



Short Communication

Understanding on the origins of hydroxyapatite stabilized gold nanoparticles as high-efficiency catalysts for formaldehyde and benzene oxidation



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ABSTRACT

Hydroxyapatite as a green and abundant material was found to enhance the stabilization of gold nanoparticles against sintering. The origins of such stabilization of HAP on supported gold nanoparticles were investigated in the present study. Phosphate groups interacted and stabilized nano-gold at lower temperature (≤ 400 °C), while hydroxyl group contributed to the stabilization at higher temperature (≤ 600 °C). Both of them contributed to the strong sintering-resistant for calcination as high as 600 °C. For the first time we found that Au/HAP and Au/CeO₂/HAP catalysts are highly active and stable for formaldehyde and benzene oxidation.

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1. Introduction

Supported gold catalysts have attracted tremendous attention owing to the pioneering discovery by Haruta [1]. The last decade has witnessed a rapid growth of interest in the catalytic properties of gold, a variety of oxide-supported Au catalysts, such as Au/CeO₂ [2], Au/TiO₂ [3], Au/Fe₂O₃ [4], Au/ZrO₂ [5], and Au/Al₂O₃ [6] catalysts have been reported.

Despite the many potential applications of supported gold catalysts, one of the most important limitations in the use of gold catalysts is their sintering of gold nanoparticles at high temperatures. Certain applications would require the catalyst to survive and remain effective at high temperature and for long times. It is well established that catalytic activity and stability of supported gold depend strongly on the choice of the supports and the specific interaction between gold and the support [7].

Recently, hydroxyapatite (HAP, Ca₁₀(PO₄)₆(OH)₂) has attracted interest for use in a variety of applications. Notably, the use of HAP as a support for nano-gold was reported to perform excellent CO oxidation activity and enhance the stability of gold nanoparticles against sintering at temperatures as high as 600 °C [8,9]. Although the origin of this stabilization

has to date been little studied, it has been ascribed to the presence of PO₄³⁻ and OH⁻ groups [10]. The excellent sintering – resistant property of this catalyst provides a new opportunity for the development of stable nano-gold catalysts.

The present work is devoted to the understanding of the essential features of the catalysis of the gold nanoparticles loaded HAP (Au/HAP) in formaldehyde (HCHO) and benzene (C₆H₆) oxidation. In this work, we first compare Au/CeO₂ and Au/HAP catalysts to confirm the stabilizing effect of the HAP support; subsequently, we compare Au/HAP and Au/FAP (fluorapatite, Ca₁₀(PO₄)₆F₂) catalysts, the latter containing only PO₄³⁻ groups, to distinguish the stabilizing effect of PO₄³⁻ and OH⁻ groups. It is found that surface hydroxyls and phosphate groups followed an interesting regularity to stabilize the gold nanoparticles from growing up for calcination, and for the first time, HAP supported Au catalyst is reported to be very active for HCHO and benzene oxidation, even in the presence of moisture.

2. Experimental

2.1. Catalyst preparation

Three kinds of supports of HAP, FAP and CeO₂/HAP were synthesized by a chemical precipitation method. Gold nanoparticles were loaded on the supports by a deposition–precipitation method targeting at 1 wt.% Au loadings. Details were described in the Supplementary data.

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2.2. Catalyst evaluation

All the feed gases used in this work were of high-purity grade (99.99%). The gas flow rates were adjusted and controlled by mass flow controllers. Gaseous HCHO was generated by flowing N₂ over paraformaldehyde (99%, Aldrich) in a thermostated bath. (The concentration of HCHO was controlled by adjusting the flow rate of N₂ and the temperature of 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, expressed as the relative humidity (RH) at 25 °C, was controlled by adjusting the flow rate of N₂, while keeping the total flow unchanged. The HCHO and C₆H₆ concentrations used in HCHO and C₆H₆ oxidation were 80 and 120 ppm, respectively. The total flow rate was 100 ml/min, corresponding to a gas hourly space velocity (GHSV) of 30,000 h⁻¹. The concentrations of HCHO and C₆H₆ were measured by converting them to CO₂ in a homemade HCHO-to-CO₂ converter [11–13] (CuO–MnO₂/γ–Al₂O₃ catalyst) at 400 °C and determining the amount of CO₂ formed by IRAS (SICK-MAIHAK-S710, Germany). Catalyst behavior for the total oxidation of HCHO into CO₂ and H₂O was studied at 25 °C, while the total oxidation of C₆H₆ into CO₂ and H₂O was studied as a function of reaction temperature. No organic byproducts or CO for HCHO and benzene oxidation were detected in the outlet, indicating that HCHO and benzene were completely oxidized. The concentration of CO and CO₂ was measured by an infrared absorption spectrometer (SICK-MAIHAK-S710, Germany). The conversion of HCHO and benzene to CO₂ was quantified on the basis of the carbon balance with an accuracy of >98%. Thus, the HCHO and C₆H₆ conversion was calculated as follows:

$$\text{HCHO conversion (\%)} = \frac{[\text{CO}_2]_{\text{out}}}{[\text{HCHO}]_{\text{in}}} \times 100\%$$

$$\text{C}_6\text{H}_6 \text{ conversion (\%)} = \frac{[\text{CO}_2]_{\text{out}}}{6 \times [\text{C}_6\text{H}_6]_{\text{in}}} \times 100\%$$

where [CO₂]_{out} is the CO₂ concentration in the products and [HCHO]_{in} and [C₆H₆]_{in} is the HCHO and C₆H₆ concentration in the feed gas. The CO₂ concentration was directly monitored by an infrared absorption spectrometer (SICK-MAIHAK-S710, Germany), while as before the inlet HCHO and C₆H₆ concentration was measured by converting it to CO₂.

2.3. Catalyst characterization

Details were described in the Supplementary data.

3. Results and discussion

3.1. Catalyst characterization

Table 1 summarizes the physical and chemical properties of the Au/HAP-x, Au/FAP-x and Au/CeO₂/HAP-x catalysts. The slight decrease of BET surface areas with increasing calcination temperature was mainly due to loss of some of the small pores, i.e., slight sintering. The real gold contents of various Au series catalysts were determined by ICP-OES. The gold loadings of the catalysts were close to the nominal loading of 1 wt.% for all samples. The measured Ca/P ratio, 1.7 ± 0.2, was essentially the same as the nominal Ca/P ratio (1.67) for all samples.

Fig. 1 shows the XRD patterns of the samples. HAP and CeO₂/HAP catalysts exhibited Ca₁₀(PO₄)₆(OH)₂ phase without the observation of CeO₂ phase [14], and the FAP exhibited Ca₁₀(PO₄)₆F₂ phase [15]. For the Au/HAP-x and Au/CeO₂/HAP-x catalysts, the intensive and sharp diffraction peaks could still be attributed to their corresponding supports, and no diffraction peaks due to the Au species could be observed, which is mainly due to the small size and high dispersion of the Au particles on the supports. In addition, the XRD patterns of Au/FAP-200 and

Table 1

BET surface areas, measured Au (Ce) contents, Ca/P ratio, and Au particle sizes of the samples.

Catalyst	Surface area (m ² /g)	Au (Ce) content (wt.%) ^a	Ca/P ratio ^a	Au particle diameter (nm) ^b
HAP-200	83	–	1.71	–
Au/HAP-200	76	0.75	1.72	2.9
Au/HAP-400	60	0.79	1.69	3.6
Au/HAP-600	57	0.81	1.71	5.5
FAP-200	31	–	1.73	–
Au/FAP-200	29	0.95	1.72	3.2
Au/FAP-400	20	0.98	1.70	3.6
Au/FAP-600	15	0.99	1.71	8.6
CeO ₂ /HAP-200	73	–(5.2)	1.68	–
Au/CeO ₂ /HAP-200	55	0.91 (5.1)	1.69	3.2
Au/CeO ₂ /HAP-400	50	0.91 (5.2)	1.69	3.3
Au/CeO ₂ /HAP-600	42	1.11 (5.3)	1.70	3.5

^a Measured by ICP-OES.

^b Estimated according to the TEM images (>200 particles were measured).

400 catalysts were in good agreement with the parent FAP, while a discernible diffraction peaks at 2θ = 38.18°, which could be assigned to metal gold (PDF# 04 = 0784), appeared for the Au/FAP-600 catalyst, which is mainly due to its strong broadening. According to Matyi and Riello et al. [16,17], the unobserved diffraction peaks of gold mean the small crystallite size of supported Au particles less than 3 nm and considerably smaller than the mean sizes of Au particles determined by TEM (Table 1), one reason may be that the Au particles are not monocrystalline, but consist of several crystallites representing a separate coherent scattering area of <3 nm in size.

Fig. 2 and Fig S1 present typical TEM images of the Au/HAP-x, Au/FAP-x and Au/CeO₂/HAP-x samples. HAP, FAP and CeO₂/HAP supports all existed as nanorod-shaped particles. Au nanoparticles with diameters of 2–5 nm were clearly observed after calcination at 200 °C (Fig. 2 (A–C)) and 400 °C (Fig. S1 (A'–C')). After calcination at 600 °C (Fig. S1 (A''–C'')), the average diameter of Au in Au/HAP-600 increased from ca. 2.9 to ca. 5.5 nm, while those in Au/FAP-600 increased from ca. 3.2 to ca. 8.6 nm. However, gold particles remained highly dispersed in Au/CeO₂/HAP-600, being ca. 3.5 nm. The above results demonstrate that HAP and CeO₂/HAP supported Au nanoparticles show good stability with respect to sintering at elevated temperatures. In contrast, Au nanoparticles supported on FAP underwent appreciable growth upon calcination at 600 °C. Moreover, the characteristic of gold nanoparticles was also observed by UV–vis shown in Fig. S2, the maxima in the range 540–560 nm ascribed to a collective oscillation of conduction electrons in response to optical excitation – the plasmon resonance of gold metal particles [18].

XPS spectra over the Au 4f binding energy (BE) regions are presented in Fig. 3. The typical binding energies of Au 4f_{7/2} at BE = 83.5 ± 0.3 eV and 85.4 ± 0.4 eV are assigned to Au⁰ and Au^{δ+}, respectively, suggesting that there are two valence states in the Au catalyst corresponding to metallic Au⁰ and ionic Au^{δ+} [2,19]. The ratio of Au^{δ+}/Au⁰ + Au^{δ+} was calculated (Table 2). It is clear that the ratio of Au^{δ+}/Au⁰ + Au^{δ+} on Au/HAP-200 (54.7%) was significantly higher than those on Au/FAP-200 (51.8%) and Au/CeO₂/HAP-200 (34.8%), respectively. After calcination at 400 and 600 °C, most of the Au^{δ+} species on the Au/HAP-x and Au/FAP-x catalysts changed into the metallic state, which were consistent with other studies [20], the ratio of Au^{δ+}/Au⁰ + Au^{δ+} decreased to 18.7% and 12.0%, respectively. For the Au/CeO₂/HAP catalysts, besides Au⁰, there were still 33.8% positively charged gold species after calcination at 600 °C, being consistent with its better resistance for sintering as evidenced by TEM.

Fig. 4 shows the characteristic FT-IR bands corresponding to the Au/HAP-x and Au/FAP-x samples. As shown in the inset of Fig. 4A, a band is observed at 3570 cm⁻¹ for the HAP support which corresponds to structural hydroxyl groups (OH...OH...OH, ρ₀) [14,21], while a band at 1186 cm⁻¹ is assigned to P–O bond stretching associated with the PO₄³⁻ groups in HAP [22]. Neither band was affected by the applied

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