NOTE

Low-Temperature Water–Gas Shift Reaction over Au/α-Fe₂O₃

There has been growing interest in studies of the catalytic activity of gold supported on some transition metal oxides. One should mention the high catalytic activity of Au/α-Fe₂O₃ in the oxidation of carbon monoxide and hydrogen (1–4). Results have also been published concerning important environmental catalytic reactions, such as the complete oxidation of hydrocarbons (4) and decomposition and reduction of NO with CO (5). The interest shown in the catalytic activity of metallic gold is related also to the mechanism of catalytic performance of that element, considered for a long time to be catalytically inactive. The question arises of how to explain the observed synergism in catalysis between gold and the transition metal oxide support.

This paper gives a short account of results associated with the high catalytic activity of metallic gold, deposited on ferric oxide, in the water–gas shift (WGS) reaction. Until now there has been no literature data on the catalytic activity of gold in that important industrial reaction except some results for the hydrogenation of CO₂ (6).

Three samples were studied: Au/α-Fe₂O₃, Au/Al₂O₃ and α-Fe₂O₃. The samples were prepared through coprecipitation upon mixing an aqueous solution of HAuCl₄ and the corresponding nitrate (Fe(NO₃)₃·9H₂O or Al(NO₃)₃·9H₂O) with Na₂CO₃ solution at 60°C and at constant pH 8.0, the atomic Au:Fe and Au:Al ratios being 1:22. All reagents used were analytical grade (p.a.). After aging at 60°C for 1 h, the precipitate was filtered and washed with distilled water until there were no Cl⁻ and NO₃⁻ ions. Further, the precipitate was dried under vacuum at 80°C and calcinated in air at 400°C for 2 h. The surface areas of the used samples were subsequently: Au/α-Fe₂O₃, 20 m²/g; α-Fe₂O₃, 16 m²/g; and Au/Al₂O₃, 57 m²/g.

Figure 1 shows the temperature dependence of the catalytic activity of the studied samples, expressed as moles of converted CO on 1 m² of the surface area per hour (mol CO · m⁻² · h⁻¹). The catalytic measurements were performed in a flow reactor at atmospheric pressure using initial gas mixture containing 4.88 vol% CO in argon. The following experimental conditions were applied: 1 cm³ catalyst bed; space velocity 4000 h⁻¹; water vapour partial pressure in the starting mixture 223 Torr. CO and CO₂ contents at the reactor outlet were determined by means of an infrared analyzer.

The results presented in Fig. 1 show that the Au/α-Fe₂O₃ sample exhibited high catalytic activity at low temperatures in the WGS reaction. This activity is even higher than that of the most efficient catalyst for the same reaction, namely, the industrial copper–zinc–aluminium (CuO/ZnO/Al₂O₃) catalyst (7), measured under the same conditions. The catalytic activity of the Au/α-Fe₂O₃ sample was considerably higher than the activity of the sample containing only Fe₂O₃. Parallel experiments indicated that the Au/Al₂O₃ sample demonstrated very low activity in the WGS reaction.

A conclusion can be drawn that the high catalytic activity of Au/α-Fe₂O₃ at low temperatures is due to a specific interaction between gold and the ferric oxide support. Preliminary X-ray diffraction measurements showed that the working Au/α-Fe₂O₃ catalyst contained iron as Fe₃O₄ and Fe₂O₃. Electron microscopy data indicated that metallic gold occurred in a finely divided state. The gold particles of 3.5 nm average size were located in close proximity to iron oxides crystallites. The average size of the gold particles in the Au/Al₂O₃ sample is of the same order. The gold-free sample manifested significant catalytic activity only at high temperatures, typical of the well known high-temperature iron catalyst with an active magnetite component (8).

The high activity of Au/α-Fe₂O₃ in the WGS reaction at low temperatures can be attributed to synergetic effects between the two catalyst components.
ACKNOWLEDGMENT

The present work was supported by the National Foundation for Scientific Research—Bulgaria.

REFERENCES


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