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Solvent-free oxidation of 1-phenylethanol catalysed by gold nanoparticles supported on carbon powder materials

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ABSTRACT

Gold (1 wt.%) was loaded on several carbon materials, namely, polymer based carbon xerogel, activated carbon, microdiamonds, nanodiamonds, graphite and silicon carbide by double impregnation and sol immobilisation. The obtained catalysts were characterised by N₂ adsorption at -196 °C, high-resolution transmission electron microscopy, high-angle annular dark-field imaging (Z-contrast), temperature programmed desorption, atomic absorption spectroscopy and X-ray photoelectron spectroscopy. The obtained materials were tested on the microwave-assisted solvent-free oxidation of 1-phenylethanol by *tert*-butyl hydroperoxide (TBHP) to produce acetophenone. The results showed that the catalytic activity was influenced by several factors, namely, the nature of the support, reaction time and temperature, amount of catalyst, presence of additives, among others. The best values for acetophenone yield (99.9%) were obtained with Au deposited on microdiamonds by the colloidal method. Catalyst recyclability was tested up to six consecutive cycles at the optimized conditions for each catalyst, and it was found that Au on microdiamonds, prepared by the colloidal method, also maintained higher activity after several reaction cycles as compared to the other carbon supports.

1. Introduction

The catalytic activity of gold is strongly dependent on nanoparticle size, although the method of preparation and the nature of the support also play an important role [1–13]. Hvolbæk et al. [14] explained the relationship between size and catalytic activity, suggesting that the active sites of gold nanoparticles are the corners and edges. Zhou et al. [15] performed single-molecule microscopy of fluorogenic reactions, showing that when the size decreased, the substrate binding affinity was reduced, while the catalytic conversion increased per surface area. However, the product binding affinity increased when the particle size decreased.

Gold nanoparticles (on different supports) have been widely used as catalysts for several reactions, due to their exceptional catalytic properties [2,3,6,10–12,16–31]. One example is the aerobic oxidation of alcohols catalysed by gold, which has been widely investigated in

organic synthesis [28,32–46]. Benzyl alcohol derivatives are very attractive substrates [34–38,40,42,44,33–46]. When substituted benzyl alcohols contain electron-donating moieties (such as CH₃, OCH₃ or OH groups), they are much more easily oxidised, compared to the compounds without such electron-donating groups. One of the obtained products is acetophenone, which has a wide variety of uses in the chemical and pharmaceutical industries.

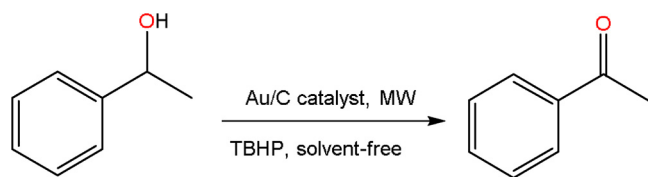
Aiming at improving the reaction conditions, Mitsudome and co-workers [38] observed that a hydrotalcite supported nanoparticle (Au/HT) was an efficient heterogeneous catalyst for the oxidation of 1-phenylethanol under mild conditions. The turnover number (TON) and turnover frequency (TOF) were 200,000 and 8300 h⁻¹, respectively. Moreover, the catalyst could be easily filtrated and recycled without loss of activity and selectivity.

Furthermore, Ni et al. [37] reported an efficient H₂O₂-Au approach for 1-phenylethanol oxidation under solvent free conditions, which was

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Scheme 1. MW-assisted oxidation of 1-phenylethanol to acetophenone.

considered an important milestone as a green oxidation with heterogeneous metal complexes.

The importance of selectivity at milder conditions was discussed by Wang et al. [40], who used gold nanoparticles supported on a layered double hydroxide and reported only acetophenone, using molecular oxygen as an oxidant, under atmospheric pressure, at room temperature, for 2 h. Upon 6 recycling cycles, the activity dropped to 97%. The size of gold nanoparticles was in the 1–5 nm range.

However, only a few studies have been conducted on the oxidation of benzyl alcohol derivatives using gold supported on carbon materials. Some of the existing reports refer to the goal of obtaining aldehydes as oxidation products [47,48] (not ketones). In order to fill that gap, we used gold nanoparticles supported on six different (carbon) materials, with different sp^2 or sp^3 hybridizations, namely, microdiamonds (MD) – primarily sp^3 , carbon xerogel (CX), activated carbon (AC), graphite (GR) – sp^2 , nanodiamonds (NDLIQ for liquid dispersion) – sp^2 in the surface (although the core is sp^3), and silicon carbide (SC) – a mixture of sp^2 and sp^3 under the oxide layer. The catalytic activity of these materials was studied for the oxidation reaction of 1-phenylethanol to acetophenone (Scheme 1).

Two different methods were used to prepare the catalysts: sol immobilisation or colloidal method (COL) [49–52] and double impregnation (DIM) [53–62]. COL refers to the simple and well known wet chemistry precipitation approach, as the solutions of diverse ions are mixed under specific temperature and pressure to form insoluble precipitates. This method proved to be very appropriate to obtain nanoparticles with controlled morphologies and prominent catalytic performance, especially when used with carbon support materials [10–12,24,49,51,63]. On the other hand, the DIM procedure involves the reaction between chloroauric acid and a base (Na_2CO_3) that produces the precipitation of gold hydroxide within the pores of the catalyst. The chemical mechanism that leads to an enhanced activity of such catalysts is due to the formation of $Au(OH)_3$ during the Au deposition process, instead of gold chloride. Therefore, the chloride ion, not being bonded with gold, is removed by the washing process. This is quite advantageous, since it is well known that chloride can poison the reaction sites of the catalyst and contributes to the sintering of gold nanoparticles, thus turning them inactive [11,12,64].

Although the selectivity and efficiency are high in traditional (alcohol) oxidation reactions, normally toxic oxidants and solvents are used, and a large amount of waste is produced. Thus, the so-called “green” oxidants [65], such as hydrogen peroxide (H_2O_2) or *tert*-butyl hydroperoxide (TBHP, $tBuOOH$) are more suitable oxidants and should be used. In this work, aqueous TBHP was used as oxidising agent, under several reaction conditions (such as different temperatures, different reaction times, different amounts of TBHP and 2,2,6,6-tetramethylpiperidin-1-yl)oxyl - TEMPO additive), with the assistance of microwave irradiation (MW). The use of MW is regarded as much more effective than conventional heating, usually with similar yields achieved in a shorter time and at lower temperatures [66,67].

2. Experimental

2.1. Carbon supports

Several types of carbon materials were used (as seen in Table 1), namely:

Table 1

Details and characterisation data of the carbon materials: surface area (S_{BET}), total pore volume (V_p), average mesopore width (L), micropore volume (V_{micro}), external area (S_{ext}), obtained by adsorption of N_2 at $-196^\circ C$, and amounts of CO and CO_2 desorbed, as determined by TPD.^a

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	L (nm)	V_{micro} (cm^3/g)	S_{ext} (m^2/g)	CO ($\mu mol/g$)	CO_2 ($\mu mol/g$)
AC	974	0.67	–	0.348	260	740	205
MD	4	0.01 ^b	3.8 ^b	~0	4	51	25
CX	611	0.90	13.6	~0	611	564	156
GR	5	0.02	4.5	~0	5	40	21
SC	~0	~0	–	~0	~0	–	–

^a Data from [24,70].

^b MD and GR are non-porous supports and the corresponding values of V_p and L refer to the voids between their aggregates.

- carbon xerogel was synthesised by the polycondensation of resorcinol and formaldehyde at pH 6, as described in earlier publications [68–70], denoted as CX;
- activated carbon Norit ROX 0.8 (AC), from Sigma Aldrich, an extruded acid washed activated carbon with cylindrical pellets of 0.8 mm diameter and 5 mm length, commercially prepared from peat by steam activation, crushed into powder;
- micro-sized diamond powder (1–2.5 μm) from Technodiamant, The Netherlands (MD), obtained by extraction from rock samples by drill core or outcrop of about 25 to 100 kg, which were crushed and dissolved in acid or a hot caustic solution;
- nanodiamonds produced by detonating carbon-containing explosives in a closed chamber and immediately cooled at a rate $\geq 3000 K min^{-1}$, as described elsewhere [71], namely, an aqueous mono-dispersion (4–5 nm) of 5% nanodiamonds (NDLIQ) from NanoCarbon Research Institute Co. Limited, Japan, known as NanoAmmando[®];
- graphite powder (< 20 μm , synthetic), supplied by Sigma Aldrich (GR);
- silicon carbide powder (SiC, carborundum < 0.2 mm) from VWR (SC).

2.2. Preparation of gold catalysts

Gold (1 wt.%) was loaded on the carbon supports by two different methods: sol immobilisation or colloidal method (COL) [49–52] and double impregnation (DIM) [53–62]. COL consists in dissolving the gold precursor, $HAuCl_4 \cdot 3H_2O$ (Alfa Aesar) in water, adding polyvinyl alcohol (Aldrich) and $NaBH_4$ (Aldrich), resulting in a ruby red sol to which the powder support is added under stirring (in the case of NDLIQ, the ND suspension was added to the solution). After a few days, the solution starts to lose colour, as Au is deposited on the support. The colourless solution is filtered, the catalyst washed thoroughly with distilled water until the filtrate is free of chloride and dried at $110^\circ C$ overnight. The organic scaffold is removed from the support by a heat treatment under nitrogen flow for 3 h at $350^\circ C$ (shown by elemental analysis to be efficient for this purpose), and then, the catalyst is activated by further treatment under hydrogen flow for 3 h also at $350^\circ C$. In previous studies, colloidal procedures were used with good success for the deposition of Au on carbon materials [49–52,72,73]. The DIM method consists in impregnating the support with an aqueous solution of the gold precursor and then with a solution of Na_2CO_3 (Sigma Aldrich), followed by washing with water and drying. This procedure leads to a chloride-free catalyst, as already mentioned.

2.3. Characterisation of carbon supports

2.3.1. Textural characterisation

The materials were analysed by adsorption of N_2 at $-196^\circ C$ in a

Quantachrome NOVA 4200e apparatus. The specific surface area (S_{BET}) was calculated by the Brunauer-Emmett-Teller (BET) equation [74], the total pore volume (V_p) was determined at $P/P_0 = 0.98$, the average mesopore width (L) by the Barrett-Joyner-Halenda (BJH) method [75], and the micropore volume (V_{micro}) and external surface area (S_{external}) were determined by the t-method using an appropriate standard isotherm [76].

2.3.2. Surface characterisation

Temperature programmed desorption (TPD) experiments were performed in a fully automated AMI-200 Catalyst Characterisation Instrument (Altamira Instruments), equipped with a quadrupole mass spectrometer (Dymaxion 200 amu, Ametek), with a $5^\circ\text{C}/\text{min}$ heating rate up to 1100°C , under helium flow. Desorbed CO and CO_2 were monitored by mass spectrometry.

2.3.3. Characterisation of gold on carbon materials

2.3.3.1. Nanoparticle sizes. Selected samples were imaged by transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field (HAADF) with energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). Conventional TEM measurements were performed with a JEOL 2010 microscope. HRTEM, EDS and Z-contrast measurements were done on a FEI Tecnai F30 instrument. The Z-contrast images were collected using an HAADF detector in scanning transmission mode (STEM). The presence of gold was confirmed by EDS. The samples were mounted on a carbon polymer supported copper micro-grid. A few droplets of a suspension of the ground catalyst in isopropyl alcohol were placed on the grid, followed by drying under ambient conditions. The average gold particle size was determined from measurements made on about 300–1000 particles, depending on the sample. The metal dispersion was calculated by $D_M = (6n_s M)/(\rho N d_p)$, where n_s is the number of atoms at the surface per unit area ($1.15 \times 10^{15} \text{cm}^{-2}$ for Au), M is the molar mass of gold (196.97g mol^{-1}), ρ is the density of gold (19.5g cm^{-3}), N is Avogadro's number ($6.023 \times 10^{23} \text{mol}^{-1}$) and d_p is the average particle size (determined by HRTEM, assuming that particles are spherical).

2.3.3.2. Oxidation state. XPS analyses of the Au 4f region were carried out for selected materials. A VG Scientific ESCALAB 200A spectrometer was used, with Al K α radiation (1486.6 eV).

2.3.3.3. Metal loading. Samples were incinerated at 600°C and the resulting ashes were dissolved in a concentrated HNO_3 and H_2SO_4 mixture. The resulting solution was diluted and analysed by atomic absorption spectroscopy (AAS) using a Unicam 939 atomic absorption spectrometer and a hollow cathode lamp Heraeus 3UNX Au.

2.3.3.4. Catalytic tests. The catalytic tests for alcohol oxidation were performed in a microwave Anton Paar Monowave 300 (25 W), using a G10 reaction tube with 10 mm of internal diameter.

A Fisons 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 . In the alcohol oxidation tests, the initial temperature was maintained at 120°C for 1 min, then raised $10^\circ\text{C}/\text{min}$ 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 helium as the carrier gas). The ionization voltage was 70 eV. GC experiments were conducted in the temperature-programming mode, using an SGE BPX5 column ($30 \text{m} \times 0.25 \text{mm} \times 0.25 \mu\text{m}$). 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.

2.3.3.5. 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 tBuOOH (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 acetonitrile (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. Reactions without catalyst and without oxidant were performed for comparison.

2.3.3.6. Recycling experiments. Recycling of the catalysts was tested up to 6 consecutive cycles. In each cycle, the method for recycling started by collecting the reaction solution from the vessel, the catalysts were separated using centrifuge (5000 rpm, 5 min), washed with acetonitrile (repeating at least 2 times) and dried under compressed air at room temperature. Afterward, the catalysts were reused for the 1-phenylethanol oxidation experiments, while the molar ratio of substrate to catalyst remained constant.

3. Results and discussion

3.1. Characterisation of the carbon supports

3.1.1. Textural and surface characterisation

Table 1 shows the textural characterisation results of the carbon samples used as supports. AC displays the highest BET surface area, while MD and GR show low surface areas of $\sim 5 \text{m}^2/\text{g}$. CX exhibits mesoporous properties with 13.6 nm mesopore width. SC is not porous.

The total amounts of released CO and CO_2 determined by curve integration of temperature programmed desorption (TPD) profiles are also shown in Table 1. AC has the largest amount of surface groups, which is expected, since it is well known that this material has a very rich surface chemistry as well [77–81]. The amounts of CO and CO_2 released from the xerogel are much lower than those from AC. GR and MD have the lowest amounts of surface groups. In fact, low amounts of desorbed CO and CO_2 species are also expected from a low surface area graphite, and also the release of far less amounts from MD, compared to AC [82]. The values determined from SC were negligible. NDLIQ was in a liquid dispersion, thus could not to be characterised by these techniques.

3.2. Characterisation of gold on carbon materials

3.2.1. Nanoparticle sizes

Fig. 1 shows bright-field high resolution transmission electron microscopy (HRTEM) images and high-angle annular dark-field (HAADF) micrographs of gold nanoparticles supported on the different carbon materials (fresh samples). In HRTEM, the gold nanoparticles are seen as darker areas, while on HAADF, they are observed as bright spots, since their detection is made through Z-contrast micrographs. The presence of gold was confirmed by energy-dispersive X-ray spectroscopy (EDS) in both cases. Figure S1 of Supporting Information shows the size distribution histograms obtained. Interestingly, DIM seems to be more efficient than COL for diamond supports (MD and NDLIQ), as seen by the size distributions (Figure S1), since the Au/MD-DIM and Au/NDLIQ-DIM samples showed predominance of smaller nanoparticles.

Table 2 shows a summary of the values of the gold nanoparticle sizes and dispersion. It can be seen that depositing gold on diamond materials (MD and NDLIQ) by different methods (COL and DIM) yields

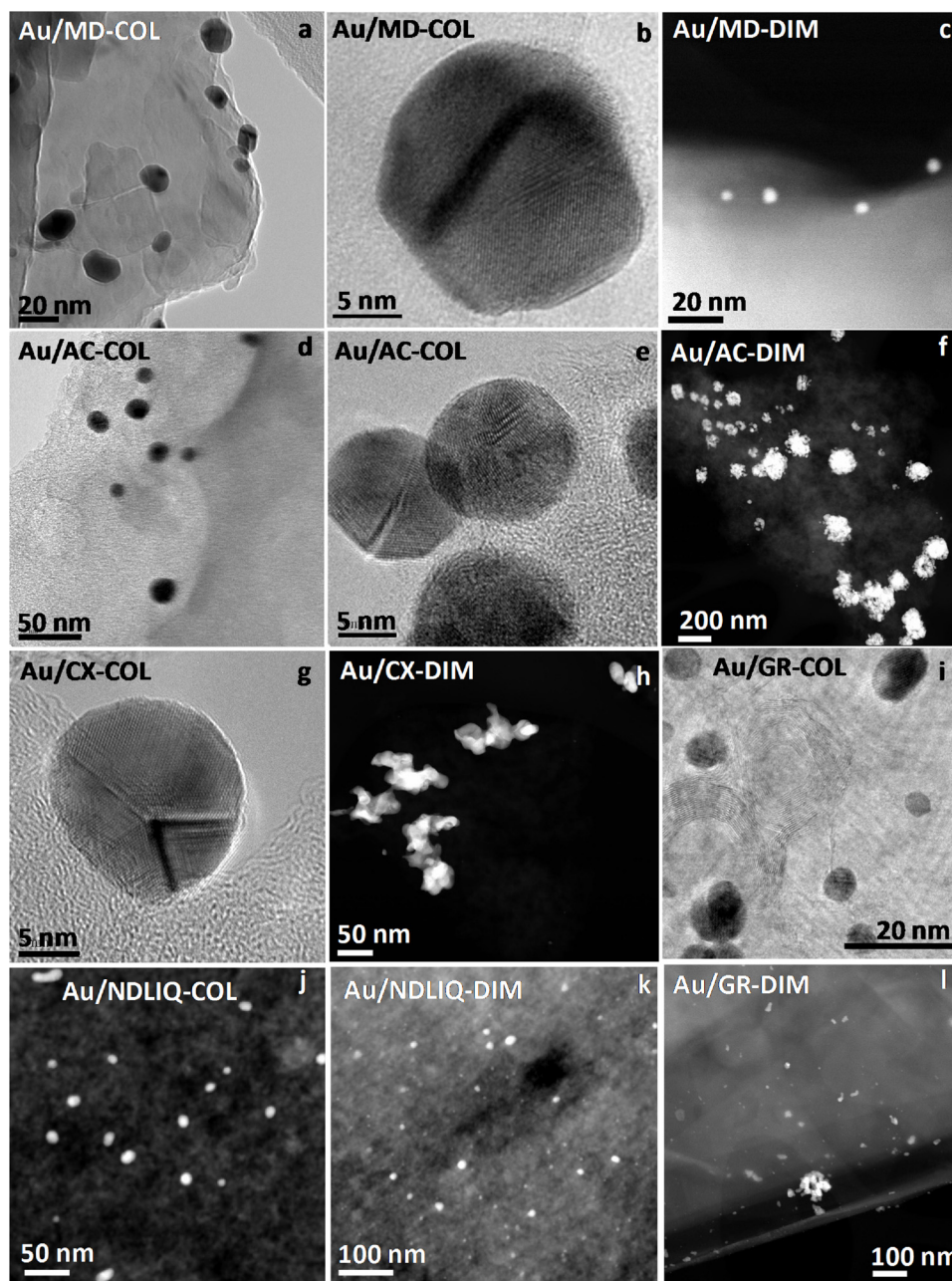


Fig. 1. HAADF micrographs and HRTEM images of Au/carbon materials: MD-COL (a,b), MD-DIM (c), AC-COL (d,e), AC-DIM (f), CX-COL (g), CX-DIM (h), GR-COL (i), NDLIQ-COL (j), NDLIQ-DIM (k), GR-DIM (l). Gold nanoparticles are seen as darker spots on HRTEM images and as bright spots on HAADF micrographs (some agglomerates are also seen as white spots).

nanoparticles with different sizes (8.2 nm for COL and ~5 nm for DIM), showing that the DIM method leads to a larger dispersion and lower average particle size on these materials. There is not much difference in terms of nanoparticle sizes for AC, CX and SC materials, when comparing deposition by the two methods. However, for GR, the COL method is more efficient, leading to smaller nanoparticle sizes (4.7 nm, compared to 5.8 nm for DIM).

In previous works, gold was deposited on carbon nanotubes following the same experimental procedures, and it was shown that COL was the most efficient method in comparison with DIM, as it led to lower sizes and better dispersions [24,51]. In fact, DIM is a very good method to prepare gold on metal oxides [53,55,56,58,59,61], but it is rarely used on carbon materials [24,51].

The smallest nanoparticles were obtained on the mesoporous CX material by COL (4.4 nm average size). According to other authors

[83,84], a large number of defects in the support structure is beneficial for gold deposition, as they act as anchoring sites, limiting the increase in nanoparticle size that occurs during further agglomeration of gold nanoparticles, before they stick onto the support. In this view, the defective structure of CX is expected to provide small gold nanoparticle sizes [83,84], as found in our work. Depositing Au on CX by DIM leads to a similar low nanoparticle size, however, agglomerates were also observed (Fig. 1h), which were not accounted for in the average size calculations, showing that, at least in our case, defects do not play such a major role. Moreover, as seen above, the use of low defect MD as a support produced Au nanoparticles with an intermediate size.

A larger average size (6.8–7.0 nm) was obtained for gold nanoparticles supported on AC. The DIM method also produced agglomerates of gold on this support (Fig. 1f).

Larger nanoparticles were formed on NDLIQ (8.2 nm). Although a

Table 2

Average gold nanoparticle size, range and dispersion, calculated from HRTEM/HAADF measurements, of the fresh samples and of selected materials used for 5 cycles of oxidation of phenylethanol (values between parenthesis).

Sample	Au average size, nm	Au range, nm	Metal dispersion, %
Au/AC-COL	6.8*	1-20*	16.9*
Au/AC-DIM	7** (9.3)	1-20 (1-25)	16.5 (12.4)
Au/NDLIQ-COL	8.2*	1-20*	14.0*
Au/NDLIQ-DIM	5.0 (7.1)	1-15 (2-15)	23.1 (16.3)
Au/MD-COL	8.2* (10.6)	1-20* (3-20)	14.0* (10.9)
Au/MD-DIM	5.8	1-20	19.9
Au/CX-COL	4.4* (6.1)	1-14* (1-14)	26.2* (19.1)
Au/CX-DIM	4.5*	1-25	25.7
Au/GR-COL	4.7	1-15	24.6
Au/GR-DIM	5.8** (7.5**)	1-25 (2-25)	19.9 (15.4)
Au/SC-COL	4.5***	1-10	26.3
Au/SC-DIM	4.8**	1-20	24.1

* Data from [24].

** With some agglomerates, not accounted for the average.

*** Very few particles seen.

complete mono-dispersed NDLIQ sample was added to the gold solution for the preparation of the gold catalyst (instead of a powder, as in the case of all other materials), a strong in situ agglomeration of the core ND particles upon gold formation might explain the different sizes. DIM was a more efficient method for preparing smaller gold nanoparticles on NDLIQ sample than COL (5 nm, compared to 8.2 nm average size), as was observed with MD. Apparently, the gold nanoparticle size does not seem to be related with the BET surface area of the supports, for the studied samples.

On GR, the COL method was also more efficient, leading to smaller (4.7 nm average size) nanoparticles, compared to DIM (5.8 nm average, plus agglomerates, as seen in Fig. 11). It is known that GR only shows a weak interaction with gold, often resulting in the formation of large gold nanoparticles, even at room temperature [85,86]. On SC, the sizes were similar (around 4.8 nm), but agglomerates were seen on the DIM sample. It was also reported that, on some SiC surfaces, Au forms clusters at room temperature, just like on graphite [87–89]. Very few particles were seen on the COL material, so the results are less trustable, as only a relatively low number of particles were counted (less than 50).

3.2.2. Oxidation state

Since the COL samples were directly reduced with hydrogen, Au 4f XPS was carried out only in selected samples (namely, Au/MD-COL and Au/AC-COL) for confirmation (results shown in Figure S2 Supporting Information). In the DIM method, the preparation included a second step of impregnation with Na₂CO₃, which can dissociate and generate hydroxyl ions (by reaction with water), which hydroxylate the Au³⁺ species of the gold precursor [51]. Subsequently, Au³⁺ can be reduced by electron transfer from coordinated OH⁻ ions on the surface of the support [90]. Therefore, it was also expected that materials prepared by the DIM technique would be in the reduced state. XPS showed that this was also the case for Au/MD-DIM, but Au⁺ was found for Au/AC-DIM, as shown in Figure S2).

3.2.3. Metal loading

The gold content obtained by atomic absorption spectroscopy (AAS) analysis was around 0.8 wt.% Au, which is lower than the nominal value (1 wt.% Au). The two preparation methods did not influence substantially the gold content of the catalysts, as the correspondingly prepared samples presented similar values. So, both COL and DIM techniques used in this work were efficient in producing catalysts with gold contents reasonably close to the expected (nominal) loading.

3.2.4. Catalytic activity

The gold nanoparticles supported on the different carbon supports

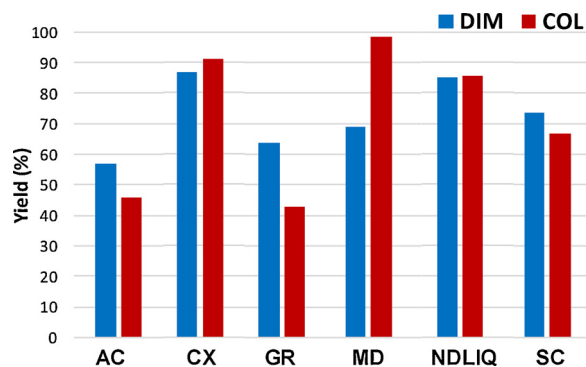


Fig. 2. Catalytic activities (in terms of yield) for the different Au/carbon materials. Reaction conditions: alcohol substrate (2.50 mmol), catalyst (1 μmol) and a 70% aqueous solution of TBHP (5 mmol), 2 h of MW irradiation (25 W power) at 150 °C.

were tested as heterogeneous catalysts for the microwave-assisted solvent-free oxidation of 1-phenylethanol by tBuOOH. The influence of several catalytic parameters, such as temperature, reaction time, catalyst amount, oxidant type/amount and loading method, on the catalytic activity (in terms of TON, TOF and yield) was investigated. The complete set of results obtained is included in Tables S1 to S12 of Supporting Information (each Table presents the results obtained for a given Au/carbon catalyst). The reaction without catalyst and the reaction without the oxidant were also performed, the acetophenone yields obtained being lower than 1% (values not included in Tables for simplicity).

3.2.5. Effect of the gold loading method

Fig. 2 shows the catalytic activity of the different Au/carbon supports at 150 °C in terms of yield. The COL method leads to better results for CX and MD. Apparently, this is not related with the Au size, since Au/MD-COL has larger nanoparticles than Au/MD-DIM, and for Au/CX, the size is similar for both methods. The COL method included a treatment in hydrogen, as referred in the Experimental section. It has been shown that, in some cases, a treatment of the catalysts with this gas can lead to better catalytic results [10,91,92].

For Au/AC, Au/GR, and Au/SC, DIM was the most adequate, although the COL method produced smaller nanoparticles (Table 2). Interestingly, the dispersion values of Au on AC, CX and SC are almost the same between COL and DIM methods (Table 2), however, the yield between DIM and COL shows a larger difference on AC (Fig. 2), being better for DIM. A possible explanation might be in the gold oxidation state (Au⁺) found on Au/AC-DIM, while Au/AC-COL had Au⁰, as seen in Figure S2). A recently published paper [93], showed that samples containing Au⁺ were more active in the oxidation of *n*-octanol.

Similar results were obtained for the NDLIQ samples, for both methods in spite of the different sizes. In this case, it seems that the effect of the support is more important than the gold nanoparticle size. As nanodiamonds were supplied in liquid form, it was not possible to characterize NDLIQ sample (as both N₂ adsorption and TPD are made on powder samples). However, it is well known that nanodiamonds have a high surface area and rich surface chemistry [24]. It is known that the presence of surface groups can affect the preparation of carbon-based catalysts, as they confer acid-base or hydrophilic character to the carbon surface, and can also affect adsorption/desorption phenomena, impacting the catalytic activity [94]. Surface groups also provide anchoring sites for the metal (namely Pt) precursors and can prevent sintering [94–97]. This was also found to be true for Au/AC catalysts on glycerol oxidation, as the amount of oxygen surface groups was found to be determining, in spite of average similar gold nanoparticle sizes [98].

Figure S3 (top) shows that, in terms of TON, at 110 °C, COL is better

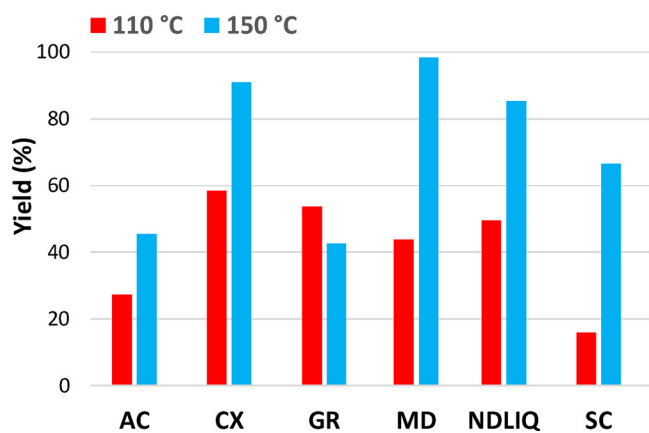


Fig. 3. Effect of reaction temperature in acetophenone yield for Au/carbon materials obtained by the COL method. Reaction conditions: alcohol substrate (2.50 mmol), catalyst (1 μ mol) and a 70% aqueous solution of TBHP (5 mmol), 2 h of MW irradiation (25 W power).

for GR, CX, MD and AC, but for the SC and NDLIQ samples the values obtained with COL and DIM are very similar. At 150 °C (Figure S3, bottom) MD and CX also show better results with COL, but for most other materials DIM is better. Very similar TON values are found for NDLIQ.

At lower temperatures (50 °C and 80 °C), the difference is not very large between the two methods for AC, SC, and GR (entries 3 and 6 of Tables S1 to S6). However, Au/CX-DIM is slightly better than Au/CX-COL (entries 3 and 6 of Tables S7 and S8). Also at 80 °C, Au/AC-DIM shows better catalytic activity than Au/AC-COL (Table S1 and S2).

3.2.6. Effect of temperature

In general, the catalytic activity increases with a temperature increase, up to 150 °C, the maximum temperature tested, as shown in entries 19 of Tables S1 and S2; entry 18 of Tables S3, S4, S5 and S7; entry 15 of Table S6; entry 3 of Table S9; entry 5 of Tables S10, S11 and S12, since better results for the tests carried out at 150 °C were obtained, in comparison with lower temperatures, under the same reaction conditions.

Figs. 3 and 4 compare two temperatures (110 °C and 150 °C) for the materials prepared by COL and DIM methods, respectively. The temperature of 150 °C gives better results, with the exception of Au/GR-COL catalyst (Fig. 3). GR only shows a weak interaction with gold, often resulting in the formation of large gold nanoparticles, even at room temperature, as already referred [85,86]. It is also known that higher temperatures promote more sintering of gold nanoparticles [1–12], so that is possibly the reason for the worse result of Au/GR-COL (Fig. 3).

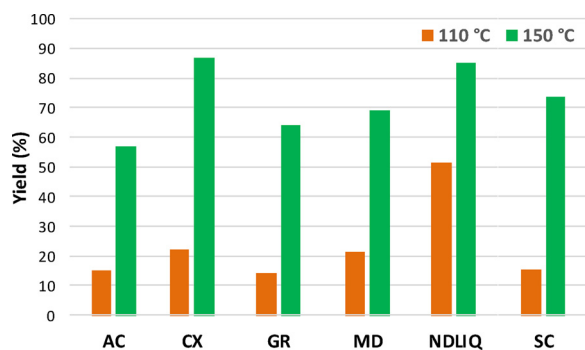


Fig. 4. Effect of reaction temperature in acetophenone yield for Au/carbon materials obtained by the DIM method. Reaction conditions: alcohol substrate (2.50 mmol), catalyst (1 μ mol) and a 70% aqueous solution of TBHP (5 mmol), 2 h of MW irradiation (25 W power).

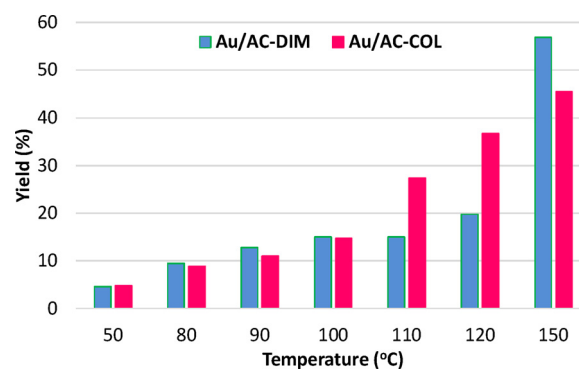


Fig. 5. Effect of temperature in acetophenone yield for Au/AC materials. Reaction conditions: alcohol substrate (2.50 mmol), catalyst (1 μ mol) and a 70% aqueous solution of TBHP (5 mmol), 2 h of MW irradiation (25 W power).

However, increasing the temperature with the Au/GR-DIM catalyst (Fig. 4) leads to a much higher yield, as is the case with all other DIM prepared catalysts. The size of gold nanoparticles is smaller in Au/GR-COL (4.7 nm) than on Au/GR-DIM (5.8 nm, with some agglomerates). Larger gold nanoparticles are more resistant to sintering [10,11], possibly explaining the different results obtained with the different preparation methods. The increase in yield with higher temperature is especially large for Au/SC materials (Figs. 3 and 4).

Fig. 5 shows the behaviour of the Au/AC materials for all the temperatures tested, as an example, to compare with the results of Haruta and co-workers [35], who used an Au/AC catalyst (2 wt.% Au) prepared by solid grinding method, and obtained a yield in the oxidation of 1-phenylethanol to acetophenone of 8%, at 80 °C after 3 h reaction (with 5.025 mol% catalyst vs. substrate). In our case, Fig. 5 shows that both the DIM and COL methods were efficient to obtain a similar yield at 80 °C, using less time (2 h reaction), and with only 0.04 mol% catalyst vs. substrate. Thus, using much less catalyst and less reaction time, we obtained yields similar to those reported in the literature [35], showing that DIM and COL are more efficient than solid grinding. Up to 100 °C, there is not much difference between DIM and COL for Au/AC materials. However, for 110–120 °C, COL shows a better performance, whereas at 150 °C, there is a superiority of DIM, in terms of yield.

In all of the above-mentioned results for the oxidation reaction, the influence of microwave irradiation is limited to pure thermal effects (i.e., bulk temperature of the reaction mixture, development of a temperature gradient) that can be responsible for higher reaction rates under microwave conditions [99]. There can be also non-thermal activation effects, mostly associated with the absorption of electromagnetic waves during rotational transitions of molecules [99]. These effects require further study.

3.2.7. Effect of reaction time

The activity also increases with reaction time. 2 h was the maximum time tested for most catalysts. The tests varying the reaction time were carried out at different temperatures, ranging from 50 °C to 100 °C, in selected samples. It was observed that, in general, 2 h reaction provided the best results for temperatures above 50–80 °C (not shown), so this time duration was used.

3.2.8. Effect of catalyst amount

Concerning the variation of the catalyst amount, it is observed that the activity, in terms of TON and TOF, increases with the increase of catalysts amount, the best results being for 1 μ mol (entries 6 and 16 of Tables S1, S2, S3, S4, S5 and S7; entry 13 of Table S6 and S8; entry 3 of Table S11 and S12; entry 1 of Table S9; entry 2 of Table S10), at different temperatures.

Figs. 6 and 7 show the results obtained for the different methods, in

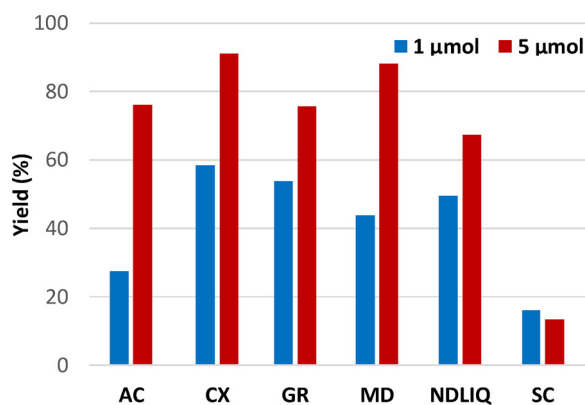


Fig. 6. Effect of catalyst amount in acetophenone yield of Au/carbon catalysts prepared by COL. Reaction conditions: alcohol substrate (2.50 mmol), and a 70% aqueous solution of TBHP (5 mmol), 110 °C temperature, 2 h of MW irradiation (25 W power).

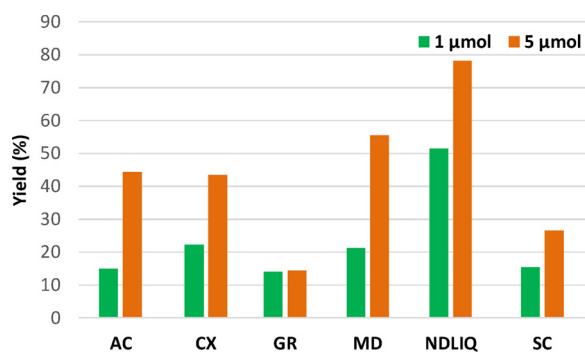


Fig. 7. Effect of catalyst amount in acetophenone yield of Au/carbon catalysts prepared by DIM. Reaction conditions: alcohol substrate (2.50 mmol), and a 70% aqueous solution of TBHP (5 mmol), 110 °C temperature, 2 h of MW irradiation (25 W power).

terms of yield. In case of the COL materials (Fig. 6), there is an improvement in the yield for all of the Au/carbon catalysts, except for Au/SC, when the catalyst quantity is changed from 1 to 5 μmol. Some agglomerates of gold nanoparticles were found on this latter support (see footnotes of Table 2). It is well known that when gold nanoparticles agglomerate, they become inactive, so part of the gold present in the material will be in an inactive form. Therefore, increasing the amount of catalyst does not lead to an improvement in the catalytic activity.

The Au/CX material showed the best performance. It was found in literature that a well-developed mesoporosity of carbon supports can be useful for the catalytic activity of Au supported on carbon materials in hydroamination of alkynes [84]. It is possible that the same happens with the oxidation of alcohols. MD also shows a good behaviour for the largest catalyst amount.

For the DIM method (Fig. 7), the yield increased for all Au/carbon catalysts, especially for AC and MD based materials, with a 5 times increase in catalyst amount, except for Au/GR, for which the yield resulted almost the same. Evidently, Au/NDLIQ-DIM showed the best performance (among the DIM materials). This could be due to the existence of a wide variety of surface groups on the nanodiamonds [100], which increase the catalytic activity, as explained above. The same does not happen for the analogue COL sample, due to its larger gold nanoparticle size (8.2 nm for COL, instead of 5 nm for DIM, as seen in Table 2).

3.2.9. Effect of oxidant

In terms of oxidant amount, all results of Tables S1–S12, unless otherwise stated, were obtained with 5 mmol of TBHP (70% aqueous

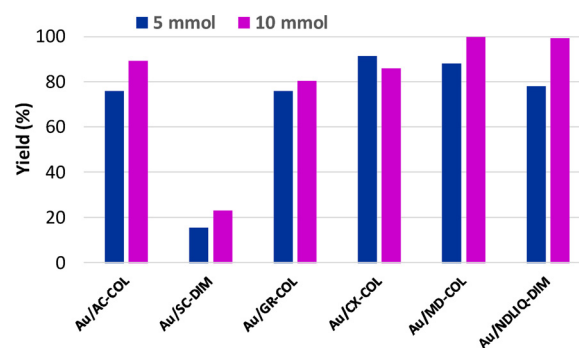


Fig. 8. Effect of TBHP oxidant amount in acetophenone yield of selected Au/carbon catalysts. Reaction conditions: alcohol substrate (2.50 mmol), catalyst (5 μmol), 110 °C temperature, 2 h of MW irradiation (25 W power). Au/AC-COL: 5 mmol; Au/SC-DIM: 2 mmol; Au/GR-COL: 5 mmol; Au/CX-COL: 5 mmol; Au/MD-COL: 5 mmol; Au/NDLIQ-DIM: 5 mmol.

solution). In most cases, this was shown to be the best option (entry 15 of Table S1; entries 15 and 16 of Table S3; and entries 12 and 14 of Table S8), compared to the results obtained with 10 mmol of TBHP (entries 20 of Tables S1 and S2; entries 19 and 21 of Table S3, and entries 15 and 17 of Table S8, respectively). However, for Au/AC-COL and Au/GR-DIM, 10 mmol was better than 5 mmol (entry 20 of Table S2 and entry 19 of Table S5). Also, in some other cases (Au/GR-COL, and Au/NDLIQ-COL), the use of TEMPO showed advantages (entry 17 of Table S6; and entry 7 of Table S11).

Fig. 8 shows that for 10 mmol of TBHP, a higher yield was obtained when compared with using 5 mmol of TBHP for most of the catalysts (except for catalyst Au/CX-COL, as will be further explained ahead). For Au/ND-LIQ, the yield increased 31.9% by doubling the TBHP amount, which is the highest increase among all the catalysts. The main reason might be that nanodiamonds have a large amount of surface groups [100], which can increase the catalytic activity, as already mentioned.

The yield obtained for Au/CX-COL (entries 13 and 15, and 14 and 17, of Table S8) decreased when the amount of TBHP was doubled. It was reported in literature that, for glycerol oxidation, a xerogel with smaller pores (5 nm width) led to the production of glyceric acid, while a xerogel with larger pores (20 nm width) favoured the production of dihydroxyacetone [52]. The explanation given was that a support with narrower pores can lead to an easier over-oxidation of the primary products. In our case, there are no secondary products. Most likely, over-oxidation occurred to a larger extent in the (~13 nm) pores, and it became an inhibitory factor for the reaction.

Fig. 9 shows that TEMPO additive does not lead to major improvement in the oxidation reaction under the tested conditions. In fact, for the Au/AC-COL, Au/SC-DIM and Au/CX-COL catalysts, the yield even decreased by 27.9%, 7.5% and 6.6% respectively, when adding

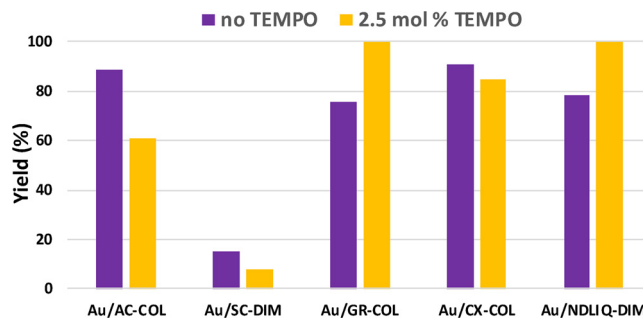


Fig. 9. Effect of TEMPO oxidant amount in acetophenone yield of selected Au/carbon catalysts. Reaction conditions: alcohol substrate (2.50 mmol), catalyst (5 μmol), TEMPO (2.5 mol %), 2 h of MW irradiation (25 W power), 110 °C; in the presence of TBHP: Au/AC-COL: 5 mmol; Au/SC-DIM: 1 mmol; Au/GR-COL: 5 mmol; Au/CX-COL: 5 mmol; Au/NDLIQ-DIM: 15 mmol.

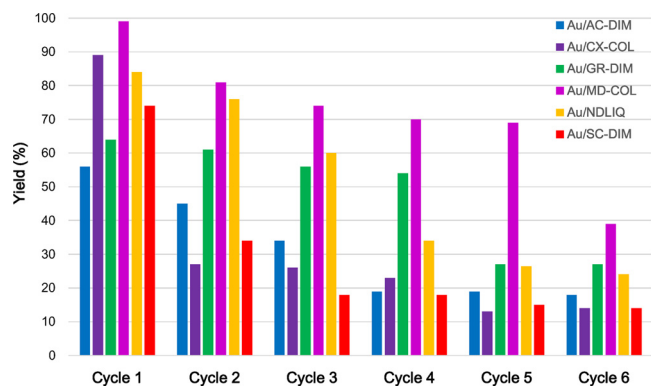


Fig. 10. Effect of the catalyst recycling in the yield of acetophenone for the different Au/carbon catalysts. Reaction conditions: alcohol substrate (2.50 mmol), catalyst (5 μ mol), 150 °C temperature, 2 h of MW irradiation (25 W power).

2.5 mol% of TEMPO. This can be considered an advantage of these systems, as they can convert 1-phenylethanol to acetophenone in good yields without the need of additive promoters (except for Au/SC).

The presence of TEMPO increased the yield by 24.2% for Au/GR-COL and by 21.7% for Au/NDLIQ-COL. The increase was less pronounced for CX. As reported in the literature [101], for the Cu(II) complex $[\text{Cu}(\text{H}_2\text{R})(\text{HL})]\cdot\text{H}_2\text{O}$ used in the MW assisted oxidation of 1-phenylethanol with TBHP, the yield was 65.9% in 15 min reaction under 25 W MW irradiation, while the yield increased up to 80% in the presence of TEMPO under the same conditions, showing the high efficiency of this additive.

3.2.10. Recycling experiments

The conditions selected for recycling tests were those leading to the highest yield obtained for each catalyst, namely the best preparation method for each support (see Fig. 2). Reactions were tested up to 6 consecutive cycles. In each cycle, the product was analysed by gas chromatography and then the catalyst was collected from the reaction vessel and centrifuged (repeated at least 2 times), thoroughly washed, dried and reused for the next 1-phenylethanol oxidation cycle experiment. The molar ratios of substrate to catalyst and oxidant to catalyst were constant. The results are shown in Fig. 10.

There was only a small loss of activity up to the 4th cycle for catalyst Au/GR-DIM, but the yield decreased to \sim 30% in the 5th cycle and stayed around that value for the final cycle. As for Au/NDLIQ-COL, the catalytic activity was above 80% in the first cycle, but it gradually decreased down to 24.7% in the last cycle. The yield for the Au/MD-COL material, in the second, third, fourth and fifth cycle, was 81%, 74%, 71% and 69%, respectively, thus it remained high in the first 5 cycles, but decreased in the 6th cycle, to 39.3%. The activity of Au/CX-COL dropped substantially after the first cycle, but after that the decrease was not so marked. For Au/AC-DIM the yield gradually decreased down to the 4th cycle, when it stabilised below 20%.

The used materials (after the 6th cycle) were analysed by TEM. The results are shown in Table 2 (between parentheses). An increase in Au particle size is observed, which can explain the decrease in catalyst activity, well known to be related with the Au nanoparticle size [1–13]. The remaining solutions were also analysed for gold determination and no metal was found, showing there is no leaching into the solution.

4. Conclusions

This study was focused on the catalytic activity of Au nanoparticles deposited on different types of carbon materials, prepared by two different methods (DIM and COL), which were used as catalysts for the microwave-assisted solvent-free oxidation of 1-phenylethanol, under different conditions. The presence of a higher catalyst amount (5 μ mol)

led to a higher yield of acetophenone, when compared with lower quantity (1 μ mol) for most catalysts. For example, for Au/MD-COL, the yield increased by 49% when the catalyst quantity was changed from 1 to 5 μ mol.

With longer reaction times, higher yields of acetophenone were obtained. For example, for Au/SC-DIM, a TON of ca.135 and a yield of 54.3% were obtained after 12 h reaction, while a TON of ca. 17.6 and a yield of 27.9% were observed after 2 h reaction.

The reaction temperature was also found to be very important for the product yield. For instance, the yield increased by 58% with catalyst Au/SC-DIM when the temperature increased from 110 to 150 °C.

The catalytic activity also changed after adding twice the amount of TBHP, depending on the different carbon supports and, in general, addition of 2.5 mol% TEMPO did not promote or even hamper the oxidation reaction. As an example, for Au/AC-COL, the yield decreased with 28% when TEMPO was added.

The preparation method had an important influence as well. The catalysts obtained by COL led, in general, to higher acetophenone yields, when compared with DIM. That is most likely because, in general, COL leads to higher dispersions and lower average nanoparticle sizes (with the exception of NDLIQ and MD samples, where the opposite was seen).

Catalyst recycling was tested up to six consecutive cycles for each material, at the best individual operation conditions found. It was seen that for catalyst Au/NDLIQ-DIM, for example, the activity dropped to 69% after the 5th cycle, but it was 55% higher when compared with Au/CX-COL in the 5th cycle. The decrease in the catalytic activity seems to be linked to an increase in the gold nanoparticle size.

The catalytic performance was different for all the Au/carbon catalysts studied; the diverse behaviours originate from differences in gold nanoparticle size, porosity and surface chemistry properties of the support and characteristics in the reaction medium.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.cattod.2019.06.041>.

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