

Magnetite and Maghemite as Gold-Supports for Catalyzed CO Oxidation at Low Temperature

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Key words A supported gold catalyst was prepared by the deposition-precipitation method from an aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ on synthesized Fe_3O_4 . Calcination at different temperatures caused transformations of Fe_3O_4 to $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$. CO oxidations over $\text{Au}/\text{Fe}_3\text{O}_4$ and $\text{Au}/\gamma\text{-Fe}_2\text{O}_3$ were superior compared to $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$.

CO oxidation
supported gold catalysts
iron oxides
magnetite (Fe_3O_4)
maghemite ($\gamma\text{-Fe}_2\text{O}_3$)
haematite ($\alpha\text{-Fe}_2\text{O}_3$)

INTRODUCTION

Haruta *et al.*^{1,2} found that Au/Fe -oxides prepared by coprecipitation and deposition-precipitation methods were active catalysts for CO oxidation after calcination at 400 °C. They caused the gold to form small metallic particles, which were active species on haematite as a support. After that, not much attention was paid to magnetite and maghemite as alternative supports. If these phases appeared in such catalysts, the results on the activities for CO oxidation would be in contradiction with each other or with this investigation. Gupta and Tripathi³ found that the activity of CO oxidation considerably decreased when $\text{Au}/\text{Fe}_2\text{O}_3$ was pre-treated in hydrogen. It was explained by the transformation of Fe_2O_3 to Fe_3O_4 and the crucial role of oxygen in the support. Kozlova and co-workers⁴ used PPh_3 as a ligand for gold, which caused $\gamma\text{-Fe}_2\text{O}_3$ formation. The most active catalyst for low temperature CO oxidation had small gold particles and a poorly crystallized mixture of $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ as a support. On the other hand, Guzzi *et al.*⁵ reported that appearance of $\gamma\text{-Fe}_2\text{O}_3$ after $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$ reduction led to a decrease in the activity of CO oxidation.

EXPERIMENTAL

Catalyst Preparation

A sample of pure magnetite⁶ was prepared by adding a stoichiometric mixture containing Fe^{II} - ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Kemika) and 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 NH_4OH containing a citric acid trisodium salt. The mixture was vigorously stirred (1500 r.p.m.) at room temperature for 30 minutes. The final pH was 9.79. The solid was separated and washed twice. After drying at 50 °C, it was ground and heated at 160 °C for 4 hours.

The prepared magnetite (Mx) was immersed into a mixture of 0.05 M $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Sigma) and 1 M NH_4OH (Kemika). The gold loading was 2 % (w) and the pH of the mixture was 11.44. After 1 hour at room temperature, the solid was separated (pH was 11.30), washed and heated at 160 °C for 4 hours.

Catalytic Measurements

Catalytic activities were measured in a fixed-bed reactor using 100 mg of a catalyst. The composition of reactant gases was: $\text{O}_2/\text{He}/\text{CO} = 20/78/2 \text{ ml min}^{-1}$ (space velocity, $\text{SV} = 60\,000 \text{ ml h}^{-1} \text{ g}_{(\text{cat.})}^{-1}$). The effluent gases were ana-

lyzed using a quadruple mass spectrometer (QMS 311, Balzers). Before the catalytic test, the samples were pre-treated by heating in a stream of $O_2/He = 20/80 \text{ ml min}^{-1}$ for 2 hours at 200 °C (M/200), 400 °C (M/400) and 600 °C (M/600). All experiments were performed at atmospheric pressure.

IR Measurements

The IR spectra were recorded at room temperature using a Perkin-Elmer spectrometer-model 283. The specimens were pressed into the KBr matrix.

RESULTS AND DISCUSSION

CO Oxidation

Figures 1 and 2 show catalytic activities expressed as a degree of reaction in percents (percent of CO conversion) and Arrhenius plots, respectively. Samples M/200 and M/400 were superior.

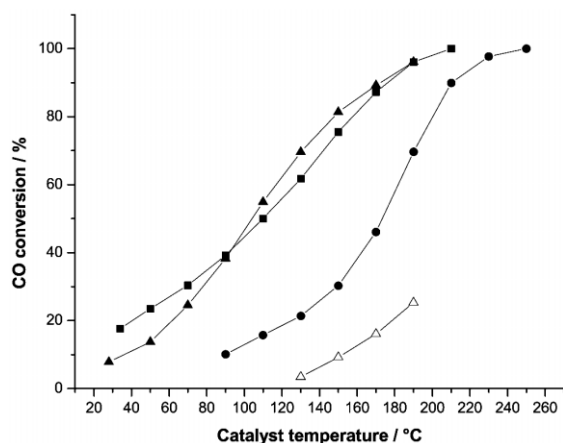


Figure 1. Conversion of CO as a function of catalyst temperature. (Δ) Mx, (\blacktriangle) M/200, (\blacksquare) M/400, (\bullet) M/600; $w(Au) = 2\%$ (loading), $\phi(CO)$ in air = 2%, $SV = 60\,000 \text{ ml h}^{-1} \text{ g}_{(cat.)}^{-1}$.

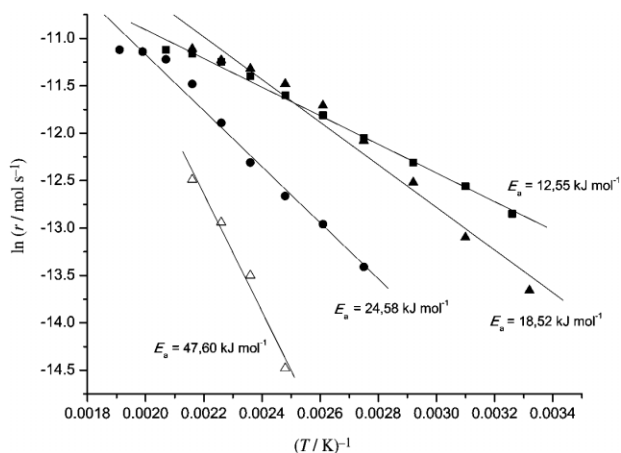


Figure 2. Arrhenius plots for CO oxidation as a function of reciprocal temperature. (Δ) Mx, (\blacktriangle) M/200, (\blacksquare) M/400, (\bullet) M/600; r , rate of CO oxidation per 1 g of catalyst.

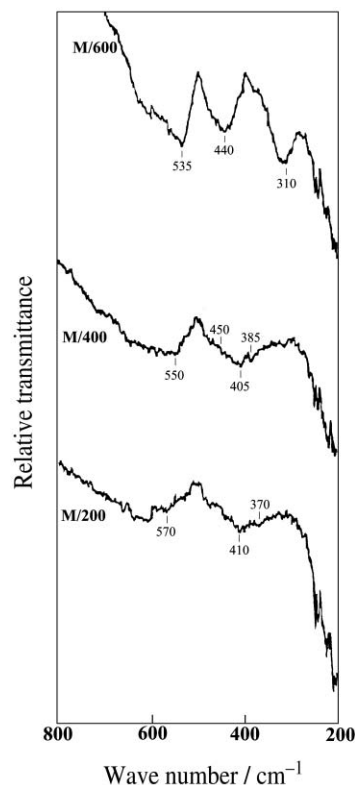


Figure 3. IR spectra of catalysts M/200, M/400 and M/600, recorded at room temperature.

The difference between magnetite with gold (M/200) and pure magnetite (Mx) is very obvious. The measurements were carried out up to 190 °C to prevent transformation of magnetite to maghemite. At that temperature, by Mx, 25 % of CO conversion was achieved while, by M/200, the same degree was achieved already at 70 °C.

Temperatures for 50 % of CO conversion were 105 °C (M/200), 110 °C (M/400) and 183 °C (M/600), which indicates that magnetite and maghemite are better gold-supports for this reaction than haematite (Figure 1).

Figure 2 shows the superiority of magnetite and maghemite in activation energy. The rates of CO oxidation at 27 °C were 1.37×10^{-6} (M/200), 2.93×10^{-6} (M/400) and 3.06×10^{-7} (M/600) mol s^{-1} per 1 g of catalyst calculated from the plots.

Superiority of maghemite as a gold-support over haematite was confirmed under milder conditions: 200 mg of the catalyst in the mixture: $O_2/He/CO = 7/26/0.7 \text{ ml min}^{-1}$ ($SV = 10\,110 \text{ ml h}^{-1} \text{ g}_{(cat.)}^{-1}$). Catalyst M/400 converted 100 % of CO at 38 °C while M/600 at 150 °C.

IR Results

Figure 3 shows the IR spectra of the catalysts used, which proved⁷ the expected transformations⁸ of magnetite to maghemite at 400 °C and maghemite to haematite at 600 °C.

CONCLUSIONS

Detailed investigations of these catalysts are still in progress but the following conclusions can be drawn:

– Magnetite and maghemite (developed from magnetite by heating) could be efficient materials as gold-supports for low temperature CO oxidation.

– Haematite (developed also from magnetite by heating) was always less active as a gold-support for CO oxidation than magnetite and maghemite. This cannot be attributed to the influence of high temperature of the pre-treatment on gold. When haematite (prepared by heating magnetite in air at 600 °C) was the support and gold was deposited in the same way, there was no difference in catalytic activity with respect to M/600 after the same pre-treatment at 400 °C.

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SAŽETAK

Magnetit i maghemit kao nosači zlata za kataliziranu oksidaciju ugljikovoga monoksida pri niskoj temperaturi

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Zlato kao katalizator na nosaču pripravljen je metodom »depozicije-precipitacije« iz vodene otopine $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ na sintetizirani Fe_3O_4 . Kalciniranje pri različitim temperaturama uzrokovalo je transformacije Fe_3O_4 u $\gamma\text{-Fe}_2\text{O}_3$ i $\alpha\text{-Fe}_2\text{O}_3$. Oksidacije CO uz $\text{Au/Fe}_3\text{O}_4$ i $\text{Au}/\gamma\text{-Fe}_2\text{O}_3$ su bile superiorne u odnosu na $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$.