AACVD synthesis of catalytic gold nanoparticle-modified cerium(IV) oxide thin films

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Co-deposition of Ce(dbm)\textsubscript{4} and NH\textsubscript{4}AuCl\textsubscript{4} precursors in acetone at 500°C via AACVD results in deposition of crystalline CeO\textsubscript{2} thin films containing/decorated with metallic gold. These particles are estimated to be ~ 70 nm in size via optical methods. Preliminary testing of catalytic activity showed the materials were surprisingly catalytically active given the very small amounts of gold present and the large estimated particle size, although the presence of smaller catalytically active particles could not be discounted.

1 Introduction The catalytic activity of gold nanoparticles (NP) increases when supported on oxide thin films, for example TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3},\textsuperscript{1} with the support playing a critical part in the activity.\textsuperscript{2} Cerium oxide (CeO\textsubscript{2}) has been found to increase the catalytic activity of supported gold NP in CO oxidation by two orders of magnitude in comparison to TiO\textsubscript{2} or Fe\textsubscript{2}O\textsubscript{3} supports due to improved dispersion of gold, and the use of an Au/CeO\textsubscript{2} catalyst in the water-gas shift reaction has been shown to be more active than the current commercial catalysts.\textsuperscript{3}

Vapour synthesis of gold nanoparticles (NP), e.g. via chemical vapour deposition (CVD), offers advantages over wet-chemical techniques; it circumvents several steps associated with solution methods such as washing, drying, calcination and reduction, and can avoid changes in metal dispersion that can occur during high temperature calcination or reduction steps.\textsuperscript{4}

For deposition of CeO\textsubscript{2} the typically low volatility of cerium CVD precursors has led to investigation of a wide-range of fluorinated \(\beta\)-diketonates in MOCVD,\textsuperscript{5,6} although these tend to lead to fluorine incorporation.\textsuperscript{7} An alternative strategy for overcoming low volatility is to introduce the precursor as a solution droplet, and this has been utilized for use of cerium nitrate in electrospray CVD,\textsuperscript{8} and for use of Ce(thd)\textsubscript{4} (thd = 2,2,6,6-tetramethyl-3,5-heptanediionato) in aerosol-assisted CVD.\textsuperscript{9,10}

Through extensive experience in the use of AACVD for co-depositing metal NP supported on metal oxides,\textsuperscript{11,12} we have previously observed that use of H\textsubscript{4}AuCl\textsubscript{4} or H\textsubscript{4}PtCl\textsubscript{6} as metal precursors, which in terms of decomposition characteristics are excellent, can be incompatible in solution with metal alkoxide and \(\beta\)-diketonates when used in a convenient one-pot system containing both precursors. Strategies to alleviate this involve use of more robust metal oxide precursors, for instance the use of Bi(dbm)\textsubscript{3} (dbm = dibenzylmethanato) instead of Bi(thd)\textsubscript{3},\textsuperscript{13} or less acidic metal precursors such as metal phosphine cluster complexes\textsuperscript{14} or NH\textsubscript{4}AuCl\textsubscript{4}.\textsuperscript{15} In this paper we describe the use of Ce(dbm)\textsubscript{4} and NH\textsubscript{4}AuCl\textsubscript{4} precursors in a one-pot AACVD strategy for co-deposition of gold NP-modified CeO\textsubscript{2}, and report on its catalytic activity for a test oxidation reaction of benzyl alcohol to benzaldehyde.
2 Results and Discussion

2.1 Experimental Ce(dbm)$_4$ was synthesised by adaption of the method for synthesis of Ce(thd)$_4$. $^1$H NMR $\delta$/ppm (CDCl$_3$, 300 MHz): 6.70 (s, 1H, (CH$_2$)$_3$); 7.4 (m, 9H, C$_6$H$_{12}$– plus CDCl$_3$ peak); 8.0 (d, 4H C$_6$H$_2$–) ($^1$H NMR dibenzyloxy methane $\delta$/ppm (CDCl$_3$, 300 MHz): 6.9 (s, 1H), 7.5 (m, 6H), 8.0 (m, 4H), 16.9 (s, 1H), indicating the loss of the H from the alcohol group after coordination). FT-IR cm$^{-1}$: 1588, 1512, 1473, 1374, 1285, 1221, 1063, 1022, 938, 784, 747, 712, 682, 603, 509, 429 (FT-IR cm$^{-1}$ dibenzyloxy methane: 11462, 1308, 1227, 998, 752, 704, 678, 607, 493).

The general AACVD method was as follows: 50 mg Ce(dbm)$_4$ was dissolved in 20 cm$^3$ acetone (and 1 mg NH$_4$AuCl$_4$ added for gold modified samples), a piezoelectric ultrasonic atomizer (Johnson Matthey Liquifog, 1.6 MHz) was used to generate an aerosol from the precursor mixture, which was then carried to the heated substrate (500°C) by an N$_2$ gas flow (200 cm$^3$/min). The substrates used were plain glass microscope slides.

Thermal Gravimetric analysis (TGA) was carried out using a NETZSCH STA-449C Jupiter balance under helium flow. X-ray diffraction measurements were completed using a Bruker D8 X-ray diffractometer with CuK$\alpha$ radiation. Survey scans were collected over a wavelength range of 300 nm to 2500 nm in the transmission mode. XRD analysis showed good agreement for cerium oxide (Fm$\overline{3}$m space group, $a = b = c = 5.507(3)$ Å; ICDD card no. 01-081-0792 a = b = c = 5.4124 Å) (Figure 1).

Deposition using Ce(dbm)$_4$ alone produced pale cream opaque films. XRD analysis showed good agreement for cerium oxide (Fm-3m space group; Figure 2).

2.2 Results and Discussion TGA data for Ce(dbm)$_4$ (Figure 1) showed the onset of first mass loss at $\sim$ 200°C, coincident with an endotherm in the DSC. This weight loss is attributed to volatilization of the precursor slightly lower than the value found previously for Ce(thd)$_4$ of 250°C. Accelerated weight loss is observed at $\sim$ 400°C, coinciding with an exotherm in the DSC and this is attributed to initial decomposition of the precursor, which continues across three distinct steps until 550°C. Assuming no decomposition prior to 400°C, the total % weight loss during decomposition is therefore approximately 50% whereas the mass loss required for complete conversion of Ce(dbm)$_4$ to CeO$_2$ is 83%, indicating incomplete decomposition (carbon contamination) may be expected during CVD. NH$_4$AuCl$_4$ decomposes in a single principle step (Figure 1) losing 43% of its mass by 300°C, although an initial loss of mass is observed from 50°C attributed to loss of water of crystallisation. The mass loss required for complete conversion to pure gold is 55%, indicating residual chloride contamination is possible. In contrast HAuCl$_4$ exhibits two main stages of weight loss after loss of water of crystallization up to 135°C, with the first step up to 220°C corresponding to the loss of HCl and Cl$_2$ and the second step up to 294°C attributed to the disproportionation of AuCl producing Au and Cl$_2$. 

![Figure 1 TGA data for Ce(dbm)$_4$ (blue line) and NH$_4$AuCl$_4$ (red line).](image-url)
Figure 2 XRD patterns of films deposited at 500°C from Ce(dbm)$_4$ only (red line) or Ce(dbm)$_4$/NH$_4$AuCl$_4$ (green line). Literature patterns for CeO$_2$ (black) and Au (blue) are also shown. Raman spectroscopy shows a peak centred at 456 cm$^{-1}$ (Figure 3), in accordance with the literature value for CeO$_2$ (465 cm$^{-1}$).

Figure 3 Raman spectra of films deposited at 500°C from Ce(dbm)$_4$ only (blue line) or Ce(dbm)$_4$/NH$_4$AuCl$_4$ (red line)

UV-vis spectra of a film deposited at 500°C is shown in Figure 4a, compared to a blank glass substrate (Figure 4c; peaks at ~850 nm are due to a detector change on the instrument). The band-gap (Eg) of a semiconductor can be inferred from its UV-Vis spectra using the following equation:

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

Where $\alpha$ corresponds to the absorption coefficient, $h\nu$ is the photon energy, and $n$ represents the index which depends on the electronic transition of the semiconductor. Estimation of the bandgap from the band edge for the CeO$_2$ film indicates a value of $\sim$ 3.1 eV, in good agreement with the literature value of 3.15 eV.

Figure 4 UV-vis spectra of films deposited at 500°C from a) Ce(dbm)$_4$ only (red line), b) Ce(dbm)$_4$/NH$_4$AuCl$_4$ (blue line) compared to, c) blank glass substrate (black line)

Bêche et al. carried out an XPS study of cerium oxide and mixed cerium oxides assigning six peaks, corresponding to pairs of spin-orbit doublets (labelled v and u), in the Ce 3d$_{3/2,5/2}$ spectrum. Analysis of a film deposited at 500°C (Figure 5) found peaks at 916.8 (u'''), 898.1 (v'''), 906.4 (u'''), 887.8 (v'''), 901.2 (u) and 882.6 (v). The u''' (916.9), v''' (898.3) and the u (901.3), v (882.7) peaks are in very good agreement with the literature values (shown in brackets) although the u'' (907.3), v'' (888.5) peaks are noticeably different. The satellite u''' peak is indicative of the presence of Ce(IV).

Figure 5 XPS spectrum of film deposited at 500°C from Ce(dbm)$_4$ only

SEM analysis showed the films were comprised of separated grains comprised of agglomerates of smaller crystallites (Figure 6A)
Addition of NH₄AuCl₄ into the reaction mixture caused deposition of blue/black coloured films. Annealing in air at 500°C resulted in films with a deep blue colouration. XRD analysis showed evidence of crystalline CeO₂ (Fm-3m space group, a = b = c = 5.492(2) Å) as previously and also the presence of metallic gold (Fm-3m space group, a = b = c = 4.070(1) Å; ICDD card no. 00-04-0784 a = b = c = 4.0786 Å) (Figure 2). Raman spectroscopy was indicative of the presence of CeO₂ (Figure 3). EDX gave a Ce/Au weight % ratio of 10:1, very close to the weight ratio of the metals in the precursor solution. SEM (Figure 6B) showed a change in morphology compared to films deposited in the absence of NH₄AuCl₄, appearing rougher with more defined island-morphology. XPS analysis agreed closely with literature values for CeO₂ with peaks at 917.0 (u'''), 898.4 (v'''), 907.0 (u''), 888.4 (v''), 901.3 (u) and 882.7 (v) eV. Peaks were also observed in the Au 4f region with binding energies 83.7 and 87.4 eV, in good agreement with the literature values for CeO₂ and CeO₂ thin film had no measurable activity during the period of test. The Au/CeO₂ film tested showed measurable conversion and turnover number (TON), with very good selectivity towards benzaldehyde. However it should be noted that the amount of reagents used in this reaction were designed to be used with 200-250 mg gold as catalyst but the amount of active catalyst present in our films being significantly lower than this hence the low total conversion (average amount of material in 2 cm² thin film, the maximum size that could fit in reactor, is 2 mg and then by using EDX the amount of gold in the sample can be estimated). The TON value is greater than a sample of gold nanoparticles supported on SiO₂ prepared via solution-phase impregnation/calcination (TON 580), although lower than gold nanoparticles supported on nanostructured tungsten oxide (~20000, although the surface area here is expected to be considerably lower).

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Table 1. Catalytic performance of film deposited from Ce(dbm)₄ and NH₄AuCl₄ at 500°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conversion to oxidized products %</th>
<th>TON (gold only)</th>
<th>Selectivity to benzaldehyde %</th>
<th>Estimated Mass Gold from EDX /mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain Glass</td>
<td>0.0</td>
<td>-</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CeO₂</td>
<td>0.0</td>
<td>-</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Au/ CeO₂</td>
<td>8.2</td>
<td>3600</td>
<td>91.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

3 Conclusions Co-deposition of Ce(dbm)₄ and NH₄AuCl₄ precursors in acetone at 500°C via AACVD results in deposition of crystalline CeO₂ thin films containing/decorated with metallic gold. These particles are estimated to be ~ 70 nm in size via optical methods. Prelimi-
nary testing of catalytic activity showed the materials were surprisingly catalytically active given the very small amounts of gold present and the large estimated particle size (although the presence of smaller particles cannot be discounted). It has been found previously that higher catalytic performance is observed in CVD deposited materials than those produced using solution-phase methods and these results may reflect this.\(^{11}\) Future work is aimed at reducing the gold loading, and in particular reducing the gold particle size, and observing the effect on the catalytic activity.

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**References**