ChemComm
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Highly effective ferric hydroxide supported gold catalyst for selective oxidation of CO in the presence of H_2†

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Received (in Cambridge, UK) 24th June 2003, Accepted 15th July 2003
First published as an Advance Article on the web 28th July 2003

Ferric hydroxide supported Au prepared with co-precipitation without heat treatment could be a very effective catalyst for selective CO oxidation in the presence of H_2 at lower temperatures.

Metal-oxide supported Au catalysts for CO oxidation at lower temperatures have been studied extensively for many years,[1–8] and several preparation methods such as conventional impregnation,[9] co-precipitation,[10] deposition–precipitation,[11] ion-exchange[12] and chemical vapour deposition[13] have been employed. The co-precipitation method has been particularly utilized to obtain highly active supported gold catalysts, in which chloroauric acid as gold precursor, including washing to remove chloride, drying and then calcinations to form appropriate nano-Au metal particles on a support were generally considered to be indispensable procedures for a successful preparation of supported Au catalyst. Due to the peculiar properties of gold as a catalytically active species, great differences from the activities usually observed for CO oxidation resulted from the co-precipitation method and various preparation parameters could strongly affect the activity of the supported gold catalysts. Recently, Gavriilidis *et al.*[14] and Kiely *et al.*[15] reported respectively that the active supported Au catalyst can be prepared by co-precipitation only by calcination at 120 K and they possessed higher activity than those which were calcined at elevated temperatures. This may imply that Au as a catalytic material may exhibit much different behavior during catalyst preparation in comparison with traditional supported Pt and Pd catalysts which were generally prepared through indispensable procedures, *i.e.* dryness, calcination in air and even reduction in H_2 at elevated temperatures.

In this communication, ferric hydroxide supported Au catalysts have been prepared with co-precipitation by drying at room temperature without any further calcining treatment at elevated temperature. Oxidations of CO or H_2 in air and selective oxidation of CO in the presence of H_2 were used as probe reactions for testing their catalytic performances. The experimental results showed that ferric hydroxide supported Au could be a highly effective catalyst for selective oxidation of CO in the presence of H_2 in comparison with Au/Fe_2O_3 derived from the ferric hydroxide supported Au which was then calcined at 200 or 400 K.

The catalysts with varied Au loadings were prepared by co-precipitation of an aqueous solution of $HAuCl_4$ ($0.1\ g\ ml^{-1}$) and $Fe(NO_3)_3$ ($1\ mol\ L^{-1}$) with an aqueous solution of $Na(CO_3)_2$ ($1\ mol\ L^{-1}$) according to the procedures described in the previously reported literatures.[16,17] The resulting precipitates without Cl^- were dried at room temperature (*ca.* 25–30 K) for 24 h to form ferric hydroxide supported Au catalyst (denoted as Au/Fe–U), or the ferric hydroxide supported Au samples were then calcined in air at 200 or 400 K for 6 h to form two different supported Au catalysts denoted as Au/Fe-2 and Au/Fe-4 respectively. In order to obtain repeatable activity the preparation process must be conducted very carefully and precisely.

Catalytic activity measurements were carried out with a micro fixed-bed reactor system, and 60 mg (60–80 mesh) of catalyst sample was charged in each time. The feed gases were 1.0 vol% CO or 1.0 vol% H_2 balanced with air, and 1.0 vol% H_2 (or 50 vol% H_2), 1.0 vol% CO and 4.0 vol% O_2 balanced with argon. The flow rate was 20 ml min^{-1} (space velocity: 20 000 $h^{-1}\cdot ml\ g\text{-}cat^{-1}$). The concentrations of CO and H_2 and O_2 in the effluent gas were on-line analyzed by a gas chromatograph (HP 6890, molecular sieve 5 Å plot column).

Complete CO oxidations in air at *ca.* 7 °C, 22 °C and 87 °C were observed over Au/Fe–U, Au/Fe-2 and Au/Fe-4 respectively, Fig. 1, indicating that CO oxidation was sensitive to heat treatment, and calcination at elevated temperatures were detrimental to the catalytic performance. Therefore, Au/Fe–U was the best catalyst for CO oxidation although its Au loading was the lowest. As expected, the catalytic activity could be markedly increased, *i.e.* complete CO oxidation in air at *ca.* −14 °C was achieved, if the Au loading was further increased from 0.76 wt% to 2.52 wt%. Since more water was contained in Au/Fe–U, the water gas shift reaction may favour to CO transformation,[18] however, H_2 formation was not observed during the reaction. In comparison with CO oxidation, oxidations of H_2 were much less sensitive to the heat treatment, and occurred above *ca.* 25 °C over all three catalysts. Since the chemical composition, structure and chemical state of Au/Fe–U are completely different with that of Au/Fe-4, it could be conjectured that CO oxidation was highly sensitive to such changes, while the active species of Au for H_2 oxidation was already formed before any heat treatment and did almost not change when they were further subjected to calcination at elevated temperatures. It is worth noting that there is about a 20 °C gap between the temperatures of complete CO oxidation and the occurrence of H_2 oxidation for Au/Fe–U. This may imply that Au/Fe–U could be an ideal catalyst for the selective CO oxidation in the presence of H_2 at lower temperatures.

When the catalysts mentioned above were exposed to a mixture gas of 1.0 vol% H_2, 1.0 vol% CO and 4.0 vol% O_2, different behaviors of catalytic oxidation were exhibited, Fig. 2.

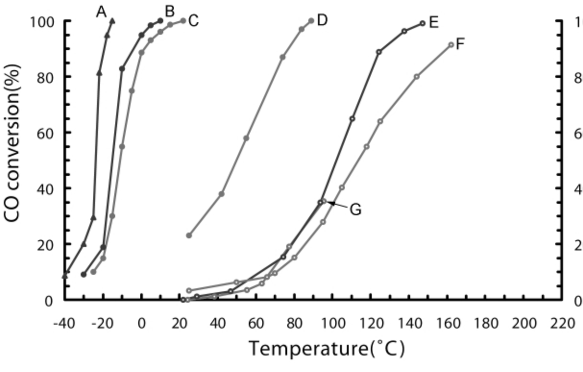

Fig. 1 Respective oxidations of CO or H_2 in air. **B G** 0.76 wt% Au/Fe-U for respective oxidations of CO or H_2. **C E** 1.05 wt% Au/Fe-2 for respective oxidations of CO or H_2. **D F** 1.48 wt% Au/Fe-4 for respective oxidations of CO or H_2. **A** 2.52 wt% Au/Fe-U for CO oxidations

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† This work was financially supported by The National Natural Science Foundation of China (No. 20173068).

DOI: 10.1039/b307181b

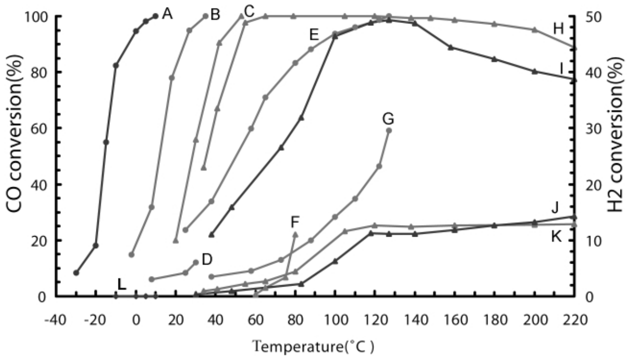

Fig. 2 Oxidations of CO or H_2 in CO + H_2 mixture gas. **A L** 0.76 wt% Au/Fe-u for oxidations of CO and H_2(1%). **B D** 1.05 wt% Au/Fe-2 for oxidations of CO and H_2(1%). **E G** 1.48 wt%Au/Fe-4 for oxidations of CO and H_2(1%). **C F** 0.15 wt%Au/Fe-U for oxidations of CO and H_2(1%). **H K** 1.05 wt%Au/Fe-2 for oxidations of CO and H_2(50%). **I J** 1.48 wt %Au/Fe-4 for oxidations of CO and H_2(50%)

Strong inhibition of CO oxidation by H_2 was observed over Au/Fe-4 and relatively high H_2 conversion occurred before all CO could be oxidized completely, indicating that highly selective CO oxidation in the presence of H_2 over Au/Fe-4 catalyst was impossible. CO oxidations were also slightly affected with H_2 over Au/Fe-2 and the temperature at which CO was completely removed, *i.e. ca.* 30 °C, was high enough to cause detectable oxidation by H_2 (*ca.* 4–6% H_2 conversion). As for Au/Fe–U, conversion of CO oxidation as a function of temperature was almost unchanged in comparison with the CO oxidation in the absence of H_2, *i.e.* the existence of H_2 did not affect the CO oxidation. CO could completely be oxidized at *ca.* 8 °C, while oxidation of H_2 was not detectable at this temperature, *i.e.* the O_2 selectivity for CO oxidation was approaching 100%.

The catalytic performances of these catalysts were also tested with the mixture gas of 50 vol% H_2, 1.0 vol% CO and 4.0 vol% O_2 in argon, Fig. 2. Conversion of CO oxidation as a function of temperature was almost not affected over Au/Fe–U although the concentration of H_2 in feed gas was greatly increased. However, CO oxidations were further inhibited over Au/Fe-2 and Au/Fe-4 in comparison with results obtained from a gas mixture of 1.0 vol% H_2, 1.0 vol% CO and 4.0 vol% O_2 in argon. At higher temperatures, conversions of CO oxidations were turned down due to competing O_2 consumption by sufficient oxidation of H_2. This suggests that selective CO oxidation was also sensitive to the catalyst heat treatments, and calcination at elevated temperatures would cause CO oxidation to be sensitive to the existence of H_2. It is worthy of note that when a Au/Fe–U with lower Au loading was employed, that the temperatures at which CO was totally removed and that H_2 oxidation was initiated was increased simultaneously, suggesting that the temperature for selective CO oxidation in the presence of H_2 could be set by adjusting the Au loadings without decreasing the selectivity of CO oxidation. Furthermore, *ca*. 15 h and 28 h of stable catalytic activities (*ca.* 100% conversion of CO oxidation) were preliminarily achieved over 0.76 wt% Au/Fe–U when it was exposed to the feed gases of 1.0 vol% H_2, 1.0 vol% CO and 4.0 vol% O_2 and 1.0 vol% CO in air, respectively.

Au loadings (3520 ICP AES, ARL Co. USA) and BET adsorption (Micromeritics ASAP 2010) analyses of three different catalysts showed that Au loadings were increased remarkably and the surface areas were decreased greatly after calcination at elevated temperatures. This should be related to losing adsorbed water and transformation of ferric hydroxide into metal-oxides, and high catalytic activity of Au/Fe–U may be partially related to its big surface area. XPS investigation (VG ESCALAB 210) indicated that the chemical states of Au species on the Au/Fe-4 and Au/Fe–U were metallic (B.E.4f$_{7/2}$ = 83.6 eV), and partially cationic (B.E.4f$_{7/2}$ = 84.1 eV), and ferric species with slightly more positive charge were observed on the surface of Au/Fe–U in comparison with that of Au/Fe-4, suggesting markedly different Au and Fe species on the catalyst surfaces, and thus exhibiting markedly different catalytic performances, between uncalcined and calcined catalysts (Table 1).

Table 1 Properties of the catalysts

	Au loading/ wt%	BET surface area m² g^{-1}	Average pore diameter/Å	B.E. of Au4f$_{7/2}$/eV	B.E. of Fe2p$_{3/2}$/eV
Au/Fe-U	2.52	328.4	22.1	84.1	711.6
Au/Fe-2	2.85	194.7	39.0	84.1	711.2
Au/Fe-4	3.32	20.13	106.6	83.6	711.0

In this work, a ferric hydroxide supported gold catalyst prepared with co-precipitation without any heat treatment was developed. It was found that such a catalyst was not only very effective for selective CO oxidation in the presence of H_2 at lower temperatures, but also much better than the corresponding catalyst calcined at elevated temperatures although the preparation method was not optimized. To the best of our knowledge, ferric hydroxide supported gold catalyst is the most effective catalyst reported so far for selective CO oxidation in the presence of H_2 at lower temperatures. Another important point of this work is that traditional preparations of supported gold catalysts was markedly innovated, which may be expanded into other supported noble metals, such as Pd or Pt *etc*., catalyst preparations.

The authors would like to thank Ms L. Gao for the XPS invesigation, Ms Q. Wu for the Au loading analysis and Ms J. Li for the measurement of BET adsorption.

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