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Journal of Molecular Catalysis A: Chemical



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

Chemometric approaches on glycerol oxidation with H₂O₂ over supported gold nanoparticles

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ARTICLE INFO

Article history: Received 29 September 2012 Received in revised form 10 January 2013 Accepted 11 January 2013

Keywords: Glycerol Gold nanoparticles Catalyst Chemometrics

ABSTRACT

This paper reports a chemometric study of effects of the catalyst preparation method and reaction conditions on the efficiency of glycerol oxidation catalyzed by gold nanoparticles supported on activated carbon using H_2O_2 as oxidant. Factorial designs and principal component analysis were used for the evaluation of experimental conditions and reaction performance. Evaluating catalyst preparation conditions we found that larger Au nanoparticles are obtained using HAuCl₄ in higher concentration. Glycerol conversion and production of glycerate and tartronate were higher using catalysts prepared with low polyvinyl alcohol (PVA) to Au ratio and low Au content. Higher HAuCl₄ concentrations resulted in larger Au nanoparticles, which contributed to higher glycolate production. Evaluating reaction conditions we found that the influence of H_2O_2 to glycerol ratio was insignificant. Glycerol conversion and production of glycerate and tartronate were higher at lower temperature. Increasing H_2O_2 to glycerol ratio contributed to higher glycolate production. Glycerol to Au ratio has a smaller influence on the reaction course.

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1. Introduction

In recent years, use of noble metal nanoparticles as catalysts in organic reactions has attracted great attention as this type of catalyst presents one of the most promising solutions to carry out reactions more efficiently under mild conditions and under the green chemistry context. An important feature that makes noble metals promising for nanoparticle preparation is their high reduction potential, which contributes to an easy metal reduction and metal stability under reaction conditions [1,2]. Gold, platinum, palladium and silver are the main metals used in the preparation of this catalyst type, although nanoparticles of other noble metals also show considerable catalytic activity [3].

Among the reactions in which catalysts based on nanoparticles of noble metals show activity, the conversion of glycerol into high value added products has stimulated research exploring the involved processes [4–7]. This interest is justified by recent advances in research and growing production of biodiesel. In this scenario, research started to be concerned with the fate of increasing growth of glycerol production which is a byproduct of biodiesel. Recent research has demonstrated high potential of glycerol as starting material for obtaining a wide variety of

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chemical compounds of great industrial interest, and noble metal nanoparticle catalysts have been shown to be effective in a series of reactions involving the conversion of glycerol into these products [3–9].

A process of considerable interest involves the oxidation of glycerol to glycerate and glycolate (Fig. 1), which can be converted into acids (glycolic and glyceric acid) [4,5]. Several applications are reported for glyceric acid and its derivatives, such as stimulating liver activity, accelerating ethanol and acetaldehyde oxidation in vivo, besides serving as a starting material for the manufacture of surfactants and functional polymers [10]. Glycolic acid has a total annual production reaching a several thousand tons. Its main application is in cosmetics, particularly in dermatological products [11].

In several studies glycerol oxidation using supported gold nanoparticles and high pressures of O_2 has been reported [9,12,13]. However, in previous work the ability of gold nanoparticles to oxidize glycerol at atmospheric pressure and mild temperatures using H_2O_2 as oxidant and to obtain good yields and selectivities to glycerate and glycolate has been demonstrated [13].

For reactions performed at high O₂ pressures, the reaction conditions such as temperature and substrate/catalyst ratio affect yield and selectivity. It has also been reported that reaction efficiency can be influenced by structural characteristics of the catalyst, such as nanoparticle size and metal content [12,14]. In these studies, the effect of each parameter was evaluated separately, i.e., each parameter was evaluated at a time, not considering possibility of existence of effects caused by interactions between them. Statistic considerations commonly have not been done.

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^{1381-1169/\$ -} see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.molcata.2013.01.006



Fig. 1. Reaction pathway for glycerol oxidation over gold nanoparticles based catalyst.

As reported several parameters influence this reaction. Each variable can influence separately the reaction performance, however, they can interact with each other and cause different effects to those observed when considered separately. Moreover, at the end of the reaction a large quantity of products can be obtained. Thus, a multivariate approach, in which a chemometric evaluation enables a more comprehensive study, would allow to extract more efficiently a greater amount of information for the process [15,16].

This paper reports a chemometric study of the effect of the catalyst preparation method and the reaction conditions on the efficiency of glycerol oxidation catalyzed by gold nanoparticles supported on activated carbon using H_2O_2 as oxidant.

2. Experimental

2.1. Synthesis and characterization of catalyst

The catalyst was prepared using the sol-gold method [13]. Initially 800 mL of a HAuCl₄·3H₂O aqueous solution was prepared followed by addition of polyvinyl alcohol (PVA) (1%, w/v aqueous solution). 0.1 mol L⁻¹ NaBH₄ was added under stirring in sufficient amount to obtain a 4:1 PVA/Au molar ratio. Then, activated carbon was added to the gold nanoparticles solution, while maintaining agitation until complete discoloration of the solution. The resulting material was filtered using a filter paper. The filtrate was washed with distilled water until complete removal of Cl⁻ (test with 0.1 mol L⁻¹ AgNO₃). Finally the material was dried in an oven at 120 °C for 24 h. The concentrations and masses of the reagents were used according to the factorial design of Table 1.

The average diameter (average of 50 measured nanoparticles) of the catalyst nanoparticles was determined by transmission electron microscopy (TEM). Sample preparation consisted of preparing

a suspension of the catalyst in methanol of 5 mg mL^{-1} . A drop of this suspension was deposited on a copper screen, specific for this analysis. The solvent was evaporated in oven at 70 °C for 10 min and the sample submitted to analysis in a Zeiss EM-109 microscope.

2.2. Glycerol oxidation

Glycerol oxidation was performed in aqueous medium using H_2O_2 as oxidant. In an Erlenmeyer flask with stopper the catalyst, NaOH, distilled water, glycerol and H_2O_2 (30%, v/v) in appropriate amounts for the factorial design were added (Table 2). The H_2O_2 load was added dropwise slowly using a microsyringe during the reaction (4 h).

Reagent and products were identified and determined by ESI-MS [17]. An aliquot of $10 \,\mu$ L was collected from the reaction medium. 750 μ L of Milli-Q water and 750 μ L of methanol were added. The resulting solution was analyzed by ESI-MS in the negative mode. Analyses were performed in an Agilent 1100-LC/MSD-Trap mass spectrometer. The conversion was calculated by measuring the glycerol content in reaction medium by a calibration curve. The relative peak intensities of the mass spectra (considering only the peaks of glyceraldehyde, glycerate, tartronate and glycolate) were used as quantitative parameter for the products formation.

2.3. Chemometric analysis

Effects of the conditions of catalyst synthesis on nanoparticle size and reaction performance were evaluated using a 2^3 factorial design (Table 1). Effects of reaction conditions on reaction performance were evaluated using a 2^{4-1} fractional factorial design (Table 2). All factorial designs were conducted with three

Table 1

Factorial design for evaluation of the catalyst preparation conditions with responses for assays.

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Assay	$HAuCl_4$ (mg L ⁻¹)	PVA/Au (w/w)	Au (%)	Au particle size (nm)	Glycolate (%)	Glyceraldehyde (%)	Glycerate (%)	Tartronate (%)	Conversion (%)
1	250	1.2	3	7.0	10.3	79.2	6.7	3.9	36.1
2	50	1.2	3	4.0	8.0	73.4	13.3	5.3	46.1
3	250	0.3	3	13.0	8.0	34.7	52.5	4.8	58.7
4	50	0.3	3	8.3	6.6	76.2	12.9	4.4	55.2
5	250	1.2	1	14.0	7.1	42.8	43.5	6.6	53.4
6	50	1.2	1	6.6	7.8	42.7	43.2	6.2	52.1
7	250	0.3	1	8.9	10.1	29.4	54.5	6.0	60.7
8	50	0.3	1	6.6	7.7	30.5	51.6	10.2	58.5
9	150	1	2	7.3	9.2	28.9	52.1	9.7	53.1
10	150	1	2	8.2	8.7	28.8	53.6	8.9	51.0
11	150	1	2	7.5	9.0	24.2	59.8	7.1	52.3

Reaction conditions: 50 °C, 30 mg catalyst, 150 mg NaOH, 4.75 mL distillated water, 100 µL glycerol and 150 µL H₂O₂.

Та	bl	e	2

Factorial design for the evaluation of the reaction conditions with responses for assays.

Assay	Glyc/Au (w/w)	OH/glyc (mol/mol)	H ₂ O ₂ /glyc (mol/mol)	Temp. (°C)	Glycolate (%)	Glyceraldehyde (%)	Glycerate (%)	Tartronate (%)	Conversion (%)
1	750	3	3	80	12.8	70.8	11.9	4.6	29.8
2	250	3	3	25	8.9	6.6	63.6	20.9	66.1
3	750	1	3	25	10.8	23.9	60.5	4.8	23.6
4	250	1	3	80	4.9	62.8	31.6	0.7	5.3
5	750	3	1	25	7.8	16.9	66.3	9.1	61.8
6	250	3	1	80	10.1	65.1	20.1	4.8	19.1
7	750	1	1	80	8.0	79.0	12.5	0.5	7.4
8	250	1	1	25	11.0	18.1	59.7	11.3	44.1
9	500	2	2	50	3.6	36.4	55.6	4.4	54.2
10	500	2	2	50	3.4	39.5	51.9	5.2	49.0
11	500	2	2	50	4.3	41.3	50.2	4.2	55.0

Catalyst preparation: HAuCl₄ 50 mg L⁻¹, PVA/Au ratio 0.6 and 1% gold.

replications on the central point. Critical effect was calculated from variance of the central point repetitions. Effects are considered significant if its absolute value is larger than the critical effect value at 95% confidence level.

Exploratory analysis by principal components analysis (PCA) was performed aiming to reveal relations between experimental conditions and reaction performance. A data matrix was constructed from independent and dependent variables of factorial designs. Data was pre-processing using autoscaling. Calculations were performed using Matlab.

2.4. Blank and leaching experiments

Blank experiments were performed. In these experiments, catalyst, H_2O_2 or NaOH was not present. After 4 h of reaction, products were analyzed by ESI-MS.

In leaching experiment, the catalyst was left in a solution under reaction conditions, containing all reagents used in the oxidation reaction, except glycerol. After 4 h stirring, the mixture was centrifuged to separate the catalyst. Then glycerol was added to the liquid phase and magnetic stirring continued for 4 h. The reaction products were analyzed by ESI-MS.

3. Results and discussion

3.1. Effects of catalyst synthesis conditions on glycerol oxidation

The catalysts were prepared by varying HAuCl₄ concentration, polyvinyl alcohol (PVA) to Au ratio (PVA/Au) and gold content (%Au) according to the factorial design of Table 1. Initially, the catalysts were characterized by TEM. The micrographs obtained for each factorial design assay are shown in Fig. 2. The images clearly show the presence of nanoparticles dispersed on the surface of activated carbon. The micrograph of activated carbon that went through all stages of catalyst preparation, without gold deposition was also obtained for comparison. The mean diameters of the nanoparticles ranged from 4 to 14 nm as expected for the preparation method used [13].

During the catalyst preparation we observed that the gold nanoparticles obtained with PVA/Au ratio of 1.2 and 3% Au, the gold sol were not promptly adsorbed on the activated carbon. This could be due to the large amount of PVA and gold to be adsorbed on the activated carbon surface.

Effects of the factorial designs are presented in Pareto's charts (Fig. 3). According to Fig. 3A the effect of HAuCl₄ concentration is the most significant on the nanoparticle sizes. The observed effect is synergistic, i.e., larger nanoparticles are obtained when using more concentrated HAuCl₄ solutions. The main effects of PVA/Au ratio and %Au present no significance when considered alone, but its interaction effects are antagonistically significant (Fig. 4C).

This corroborates with previous works [18,19] and with the idea that the Au particle size depends on the dielectric properties of the PVA–water medium, which may influence the gold reduction [20].

Fig. 4 shows the surface responses to the variation of the average diameter of gold nanoparticles as a function of HAuCl₄ concentration, PVA/Au ratio and %Au. It is observed that the main variation in diameter mainly occurred along the HAuCl₄ concentration axis, and increased proportionally with increasing concentration.

The significance of the catalyst preparation conditions on the catalytic performance in glycerol oxidation was also evaluated. The dependent variables evaluated were glycerol the conversion and the production of glycerate and glycolate, which are products of interest. Pareto's charts were used to evaluate significance and type (synergistic or antagonistic) of effects, and a more global discussion was done by PCA approaches.

The Pareto's chart for glycerol conversion (Fig. 3B) shows that the PVA/Au ratio and %Au main effects were antagonistically significant. The major effect was the PVA/Au ratio. The catalyst prepared with higher PVA/Au ratio results in low glycerol conversion. A hypothesis for this is that although PVA is highly porous and allows the adsorption of the reactant on the active site [21], a thick PVA layer can block the nanoparticle interaction. It is also important to note that a high %Au, which contributed for larger Au nanoparticles, provides lower conversion. The production of glycerate is also antagonistically influenced by %Au and PVA/Au ratio (Fig. 3C). The production of glycolate was favored when using higher HAuCl₄ concentration (Fig. 3D), i.e., more glycolate was produced by larger Au nanoparticles. PVA/Au ratio and %Au also present significant interaction synergistic effect.

PCA was used in order to have a global view of the influence of the catalyst preparation conditions on the reaction performance. Only loadings are evaluated (Fig. 5), since the main goal of this analysis was to study the relationship between catalyst synthesis variables and reaction performance parameters.

The first principal component (PC1), which explains the highest variance of the system (45.59%), indicates that the PVA/Au ratio and %Au are the variables that most influence the reaction performance. According to PC1, glycerol conversion and production of glycerate and tartronate were higher when using catalysts prepared with low PVA/Au ratio and low %Au. As previously explained, this may be due to the thick layer of PVA, blocking the interactions between reactant and active sites.

The second principal component (PC2), which explains 19.93% of total variance, indicates that HAuCl₄ concentration also has an important effect on the system. According to PC2, higher HAuCl₄ concentrations result mainly in larger nanoparticles, and this effect causes a higher production of glycolate.

The production of glyceraldehyde was higher when low HAuCl₄ concentration (smaller nanoparticles), higher PVA/Au ratio and high %Au are used. This corroborates with the reaction pathway



Fig. 2. TEM micrographs of the catalysts prepared according to the factorial design of Table 1. Image numbers refer to assay numbers of Table 1.

shown in Fig. 1, which suggests that glyceraldehyde is the first oxidation product. So, the lesser efficient oxidation system is the more glyceraldehyde will remain in the reaction mixture.

3.2. Effect of reaction conditions on glycerol oxidation

It has been reported that the first step in the formation of oxidized products from glycerol involves the deprotonation of a glycerol hydroxyl to form a glycerolate intermediate, which is then dehydrogenated to glyceraldehyde [22]. Mechanisms described in literature suggest the formation of glycerate by glyceraldehyde oxidation, and the glycerate can be oxidized to form tartronate. Glycolate can be obtained via tartronate decarboxylation. A possible reaction pathway for the formation of oxidation products from glycerol, according to the literature was presented in Fig. 1 [13,23].

The evaluation of the influence of the reaction conditions on glycerol conversion and production of the major products was performed by fractional factorial design shown in Table 2.

Pareto's chart for effects of the reaction conditions on glycerol conversion is shown in Fig. 6A. Significant parameters are the temperature and $OH^-/glycerol$ ratio. Temperature has an antagonistic effect and the $OH^-/glycerol$ ratio presents a synergistic effect. Glycerol/Au ratio, $H_2O_2/glycerol$ ratio and interaction effects are not significant at a 95% confidence level.



Fig. 3. Pareto's charts for the effects of Au nanoparticle size (A), glycerol conversion (B) and production of glycerate (C) and glycolate (D) considering the factorial design of Table 1. Vertical lines represent the critical effect at 95% confidence level.

Pareto's chart for production of glycerate (Fig. 6B) indicates that only the temperature has a significant effect, with a considerably magnitude larger than the other effects. The negative value obtained for the temperature effect indicates that higher production of glycerate is obtained at lower temperature.

The effect of reaction conditions on the production of glycolate is shown in Fig. 6C. Pareto's chart shows that the effects of temperature, glycerol/Au, OH/glycerol and $H_2O_2/glycerol$ ratio are not significant when considered alone, however the effect of interaction between these variables have an important significance on the production of glycolate. As a factorial design 2^{4-1} was used, the 2nd order interactions are confusing, not allowing, in principle, to tell whether the significant interaction is between glycerol/Au–H₂O₂/glycerol or between OH/glycerol-temperature. For the same reason it is not possible to define whether the significant interaction is between glycerol/Au-temperature or between OH/glycerol-H₂O₂/glycerol. Therefore, PCA was carried out in order to elucidate the significant interaction effects, and give a more global view of the effects of reaction conditions on the glycerol oxidation performance.

PCA loading plots for the first two principal components are shown in Fig. 7. The graph shows low loadings for $H_2O_2/glycerol$ in PC1 and PC2, indicating a small influence of $H_2O_2/glycerol$ ratio. From this information the interaction effects in the production of glycolate study were elucidated. The significant interaction effects on the production of glycolate should be those that



Fig. 4. Response surfaces for variation of Au particle size as function of HAuCl₄ concentration, PVA/Au ratio and %Au. Size (nm) = 0.97 + 0.02 HAuCl₄ + 5.69 PVA/Au + 3.11 Au% + 0.01 HAuCl₄·PVA/Au - 0.002 HAuCl₄·Au% - 4.28 PVA/Au·Au%; $R^2 = 0.90$; $p_{(regression)} = 0.048$; $p_{(lack-of-fit)} = 0.056$.



Fig. 5. PCA loadings for the catalyst preparation conditions according to factorial design of Table 1.

do not include H_2O_2 /glycerol, i.e., the interactions between OH/glycerol-temperature, and between glycerol/Au-temperature. More glycolate is produced using high OH/glycerol and glycerol/Au ratios, and low temperature.

According to PC1, which explains most variance (48.49%), temperature is the factor that mostly influences the reaction performance. The plot indicates that glycerol conversion and production of glycerate and tartronate is higher at lower temperature. The lower glycerol conversion at higher temperatures may be related to lower stability of H_2O_2 at higher temperatures [13], especially in alkaline medium [24]. Besides, PVA is soluble in water at temperatures higher than $60 \,^{\circ}$ C [21]. Thus, higher reaction temperature ($80 \,^{\circ}$ C) can affect the PVA ability to stabilize the gold nanoparticles and its catalytic activity.

PC2, which explains 16.12% of variance, indicates that the OH/glycerol ratio has a secondary effect on the reaction. Increased OH/glycerol ratio contributed mainly to higher production of glycolate. The glycerol/Au ratio also influences the reaction, but by a less relevant manner. Smaller glycerol/Au ratio favors glycerol conversion and production of glycerate and tartronate. Again the production of glyceraldehyde is higher under unfavorable conditions for the formation of other products, i.e., high temperature and low OH/glycerol ratio, corroborating again with the reaction pathway shown in Fig. 1.

3.3. Blank and leaching experiments

In order to investigate the role of catalyst, promoter base (NaOH) and oxidizing agent (H_2O_2) in glycerol oxidation, blank reactions were performed in absence of these components. For comparison, we performed a control reaction containing all components. We also analyzed the possibility of leaching of the nanoparticles and its role as homogeneous catalyst. The results are shown in Fig. 8.

The reaction conducted in absence of the catalyst presented negligible conversion as expected. Only formation of a very small amount of glyceraldehyde was observed. Oxidation in absence of NaOH, a slightly higher conversion was obtained, but it was considerably lower than in the control. Glyceraldehyde was the only observed product. This is consistent with a previous study on the mechanism of this reaction [17], where it is reported that reaction steps occurring in presence of the hydroxyl group present



Fig. 6. Pareto's charts for the effects of glycerol conversion (A) and production of glycolate (B) and glycerate (C) considering the factorial design of Table 2. Vertical lines represent the critical effect at 95% confidence level.

activation barriers considerably smaller and more favorable than those in its absence. Furthermore, it was demonstrated that the oxygen atoms incorporated into the glycerol oxidation products are from the hydroxyl groups instead of the oxidizing agent, which acts in the base regeneration.

The reaction performed in the absence of H_2O_2 presented a significant conversion, although lower than in the control experiment, and produced mainly glyceraldehyde and glycerate. In this case, although no oxidizing agent was added, atmospheric oxygen may have acted as such and made the formation of oxidized products possible. Previous work on the mechanism of this reaction [17] indicated an indirect effect of the oxidizing agent. Calculations by DFT (Density Functional Theory) indicate that there is formation of H_2O_2



Fig. 7. PCA loadings for the reaction conditions according to the factorial design of Table 2.



Fig. 8. Glycerol oxidation in blank and leaching experiments.

by reduction of O_2 with H_2O on the metal surface, and the hydrogen peroxide formed is decomposed to OH^- which promotes the base regeneration.

In the leaching experiment no significant glycerol conversion was observed, indicating that if any leaching occurred, the gold species in solution were not active on glycerol oxidation. TEM analysis of the catalyst after the leaching experiment showed the presence of nanoparticles on the surface of the activated carbon.

4. Conclusion

Gold nanoparticles supported on activated carbon are active in glycerol oxidation using hydrogen peroxide under mild conditions, favoring formation of high value added products, such as glycerate and glycolate. The production of these products depends on the parameters related to catalyst synthesis, as gold nanoparticle size (large nanoparticles, lower conversion and higher glycolate formation), and reaction conditions such as temperature (high temperature, lower conversion and glycerate formation) and amount of alkali (high alkali ratio, higher glycolate formation). Some process conditions observed in this study proved to be advantageous under a technical point of view and are also favored environmentally and economically, as higher glycerol conversions were achieved at mild temperatures and catalysts with low gold content.

Acknowledgments

The authors acknowledge financial support from the Brazilian agencies Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG), Petróleo Brasileiro S/A (PETROBRAS), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Financiadora de Estudos e Projetos (FINEP). We are also grateful to the Laboratório de Microscopia Eletrônica and to the Central de Análise e Prospecção Química of the Federal University of Lavras the technical support. We are also grateful to Prof. Dr. U. Schuchardt for suggestions and corrections on the manuscript.

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