

# Influence of Calcination Temperature on Properties of Au/Fe<sub>2</sub>O<sub>3</sub> Catalysts for Low Temperature Water Gas Shift Reaction

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**Abstract:** A series of Au/Fe<sub>2</sub>O<sub>3</sub> catalysts for the water gas shift (WGS) reaction were prepared by modified deposition-precipitation method. The sample calcined at 300 °C showed higher catalytic activity and better stability than other samples. Using N<sub>2</sub> physisorption, *in situ* XRD, H<sub>2</sub>-TPR, and XPS techniques, the influence of calcination temperature on properties of Au/Fe<sub>2</sub>O<sub>3</sub> catalyst was explored, and the cause of deactivation was analyzed as well. The results showed that the catalytic behaviors were related to the interaction between Au and Fe<sub>2</sub>O<sub>3</sub>, and the reductive property of support, both of which were significantly affected by calcination temperature. Furthermore, according to the results of XPS, although stable carbonate and carbonyl surface species were found on the spent catalysts, the semiquantitative analysis of these species indicated that they were not the main cause of the deactivation. In fact, the deactivation of Au/Fe<sub>2</sub>O<sub>3</sub> was sensitive to the structure change of support. During the water gas shift reaction, Fe<sub>3</sub>O<sub>4</sub> particle would aggregate and crystallize leading to increase in the crystallinity of support and a significant reduction in the surface area of the catalysts, which resulted in the deactivation of Au/Fe<sub>2</sub>O<sub>3</sub>.

**Key Words:** Water gas shift; Calcination temperature; Deactivation; Au/Fe<sub>2</sub>O<sub>3</sub> catalyst

The water gas shift (WGS) reaction is a key reaction in the production of hydrogen for a number of process, including petroleum refining and chemical synthesis. An emerging application for the WGS is in the production of hydrogen for proton exchange membrane (PEM) fuel cells. This reaction is important because it removes CO, a poison to the fuel cell electrocatalysts, which is produced during the steam reforming and/or partial oxidation reactions. Cu-based and Fe-Cr-based WGS catalysts are commercially used in current chemical plants. However, they are unsuitable for PEM system because they are pyrophoric and they do not have sufficient activity at low temperature. So, there is substantial interest in development of better performance and more durable WGS catalysts<sup>[1–5]</sup>.

Recently, it has been reported that Au supported catalysts are interesting candidates for novel WGS reaction<sup>[6–11]</sup>. High activities of Au/Fe<sub>2</sub>O<sub>3</sub> and Au/CeO<sub>2</sub> for WGS reaction have

been observed by Andreeva<sup>[6]</sup> and Fu<sup>[7]</sup> *et al.* It is generally known that high catalytic activity of the gold/metal oxide catalysts depends strongly on the dispersion of gold particles and the interaction between gold and support. Therefore, most of the interest in gold catalysis has geared to the study of preparation method<sup>[6,12–14]</sup>, the synthesis parameters<sup>[15,16]</sup>, pre-treatment conditions<sup>[17,18]</sup>, and the choice of supports<sup>[19,20]</sup>, all affecting the dispersion of the gold particles. However, there is relatively little work devoted to the effect of the state and structure of support in the WGS reaction. Zhang *et al.*<sup>[21]</sup> reported the remarkable nanosize effect of zirconia in Au/ZrO<sub>2</sub> catalyst for CO oxidation. In addition, supported gold catalysts have been reported to be susceptible to deactivation. There are several reports describing deactivation mechanisms for gold-based CO oxidation catalysts<sup>[22–26]</sup>. Some of the studies have considered sintering of Au particles as a reason for the deactivation<sup>[24–26]</sup>. Change of Au particle size from 4 to 5.5

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nm has been taken as a significant change influencing the catalytic performance<sup>[26]</sup>. For WGS reaction, catalysis process of gold-containing systems generally involves the formation of carbonyl or carbonate-like species on ultrafine gold particles. Kim *et al.*<sup>[27]</sup> reported that it is these species blocking the active surface sites that contribute to the deactivation of Au/CeO<sub>2</sub> catalyst. There is only one another work<sup>[28]</sup>, which is devoted to the study of deactivation mechanisms of the gold-based WGS catalyst. With the help of DRIFTS, MS, TGA, TEM, N<sub>2</sub> physisorption, ICP, and XRD, Silberova *et al.*<sup>[28]</sup> put forward that the decrease of the surface area can almost solely explain the decrease on the activity when Au/Fe<sub>2</sub>O<sub>3</sub> catalyst was exposed to a steam with 0.5% CO, 1.5% H<sub>2</sub>O, and 98% He. Because WGS gas composition in the production of hydrogen for proton exchange membrane (PEM) fuel cells is typically with 10% CO, furthermore work is needed to clarify whether the decrease of the surface area is the essential reason for the deactivation of Au/Fe<sub>2</sub>O<sub>3</sub> catalysts in higher CO concentration.

In this article, temperature-programmed and long-term stability tests of Au/Fe<sub>2</sub>O<sub>3</sub> catalysts calcined at different temperatures for the WGS reactions were studied. The influence of calcination temperature on the structure and catalytic performance of Au/Fe<sub>2</sub>O<sub>3</sub> catalysts for WGS reaction were investigated by applying different characterization techniques (e.g. *in situ* XRD, N<sub>2</sub> physical adsorption, TPR, and XPS). Finally, all of above characterizations of the physical and chemical properties of the fresh and used catalysts helped to define the deactivation mechanism.

## 1 Experimental

### 1.1 Catalyst preparation

Supported gold catalysts used in this article were designed with mass fraction of 4.0% Au and prepared by the following general route. The aqueous solutions of 1.0 mol·L<sup>-1</sup> Fe(NO<sub>3</sub>)<sub>3</sub> and 1.0 mol·L<sup>-1</sup> K<sub>2</sub>CO<sub>3</sub> were simultaneously added dropwise to 20 mL deionized water at 60 °C and at a constant pH value of 8.0 under vigorous stirring. After being centrifuged and washed with deionized water several times, the obtained precipitate was redispersed into 30 mL deionized water at 60 °C. Then the 0.2 mol·L<sup>-1</sup> HAuCl<sub>4</sub> was pumped into the support slurry under vigorous stirring at ca 8.0 cm·min<sup>-1</sup>. And the base (0.5 mol·L<sup>-1</sup> K<sub>2</sub>CO<sub>3</sub>) was pumped in at a variable rate to maintain pH as close as possible to 8.0 throughout the addition of gold chloric acid. After the aqueous solution addition was complete, stirring was continued for a further 1 h at 60 °C. The acquired samples were alternatively centrifuged and washed with deionized water until no Cl<sup>-</sup> ion was detected by AgNO<sub>3</sub> solution. Following that, the samples were dried at 110 °C for 8 h, then heated to desired temperature (200, 300, 400, or 500 °C) in air at a rate of 5 °C·min<sup>-1</sup> and held at concerned temperature for 2 h. The as-prepared samples were la-

beled as Au/Fe-200, 300, 400, or 500, respectively. For comparison, Fe<sub>2</sub>O<sub>3</sub> was prepared in a similar way.

### 1.2 Catalyst characterization

The textures of the samples were obtained from nitrogen absorption-desorption isotherms which were measured at liquid nitrogen temperature, using 'OMINSORP100CX' instrument. Before analysis, the samples were degassed at 150 °C to final pressure of 1×10<sup>-3</sup> Pa.

Powder X-ray diffraction (XRD) data of all samples were collected *via* a Panalytical X'Pert Pro diffractometer with X'Celerator Detector, using the Co K<sub>α</sub> radiation (0.1790 nm) at a voltage and current of 40 kV and 40 mA, respectively. Diffraction patterns were recorded at room temperature (25 °C) in the step scanning mode, with a 2θ step of 0.0333° and every step standing for 10 s in the range of 20°≤2θ<80°.

Temperature-programmed reduction (TPR) of the catalysts in fine powder form was carried out in a 'Micromeritics Autochem 2910' instrument equipped with a thermal conductivity detector (TCD). About 100 mg of the fresh sample was packed into a reactor with quartz tubing of 6 mm i.d. (inner diameter), and pretreated with high purity helium gas at 120 °C for 1 h. Then TPR traces of samples were pursued in a reductive flow of 30 mL·min<sup>-1</sup> 10% (φ) H<sub>2</sub> in helium, on raising the system temperature linearly from room temperature to 700 °C at a ramp rate of 5 °C·min<sup>-1</sup>.

In addition, the chemical transformation of uncalcined Au/Fe<sub>2</sub>O<sub>3</sub> catalyst was studied with *in situ* XRD by heating the samples in a gas mixture of H<sub>2</sub>/N<sub>2</sub> (φ(H<sub>2</sub>)=10%) at a rate of 2 °C·min<sup>-1</sup>. Diffraction patterns were recorded within 2θ=30°–50° during the reduction process since the most intense diffraction peaks of Fe<sub>2</sub>O<sub>3</sub> phases are located in this 2θ range.

The X-ray photoelectron spectroscopy (XPS) measurements were performed with a Phi Quantum 2000 spectrophotometer with Al K<sub>α</sub> radiation (1486.6 eV). The samples were preliminarily pressed into pellets and reduced at 150 °C for 9 h in H<sub>2</sub>/N<sub>2</sub> mixture (φ(H<sub>2</sub>)=10%), then transferred to a test chamber. An electron takeoff angle of 45° was used. The vacuum in the test chamber was maintained below 1.33×10<sup>-7</sup> Pa during the collection. Binding energies were corrected for surface charging by referencing them to the energy of C 1s peak of contaminant carbon at 284.8 eV.

### 1.3 Activity and stability measurements

The catalytic activity of the samples in the WGS reaction was measured using 'CO-CMAT 9001 apparatus (Beijing Hangdun, China)' at atmospheric pressure. A stainless steel tube with an inner diameter of 9 mm was used as the reactor tube. The samples were all 0.5 cm<sup>3</sup> (20–40 mesh size) in volume and preliminarily reduced at 150 °C for 9 h in H<sub>2</sub>/N<sub>2</sub> mixture (φ(H<sub>2</sub>)=10%). The mixture reactant gas, containing 10% (φ) CO diluted by nitrogen, passed through a vaporizer

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