sample used to develop tested catalysts through different pre-treatments.

## 2.2. Characterization

TEM microphotographs were collected using a microscope model FEI-MORGAGNI 268D operated at 70 kV with magnification of 40,000 times. The samples were deposited on a grid covered by a polymer previously coated by a carbon film.

X-ray diffractograms of the supported gold particles were taken on a Philips 3710 diffractometer operated at 40 kV and 40 mA using monochromatic  $\text{Cu K}\alpha$  radiation. The range in  $2\theta$  from 5 to  $60^\circ$  was scanned by speed of  $0.02^\circ \text{ s}^{-1}$  at room temperature.

$^{57}\text{Fe}$  Mössbauer spectra were obtained at ambient temperature and at 77 K by conventional KFKI spectrometer operated in a constant acceleration mode. Isomer shifts data were referred to metallic  $\alpha$ -iron as a standard. The accuracy of positional parameters was  $\pm 0.03 \text{ mm s}^{-1}$  and the spectra were decomposed to Lorentzian shape lines.

$^{197}\text{Au}$  Mössbauer experiments were performed with sources made by irradiation with thermal neutrons of Pt powder, enriched in  $^{196}\text{Pt}$  to 97%. The formed  $^{197}\text{Pt}$  decays to the Mössbauer isotope  $^{197}\text{Au}$  which decays to the ground state by emission of the 77.3 keV  $\gamma$ -photon that is used for Mössbauer spectroscopy. Both, source and absorber were cooled to temperature of 4.2 K (liquid helium). The transmitted photons were detected using a high purity Ge detector that enables us to selectively count 77.3 keV  $\gamma$ -rays only. The spectra were recorded in 1024 channels for a complete period of the sinus and then were folded to 512 channels to remove the background. Subsequently, the spectra had to be linearized. Calibration of the spectra was done by recording a spectrum of sodium nitroprusside (SNP) using a  $^{57}\text{Co}:\text{Rh}$  source and the velocity was reported relative to the centre of that spectrum.

## 2.3. Catalytic measurements

The activity of the catalysts, prepared after different pre-treatments of the original sample, for CO oxidation was measured in a fixed-bed reactor at atmospheric pressure using 0.1 g of the catalysts. The  $\text{O}_2 + \text{He} + \text{CO}$  ( $20/78/2 \text{ cm}^3 \text{ min}^{-1}$ ) mixture passed through the catalyst bed with a space velocity (SV) of about  $60,000 \text{ cm}^3 \text{ g}_{(\text{CAT.})}^{-1} \text{ h}^{-1}$ . The effluent gases were analyzed by a quadrupole mass spectrometer (QMS 311, Balzers). Before the catalytic activity tests, the original sample was pre-

treated by heating in a stream of  $\text{O}_2 + \text{He}$  ( $20/80 \text{ cm}^3 \text{ min}^{-1}$ ) for 2 h at 473 K (MD-200), 673 K (MD-400) and 873 K (MD-600).

## 2.4. FT-IR measurements

FT-IR experiments were carried out in a standard vacuum line (pressure:  $1 \times 10^{-3} \text{ Pa}$ ) with a quartz infrared cell contained  $\text{CaF}_2$  windows and an external furnace section. Catalyst samples were used as 16 mm diameter self-supporting discs of 0.03 g by pressing (2 tonnes) the original sample between two polished steel dies. Before the experiments, the prepared disc was calcined in situ by flowing air ( $100 \text{ cm}^3 \text{ min}^{-1}$ ) for 2 h at 473 K (MD-200), 673 K (MD-400) and 873 K (MD-600). After calcination, the cell was evacuated for 30 min with the disc at the same temperature and then cooled to room temperature. Three spectra were obtained: before (label “start” in the figures) and after introducing a pulse of CO under pressure of 3999 Pa and, finally, after evacuation of the cell for 10 min. In general, 100 scans were recorded at 298 K using a Perkin-Elmer Model 1710 FT-IR spectrometer fitted with an MCT detector and operating at  $4 \text{ cm}^{-1}$  resolution.

## 2.5. In situ DRIFTS

In situ DRIFTS measurements were conducted using a Perkin-Elmer 1750 FT-IR fitted with an MCT detector. The DRIFTS cell was equipped with  $\text{CaF}_2$  windows and a heating cartridge controlled by REX-P200. The spectra were recorded at different temperatures of the reaction by accumulating 200 scans and with employed resolution of  $4 \text{ cm}^{-1}$ . (Label “start” in the figures indicates a spectrum before introducing the inlet gases.)

# 3. Results and discussion

## 3.1. Characterization

Microphotographs of the samples are displayed in Fig. 1. MD-200 is amorphous, particles of the support are not shaped and particles of gold are not visible. MD-400 and MD-600 have formed particles of the supports and gold. The average sizes of gold particles in these two samples were estimated, through the observation of 100 particles, as approximate to 4 and 10 nm, respectively.

Fig. 2 shows the XRD patterns of the samples. MD-200 has very broad maxima at  $2\theta = 31^\circ, 36^\circ, 43^\circ$  and  $58^\circ$ , that is it contains magnetite and/or maghemite. Namely, these two oxides of iron show almost identical diffraction of X-rays, so it is very difficult to distinguish them by this technique [21]. Very broad lines prove that this sample has very small and/or amorphous particles. The same was observed by TEM. Presence of metallic gold is confirmed by very broad pattern at  $2\theta = 39^\circ$  [21,22]. MD-400, besides previously observed maxima, has the new ones at  $2\theta = 24^\circ, 34^\circ, 41^\circ, 50^\circ$  and  $54^\circ$  which are proofs of haematite formation [21,23]. A small portion of maghemite (magnetite would be converted to maghemite already at 523 K in these conditions [24]) can be proposed because of the peak at  $31^\circ$ .

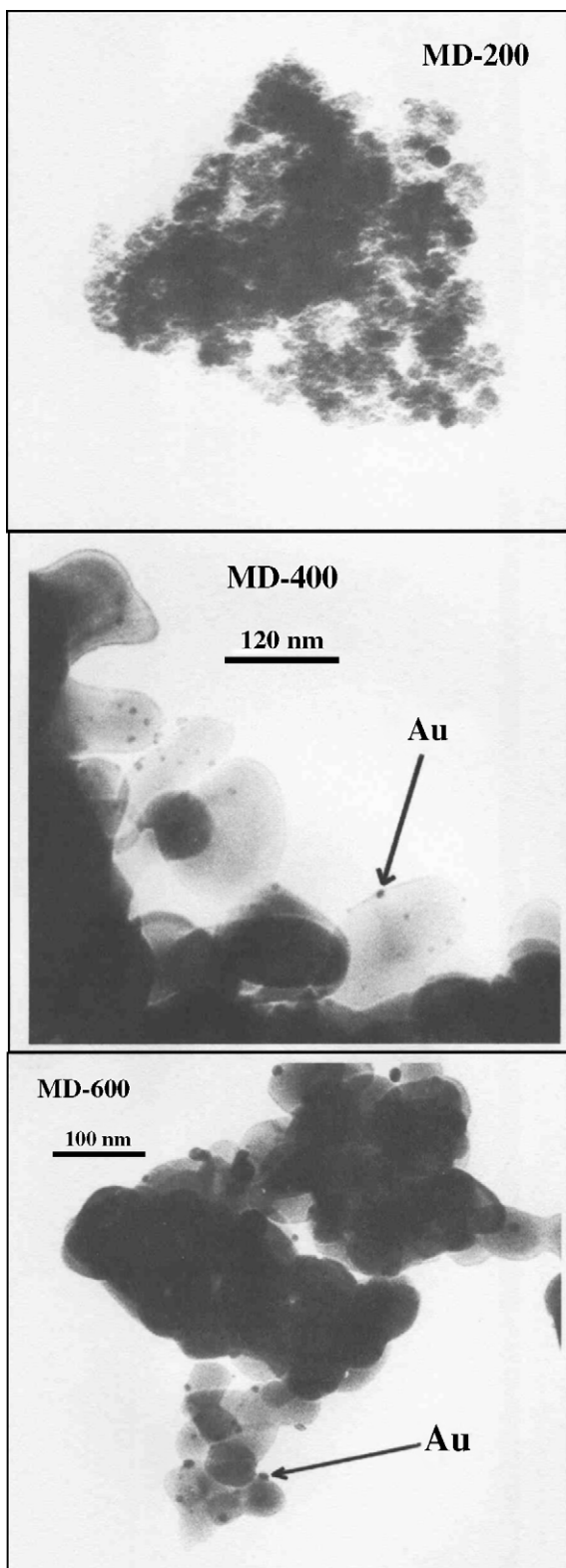


Fig. 1. TEM photographs of MD-200, MD-400 and MD-600 catalysts.

Metallic gold is characterized by patterns at  $39^\circ$  and  $44^\circ$  [21,22]. All peaks of this sample are much narrower and higher, what is a consequence of increase in particles during the pre-treatment. MD-600 has only peaks of haematite and metallic gold. It is important to notice that the ratio of intensities of peaks 104 and

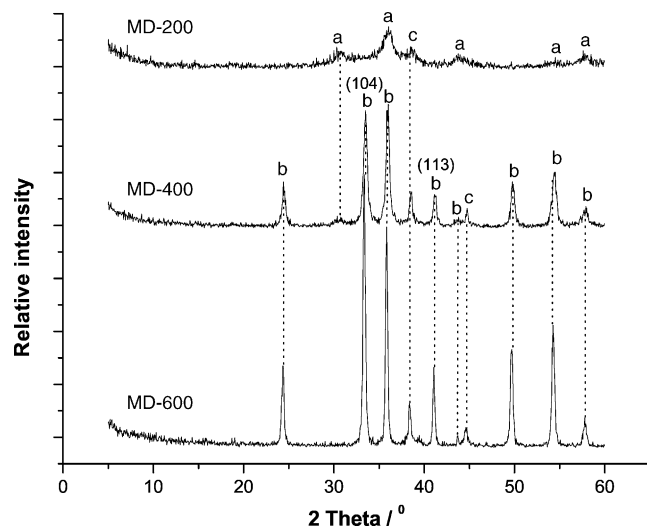


Fig. 2. XRD patterns of MD-200, MD-400 and MD-600 catalysts: (a)  $\text{Fe}_3\text{O}_4$  or  $\gamma\text{-Fe}_2\text{O}_3$ , (b)  $\alpha\text{-Fe}_2\text{O}_3$  and (c) Au.

113 [23], expressed in counts per second (CPS), is greater than 4 ( $I_{104}/I_{113} = 506.41 \text{ CPS}/122.64 \text{ CPS} = 4.1292$ ). It means that haematite in this sample has no water or  $-\text{OH}$  groups [25]. Considering the peak for metallic gold at  $39^\circ$ , which is common for all three samples, particle size of gold in sample MD-200 could be estimated according to Scherrer formula and to data provided by TEM photographs. Ratio of full width at half maximum (FWHM) of the peak at  $39^\circ$  in MD-200:MD-400:MD-600 =  $0.4723^\circ:0.1968^\circ:0.0787^\circ = 6.00:2.50:1.00$ . If the size of gold particles in MD-600 on the TEM photograph has taken as 10 nm, then from FWHM ratio particle size of gold in MD-200 is 1.67 nm and in MD-400 is 4 nm, just like in Fig. 1.

Fig. 3 shows  $^{57}\text{Fe}$  Mössbauer spectra of tested samples, while Table 1 contains their chemical compositions and  $^{57}\text{Fe}$

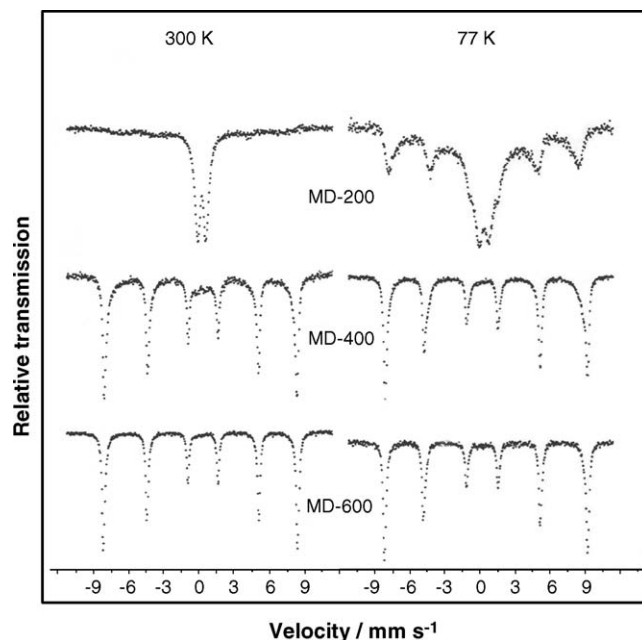


Fig. 3.  $^{57}\text{Fe}$  Mössbauer spectra of MD-200, MD-400 and MD-600 catalysts recorded at 300 and 77 K.

Table 1  
<sup>57</sup>Fe Mössbauer parameters of MD-200, MD-400 and MD-600 catalysts recorded at 300 and 77 K

Sample	Composition	IS (mm s <sup>-1</sup> )		QS (mm s <sup>-1</sup> )		MHF (T)		LW (mm s <sup>-1</sup> )		RI (%)	
		300 K	77 K	300 K	77 K	300 K	77 K	300 K	77 K	300 K	77 K
MD-200	FeO (spm)	0.35	0.43	0.73	0.93	–	–	0.54	1.15	87 <sup>a</sup>	74 <sup>a</sup>
	Maghemite	0.37	0.43	–	–	42.4	50.5	1.36	0.51	13	15
				0.42		–		47.0		0.75	
MD-400	FeO (spm)	0.32		1.05		–		1.26		27 <sup>a</sup>	
	α-Fe <sub>2</sub> O <sub>3</sub> <sup>(1)</sup>	0.37	0.47	0.22	0.35	50.9	53.7	0.29	0.26	54	51
	Fe <sub>2</sub> O <sub>3</sub>	0.37	0.43	0.21	0.11	48.5	51.8	0.55	0.54	19	49
MD-600	α-Fe <sub>2</sub> O <sub>3</sub> <sup>(1)</sup>	0.37	0.47	0.20	0.37	51.5	54.0	0.23	0.28	61	75
	α-Fe <sub>2</sub> O <sub>3</sub> <sup>(2)</sup>	0.37	0.43	0.21	0.19	50.7	52.7	0.33	0.33	39	25

IS, isomer shift related to metallic α-iron; QS, quadrupole splitting; MHF, magnetic hyperfine field; LW, line width (full width at half maximum); RI, relative intensity (spectral contribution).

<sup>a</sup> Sum of the doublet and the curved superparamagnetic background. spm: superparamagnetic component.

Mössbauer parameters recorded at 300 and 77 K [26,27]. As can be seen, MD-200 exhibits typical superparamagnetic behaviour: the extent of magnetic ordering increases with decrease of the measuring temperature. The average particle size of 3 nm can be taken as a very rough approximation. A small portion of maghemite in that sample can be proposed because of moderated magnetic field values. The overwhelming parts of the MD-400 spectra are characteristic for haematite but at 300 K, there is still visible a small contribution of the superparamagnetic component. MD-600 has typical haematite spectra but the sample is not completely homogeneous (labels <sup>(1)</sup> and <sup>(2)</sup> in the tables) because slightly different MHF values can be distinguished.

Fig. 4 shows <sup>197</sup>Au Mössbauer spectra of tested samples, while their <sup>197</sup>Au Mössbauer parameters are reported in Table 2. Isomer shifts of –1.20 and –1.27 mm s<sup>-1</sup> confirm only metallic gold in the samples [28,29]. Fitting of a second contribution in the spectra did not make any improvement.

### 3.2. Catalytic measurements

Figs. 5 and 6 represent catalytic activities expressed as a degree of reaction in percent of CO conversion and Arrhenius plots, respectively. Samples MD-200 and MD-400 were superior despite the facts that pure metallic gold is on the supports which are chemically and structurally completely different, while MD-400 and MD-600 are almost identical in those characteristics. Temperatures for 50% of CO conversion were 378 K (MD-200), 383 K (MD-400) and 456 K (MD-600). Fig. 6 confirms the superiority of MD-200 and MD-400 in activity through the activation energy. The rates of CO oxidation at 300 K were 1.37 × 10<sup>-6</sup> (MD-200), 2.93 × 10<sup>-6</sup> (MD-400) and 3.06 × 10<sup>-7</sup> (MD-600) mol(CO) g(CAT.)<sup>-1</sup> s<sup>-1</sup> calculated from

Table 2  
<sup>197</sup>Au Mössbauer parameters of MD-200, MD-400 and MD-600 catalysts recorded at 4.2 K

SAMPLE	IS (mm s <sup>-1</sup> )	QS (mm s <sup>-1</sup> )	RAA (a.u.)
MD-200	–1.20	2.73	0.77
MD-400	–1.27	2.15	0.97
MD-600	–1.20	2.10	1.03

IS, isomer shift; QS, quadrupole splitting; RAA, resonant absorption area.

the plots. In the same experiment, the similar behaviour showed by pure supports [30]: supports of MD-200 and MD-400 had almost identical activity which was superior considering the support of MD-600.

### 3.3. FT-IR measurements

In Fig. 7, FT-IR spectra of tested samples before and after adsorption of CO in a vacuum are shown.

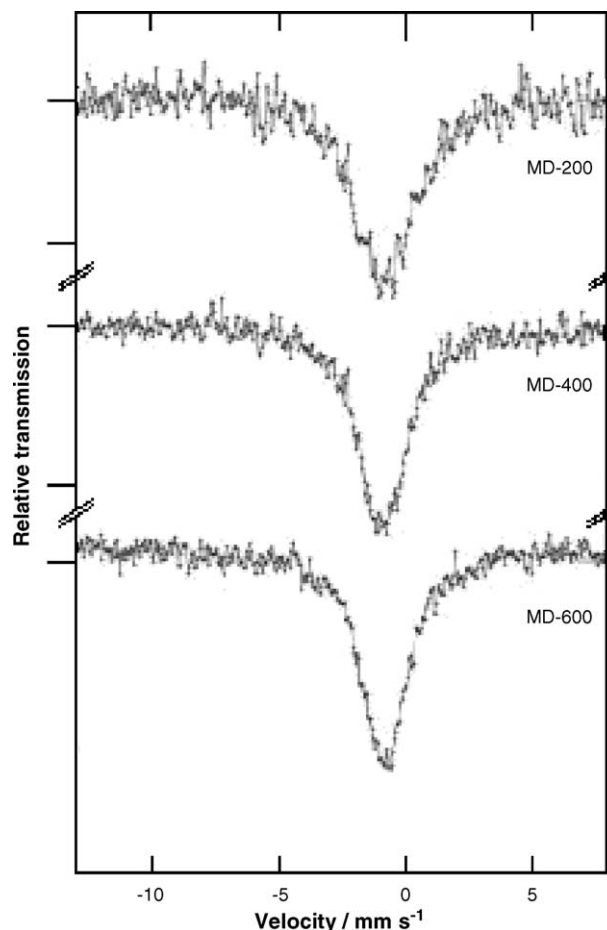


Fig. 4. <sup>197</sup>Au Mössbauer spectra of MD-200, MD-400 and MD-600 catalysts recorded at 4.2 K.

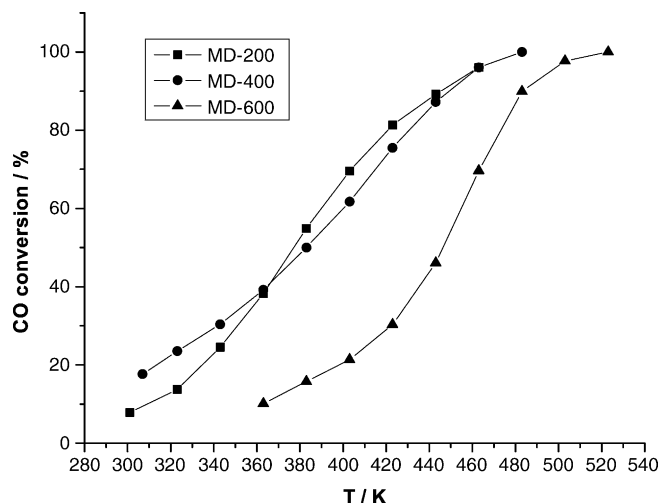


Fig. 5. Conversion of CO over MD-200, MD-400 and MD-600 as a function of catalyst temperature.

Introduction of CO in the chamber with MD-200 almost completely decreases bands characteristic for water and  $\text{-OH}$  groups [31,32]: 3687 (free  $\text{-OH}$  groups), 3637 ( $\text{-OH}$  groups H-bonded to water), 3400 (stretching of adsorbed water) and a shoulder at  $1646\text{ cm}^{-1}$  (bending of adsorbed water) indicating their almost complete consumption. An appearance of a new band at  $2353\text{ cm}^{-1}$  from produced and adsorbed carbon dioxide [33] and a small doublet at  $2142\text{ cm}^{-1}$  due to gaseous carbon monoxide [34] are visible. New bands appear also at 1621, 1414 and  $1222\text{ cm}^{-1}$  assigned to bicarbonates which were formed after adsorption of  $\text{CO}_2$  on  $\text{-OH}$  groups [17,33]. This is the reason for reduced intensities of the bands for  $\text{-OH}$  groups but also the bands of residual adsorbed citrates: 2957, 2876, 1538, 1444, 1378 and  $1361\text{ cm}^{-1}$  [35]. After evacuation of the chamber, bands at 1621, 1414 and  $1222\text{ cm}^{-1}$  lost in intensity, doublet at  $2142\text{ cm}^{-1}$  disappeared and the band of irreversibly adsorbed  $\text{CO}_2$  at  $2353\text{ cm}^{-1}$  stayed.

A decrease in intensities of bands at 3691, 3628, and  $3470\text{ cm}^{-1}$  with an appearance of a shoulder at  $2350\text{ cm}^{-1}$  is

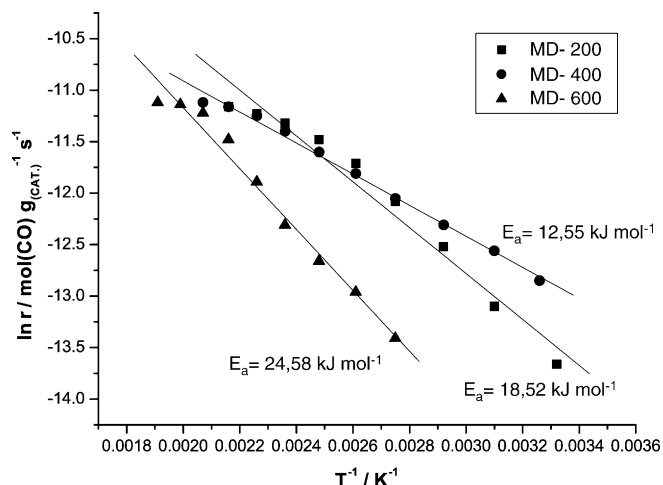


Fig. 6. Arrhenius plots for the rates of CO oxidation over MD-200, MD-400 and MD-600 catalysts.

also evident on sample MD-400, as it was in the case of sample MD-200. A less intense band at  $\approx 3400\text{ cm}^{-1}$  and absence of the band at  $1646\text{ cm}^{-1}$  indicate less adsorbed water considering MD-200 but, consequently, similarity in amount of  $\text{-OH}$  groups. Another difference is in very small bands at 2172, 2115 and  $2071\text{ cm}^{-1}$  which could be attributed to irreversibly adsorbed CO at different sites of metallic gold particles [3,16,33,36].

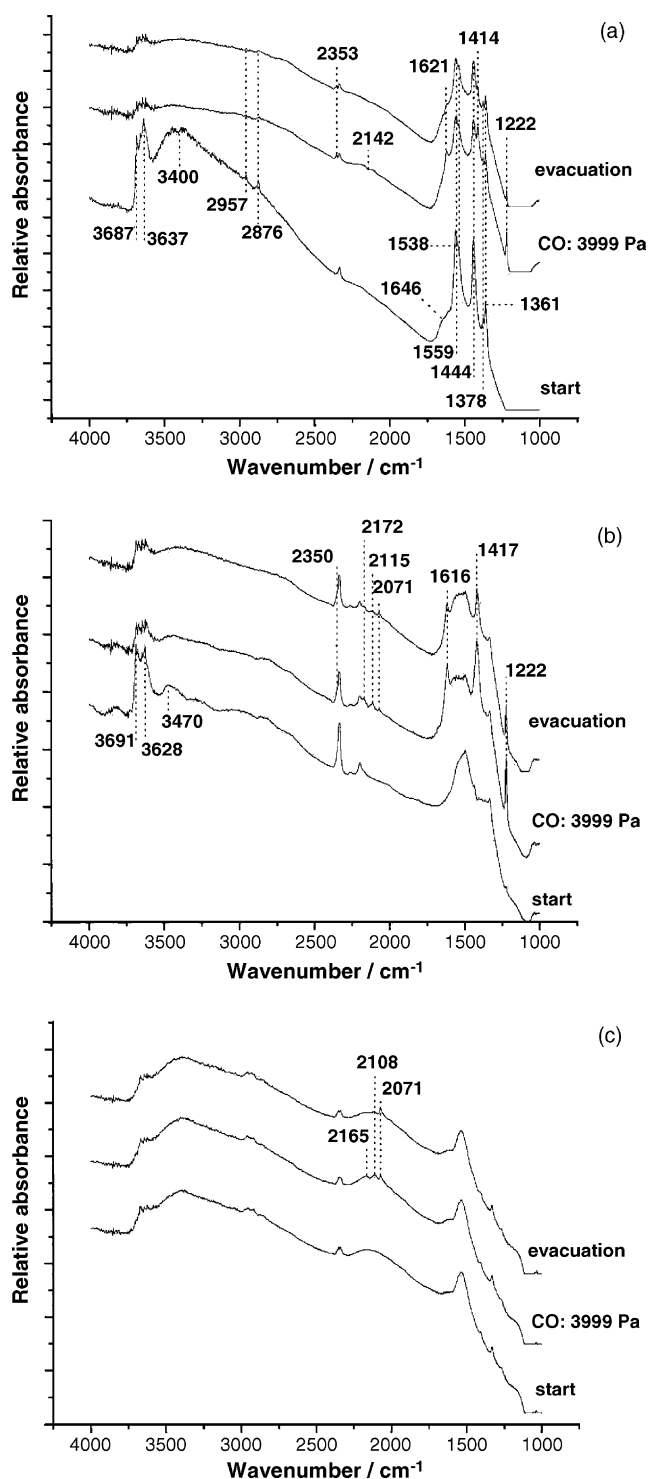


Fig. 7. FT-IR spectra of the catalysts recorded before and after adsorption of CO and after evacuation of the IR cell: (a) MD-200, (b) MD-400 and (c) MD-600.

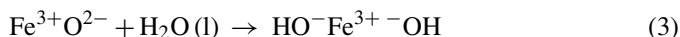
Namely, in bands at 2172 and 2115  $\text{cm}^{-1}$  possible contribution of gaseous CO cannot be excluded, but they are well visible after evacuation. Also, the band at 2172  $\text{cm}^{-1}$  is not from adsorbed CO at oxidized gold [36] or  $\text{Fe}^{3+}$  ions [37] because on this sample exists only metallic gold and adsorption of CO on the same support without deposited gold on it did not show that band in the same experiment [30]. Very intensive bands of bicarbonates are also present at 1616, 1417 and 1222  $\text{cm}^{-1}$ . After evacuation, the shoulder at 2350  $\text{cm}^{-1}$  again stayed while the intensity of all bands, except the one at 2071  $\text{cm}^{-1}$ , decreased. This sample did not show the bands of adsorbed citrates because they were removed by calcination at 673 K.

In the same conditions, sample MD-600 shows a new band only at 2165 and two peaks at 2108 and 2071  $\text{cm}^{-1}$ . The band at 2165  $\text{cm}^{-1}$  cannot be surely connected with adsorption of CO on a gold site, unlike the band at 2172  $\text{cm}^{-1}$  on MD-400, because of its shape and completely disappearance after evacuation. On the other hand, considering the intensity and shape of the peak at 2108  $\text{cm}^{-1}$ , it can be concluded that there is a significant contribution of CO reversibly adsorbed on gold because evacuation almost completely reduced this peak. The peak at 2071  $\text{cm}^{-1}$ , associated with irreversibly adsorbed CO on gold, stayed unchanged after evacuation, just as it was on MD-400. Anyway, absence of adsorbed  $\text{CO}_2$  (band at 2350  $\text{cm}^{-1}$ ) means that oxidation of CO by oxygen adsorbed on gold particles and/or from the support did not happen on this sample despite the fact that it has almost identical chemical and structural composition as sample MD-400.

This last result could be explained only by a lack of surface  $-\text{OH}$  groups on this sample as it was revealed by XRD results. In that case, main path in CO oxidation over MD-200 and MD-400 in a vacuum is in direct reaction between CO and  $-\text{OH}$  groups forming very reactive formates which can be easily oxidized mainly by oxygen adsorbed at gold particles and partially by oxygen from the supports [30,38]:



Water formed in this reaction can easily dissociate and keep a constant amount of  $-\text{OH}$  groups on a surface of the oxide [34]:



Namely, the reaction was very intense on both samples (which are almost equal in the catalytic activity) despite the facts that MD-200 is covered with citrates, has more adsorbed water and did not adsorb CO on gold particles. Formation of formates was visible in the same experiment with the pure support [30] because the reaction was not so intense on the support covered by citrates.

In the experiment over MD-600, there is no band at 2350  $\text{cm}^{-1}$  as an evidence of  $\text{CO}_2$  production which indicates that the direct reaction (Eley–Rideal mechanism) between CO and adsorbed oxygen does not occur in these conditions. Also, the absence of bands between 2140 and 2130  $\text{cm}^{-1}$ , characteristic of co-adsorbed CO and O on gold particles [16,39], shows

that Langmuir–Hinshelwood mechanism does not occur over the same gold particles, either.

### 3.4. In situ DRIFTS

Fig. 8 shows in situ DRIFTS spectra of the tested catalysts.

Introduction of the reaction mixture through MD-200 caused an appearance of a doublet characteristic for gaseous CO in these conditions with two peaks at 2176 and 2116  $\text{cm}^{-1}$  where the first one is more intense [40,41]. Increase of a band at 2341  $\text{cm}^{-1}$  with an appearance of a new band at 2362  $\text{cm}^{-1}$  at higher temperature, which form a doublet of gaseous  $\text{CO}_2$  [40], proves activity of this catalyst from the beginning. Rise of the reaction temperature caused increase of bands at 2362 and 2341  $\text{cm}^{-1}$  and decrease of bands at 2176 and 2116  $\text{cm}^{-1}$ . During the reaction, a stability of bands of  $-\text{OH}$  groups at 3681 and 3633  $\text{cm}^{-1}$  (Eq. (3)) with a moderate decrease of band for water at  $\approx 3400 \text{ cm}^{-1}$  above 373 K is visible. Citrates are present all the time (1560, 1538, 1440, 1378 and 1358  $\text{cm}^{-1}$ , while 2957 and 2876  $\text{cm}^{-1}$  are not intense and distinguished in these conditions) which confirms the previous statement that the main path for oxygen in this oxidation is over gold particles and not from the support. Shoulder at 1621 and a band at 1220  $\text{cm}^{-1}$  (1414 is not so intense), typical for bicarbonates formed after adsorption of  $\text{CO}_2$  at  $-\text{OH}$  groups, are present before introducing the reaction mixture. It has already been reported [42] and the reason is probably in  $\text{CO}_2$  adsorption from used air. Bicarbonates are stable at temperatures below 400 K [43] and removable completely above 475 K [33], so that they are still visible at 423 K (1220  $\text{cm}^{-1}$ ). Anyway, it is hard to characterize them as some intermediates in this reaction because the amount of citrates is constant all the time. This is the difference compared to the measurement in vacuum where the bicarbonates formed were replacing them (Fig. 7a).

The beginning of the reaction at MD-400 leads to very intensive rise of the broad band at 3400  $\text{cm}^{-1}$  indicating forming of water because of high activity from the beginning of the reaction (Eq. (2)). This catalyst has a little bit higher activity at the start in comparison to MD-200 (Fig. 5), which could be explained by the absence of adsorbed citrates and additional oxidation by oxygen from the support. (In any case, they are very similar considering the activity.) It is connected with appearance and rise of the doublet for gaseous  $\text{CO}_2$  (2360 and 2343  $\text{cm}^{-1}$ ) and with decrease of gaseous CO (2175 and 2115  $\text{cm}^{-1}$ , where the first one is more intense, again). Like in the case of MD-200, bands at 3681 and 3630 are stable while 3400  $\text{cm}^{-1}$  loses a little bit at higher temperature. The same thing happened with the bands at 1621, 1409 and 1220  $\text{cm}^{-1}$  which disappeared, except the last one, above temperature of 383 K. Absence of the bands characteristic for CO adsorbed at gold particles (especially 2070  $\text{cm}^{-1}$ ) and the fact about the same activities of MD-200 and MD-400 confirms previous statement about reaction between CO and  $-\text{OH}$  groups and oxidation of formed formates where size of gold particles does not have any influence if they are less than 5 nm. This observation is very similar to Guzzi's conclusion about no need for change in the size of the metallic gold particles to reach a high activity in CO oxidation [9].

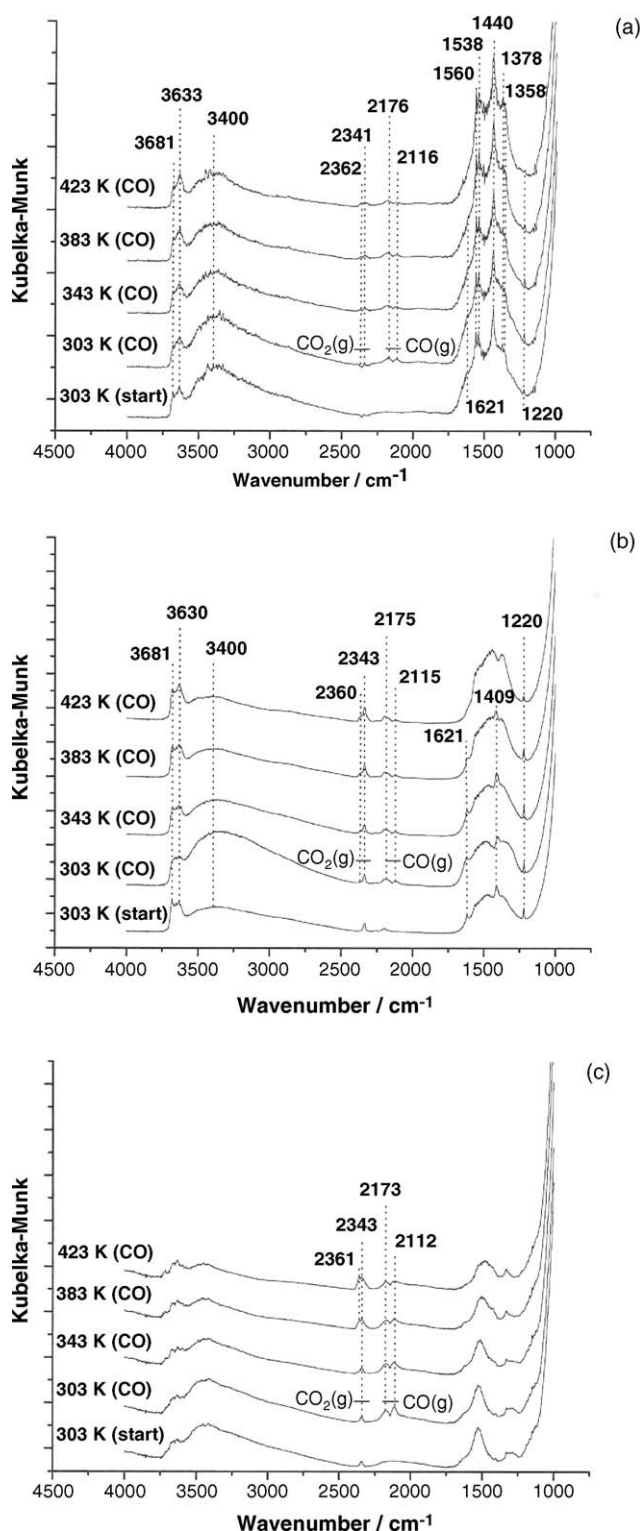
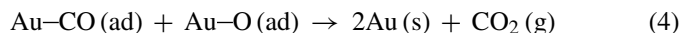


Fig. 8. In situ DRIFTS spectra of the catalysts recorded at the indicated temperatures during oxidation of CO: (a) MD-200, (b) MD-400 and (c) MD-600.

Sample MD-600 which has significantly less activity considering the other two (Figs. 5 and 6) shows very intensive bands at 2173 and 2112  $\text{cm}^{-1}$ , where the last one is more intense. This is a discrepancy from the characteristic doublet of gaseous CO which indicates considerable adsorption of CO on gold particles.

Faster diminishing of that band at 2112  $\text{cm}^{-1}$  in comparison with the band at 2173  $\text{cm}^{-1}$  suggests that the reaction occurs between CO reversibly adsorbed at gold (2108  $\text{cm}^{-1}$  in Fig. 7c) and oxygen adsorbed on other gold particles [18,19]:



Namely, direct oxidation of CO at the same sample in a vacuum did not give any result, while oxidation over formates on the other two samples were more intense by oxygen adsorbed on gold than by oxygen from the supports. The reaction over MD-600 started at 363 K (Fig. 5), so the increase of bands at 2361 and 2343  $\text{cm}^{-1}$  is visible just in the spectra recorded at 383 and 423 K. Absence of bands for bicarbonates before introducing the reaction mixture and the fact that forming of  $\text{CO}_2$  did not cause their appearance, at least the band at 1220  $\text{cm}^{-1}$  which was visible at the other two samples at 423 K, confirm previous conclusions that they are not intermediates in this reaction and XRD analysis about missing  $-\text{OH}$  groups and their importance in CO oxidation over these catalysts at temperatures below 363 K.

#### 4. Conclusions

- Low-temperature CO oxidation on metallic gold supported at used iron oxides depends only about presence of  $-\text{OH}$  groups and not about chemical or structural composition of the supports.
- The importance of  $-\text{OH}$  groups is in possibility of direct reaction with CO. They form very reactive formates which can be oxidized to  $\text{CO}_2$  by oxygen adsorbed at gold (particle size is not important when their diameter is less than 5 nm) and partially by oxygen from the supports.
- Gold particles with 1.5 nm size does not adsorb CO, with 4 nm have three sites suitable for CO adsorption (2172, 2115 and 2071  $\text{cm}^{-1}$ ; all irreversible) and with 10 nm two sites (2108 and 2071  $\text{cm}^{-1}$ ; the latter is irreversible).
- Reaction of CO from gaseous phase with adsorbed oxygen (Eley-Rideal mechanism) is not possible, and between CO and oxygen adsorbed at different metallic gold particles occurs just at higher temperatures (363 K).
- During low-temperature CO oxidation, bicarbonates are not intermediates of the reaction but they appear after adsorption of  $\text{CO}_2$  at  $-\text{OH}$  groups during oxidation in a vacuum or before measurement in the reaction conditions ( $\text{CO}_2$  from air).
- FT-IR and in situ DRIFTS spectroscopies offered different results about low-temperature CO oxidation over supported gold on different iron oxides but their recombination gave very valuable and interesting information which could be used for suggestion of mechanism of the reaction.

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