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## Accepted Article

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# Commercial gold(I) and gold(III) compounds supported on carbon materials as greener catalysts for the oxidation of alkanes and alcohols

Sónia A.C. Carabineiro,<sup>\*[a]</sup> Luísa M.D.R.S. Martins,<sup>\*[b]</sup> Armando J.L. Pombeiro,<sup>[b]</sup> José L. Figueiredo<sup>[a]</sup>

**Abstract:** The present paper reports strategies for single-pot efficient oxidative functionalization of cyclohexane and alcohols, under mild conditions, catalysed by Au(I or III) compounds, namely, dichloro(2-pyridinecarboxylato)gold(III) (**1**), tetrabutylammonium tetrachloroaurate(III) (**2**), chlorotrimethylphosphinegold(I) (**3**), chlorotriphenylphosphinegold(I) (**4**) and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidenegold(I) chloride (**5**) supported on different carbon materials: activated carbon (AC), multi-walled carbon nanotubes (CNT) and carbon xerogel (CX), with three different surface treatments: original, as purchased/prepared, oxidized with nitric acid (-ox), and oxidized with nitric acid and subsequently treated with NaOH (-ox-Na). The obtained materials were tested for the oxidation of cyclohexane under mild conditions (room temperature and atmospheric pressure), using an environmentally friendly oxidant (*tert*-butyl hydroperoxide, TBHP, 70% aqueous solution). All materials were very selective to the production of cyclohexanol and cyclohexanone with no trace of by-products detected. The same catalysts were also tested in the selective oxidation of methyl benzyl alcohol, cyclohexanol and 2-octanol with TBHP, under microwave irradiation, to the corresponding aldehydes or ketones. The obtained results showed that, in general, better results are obtained for the heterogenised complexes and that the most efficient support is CNT-ox-Na for both reactions. The best result for cyclohexane oxidation was obtained for 5/CNT-ox-Na, which showed recyclability up to 5 cycles without decrease of activity. The highest activity for methyl benzyl alcohol oxidation was found for the 3/CNT-ox-Na material, which could be recycled to 7 cycles without loss of activity. This is the first report so far on the oxidation of C,H bonds using the mononuclear gold complexes above (as only the oxidation of unsaturated units had been reported until now). The sp<sup>3</sup>-C,H activation is much more difficult than the oxidation of unsaturated molecules with molecular oxidants.

## Introduction

Although heterogeneous catalysis by (supported) gold nanoparticles is still predominant, an explosive growth of homogeneous catalysis by gold took place a few years ago and keeps increasing.<sup>[1]</sup> Homogeneous gold catalysts (in the form of soluble complexes) can have high activity,<sup>[2]</sup> enantioselectivity<sup>[1a, 3]</sup> and well characterized structures, but heterogeneous gold systems show longer lifetimes, easier separation of the catalyst from the products, possible catalyst recycling and adaptation to continuous flow processes (for the problems with continuous flow processes in homogeneous gold catalysis, see <sup>[4]</sup>). Thus, the possibility to combine the remarkable properties of homogeneous catalysts with the well-known advantages of heterogeneous systems by anchoring soluble gold complexes on solid supports, is a very promising interface area of research.<sup>[5]</sup>

Heterogenisation was already accomplished for complexes of several metals, however, examples of heterogenisation of Au complexes are still not much abundant.<sup>[5]</sup> They dealt mostly with the work of Gates *et al.* using the [Au(CH<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)] complex,<sup>[6]</sup> Corma *et al.*<sup>[7]</sup> and Parida *et al.*<sup>[8]</sup> heterogenised Au complexes that contained Au(III) Schiff bases. Corma *et al.* also used compounds with ONN-tridentate<sup>[9]</sup> and CNN-tridentate pincer-type ligands,<sup>[10]</sup> chiral (NHC)-dioxolane-amino Au(I) and Au(III) complexes<sup>[11]</sup> and a mononuclear asymmetrical *N*-heterocyclic carbene-Au complex.<sup>[12]</sup> A *N*-heterocyclic carbene-Au(I) complex was also reported by Fujita and co-workers.<sup>[13]</sup> Ganai *et al.*<sup>[14]</sup> used a Au(III) complex with a 1,2,3-triazole linkage, which can be used as bridge to the support. A triazole-Au(I) complex was also reported by Cai and co-workers.<sup>[15]</sup> Malliserry *et al.*<sup>[16]</sup> used phosphinine Au(I) complexes. Dubarle-Offner *et al.*<sup>[17]</sup> synthesised  $\pi$ -complexes of phosphino ligands, [Cp\*Ru( $\eta^6$ -arene-PAr<sub>2</sub>)] [OTf], in which the diarylphosphine unit was attached to a metalated  $\pi$ -arene scaffold, with either an electron-donating methyl group (-PAr<sub>2</sub> = -P(p-tol)<sub>2</sub>) or electron-withdrawing trifluoromethyl group (-PAr<sub>2</sub> = -P(p-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)<sub>2</sub>). Those metallo ligands were converted to heterodinuclear gold complexes upon treatment with [AuCl(tht)]. [Cp\*Ru( $\eta^6$ -p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-P(p-tol)<sub>2</sub>-Au-Cl)] [OTf] and [Cp\*Ru( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>-P(p-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)<sub>2</sub>-Au-Cl)] [OTf] materials were obtained.<sup>[17]</sup> Cao and Yu used a (benzotriazole)(triphenylphosphine)Au(I) complex prepared using a pre-anchored ligand.<sup>[18]</sup> Anchoring of a gold chiral sulfinamide monophosphine complex was also reported by Chen *et al.*,<sup>[19]</sup> while the immobilisation of phosphine Au(I) complexes was reported by other authors.<sup>[20]</sup> Vriamont *et al.* reported the heterogenisation of the gold complex [Tf<sub>2</sub>NAuPPh<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>]<sup>[21]</sup> and new pyrene-tagged gold complexes.<sup>[22]</sup> A cationic Au(I) complex with a BF<sub>4</sub> moiety was

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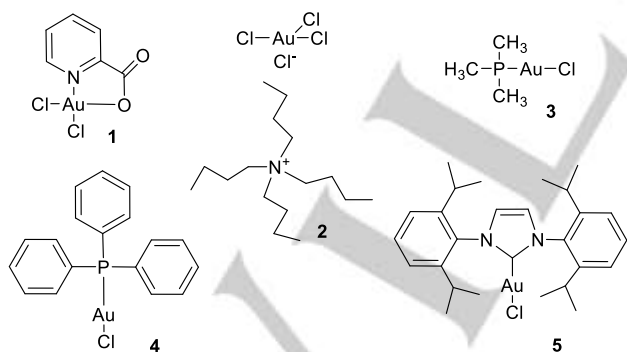
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reported by Somorjai's and Toste's groups,<sup>[23]</sup> while other authors reported heterogenisation of Au(I)-carbene compounds.<sup>[24]</sup> Immobilisation of a Au(III)-bipy complex was also reported by Yang et al.<sup>[25]</sup> and of strongly luminescent cationic cyclometalated Au(III) complexes with various dimensions by other authors.<sup>[26]</sup>

Several supports were used for these works, like silica,<sup>[12a, 14, 20c, 23]</sup>  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,<sup>[6b]</sup> MgO,<sup>[6a]</sup> La<sub>2</sub>O<sub>3</sub>,<sup>[6f]</sup> TiO<sub>2</sub>,<sup>[16]</sup> CeO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>,<sup>[7a]</sup> zeolites,<sup>[12a]</sup> polystyrene,<sup>[18-19, 24]</sup> porous organic polymers,<sup>[15]</sup> metalated arene scaffold,<sup>[17]</sup> magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>),<sup>[13, 20a, 20b, 25]</sup> metal-organic frameworks,<sup>[26]</sup> etc. Yet, to the best of our knowledge, comparatively, not much work has been done on heterogenization of Au complexes on carbon materials (although carbon materials have advantages as supports since their texture and surface chemistry can be easily tuned as needed<sup>[27]</sup>). The first report on the heterogenization of gold complexes was a publication of ours, dealing with Au (C-scorpionate) complexes immobilized on activated carbon, carbon xerogel and carbon nanotubes,<sup>[28]</sup> that showed superior performance to Au nanoparticles on similar supports<sup>[29]</sup> for the oxidation of cyclohexane to cyclohexanol and cyclohexanone. Also the yield achieved with supported gold complexes was much better than that obtained with the unsupported (soluble) complexes, and the best reported result was also larger than the obtained in the currently used industrial process (that uses a homogeneous cobalt species as catalyst and dioxygen as oxidant, at a considerably high temperature of 150 °C, with selectivities of ca. 85%).<sup>[28]</sup> Since then, the only other reports on the heterogenisation of gold compounds on carbon materials were from Vriamont et al., which dealt with the heterogenisation of a [Tf<sub>2</sub>NAuPPh<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>] complex<sup>[21]</sup> and a new pyrene-tagged Au(I) complex<sup>[22a]</sup> on carbon nanotubes. Ventura-Espinosa et al. also reported gold complexes of general formula [(NHC)AuX] (where X = Cl, Br) immobilized on reduced graphene oxide by  $\pi$ -stacking interactions.<sup>[22b]</sup> Thus, to the best of our knowledge, those four publications are the only reports so far on the subject.



**Scheme 1.** Dichloro(2-pyridinecarboxylate)gold(III) (1) – firstly used as a catalyst by Hashmi et al.,<sup>[30]</sup> tetrabutylammonium tetrachloroaurate(III) (2), chlorotrimethylphosphinegold(I) (3), chlorotriphenylphosphinegold(I) (4) and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidenegold(I) chloride (5) complexes.

In order to contribute to the development of this area, herein, we report on the heterogenization of five different Au(I) and Au(III) complexes (Scheme 1) on three different types of carbon

materials (activated carbon, carbon xerogel and carbon nanotubes). Four of these compounds have the advantage of being commercially available, which avoids the need to troublesome often low yield syntheses. The hybrid catalysts were tested in the oxidation of cyclohexane and alcohols under mild conditions. Those are reactions of industrial importance for the synthesis of fine chemicals and intermediates.<sup>[31]</sup> So far, such mononuclear gold complexes have only been reported for the oxidation of unsaturated units,<sup>[32]</sup> but not for C,H bonds. It is worth to point out that the sp<sup>3</sup>-C,H activation is a more difficult challenge than the “easier” oxidation of unsaturated molecules with molecular oxidants.

## Results and Discussion

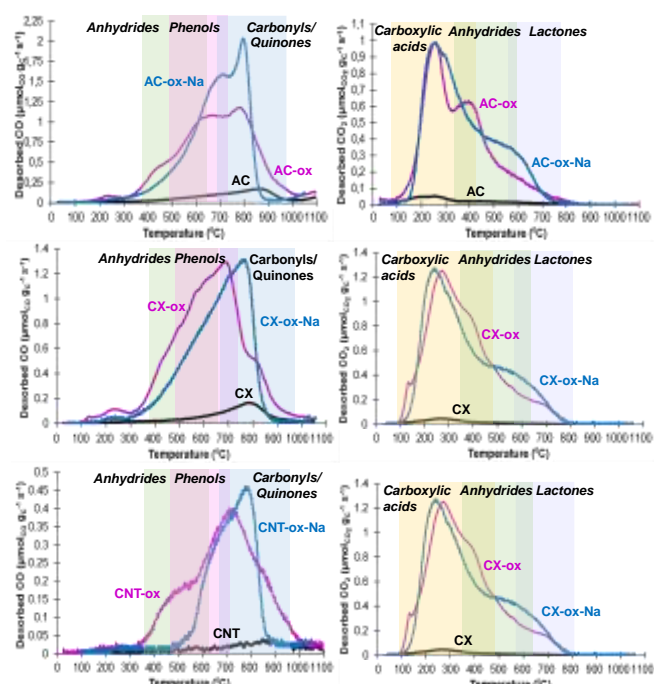
### Characterisation of carbon supports

The carbon supports were used in their original forms: as purchased (AC and CNT) or as prepared (CX), oxidised (-ox) and oxidised with nitric acid and subsequently treated with sodium hydroxide (-ox-Na). The characterization details of the nine carbon samples are displayed in Table 1 and Figure 1.

As expected, AC has the largest surface area and has abundance of micropores,<sup>[27a, 27b, 27d, 27e, 33]</sup> while CX is mesoporous and has a large pore size.<sup>[29, 33]</sup> Carbon nanotubes have a cylindrical structure and the pores result from the free space in the bundles, so they show lower surface areas than the other carbon materials.<sup>[29, 33]</sup>

**Table 1.** Description and characterisation of (powder) carbon samples: surface area ( $S_{\text{BET}}$ ), total pore volume ( $V_p$ ), average mesopore width ( $L$ ), micropore volume ( $V_{\text{micro}}$ ), external area ( $S_{\text{ext}}$ ), obtained by adsorption of N<sub>2</sub> at -196 °C, and amounts of CO and CO<sub>2</sub> desorbed, as determined by TPD (adapted from [34]).

Sample	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_p$ (cm <sup>3</sup> /g)	$L$ (nm)	$V_{\text{micro}}$ (cm <sup>3</sup> /g)	$S_{\text{ext}}$ (m <sup>2</sup> /g)	CO (μmol/g)	CO <sub>2</sub> (μmol/g)
AC	974	0.67	-	0.348	260	643	179
AC-ox	914	0.62	-	0.324	247	4930	2596
AC-ox-Na	610	0.35	-	0.251	80	5012	2883
CNT	257	2.89	-	~0	257	142	89
CNT-ox	400	1.89	-	~0	400	1475	729
CNT-ox-Na	350	1.45	-	~0	350	1079	838
CX	604	0.91	13.7	~0	604	492	135
CX-ox	570	0.80	18.8	0.038	512	4609	3774
CX-ox-Na	560	0.75	17.6	0.036	496	3720	3793



**Figure 1.** TPD profiles for the AC (top), CX (middle), and CNT (bottom) materials. Desorption of CO (left) and CO<sub>2</sub> (right), with identification of types of groups desorbing at different temperature ranges. The different colour bars are only indicative of the temperature ranges expected for desorption of different groups, and do not provide any information on their amounts (adapted from [34]).

Not surprisingly, the -ox treatment greatly increases the CO and CO<sub>2</sub> amounts (Table 1 and Figure 1). The CO desorption profiles (Figure 1, left) show that the desorption process starts around 350 °C for the -ox materials, being slightly higher for the -ox-Na samples. That can be explained by destruction of carboxylic anhydrides, which are known to desorb as CO (and CO<sub>2</sub>) in that temperature range,<sup>[27a-d, 33a]</sup> which also contribute to the increase of the carboxylate groups.<sup>[35]</sup> The peaks of the -ox-Na samples sharper, more intense and have their maxima at a temperature higher than the -ox materials, suggesting that phenol groups (that desorb as CO in this temperature range<sup>[27a-d, 33a]</sup>) are converted into phenolates, that are more stable.<sup>[35]</sup> The CO<sub>2</sub> desorption profiles (Figure 1, right) of the -ox and -ox-Na supports show a substantial increase in the carboxylic acids (that are known to decompose around 200-350 °C<sup>[27a-d, 33a]</sup>) in compared with the pristine materials. The peaks of -ox-Na supports are generally narrower with centers slightly shifted to higher temperatures, which suggests possible conversion of the carboxylic acids to (sodium) carboxylates, which increases stability.<sup>[35]</sup>

#### Heterogenisation efficiency

The gold complexes were heterogenised on the different carbon materials (~2% Au was the target value, but different loadings were obtained as will be explained ahead) on the different carbon materials, their original forms (AC, CX and CNT), oxidised with refluxing HNO<sub>3</sub> 7 M (-ox) and oxidised with HNO<sub>3</sub> followed by refluxing with NaOH 20 mM (-ox-Na). As seen above, the different treatments affect the porous structure and surface

chemistry of the supports, but the obtained materials were able to anchor all the Au complexes, although with different efficiencies (Table S1). It can be seen that complex **1** heterogenises equally on all supports. The other compounds, in general, heterogenise better on -ox-Na or -ox samples, than on pristine supports. It is well known that functionalization of the supports increases the number of surface groups which act as "anchors" for the complexes.<sup>[28, 34-36]</sup>

#### Cyclohexane oxidation

The catalytic systems were based on the chlorogold complexes **1-5**, bearing phosphinic or *N,O*-donor ligands, supported on the different carbon supports with different surface chemistries, TBHP (70% aqueous solution) as the oxidizing agent, and acetonitrile as the solvent, in a slightly acidic medium (HNO<sub>3</sub>) at room temperature and 6 h reaction time.

It was found that complexes **1-5** supported on carbon materials exhibit a remarkable catalytic activity as catalysts for the single-pot peroxidative oxidation of cyclohexane to a cyclohexanol and cyclohexanone mixture (final products), under mild conditions (Table 2). These compounds are important reagents for the production of adipic acid and caprolactam used for the industry of manufacture of nylon.<sup>[28-29, 37]</sup>

All heterogenised systems show activities higher than the homogenous counterparts, independently of the type of support and surface chemistry. The positive effects of immobilisation of complexes on solid supports include confinement effect, site-isolation, prevention of dimerization, cooperative effect of support, among others.<sup>[38]</sup> The largest increases are about 10-fold (comparing the homogenous catalyst with that supported on CNT-ox-Na), reaching almost 14-fold for the **2**/CNT-ox-Na, compared with unsupported **2** (entries 20 and 11, respectively, of Table 2).

It was also shown that the complexes supported on CNT-ox-Na yield the best results (Table 2, entries 10, 20, 30, 40 and 50). The presence of more stable phenolate and carboxylate moieties, originated by the -ox-Na treatment, might explain the good results, since these groups can act as coordination sites for the complexes.<sup>[28, 34-36]</sup>

The best results were always obtained with the CNT materials (Table 2, entries 8-10, 18-20, 28-30, 38-40, 48-50). This might be due to a textural effect, the absence of porosity of these materials allowing easier accessibility of the reactants to the active centers, or to an electronic effect, since the more graphitic structure of these materials might lead to enhanced interactions with the reactants or intermediate radicals.<sup>[28]</sup>

Depending on the complexes, CX or AC are the less adequate supports (entries 2, 12, 22, 32, 42 of Table 2). However functionalization is beneficial, as -ox materials (entries 3, 6, 9, 13, 16, 19, 23, 26, 29, 33, 36, 39, 43, 46, 49 of Table 2) are always more active than the pristine samples (entries 2, 12, 22, 32, 42 of Table 2). And the -ox-Na treatment is even better (entries 10, 20, 30, 40 and 50 of Table 2), as already explained above. That is valid not just for CNT, but also for CX and AC. The oxidation treatments provide sites to anchor of the complexes. However, it was found that the carbon supports (with no anchored complexes) showed negligible catalytic activity (results not shown in Table 2 for simplicity).



**Table 2.** Selected optimized results<sup>a</sup> for the oxidation of cyclohexane with TBHP.

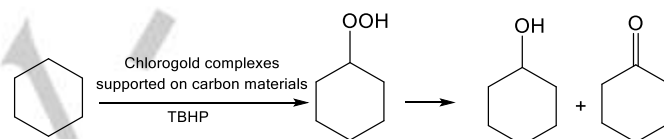
Entry	Au compound	carbon support	TON <sup>b</sup>	Total yield <sup>c</sup> /%
1	1	-	58	2.3
2		CX	78	3.1
3		CX-ox	120	4.8
4		CX-ox-Na	195	7.3
5		AC	105	4.2
6		AC-Ox	130	5.2
7		AC-Ox-Na	245	9.8
8		CNT	243	9.7
9		CNT-Ox	388	15.1
10		CNT-Ox-Na	608	24.3
11	2	-	13	0.5
12		CX	93	3.7
13		CX-Ox	110	4.4
14		CX-ox-Na	123	4.9
15		AC	75	3.0
16		AC-ox	195	7.8
17		AC-ox-Na	213	8.5
18		CNT	158	6.3
19		CNT-ox	180	7.2
20		CNT-ox-Na	240	9.6
21	3	-	35	1.4
22		CX	58	2.3
23		CX-ox	105	4.2
24		CX-ox-Na	153	6.1
25		AC	130	5.2
26		AC-ox	215	8.6
27		AC-ox-Na	243	9.7
28		CNT	155	6.2
29		CNT-ox	238	9.5
30		CNT-ox-Na	333	13.3
31	4	-	43	1.7
32		CX	113	4.5
33		CX-ox	153	6.1
34		CX-ox-Na	203	8.1
35		AC	180	7.2
36		AC-ox	223	8.9
37		AC-ox-Na	303	12.1
38		CNT	173	6.9
39		CNT-ox	355	14.2
40		CNT-ox-Na	405	16.2
41	5	-	63	2.5
42		CX	118	4.7
43		CX-ox	150	6.0
44		CX-ox-Na	153	6.1
45		AC	78	3.1
46		AC-ox	125	5.0
47		AC-ox-Na	180	7.2
48		CNT	303	12.1
49		CNT-ox	330	13.2
50		CNT-ox-Na	653	26.1

<sup>a</sup> Reaction conditions: cyclohexane (5.0 mmol), TBHP (10.0 mmol), 2  $\mu$ mol (0.04 mol% vs. substrate) of 1 - 5, HNO<sub>3</sub> (1.40 mmol), acetonitrile (3.0 mL), 6 h, 20 °C; 2  $\mu$ mol of 1-5 supported on different carbon materials (CM): carbon xerogel (CX), activated carbon (AC) or multi-walled carbon nanotubes (CNT), used in their original forms, oxidised with nitric acid (-ox) or oxidised with nitric acid and subsequently treated with sodium hydroxide (-ox-Na). Percentage of yield, TON determined by GC analysis (upon treatment with PPh<sub>3</sub>). <sup>b</sup> Turnover number (moles of product per mol of Au catalyst). <sup>c</sup> Molar yield (%) based on substrate, i.e. moles of products (cyclohexanol and cyclohexanone) per 100 mol of cyclohexane.

It was found that the best results were obtained for the 5/CNT-ox-Na material with overall yields up to ca. 26% (Table 2, entry 50), five times more than those of the industrial process [39] and overall turnover number (TON, mol of product/mol of catalyst) of 653 after 6 h reaction. This suggests that the imidazole moiety is able to efficiently assist the catalytic oxidation reaction. The reaction was also monitored with time. Figure S1 shows those results. It can be seen that the yield increases sharply up to 4-5 h, with 6 h being the optimum. Leaving the reaction more time is not needed and detrimental.

Unsupported 5 was also the best among the homogenous catalysts. The second result was achieved for complex 1, showing also the good effect of the pyridine group. The presence of nitrogen in the ligands is beneficial, since it can assist proton-transfer steps that are believed to be involved in key catalytic processes.<sup>[40]</sup>

This reaction is carried out through formation of the cyclohexyl hydroperoxide (primary product), according to Scheme 2. The formation of CyOOH is proved by using the method proposed by Shul'pin.<sup>[41]</sup>

**Scheme 2.** Oxidation of cyclohexane to cyclohexanol and cyclohexanone.

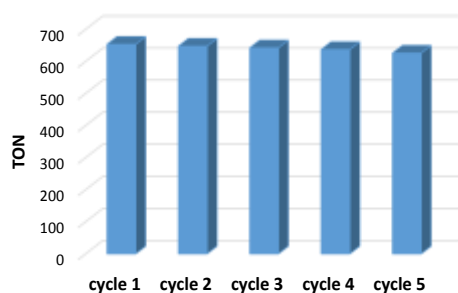
A high selectivity towards the formation of cyclohexanol and cyclohexanone is exhibited by our systems, since no traces of by-products were detected by GC-MS analysis of the final reaction mixtures. The well-known recognized promoting effect of an acidic medium on the peroxidative oxidation of alkanes catalyzed by homogeneous complexes of several metals,<sup>[37a-d, 42]</sup> pyrazole-rhenium complexes supported on modified silica gel<sup>[37e]</sup> or by other metallic catalysts<sup>[43]</sup> is also observed here. The favourable effect of the acid presumably can be associated with: (i) the activation of the metal centre by further unsaturation upon protonation of a ligand, (ii) the enhancement of oxidative properties of metal complexes, and (iii) the stabilization of the peroxide towards decomposition and promotion of peroxo (or hydroperoxo)-complexes formation. This is unlike what was found for the C-scorpionate complexes where the presence of acid (either organic or mineral) has an inhibiting effect on the catalytic activity.<sup>[28]</sup> In that work, H<sub>2</sub>O<sub>2</sub> was used (instead of TBHP), but the results were not so good as those reported here (the highest activity was ca. 10% with a TON of 300 for the [AuCl<sub>2</sub>(κ<sup>2</sup>-Tpm<sup>OH</sup>)]Cl [Tpm<sup>OH</sup> = HOCH<sub>2</sub>C(pz)<sub>3</sub>, pz = pyrazol-1-yl] complex heterogenised on CNT-ox-Na<sup>[28]</sup>).

The activities (yield) of supported gold complexes were higher than the values found for gold nanoparticles (NP) on carbon supports.<sup>[29]</sup> These systems also required the presence of acid. The values were also higher than those reported for Au nanoparticles supported on several oxides (yields varying from 1.3 to 13.5%)<sup>[31]</sup>. A comparison is not straightforward since H<sub>2</sub>O<sub>2</sub> was also used in these systems, instead of TBHP. The advantage of the Au/oxide systems is that they did not require the presence of acid.<sup>[31]</sup>

The results are presented in terms of TON, however TOF (turnover frequency, moles of product per mol of Au catalyst per time) is also an important measurement.<sup>[44]</sup> TOF is the reaction rate, normalised by the amount of active centres, and can be calculated from the rate constants after adequate kinetic analysis.

Catalyst recyclability was tested for up to five consecutive cycles for the most active catalyst: **5**/CNT-ox-Na. After completion of each cycle, the products were analyzed as normally and the hybrid catalyst was recovered by filtration from the reaction mixture, washed several times with acetonitrile and dried overnight. The subsequent cycle was initiated upon addition of new standard portions of all other reagents. The filtrate was tested in a new reaction (by addition of fresh reagents), and no oxidation products were detected, thus excluding the hypothesis of catalyst leaching. The recyclability of the system **5**/CNT-ox-Na is shown in Figure 2: it maintains almost the original level of activity after several reaction cycles (in a second, third, fourth and fifth run, the observed activities were 99.1, 98.3, 97.5 and 95.8% of the initial one, respectively) to cyclohexanol and cyclohexanone.

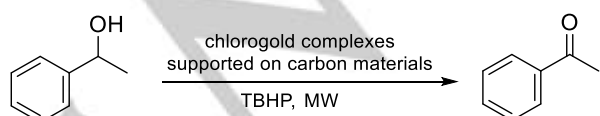
A small amount of Au (near 0.97 % of the initial amount loaded) was found by ICP in the supernatant liquid after 5 cycles. This explains the small decrease in the activity, together with small losses of the solid material, when the catalyst is separated by filtration and re-used again.



**Figure 2.** Effect of the catalyst recycling on the overall yield of products for cyclohexane oxidation catalysed by **5**/CNT-ox-Na. Reaction conditions: C<sub>6</sub>H<sub>12</sub> (5.00 mmol); NCMe (3.0 mL); TBHP (10.00 mmol); HNO<sub>3</sub> = (1.40 mmol), 20 °C; 6 h.



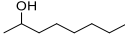
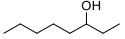
#### Oxidation of secondary alcohols

The oxidation of secondary alcohols was carried out using microwave (MW) irradiation and TBHP as the oxidant. The oxidation of methyl benzyl alcohol to acetophenone (Scheme 3) was tested for all the catalysts (Table 3). This ketone is an important industrial organic synthesis precursor to other organic compounds that range from pharmaceuticals to plastic additives.<sup>[31, 36, 45]</sup>



**Scheme 3.** Oxidation of methyl benzyl alcohol to acetophenone using MW irradiation.

**Table 3.** Selected optimized results<sup>a</sup> for the MW-assisted solvent-free oxidation of selected secondary alcohols to the respective ketones

Entry	Au compound	CM	TON <sup>b</sup>	Total yield <sup>c</sup> /%
<div><div></div><div>methyl benzyl alcohol</div></div>				
1	1	-	604	48.3
2		CX	619	49.5
3		CX-ox	714	57.1
4		CX-ox-Na	1031	82.5
5		AC	473	37.8
6		AC-ox	441	35.3
7		AC-ox-Na	659	52.7
8		CNT	536	42.9
9		CNT-ox	826	66.1
10		CNT-ox-Na	1113	89.0
11	2	-	326	26.1
12		CX	389	31.1
13		CX-ox	375	30.0
14		CX-ox-Na	394	31.5
15		AC	509	40.7
16		AC-ox	773	61.8
17		AC-ox-Na	894	71.5
18		CNT	570	45.6
19		CNT-ox	723	57.8
20		CNT-ox-Na	851	68.1
21	3	-	698	55.8
22		CX	868	69.4
23		CX-ox	891	71.3
24		CX-ox-Na	920	73.6
25		AC	806	64.5
26		AC-ox	845	67.6
27		AC-ox-Na	961	76.9
28		CNT	835	66.8
29		CNT-ox	985	78.8
30		CNT-ox-Na	1201	96.1
31	4	-	569	45.5
32		CX	664	53.1
33		CX-ox	780	62.4
34		CX-ox-Na	993	79.4
35		AC	755	60.4
36		AC-ox	890	71.2
37		AC-ox-Na	983	78.6
38		CNT	1010	80.8
39		CNT-ox	1094	87.5
40		CNT-ox-Na	1185	94.8
41	5	-	759	60.7
42		CX	820	65.6
43		CX-ox	819	65.5
44		CX-ox-Na	889	71.1
45		AC	773	61.8
46		AC-ox	925	74.0
47		AC-ox-Na	971	77.7
48		CNT	853	68.2
49		CNT-ox	980	78.4
50		CNT-ox-Na	1159	92.7
<div><div></div><div>cyclohexanol</div></div>				
51	3	CNT-ox-Na	1104	88.3
<div><div></div><div>2-octanol</div></div>				
52	3	CNT-ox-Na	871	69.7
<div><div></div><div>3-octanol</div></div>				
53	3	CNT-ox-Na	661	52.9

<sup>a</sup> Reaction conditions: 2.50 mmol of substrate, 5.00 mmol of TBHP (2 eq., 70% in H<sub>2</sub>O), 2 μmol (0.08 mol% vs. substrate) of **1** - **5**, 80 °C, 1 h of MW irradiation (25 W power). <sup>b</sup> Turnover number = number of moles of product per mol of catalyst precursor. <sup>c</sup> Moles of ketone product per 100 moles of alcohol.

It was found that, in general, the supported complexes show higher catalytic activity than the homogenous counterparts (Table 3), possibly on account of the stabilizing effect of the support which, e.g., can hamper the formation of less active di- or polynuclear species. However that effect is not as intense as the one found for cyclohexane oxidation (Table 2), as the increase is only around 2-fold (while from cyclohexane it varied

from 10- to 14-fold). The only exception is complex **1**, in which heterogenisation on AC and AC-ox (entries 5 and 6 of Table 3) gave worse results than unsupported **1** (entry 1 of Table 3). That can be due to the fact that **1** is a small compound that can possibly penetrate inside the micropores of activated carbon preventing access to the reagents. Unsupported **1** (and similar complexes) have already been investigated in the oxidation of alcohols with TBHP by Hashmi et al.<sup>[46]</sup> The methyl benzyl alcohol oxidation in the absence of a chlorogold catalyst was evaluated and it was found that it occurred in a very low extent. In fact, only 12.4% of acetophenone was obtained after 1 h of MW irradiation (25 W power) under the above conditions (but without catalyst).

In general, the complexes supported on CNT-ox-Na yield the best results (Table 3, entries 10, 30, 40 and 50), similarly to what was found for cyclohexane oxidation (Table 2). As explained above, that can be due to the presence of more stable phenolate and carboxylate groups<sup>[28, 34-36]</sup> and to a textural or electronic effect of CNT.<sup>[28]</sup> The exception is complex **2**, since the best result was obtained for AC-ox-Na (entry 17 of Table 3), which was slightly higher than the obtained for CNT-ox-Na (entry 20 of Table 3).

In general, functionalization is beneficial, as complexes supported on -ox materials (entries 3, 9, 16, 19, 23, 26, 29, 33, 36, 39, 43, 46, 49 of Table 2) are more active than the complexes supported on pristine samples (entries 2, 12, 22, 32, 42 of Table 2). The exception is **1**/AC-ox (entry 6) and **2**/CX-ox (entry 13), that are less active than **1**/AC (entry 5) and **2**/CX (entry 12). However the -ox-Na treatment always provides better catalysts (entries 10, 20, 30, 40 and 50), than the -ox or pristine counterparts. As already explained that treatment provides more efficient anchorage sites for catalysts. It was found that the carbon supports (with no anchored complexes) showed negligible catalytic activity (results not shown in Table 3 for simplicity).

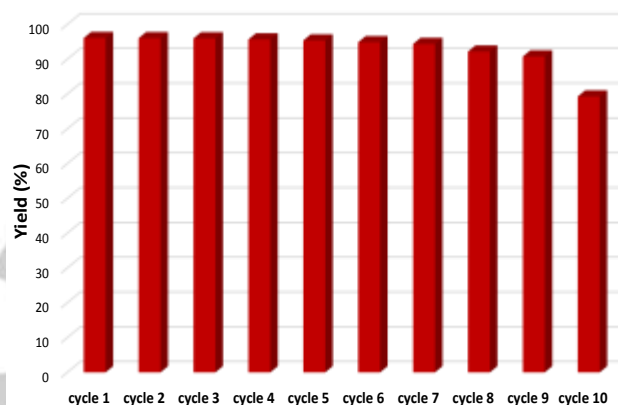
The best results were obtained for the **3**/CNT-ox-Na material with overall yields up to ca. 96.1% (entry 30). This reaction also monitored with time, as shown in Figure S2. The yield increases very fast up to 1 h, and then is kept constant up to 2 h (the maximum studied).

However unsupported **5** was the best homogenous catalyst (just like it had been for cyclohexane oxidation), and **3** was only the second best (among the homogenous catalysts). The selectivity was always very high in all cases, with no trace of byproducts detected.

The best catalytic system (**3**/CNT-ox-Na) was also tested for the oxidation of other alcohols: cyclohexanol, 2-octanol and 3-octanol (Table 2). The highest yield was obtained for cyclohexanol oxidation (TON = 1104, yield = 88.3%), which was smaller than the obtained for methyl benzyl alcohol (TON = 1201, yield = 96.1%). This value is higher than those reported for Au nanoparticles supported on several oxides, obtained at 100°C (TON=1095).<sup>[31]</sup>

Catalyst recyclability was tested for up to ten consecutive cycles for the most active catalyst: **3**/CNT-ox-Na. After completion of each cycle, the products were analyzed as normally and the hybrid catalyst was recovered by filtration from the reaction

mixture, washed and dried overnight. The subsequent cycle was initiated upon addition of new standard portions of all other reagents. The filtrate was tested in a new reaction (by addition of fresh reagents), and no oxidation products were detected, thus excluding the hypothesis of catalyst leaching. The recyclability of the system **3**/CNT-ox-Na is shown in Figure 3: it maintains almost the original level of activity until seven reaction cycles, starting to loose activity on the 8<sup>th</sup>, which is decreased on the 10<sup>th</sup>. Just like with the cyclohexane oxidation experiments, the decrease in the activity on the 10<sup>th</sup> cycle can be due to some small leaching, together with small losses of the solid material, when the catalyst is separated by filtration and re-used again.



**Figure 3.** Effect of the catalyst recycling on the overall yield of products for the MW-assisted oxidation of methyl benzyl alcohol by **3**/CNT-ox-Na. Reaction conditions: Reaction conditions: 2.50 mmol of alcohol, 5.00 mmol of TBHP, 80 °C, 1 h of MW irradiation (25 W power).

## Conclusions

The heterogenised chlorogold complexes were tested as catalysts for cyclohexane and alcohol oxidation, with TBHP as the oxidizing agent. The highest catalytic activities were observed in the presence of CNT-ox-Na with complexes **5** and **3**, respectively. The advantages of the present systems are the recyclability (up to 5 cycles without decrease of activity for **5**/CNT-ox-Na in cyclohexane oxidation and up to 7 cycles for **3**/CNT-ox-Na in methyl benzyl oxidation) using TBHP. The ease of separation of the catalysts from the reaction mixtures minimises additional work-up procedures, reducing costs and decreasing the production of toxic waste.

## Experimental Section

### General reagents

Cyclohexane (Merck), methyl benzyl alcohol (Aldrich), cyclohexanol (Alfa Aesar), 2-octanol (Aldrich), 3-octanol (Aldrich), acetonitrile (Riedel-de-Haën), nitric acid (65%, Riedel-de-Haën), diethyl ether (LabScan), cycloheptanone (Riedel-de-Haën), *tert*-butyl hydroperoxide (TBHP, 70%, Aldrich), were used as received from the suppliers.



### Gold complexes

Different Au(III) and Au(I) complexes were used (Scheme 1). Concerning the Au (III) compounds, dichloro(2-pyridinecarboxylato)gold(III) (**1**) was purchased from Aldrich, while tetrabutylammonium tetrachloroaurate(III) (**2**) was synthesized by adding dropwise, under stirring, 1 mL of the aqueous HAuCl<sub>4</sub> solution (0.01 mmol) to an equimolar quantity (0.01 mmol) of [nBu<sub>4</sub>N][BF<sub>4</sub>] dissolved in 4 mL of water. The [nBu<sub>4</sub>N][AuCl<sub>4</sub>] (**4**) yellow precipitate was formed within a few minutes. The Au(I) complexes chlorotrimethylphosphinegold(I) (**3**), chlorotriphenylphosphinegold(I) (**4**) and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidenegold(I) chloride (**5**) were purchased from Strem Chemicals.

### Carbon supports

The carbon supports used in this work were the following: activated carbon Norit® RO 0.8 (AC) from Sigma-Aldrich, multi-walled carbon nanotubes NC3100 (CNT) from Nanocyl™, and carbon xerogel (CX) prepared by a protocol described elsewhere.<sup>[33a, 47]</sup> These carbon materials were used in their original forms, as purchased (AC and CNT) or as prepared (CX); oxidised with nitric acid (-ox); and oxidised with nitric acid with a subsequent treatment with NaOH (-ox-Na). The -ox supports were obtained by treating the pristine ones with 75 mL of a 5 M nitric acid solution per gram of carbon material for 3 h in reflux. The solid was then filtrated and washed with deionized water until a neutral value of pH was obtained.<sup>[28, 34, 36, 48]</sup> The -ox-Na materials were achieved by subsequent treatment of the -ox ones with 75 mL of a 20 mM NaOH aqueous solution (per gram of carbon material) for 1 h in reflux, followed by filtration and washing until neutral pH.<sup>[28, 34-36, 48]</sup>

### Supports characterisation

The carbon materials were analysed by N<sub>2</sub> adsorption at -196 °C using a Quantachrome Nova 4200e apparatus. The specific surface area (S<sub>BET</sub>) was calculated by the Brunauer-Emmett-Teller (BET) equation, the external surface area (S<sub>ext</sub>) and the micropore volume (V<sub>mic</sub>) were determined by the *t*-method using an appropriate standard isotherm, the total pore volume (V<sub>p</sub>) was determined at P/P<sub>0</sub> = 0.99, and the average mesopore size (d<sub>meso</sub>) was calculated using area and volume data (assuming cylindrical pores). The surface chemistry was characterised by temperature programmed desorption (TPD) using an Altamira AMI-300 apparatus, coupled with a Ametek Dycor DyMaxion quadrupole mass spectrometer.

### Heterogenisation procedure

The complexes were anchored onto the nine different carbon materials (0.15 g). The necessary amount to obtain ~3% Au per mass of carbon was weighted and dissolved in 25 mL of methanol. Samples were left stirring at room temperature for overnight, filtered, washed with methanol and dried overnight at 40 °C, under in a vacuum oven. The gold loading was confirmed by inductively coupled plasma (ICP) by the Analytical Services of Instituto Superior Técnico.

### Catalytic tests

The catalytic tests for alcohol oxidation were performed in a microwave CEM discover reactor (25 W), using a 10 mL reaction tube with 13 mm of internal diameter.

A FISOONS Instruments GC 8000 gas chromatograph (GC) equipped with a DB-624 (J&W) capillary column (FID detector) and Jasco-Borwin v.1.50 software was used for the GC measurements. Helium was the carrier gas.

The temperature of injection was 240 °C. For alkane oxidation experiments, the initial temperature was maintained at 100 °C for 1 min, then raised 10 °C/min to 180 °C, while for the alcohol oxidation tests the initial temperature was maintained at 120 °C for 1 min, then raised 10 °C/min to 200 °C and held at this temperature for 1 min.

GC-MS analyses were performed using a Perkin Elmer Clarus 600 C instrument (using He as the carrier gas). The ionization voltage was 70 eV. GC experiments were conducted in the temperature-programming mode, using a SGE BPX5 column (30 m x 0.25 mm x 0.25 µm). Reaction products were identified by comparing their retention times with known reference compounds, and by comparison of their mass spectra to fragmentation patterns obtained from the NIST spectral library stored in the computer software of the mass spectrometer.

### Typical procedures for the catalytic oxidation of alkanes and products analysis

In typical conditions the reaction mixtures were: catalyst (0.1-10 µmol, 0.002-0.2 mol% vs. cyclohexane) in acetonitrile (3.00 mL), then 10.00 mmol of oxidant, HNO<sub>3</sub> (0.10 mL) and 5.00 mmol of cyclohexane (0.54 mL) were added (by this order) and the reaction solution was stirred at the desired temperature (usually room temperature) and time at normal pressure. For the products analysis, 90 µL of cycloheptanone (internal standard for cyclohexane oxidation) and 5.0 mL of diethyl ether (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred during 10 min and then a sample (1 µL) was taken from the organic phase and analyzed by GC using the internal standard method. Blank experiments confirmed that no cyclohexanol or cyclohexanone were formed without the presence of catalyst. The amount of alkyl hydroperoxide was estimated from the variations in the alcohol and ketone yields, determined by GC, analyses, upon addition of PPh<sub>3</sub> to the final reaction solution, according to a method reported by Shul'pin.<sup>[41]</sup>

### Typical procedures for the catalytic oxidation of alcohols and product analysis

Oxidation reactions of the alcohols were carried out in sealed cylindrical Pyrex tubes under focused microwave irradiation as follows: the alcohol substrate (2.50 mmol), catalyst (0.1-15 µmol, 0.004-0.6 mol% vs. substrate) and a 70 % aqueous solution of Bu'OOH (5.00 mmol) were introduced in the tube, which was placed in the microwave reactor. The system was stirred and irradiated (25 W) for 0.25-1 h at 80 °C. After the reaction, the mixture was cooled to room temperature. 150 µL of benzaldehyde (internal standard) and 2.50 mL of NCMe (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred during 10 min and then a sample (1 µL) was taken from the organic phase and analysed by GC using the internal standard method.

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**Keywords:** gold complexes • carbon supports • oxidation • heterogenisation • recyclability

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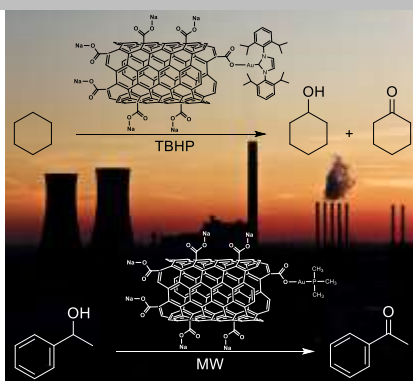
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## Entry for the Table of Contents

Layout 1:

## FULL PAPER

Single-pot efficient oxidative functionalization of cyclohexane and alcohols, under mild conditions, was catalysed by Au(I) or Au(III) complexes supported on activated carbon, carbon xerogel and multi-walled carbon nanotubes.



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Commercial gold(I) and gold(III) compounds supported on carbon materials as greener catalysts for the oxidation of alkanes and alcohols