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TPR and TPD investigation of Au/α-Fe_2O_3

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Abstract

Temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) studies of Au/α-Fe_2O_3 and α-Fe_2O_3 samples have been carried out. It was found that the peak maximum due to the $Fe_2O_3 \rightarrow Fe_3O_4$ reduction of the gold-containing sample was shifted by ~140 K to lower temperatures in comparison with α-Fe_2O_3. A scheme of low-temperature reduction with the participation of reactive surface hydroxyl groups is proposed. By means of TPD, it was established that the hydroxyl coverage on Au/α-Fe_2O_3 was about two times higher than that on α-Fe_2O_3. A scheme is suggested which explains the continuous desorption of water to 1083 K from the surface of the gold-containing sample. The results obtained are in agreement with earlier proposed water–gas shift (WGS) reaction mechanism over Au/α-Fe_2O_3 catalysts. © 1997 Elsevier Science B.V.

Keywords: Au/α-Fe_2O_3; Effect of hydroxyl coverage; Reduction mechanism; Temperature-programmed desorption; Temperature-programmed reduction

1. Introduction

Recently, studies of gold-containing catalysts, deposited on metal oxides from the first transition-metal series, have received considerable attention. These catalysts manifest high activity at low temperatures in a number of important reactions, such as oxidation of CO and H_2 [1–4], CO_2 hydrogenation [5], etc.

Our investigations [6,7] have shown that the gold-containing catalysts also exhibit high activity in the low-temperature water–gas shift (WGS) reaction. A possible reaction mechanism of this process over Au/α-Fe_2O_3 has been suggested, which involves the formation of intermediate species on interaction between CO, adsorbed on iron cations, and OH groups from the catalyst surface. The occurrence of ultrafine gold particles presumes high surface hydroxyl coverage, experimentally verified by electrocatalysis [8], and is in agreement with the proposed mechanism, including water dissociative adsorption onto energetically rich gold particles on the surface.

By carrying out a parallel study of Au/α-Fe_2O_3 and α-Fe_2O_3 samples, this work aims at looking for new evidence in favour of the suggested WGS reaction mechanism as well as for the effect of gold as promoter on iron oxide reducibility and formation of reactive surface hydroxyl coverage.

2. Experimental

Two samples, Au/α-Fe_2O_3 and α-Fe_2O_3, were investigated. They were prepared through co-precipi-

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tation by means of Contalab automated laboratory reactor (Contraves, Switzerland) under complete control of all parameters: temperature, pH, stirrer speed, reactant feed flow, etc. The chemicals used were all 'analytical grade': $Fe(NO_3)_3 \cdot 9H_2O$, $HAuCl_4 \cdot 3H_2O$ and Na_2CO_3. The following conditions of co-precipitation were employed: 333 K, pH 8.0, stirrer speed 250 rpm, reactant feed flow rate 8 ml min^{-1}. The precipitate was filtered and carefully washed until disappearance of NO_3^- and Cl^- ions. Further, the samples were dried at 353 K under vacuum and calcined at 673 K for 2 h. Gold content in the Au/α-Fe_2O_3 sample was 3 wt.%. The BET area of the Au/α-Fe_2O_3 and α-Fe_2O_3 samples was 59 and 56 m^2g^{-1}, respectively. Fresh samples were characterized by means of X-ray diffraction and transmission electron microscopy (TEM) [7]. The Au/α-Fe_2O_3 sample contained finely divided gold on α-Fe_2O_3, the average gold particle size being 3.5 nm.

The temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) measurements were performed by means of an apparatus described elsewhere [9]. An argon–hydrogen mixture (10 vol.% H_2), dried by passing through molecular sieve at 233 K, was used for the TPR experiments (flow rate 24 ml min^{-1}). The sample, 0.01 g, was heated at a rate of 15 K min^{-1}. A cool trap, 233 K, for collecting released water during reduction was mounted in the gas line between the reactor and the thermal conductivity detector.

Two types of TPR measurements were carried out: TPR experiments of fresh samples (direct TPR) and TPR after preliminary dehydroxylation by heating in helium flow to 823 K and subsequent cooling to room temperature.

The TPD measurements were conducted with 0.15 g samples which were heated at a rate of 17 K min^{-1}. Specially purified helium [9] was applied as a carrier gas (50 ml min^{-1}). Following reduction of samples to magnetite, TPD experiments on Au/α-Fe_2O_3 at 580 K and α-Fe_2O_3 at 700 K were also carried. Pulses of 0.4×10^{-6} ml water were introduced at 373 K until saturation of the surface. This was followed by TPD to 1073 K.

The amount of desorbed water in the 513–908 K range was determined on a preliminarily calibrated thermal conductivity detector by freezing in a liquid nitrogen trap and subsequent thawing.

Infrared (IR) spectra of the fresh samples were recorded on a Bruker-IFS 66 FTIR spectrophotometer, equipped with throughput Michelson interferometer and ASPECT-1000 computer, in the 3800–600 cm^{-1} range, at a spectral resolution of 0.5 cm^{-1}. The samples were pressed in KBr discs.

3. Results

3.1. Temperature-programmed reduction

Fig. 1 shows TPR profiles of the two investigated samples. Direct TPR of the α-Fe_2O_3 and Au/α-Fe_2O_3 samples is presented in Figs. 1.1 and 1.3, respectively. The TPR profiles of prior dehydroxylated α-Fe_2O_3 and Au/α-Fe_2O_3 are shown in Figs. 1.2 and 1.4, respectively. It is seen that the TPR spectrum of α-Fe_2O_3 is composed by two overlapping peaks, one of them with T_{max} at ~700 K is related to the $Fe_2O_3 \rightarrow Fe_3O_4$ reduction step, whereas the other peak is attributed to the transition $Fe_3O_4 \rightarrow FeO \rightarrow Fe$ [10]. A low-temperature shoulder at ~618 K in the TPR profile of fresh α-Fe_2O_3 was also observed which disappeared on preliminary dehydroxylation of the sample (cf. Figs. 1.1 and 1.2).

The TPR spectra of Au/α-Fe_2O_3 (Figs. 1.3, 1.4) substantially differ from those of α-Fe_2O_3. The two peaks, due to the two reduction steps (hematite to magnetite and magnetite to metal iron) do not overlap in the presence of gold. T_{max} of the peak related to the reduction step $Fe_2O_3 \rightarrow Fe_3O_4$ for fresh Au/α-Fe_2O_3 is by ~140 K lower than that for the same transition in the absence of gold (cf. Figs. 1.1 and 1.3). X-ray diffraction and TEM analysis of Au/α-Fe_2O_3 sample conducted after the end of the first reduction peak, T=580 K, indicated pure magnetite. Kang et al. [11] have also observed a shift to lower temperatures for that transition in a TPR study of Au-Fe/zeolite Y. The second reduction step $Fe_3O_4 \rightarrow FeO \rightarrow Fe$ starts after the reduction of hematite to magnetite has been completed. After preliminary dehydroxylation of the Au/α-Fe_2O_3 sample, the first TPR peak was displaced to higher temperatures (T_{max}=588 K) but did not overlap with the second peak.

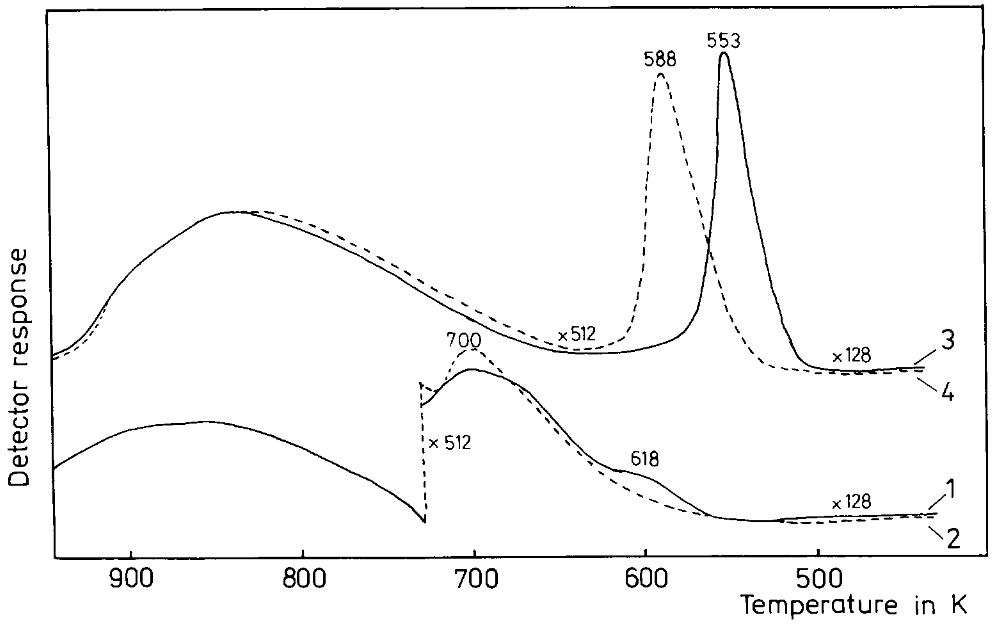


Fig. 1. TPR spectra of the following samples: (1) α-Fe_2O_3; (2) α-Fe_2O_3 after preliminary dehydroxylation; (3) Au/α-Fe_2O_3; and (4) Au/α-Fe_2O_3 after preliminary dehydroxylation.

3.2. TPD

Fig. 2 shows direct TPD profiles of the two investigated samples. Two TPD peaks were observed with the α-Fe_2O_3 sample (Fig. 2.1): a low-temperature peak (T_{max}=398 K), attributed to non-dissociatively bonded water, and a high-temperature peak which we assign to the surface hydroxyl coverage. The Au/α-Fe_2O_3 sample (Fig. 2.2) gave rise to only one well-resolved peak in the low-temperature range

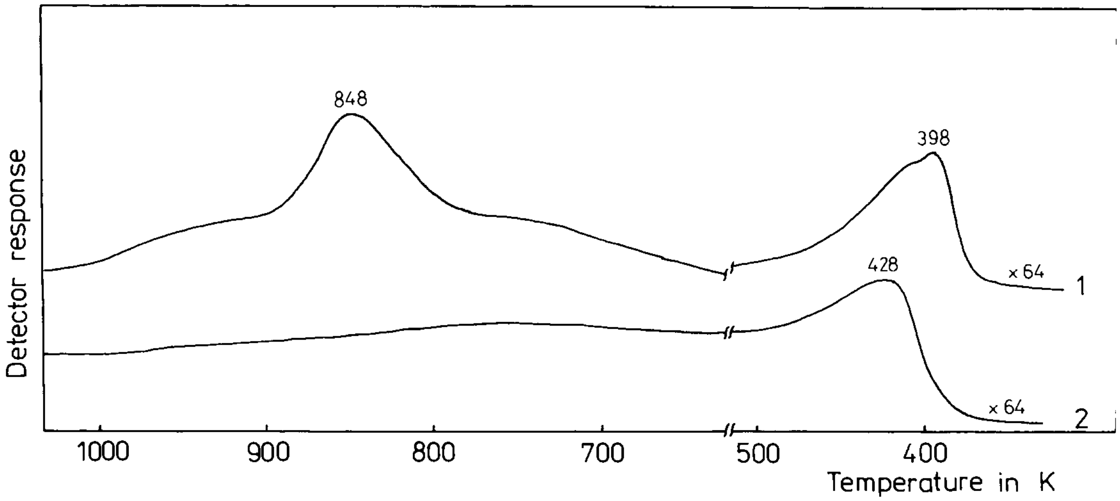


Fig. 2. TPD spectra of (1) α-Fe_2O_3, and (2) Au/α-Fe_2O_3 samples.

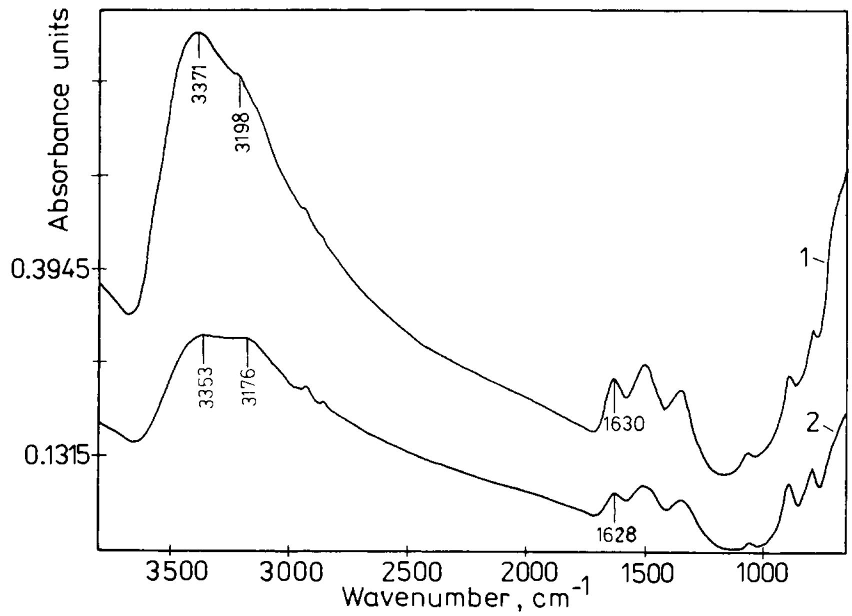


Fig. 3. IR spectra of (1) Au/α-Fe_2O_3 and (2) α-Fe_2O_3 samples.

(T_{max}=428 K). Following that, a continuous desorption to 1073 K was observed without clearly resolved maxima.

TPD experiments with magnetite samples with prior adsorbed water, demonstrated profiles similar to those presented in Fig. 2. Again, after the first well-resolved peak from the Au/α-Fe_2O_3 sample, a continuous desorption from the surface was registered.

Concerning the amount of desorbed water, corresponding to the surface hydroxyl coverage due to non-dissociatively bonded water in the temperature range after the first peak, the following values were determined: 8.9×10^{-8} and 16.6×10^{-8} ml m^{-2} for the α-Fe_2O_3 and Au/α-Fe_2O_3 samples, respectively.

3.3. IR spectra

IR spectra of the two fresh samples are shown in Fig. 3. A band from the bending H–OH vibrations was observed at 1627.7 and 1629.6 cm^{-1} for the α-Fe_2O_3 and Au/α-Fe_2O_3 samples, respectively. The integrated intensity of this band from the gold-containing sample was calculated at a 2.1 times higher value than that of α-Fe_2O_3. An intense absorbance in the OH stretching region, 3200–3400 cm^{-1}, due to hydroxyl groups and non-dissociatively adsorbed water molecules was also observed. Comparison of the integrated band intensities showed a 1.7 times higher value for the gold-containing sample.

4. Discussion

Previous investigations from this laboratory [7] have shown that the Au/α-Fe_2O_3 catalyst manifested a higher catalytic activity in the low-temperature WGS reaction (410–530 K) as compared to α-Fe_2O_3. Essential aspects of the proposed reaction mechanism [7] involve water-dissociative adsorption on ultrafine gold particles followed by a spillover of activated hydroxyl groups onto adjacent sites of the ferric oxide. The formation and decomposition of intermediate species is accompanied by a redox transfer $Fe^{3+} \Leftrightarrow Fe^{2+}$ in Fe_3O_4.

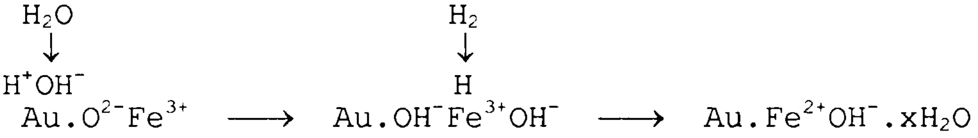
According to this reaction mechanism, one should expect magnetite as the working catalytic system and the presence of high surface hydroxyl coverage – which takes part in the formation of surface intermediates – in order to achieve high catalytic activity.

The TPR study performed in the present work showed that the hematite–magnetite transition in Au/α-Fe_2O_3 takes place at a considerably lower temperature (~140 K) than in α-Fe_2O_3. At 580 K, the iron oxide in Au/α-Fe_2O_3 was pure magnetite, whereas the reduction of α-Fe_2O_3 started at about the same temperature. Therefore, in the presence of gold, the working state of the catalyst was attained at a significantly lower temperature – which explains the low-temperature activity of the gold-containing catalysts in the WGS reaction.

The high dispersion of gold in Au/α-Fe_2O_3 samples [7], justifies the occurrence of considerable quantities of energetically rich gold atoms on the surface of these samples, such atoms being able to generate reactive hydroxyl groups. A semiquantitative estimation from the IR spectra (Fig. 3) points to a substantial increase of OH groups and non-dissociatively bonded water molecules in the gold-containing sample (~2 times) than in the α-Fe_2O_3 sample.

The TPD measurements provide a possibility for quantitative evaluation of water amount, corresponding to hydroxyl coverage, after desorption of the non-dissociatively bonded water molecules. The results obtained show that the amount of water desorbed from the gold-containing sample, corresponding to the surface hydroxyl coverage, is about two times higher than that with α-Fe_2O_3. The presence of high hydroxyl coverage explains satisfactorily the higher catalytic activity of Au/α-Fe_2O_3 in the WGS reaction, in agreement with the suggested mechanism.

Results of the TPR study can be interpreted on the assumption that coordinated water and hydroxyl coverage take part in the process of reduction. The ability of finely divided gold to dissociate water and form reactive species is consistent with the participation of that species in the reduction, according to the scheme:

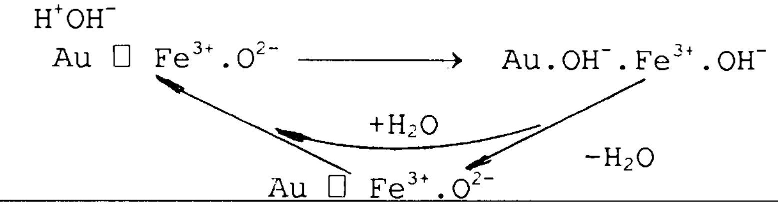


$$\overset{\substack{\mathrm{H_2O}\\ \downarrow \\ \mathrm{H^+OH^-}}}{\mathrm{Au.O^{2-}Fe^{3+}}} \longrightarrow \overset{\substack{\mathrm{H_2}\\ \downarrow \\ \mathrm{H}}}{\mathrm{Au.OH^-Fe^{3+}OH^-}} \longrightarrow \mathrm{Au.Fe^{2+}OH^-.xH_2O}$$

Further, the participation of activated hydroxyl groups, generated on gold, leads to the low-temperature reduction of α-Fe_2O_3 in the gold-containing sample. After removing the major part of the hydroxyl coverage on prior heated to 823 K, the peak due to the reduction step $Fe_2O_3 \rightarrow Fe_3O_4$ is shifted to higher temperatures (cf. T_{max}=553 K and T_{max}=588 K). However, T_{max} remains considerably lower than that for the same step in the absence of gold. By removing the major part of the hydroxyl coverage, the effect of gold on the low-temperature reduction is, very likely, due to a facilitated electron transfer from gold to Fe^{3+}.

The presence of a low-temperature shoulder in the TPR spectrum of α-Fe_2O_3, which disappears after preliminary dehydroxylation, is also associated with facilitated hematite–magnetite transition for a small part of the sample because of a less significant hydroxyl coverage.

A probable explanation of the interesting behaviour of Au/α-Fe_2O_3 during TPD, namely, a continuous desorption of water to 1073 K after the first well-resolved peak, can be related to incorporation of part of the desorbed water in a cycle, according to the following scheme:



This scheme explains satisfactorily the role of energetically rich finely devided gold particles in the dissociative adsorption of water onto Au/α-Fe_2O_3 catalysts.

5. Conclusions

1. The presence of gold in the Au/α-Fe_2O_3 sample, giving rise to dissociative decomposition of water on gold and high hydroxyl coverage, leads to a considerable lowering of the temperature of the reduction step $Fe_2O_3 \rightarrow Fe_3O_4$.
2. Results obtained from the TPD study are in agreement with the proposed reaction mechanism of the water–gas shift over Au/α-Fe_2O_3 catalysts which involves a step of water dissociative adsorption onto finely divided gold particles.

Acknowledgements

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