Journal of Catalysis 268 (2009) 350–355

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Gold nanoparticles supported on ceria promote the selective oxidation of oximes into the corresponding carbonylic compounds

Abdessamad Grirrane, Avelino Corma *, Hermenegildo Garcia *

Instituto Universitario de Tecnología Química CSIC-UPV, Universidad Politécnica de Valencia, Av. De los Naranjos s/n, 46022 Valencia, Spain

ARTICLE INFO

Article history:
Received 31 July 2009
Revised 1 October 2009
Accepted 2 October 2009
Available online 4 November 2009

Keywords:
Heterogeneous catalysis
Gold nanoparticles as catalysts
Aerobic oxidation
Oximes

ABSTRACT

Gold supported on ceria (Au/CeO_2) is a highly active and selective catalyst for the aerobic oxidation of oximes to the corresponding carbonylic compounds. This reaction can be carried out in a mixture of ethanol–water by oxygen with a complete selectivity and very high conversion using Au/CeO_2 as a catalyst. This process appears to be general and aliphatic as well as oximes from aromatic ketones can be converted to the carbonylic compound in the absence of corrosive Brönsted acids and without producing aqueous wastes. One example of particular industrial relevance is the transformation of carvone oxime into carvone.

1. Introduction

Oximes are most generally obtained from carbonylic compounds by condensation with hydroxylamine [1], but another route through the hydrogenation of nitroalkanes has also been proposed that avoids the use of hydroxylamine [2]. When oximes are prepared by methods others than those requiring carbonyl compounds as the starting materials, oximes can be used in turn as synthetic precursors of the corresponding carbonyl compounds. One particular case that exemplifies the above-mentioned route of ketones from oximes is the commercial synthesis of carvone, which is an essential oil used in fragrance industry [3]. D-Carvone has a caraway odor and L-carvone has a sweet spearmint odor and is the main constituent of spearmint [4]. Carvones can be synthesized from carvone oxime that is prepared from limonene by reaction with nitrosyl chloride [5,6]. Scheme 1 shows the synthetic route for the preparation of carvone.

Generally, compounds having a C=N double bond undergo hydrolysis to the corresponding carbonylic compounds [1]. However, compared to imines and other C=N double bond compounds, oximes are typically stable and notably reluctant to undergo hydrolysis. An alternative to the conventional hydrolysis of oximes to carbonylic compounds under acid or basic conditions is the oxidation of the C=N bond. It has been reported that metal oxides, peracids, ozone, and other chemical oxidizing reagents can convert oximes into the corresponding ketones through an oxidative mechanism [7–9]. Also the photochemical oxidation of oximes can render the corresponding carbonylic compound through the intermediacy of the oxetane derivative [10,11].

From the environmental point of view, the use of oxidizing reagents that do not generate wastes constitutes a considerable advantage. This requires the shift from the use of stoichiometric oxidizing reagents to catalytic oxidations [12–15]. In this context, it has been reported that titanium silicalite TS-1 is a heterogeneous catalyst that can promote the oxidation of oximes to carbonylic compounds using hydrogen peroxide [16]. Although the by-product of hydrogen peroxide is water, it is always more advantageous to use oxygen instead of H_2O_2 as an oxidizing reagent. In addition TS-1 is a medium pore size zeolite (~0.54 nm) and there is a limit in the molecular dimensions of the substrates that can undergo oxidation.

Herein we report that supported gold nanoparticles can be efficient solid catalysts to promote the aerobic oxidation of oximes to the corresponding carbonylic compounds in the absence of acids.

The use of gold nanoparticles as catalysts has attracted considerable attention in the recent years [17–19]. It has been found that gold is an excellent catalyst for the aerobic oxidation of alcohols and amines among other compounds [20–22]. In the present work, we expand the scope of gold nanoparticles as catalysts for aerobic oxidations by showing that they are general catalysts to perform the selective transformation of oximes into carbonylic compounds.

2. Experimental section

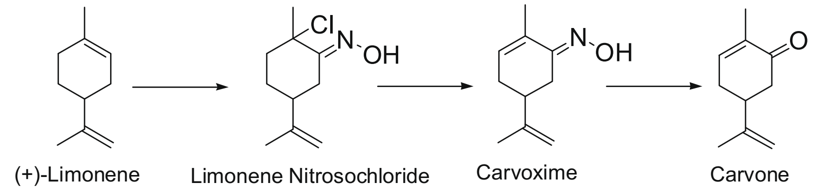
2.1. Catalyst preparation

Nanoparticulated ceria was obtained as reported [23] by the hydrolysis of cerium nitrate aqueous solutions at pH 5 using

---

* Corresponding authors. Fax: +34 963877809 (H. Garcia).
E-mail address: hgarcia@qim.upv.es (H. Garcia).

0021-9517/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2009.10.005



Scheme 1. Synthesis of carvone from limonene.

ammonia as a base. The colloid was purified by dialysis. Au was deposited on the nanoparticulated cerium oxide by the following procedure: a solution of 300 mg of $HAuCl_4{\cdot}3H_2O$ in 50 ml of deionized water was brought to pH 10 by the addition of a solution of NaOH 0.2 M. Once the pH value was stable the solution was added to a slurry containing colloidal CeO_2 (10 g) in H_2O (80 ml). After adjusting the pH with NaOH 0.2 M, the slurry was left under vigorous stirring for 18 h at room temperature. The Au/CeO_2 solid was then filtered and exhaustively washed with distilled water until no traces of chlorides were detected by the $AgNO_3$ test. This is an important treatment since traces of Cl^- remain strongly bonded to gold and are highly detrimental for the overall activity. The catalyst was dried at room temperature under vacuum. Finally the Au/CeO_2 was activated by reduction by pouring the solid into boiling 1-phenylethanol for 2 h. After recovering, washing, and drying the solid, it was ready to be used as a catalyst. The total Au content of the final catalyst was 0.72% as determined by chemical analysis. The average particle size of the gold nanoparticles as determined by statistical analysis of a sufficiently large number of particles was 3.97 nm. A second Au/CeO_2 catalyst containing higher gold loading (1.85 wt.%) was prepared following exactly the above-mentioned procedure, but using 750 mg of $HAuCl_4$. The average particle size of this $Au(1.85)/CeO_2$ catalyst was 5.45 nm.

The $Au(0.72\%)Pd(0.15\%)/CeO_2$ sample was prepared by stirring a suspension of 2 g of 0.72% Au/CeO_2 in acetone (150 ml) containing $PdCl_2(PhCN)_2$ (2.5×10^{-4} M), the slurry was left under vigorous stirring for 4 h at room temperature. The solid was then filtered, exhaustively washed with distilled water, and dried at 373 K overnight. Then $Au(0.72\%)Pd(0.15\%)/CeO_2$ catalyst was activated by the reducing the solid with 1-phenyletanol at 433 K for 2 h. The catalyst was then washed, filtered, and dried at room temperature for 12 h. The final Pd content was 0.15 wt.% as determined by quantitative atomic absorption analysis.

Using also as support nanoparticulated ceria, two other supported noble metal catalysts were prepared. Pd/CeO_2 and Pt/CeO_2 catalysts containing 0.73 and 0.70 wt.% of Pd or Pt, respectively. These catalysts were prepared by impregnation of 2 g of nanoparticulated CeO_2 with a H_2O (5 ml)/acetone (5 ml) solution of 42 mg of $PdCl_2$ (Aldrich, 60% purity) or an aqueous solution (10 ml) of 45 mg of $H_2PtCl_6{\cdot}6H_2O$ (Aldrich). The resulting slurry was stirred for 3 h at room temperature. Then, the liquid phase was evaporated and the solid was dried at 373 K overnight. The samples were activated by reduction with excess of 1-phenyletanol at 433 K for 3 h. The catalyst was then washed, filtered, and dried at 373 K for 12 h. The Pd or Pt content present on the solids was determined by quantitative atomic absorption spectroscopy.

The Au/TiO_2 catalyst consists of 1.5 wt.% gold on TiO_2 and was supplied by the World Gold Council (reference catalysts, Type A). It can also be prepared by depositing the gold from an aqueous solution of $HAuCl_4$ (Alfa Aesar) on a sample of TiO_2 (P25 Degussa). The deposition precipitation procedure is done at 343 K and pH 9 for 2 h, using (0.2 M) NaOH to maintain the pH constant. Under these conditions, gold deposition occurs with 80% efficiency. The catalyst is then recovered, filtered, washed with deionized water, and dried at 373 K overnight. Finally, the powder is calcined at 673 K in air for 4 h. Following this procedure, 3.5 nm gold nanoparticles supported on TiO_2 are obtained.

Pt/TiO_2 (5 wt.%) catalyst is prepared by the impregnation of 2 g of TiO_2 (Degussa P25, 10 g, $S_{BET} = 55\ m^2\ g^{-1}$) with a solution of $H_2PtCl_6{\cdot}6H_2O$ (Aldrich) in 7 ml of H_2O (milliQ). The slurry was stirred for 2 h at room temperature, then all the liquid was evaporated and the solid was dried at 373 K overnight and reduced with 1-phenyletanol at 433 K for 2 h. The catalyst was then washed, filtered, and dried at room temperature for 12 h. The final Pt content was found to be 5 wt.% by atomic absorption analysis.

The Pd/TiO_2 catalyst containing 1.81 wt.% of palladium was prepared by the impregnation of 2 g of TiO_2 (Degussa P25, 10 g, $S_{BET} = 55\ m^2\ g^{-1}$) with a solution of 104 mg of $PdCl_2$ (Aldrich, 60% purity) in a mixture of 5 ml of H_2O (milliQ) and 5 ml of acetone. The slurry was stirred for 3 h at room temperature. Then, the liquid phase was evaporated and the solid was then washed, filtered, and dried at 373 K overnight. The catalyst was activated by reduction under H_2 flow (50 ml min^{-1}) at 473 K for 2 h. The final Pd content on the solid was determined by quantitative atomic absorption analysis.

The Au/C catalyst consists of 0.8 wt.% gold on active carbon and was supplied by the World Gold Council (reference catalysts, Type D).

The Pt/C catalyst consists of 5 wt.% gold on active carbon and was supplied from Sigma–Aldrich Company.

2.2. Catalytic experiments

Catalytic experiments were performed in reinforced glass semi continuous reactors equipped with temperature and pressure controllers. For each reaction, a 2-ml mixture of reactants and solvent was placed into the reactor (3 ml capacity) together with appropriate amount of catalyst. Using toluene as a solvent care has to be taken to avoid vapor mixtures within the explosion range. Working under the experimental conditions 373 K and 5 bars of oxygen, the composition of the vapor phase is outside the explosion mixture range.

All the reactants used in this study, except carvoxime **5**, are commercially obtained from Sigma–Aldrich Company with purities higher than 95%. Compound **5** was synthesized from carvone and hydroxylamine as described in the literature [24], but using only methanol as a solvent. Carvoxime **5** was obtained in 85% yield as white crystals. Anal. Calc. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.39; H, 9.48; N, 8.42. The ^1H and ^{13}C NMR spectral data of compound **5** agree with those reported in the literature [25,26].

In the cases in which no water was used as a solvent, conversion and yields were estimated using dodecane as an internal standard. After sealing the reactor, air was purged by filling the reactor with oxygen (5 bar) and pumping out three times before final pressurization of the reactor with O_2 at 5 bar. The reactor was deeply introduced into a silicone bath that was preheated at the reaction temperature. During the experiment, the pressure was maintained constant and the reaction mixture was magnetically stirred at 1000 rpm. Aliquots were taken from the reactor at different reaction times. Once the catalyst particles were removed from the solution by centrifuging at 12,000 rpm, the products were identified by GC–MS and also by comparing the retention time with commercial (Sigma–Aldrich Company) pure samples when available. When mixtures of water–ethanol were used as a solvent, quantification was performed adding a known weight of dodecane as an external standard to aliquots of the reaction mixtures diluted in dichloromethane. Only experiments with mass balances ⩾95% were considered.

3. Results and discussion

In the first stage of our work we selected cyclohexanone oxime (**1**) as a model compound and studied the aerobic oxidation of this oxime **1** in the presence of the commercially available titania-supported gold nanoparticles [Au (1.5 wt.%)/TiO_2] in various solvents. The results presented in Table 1 show that although reactant **1** is partially converted using acetonitrile or toluene as solvents (entries 1 and 2 in Table 1), the conversion achieved at long reaction time was low. Besides this it can be seen that after an initial period, the reaction stops and the conversion measured at 3 and 23 h in toluene using Au (1.5 wt.%)/TiO_2 was identical (compare entries 2 and 3 in Table 1). This indicates deactivation of the catalyst. Other commercial gold catalysts such as Au (0.8 wt.%)/C were more active promoting the disappearance of the oxime **1,** although the selectivity to the ketone was very low (entry 4 in Table 1). Gold was not the only noble metal exhibiting activity toward this aerobic oxidation. Platinum nanoparticles supported on active carbon, working in toluene also exhibit a behavior similar to that of gold (entry 5 in Table 1), i.e. they are able to convert the oxime **1**, but again with unsatisfactorily low selectivity toward cyclohexanone (entry 5 in Table 1). The reason for the low selectivity toward cyclohexanone **2** was the formation of other oxidation products accompanying cyclohexanone (see footnote "a" in Table 1).

In the aerobic oxidation of alcohols [20] and benzyl amines [27], it has been found that the nature of the support plays an important role influencing the catalytic activity of the supported Au nanoparticles. For those transformations as well as for the low-temperature CO oxidation and other reactions [17–19], a comparison among different carriers has established that the use of cerium nanoparticles as a gold support boosts the activity of gold nanoparticles or *vice versa*. Therefore, an obvious catalyst to be tested will be gold supported on nanoparticulated ceria. Using this Au (0.72 wt.%)/CeO_2 material as a catalyst in toluene, conversion and selectivity increased substantially to high values (entry 6 in Table 1). Furthermore, since water has been found to be a suitable solvent for aerobic alcohol oxidation using ceria supported gold, and considering that in the transformation of the oxime into ketone a hydrolysis pathway could contribute to the formation of the target cyclohexanone, we also performed the reaction using Au (0.72 wt.%)/CeO_2 as a catalyst in a mixture of ethanol and water. The results show that in the presence of water the conversion was increased to very high values with essentially complete selectivity toward cyclohexanone **2** at very short times (entry 7 in Table 1). Even more, the reaction time can be substantially reduced if the reaction temperature is increased to 130 °C (entry 8 in Table 1).

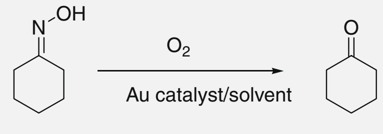
We tested the catalytic activity of the nanoparticulated ceria used as support without gold. In related precedents [28], it has been observed that CeO_2 nanoparticles already exhibit some activity that is further promoted by the presence of supported gold nanoparticles that increase activity and selectivity. In the present case it was also observed that nanoparticulated CeO_2 has a notable activity toward oxidation (entry 9 in Table 1). However, the presence of gold more than doubles the activity and makes the reaction totally selective toward the target cyclohexanone. This is attributed to the influence of gold nanoparticles increasing the oxygen vacancies and structural defects already inherent to nanoparticulated ceria [29].

Finally, other more elaborated catalysts, as those based on core–shell alloys of gold (core) and palladium (shell) supported on nanoparticulated ceria were also efficient even in toluene as a solvent (entry 10 in Table 1), but they have the drawback of a more complex preparation. Thus, from the results shown in Table 1 it can be concluded that the use of Au (0.72 wt.%)/CeO_2 as a catalyst and of ethanol/water as a solvent are suitable conditions to perform the aerobic oxidation of cyclohexanone oxime (**1**) to the corresponding ketone **2**.

The Au (0.72 wt.%)/CeO_2 catalyst acts as a heterogeneous catalyst as it can be deduced from the fact that the conversion stops when this solid catalyst is filtered from the reaction medium. Also the Au (0.72 wt.%)/CeO_2 was reused three times without observing any decay in activity or selectivity for the oxidation of **1** into **2.**

We have expanded the results achieved for compound **1** to show the general applicability of the oxidation process to obtain not only cycloalkanones but also ketones and, more importantly,

Table 1
Conversion and selectivity toward cyclohexanone (**2**) for the oxidation of cyclohexanone oxime (**1**) by oxygen in the presence of a series of supported gold catalysts. Reaction conditions: compound **1:** 1 mmol, solvent: 2 ml, oxygen pressure: 5 bar, Au/substrate ratio 1 mol%.



1 2

Run	Catalyst	Time (h)	Solvent	*T* (°C)	Conversion (%)	Selectivity (%)
1	Au (1.5 wt.%)/TiO_2	23	Acetonitrile	100	23	95
2	Au (1.5 wt.%)/TiO_2	3	Toluene	100	41	99
3	Au (1.5 wt.%)/TiO_2	23	Toluene	100	41	99
4	Au (0.8 wt.%)/C	2	Acetonitrile	100	71	27[a]
5	Pt (5 wt.%)/C	6	Toluene	100	76	23[a]
6	Au (0.72 wt.%)/CeO_2	6.5	Toluene	100	90	100
7	Au (0.72 wt.%)/CeO_2	1	Ethanol/water 1/1	100	99	100
8	Au (0.72 wt.%)/CeO_2	0.5	Ethanol/water 1/1	130	100	100
9	CeO_2	1.1	Ethanol/water 1/1	130	95	70[a]
10	Au (0.72 wt.%)–Pd (0.15 wt.%)/CeO_2	5.5	Toluene	110	99	98

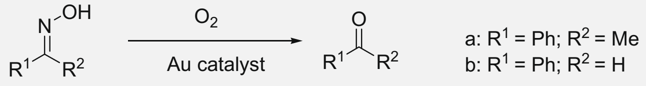
[a] Formation of other products reaction for example, 1,2-cyclohexanedione and 2-cyclohexenone oxime.

also aldehydes. Since efficient aerobic oxidation of aldehydes to the corresponding carboxylic acids using supported gold catalysts has been reported [30], it is of interest to establish whether or not it is possible to stop selectively the aerobic oxidation of an aldoxime at the stage of aldehyde or if consecutive cascade reactions occur leading to a more complex reaction mixture.

The results obtained with the aerobic oxidation of keto- and aldoximes are shown in Table 2. As it can be seen there, Au (0.72 wt.%)/CeO_2 in a mixture of ethanol water (1:1) or toluene is also efficient to promote the aerobic oxidation of oximes **3a** and **3b** to acetophenone (**4a**) and benzaldehyde (**4b**). The aerobic oxidation of compound **3b** to render benzaldehyde was particularly easy and can take place in very short times (5 min), even in toluene. For this transformation we checked that water, even in trace amounts, is not needed to produce the formation of the aldehyde, since the reaction takes also place with dried toluene in the absence of moisture. Moreover, as it can be seen there, water as solvent exerts a negative influence since in this case concurrent overoxidation of benzaldehyde to benzoic acid is observed in a large extent. This is in agreement with the fact that water favors the oxidation of aldehydes probably through the intermediacy of their *gem*-diols [30].

Although catalysts containing higher gold loading on the nanoparticulated ceria support and working to the same oxime/Au mol ratio are also efficient to promote the aerobic oxidation, no advantages derived from the use of higher Au loadings were apparent.

Table 2
Conversion and selectivity toward carbonylic compounds determined for the oxidation of a series of oximes in the presence of Au/CeO_2 catalyst at two different Au loadings (0.72 and 1.85 wt.%). Reaction conditions: substrate 0.5 mmol, solvent 1 ml, oxygen pressure 5 bar, Au/substrate mol ratio 1%.



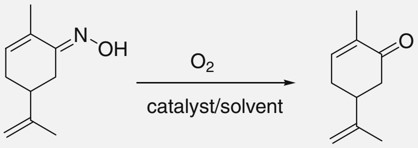
3a,b

4a,b

Oxime	Catalyst	Time (h)	Solvent	T (°C)	Product	Conversion (%)	Selectivity (%)
3a	Au (0.72 wt.%)/CeO_2	4	EtOH/H_2O 1:1	130	**4a**	99	100
	Au (0.72 wt.%)/CeO_2	15	Toluene	100	**4a**	85	100
3b	Au (0.72 wt.%)/CeO_2	2	EtOH/H_2O 1:1	130	**4b**	98	58[a]
	Au (0.72 wt.%)/CeO_2	0.1	Toluene[b]	130	**4b**	98	98
	Au (1.85 wt.%)/CeO_2	0.25	Toluene[b]	130	**4b**	93	96[a]

[a] Formation of benzoic acid in 42% selectivity was also observed.
[b] Anhydrous toluene.

Table 3
Conversion and selectivity toward carvone **6** determined for the oxidation of carvoxime **5** with supported noble metal catalysts. Reaction conditions: substrate 0.5 mmol, solvent 1 ml, oxygen pressure 5 bar, metal/substrate mol ratio 1%.



(**5**)

(**6**)

Catalyst	Time (h)	Solvent	T (°C)	Conversion (%)	Selectivity (%)
Au (0.72 wt.%)/CeO_2	20	EtOH/H_2O 1:1	100	78	100
Au (0.72 wt.%)/CeO_2	20	EtOH/H_2O 1:1	110	97	100
Au (0.72 wt.%)/CeO_2	7.5	EtOH/H_2O 1:1	120	99	100
Au (0.72 wt.%)/CeO_2	5	EtOH/H_2O 1:1	130	99	100
Au (0.72 wt.%)/CeO_2	5	EtOH	130	45	12[a]
Au (0.72 wt.%)/CeO_2	5	$CH_3C{\equiv}N$	130	80	10[a]
Au (0.72 wt.%)/CeO_2	6	Toluene	130	75	13[a]
Au (1.85 wt.%)/CeO_2	5	EtOH/H_2O 1:1	130	75	100
Pt (0.7 wt.%)/CeO_2	8	EtOH/H_2O 1:1	100	81	100
Pt (0.7 wt.%)/CeO_2	8	EtOH/H_2O 1:1	110	92	100
Pt (0.7 wt.%)/CeO_2	5	EtOH/H_2O 1:1	120	96	100
Pt (0.7 wt.%)/CeO_2	3.5	EtOH/H_2O 1:1	130	99	100
Pd (0.73 wt.%)/CeO_2	22	EtOH/H_2O 1:1	100	51	100
Pd (0.73 wt.%)/CeO_2	8	EtOH/H_2O 1:1	110	18	100
Pd (0.73 wt.%)/CeO_2	8	EtOH/H_2O 1:1	120	27	100
Pd (0.73 wt.%)/CeO_2	5	EtOH/H_2O 1:1	130	35	100
Pd (1.81 wt.%)/TiO_2	5	EtOH/H_2O 1:1	130	32	100
CeO_2	5	EtOH/H_2O 1:1	130	85	69
Au (1.5 wt.%)/TiO_2	5	EtOH/H_2O 1:1	130	42	100
Pt (5 wt.%)/TiO_2	3.5	EtOH/H_2O 1:1	130	98	100
TiO_2	5	EtOH/H_2O 1:1	130	30	66
Zeolite(HB-20) Si/Al(13/1)	5.5	EtOH/H_2O 1:1	130	93	10[a]

[a] Formation of other unidentified products, particularly two with molecular weights 281 and 341 Da was also observed.

As commented earlier in the introduction, the efficient conversion of carvone oxime (**5**) into carvone (**6**) constitutes an example of industrial relevance in which oximes act as synthetic precursors of ketones. The structure of carvoxime contains two tri-substituted C=C double bonds that can also undergo oxidation to epoxides and other oxygen containing products if the oxidation process does not exhibit sufficient chemoselectivity toward oxime oxidation. Thus, it was of interest to apply the gold supported catalyst for the conversion of oxime **5** into carvone **6**. The results obtained are summarized in Table 3.

As it can be seen there, Au (0.72 wt.%)/CeO_2 was also efficient to selectively catalyze the aerobic oxidation of oxime **5** into carvone. Ethanol and toluene were not suitable solvents to attain high conversions. Even the selectivity toward carvone decreases when toluene is present due to the occurrence of reaction involving the C=C double bonds. On the other hand, water was also not an appropriate solvent since it does not dissolve carvoxime **5** at room temperature. A 1:1 mixture of ethanol and water was found to be the most adequate. At 100 °C in 1:1 ethanol–water, the conversion of oxime **5** into ketone **6** was not complete after 23 h. In contrast, the reaction goes to completion in less than 5 h when the reaction temperature is increased at 130 °C (see Fig. 1).

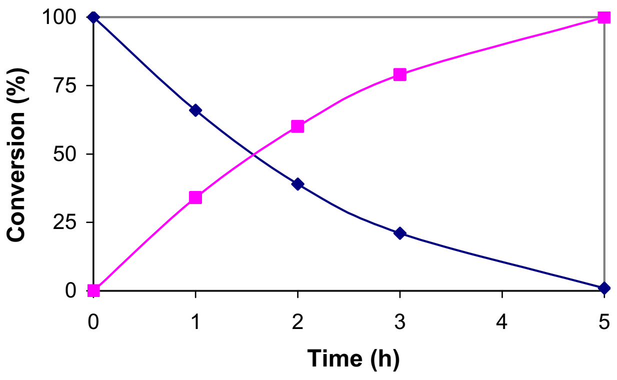


Fig. 1. Time conversion plot for the oxidation of carvoxime **5** into carvone **6** in the presence of Au (0.72 wt.%)/CeO_2. (♦): conversion of **5**; (■): yield of **6**. Reaction conditions: carvoxime, 0.5 mmol; ethanol/water (1/1), 1 ml; temperature, 403 K; oxygen pressure, 5 bar; Au/substrate mol ratio 1%.

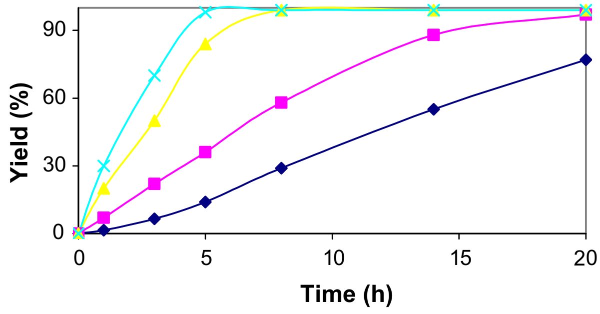


Fig. 2. Time-yield plots for the oxidation of carvoxime **5** in the presence of Au (0.72 wt.%)/CeO_2 at (100 °C) (♦), (110 °C) (■), (120 °C) (▲), (130 °C) (×). Reaction conditions: carvoxime, 0.5 mmol; ethanol/water (1/1), 1 ml; oxygen pressure, 5 bar; Au/substrate mol ratio 1%.

Higher gold loadings on ceria play an adverse role, decreasing the conversion. Thus, the activity of Au (1.85 wt.%)/CeO_2 was lower than that of Au (0.72 wt.%)/CeO_2 under the same conditions (see Table 3). Related precedents on the negative influence of excessive gold loading and the existence of an optimal gold loading can be found in the literature [17]. Several possible reasons for this activity decrease upon gold loading increase such as increase in the average size of the nanoparticles (see Section 2) and reduction on the exposed support surface have been proposed [17].

As it was observed already for the oxidation of cyclohexanone oxime **1**, Au (0.72 wt.%)/CeO_2 and Au (1.85 wt.%)/CeO_2 were more efficient than Au (1.5 wt.%)/TiO_2. The latter sample was not able to carry out the complete conversion of **5** under the optimal conditions of the oxidation, once again exemplifying the influence of the support on the efficiency of the gold catalyst. Fig. 2 shows the time-yield plots for the oxidation of carvoxime **5** in the presence of 0.72 wt.% Au/CeO_2 at different temperatures.

Also in line with the results commented for cyclohexanone oxime, it was observed that besides gold catalysts, analogous platinum and palladium catalysts supported on ceria at similar loadings as the most active Au (0.72 wt.%)/CeO_2 also exhibit activity for the aerobic oxidation of carvoxime **5** to carvone **6**. It was found that the activity of the platinum catalysts was similar to that of gold and much higher than that of palladium (see Table 3). Table 4 shows the calculated turnover frequency (TOF) for the two Au/CeO_2 catalysts based on the estimated number of external gold atoms present in the catalysts. As it can be seen in Table 4, the inherent catalytic activity for gold in Au (0.72 wt.%)/CeO_2 is about 1.5 times that of Au (1.85 wt.%)/CeO_2 and the TOF absolute value for carvoxime oxidation is somewhat in the lower range compared to TOF values for alcohol oxidation [17].

Activation energies of the overall kinetics for Au (0.72 wt.%)/CeO_2, Pt (0.70 wt.%)/CeO_2, and Pd (0.73 wt.%)/CeO_2 were obtained from the Arrhenius plot of the logarithm of the initial reaction rates (r_0) vs. the inverse of the absolute temperature (see Fig. 3). The r_0 values were determined from the slope at zero time of the time-yield plots as those shown in Fig. 2 for Au (0.72 wt.%)/CeO_2.

The activation energies (E_a) obtained from the slope of the best fitting of the experimental points to a straight line and applying the Arrhenius equation [$\ln r_0 = -(E_a/RT) + \ln A$] were 30.28, 15.23, and 41.90 kcal mol^{-1} for Au (0.72 wt.%)/CeO_2, Pt (0.70 wt.%)/CeO_2, and Pd (0.73 wt.%)/CeO_2, respectively. These values indicate that Pt is the metal for which the energy barrier is the lowest and about one half that of gold.

Overall the data shown in Table 3 and Fig. 1 shows that gold supported catalysts can effect the conversion of carvoxime into carvone under neutral conditions avoiding highly corrosive Brönsted acids and without forming any waste or by-product.

As a summary of the previous data, it can be concluded that gold on nanoparticulated ceria is a suitable and general catalyst to effect the aerobic oxidation of oximes into carbonylic compounds. The process is heterogeneous and the catalysts can be reused without decay. The reaction is quite sensible to the solvent, a

Table 4
Number of external gold atoms present in the catalyst used to oxidize carvoxime **5** (0.5 mmol) into carvone **6** and the corresponding turnover frequency (TOF).[a]

Catalyst	⟨*d*⟩ (nm)	N_T (per nanoparticle)	*m*	N_s (per nanoparticle)	% N_s	$N_s \times 10^{-20a}$ (in the reaction)	TOF (h^{-1})
Au (0.72 wt.%)/CeO_2	3.97	1941	8.83	616.18	31.74	9.56	6800
Au (1.85 wt.%)/CeO_2	5.45	5022	11.95	1201.02	23.91	7.20	4200

[a] ⟨*d*⟩: average gold nanoparticle size; N_T: number of total gold atoms per particle; *m*: number of full shells in an average gold nanoparticle; N_s: number of surface gold atoms per nanoparticles; % N_s: percentage of external gold atoms.

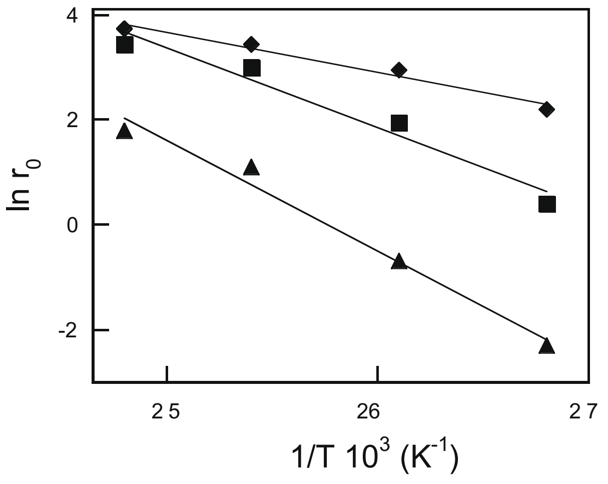


Fig. 3. Arrhenius plot correlating the inverse of the absolute temperature with the initial reaction rates in the presence of Au (0.72 wt.%)/CeO_2 (■), Pt (0.70 wt.%)/CeO_2 (◆), and Pd (0.70 wt.%)/CeO_2 (▲). The activation energies (E_a) were obtained from the slope of the best fitting of the experimental points to a straight line and applying the Arrhenius equation [$\ln r_0 = -(E_a/RT) + \ln A$]. The experimental equations for the three catalysts were: $y_{Au} = -15239x + 41.469$; $y = -7665.2x + 22.83$, and $y_{Pd} = -21088x + 54.329$.

mixture of ethanol/water being generally a convenient medium. Other supports such as titania and active carbon are less suitable than ceria that already exhibits an intrinsic activity for this oxidation process. Low gold loading is optimal with respect to the activity for this aerobic oxidation. Palladium was much less efficient than gold, but platinum exhibits a similar catalytic behavior as gold, but platinum exhibits remarkably lower (about one half) activation energy than gold.

The process described here fulfills all the requirements of Green Chemistry and can replace advantageously current processes that use Brönsted acids that are notoriously unsatisfactory from the environment point of view due to corrosion and the generation of aqueous wastes. Furthermore, these results expand the list of selective aerobic oxidations that are efficiently catalyzed by gold nanoparticles.

Acknowledgments

Financial support by the Spanish Ministry of Science and Innovation (projects CTQ2006-5678) and Generalitat Valenciana (Prometeo 2008) is gratefully acknowledged. A.G. thanks the CSIC for a research associate JAE contract.

References

[1] J. March, Advanced Organic Chemistry: Reactions, Mechanisms and Structures, McGraw Hill, New York, 1993.
[2] P. Serna, M. Lopez-Haro, J.J. Calvino, A. Corma, J. Catal. 263 (2009) 328.
[3] D.G. Williams, The Chemistry of Essential Oils: An Introduction for Aromatherapists, Beauticians, Retailers and Students, Micelles Press, Dorset, 2008.
[4] C.C.C.R. De Carvalho, M.M.R. Da Fonseca, Food Chem. 95 (2006) 413.
[5] R.H. Reitsema, J. Org. Chem. 23 (1958) 2038.
[6] P.N. Davey, C.P. Newman, W.A. Thiam, C.-L. Tse, Preparation of Carvone, Quest Int., US, 2001.
[7] V.K. Jadhav, P.P. Wadgaonkar, P.L. Joshi, M.M. Salunkhe, Synth. Commun. 29 (1999) 1989.
[8] J.W. Bird, D.G.M. Diaper, Can. J. Chem. 47 (1969) 145.
[9] Y.T. Yang, T.S. Li, Y.L. Li, Synth. Commun. 23 (1993) 1121.
[10] M.F. Haley, K. Yates, J. Org. Chem. 52 (1987) 1817.
[11] H.J.P. de Lijser, F.H. Fardoun, J.R. Sawyer, M. Quant, Org. Lett. 4 (2002) 2325.
[12] R.A. Sheldon, Catal. Oxid. (1995) 239.
[13] R.A. Sheldon, R.A. van Santen (Eds.), Catalytic Oxidation: Principles and Applications, Elsevier Science Publication BV, Amsterdam, 1995.
[14] R.A. Sheldon, Stud. Surf. Sci. Catal. 59 (1991) 33.
[15] R.A. Sheldon, Chemtech 21 (1991) 566.
[16] R. Joseph, A. Sudalai, T. Ravindranathan, Tetrahedron Lett. 35 (1994) 5493.
[17] A. Corma, H. Garcia, Chem. Soc. Rev. 37 (2008) 2096.
[18] A.S.K. Hashmi, J. Hutchings Graham, Angew. Chem. Int. Ed. 45 (2006) 7896.
[19] S.A.K. Hashmi, Chem. Rev. 107 (2007) 3180.
[20] A. Abad, C. Almela, A. Corma, H. Garcia, Tetrahedron 62 (2006) 6666.
[21] A. Abad, A. Corma, H. Garcia, Chem. Eur. J. 14 (2008) 212.
[22] A. Grirrane, A. Corma, H. Garcia, Science 322 (2008) 1661.
[23] J.Y. Chaneching, J. Chane-Ching, Cerium oxide prodn|easily dispersible in water to form stable sols, Rhone Poulenc Specialites Chim; Rhone-Poulenc Spec, 1987.
[24] A.M. Nilsson, M.A. Bergström, K. Luthman, J.L.G. Nilsson, A.T. Kalberg, Food Chem. Toxicol. 43 (2005) 1626.
[25] S. Sivasubramanian, S. Muthusubramanian, N. Arumugam, Ind. J. Chem. Sect. B 23 (1984) 1128.
[26] A.V. Tkachev, A.M. Chibiryaev, A.Y. Denisov, Y.V. Gatilov, Tetrahedron 51 (1995) 1789.
[27] A. Grirrane, A. Corma, H. Garcia, J. Catal. 264 (2009) 138.
[28] R. Juarez, A. Corma, H. Garcia, Green Chem. 11 (2009) 949.
[29] A. Corma, P. Atienzar, H. Garcia, J.-Y. Chane-Ching, Nat. Mater. 3 (2004) 394.
[30] A. Corma, M.E. Domine, Chem. Commun. (2005) 4042.