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Gold on Carbon as a New Catalyst for Selective Liquid Phase Oxidation of Diols

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Catalytic oxidation of vicinal diols to α-hydroxy carboxylates with dioxygen in alkaline solution has been performed by using gold based catalysts. The optimization of the catalytic system has highlighted the influence of the support and preparation method on both activity and selectivity. Under mild conditions ($T = 343$–363 K, $pO_2 = 300$ kPa (absolute)) high selectivities (90–100%) toward monooxygenation in the cases of ethane-1,2-diol and propane-1,2-diol were achieved at high diol conversions (80–94%). The racemization of optically active propane-1,2-diol during its oxidation as well as isotopic H-D exchange experiments allowed us to deduce new features in the mechanism of diol oxidation and concerning the dependence of selectivity on reaction conditions. The recycling of gold on carbon catalyst revealed its good resistance toward deactivation, greater than palladium or platinum on carbon catalysts which were respectively affected by metal leaching and a considerable loss of selectivity. © 1998 Academic Press

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1. INTRODUCTION

Catalytic oxidation involving the use of dioxygen as the oxidant has attracted great interest as a *clean* alternative to stoichiometric or enzymatic oxidation. Unfortunately the activation of dioxygen by means of metals can induce radical reactions that decrease selectivity, particularly in the case of polyfunctional molecules (1). Moreover such reactants usually present low thermal stability, thus requiring mild experimental conditions normally achieved in the liquid phase. However, under these conditions, there are a few drawbacks that limit industrial application (2). In addition to the problem of selectivity, catalyst deactivation tends to occur that appears to be caused either by the chemical species being strongly adsorbed on active sites or by a poisoning effect of the dioxygen itself on the catalyst (3).

Solutions to both problems have been proposed (particular experimental conditions (2), diffusion stabilized carriers (4)), but a decisive factor is the chemical nature of the metal catalyst. Until now the most promising innovation has been the use of promoters (e.g., bismuth or lead) to modify the platinum or palladium catalysts. In fact, in the field of carbohydrates, as in the transformation of glucose to gluconic acid, the use of the above-mentioned bimetallic catalysts has led to excellent results in term of both selectivity and catalyst lifetime (5). Less investigated are the new catalytic materials showing intrinsic high selectivity and catalytic resistance to chemical poisoning.

This paper deals with our studies, following preliminary catalytic tests reported recently (6), on new gold-based catalysts and their application to catalytic oxidation of vicinal diol in water solution. In particular, a valuable target for the synthesis of glycolic acid and lactic acid lies in the monooxygenation of ethane-1,2-diol and propane-1,2-diol to these important products. Present-day chemical methods involve the use of toxic or corrosive reagents as well as high pressure apparatus (Scheme 1) (7). A fermentation process, available for lactic acid production, is affected by low productivity and severe purification problems.

Moreover, isotopic H-D exchange experiments in D_2O have given new insight into the reaction pathway of diol oxidation under basic conditions.

2. EXPERIMENTAL

2.1. Reagents and Apparatus

Diols, glyoxal, hydroxyacetone and pyruvic aldehyde were of the highest purity from Fluka and were used without any further purification. R(-)-propylene glycol was from Fluka, showing $[\alpha]_D$ $-16.5 \pm 1^\circ$ (in substance). NaOH and D_2O were 99.9% pure from Merck and stored under nitrogen. NaOD was 40% in D_2O (>99.5 at% D) from Fluka. Gaseous oxygen from SIAD was 99.99% pure. Gold powder was of the highest purity grade from Fluka. Commercial 5% Pd/C was supplied by Süd Chemie-M.T., 5% Pt/C by Engelhard.

Activated carbon (5–100 μ) had a specific area of 1200 m^2/g; Al_2O_3 from La Roche had a specific area of 420 m^2/g.

Reactions were carried out at the appropriate temperature in a thermostat-controlled glass reactor (30 ml) provided with an electronically controlled magnetic stirrer connected to a large reservoir (5000 ml) containing oxygen at

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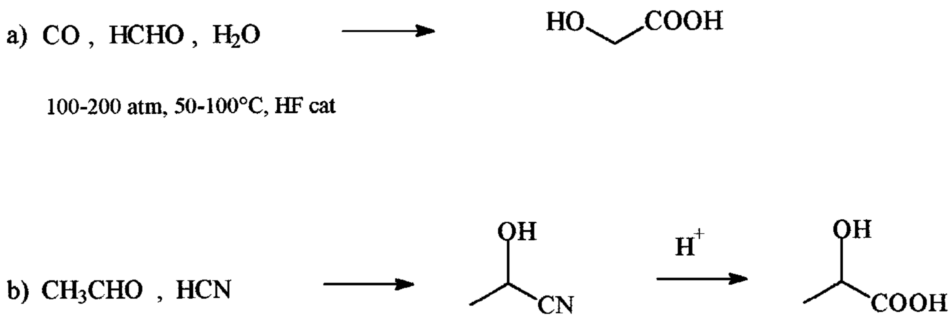


SCHEME 1. Industrial chemical route to glycolic acid (a) and lactic acid (b).

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.

2.2. *Catalysts Preparation*

Gold catalysts were prepared using a $HAuCl_4$ 0.1 *M* solution obtained by dissolving 1.97 g of gold powder in a minimum amount of a 3 : 1 (v/v) mixture of concentrated HCl and HNO_3 and then diluted to 100 ml with distilled water. After reduction all the catalysts were filtered and then washed with hot water until the filtrate was chloride free (AgCl test). The catalysts were used in wet form.

2.2.1. Gold on alumina. 1% Au on Al_2O_3 was prepared by using either incipient wetness impregnation (see below) or a deposition–precipitation method previously reported (8). The reduction step was performed by calcinating the catalyst at 623 K for 3 h in air.

2.2.2. Gold on carbon. (a) Incipient wetness impregnation. The support (2 g) was impregnated with 1 ml of 0.1 *M* $HAuCl_4$ diluted with distilled water to a volume equal to its pore volume. The suspension was mixed for 20 min and then added to a hot solution of HCOONa (20 ml of water and 200 mg of sodium formate).

(b) Deposition–precipitation method. The solution of $HAuCl_4$ 0.1 *M* (1 ml) was diluted with distilled water (10 ml) and a saturated solution of Na_2CO_3 was added until a fixed pH of 10 was reached. Then the mixture was added to a stirred slurry of carbon (2 g) in distilled water (20 ml). The slurry was allowed to stand for 1 h and then heated to 343 K and reduced by adding HCHO 37% (1.5 ml) dropwise.

On carbon support we have some evidence that the carbon itself acts as the reductant. In fact a catalyst prepared without adding HCHO is already active (although to in a minor extent) and contains all the gold added (ICP analysis). The HCHO is added to ensure a complete reduction of gold.

2.2.3. XRPD. X-ray diffraction experiments were performed on a Rigaku D III-MAX horizontal-scan powder diffractometer with Cu-Kα radiation, equipped with a graphite monochromator in the diffracted beam. Crystallite sizes of gold were estimated from peak half-widths by using Scherrer's equation with corrections for instrumental line broadening.

2.3. *Oxidation Procedures*

2.3.1. Oxidation under strong alkaline conditions. The reactant (8 mmol), NaOH (8.25 mmol), and the catalyst (reactant/metal = 1000) were mixed in distilled water (total volume 10 ml). The reactor was pressurized at 300 kPa of O_2 and thermostat-controlled at the appropriate temperature. The mixture was stirred and the samples analyzed at various times by HPLC and ^{13}C-nmr.

2.3.2. Stability tests of intermediates. Reactant (8 mmol), NaOH (8 mmol), and eventually the catalyst (reactant/metal = 1000) were mixed in distilled water (total volume 10 ml). The reactor was closed in an inert atmosphere (N_2) and thermostat-controlled at 343 K. The mixture was stirred and then analyzed by HPLC and ^{13}C-nmr.

2.3.3. Oxidation of propane-1,2-diol at pH 8. The reactant (0.52 g, 6.8 mmol) and the catalyst (diol/M = 1000) were mixed in distilled water (total volume 10 ml). Dioxygen was bubbled at atmospheric pressure into the stirred mixture thermostat-controlled at the appropriate temperature. A solution of NaOH 0.1 *M* was added dropwise to maintain the pH of the solution at 8. The pH was measured by a Metrohom 744 pH meter. Samples were analyzed at various times by HPLC.

2.3.4. Recycling tests. After the first run the catalyst was filtered off and reused in the next run with a freshly prepared solution of glycol. After four runs the catalyst was filtered and washed several times with water until the neutral pH of water was reached. The metal content was determined by ICP analysis on a Jobin Yvon JY24.

2.4. *H-D Exhange Experiments*

All the reagents were handled under N_2 after exchange of labile hydrogen (OH) which was performed by dissolving the reactants in D_2O and then evaporating the solution. The reagent was then redissolved in D_2O and allowed to react with O_2, following the same oxidation procedure as reported above, except that NaOD was used instead of NaOH. ^{1}H and ^{13}C-nmr spectra were registered and the solution evaporated. The D-nmr spectrum was registered by dissolving the residue in H_2O and the D-H exchange evaluated by comparison of ^{1}H and D-nmr spectra.

2.5. *Analysis of Products*

The products were identified by comparison with authentic samples. Quantitative analyses were performed by either HPLC or ^{13}C-nmr methods, using an internal standard (propionic acid).

2.5.1. HPLC analysis. Analyses were performed on a Varian 9010 instrument equipped with a Varian 9050 UV detector (210 nm) in the cases of deuterated reagents, whereas a Varian R.I. detector was used in other cases. An Alltech OA-1000 column (300 mm × 6.5 mm) was used with aqueous H_2SO_4 0.01 *M* (pH 2.1) (0.8 ml/min) as the eluent. Samples of reaction mixture (0.1 ml) were diluted (10 ml) by using the eluent after adding the standard.

2.5.2. NMR analysis. ^{13}C-^{1}H- and D-nmr spectra were recorded in water on a Varian 200 MHz. Samples of reaction mixture were neutralized with HCl 12N before adding the standard.

3. RESULTS AND DISCUSSION

Gold has long been used in electrooxidation (9); however, in heterogeneous catalysis it has been regarded as a poorly active metal until the discovery of suitable methods for its deposition as nanoparticles on oxidic supports has led to a revaluation of its use also in this field (10). In fact the behaviour of gold that is finely dispersed on a support differs drammatically from a smooth surface or relatively large particles and it has been found that there is a marked interaction between the support and the metal (10a). Moreover, gold is reported to decrease the dissociative adsorption of dioxygen in favour of a molecular one and to inhibit subsurface oxygen diffusion (11). Thus, as catalyst deactivation during alcohol oxidation in water solution has partly been ascribed to the formation of less active oxidized metal species, we were led to hypothesized a smaller poisoning effect of O_2 on supported gold catalysts with respect to palladium or platinum ones.

3.1. *Oxidation of Ethane-1,2-diol*

In ethane-1,2-diol catalytic oxidation, a few studies have indicated a limited application of platinum and palladium catalysts because of the overoxidation that normally occurs with C–C bond cleavage, forming CO_2. As a consequence, patent literature mainly reports catalytic processes on protected reactants such as methoxy glycol and polyethylene glycol (12), or claims high selectivity (95%) by using palladium or platinum on carbon doped with lead (13). To the best of our knowledge, the most notable result in glycolic acid production from ethane-1,2-diol was claimed using an Ir on carbon catalyst operating at 10 atm and 80°C (87% selectivity at 98% conversion) (14). We recently reported that 1% Au on carbon allows a selectivity of 90% at 94% conversion of ethane-1,2-diol under mild conditions (343 K, 300 kPa O_2) in alkaline solution, whereas, at comparable conversion, by using commercial Pd or Pt on a carbon catalyst glycolic acid is produced in 70% selectivity, forming oxalate, formate, and carbonate by-products (6). On comparing various supports such as carbon, aluminum oxide, cerium oxide, and iron oxide, carbon was found to be peculiar. Using gold-supported catalysts on carbon and alumina prepared by two different methods, incipient wetness impregnation (15) and deposition–precipitation (8) (reported to produce differently sized gold particles (10b)) we confirmed that the particular behaviour of Au/C greatly depends on the nature of the supports. In particular, as reported in Table 1, XRDP measurements revealed comparable nanoparticles with the deposition–precipitation method on both carbon (7 nm) and alumina (8 nm), these being smaller than those obtained by incipient wetness impregnation (12 nm on carbon and 20 nm on Al_2O_3). Nevertheless, higher activities correspond to smaller particle diameter only on comparing carbon and alumina separately, and the same trend was also observed for selectivity. In fact larger particles on carbon (12 nm) are more active and selective than smaller ones on Al_2O_3 (8 nm). Figure 1 shows that gold on carbon is more selective than gold on alumina at all the conversions, the selectivity in both cases being almost constant. Therefore, the higher activity and selectivity of gold on carbon with respect to the alumina seem to be correlated to a different cooperative effect of the support.

The stability of the reaction product and the intermediates in alkaline solution under oxidative conditions plays an important role in considering the selectivity obtained with different catalytic systems. As shown in Table 2, a solution of sodium glycolate is quite stable at 343 K in the presence of

TABLE 1

Influence of Preparation Methods and Supports on Activity and Selectivity of 1% Au Catalysts

Preparation method	Support	Gold particles diameter (nm)	TOF^c mol conv./ mol Au/h	Select.% to glycolate at 80% conv.
a	Al_2O_3	20	117	50
b	Al_2O_3	8	273	68
a	carbon	12	325	86
b	carbon	7	405	93

Note. Reaction conditions: ethane-1,2-diol/Au = 1000; NaOH/ethane-1,2-diol = 1; T = 343 K; pO_2 = 300 kPa. (a) incipient wetness impregnation; (b) deposition–precipitation.

[c] TOF numbers were calculated on the basis of total gold.

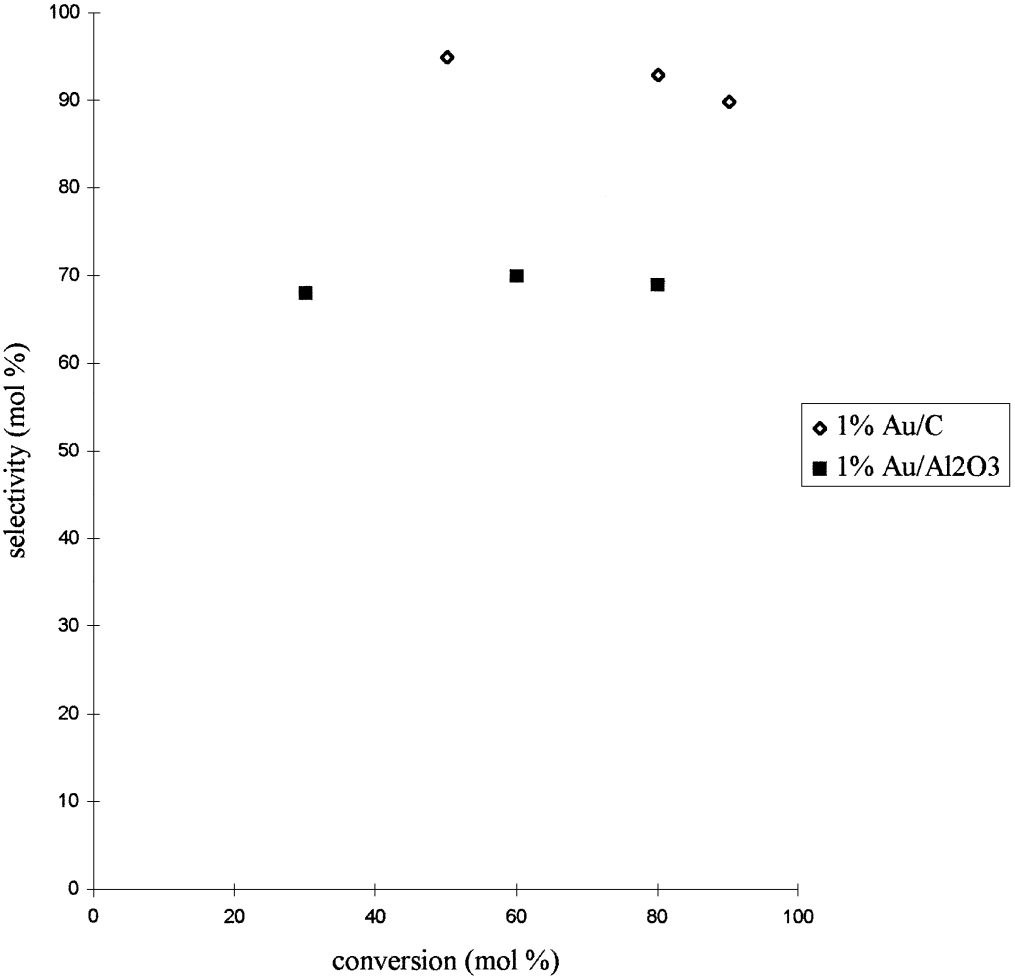


FIG. 1. Oxidation of ethane-1,2-diol to glycolate. Reaction conditions as reported in Table 1; detectable byproducts are formate and carbonate. Both catalysts were prepared by deposition–precipitation method.

1% gold on carbon, whereas it is oxidized in the presence of 5% palladium on carbon or 5% platinum on carbon to produce relevant amounts of oxalate and carbonate.

Considering the facile Canizzaro reaction which occurs under alkaline conditions with glyoxal (I) and glyoxylate (II) we can also derive a different route for glycolate formation with respect to the oxidation of a single alcoholic function.

(I) $\mathrm{CHOCHO} \rightarrow \mathrm{HOCH_2COO^-}$

(II) $2\,\mathrm{CHOCOO^-} \rightarrow \mathrm{HOCH_2COO^-} + {}^-\mathrm{OOCCOO^-}$

However, the absence of oxalate in the products in both Au-catalyzed oxidation of glycolate (Table 2) and ethane-1,2-diol (6) seems to exclude, in the case of gold, the formation of glyoxylate as an intermediate. Moreover, the absence of glyoxylate does not exclude the formation of glyoxal as, under basic conditions, this dialdehyde immediately leads to the Canizzaro reaction, limiting any further oxidation to glyoxylate.

In conclusion, the reaction pathway in the case of the gold on carbon catalyst could be represented by Scheme 2, where glycolic acid could either be directly produced by a stepwise oxidation of a single alcoholic function or produced by an intramolecular Canizzaro reaction from glyoxal. Considering the product distribution, in the case of

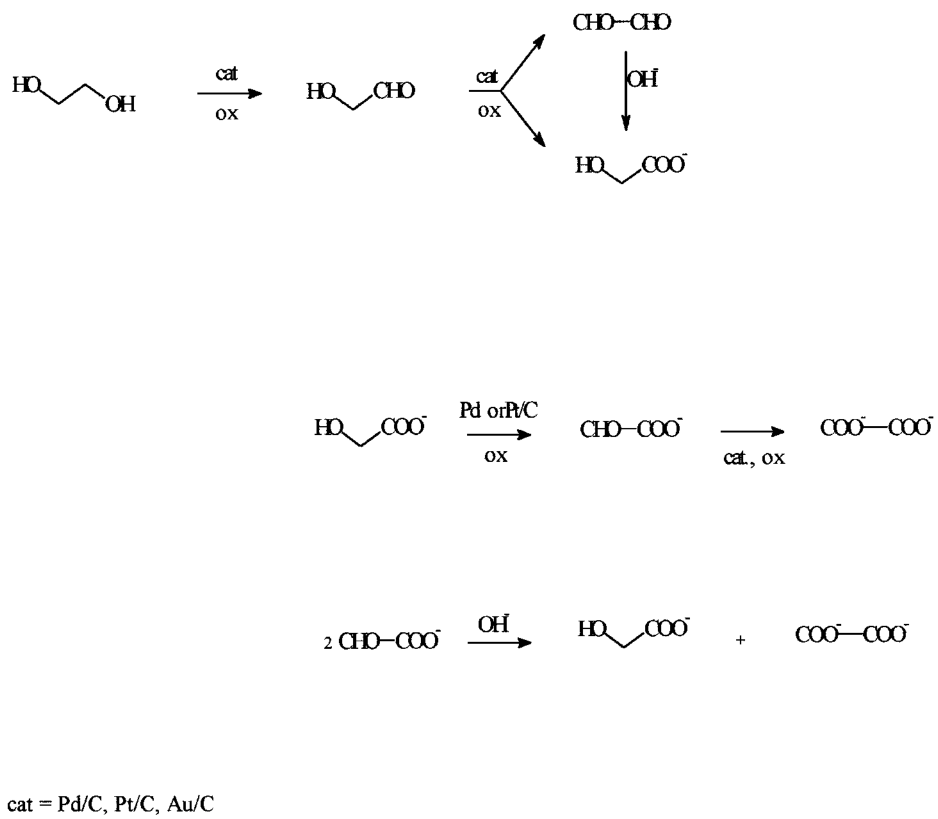
TABLE 2

Oxidation of Glycolic Acid

Entry	Catalyst	OXA (mol%)	CAR (mol%)	Conv. %
1	1% Au/C[a]	—	<1	<1
2	5% Pd/C	9	9	18
3	5% Pt/C	16	24	40

Note. Reaction conditions: glycolic acid/M = 1000; NaOH/glycolic acid = 1; $pO_2 = 300$ kPa; T = 343 K; t = 2 h; OXA = oxalate; CAR = carbonate.

[a] Prepared by deposition–precipitation method.



SCHEME 2. Reaction scheme for ethane-1,2-diol under alkaline conditions.

palladium or platinum on carbon catalysts, glyoxylic acid should be formed, thus providing a route for oxalate either via the intermolecular Canizzaro reaction or via oxidation of the aldehydic group (Scheme 2).

Glycolate is stable in the basic solution, whereas glyoxylate or glyoxal undergo only the Canizzaro reaction, thus excluding the formation of C1-byproducts from these intermediates by alkali catalyzed reactions. In the presence of Pd or Pt/C catalysts the C—C bond scission most probably derives from oxalate overoxidation. However, as also in the case of gold catalyzed oxidation we observed the presence of C—C cleavage, and considering that glycolate does not yield oxalate, we cannot exclude the oxidative scission of another possible intermediate like glyoxylic aldehyde or, alternatively, the direct scission of glycol. This latter alternative agrees with the independence of selectivity from the conversion that supports the hypothesis of two separate reaction pathways, one leading to monooxidation and the other to C—C bond rupture.

3.2. *Oxidation of Propane-1,2-diol*

In this case the problem of chemoselectivity, arising from the presence of a primary and a secondary alcoholic function, is of great interest as both hydroxyacetone and lactic acid are products of synthetic importance. Supported platinum group metals, doped with heavy metals like bismuth, have been claimed to selectively oxidize propane-1,2-diol to hydroxyacetone (16), whereas palladium on carbon has been reported to oxidize propane-1,2-diol in a nonselective manner (17).

However, in our experiments in alkaline solutions at 343 K under 300 kPa of O_2, commercial 5% Pd/C and 5% Pt/C produced lactate in good selectivity (89–90%) at high glycol conversion (73–84%) (6). Nevertheless, gold on carbon shows a remarkable improvement in selectivity, being as high as 100% at 78% conversion (Table 3), although with minor activity compared to that of Pd or Pt. Figure 2 shows the selectivity/conversion plot with Au, Pd, and Pt on carbon catalysts.

As in the case of ethane-1,2-diol, by oxidizing propane-1,2-diol, the reaction pathway is affected by basic reaction conditions which produce undesired drawbacks. One problem emerged when, owing to the importance of the synthesis of optically pure enantiomers of lactic acid, we performed the oxidation of R(-)-propyl glycol. Only racemic lactic acid was obtained by using either gold or platinum and palladium on carbon catalysts. We first ascribed this process to the enolization of the intermediate aldehyde in alkaline solution, in agreement with the accepted dehydrogenation mechanism and the normally observed trend of reactivity which suggest the more rapid oxidation of primary alcoholic functions with respect to the secondary one (2, 18).

TABLE 3

Oxidation of Propane-1,2-diol with Various Catalysts

Entry	Catalyst	T (K)	LA (mol%)	AC (mol%)	PYR (mol%)	CAR (mol%)	Conv. %	Selec.% to lactic a.
1	5% Pd/C	343	72	6	2	—	80	90
2	5% Pt/C	343	65	7	1	—	73	89
3	1% Au/C[a]	363	78	—	—	—	78	100

Note. Reaction conditions: NaOH/propane-1,2-diol = 1; diol/M = 1000; $pO_2 = 300$ kPa; t = 1 h. LA = lactate; AC = acetate; PYR = pyruvate; CAR = carbonate. Among the products hydroxyacetone was not detected.

[a] Prepared by deposition–precipitation method.

However, a series of H-D exchange experiments, performed in deuterium oxide and sodium deuterium oxide, highlighted a more complex reaction mechanism. As reported in Table 4 we confirmed that optically active sodium lactate does not racemize under reaction conditions, nor does it exchange with deuterium oxide in the presence of a base. Not even the starting diol, propane-1,2-diol, exchanges under alkaline conditions but, during its oxidation, we showed H-D exchange in the resulting lactate, not only in the expected α-position but also at the methyl group (Scheme 3). As propionic acid obtained by oxidizing either n-propanol or propanal in deuterium oxide shows H-D exchange only in the α-position (Table 4), we concluded that the hydroxyl group in the C2 position is responsible for the H-D exchange at the C3 position.

Thus, a possible mechanism for H-D exchange in the lactate-C2 and C3 positions involves the formation of hydroxyacetone as an intermediate that in an alkaline solution

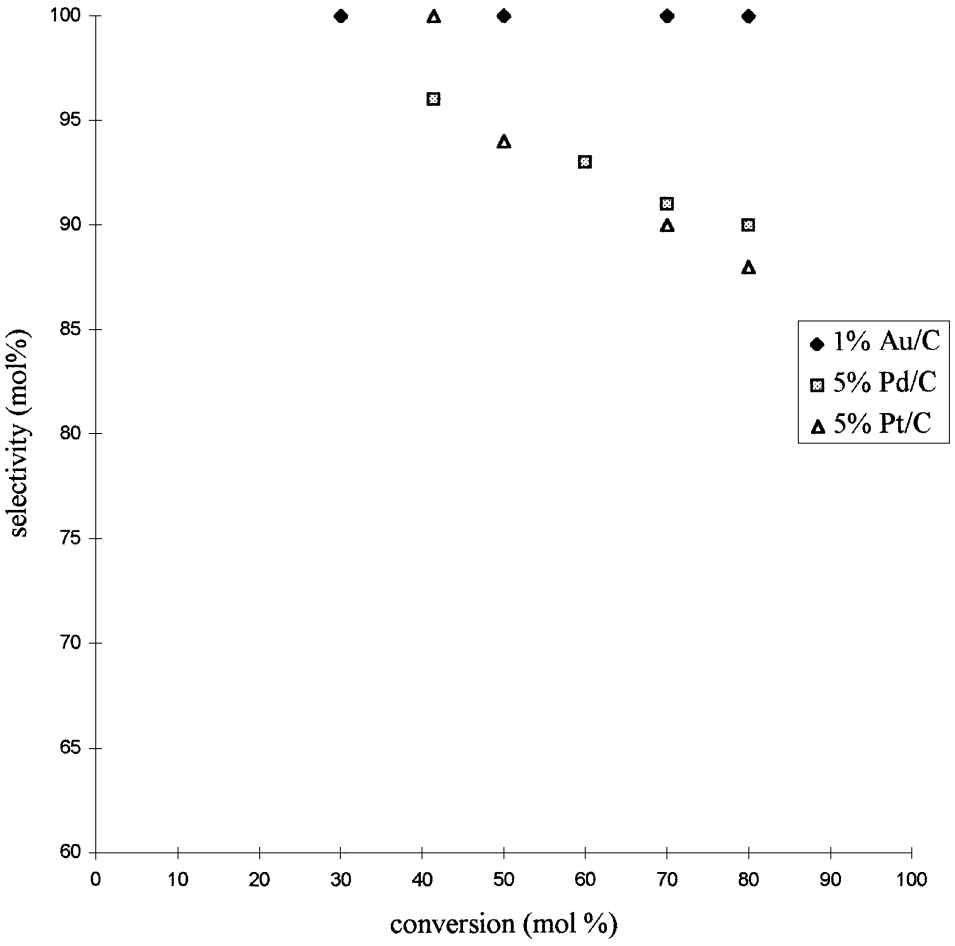
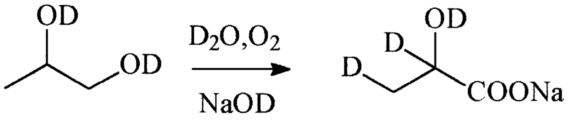


FIG. 2. Oxidation of propane-1,2-diol. Reaction conditions as reported in Table 3; gold on carbon catalyst was prepared by deposition–precipitation method.



SCHEME 3. H-D exchange in propane-1,2-diol oxidation.

TABLE 4

H-D Exchange Experiments

Reactant	NaOD	Catalyst	O_2	N_2	C2-exchange	C3-exchange
Propane-1,2-diol	X	—	X	—	No	No
	X	X	—	X	No	No
	X	X	X	—	Yes	Yes
Lactic acid	X	—	X	—	No	No
	X	X	X	—	No	No
Propionic aldehyde	X	—	—	X	Yes	No
	X	X	—	X	Yes	No
	X	X	X	—	Yes	No
n-propanol	X	X	X	—	Yes	No

forms two different enols (Scheme 4). To confirm this point hydroxyacetone was oxidized at 343 K in an alkaline solution with O_2 and, surprisingly, lactate was obtained in high yield. The reaction was totally selective in the presence of Au/C, whereas by using Pt/C or Pd/C a small amount of pyruvate was detected (2–3%). As a working hypothesis, we assumed that the oxidation of hydroxyacetone proceeds via pyruvic aldehyde to produce the lactate by means of an intramolecular Canizzaro reaction. This point was confirmed by experimental tests which stated that pyruvic aldehyde quantitatively yields lactate under basic conditions at 343 K in the absence of metal catalysts. Under oxidative conditions, in the presence of Pd, Pt, and Au catalysts, it gave, along with the lactate, variable amounts of pyruvate (2–4%).

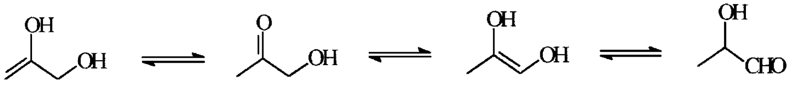
Therefore, a general reaction scheme for the catalyzed oxidation of propane-1,2-diol under basic conditions, must consider lactic acid production either by oxidation of the primary alcoholic function via lactaldehyde or by the intramolecular Canizzaro reaction of pyruvic aldehyde. This latter can be formed by oxidation of propandiol at the secondary hydroxyl group giving hydroxyacetone, but the lactaldehyde and hydroxyacetone could also be in equilibrium via their enols (Scheme 5). Although the oxidation of 2-hydroxy-propanal (lactaldehyde) to lactic acid was not proven in our laboratory, not being commercially available because of its instability, its presence as an intermediate during the oxidation of propane-1,2-diol appears likely, considering the facile oxidation of primary alcoholic function observed in the case of ethane-1,2-diol.

As already reported for palladium on carbon catalyst (17) we verified that lactic acid is stable under oxidative conditions also by using gold or platinum on carbon catalyst and that it is not further oxidized to pyruvic acid. Therefore the pyruvate detected in the reaction products from propane-1,2-diol with palladium or platinum catalysts derives from the hydroxyacetone intermediate. However, in alkaline solution, the presence of pyruvate does not give no indication of the selectivity of the first dehydrogenation step of propane-1,2-diol leading to carbonyl intermediates. In the case of gold the absence of pyruvate but the formation of hydroxyacetone as an intermediate, proven by H-D exchange at the C3-position, supports the hypothesis that under basic conditions lactaldehyde, in equilibrium with hydroxyacetone, is rapidly oxidized to lactic acid, this reaction being faster than that of hydroxyacetone to pyruvic aldehyde.

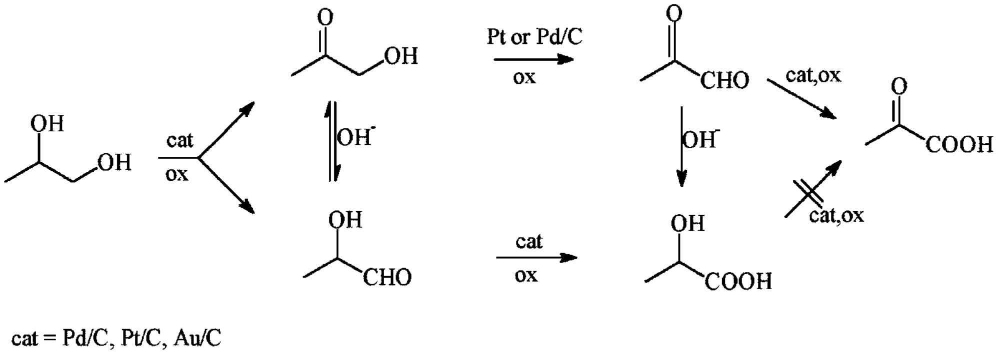
By considering that hydroxyacetone is unstable under alkaline conditions (producing condensed products) and that in the case of gold-catalyzed oxidation we did not detect any by-products, we presume that hydroxyacetone is present at the equilibrium in very low amounts or its oxidation rate through lactaldehyde is more rapid than its degradation. On the contrary, in the presence of Pd and Pt/C catalysts, we found acetate among the reaction products. In these cases the direct oxidation of hydroxyacetone, as outlined before, yields, along with lactate, pyruvate that is as unstable under basic conditions as hydroxyacetone. However, under basic conditions neither hydroxyacetone nor pyruvate yields acetate, acetate being obtainable only under oxidative conditions. Thus, we can assume that acetate derives from the oxidative scission of pyruvate or through the C−C bond oxidative scission directly from glycol.

A careful investigation of the stability of pyruvic aldehyde in alkaline solution was done to find the limiting pH value for observing the aldehyde dismutation according to the Canizzaro reaction. At 343 K in 10% (w/w) solution no lactate was detected after 2 h reaction at $pH = 8$. Therefore, a set of experiments on the oxidation of propane-1,2-diol was done at controlled pH ($pH = 8$).

As reported in Table 5 gold on carbon yields lactic acid with total selectivity, whereas platinum and palladium on carbon catalysts produce relevant quantities of hydroxyacetone and pyruvate. From these data, we can derive that gold shows an intrinsic high selectivity toward the oxidation



SCHEME 4. Equilibria from hydroxyacetone in basic solution.



SCHEME 5. Reaction scheme for propane-1,2-diol under alkaline conditions.

of the primary hydroxyl, at both low and high pH values, whereas Pd and Pt do not discriminate between primary and secondary hydroxyls. Therefore, the high selectivity shown by palladium and platinum catalysts under stronger basic conditions is interpreted by rapid equilibria (Scheme 6) and the intramolecular Canizzaro reaction favouring the formation of lactate also from pyruvic aldehyde.

The high chemoselectivity toward the primary alcoholic function shown by the gold catalyst was also demonstrated by the inertness of butan-2,3-diol and 2-propanol under oxidative conditions in the presence of such a catalyst (4-h experiments).

3.3. *Catalyst Deactivation*

Beside the benefits to activity and selectivity observed in the oxidation of ethane- and propane-1,2-diols in strong alkaline solution, we also expected some benefits in terms of catalyst life (2). At $\mathrm{pH} > 13$ and with a high reactant/metal ratio (1000) we did not observe any deactivation with any of the catalysts in single runs. However, a four-recycle test on the oxidation of ethane-1,2-diol showed a clear difference between gold and the other two metals, as shown in Table 6. The analytical data obtained in the susequent runs, where the catalyst used in the previous ones was simply filtered off and reused without any washing, indicate a large transfer of palladium to the solution (45% leaching from the catalyst after four cycles), a smaller transfer of platinum (2% leaching), and no detectable transfer of gold (<0.1% leaching). At the same time, the composition of the reaction products shows a very strong decline in terms of both activity (−25%) and selectivity (−56%) in the case of Pd catalyst, whereas in the case of Pt only the selectivity is affected by aging (−31%).

On the contrary, the recycling test for gold revealed an almost constant activity and selectivity because the small differences (−3% activity, −2% selectivity) can be ascribed to a small loss of catalyst during the workup.

TABLE 5

Oxidation of Propane-1,2-diol at pH 8

Catalyst	t (h)	T (K)	PYR (mol%)	HYDR (mol%)	LA (mol%)	Conv. %	Selec. %
1% Au/C[a]	10	363	—	—	30	30	100
5% Pd/C	5	343	8	13	5	46	11
5% Pt/C	5	343	4	24	18	56	32

Note. Reaction conditions: diol/M = 1000; $pO_2 = 100$ kPa. The pH was maintained at 8 by dropping NaOH 0.1 *M*. PYR = pyruvate; HYDR = hydroxyacetone; LA = lactate.

[a] Prepared by deposition–precipitation method.

4. CONCLUSIONS

This study shows that gold can be conveniently employed as a catalyst for liquid phase oxidation of diols under mild conditions, in competition with the more commonly used Pd and Pt catalysts. An intrinsic high selectivity for the oxidation of primary hydroxy groups can be coupled with good activity by a careful choice of support, preparation method, and experimental conditions.

The promoting effect of basic solutions is interpreted by keto–enol equilibria and Canizzaro dismutation which tend to favour the selectivity of Pd/C and Pt/C catalysts more than that of Au/C.

TABLE 6

Recycling Tests

	1% Au/C[a]		5% Pt/C[b]		5% Pd/C[b]	
Run	Conv.%	Select.%	Conv.%	Select.%	Conv.%	Select.%
1	80	93	89	79	75	82
2	78	91	88	68	71	70
3	75	92	85	55	65	53
4	77	90	89	48	50	26

Note. Reaction conditions: reactant/metal = 1000; reactant/NaOH = 1; $pO_2 = 300$ kPa.

[a] T = 343 K, t = 3 h; the catalyst was prepared by deposition–precipitation method.

[b] T = 323 K, t = 2 h.

Moreover, gold on carbon shows the best stability in recycling tests, where neither deactivation nor metal leaching were observed.

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