Synthesis of High Performance Hydroxyapatite-Gold Catalysts for CO Oxidation

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Abstract

Catalysts for low temperature CO oxidation were prepared by decorating hydroxyapatite (HAp) ceramic foam scaffolds with highly dispersed gold nanocrystals using a deposition-precipitation (DP) process. Catalytic activity, microstructure and crystallinity were studied as a function of reagent pH (4-12) and aging time (10, 30, 60 min) for powders and porous supports. Superior products with small (≤ 5 nm) gold crystals distributed homogeneously over HAp foam were obtained at pH 8-9. Larger crystal sizes and colloidal gold agglomeration appeared at longer aging times. The optimized catalyst prepared by reaction at pH 9 for 30 min showed 100% CO conversion to CO₂ at 150°C. The Au-HAp composite demonstrated excellent durability by retaining structural and crystallographic integrity with no loss of activity when tested at 65°C out to 166 h.

Keywords

CO oxidation, deposition-precipitation process, gold nanocrystal, hydroxyapatite.

Introduction

The catalytic activity of oxide-supported gold nanoparticles has been exploited in many applications including chemical sensing, hydrogen production, fuel cells, and various chemical processes [1] of which carbon monoxide oxidation is the best known [2]. Several mechanisms have been proposed to explain the enhanced activity at the metal-oxide interface including the presence of highly reactive surface gold atoms at growth steps [3], the ease of charge transfer at the boundary [4], and in the case of reducible supports, the provision of activated oxygen that can be trapped at reaction sites [5]. Whatever the means, it is evident that interactions between the support and the gold must be tailored for performance enhancement. While porous binary oxides such as alumina [6] or zirconia [7] are frequently used as catalytic scaffolds, the search for supports whose properties will amplify the reactivity of nanosized gold continues. One such material is hydroxyapatite (HAp) whose potential as a component of environmentally benign catalysts has not been widely considered, although photocatalytic mineralisation of pollutants [8] and oxidative decomposition of methanol [9], hydrocarbon [10], trichlorobenzene and chloroethylene [11, 12] have been demonstrated. Progress in this field has been hampered partly because HAp is crystallochemically complex [13], and also because it has been difficult to prepare with porous architectures, although methods to construct inverse opaline structures [14, 15] and foams [16, 17] are now available. Indeed, apatitic chemistry is diverse with some analogues intrinsically catalytic [18-21], and these forms may interact favorably with metallic co-catalysts such as gold to invigorate reactivity.

Deposition-precipitation (DP) is a reliable method to prepare oxide-supported gold [22, 23] in which the key parameter is the isoelectric point (IEP) of the scaffold material. Moreau et al [24] found that the deposition rate of agglomerated gold crystals on titania accelerated with pH < IEP as the positive surface charge at lower pH attracted gold-bearing anions (AuCl₄⁻). However, with pH > IEP the titania surface carried a net negative charge, and electrostatic repulsion of anions resulted in highly dispersed gold crystals with the coverage influenced by many factors including the concentration of HAuCl₄, the volume to mass ratio of HAuCl₄ to support, the base type (NaOH, NH₄OH, urea), aging time and temperature, processing steps (filtration, washing and drying steps) and calcination temperature [25]. Selection of the alkaline solution proves especially critical in controlling the yield, dispersion and size of gold crystals. For example, Zanella et al [26] found that during DP in NaOH the gold was partially reduced to metal after drying at 100°C, but a comparable experiment in urea delayed metallization to calcination temperatures >150°C.

While DP syntheses of gold nanoparticles on reducible (TiO₂, Fe₂O₃, Co₂O₃) [27-29] and non-reducible oxides (SiO₂, Al₂O₃) [30, 31] have been widely reported and the catalytic mechanisms investigated, corresponding examination of HAp supports are sparse. The notable exception is the study of

Vemugopal et al [32] where 3% Au and Ru, deposited from $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ at pH 8.8 for 3h, produced a catalyst used to promote a low temperature water-gas shift reaction. It was found that Au/HAp showed the higher activity with 95% conversion to CO_2 and H_2 achieved at 300°C , but correlation of preparative conditions with respect to the size, dispersion and catalytic activity of the gold crystals requires clarification. This report describes a DP method that homogeneously distributes gold nanocrystals (5 nm average diameter) over porous HAp to create a highly efficient and durable catalyst for CO oxidation. Techniques to control the size and dispersion of metallic crystals on HAp are detailed, particularly with respect to the manner of support synthesis, pH control and aging time.

Experimental

Hydroxyapatite (HAp) support fabrication

HAp was synthesized by mixing 3.59 g calcium nitrate ($\text{Ca}(\text{NO}_3)_2$, 99.0%, Merck) and 1.18 g $(\text{NH}_4)_2\text{HPO}_4$ (99.0%, Aldrich) in 34 ml NH_4OH (Merck) and 145 ml doubly deionized water. The suspension was heated to 65°C with magnetic stirring for 90 min after which the temperature was raised to 100°C and stirring continued for 120 min. The precipitated HAp was separated using vacuum filtration and washed several times prior to oven drying overnight at 100°C . Crystallization was promoted by dewatering at 250°C (with a heating rate of $0.7^\circ\text{C min}^{-1}$) for 30 min followed by soaking at 1200°C for 5 hr with a heating rate of $3.3^\circ\text{C min}^{-1}$.

The HAp foam support was prepared in a two stage process [16]. First, methyl cellulose (4000 cPs viscosity, Alfa Aesar) was dissolved in 45 ml of deionized water then aerated with a stainless steel blade agitator at 20,000 rpm for 5 min. Second, a suspension of 5 ml H_2O and 0.512 g HAp was added to the polymer solution with aggressive mixing for 10 min. The polymer foam impregnated with HAp was calcined at 250°C ($0.7^\circ\text{C min}^{-1}$) for 30 min to remove organics prior to final sintering for 5 hrs (1200°C ; $3.3^\circ\text{C min}^{-1}$).

Gold deposition-precipitation (DP)

Gold stock solutions were prepared by adding 0.1 M NaOH (Sigma-Aldrich) dropwise to 20 ml of 6.25 mM HAuCl_4 ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, Alfa Aesar) until the pH stabilized at predetermined values ranging from 4 to 12. HAp (0.3 g) was dispersed in the solution which was aged at 65°C with vigorous stirring for 60 min after which the gold loaded catalysts were collected by filtration and washed repeatedly with deionized water to remove chloride. The powder was oven dried overnight at 100°C prior to air calcination at 400°C (5°C min^{-1}) for 3h.

Materials characterization

The crystallographic parameters and phase content of the HAp support and gold loaded catalysts were determined

from powder X-ray diffraction (XRD) patterns (Shimadzu LAB-XRD-6000) collected at 4 kW using $\text{CuK}\alpha$ radiation. Specimens were prepared for diffraction by packing powder into a glass holder (2×2 cm) with intensity collected by step scanning over the 2θ range 10° to 90° in increments of 0.02° and a dwell time of 0.60 s. Rietveld analysis as implemented in TOPAS [33, 34] was used for quantitative phase determination with hydroxyfluorapatite [35] and gold [36] employed as crystallographic models in a simulation that included a background polynomial, scale factor, cell parameters, preferred orientation and zero point correction. In this way, powder XRD was used to determine phase content, conduct mass balance and estimate crystal size. Catalyst morphology was examined using a field emission scanning electron microscope (SEM, JEM 6360) operated in secondary electron imaging (SEI) mode at 10 kV. To avoid charging, the powders were pressed into a carbon tape attached to an aluminum stub followed by gold coating using a low energy plasma. Micrographs of the pyrolyzed samples were obtained at magnifications of $\times 1,000$ and $\times 3,500$. Bright field transmission electron microscopy (TEM, JEM 2100F) was conducted at 200 kV. Nitrogen adsorption-desorption isotherms were used to determine surface area and porosity (Micromeritics ASAP 2020) via the Brunauer-Emmett-Teller (BET) method. A mixed gas of nitrogen and helium was allowed to flow through the analyzer at a constant rate of 30 cc/min. Nitrogen was used to calibrate the analyzer and also served as the adsorbate at liquid nitrogen temperature. The samples were thoroughly outgassed for 5h at 150°C before exposure to the adsorbent gas.

Catalytic testing

Catalytic oxidation of CO was conducted in a fixed-bed microreactor using a catalyst charge of 50mg. Prior to testing, the material was heated in air at 200°C for 1 h to remove impurities. After cooling to room temperature, a reactant gas containing 1 vol% CO in air was passed through the catalyst bed with a gas hourly space velocity (GHSV) of 15000 h^{-1} . The outlet gases were analyzed by an on-line gas chromatograph (GC) (Shimadzu-14B) equipped with thermal conductivity (TCD) and flame ionization (FID) detectors. Catalyst durability was established by fixing the temperature of the reactor at 65°C for 166 h under the same feed conditions using the Au-HAp material prepared at pH 9.

Results and Discussion

Structure of HAp support

Both the dried and calcined powders contained single phase HAp as determined by powder X-ray diffraction (Figure 1) with the average crystallite size increasing from 22 to 218 nm after heat treatment (Table 1). Matching of simulated and experimental diffracted patterns invariably required correction of (00l) reflection intensities that were enhanced as a result of acicular faceting. Subsequent incorporation of HAp in the

Table 1*Physical properties of dried, calcined and foam HAp supports*

Sample	BET surface area (m ² g ⁻¹)	Pore size (nm)	HAp crystal size* (nm)
Dried HAp	79	12.5	20
Calcined HAp	1	-	123
Calcined foam HAp	3	-	218

*determined by XRD

ceramic foam and firing at 1200°C did not perceptibly change the crystallinity or texture (Table 1). The calcined powder contained large aggregates (2-5 µm) of HAp crystals while the ceramic foam consisted of spongy macropore walls of high porosity (Figure 2).

The highest surface area with the largest pore size (12.5 nm) as determined by the BET procedure was obtained from dried HAp, but decreased dramatically after calcination at 1200°C due to crystal growth (Table 1). Prior to calcination, the dried HAp powder showed a type IV nitrogen adsorption-desorption isotherm (Figure 3a) with a hysteresis loop of type H3 consistent with slit-pore mesoporosity [37-43]. After

Figure 1

Rietveld plots of XRD patterns of (a) powder HAp and (b) foam HAp calcined at 1200°C. The experimental intensity is shown as circles and the simulated pattern as a solid line. The intensity difference between these patterns is shown below. The Bragg diffraction markers for HAp are shown at the bottom of each plot

Table 2

Correlation of HAp support and deposition-precipitation conditions on gold crystal size and loading

HAp	pH	Aging time (min)	%Au loading	Au crystal size (nm)*
Powder	8	60	0.1	14
Foam	6	60	1.5	8
Foam	7	60	4	11
Foam	8	60	4.8	8
Foam	8	30	4	7
Foam	8	10	3.1	5
Foam	9	60	2.4	5
Foam	12	60	0.8	6

*determined by XRD

calcination the powder and foam gave type II isotherms (Figure 3b) as the mesopores collapsed leading to unrestricted monolayer-multilayer adsorption [39]. This confirms that while the ceramic foam is macroporous, its pore walls are composed of dense HAp particles rather than mesoporous material.

Figure 2

SEI micrographs of calcined (a) powder HAp and (b) foam HAp

Effect of HAp support on CO oxidation

Gold nanocrystals deposited on ceramic foam HAp were generally evenly distributed, and of smaller and more regular size, than those fixed to the powder (Table 2, Figure 4). The Au-loaded foam was always more active with the optimized material achieving 100% CO conversion at 190°C, a temperature 110°C lower than the analogous calcined powder (Figure 5). As the apatite foam without gold was not catalytic, it is clear that the size and dispersion of gold particles control CO oxidation activity.

The precise function of the HAp support during catalysis will require clarification, but recent studies of gold nanocrystals loaded on phosphate-doped titania, or attached to monoclinic and hexagonal LaPO_4 , suggest the phosphate groups stabilize Au crystals, preventing their agglomeration and enhancing CO conversion at high temperatures [44, 45]. The function of the crystal structure support is subtle, as in the case of LaPO_4 , greater CO conversion was achieved only with catalysts using the hexagonal dimorph. These results are in accord with the present investigation, where the size of the gold crystals decorating HAp remained constant after calcination to 400°C. However, the mechanism of CO conversion must be distinct, due to the different chemistry, crystal structure and oxygen transference efficiency of apatite. As HAp is both

Figure 3

Nitrogen adsorption-desorption isotherms of (a) dried and (b) calcined foam HAp

Figure 4
Bright field TEM images of gold decorating (a) calcined powder and (b) foam HAp synthesized at pH 8 and an aging time of 30 min

Figure 5
Comparison of the CO conversion efficiency of calcined foam HAp, gold loaded calcined powder and foam HAp

Figure 6
HAp loaded gold nanocrystal growth and dispersion at pH (a) 6, (b) 7, (c) 9 and (d) 12 (aging time 60 min)

Figure 7
TEM image of anhedral gold nanocrystals (pH 7)

polymorphic and zeolitic [46] with a wide range of chemical analogues, a systematic study of crystallochemical variants (e.g. iron, zinc or magnesium replacement of calcium and phosphorous) may produce superior catalytic supports.

Effect of pH on CO oxidation activities

The distribution and size of gold nanocrystals was controlled by adjusting the pH from 4 to 12 to increase hydrolysis of $[\text{AuCl}_4]^-$ to $[\text{Au}(\text{OH})_4]^-$ and reduce the adsorption of chloride (Figure 6, Table 2). While neutral $\text{AuCl}_3 \cdot \text{H}_2\text{O}$ is the principle species at pH ~ 3-4 [24, 25, 47, 48] hydroxychloride anions $(\text{AuCl}_x\text{OH}_{4-x})^-$ occur from mid-pH until at pH 10 $\text{Au}(\text{OH})_4^-$ is dominant. Therefore, in acidic conditions adsorption of gold complexes on HAp surfaces takes place slowly and is of limited extent. At pH 5 and 6, the concentration of $[\text{AuCl}_x(\text{OH})_{4-x}]^-$ increases as does the nucleation and growth of gold. At pH 8-9 which spans the IEP of HAp (around 8.7) [49], anionic

Figure 8
XRD patterns of (a) the pure foam HAp and after gold deposition at pHs (b) 6, (c) 7, (d) 8, (e) 9 and (f) 12 (aging time 60 min)

Figure 9
Large colloidal gold cluster formation (pH 7, aging time 30 min)

$[\text{AuCl}(\text{OH})_3]^-$ is prevalent, depositing on many nucleation sites that leads to gold crystals of smaller size and higher dispersion. When the pH increases to 12 which exceeds the IEP gold deposition is impeded by electrostatic repulsion between the HAp surface and gold hydroxide complexes. The geometrical configuration of the gold nanocrystals controls the number of co-ordinatively unsaturated sites. Spherical topology was dominant (Figure 7) and provides higher selectivity and turnover frequency (TOF) [50, 51] compared to faceted or multiply-twinned particles (MTPs).

Quantitative X-ray diffraction clearly shows the pH dependence of gold loading and crystallinity (Table 2, Figure 8). From pH 4-8 the gold loading increases by more than an order of magnitude, but declines at higher pH. The gold crystal size determined from the XRD peak width is characteristically slightly smaller than direct observations by TEM, as each particle is composed of crystal domain mosaics.

Figure 10
Correlation of pH with CO conversion of gold loaded-calcined foam HAp

Figure 11

Correlation of Au crystal growth time with CO conversion efficiency of HAp loaded gold

In addition, the large gold clusters that appear at pH 7 independent of the HAp support are only recognized by microscopy (Figure 9).

Complete CO conversion was obtained at $\sim 190^\circ\text{C}$ for the catalysts prepared at pH 8 and 9 (Figure 10) with the latter proving marginally superior, as the gold crystals were slightly smaller (5 nm versus 8 nm). The least %CO conversion was observed for pH 6 material which had the largest gold size (8 nm) with least dispersion as evident from TEM images (Figure 6).

Effect of gold particle size on CO oxidation activity

For the optimal pH 8 catalysts, the DP aging time was varied from 10, 30 and 60 min to systematically adjust crystal size. The smallest uniform Au size (2 nm) was obtained at the shortest aging time (10 min). This material gave the fastest

Figure 13

Bright field TEM image showing that the small size and high dispersion of Au nanocrystals is maintained after the durability test was conducted at 65°C for 166 h

Figure 12

CO conversion of Au-loaded HAp at pH 9 as a function of reaction time at 65°C

reaction rate with 100% CO conversion at a temperature of 150°C (Figure 11).

Durability

The durability and stability of Au-loaded HAp at pH 9 was tested by maintaining the temperature of the reactor at 65°C for 166 h (Figure 12). The CO oxidation activity remains constant as a function of reaction time, unlike metal oxide supported Au catalysts such as CuMn_2O_3 [29] and TiO_2 [52, 53] where deactivation occurred rapidly due to growth of the Au crystals [52, 53]. This is a significant problem for nanogold catalysts that makes them unsuitable for long term use has been overcome using the HAp scaffold. From the TEM image of the catalyst after the durability test (Figure 13) it is evident that the average size and dispersion of Au particles has not changed. The reason for the enhanced stability of nanogold on HAp remains to be investigated.

Conclusions

Catalysts composed of highly dispersed gold nanocrystals on a macroporous HAp foam were prepared using a DP method from a NaOH buffered solution of gold chloride. The phase pure HAp was synthesized as calcined powder and ceramic foam with crystal sizes of 123 and 218 nm respectively. Although the surface areas were equivalent, the foam favoured the deposition of anedral gold crystals of smaller size and higher dispersion to create effective catalysts. The pH of the HAuCl_4 solution controls the speciation of $\text{AuCl}_x(\text{OH})_{4-x}$ anions which attenuates the rates of deposition such that smaller crystals (≤ 5 nm) and homogeneous distributions were obtained from pH 8-9, near the IEP of HAp. Longer reaction times resulted in larger crystal sizes and colloidal gold clusters separated from the HAp. For samples prepared at pH 8-9 with an aging time of 10 min, 100% conversion of CO to CO_2 at the low reaction temperature 150°C was achieved. Over a test period of 166 h and a reaction temperature of 65°C the catalyst showed structural

and crystallographic stability without measurable loss of activity.

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