

Adsorption and low-temperature oxidation of CO over iron oxides

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Abstract

Different iron oxides, usually used as gold supports, were tested as catalysts for CO oxidation at low temperature. Calcinations of synthesized magnetite at different temperatures, before the activity test, caused its chemical transformations but differences in the activity were not noticeable in all the cases. A sample calcined at 873 K was significantly less active than samples calcined at 473 and 673 K. FTIR measurements in a vacuum showed that the differences in the activity were not caused by the chemical composition but by amount of surface –OH groups.

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1. Introduction

Roles of different iron oxides as gold supports in CO oxidation were doubtful so far. Namely, opposite opinions about influences of magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃) and haematite (α-Fe₂O₃) on the mentioned reaction were published. During pre-treatment, there is always some possibility for transformations of those oxides to each other but reported results about their influences on the activity were contradicted. One of the most active catalysts for CO oxidation was prepared by co-precipitation when gold was supported on haematite [1]. Formation of magnetite [2] and maghemite [3] after pre-treatment in hydrogen decreased the activity of Au/Fe₂O₃ catalysts. But in some articles, appearance of maghemite with haematite [4] or pure maghemite [5,6] as gold supports was attributed for increased activity. In this paper, the catalytic activity of those iron oxides for low-temperature oxidation of CO was investigated as a part of a project about their roles in gold catalysis.

2. Experimental

2.1. Catalyst preparation

A starting material was magnetite [7] prepared by adding a stoichiometric mixture of Fe(II)-(FeSO₄·7H₂O, Kemika) and Fe(III)-ions (FeCl₃·6H₂O, Riedel-de Haën) at a ratio 1:2 into 0.7 M NH₄OH containing a citric acid trisodium salt. After vigorously stirring (1500 rpm) for 30 min at room temperature and pH 9.79, the solid was separated and washed twice, dried at 323 K, ground and heated in air at 433 K for 4 h.

2.2. Characterization

⁵⁷Fe Mössbauer spectra were obtained at ambient temperature and at 77 K by conventional KFKI spectrometer operated in a constant acceleration mode. The reported isomer shift values were related to metallic α-iron and the accuracy of the positional data was ±0.03 mm s⁻¹. The characteristic data were extracted from the spectra presuming they were composed of Lorentzian shaped peaks.

2.3. FTIR measurements

FTIR experiments were performed in a standard vacuum line (pressure of 1 × 10⁻³ Pa) with a quartz infrared cell contained

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CaF₂ windows and an external furnace section. Catalyst samples were prepared as 16 mm diameter self-supporting discs of 0.03 g by pressing (2 tonnes) the powder between two polished steel dies. Before the experiments, the samples were calcined in situ by flowing air (100 cm³ min⁻¹) for 2 h at 473 K (code: M-200), 673 K (code: M-400) and 873 K (code: M-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 after evacuation of the cell for 10 min. In general, 100 scans were recorded at 298 K using a Perkin-Elmer Model 1710 FTIR spectrometer fitted with an MCT detector and operating at 4 cm⁻¹ resolution.

2.4. Catalytic measurements

The activity of iron oxides for CO oxidation was measured in a fixed-bed reactor at atmospheric pressure using 0.1 g of the catalysts. The O₂ + He + CO (20/78/2 cm³ min⁻¹) mixture passed through the catalyst bed with a space velocity (SV) of about 60,000 cm³ g_(CAT.)⁻¹ h⁻¹. The effluent gases were analyzed by quadrupole mass spectrometer (QMS 311, Balzers). Before the catalytic activity tests, the samples were pre-treated by heating in a stream of O₂/He = 20/80 cm³ min⁻¹ for 2 h at 473 K (M-200), 673 K (M-400) and 873 K (M-600).

3. Results and discussion

Fig. 1 shows Mössbauer spectra of tested samples, while Tables 1 and 2 contain their chemical compositions and ⁵⁷Fe Mössbauer parameters recorded at 300 and 77 K, respectively [8,9]. As can be seen, M-200 exhibits typical superparamag-

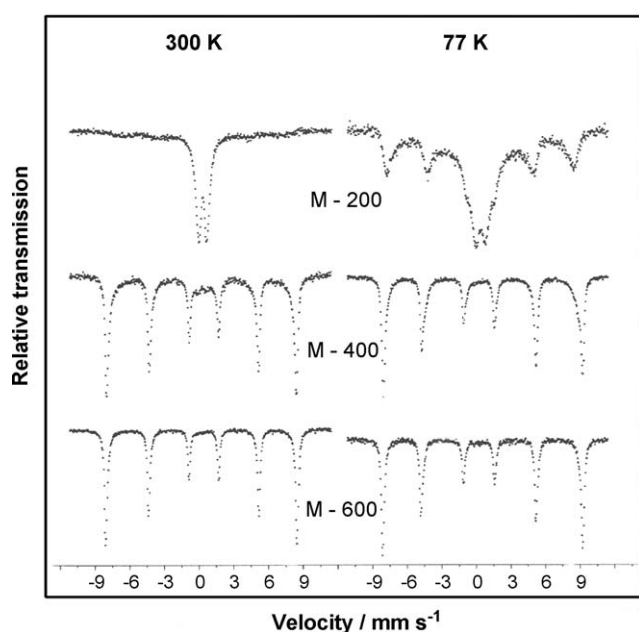


Fig. 1. ⁵⁷Fe Mössbauer spectra of M-200, M-400 and M-600 catalysts recorded at 300 and 77 K.

Table 1
⁵⁷Fe Mössbauer parameters of M-200, M-400 and M-600 catalysts recorded at 300 K

Sample	Composition	IS (mm s ⁻¹)	QS (mm s ⁻¹)	MHF (T)	LW (mm s ⁻¹)	RI (%)
M-200	FeO (spm)	0.35	0.73	–	0.54	87 ^a
	Maghemite	0.37	–	42.4	1.36	13
M-400	FeO (spm)	0.32	1.05	–	1.26	27 ^a
	α-Fe ₂ O ₃ ⁽¹⁾	0.37	0.22	50.9	0.29	54
	Fe ₂ O ₃	0.37	0.21	48.5	0.55	19
M-600	α-Fe ₂ O ₃ ⁽¹⁾	0.37	0.20	51.5	0.23	61
	α-Fe ₂ O ₃ ⁽²⁾	0.37	0.21	50.7	0.33	39

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).

^a Sum of the doublet and the curved superparamagnetic background; spm: superparamagnetic component.

netic behaviour. A small portion of maghemite in that sample can be proposed because of moderated magnetic field values. An average particle size of 3 nm can be taken as a very rough approximation and this sample is not recognizable by XRD. The overwhelming parts of the M-400 spectra are characteristic for haematite but at 300 K there is still visible a small contribution of the superparamagnetic component. M-600 has typical haematite spectra but the sample is not completely homogeneous (labels (1) and (2) in the tables) because slightly different MHF values can be distinguished.

Figs. 2–4 represent FTIR spectra before and after adsorption of CO on the iron oxides in a vacuum and after evacuation of the IR cell.

After introduction of CO, M-200 shows increased bands at 3637 and ≈3400 cm⁻¹ which could be ascribed to H-bonded –OH groups and adsorbed water, respectively [10]. Increase of peaks at 2958, 2870 and 1563 cm⁻¹, which originate from adsorbed residual citrates [11] added during the synthesis, proves formation of adsorbed formates, HCOO_(ad) [12,13]. (Increase of bands at 1377 and 1360 cm⁻¹ is not shown for the sake of brevity.) Appearance of a small band at 2364 cm⁻¹, as

Table 2
⁵⁷Fe Mössbauer parameters of M-200, M-400 and M-600 catalysts recorded at 77 K

Sample	Composition	IS (mm s ⁻¹)	QS (mm s ⁻¹)	MHF (T)	LW (mm s ⁻¹)	RI (%)
M-200	FeO (spm)	0.43	0.93	–	1.15	74 ^a
	Maghemite	0.43	–	50.5	0.51	15
		0.42	–	47.0	0.75	11
M-400	α-Fe ₂ O ₃ ⁽¹⁾	0.47	0.35	53.7	0.26	51
	Fe ₂ O ₃	0.43	0.11	51.8	0.54	49
M-600	α-Fe ₂ O ₃ ⁽¹⁾	0.47	0.37	54.0	0.28	75
	α-Fe ₂ O ₃ ⁽²⁾	0.43	0.19	52.7	0.33	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).

^a Sum of the doublet and the curved superparamagnetic background; spm: superparamagnetic component.

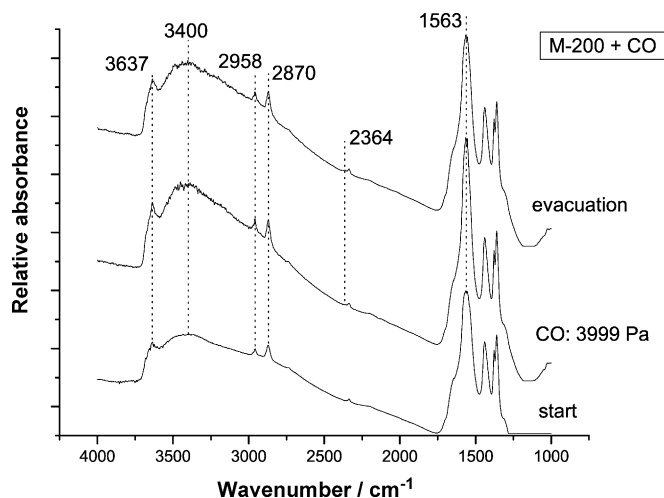


Fig. 2. FTIR spectra of M-200 catalyst recorded before and after adsorption of CO and after evacuation of the IR cell.

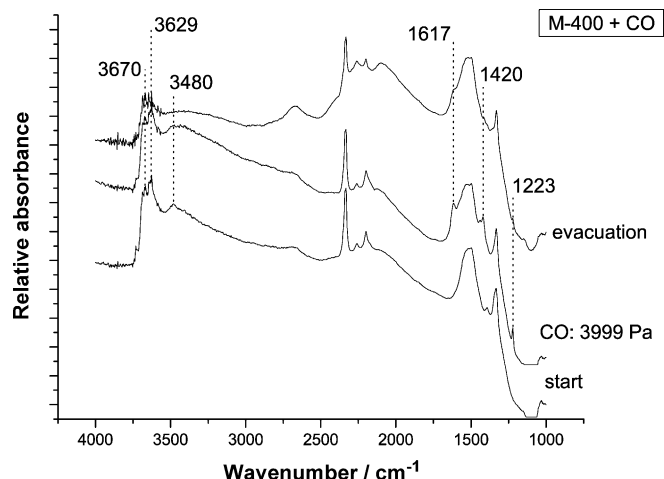


Fig. 3. FTIR spectra of M-400 catalyst recorded before and after adsorption of CO and after evacuation of the IR cell.

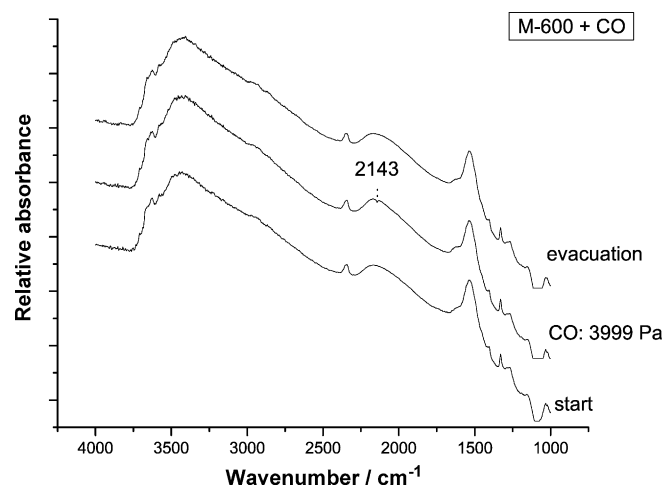
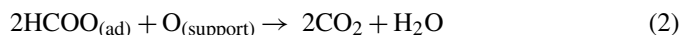
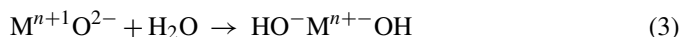


Fig. 4. FTIR spectra of M-600 catalyst recorded before and after adsorption of CO and after evacuation of the IR cell.

a result of CO₂ adsorption [14], indicates partial oxidation of very reactive formates what explains increased amount of water as well [15]:



Water formed in this reaction can easily dissociate and keep a constant amount of -OH groups on a surface of the oxide with uncoordinated metal cations and oxide anions [16]:



This reaction is not so intensive on this sample because of adsorbed citrates and that is the reason for more adsorbed water and H-bonded -OH groups.

M-400, besides a band characteristic for H-bonded -OH groups (3629 cm⁻¹), has a band of free or almost free -OH groups at 3670 cm⁻¹ [12] because of less surface water in comparison with M-200. Also, on this sample there are no adsorbed citrates which were removed by calcination at 673 K. Increase of a band at 3480 cm⁻¹ is a consequence of adsorbed water produced during the oxidation of formates (Eq. (2)). Differently from the sample M-200, appearance of the water on this sample is not so obvious. Namely, dissociation (Eq. (3)) is more feasible because cations of iron are free of citrates but the signals for surface -OH groups decreased: carbonate-type species (bands at 1617, 1420 and 1223 cm⁻¹) were formed after adsorption of CO₂ on -OH groups [14,17].

In the same conditions, on M-600 there is only appearance of doublet at 2143 cm⁻¹, corresponds to gaseous CO [16] which disappears after evacuation. It means there is no oxidation of CO and it could be explained only by lack of adsorbed water and -OH groups because the chemical compositions of M-400 and M-600 are almost the same.

The catalytic behaviour of iron oxides M-200, M-400 and M-600 are shown in Fig. 5. It is obvious that sample M-600 is less active than the other two. On this oxide, the reaction starts

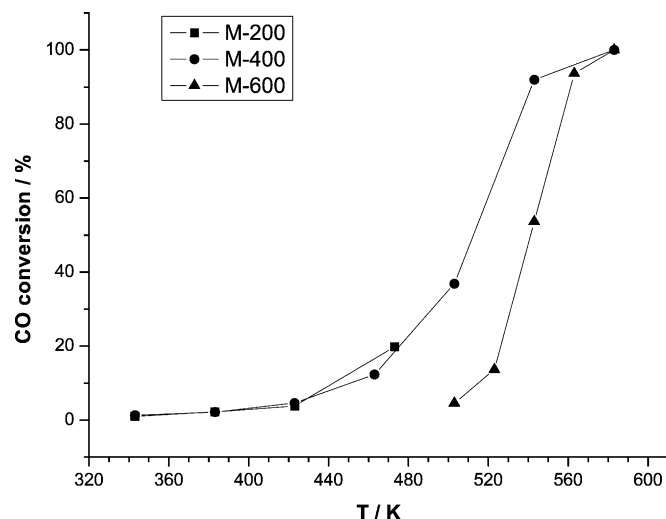


Fig. 5. Conversion of CO as a function of catalyst temperature.

at 500 K, while samples M-200 and M-400 are active even at 340 K. Samples M-200 and M-400 show almost identical activity. (The reaction over M-200 was stopped at 473 K to prevent possible transformation of magnetite and maghemite which usually occurs at this temperature.) It seems that the main path in low-temperature CO oxidation over formates is by oxygen from a gas phase because adsorbed citrates on M-200 did not influence on the activity. Complete conversion of CO over M-400 and M-600 are practically achieved at the same temperature (583 K), but sample M-400 is more active at lower temperature. As can be seen from Fig. 5, 50% conversion over M-400 is achieved at 515 K and over M-600 at 542 K, respectively. Those results are in accordance with our preliminary results [18] with gold dispersed at the same supports.

4. Conclusion

A crucial role in the activity of iron oxides, which could be used as gold supports ($\text{Au}/\text{Fe}_x\text{O}_y$) for CO oxidation at low temperature, plays the amount of surface $-\text{OH}$ groups. It is independent of chemical composition but is dependent of calcination temperature during the pre-treatment. Lower calcination temperature means more $-\text{OH}$ groups. In that case, CO reacts with $-\text{OH}$ groups forming very reactive adsorbed formates, $\text{HCOO}_{(\text{ad})}$. They can be oxidized even in a vacuum to carbon dioxide and water by lattice oxygen, and more easily at the reaction conditions.

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