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Gold catalysts for the direct oxidation of aminoalcohols to aminoacids

Aureliano Gaiassi, Laura Prati *

Dipartimento di Chimica Inorganica Metallorganica e Analitica, Centre of Excellence CIMAINA, Università degli Studi di Milano, Via Venezian 21, I-20133 Milano, Italy

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ABSTRACT

Gold catalysts on different supports, prepared by sol immobilization and deposition–precipitation, were tested in aminoalcohol oxidation for the direct preparation of aminoacids. Nitrogen substitution appeared to be crucial for avoiding parallel reaction pathway, but also the reaction conditions play an important role. Basic conditions and moderate temperature (40 °C) represent a good compromise for enhancing selectivity to aminoacids. TiO_2 represents the most versatile support.

1. Introduction

Aminoacids are very abundant in natural materials, and were usually obtained from hydrolyzed protein by fractionated precipitation or ion-exchange chromatography. Presently, single aminoacids are mainly produced by fermentation from micronutrients using genetically modified bacteria [1].

When proteinaceous materials lack of a specific aminoacid, or when it cannot be obtained by biotechnology, it can be prepared by classical synthetic methods. The most common ones are amination of halo acids [2] Gabriel synthesis (treatment of halo acids with potassium phtalimide, followed by hydrolysis of the intermediate) [3], alkylation of *N*-acetylaminomalonic esters (Sorensen method) [4], and Strecker synthesis (addition of ammonium and cyanide ions to aldehydes or ketones, followed by hydrolysis of the α-amino nitrile) [5]. These latter methods presented a high environmental impact due to both reagents and co-products.

Glycine, sarcosine (*N*-methylglycine) and *N*,*N*-dimethylglycine are important intermediates in organic chemical industry; they are mainly employed to produce their *N*-cocoyl derivatives, used as surface-active agents. Glycine is commonly obtained from chloroacetic acid by amination with excess of ammonia [2]. Using dibenzylamine instead of ammonia as aminating agent, overalkylation is avoided, but the intermediate (dibenzylglycine) have to be hydrogenated to remove the protective groups [6]. *N*,*N*-dimethylglycine is usually prepared by amination of α-halo acetic acids or their esters with dimethylamine, followed by hydrolysis of the ester if necessary [7]. Also some other methods are employed: Strecker synthesis (addition of dimethylamine and sodium cyanide to formaldehyde, and following hydrolysis) [8], reductive alkylation of glycine using formaldehyde and a reducing agent (formic acid, $NaBH_4$, $NaBH_3CN$) [9], and reductive amination of glyoxylic acid, using boronic acid (H_3BO_2) as reducing agent [10]. Sarcosine is usually synthesized by amination of α-halo acetic acids with methylamine [11], Strecker synthesis [12], and reductive alkylation of glycine [13], as described above for *N*,*N*-dimethylglycine.

The direct catalytic oxidation of aminoalcohols, using O_2 as the oxidant, represent a suitable alternative to produce aminoacids avoiding dangerous stoichiometric reactants and by-products being environmentally begnin. Since ethanolamine (EA), 2-methylaminoethanol (MAE) or 2-dimethylaminoethanol (DMAE) can be easily prepared from ethylene oxide by reaction with ammonia, methylamine or dimethylamine, they can be used as low cost starting materials for the synthesis of the corresponding aminoacids.

Recently, the role of transition metals as catalysts in oxidation reactions has been investigated. It is well known that organic substrates such as primary or secondary alcohols can be oxidized to aldehydes, carboxylic acids or ketones, in the presence of dioxygen and using supported Au, Pd and Pt nanoparticles as the catalysts [14]. These catalysts have been applied also in aminoalcohol oxidation: ethylglycine has been obtained from ethylglycinol by protecting the amino group with phenyl sulfonyl chloride, oxidizing the protected aminoalcohol using platinum catalyst, and finally removing the protective group [15], while betaines (surfactants) were prepared by direct oxidation from ethoxylated quaternary ammonium compounds in the presence of a supported and promoted Pt catalyst [1].

In the last years gold catalysts have been fruitfully introduced in the liquid phase oxidation reactions because gold nanoparticles

* Corresponding author.
E-mail address: Laura.Prati@unimi.it (L. Prati).

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have a greater resistance to deactivation compared to palladium and platinum nanoparticles [14]. It has been shown that by choosing the proper catalyst aminoalcohols can be directly oxidized using water as the solvent under basic conditions: alanine has been thus obtained from alaninol by direct oxidation using Au/Al_2O_3 as catalyst [16], while *N*,*N*-dimethylglycine has been prepared from 2-*N*,*N*-dimethylaminoethanol using Au/Co_3O_4 as the catalyst, dioxygen as the oxidizing agent and water as the solvent [1].

In addition it has been shown that primary, secondary and tertiary amines can be respectively oxidized to nitriles, imines and N-oxides with good selectivities [17,18]. Particularly, 3-dimethylamino-1-propanol can be selectively oxidized to the corresponding N-oxide derivative [18] in the presence of Au supported on C, Al_2O_3 and TiO_2 under mild basic conditions (pH 10.5) and atmospheric pressure of O_2, Moreover, 1,6-hexanediamine can be oxidized to caprolactam [19] using Au/TiO_2 catalyst and dioxane as the solvent. Thus, the aim of this work is to investigate reaction conditions, catalyst activities and selectivity in liquid phase oxidations of aminoalcohols, for the potential development of a process for the production of aminoacids from aminoalcohols.

2. Experimental

2.1. Materials

Gold of 99.99% purity in sponge from Fluka was used.

Activated carbon (AC) from Camel (S.A. = 1200 m^2/g), γ-Al_2O_3 from Condea (S.A. = 90 m^2/g), MgO from Merck (S.A. = 35 m^2/g), and TiO_2 (P25) from Degussa (S.A. = 50 m^2/g) were employed as supports for catalysts. Commercial 5% Au/Fe_2O_3 from World Gold Council was also tested.

Tetrakis(hydroxymethyl)phosphonium chloride (THPC, 98% solution) from Aldrich was used. NaOH of the highest purity available and urea (purity > 99%) were from Fluka. Gaseous oxygen from SIAD was 99.99% pure. Ethanolamine (purity > 99.0%) from Fluka, 2-methylaminoethanol (99% purity) from Degussa and 2-dimethylaminoethanol (99% purity) from Aldrich were used. DSS (3-trimethylsilyl-1-propanesulfonic acid, sodium salt) and all the products used as standard samples were from Fluka.

2.2. Catalyst preparation

The symbol for each catalyst indicates the preparation method (THPC for sols, DP for deposition–precipitation) and the type of support. The gold content was checked by ICP analysis of the filtrate or alternatively directly on the catalyst after burning off the carbon or digestion with aqua regia.

2.2.1. Metallic sol immobilization (THPC-protected sol)

Gold sols generated in the presence of the THPC/NaOH system were prepared as reported elsewhere [20] and used as such. A freshly prepared 0.05 M solution of THPC (0.5 mL) was added to a 10^{-3} M solution of NaOH. After 6 min, 2 mL of $HAuCl_4$ (5.0 mg/mL Au) was added dropwise, yielding a brown metallic sol. Within a few minutes of sol generation, the support was added under vigorous stirring. The amount of support was calculated for having a final gold loading of 1% wt. After 2 h the slurry was filtered and the catalyst washed thoroughly with distilled water; it was then used in the wet form. The actual loading of metal was checked by ICP analysis on the filtered solution.

2.2.2. Deposition–precipitation with urea

Au/Al_2O_3 and Au/MgO were prepared by the deposition–precipitation method reported by Louis and co-workers [21] using urea as the precipitating agent. The support (1.00 g) was added to 100 mL of an aqueous solution of $HAuCl_4$ (100 mg/L Au) and of urea (0.42 M). The suspension, thermostated at 80 °C, was vigorously stirred for 4 h, until pH 7 was reached. The slurry was then filtered, washed thoroughly with water, dried at 80 °C for 2 h and then calcined in air at 450 °C for 4 h. The loading was calculated by checking the residual metal with ICP analysis of the filtrate.

2.3. Oxidation experiments

The reactions were carried out in a thermostated glass reactor (30 mL), provided with an electronically controlled magnetic stirrer, connected to a large reservoir (5000 mL) containing oxygen at 300 kPa. The oxygen uptake was followed by a mass-flow controller connected to a PC through an A/D board, plotting a flow/time diagram. The aminoalcohol, NaOH and gold catalyst (reactant/Au = 500 mol/mol) were mixed in distilled water (total volume 10 mL). 0.3 M reactant solutions were used. The reactor was pressurized at 300 kPa with O_2 and thermostated at the appropriate temperature. After an equilibration time of 10 min the reaction was started by stirring; samples were taken after 30, 60, 120, 240 min and analysed by ^{1}H NMR spectroscopy.

The pH-controlled oxidation experiments were performed in a Metrohm 718 STAT Titrino. The aminoalcohol (0.3 M aqueous solution, total volume 50 mL) and the gold catalyst (reactant/Au = 500 mol/mol) were mixed in the reactor, which was pressurized at 300 kPa of O_2 and thermostated at 60 °C. The pH was stated at 11.0 by adding a 1 M aqueous solution of NaOH. Samples were taken after 30, 60, 120, 240 min and analysed by ^{1}H NMR spectroscopy.

2.4. Analysis of products

Analyses were performed by ^{1}H NMR [22], using DSS (sodium 3-trimethylsilyl-1-propanesulfonate) as external standard to quantify the products. Proton NMR spectra were recorded on a Bruker AC 300 NMR spectroscope. Water signal was suppressed using a low power PRESAT pulse in order to minimize signal distortions. 100 μL of DSS solution in D_2O (20 mg/mL), equivalent to 2.0 mg of DSS, were added to each sample (500 μL). Products were recognised by comparison with authentic samples, and their concentrations were determined by comparing the integration of products signals to standard ones.

Chemical shifts (ppm), multiplicity and coupling constants (Hz) are reported for each aminoalcohol and for oxidation products:

- Ethanolamine: $NH_2C\underline{H}_2CH_2OH$ (δ = 2.7, triplet, J = 5.6), $NH_2CH_2C\underline{H}_2OH$ (δ = 3.5, triplet, J = 5.6).
- Glycine: $NH_2C\underline{H}_2COOH$ (δ = 3.1, singlet).
- 2-Methyaminoethanol: $C\underline{H}_3NHCH_2CH_2OH$ (δ = 2.2, singlet), $CH_3NHC\underline{H}_2CH_2OH$ (δ = 2.5, triplet, J = 5.6), $CH_3NHCH_2C\underline{H}_2OH$ (δ = 3.5, triplet, J = 5.6).
- Sarcosine: $C\underline{H}_3NHCH_2COOH$ (δ = 2.2, singlet), $CH_3NHC\underline{H}_2COOH$ (δ = 3.0, singlet).
- 2-Dimethyaminoethanol: $(C\underline{H}_3)_2NCH_2CH_2OH$ (δ = 2.10, singlet), $(CH_3)_2NC\underline{H}_2CH_2OH$ (δ = 2.4, triplet, J = 6.4), $(CH_3)_2NCH_2C\underline{H}_2OH$ (δ = 3.6, triplet, J = 6.4).
- *N*,*N*-dimethylglycine: $(C\underline{H}_3)_2NCH_2COOH$ (δ = 2.1, singlet), $(CH_3)_2NC\underline{H}_2COOH$ (δ = 2.8, singlet).
- Glycolic acid: $HOC\underline{H}_2COOH$ (δ = 3.8, singlet).
- Formic acid: $\underline{H}COOH$ (δ = 8.30, singlet).

Fig. 1 reports as an example ^{1}H NMR signal evolution for DMAE oxidation at t: (a) 0 min; (b) 30 min; (c) 1 h; (d) 2 h.

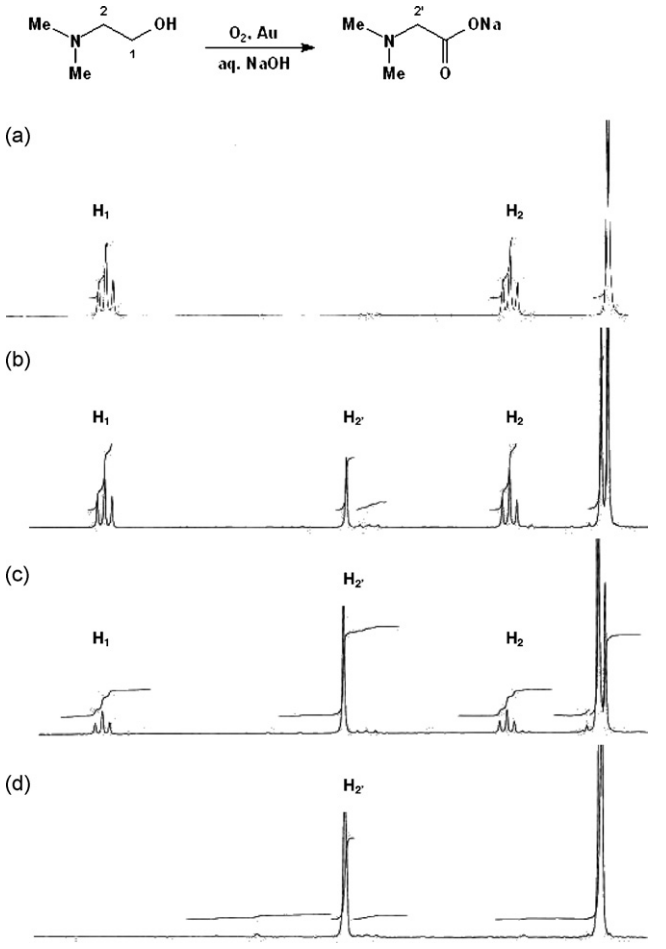

Fig. 1. ^{1}H NMR signal evolution for DMAE oxidation at *t*: (a) 0 min; (b) 30 min; (c) 1 h; (d) 2 h.

3. Results and discussion

We principally investigate the behaviour under oxidative conditions of three aminoalcohols: ethanolamine (EA), 2-methylaminoethanol (MAE), 2-dimethylaminoethanol (DMAE), differing each other by the groups beared by nitrogen. This study was performed in order to investigate the influence of N-substitution and reaction conditions on the activity/selectivity of gold catalysts in the liquid phase oxidation of β-aminoalcohols using O_2 as the oxidant.

It has been already shown that basic conditions promoted the oxidation of alcohols in aqueous phase [14], and this happened also in the case of aminoalcohol despite amino group provides a basic environment. For aminoalcohol oxidation it was also shown that gold on oxides resulted more active than gold on active carbon [16].

Thus, first of all we tested two different oxide-supported Au catalysts, varying the NaOH/reactant molar ratio (from 0 to 4 mol/mol) and the temperature (range 40–70 °C), the DP prepared 5% Au/Fe_2O_3 (Table 1) and sol prepared 1% Au/MgO (Table 2). For both the catalysts the results showed that the use of strong basic conditions (pH > 14) improves the selectivity to the corresponding aminoacid as well as the conversion. At 60 °C, without the presence of an additional base as well as at controlled pH (11 ± 0.2), the selectivity was really poor (even at low conversion) except in the case of DMAE that can be smoothly oxidized to aminoacid with always a pretty good selectivity (68–75% without pH control; 79–83% at pH 11). The main product is usually the corresponding aminoacid, but also variable amounts of glycolic acid (up to 17%), formic acid (up to 40%) and unknown by-products are formed. The selectivity more than the activity is affected by the variation of conditions. In the cases of EA and MAE we observed that by increasing the temperature the activity of the catalysts decreased, on the contrary of what is generally expected in catalytic experiments. Although the selectivity to aminoacid increases, we correlated this behaviour to the *nature* of by-products: in fact by increasing the temperature an increased amount of unknown by-products was formed. These could be responsible through irreversible adsorption on the surface of the catalyst, of a decreasing of active sites amount and thus producing a deactivating effect on the catalyst. As a consequence we observed that conversion decreases by increasing the temperature. Indeed, when negligible amount of by-products are produced, as in the case of DMAE, the expected behaviour of catalysts was observed with increasing of conversion with the temperature.

Table 1
Aminoalcohol oxidation with 5% Au/Fe_2O_3 (WGC)

NaOH/reactant	Temperature (°C)	EA		MAE		DMAE[a]	
		%C	%S	%C	%S	%C	%S
0[b]	60	13	38	4.4	60	48	68
pH = 11	60	59	24	11	71	54	79
1	40	33	63	53	47	33	>95
4	40	50	93	60	72	42	>95
1	70	16	55	69	57	71	>95
4	70	53	69	70	74	68	>95

Reaction conditions: [reactant] = 0.3 M; reactant/Au = 500; $p(O_2)$ = 3 atm; time = 4 h.
[a] Time = 30 min.
[b] Initial pH about 10.5.

N-oxidation and formation of the N-oxides is only observed when DMAE is oxidized under mild basic conditions (pH 10.5 or 11, selectivity to N-oxide up to 21%). This result is in agreement to previous observations that reported a high selectivity to N-oxide when 3-(dimethylamino)-1-propanol was oxidized in the presence of Au/C, Au/Al_2O_3 and Au/TiO_2 at pH 10 [18] and formation of caprolactam when 1,6-hexanediamine is oxidized with Au/TiO_2 using dioxane as the solvent [19]. However, as mentioned above, when strong basic conditions were employed, regardless the catalytic system employed, the selectivity to aminoacid resulted >95%.

It should be also noted that increasing the base amount (from 1 to 4 equivalents) the effect on selectivity was negligible whereas we observed enhancement in the activity of catalysts (Tables 1 and 2). The basic properties of MgO probably mask the effect of increasing the NaOH amount. Indeed the effect becomes strong in the case of Fe_2O_3. However we cannot exclude that also the preparation method (DP or sol immobilization) plays an important role.

Table 2
Aminoalcohol oxidation with 1% Au/THPC/MgO

NaOH/reactant	Temperature (°C)	EA		MAE		DMAE[a]	
		%C	%S	%C	%S	%C	%S
0[b]	60	20	21	13	<5	29	75
pH = 11	60	21	36	46	14	34	83
1	40	91	44	38	89	35	>95
4	40	92	54	44	95	39	>95
1	70	80	74	22	37	67	>95
4	70	84	87	37	49	65	>95

Reaction conditions: [reactant] = 0.3 M; reactant/Au = 500; $p(O_2)$ = 3 atm; time = 4 h.
[a] Time = 30 min.
[b] Initial pH about 10.5.

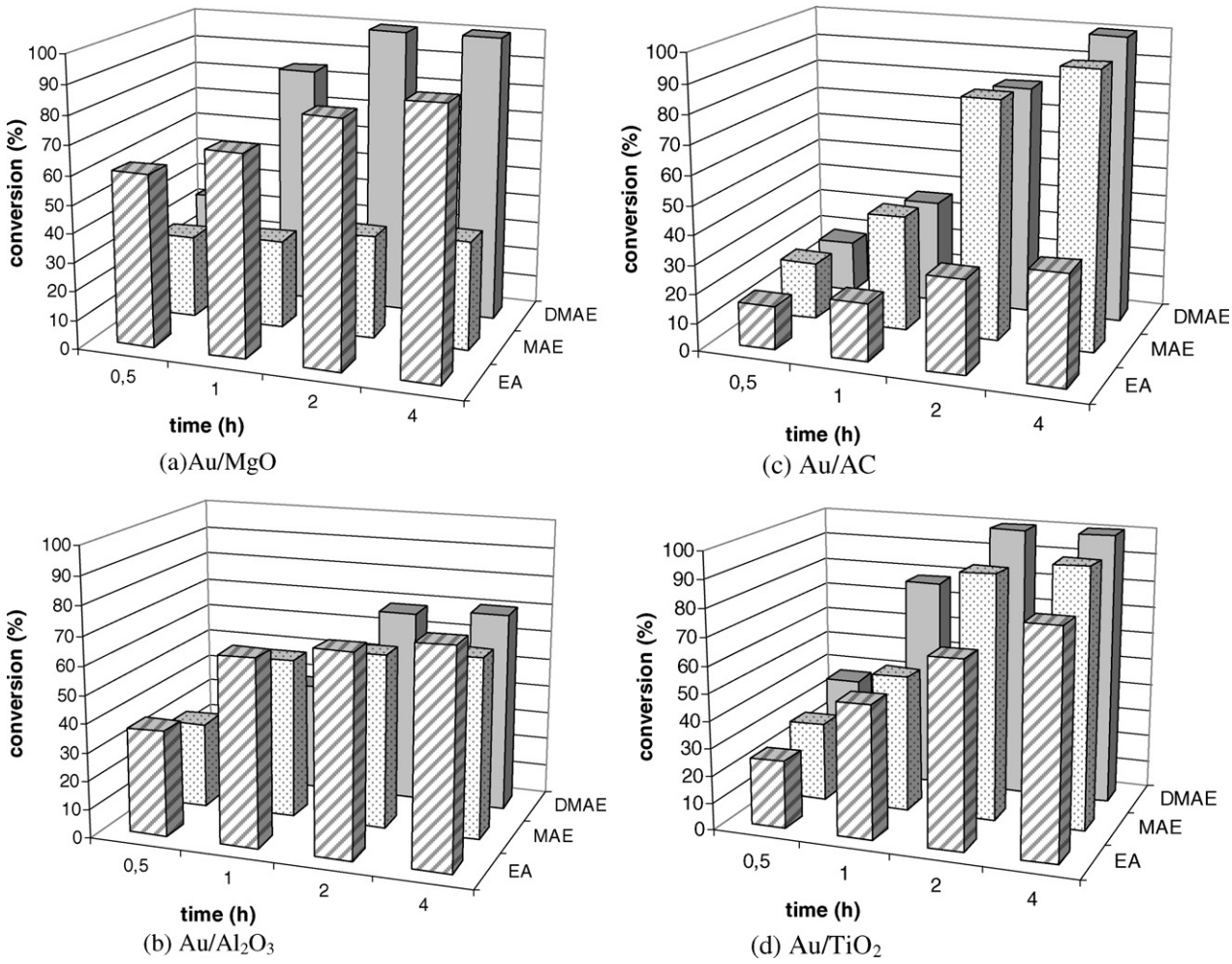

Fig. 2. Conversions of aminoalcohols using sol derived catalysts: (a) 1% Au(THPC)/MgO; (b) 1% Au(THPC)/Al_2O_3; (c) 1% Au(THPC)/AC; (d) 1% Au(THPC)/TiO_2. Reaction conditions: [reactant] = 0.3 M, NaOH/reactant = 4 mol/mol, reactant/Au = 500 mol/mol, $p(O_2)$ = 300 kPa, T = 313 K.

Thus we prepared gold catalysts by two different methodologies (sol immobilization and deposition–precipitation) using supports of different acid–base properties (activated carbon, TiO_2, Al_2O_3, MgO, Fe_2O_3). We choose to test them under the following experimental conditions in order to maximize the selectivity to aminoacids: 0.3 M solution, NaOH/reactant = 4 mol/mol, reactant/Au = 500 mol/mol, T = 40 °C, $p(O_2)$ = 3 atm.

Fig. 2a–d reported the results obtained using gold catalysts prepared by immobilization of a THPC sol on MgO, Al_2O_3, activated carbon, and TiO_2. Conversions versus time are shown for the three reactants. Conversely, Fig. 3a–d show the results with DP prepared catalysts (Fe_2O_3, Al_2O_3, MgO, TiO_2) some of them available commercially from WGC. To be noted that Au/C could not be prepared by DP [23] and Au/Fe_2O_3 could not be prepared by sol immobilization as the support is not available commercially.

The gold sol resulted in a narrow particle distribution centred at 3.0 nm. The immobilization step did not affect the distribution (3.6 nm for Au/TiO_2) except in the case of carbon where some aggregation can be seen (mean size 8 nm) [24]. Among DP prepared samples, commercial ones (Au/Fe_2O_3 and Au/TiO_2) are reported to show a similar mean size (3.7 nm) [25] as the sol preparations, and also on Al_2O_3 and MgO the metal mean size resulted similar (4.0 nm).

Moreover the loading of DP catalysts was not strictly the same, as the preparation method does not allow to finely control this parameter. Consequently, catalytic tests were carried out slightly varying the catalyst amount for obtaining always the same molar ratio (reactant/Au = 500 mol/mol).

Generally, following the conversion as a function of time, what clearly appeared is that catalysts underwent very often to deactivation. This phenomenon appeared to be correlated not only to the catalyst used but also to the reactant structure. This latter point will be discussed later. Deactivation seems to be not correlated to the low selectivity: AC, that produced the lowest selectivity to aminoacid (50%), resulted one of the most resistant catalyst (Fig. 2c). On the contrary the most deactivated, and also poorly active, catalyst resulted Au/Al_2O_3 prepared with both method (Figs. 2b and 3b), but the selectivity was in the range 75–95%.

Generally the preparation method appeared important though the influence varied from support to support. Au/MgO presented the most strong difference between the two preparations (Figs. 1a and 3d, Table 3), being the activity of the one prepared by DP almost negligible. The strong difference is maintained with all the three reactants. Au/MgO prepared by sol immobilization was really more active than the one prepared by DP even much less selective. The two preparations on Al_2O_3 (Figs. 2b and 3b) behaved similarly when EA and MAE were used as the reactants in terms of either activity and selectivity. However, when DMAE was used, full conversion (and selectivity >95%) was obtained only using the DP preparation.

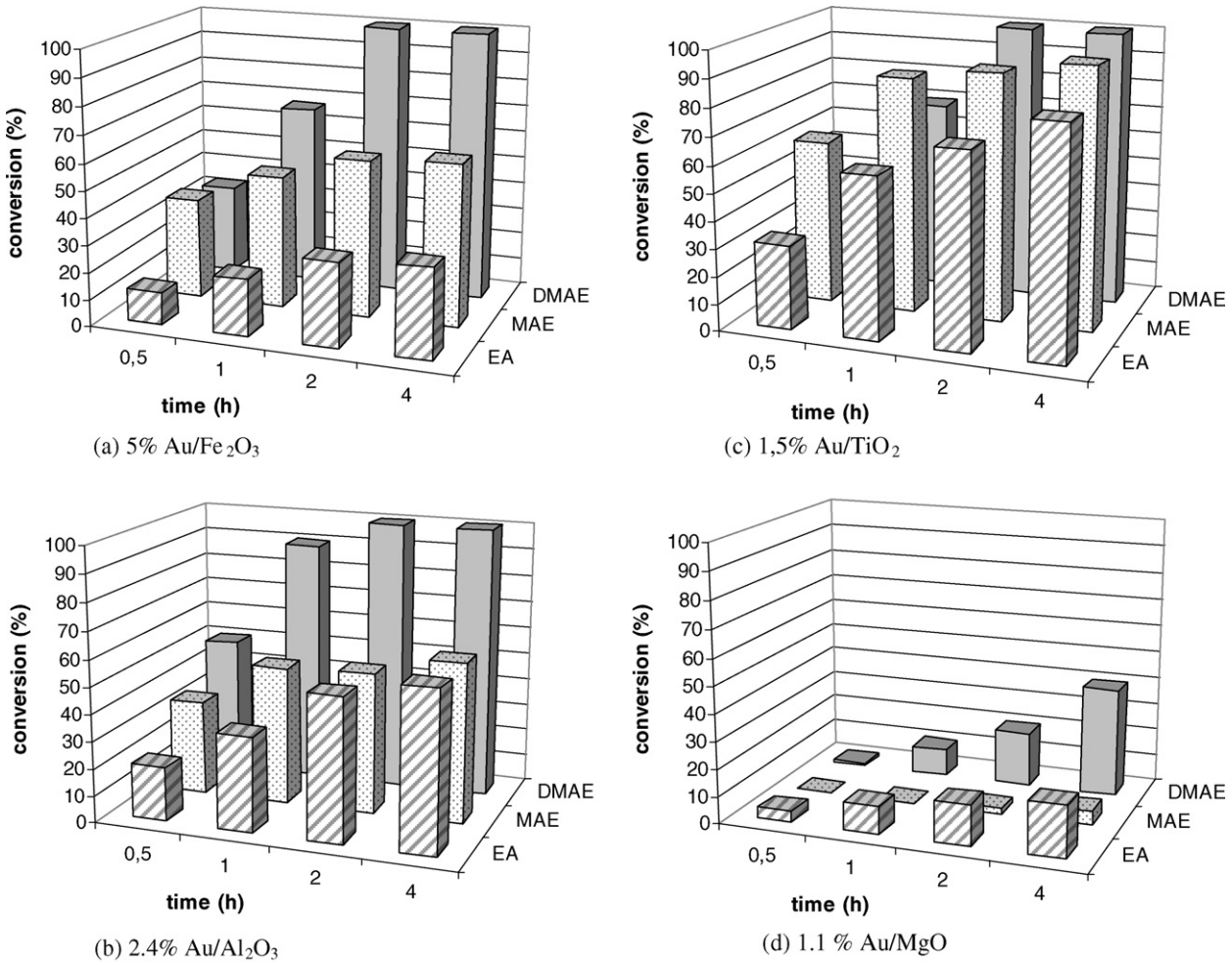

Fig. 3. Conversions of aminoalcohols using DP prepared catalysts: (a) 5% Au/Fe_2O_3 (WGC); (b) 2.33% Au(DP)/Al_2O_3; (c) 1.5% Au/TiO_2 (WGC); (d) 1.1% Au(DP)/MgO. Reaction conditions: [reactant] = 0.3 M, NaOH/reactant = 4 mol/mol, reactant/Au = 500 mol/mol, $p(O_2)$ = 300 kPa, T = 313 K.

Considering the TiO_2 support (Figs. 2d and 3c, Table 4) we observed an initial activity of DP preparation superior than the sol one. However, due to different conversion profiles, the same conversion was reached in about the same time (Table 5). Selectivities were comparable for the two preparations in the case of EA (86% for DP and 87% for sol preparation at 82% conversion) and in the case of MAE (78% for the DP preparation and 75% for the sol technique at 95% conversion), but it was better with DP preparation in the case of DMAE (>95% for DP preparation vs. 70% for the sol one at full conversion).

Au/Fe_2O_3 (Table 2, Fig. 3a) did not appear the most active but one of the most selective especially in the case of EA ($S_{30} > 90\%$). However, also in this case deactivation represents the main problem.

The Au sol prepared catalysts in liquid phase oxidation using O_2 as the oxidant generally show a better resistance to deactivation either in terms of resistance to oxygen poisoning or for irreversible adsorption. Normally this behaviour is addressed to the presence of a protective agent on the surface of Au nanoparticles, which can prevent metal migration and restructuring of the catalyst [26].

Table 3
Comparison between Au/MgO catalysts prepared by two different methods

Catalyst preparation	Time (h)	EA		MAE		DMAE	
		%C	%S	%C	%S	%C	%S
THPC	0.5	73	54	7	>95	39	>95
	1	84	49	24	>95	93	>95
	2	92	49	31	95	100	>95
	4	92	44	44	89	100	>95
DP	0.5	4	>95	0.0	nd	0.7	nd
	1	10	>95	0.0	nd	8.4	90
	2	15	>95	2.2	0.0	21	84
	4	19	>95	4.7	0.0	40	76

Reaction conditions: [reactant] = 0.3 M; NaOH/reactant = 4 mol/mol; reactant/Au = 500; $p(O_2)$ = 3 atm; T = 40 °C.

Table 4
Comparison between Au/TiO_2 catalysts prepared by two different methods

Catalyst preparation	Time (h)	EA		MAE		DMAE	
		%C	%S	%C	%S	%C	%S
THPC	0.5	25	>95	29	>95	37	82
	1	49	>95	50	90	78	75
	2	68	87	90	78	100	70
	4	82	87	95	75	100	56
DP	0.5	31	>95	60	84	34	>95
	1	59	91	86	80	69	>95
	2	71	88	90	78	100	>95
	4	83	86	95	78	100	>95

Reaction conditions: [reactant] = 0.3 M; NaOH/reactant = 4 mol/mol; reactant/Au = 500; $p(O_2)$ = 3 atm; T = 40 °C.

Table 5
Comparison between Au on TiO_2 and MgO prepared by sol immobilization

Catalyst	Time (h)	EA		MAE		DMAE	
		%C	%S	%C	%S	%C	%S
Au/TiO_2	0.5	20	>95	29	>95	37	82
	1	49	>95	40	95	78	75
	2	68	87	95	78	100	70
	4	82	87	98	75	100	56
Au/MgO	0.5	73	54	7	>95	39	>95
	1	84	49	24	>95	93	>95
	2	92	49	31	95	100	>95
	4	92	44	44	95	100	>95

Reaction conditions: [reactant] = 0.3 M; NaOH/reactant = 4 mol/mol; reactant/Au = 500; $p(O_2)$ = 3 atm; T = 40 °C.

Table 6
Comparison between Au on TiO_2 and Fe_2O_3 prepared by DP (commercial)

Catalyst	Time (h)	EA		MAE		DMAE	
		%C	%S	%C	%S	%C	%S
Au/TiO_2	0.5	31	>95	60	84	34	>95
	1	59	91	86	80	69	>95
	2	70	88	92	80	100	>95
	4	83	86	95	78	100	>95
Au/Fe_2O_3	0.5	12	>95	37	95	33	>95
	1	21	>95	49	95	67	>95
	2	31	>95	58	88	100	>95
	4	33	93	60	72	100	>95

Reaction conditions: [reactant] = 0.3 M; NaOH/reactant = 4 mol/mol; reactant/Au = 500; $p(O_2)$ = 3 atm; T = 40 °C.

However we highlighted that in this reaction the deactivation seems comparable in the case of sol and DP prepared catalysts.

Moreover, evaluating the conversion profiles reported in Fig. 2a–d, it is clear that among the sol prepared catalysts, Au/MgO and Au/TiO_2 were the most promising ones. Table 5 reported the data of conversion and selectivity to aminoacid. With EA selectivity at almost isoconversion (82% for Au/TiO_2 and 84% for Au/MgO) resulted 87% for Au/TiO_2 but only 44% for Au/MgO. Deactivation was very strong for Au/MgO when MAE was used as the reactant (Fig. 2, Table 5). On the contrary Au/TiO_2, in this latter case, allowed to reach 95% conversion with a good selectivity (78%). An opposite behaviour was observed in the case of DMAE: both the catalysts reached full conversion, but Au/TiO_2 presented a worse selectivity (70%) than Au/MgO (>95%). It should be also observed that in the case of Au/TiO_2 the reaction proceeded towards a degradation of aminoacid (the selectivity decreases from 70% to 56% in 2 h, see Table 5). On the contrary, the aminoacid seems stable in the presence of Au/MgO, this behaviour being a possible explanation of the observed high selectivity.

Table 6 reported the comparison of the catalytic performances of the two commercial catalysts: 5% Au/Fe_2O_3 and 1.5% Au/TiO_2, both prepared by DP. From a selectivity point of view the two catalysts appeared similar but the data of conversion versus time clearly show that Au/Fe_2O_3 underwent strong deactivation except when DMAE was used.

The behaviour of different oxides were highlighted but it is really difficult to have a definite answer on the effect of support composition as many parameters (reactant structure, preparation methods, and so on) are present. TiO_2 appeared the most generally applicable support.

Considering the reactant structure, DMAE oxidation showed in the most tests very high selectivity to aminoacid. Best results (selectivity > 95% at full conversion) can be reached using Au catalyst prepared via sol immobilization on MgO or by deposition–precipitation on Fe_2O_3, TiO_2 or Al_2O_3. Moreover, only two of the eight catalysts tested (sol prepared Au/Al_2O_3 and DP prepared Au/MgO) underwent deactivation in this reaction. On the contrary, for the other two reactants (EA and MEA) we *always* observed deactivation and lower selectivity, thus making the choice of the catalytic system more important. Since DMAE and MAE differ by N-methyl substitution, we addressed this behaviour to this structural feature. In fact by using EA (not substituted amino group) deactivation appeared even more important.

A possible explanation could be derived from the proposed reaction mechanism. In fact a similar mechanism as the one accepted for gold-catalyzed alcohol oxidation [14] has been recently proposed for primary and secondary amines, which can be oxidized towards nitriles and imines on the surface of ruthenium nanoparticles [17]. Nevertheless, some differences have been recently underlined between Au and Pd catalyzed oxidation [27], this making a similarity among different metals little significant. However, on the basis of this oxidative dehydrogenation mechanism we could explain the formation of the principal by-products (formic acid and glycolic acid) that we observed during EA and MAE oxidation. In Fig. 4a possible reaction pathway for MAE is reported. When DMAE is used as the reactant, the proton abstraction does not take place and imine formation is neglected. Thus aminoacid represents the main product of the oxidation and the reaction show higher selectivity.

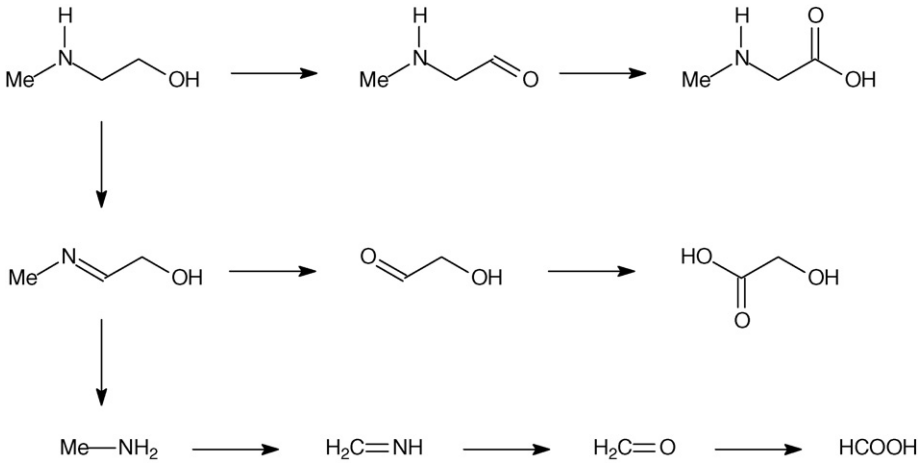

Fig. 4. Proposed reaction pathway for aminoalcohol oxidation.

The presence of a tertiary amino group have also a positive influence on the durability of the catalyst: DMAE oxidation reached full conversion with almost all the catalysts tested. For this reason, deactivation seems more influenced by the reactant structure than by any other experimental parameters. A reasonable explanation for this behaviour could be the sterical hindrance of the tertiary amino group. In fact it is known that aliphatic amines strongly interact with noble metals, resulting in their catalytic deactivation [28]. Probably, a sterically hindered amino group cannot interact strongly with the metal surface and the catalyst is not deactivated. Another possible explanation is that catalyst deactivation occurs because of the formation, and subsequent adsorption, of oligomers (oligoamides) on the metal surface. So, when DMAE is used as the reactant, amide formation is prevented and deactivation does not occur. However, in the future this phenomenon will be investigated thoroughly.

4. Conclusions

Different gold catalysts have been compared in the selective oxidation of aminoalcohols to aminoacids. The experimental conditions appeared to be very important as using strong basic conditions we are able to avoid the oxidation of the amino group, that should have been expected as the most important parallel reaction. Only a few percent of N-oxide derivative have been detected in the case of DMAE. Basic conditions and moderate temperature (40 °C) represent a good compromise for enhancing selectivity to aminoacids. Nevertheless the experimental conditions don't represent the sole parameter to be considered. Indeed the N-substitution of the amino group appeared fundamental, being DMAE generally producing a better selectivity. We principally addressed this behaviour to parallel reactions that could take place when N is bearing H (i.e. primary or secondary amines) thus producing imines as intermediates (Fig. 4). We also investigated the influence of preparation methods, comparing deposition–precipitation (DP) with sol immobilization. Though normally sol prepared catalysts appeared more resistant to deactivation than DP prepared catalysts, in this reaction we highlighted a strong effect due to products, and deactivation became the principal problem of the reaction. Support nature has been revealed also important and TiO_2 resulted the most versatile support.

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