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NOTE

Low-Temperature Water–Gas Shift Reaction over Au/α-Fe_2O_3

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-Fe_2O_3 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 have been no literature data on the catalytic activity of gold in that important industrial reaction except some results for the hydrogenation of CO_2 (6).

Three samples were studied: Au/α-Fe_2O_3, Au/Al_2O_3 and α-Fe_2O_3. The samples were prepared through coprecipitation upon mixing an aqueous solution of $HAuCl_4$ and the corresponding nitrate ($Fe(NO_3)_3 \cdot 9H_2O$ or $Al(NO_3)_3 \cdot 9H_2O$) with Na_2CO_3 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 NO_3^- 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-Fe_2O_3, 20 m^2/g; α-Fe_2O_3, 16 m^2/g; and Au/Al_2O_3, 57 m^2/g.

Figure 1 shows the temperature dependence of the catalytic activity of the studied samples, expressed as moles of converted CO on 1 m^2 of the surface area per hour (mol $CO \cdot m^{-2} \cdot h^{-1}$). 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 cm^3 catalyst bed; space velocity 4000 h^{-1}; water vapour partial pressure in the starting mixture 223 Torr. CO and CO_2 contents at the reactor outlet were determined by means of an infrared analyzer.

The results presented in Fig. 1 show that the Au/α-Fe_2O_3 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 ($CuO/ZnO/Al_2O_3$) catalyst (7), measured under the same conditions. The catalytic activity of the Au/α-Fe_2O_3 sample was considerably higher than the activity of the sample containing only Fe_2O_3. Parallel experiments indicated that the Au/Al_2O_3 sample demonstrated very low activity in the WGS reaction.

A conclusion can be drawn that the high catalytic activity of Au/α-Fe_2O_3 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-Fe_2O_3 catalyst contained iron as Fe_3O_4 and Fe_2O_3. 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/Al_2O_3 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-Fe_2O_3 in the WGS reaction at low temperatures can be attributed to synergetic effects between the two catalyst components.

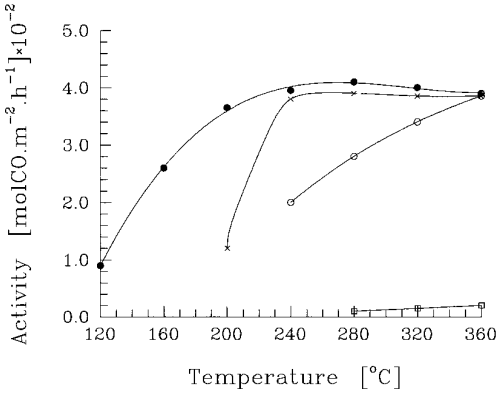

FIG. 1. Temperature dependence of the catalytic activity of the samples studied: ●, Au/α-Fe_2O_3; ○, α-Fe_2O_3; □, Au/Al_2O_3; ×, $CuO/ZnO/Al_2O_3$.

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