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

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A supported gold catalyst was prepared by the deposition-precipitation method from an aqueous solution of HAuCl₄·3H₂O on synthesized Fe₃O₄. Calcination at different temperatures caused transformations of Fe₃O₄ to γ-Fe₂O₃ and α-Fe₂O₃. CO oxidations over Au/Fe₃O₄ and Au/γ-Fe₂O₃ were superior compared to Au/α-Fe₂O₃.

Key words: CO oxidation, supported gold catalysts, iron oxides, magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), haematite (α-Fe₂O₃)

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 Au/Fe₂O₃ was pre-treated in hydrogen. It was explained by the transformation of Fe₂O₃ to Fe₃O₄ and the crucial role of oxygen in the support. Kozlova and co-workers⁴ used PPh₃ as a ligand for gold, which caused γ-Fe₂O₃ formation. The most active catalyst for low temperature CO oxidation had small gold particles and a poorly crystallized mixture of γ-Fe₂O₃ and α-Fe₂O₃ as a support. On the other hand, Guczi et al.⁵ reported that appearance of γ-Fe₂O₃ after Au/α-Fe₂O₃ 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 Fe²⁺ (FeSO₄·7H₂O, Kemika) and Fe³⁺-ions (FeCl₃·6H₂O, Riedel-de Haën) at a ratio 1:2 into 0.7 M NH₄OH 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 HAuCl₄·3H₂O (Sigma) and 1 M NH₄OH (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: O₂/He/CO = 20/78/2 ml min⁻¹ (space velocity, SV = 60 000 ml h⁻¹ g⁻¹ (g 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 O2/He = 20/80 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.

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 \(\times\) 10\(^{-6}\) (M/200), 2.93 \(\times\) 10\(^{-6}\) (M/400) and 3.06 \(\times\) 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 ml min\(^{-1}\) (SV = 10 110 ml h\(^{-1}\) g\(_{\text{cat.}}\)\(^{-1}\)). 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 proved the expected transformations of magnetite to maghemite at 400 °C and maghemite to haematite at 600 °C.

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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.

REFERENCES


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 HAuCl₄·3H₂O na sintetizirani Fe₃O₄. Kalciniranje pri različitim temperaturama uzrokovalo je transformacije Fe₃O₄ u γ-Fe₂O₃ i α-Fe₂O₃. Oksidacije CO uz Au/Fe₃O₄ i Au/γ-Fe₂O₃ su bile superiorne u odnosu na Au/α-Fe₂O₃.