Catalytic performance of gold nanoparticles using different crystallinity HAP as carrier materials

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A B S T R A C T

Gold (Au) was loaded on hydroxyapatite (HAP) supports with three different degree of crystallinity by deposition-precipitation method. Amorphous HAP and higher crystalline HAP nanoparticles were synthesized respectively by a direct precipitation process of which the aging time was 12 h or hydrothermal treatment at 180 °C. CO oxidation reaction was used to evaluate the behavior of catalysts. The physical properties of the catalysts were characterized by BET and TEM. The result found the catalyst with the lowest specific surface area had the highest initial activity. Patterns of XRD and XPS revealed that the HAP supports with higher crystallinity could produce more Au° over their surface which resulted in higher initial activity. This study suggested that the crystallinity of HAP supporter was another main factor to improve catalytic activity despite of specific surface area of the Au/HAP nanocatalysts.

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1. Introduction

Environmental contamination is always a worldwide issue in the 21st century. With the great industrialization process, carbon monoxide (CO), concerned by all over the world, had become an increasingly severe problem on air pollution. The main source of this toxic pollutant was incomplete combustion of fossil fuel from industrial manufacture and automobile exhaust emissions [1,2]. CO oxidation was an important research subject due to its widespread applications in the fields of industry, military, environment protection and citizens' daily life, as well as stringent environmental regulations [3–5]. Noble metal catalysts and non-noble catalysts were generally used in CO oxidation reaction. Comparing with the traditional metal oxide catalysts, the noble metal catalysts owned better water resistance and initial activity. Among these noble metal, gold (Au) was frequently used to prepare oxide catalysts. However, the high price of Au limited the practical application of Au catalysts. In the present work, HAP nanocatalysts loaded with 1.0 and 3.0 wt.% were prepared to investigate the relevance between cost and activity.

Since pioneer Haruta et al. [6] firstly demonstrated that gold nanoparticles had high catalytic activity in the oxidation of CO when they were well dispersed on some supports, a great variety of supports had been used to investigate the mechanisms between amplification of catalytic activity in the oxidation of CO and supported gold catalyst, especially on metallic oxides supports such as Al_2O_3 [7–9], Fe_2O_3 [10], ZnO [11], TiO_2 [12], ZrO_2 [13], Co_3O_4 [14,15]. However, less attention has been paid to non-oxide supports. Recently, Dai et. al synthesized an ultrastable gold nanocatalyst supported by lanthanum phosphate [16,17]. This nanosized phosphate substrate could stabilize gold nanoparticles on the catalysts. Based on former study, Dai and co-workers, via a deposition–precipitation method (DP method), systematically synthesize an array of Au/metal phosphates catalysts (metal = Ca, Fe, Co, Y, La, Pr, Nd, Sm, Eu, Ho, Er) of which the initial activity were tested. It suggested that many other phosphate salts were also good supports for Au catalysts [18]. According to the works mentioned above, the support had a obvious effect on the catalytic activity in the oxidation of CO.

Hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) as one kind of phosphate salt contained various morphologies [19], excellent biocompatibility [20], high physical and chemical activities. [21] Its excellent ion-exchange capacity for many cationic heavy metals [22,23], had been widely used in artificial bone repair, carriers for drug delivery system [24] and water and soils treatment processes [25,26]. Although the complex structure of HAP might cause its limited usage in supported Au catalyst, Phonthammachai et al. [27] found that DP method could distribute Au nanoparticles homogeneously over HAP to create a highly durable catalyst. During 16 h of continuous CO testing at 338 K, it was shown that both the catalyst structure and activity were stable. Domínguez et al. [28] found out that HAP supports with high surface might improve

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catalytic activity for CO oxidation at room temperature. Pre-treatment temperature influenced the catalytic activity by modifying the gold oxidation state. Huang et al. [29] found that Au/HAP catalyst calcinated in helium (He) atmosphere attained the highest initial activity for CO oxidation, comparing with those calcinated in H_2 and O_2 atmosphere. But among these researches, few reported the relevance between the crystallinity of HAP support and catalytic efficiency.

The objective of this work was to develop three HAP samples of different crystallinity degree. Amorphous HAP (HA0) was synthesized by direct precipitation. Higher crystalline HAP (HA12) was obtained after aging for 12 h [30] and the highest crystalline HAP sample (HR) was prepared by hydrothermal treatment [31]. Au was loaded by DP method. Urea was used as precipitant to achieve efficient gold content on the supports. In this study, the effect of different morphologies, and the crystallinities of HAP supports on the catalytic activity in the CO oxidation was explored. A feasible mechanism was established according to the results obtained from our research. The results of this study were constructive for the practical production and applications.

2. Experimental

2.1. Chemicals

Calcium chloride anhydrous ($CaCl_2$, 96%), potassium dihydrogen phosphate (KH_2PO_4, 99.5%), ethylenediamine ($C_2H_8N_2$, 98%), hydrogen tetrachloroaurate ($HAuCl_4 \cdot 3H_2O$, 99.99%), and urea [$CO(NH_2)_2$, 99.00%] were purchased from National Chemical Corporation. All chemicals were analytical purity class, and used without further purification. Deionized water was used throughout the experiments.

2.2. HAP supports preparation

The amorphous HAP (HA0) was precipitated through a direct precipitation process outlined in Eq. (1). In a typical experiment, 0.1 mol/L $CaCl_2$ aqueous solution and 0.06 mol/L KH_2PO_4 aqueous solution (ratio: Ca/P = 1.67) were respectively adjusted by ethylenediamine to pH 8. The phosphate solution (100 mL) was vigorously stirred at room temperature, and $CaCl_2$ aqueous solution (100 mL) was added dropwise to the KH_2PO_4 aqueous solution within 60 min to produce a white precipitate.

$$10CaCl_2 + 6KH_2PO_4 + 2H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 6KCl + 14HCl$$
(1)
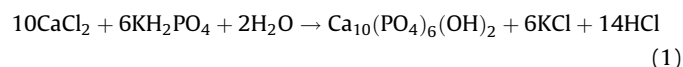
The reaction system was kept at room temperature for 12 h to prepare sheet-like HAP (HA12). During aging process, higher crystallization would be achieved.

Above-mentioned HA0, transferred into a Teflon bottle held in a high-pressure tank, were processed hydrothermally at 180 °C for 72 h to prepare rod-like HAP (HR). The products were centrifugalized at 3000 rmp and washed by deionized water. The final products were obtained after being dried for 12 h in a desiccator.

2.3. Au/HAP catalysts preparation

Gold was deposited to the obtained HAP nanoparticles by a DP process. The required amount of $HAuCl_4$ and 1 g HAP support were dissolved in 100 mL distilled water to synthesize 1.0 wt.% and 3.0 wt.% gold catalysts. After stir for 20 min and ultrasonic vibration for 5 min at room temperature, the mixture was heated to 90 °C. Urea (urea/Au = 150, molar ratio) was added. Urea was used as precipitant to achieve efficient gold content on the supports. The products were separated by a centrifuge at 3500 rmp

and washed by deionized water for three times after the suspension was kept at 90 °C for 4 h. The resulting products were collected and dried at 95 °C for 12 h in a desiccator. The precursors, pre-actived at 350 °C in the steam of 1% CO and 20% O_2, were balanced by N_2 at a space velocity of 15,000 mL/(h × g_{cat}) for 1 h. The catalysts were refrigerated to room temperature before the light-off curve started.

2.4. Materials characterization

The actual Au loading was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian, 710ES).

The purity, crystal phase, and crystallinity of the products were characterized by X-ray powder diffraction (XRD, Shimadzu XD-3A diffractometer) with a graphite-monochromated Cu-Kα radiation (λ = 0.15406 nm), operating at 40 kV and 40 mA, at a scanning rate of 6 °/min in the 2θ range from 10 to 80°.

The specific surface area of the products were analyzed by nitrogen adsorption and Brunauer–Emmett–Teller (BET, Micometrics, ASAP 2010) at 79 K.

The morphologies of the products were characterized by transmission electron microscopy (TEM, Hitachi-800) with an acceleration voltage of 200 kV. Before experiments, the products were dispersed well in anhydrous ethanol by ultrasonic irradiation.

The binding energy (BE) of the surface Au species was determined by X-ray photoelectron spectra (XPS, PerkinElmer, 580B). The contaminated C 1s (285 eV) was used as an internal standard.

2.5. Measurement of catalytic activities

The measurements of CO oxidation catalytic activity were carried out in a quartz tubular (i.d. = 5 mm) fixed-bed reactor with 200 mg of catalyst under atmospheric pressure. The reaction temperature was monitored by a thermocouple placed in the middle of the catalyst bed. The feed gas for reactants was a mixture of 1 vol.% CO and 20 vol.% O_2 balanced by N_2. The gas flow rate was 50 mL/min, which resulted in a space velocity of 15,000 mL/(h × g_{cat}). The catalyst was directly exposed to the reaction without any pre-treatment. The concentration of CO and CO_2 in the effluent gas were obtained from room temperature (20 °C) to 300 °C at a heating rate of 5 °C/min, and analyzed by a GC-9790 gas chromatograph equipped with a TID detector. Conversion of CO was calculated as follows, where $[CO]_{in}$ and $[CO]_{out}$ were the CO concentrations in the feed gas (vol.%) and products (vol.%), respectively.

$$\text{COonversion}(\%) = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100$$

3. Result and discussions

Au/HAP precursors were prepared by DP method, drying at 95 °C (denoted as Au/HAP-95). After calcination at 350 °C, the catalysts were denoted as Au/HAP-95-Re. The real gold content of two series loading amounts Au/HAP-95-Re samples were determined by ICP-AES. The average measured gold contents were 0.93 and 2.8 wt.% respectively, which was basically the same as the target Au loadings (1.0 and 3.0 wt.%) for both series. As shown in Table 1, an ICP measurement showed the different loss of Au on three HAP supports in both desirable series. It was interesting to find no matter whether the nominal Au loading is 1.0 or 3.0 wt.%, the loss of Au in the three fresh samples increased in the following order: Au/HR-95 < Au/HA12–95 < Au/HA0–95. It indicated that the Au loadings of Au/HA0–95 was the lowest while that of Au/HR–95 was the highest.