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Gold stabilized on various oxide supports catalyzing formaldehyde oxidation at room temperature

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ABSTRACT

Gold stabilized on reducible oxide (CeO_2 and FeO_x) and irreducible oxide ($\gamma\text{-Al}_2\text{O}_3$, SiO_2 , and HZSM-5) were prepared by deposition precipitation method and tested for catalytic oxidation of formaldehyde (HCHO) at room temperature under high GHSV of 600000 ml/(g·s). Au/ $\gamma\text{-Al}_2\text{O}_3$ catalyst showed distinctive catalytic performance, presenting the highest initial HCHO conversion and stability. Correlating the reaction rate with Au particle size, there is a linear relationship, suggesting that the smaller Au particle size with higher dispersion possesses high reactivity for HCHO oxidation. All the catalysts deactivated at high GHSV (600000 ml/(g·s)), but in a quite different rate. Reducible oxide (CeO_2 and FeO_x) could stabilize gold through O linkage and therefore exhibits a better stability for HCHO oxidation reaction. However, the aggregation of gold particles occurred over Au/ SiO_2 and Au/HZSM-5 catalysts, which result in the fast deactivation. Therefore, our results suggest that the reducibility of the supports for Au catalysis has no direct influence on the activity, but affects the catalytic stability.

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1. Introduction

Given that formaldehyde is a major indoor air pollutant, significant efforts have been directed at indoor HCHO removal to meet environmental regulations and human health needs [1–4]. Catalytic oxidation is recognized as the most promising HCHO removal technology. Catalysts applied for HCHO oxidation include both supported base metals and noble metals [5,6]. However, base metals require the use of elevated temperatures for HCHO oxidation. For example, the operating temperatures of $\text{MoO}_3\text{-SnO}_2$, $\text{MnO}_x\text{-CeO}_2$ and Ag/CeO_2 catalysts are in the range of 100–300 °C [7–9]. In contrast, noble metal catalysts such as Ru, Pd and Pt can effectively remove HCHO at low temperature [10–12]. Among them, supported Pt catalysts have

been proven to be the most active [10,13–15].

A variety of oxide-supported Au catalysts, such as Au/ $\text{Co}_3\text{O}_4\text{-CeO}_2$, Au/ ZrO_2 , and Au/ CeO_2 , have been tested for HCHO catalytic oxidation [16–22]. Zhang et al. [20] successfully synthesized three-dimensionally ordered macroporous 3DOM Au/ CeO_2 catalyst, which was found to exhibit superior catalytic activity as exemplified by 100% HCHO conversion at 75 °C. The unique structure of 3DOM CeO_2 favored high gold dispersions, which was believed to be a key factor in the enhancement of catalytic efficiency for HCHO oxidation. Recently, Ma et al. [17] reported that 50% HCHO conversion was achieved over a mesoporous Au/ Co_3O_4 catalyst at room temperature. It was found that HCHO could be oxidized into formate by Co^{3+} , and could be further transformed into bicarbonate or carbonate

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species, which then decomposed into CO₂ and H₂O.

In our previous study, reducible CeO₂ and FeO_x supported nano-gold catalysts were investigated for catalytic HCHO oxidation, Au/CeO₂ catalyst prepared by deposition-precipitation (DP) method using urea as precipitants and Au/FeO_x catalyst prepared by co-precipitation and calcined at 200 °C showed the best catalytic activity, complete oxidation of HCHO into CO₂ and H₂O being achieved at room temperature and in humid air [23,24]. Such reducible oxides show strong interaction with supported nano-gold particles, leading to weaken Ce–O and Fe–O band, and increase the reducibility reactivity of these surface active oxygen species towards HCHO oxidation [25–27].

In a recent study, we reported for the first time that γ -Al₂O₃ supported Au was a very active catalyst for HCHO oxidation at room temperature even in the presence of moisture [28]. It is found that although there is no active surface oxygen on γ -Al₂O₃, surface hydroxyls have the ability to partially oxidize HCHO into formate intermediates, which can be further oxidized into CO₂ and H₂O by nano-Au [28]. This study challenges the traditional idea of supporting noble metals on reducible oxides for HCHO oxidation at room temperature [28].

Herein, under similar conditions, we compare the catalytic properties of Au/CeO₂, Au/FeO_x, Au/ γ -Al₂O₃, Au/HZSM-5 and Au/SiO₂ catalysts for HCHO oxidation at room temperature. The goal of the present study is to provide a clear image on the effect of reducibility of the supports for gold catalysis and the factors that influence the gold catalysts' activity and stability for HCHO oxidation.

2. Experimental

2.1. Catalysts preparation

Au/ γ -Al₂O₃, Au/CeO₂ and Au/FeO_x samples with nominal gold contents of 1 wt% were prepared by DP method with urea as the precipitant. Typically, 2.1 mL of HAuCl₄ solution (0.024 mol/L), 0.38 g of urea (urea/Au = 125, molar ratio), 1.0 g γ -Al₂O₃, CeO₂ or FeO_x (γ -Al₂O₃ provided by Lanzhou Petrochemical Company Petroleum, CeO₂ provided by Tianjin anylink new materials Co., Ltd. and FeO_x was prepared according to a co-precipitation method [29]) powders (mesh size >100) and 150 mL of deionized water were co-added into a three-neck flask mixed adequately in the water bath thermostated at 80 °C, and the flask was covered with an opaque package to keep off the room light. The suspensions were then stirred vigorously for 8 h (final pH \approx 7.0), followed by overnight aging at room temperature. The solid was filtered and washed extensively with deionized water until it was free of chloride ions, then dried at 80 °C for 8 h and calcined at 300 °C in air for 4 h.

The Au/HZSM-5 (SiO₂/Al₂O₃ = 500) and Au/SiO₂ catalysts with nominal Au contents of 1 wt% were prepared by a DP method with NH₃·H₂O as the precipitant. Typically, an aqueous solution of HAuCl₄ (0.024 mol/L), HZSM-5 or SiO₂ support (1.0 g) (HZSM-5 SiO₂/Al₂O₃ = 500, Nankai University, China and SiO₂ is provided by Qingdao Haiyang Chemical Co., Ltd) and distilled water (50 mL) were co-added to a three-necked flask and

mixed adequately. The slurry was stirred at 60 °C for 30 min, then aqueous NH₃·H₂O solution (1 mol/L) was added under stirring to adjust the pH of the system to about 9, followed by stirring at 60 °C for 8 h. After that, the resulting precipitate was filtered and washed with hot distilled water, then dried at 60 °C for 6 h and stored in darkness. The solid was then treated at 300 °C in reducible atmospheres (10% H₂ in N₂, 80 mL/min) for 4 h to obtain the final catalysts.

2.2. Catalyst characterization

The actual Au content in each sample was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima 2000DV, USA). BET surface area determinations were performed using a nitrogen adsorption apparatus (Micromeritics, Tristar 3000). High-resolution transmission electron microscopy (HRTEM) micrographs were obtained with a Tecnai G2 20 S-TWIN microscope and operated at 200 kV.

Transmission electron microscopy (TEM) images of the catalysts were obtained on a JEOL JEM-2000EX microscope operated at 200 kV. Before observation, the samples were ultrasonically dispersed in ethanol and then a drop of the solution was put onto microgrid carbon polymer supported on copper grid. At least 100 Au nanoparticles were measured to analyze the particle size distribution.

Temperature programmed oxidation (TPO) experiments were used to study the deposits on the all the spent Au/ γ -Al₂O₃, Au/SiO₂, Au/HZSM-5, Au/CeO₂ and Au/FeO_x catalysts, after 360 min of reaction. The catalysts were purged with a dry simulated air stream (100 mL/min) at room temperature for 30 min prior to the experiment. The temperature was heated from room temperature to 400 °C at a rate of 10 °C/min in an air flow and the gas products were analyzed by the on-line CO_x analyzer and mass spectrometer (MS). No other carbon-containing compounds except CO₂ in the products were detected for all the tested catalysts.

2.3. Measurement of catalytic activity

The activity of catalysts in HCHO oxidation was carried out in a fixed-bed quartz reactor (i.d. = 4 mm). 10 mg catalyst powder diluted with 50 mg SiO₂ was loaded in the quartz reactor. A feed gas (80 ppm HCHO, 21 vol% O₂, 1.6 vol% H₂O (RH = 50%, 25 °C), and balanced with N₂) was allowed to pass through the catalyst bed at a flow rate of 100 ml/min, resulting in a space velocity (SV) of 600000 ml/(g·h). All the feed gases used in this work were of high-purity grade (99.999%). The gas flow rates were controlled by mass flow controllers. Gaseous HCHO was generated by flowing N₂ over paraformaldehyde (99%, Aldrich) in a thermostated bath and the concentration of HCHO was controlled by adjusting the flow rate of N₂ and the temperature of the thermostated bath. Gaseous H₂O was carried into the gas stream by passing N₂ through a bubbler in a water bath at room temperature. The amount of water was controlled by adjusting the flow rate of N₂, while keeping the total flow constant. The HCHO/N₂ and H₂O/N₂ streams were

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