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New insights for the catalytic oxidation of cyclohexane to K-A oil

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ABSTRACT

Au-based catalysts have been reported to be active in the cyclohexane oxidation to K-A oil, but they showed some limitiations in terms of productivity, selectivity and required reaction conditions. The possibility to overcome some of these limits has been explored coupling Au with Cu, which can be suitable for undergoing the electron-switch in the initial step of the cyclohexane oxidation. Hence, a bimetallic 2 wt% AuCu/Al_2O_3 catalyst was tested in the oxidation of cyclohexane, working at mild conditions of 120 °C and 4 bar of O_2. The combination of the catalyst with a very small amount of benzaldehyde used as cheaper and non-toxic radical initiator allowed to obtain a very high productivity of cyclohexanol and cyclohexanone (45 mmol*mL/mg$_{met}$*h) with a selectivity of 94%. Moreover, comparing the catalysed reaction with the non-catalysed one, the role of the catalyst has been disclosed.

1. Introduction

The selective oxidation of cyclohexane (Cy) is a key reaction in industrial chemistry, since the products that can be obtained are a mixture of cyclohexanol (CyOH, A) and cyclohexanone (Cy = O, K) (K-A oil), which are the starting reactants for the production of adipic acid and ε-caprolactam [1]. These latter are in turn mainly employed for the synthesis of Nylon-6,6 and Nylon-6 [2]. The massive demand of nylon fibers makes adipic acid the most important dicarboxylic acid from an industrial point of view [3], as well as ε-caprolactam is forecast to reach a global production of around 6.5 million tons per year by 2023 [4]. An annual growth rate of 6.1% for the combined global market of the two nylon varieties is also expected from 2017 to 2025 [5].

Cyclohexane oxidation to K-A oil is still a challenge, considering the issues represented by the ease of oxidation of K-A oil compared to the initial difficulty to activate the C–H bond [2]. For this reason, mild conditions of temperature and pressure would be required to avoid the formation of over-oxidation byproducts. However, mild conditions limit the first step of the reaction, resulting in a low conversion.

In the classical industrial process cyclohexane is air-oxidized at 140–160 °C and 10–15 bar in the presence of cobalt(II) naphthenate salt ($CoC_{22}H_{14}O_4$) [6,7], reaching a cyclohexane conversion of around 4%-5% with a selectivity towards the K-A mixture of 70 to 80% (K/A molar ratio from 1:1 to 1:3.5) [8–10]. The remaining 20% consists of by-products such as n-butyric, n-valeric, succinic, glutaric and adipic acids [11]. The excessive by-product formation derives from the ring cleavage of cyclohexanone [12], as well as from the propagation of cyclohexyl hydroperoxide CyOOH into a cyclohexoxy radical (CyO$^\bullet$) and the subsequent b-cleavage forming a ring-opened x-formyl radical [13].

In the condition used in the industrial process, it was seen that the addition of boric acid allows increasing the conversion up to 10% and the selectivity up to 90% (K/A molar ratio of 1:9), because boric acid forms insoluble adducts with cyclohexanol and its hydroperoxide thus limiting the over-oxidation. However, the large amount of solid which is formed needs to be separated and decomposed, increasing the operational costs [11].

From there, in the last few years two commercial processes have been optimized, one based on the non-catalytic autoxidation process and one based instead on the catalysed process [14]. In the first process, cyclohexyl hydroperoxide (CyOOH) is formed by a non-catalytically mechanism, and then further converted to KA-oil [15]. In the second case, a radical initiator is used to accelerate the entire process, which is mostly dissolved cobalt(II)naphthenate [16]. In fact, transition metals such as Co^{2+}, Mn^{2+}, and Cr^{2+}, are capable of undergoing a one-electron switch and catalyse this initiation through the Haber- Weiss cycle [15].

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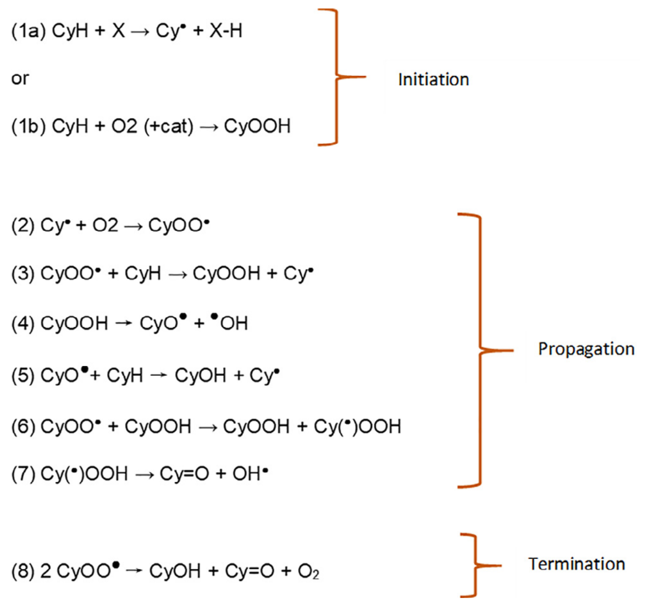
Both the autoxidation and the catalysed reaction proceed via a radical-chain mechanism, reported in Scheme 1.

The chain initiation can proceed through the activation of the C–H bond by abstraction of an H atom due to the cleavage by an unsaturated metal centre, a peroxide species or a superoxide species bound to metal centres or metal oxides [17]. For this reason the use of a suitable radical initiator would be able to favor the initiation of the cycle and improve the kinetics of the reaction. Alternatively, the chain initiation can be started by the catalytic oxditation of cyclohexane to cyclohexyl hydroperoxide (CyOOH) [16,18], where the formation of the CyOOH is the rate determining step of the reaction [19,20]. The formation of cyclohexanol (CyOH) and cyclohexanone (Cy = O) takes place from the mutual destruction of two peroxyl radicals according to reaction (8), but can also occur during the steps (5–7) (see scheme 1).

Since the classical industrial process is based on a homogeneous catalyst, some efforts have been done in order to improve the process by replacing it with a heterogeneous catalyst, which is more advantageous in terms of separation, recyclability and disposal, and would also represent an interesting way to implement a continuous process. The use of an heterogeneous catalyst however required in most cases the presence of a radical initiator that is often tert-butyl hydroperoxide (TBHP), which is effectively employed even if the very high price makes it unattractive for industry [10]. In combination with TBHP as initiator, Au-based catalysts have been reported as active and very selective toward K/A oil formation [21–24]. However, a study reported by Weckhuysen et al. [14] showed that results on gold-based catalysts are often masked by the difficult product analysis. In particular, they investigated the activity and selectivity of a Au/Al_2O_3, Au/TiO_2 and a Au/SBA-15 catalysts taking into account the product analysis of both the gas and the liquid phases. Considering the real formation of by-products, which included in particular adipic acid and CO_2, the combined selectivity toward cyclohexanone and cyclohexanol decreased to 70%, thus concluding that Au catalysts performed poorly compared to the autoxidation in terms of selectivity and in initiating the reaction.

This fact is fundamental to understand the real performance of some catalysts in cyclohexane oxidation. Many more recent papers which reported good results in cyclohexane oxidation to KA oil, using metal based catalysts including some gold-based even without the use of a radical initiator, did not in fact really perform a precise and complete by-product analyses. For example, one of the best claimed achievements recently reported by Luo et al. [25], showed the possibility to reach 50% of cyclohexane conversion with a selectivity toward cyclohexanol and cyclohexanone higher than 90% using Ag clusters supported on graphene oxide and TBHP as radical initiator. However, in this case as in others it is not clear how conversion and selectivity have been calculated. There are in fact difficulties and quite often lacking of quantitative mass balance in the analysis of by-products.



Scheme 1. Representation of the possible free radical pathways occurring in the oxidation of cyclohexane.

In Table 1, the most recent and best achievements, mostly without the need of using a radical initiator are reported. In order to compare results obtained at different conditions, we considered the amount of the catalyst used, taking into account the metal loading, the conditions of temperature and pressure at which the reaction occurred, the cyclohexane conversion, as the K-A oil productivity and selectivity. In particular, the productivity of K-A oil was calculated as mmol of formed cyclohexanol and cyclohexanone per hours of reaction and mg of metal used per mL of cyclohexane (mmol K-A oil * mL of cyclohexane * mg^{-1} metal * h^{-1}).

Results of only three of the catalysts reported in the table (i.e. 1% AgPd/MgO, 1%Au/CNT and 1.21% Au/MCM-41) are obtained using an internal standard in the analyses, thus reported more reliable values of conversion and selectivity to K-A oil. Moreover, most often high O_2 pressure (≥10 bar) and/or high temperature (≥120 °C), or high catalyst:substrate ratio are required.

1%Au/CNT and 1.21%Au/MCM-41 appear the most performing catalysts in terms of selectivity or productivity, thus proving the still promising performance of gold in this reaction. However, in the case of 1%Au/CNT [28] the high selectivity is accompained by a very low productivity of K-A oil, while in the case of the Au/MCM-41 catalyst [31] high temperature and pressure are required.

Considering the potential of gold-based catalysts, the present paper reports a study on the activity of bimetallic Au supported on Al_2O_3 catalyst in cyclohexane oxidation at mild reaction conditions. In particular, we explored the possibility to overcome the limits of Au (very low selectivity) coupling it with a transition metal such as Cu. Indeed, as already mentioned transition metals such as Co^{2+}, could favour the electron switch for undergoing the Haber-Weiss mechanism at the beginning of the reaction [32 15].

In addition, as alternative to the use of expensive and toxic radical initiators, a possible non-toxic and cheaper alternative initiator can be found in the use of some aromatic molecules which can be oxidized through a radicalic mechanism. For example, the oxidation of benzaldehyde (BALD) to benzoic acid proceeds through a radicalic chain mechanism [33–35], which can be employed to supply free radical species for activation of cyclohexane. Studies at different benzaldehyde concentrations and the use of a radical scavenger have been performed to highlight the impact on the oxidation rate and selectivity of this parameter. The catalytic approach was also probed with particular focus on reaction conditions, selectivity and productivity of K-A oil.

2. Experimental

2.1. Materials

Cyclohexane (C_6H_{12}, Sigma Aldrich, ≥99%) and benzaldehyde (C_6H_5CHO, Sigma Aldrich, ≥99%) were used for the oxidation reaction. Tetrachloroauric(III) acid trihydrate ($HAuCl_4{\cdot}3H_2O$, 99%) and copper(II) nitrate hydrate ($Cu(NO_3)_2{\cdot}xH_2O$, 99.99%) were used as precursors for catalysts synthesis, using alumina (Degussa Aluminium oxide C, 100 m^2/g) as support and polyvinyl alcohol

Table 1
Recent results obtained in cyclohexane oxidation using heterogeneous metal-based catalysts.

Me-based catalyst	Catalyst am. (mg/mL) [a]	*T* (°C)*P* (bar)	Conv.% (h)	Productivity [b]	Sel. to K-A	K/A
1wt% AgPd/MgO [26]	6 mg/10 mL	140 °C3 bar O_2	9.5% (17 h)	67.24	78%	0.51
Pt-Sn/MWCNTs [19]	50 mg/10 mL	120 °C15 bar O_2	24.1% (6 h)	30.55	83.4%	0.51
5 wt%Pt/16 wt%Ce0.68Zr0.17Sn0.15O2.0/SiO_2 [27]	10 mg/6.5 mL	130 °C5 bar O_2	24.1% (7 h)	22.46	83,4%	0.51
1%Au/CNT [28]	2 mg/0.54 mL	RTP_{atm} H_2O_2	3.6% (6 h)	0.80	99%	0.80
1%Au/MgO [17]	6 mg/10 mL	140 °C3 bar O_2	5% (17 h)	36.75	81%	0.58
4.63 wt%Au/MIL-53(Cr) [29]	100 mg/10 mL	130 °C12 bar O_2	23% (6 h)	6.57	84.6%	1.85
1.21% Au /MCM-41 [30,31]	5 mg/2 mL	150 °C10 bar O_2	19% (6 h)	18.22	94%	3.48

[a] mg of catalyst in mL of cyclohexane;
[b] productivity calculated as: mmol K-A oil * mL of cyclohexane * mg^{-1} metal * h^{-1})

(PVA, MW = 9000–10,000, 80% hydrolysed) as capping agent. Reagents were purchased and used without further purification.

2.2. Catalyst syntheses

A monometallic 2 wt% Au supported on Alumina (Au/Al_2O_3) was synthesized by sol-immobilization as already reported in [36]. For the synthesis, an aqueous Au monometallic sol was obtained by reduction of $HAuCl_4$ precursor with $NaBH_4$ in the presence of PVA used as protecting agent. Precisely, 75 mL of a solution of $NaBH_4$ (25.6 mM) was added rapidly to 685 mL of a $HAuCl_4$ (0.33 mM) and PVA (0.013 wt%) solution, under vigorous stirring. After 1 h of stirring, a proper amount of alumina support (Degussa Aluminium oxide C, 100 m^2/g) was added to have a final metal loading equal to 2 wt%. After the complete decolouration of the sol (≅2h) the catalyst was filtered and dried in air at 80 °C.

A monometallic 2 wt% Cu/Al_2O_3 was then prepared with the same methodology. In this case, the Cu monometallic sol was obtained by reduction of $Cu(NO_3)_2$ precursor with $NaBH_4$ and in the presence of PVA as stabilizing agent as in the case of monometallic Au. Accordingly, 658 mL of a solution of $Cu(NO_3)_2$ (0.33 Mm) and PVA (0.013 wt%) was reduced adding 75 mL of $NaBH_4$ (25.6 Mm) under continuous stirring. Alumina was added after 1 h, then after 2 h the final catalyst was filtered and dried in air at 80 °C, having a final metal loading of 2 wt%.

The bimetallic catalyst 2 wt% Au_1Cu_1/Al_2O_3 was synthesized as well using the same method [37], with a Au/Cu molar ratio equal to 1. For the preparation of the bimetallic sample an aqueous Au-Cu bimetallic sol of Au/Cu = 1/1 molar ratio was fabricated in this case by co-reduction of $HAuCl_4$ and $Cu(NO_3)_2$ precursors by $NaBH_4$ as reducing agent and in the presence of PVA as protecting agent. The amount and concentration of the precursor solutions used for the synthesis of the bimetallic sample were the same used in the preparation of the corresponding monometallic sols. To obtain the final bimetallic catalyst, also in this case a proper amount of alumina was added for having a final metal loading of 2 wt%. For each catalyst preparation, the solid was filtrated after the complete decolouration of the sol (≅2h) and dried in air at 80 °C.

2.3. Oxidation of cyclohexane

The oxidation of cyclohexane (10 mL) was carried out in a 100 mL stainless-steel autoclave, at 120 °C and 4 bars of oxygen pressure using biphenyl as internal standard (0.2 M) and 20 mg of catalyst. When the reaction was performed in the presence of benzaldehyde as radical initiator, it was added to the initial solution before starting the reaction. The concentration of the initial benzaldehyde ranged from 0.004 M to 0.4 M, in order to study the influence of different benzaldehyde concentrations on the reaction. Stirring was set to 1125 rounds per minute. Oxygen was refilled after each withdraw of sample at t = 0, 30 min, 1 h, 3 h, 4 h and 5 h (restoring the internal pressure at 4 bar O_2). The reactor was cooled down in an ice bath each time to withdraw a sample. For the characterisation of the reaction products, samples (300 μL) were centrifuged to separate the catalyst from the solution, and the liquid solution was analysed using a GC (Thermo Scientific TRACE 1300) equipped with an Agilent HP-5 column.

2.4. Characterization analyses

X-ray photoelectron spectra (XPS) of the bimetallic sample was taken in an M−probe apparatus (Surface Science Instruments), for the determination of surface composition and oxidation state of the metals. The source was monochromatic Al K radiation (1486.6 eV). Data processing was performed by Esca Hawk software. The XPS lines of C 1 *s*, O 1 *s*, Au 4*f* and Cu 2*p* regions were recorded.

High angular annular dark field scanning transmission electron microscopy (HAADF-STEM) analysis was carried out using a ZEISS LIBRA200FE microscope equipped with a 200 kV FEG source. Before the analysis, the samples were finely smashed in an agate mortar, suspended in isopropanol and sonicated, then each suspension was dropped onto a lacey carbon-coated copper grid (300 mesh) and the solvent was evaporated. Histograms of the particle size distribution were obtained by counting onto the micrographs at least 300 particles. The mean particle diameter (d_m) was calculated using the formula $d_m = \Sigma d_i n_i / \Sigma n_i$ where n_i was the number of particles of diameter d_i. The standard deviation was calculated using the formula SD = $[\Sigma_{ni}(d_i - d_m)^2/n_i]^{0.5}$.

An ICP Perkin Elmer optical emission spectrometer Optima 8000ICP-OES was used to evaluate the actual metal loading of each catalyst. The samples were dissolved using a CEM MARS One Microwave Digester and the digestion was performed at 180 °C using an acidic solution of HCl (37%) and H_2SO_4 (98%) (2:3 molar ratio).

3. Results and discussion

3.1. Catalysts characterization

The monometallic 2%Au/Al_2O_3, 2%Cu/Al_2O_3 and the corresponding bimetallic 2%Au_1Cu_1/Al_2O_3 were prepared and characterized accordingly to our previous research [35,38]. The specific Au:Cu ratio of 1:1 was chosen as in a previous study [37], considering that with this ratio we already obtained good results in terms of intimate contact between the two metals and catalytic activity in the oxidation of benzyl alcohol compared to other Au/Cu ratios. On the basis of the characterization already reported in [38], here we confirmed the metal loading of both the monometallic and bimetallic sample by ICP measurements, obtaining an actual metal loading of 1.8 wt% for the monometallic Au catalyst, 2.0 wt% for the Cu/Al_2O_3 and of 1.82 wt% for the bimetallic one. In the bimetallic catalyst the Au/Cu molar ratio was 0.9.

The TEM characterizations of the monometallic catalyst 1.8 wt% Au/Al$_2$O$_3$ and of the bimetallic 1.82 wt%AuCu/Al$_2$O$_3$ are reported in Figs. 1 and 2. The monometallic sample showed very well dispersed Au nanoparticles with narrow particle size distribution and NPs average diameter of 2.5 nm (Fig. 1), as well as a high metal dispersion with narrow particle size distribution (av. Diam. of 1.9 nm) was observed in the case of the bimetallic sample (Fig. 2). Fig. 3.

EDX analyses on single particles (Fig. 2c), revealed a mean composition of about 35 at% of Cu and 65 at% of Au. Therefore, the bimetallic nature of nanoparticle is confirmed even the composition is more rich in Au compared to the nominal value. In Au$_1$Cu$_1$ sol, the Au and Cu elemental maps showed the co-existence of the two metals in the single particles, with a Au/Cu atomic ratio between 44/66 and 61/39 (EDS spectra collected on nine particles) [37].

In addition, XPS analysis (Table 2) showed a Au/Cu ratio equal to 0.76, thus showing that Cu species are prevalent on the surface compared to the bulk composition observed (0.9). From the high-resolution spectra of Au 4*f* 7/2 we identified as expected the presence of two different species of Au, i.e. Au^0 (83.5–84.4 eV) and Au$^{\delta+}$ (85.4–86.1 eV), showing an amount of 83% and 17%, respectively. In the case of Cu 2*p* 3/2 the presence of both Cu^0/Cu$^+$ and Cu^{2+} species was observed, with an amount of 61% and 39%, respectively.

3.2. Oxidation of cyclohexane

The catalysts have been tested in the catalytic oxidation of cyclohexane, working at 120 °C and 4 bar of O$_2$ pressure, which are milder reaction conditions compared to those most reported in the literature for heterogeneous processes (Table 1). At these conditions, cyclohexane is not oxidized without a catalyst or a radical initiator. The reaction was carried out using 10 mL of cyclohexane and 20 mg of each catalyst, analysing the products by a GC and using biphenyl as internal standard.

The reaction has been then carried out testing the catalysts without the use of a radical initiator. In such conditions the catalysts were not active, as no products were observed and the amount of cyclohexane remained constant overtime.

Considering benzaldehyde auto-oxidation as radical driven reaction, we thus investigate the cyclohexane oxidation by adding benzaldehyde in the reaction solution, in order to probe if the radical mechanism of the benzaldehyde oxidation to benzoic acid [33–35] could aid the initiation of the radical mechanism of the cyclohexane oxidation. The reaction was performed using 10 mL of cyclohexane and working at 120 °C and 4 bar of O$_2$ pressure as in the case of the previous tests, but adding 1.5 mmol of benzaldehyde to have a benzaldehyde initial concentration 0.15 M. Both the reactions, i.e. with or without the catalyst, were performed. In particular, Fig. 3(a) reported the reaction profile without the catalyst, Fig. 3(b) represents the reaction in the presence of the monometallic Cu/Al$_2$O$_3$ catalyst, Fig. 3(c) is the reaction in the presence of Au/Al$_2$O$_3$ catalyst and finally Fig. 3(d) corresponds to the reaction profile using the bimetallic Au$_1$Cu$_1$/Al$_2$O$_3$ catalyst.

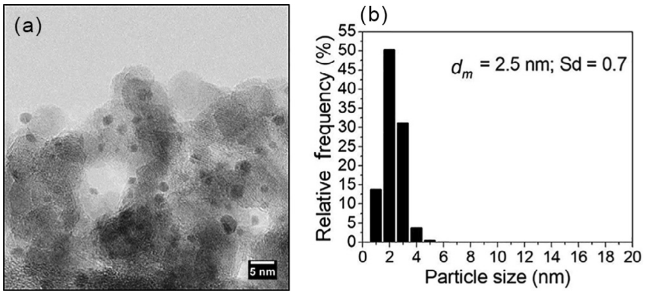


Fig. 1. (a) TEM micrograph and (b) particle size distribution for 1.8 wt% Au/Al$_2$O$_3$.

Table 3 reports the K-A oil productivity calculated as mmol of formed cyclohexanone and cyclohexanol per hours of reaction and mL of cyclohexane, and per mg of metal used for catalysed reactions as reported in the introduction for comparing the productivity obtained in the previous papers.

In all four reaction profiles, benzaldehyde oxidation to benzoic acid occurred in the first hour of reaction, forming benzoic acid and a certain amount (4–13%) of benzyl alcohol, which is assumed to be formed by the disproportion of two molecules of α-hydroxybenzyl radicals [35]. Looking at the reaction profile without the catalyst (Fig. 3a), cyclohexanol and cyclohexanone started to be formed contemporarily to the consumption of benzaldehyde, with a productivity of 4.32 mmol of K-A oil*mL/*h and a K/A ratio of 1.7 after 5 h of reaction (Table 3). This K/A ratio was expected because, as reported in the literature, when a pure radical mechanism is present ketone is formed in excess with respect to the alcohol [26], usually with a K/A ratio of 1–1.5 [39].

The introduction of 20 mg of catalyst changed significantly the reaction, considering both the productivity of K-A oil and the final K/A ratio. When the catalyst is present and it takes part into the oxidation mechanism, the K/A molar ratio is expected to decrease with respect to auto-oxidation being the alcohol formed in excess compared to the ketone [17].

Using the monometallic Cu/Al$_2$O$_3$ (Fig. 3b) the amount of K-A oil formed at the end of the reaction decreased compared to the non-catalysed reaction (Fig. 3a) (2.11 and 4.32 mmol*mL/h respectively, Table 3), while the K/A ratio (0.70) overturns, having in this case, a higher amount of cyclohexanol compared to cyclohexanone. The role of the catalyst in modulating the K/A ratio is thus confirmed. Compared to Cu/Al$_2$O$_3$ and also compared to the non-catalysed reaction, the monometallic Au/Al$_2$O$_3$ (Fig. 3c) led to a higher productivity of K-A oil, which increased to 6.35 mmol*mL/h (Table 3), while the K/A ratio of 0.62 confirmed the role of the catalyst in increasing the formation of cyclohexanol. The productivity normalized by the metal mg also increased (17.64 and 5.03 mmol*mL/mg met*h ,Table 3).

In the presence of the bimetallic catalyst (Au$_1$C$_1$/Al$_2$O$_3$) (Fig. 3d), the productivity of K-A oil grew up to 7.20 mmol*mL/h and 19.78 mmol*mL/mg$_{met}$*h (table 3). A higher catalytic activity and higher KA oil productivity (19,78 mmol*mL/mgmet*h)) were obtained using the bimetallic catalyst compared with the ones obtained using the corresponding monometallic samples (5.03 and 17.64 mmol*mL/mgmet*h respectively). Considering the actual loading of Au and Cu in bimetallic catalyst the productivity calculated for a simply physical mixture of Au and Cu catalyst should have been 13,22 mmol*mL/mgmet*h. It is therefore clear that there is the presence of a synergistic effect. The K/A ratio raises to 0.91 being a signal of slightly different catalytic pathway.

Further investigation has been carried out on the effect of the amount of benzaldehyde as initiator of the reaction. In fact, benzaldehyde oxidation produces, beside benzoic acid, benzyl alcohol which can be considered a radical scavenger thus inhibiting the radicalic propagation of the reaction [35]. Therefore, the lower formation of benzyl alcohol due to a lower amount of benzaldehyde should be advantageous for the proceeding of the reaction.

We first proved this fact adding benzyl alcohol (1.5 mmol) as radical scavenger and we verified the reaction was effectively stopped. Then, accordingly, we performed the reaction with different initial amounts of benzaldehyde, both without and with the AuCu catalyst.

Benzaldehyde initial concentration effect was investigated in the range 0.010–0.4 M (tables 4 and 5).

Looking at the results obtained in the reactions performed without the catalyst, we observed almost the same productivity using a

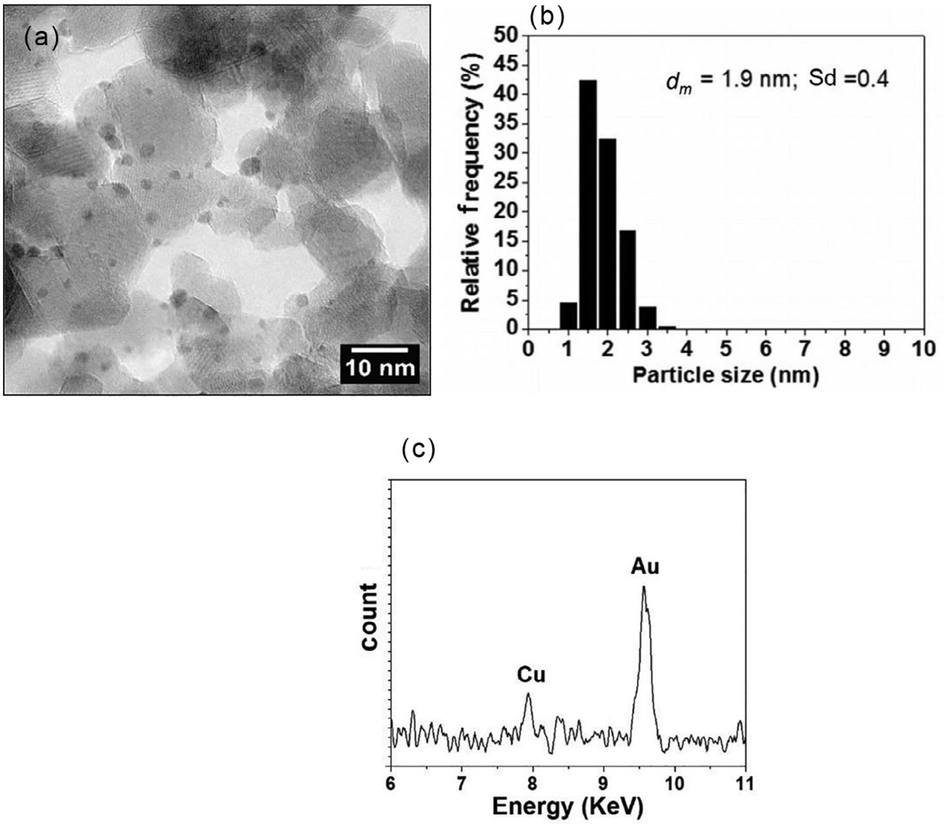


Fig. 2. (a) TEM micrograph; (b) particle size distribution of 1.82 wt% AuCu/Al_2O_3 and (c) EDX analyses on single particle.

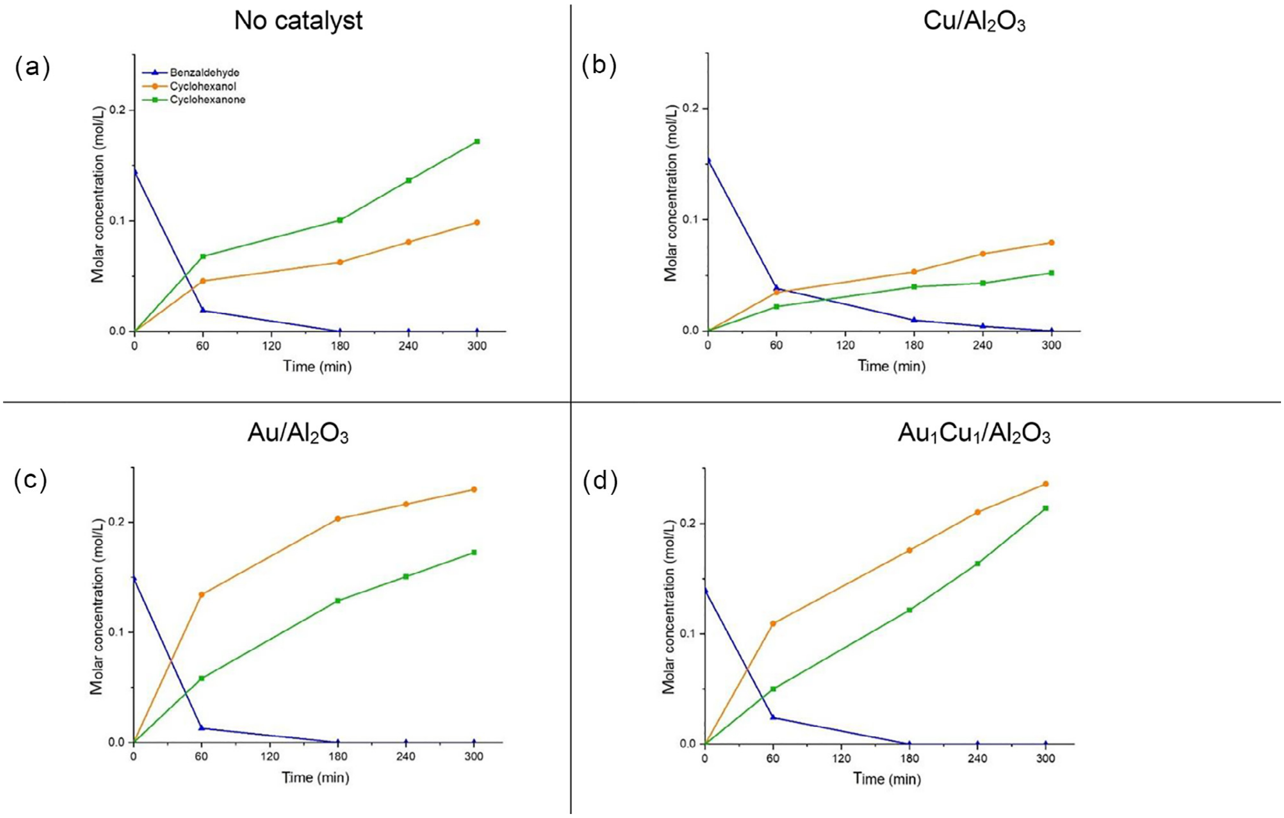


Fig. 3. Cyclohexane oxidation in the presence of benzaldehyde (0.15 M) at 120 °C and 4 bar of O_2. Reaction performed without a catalyst (a), in the presence of 20 mg of Cu/Al_2O_3 (b), 20 mg of Au/Al_2O_3 (c) and 20 mg of AuCu/Al_2O_3 (d).

Table 2
XPS survey analyses and high-resolution spectra of Au(4*f*) and Cu(2*p*) of the monometallic 1.8 wt% Au/Al_2O_3 sample and the corresponding bimetallic 1.82 wt% $AuCu/Al_2O_3$.

Sample		Survey	HR			
			$Au(4f)_{7/2}$		$Cu(2p)_{3/2}$	
		Au/Cu	Au^0	$Au^{\delta+}$	Cu^0-Cu^+	Cu^{2+}
2 wt% $AuCu/Al_2O_3$	B.E. (eV)		83.5	86.1	932.9	935.6
	%At	0.76	83	17	61	39

Table 3
K-A oil formation after 5 h of reaction in the presence of BALD 0.15 M, performed at 120 °C and 4 bar of O_2.

Catalyst	K/A	K-A productivity (mmol*mL/*h)	K-A productivity (mmol*mL/mg_{met}*h)
No cat.	1.70	4.32	-
Cu/Al_2O_3	0.70	2.11	5.03
Au/Al_2O_3	0.62	6.35	17.64
Au_1Cu_1/Al_2O_3	0.91	7.20	19.78

Table 4
K-A oil formation after 5 h of reaction in the presence of different BALD concentrations, without catalyst at 120 °C and 4 bar of O_2.

$BALD_{in}$ [M]	K/A	K-A productivity (mmol*mL/h)
0.40	0.60	2.64
0.15	1.70	4.32
0.08	1.88	4.02
0.04	2.22	4.56
0.01	2.25	4.09

Table 5
K-A oil formation after 5 h of reaction in the presence of different BALD concentrations, in the presence of $AuCu/Al_2O_3$ (20 mg) at 120 °C and 4 bar of O_2.

$BALD_{in}$[M]	K/A	K-A productivity(mmol*mL/*h)	K-A productivity (mmol*mL/mg_{met}*h)
0.40	0.85	3.85	10.59
0.20	0.89	5.78	15.87
0.15	0.91	7.20	19.78
0.10	0.77	5.07	13.93
0.01	0.73	3.60	9.89

Table 6
Productivity of K-A oil at 5 h with and without $AuCu/Al_2O_3$ catalyst and BALD concentration 4 × 10^{-3} M.

Catalyst	K/A	K-A productivity (mmol*mL/*h)	K-A productivity (mmol*mL/mg_{met}*h)
No catalyst	2.66	10.40	-
$Au/Cu\_Al_2O_3$	0.60	16.40	45.05

benzaldehyde concentration in the range 0.01–0.15 M whereas a decrease of productivity is observed when a higher (0.40 M) concentration of benzaldehyde is used (Table 4). We then stated that cyclohexanol and cyclohexanone production is dependent on the initial addition of benzaldehyde when benzaldehyde was present in a high amount (0.4 M) because the reaction is probably inhibited by the higher amount of produced benzyl alcohol. Moreover, in this latter case, also the higher production of benzoic acid can lead to a phase separation due to a precipitate formation. The K/A ratio seems to depend on the different BALD concentration being increased by decreasing the amount of BALD. To be noted that the K/A ratio in the case of 0.4 M BALD is very similar to the number expected for catalysed reaction.

The effect of the benzaldehyde amount is different when the reaction was performed in the presence of the AuCu catalyst. In this case we obtained a volcano type dependence of the productivity from the initial amount of benzaldehyde (Table 5). The productivity of K-A oil presented a maximum when 0.15 mmol/mL of benzaldehyde was used (19.78 mmol*mL/mg_{met}*h). The productivity decreased using lower or higher amount of benzaldehyde. Considering that the K/A ratio always is below 1 indicating that the catalyst affects the pure radical pathway. However, the different values obtained indicate a correlation between the amount of BALD not monotone with the higher value obtained with 0.15 M BALD (0.91, Table 5). Therefore, the presence of different amount of benzaldehyde influences not only the benzyl alcohol production (which inhibits the radical propagation when benzaldehyde is in large amount) but also the rate of the radical starting step (when benzaldehyde is in a lower amount). Moreover, the presence of benzoic acid formed from oxidation of benzaldehyde could have a detrimental effect poisoning the catalyst surface, accordingly to what already reported in [40–43], where it was shown that benzoic acid can act as strong inhibitor of gold catalysts.

To find a proper balance between the amount of BALD and the catalyst, we carried out an experiment reducing both initial concentration of benzaldehyde (4*10^{-3} M) and the amount of catalyst (10 mg). The results obtained in the new reaction conditions are reported in table 6.

Surprisingly, the K-A oil productivity almost doubled in both cases increased from 4.56 to 10.40 mmol*mL/*h in the non-catalysed reaction and from 7.20 to 16.40 mmol*mL/*h for the catalysed reaction. In this latter case we observed that the productivity normalized by the amount of metal also doubling from 19.78 mmol*mL/mg_{met}*h (table 3) to 45.05 mmol*mL/mg_{met}*h (Table 6).

As already noted the K/A ratios are affected by both the amount of catalyst and the amount of BALD. In the non-catalysed reaction a particular high value was obtained (2.66-Table 6) whereas a particular low value was obtained in the catalysed reaction (0.60, Table 6).

Considering the selectivity of the catalysed reactions, the gold-based catalyst under the reported reaction conditions are always 93–94% selective to K-A oil being adipic acid formed as only other oxidation product in liquid-phase.

4. Conclusions

Cyclohexanol and cyclohexanone can be obtained with a productivity of 45 mmol*mL/mg_{met}*h from the $AuCu/Al_2O_3$ catalysed oxidation of cyclohexane at 120 °C and 4 bar of O_2 adding benzaldehyde (4*10^{-3} M) in the initial volume of cyclohexane. Benzaldehyde acts as radical initiator, as its oxidation to benzoic acid proceeds through a radical mechanism which in turn induces the initiation of the radical mechanism of the cyclohexane oxidation.

The productivity of K-A oil using Cu/Al_2O_3 decreased compared to that obtained in the non-catalysed reaction, while it increased using Au/Al_2O_3, or even more using the bimetallic $AuCu/Al_2O_3$. In particular, the results showed the presence of synergistic effect between Au and Cu due to the presence of alloyed nanoparticles. The selectivity of the reaction is 94% being adipic acid the only by-product detected in the liquid phase.

Benzaldehyde as radical initiator and the amount of the catalyst play a fundamental role in determining the K/A ratio.

The productivity of K-A oil normalized per mg of metal used in the reaction, allows the comparison with most of literature data. The productivity obtained in the reported conditions (120 °C and 4 bar O_2) and the use of 4*10–3 M BALD, is higher than most of the previous publications (Table 1). Moreover, the reaction conditions used in this study are mildest compared to the others probably contributing to enhance the reaction selectivity (94%).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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