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Article

Determination of Metal Loading in Heterogeneous Catalyst by Slurry Sampling Flame Atomic Absorption Spectrometry

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Quantification of metal loading in supported catalysts is imperative; however, the analytical methods are usually time-consuming, expensive, and require sophisticated equipment and sample extraction with hazardous and corrosive strong acids. Herein, we report a new method for quantification of metal in supported catalysts using slurry sampling flame atomic absorption spectrometry. The slurry sampling method was used for determination of gold and the results were similar to those obtained with the traditional extraction method using *aqua regia*; however, it overcomes the main drawbacks associated with sample digestion by avoiding the use of concentrated toxic reagents, minimizing sample manipulation, and consequently, reducing the risks of contamination and the sample preparation time. Ultrasound radiation optimization associated with the solvent, mass of sample, concentration, and matrix effect in the slurry analysis allowed direct analysis by using the calibration in aqueous medium. The slurry sampling procedure could be applied to other catalysts with different supports and in bimetallic systems.

Keywords: slurry sampling, flame atomic absorption spectrometry, gold determination, heterogeneous catalyst

Introduction

Among many different transition metals used as catalysts, gold was conventionally considered inert until the pioneer work accomplished by Haruta *et al.*[1,2] Since then, many studies have been devoted to gold catalysis in a wide variety of reactions under comparatively mild conditions, including oxidation, hydrogenation, and many others. Gold catalysts are used in selective oxidation of alcohols, silanes, hydroquinone, amines, and alkyl aromatic compounds with simple model substrates or with more complex molecules. It is a very attractive synthetic method that uses molecular oxygen or hydrogen peroxide for green catalyzed oxidation reactions.[3] Attempts have been made to use gold catalysts in the synthesis of fine chemicals.[4] Examples include the use of gold-based catalysts in the preparation of azo compounds,[5] synthesis of dipolar cycloaddition products,[6] applications in more difficult organic pathways such as Michael additions,[7] and others.[8] The efficiency of gold-based catalysts depends on many parameters, such as the size of the gold nanoparticle and its electronic state, the nanoparticle stabilizer, the support, and the gold loading on the support.[9] Many of these parameters are chosen and can be adjusted by selecting the synthetic method.

Generally, the nominal metal content in supported gold catalysts varies between 1 and 2 wt.%; however, the exact metal loading depends on the preparation method, metal-support interactions, and washing steps. Metal loading can also vary from batch to batch. Therefore, it is strongly recommended to determine the metal loading after each preparation. The amount of substrate necessary for the catalytic tests is thus adjusted based on the actual metal loading. The correct calculation of the catalyst to substrate ratio is necessary to evaluate the activity of the catalyst; i.e., how many mol of substrate are converted *per* mol (or single site) of gold in a certain period of time.[10]

Typically, emission or absorption analytical instrument techniques are widely used in the determination of gold loading. Inductively coupled plasma optical emission spectroscopy (ICP OES) is an emission technique used to detect gold and other metals in catalysts[11-13] over a very broad range of concentrations, down to ppb. Atomic absorption spectrometry (AAS) is used for the same purpose and is capable of detecting the same range of concentrations, with the advantage of lower price compared with ICP OES equipment. For this purpose, two different types of atomizers, electrothermal (ET AAS) and flame (F AAS) atomizers,

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enable analysis in ranges of μg kg^{-1} and mg kg^{-1}, respectively. In all of these optical analysis techniques, the sample (gold or other metal) must be extracted from the support matrix before analysis. This sample preparation step is performed by means of dry decomposition (fusion or pyrohydrolysis) or wet decomposition with oxidants and non-oxidant acids using thermal heating or microwave. For noble metals, a highly effective method of decomposition uses concentrated *aqua regia* as the digester, prepared from pure analytical grade acids. *Aqua regia* (1:3 HNO_3:HCl) provides oxidant compounds such as molecular chlorine and nitrosyl chloride (NOCl). Along with chlorine ions available in solution, this reagent is very efficient for gold dissolution.[14] However, this decomposition method requires the use of unsafe strong acids, produces large volumes of acid residues, and is time consuming (usually 2-3 h for the preparation of the samples, including a dilution step after the treatment).[15]

The direct analysis of a slurry containing an ultrasound homogenized analyte is an alternative method.[16] As far as we know, this method has not yet been explored in the determination of metal loading in a heterogeneous catalyst. The slurry sampling method overcomes the main drawbacks associated with sample digestion by avoiding the use of toxic reagents, minimizing sample manipulation, and consequently, reducing the risks of contamination and the sample preparation time. Many spectroscopy techniques allow solid sampling analysis; however, specific sampling instruments are required.[17] Slurry sampling analysis presents all the same characteristics associated with solid sampling procedures, but it does not require a graphite furnace. The instruments commonly adopted for solution analysis can be used, such as F AAS. In slurry sampling analysis, solid samples should be ground and suspended in an adequate solvent. The stability of the suspension is one of the difficulties associated with this method. Other parameters, such as particle size, solvent, and calibration influence the quality of the analytical results. Taking these parameters into consideration, this paper describes the development of a method for direct determination of gold in catalysts by slurry sampling flame atomic absorption spectrometry (SLS-F AAS). The results obtained by this method were compared with those obtained by the dissolution method using concentrated *aqua regia*, which is the conventional procedure used for heterogeneous catalyst analysis.

Experimental

Instrumentation

A Shimadzu GFA-EX7i (Kyoto, Japan) flame atomic absorption spectrometer equipped with a pneumatic nebulizer system was used for the analysis. A gold hollow cathode lamp was used throughout. The instrumental parameters and experimental conditions used for Au measurement by F AAS were: wavelength = 242.8 nm; lamp current = 5 mA; bandpass = 0.7 nm; height of observation = 7 mm; air flow rate = 15 L min^{-1}; acetylene flow rate = 2.0 L min^{-1}; reading time = 5 s; nebulizer aspiration flow rate = 4 mL min^{-1}. A Branson 2510 ultrasonic bath (Dunbury, USA) operating at 42 kHz and 100 W, was used in the metal extraction. For comparison, a Phoenix Luferco vortex shaker AP 56 (Araraquara, Brazil) working at ca. 3000 rpm was also used. An Eppendorf 5804 centrifuge (Hamburg, Germany) with an eight-tube capacity was used to separate the sample solid particles from the solvent for supernatant analysis. For digestion procedures, a 1020-W, 60-Hz Ika heater plate (Königswinter, Germany) was used.

The limit of detection (LOD) and the limit of quantification (LOQ) were calculated according to the International Union of Pure and Applied Chemistry (IUPAC)[18] (LOD = 3σ / S and LOQ = 10σ / S, in which σ is the standard deviation of ten consecutive measurements of the analytical blank solution and S is the slope of the respective calibration curves).

Reagents and sample

All samples and solutions were prepared using deionized water (Millipore, Model Direct 8) with 18.2 MΩ cm resistivity. The glassware was washed with commercial detergent and rinsed with deionized water from the same source. Standard solutions of gold were prepared in 0.1% v/v of HNO_3 by successive dilution from a Au(III) stock solution (1000 mg L^{-1}, SpecSol®). *Aqua regia* solution was prepared by mixing hydrochloric acid (37% m/v, J. T. Backer) and concentrated nitric acid (70% m/v, Merck) in a proportion of 3:1 v/v, respectively, with no further purification. Titanium(IV) oxide (TiO_2) and cerium(IV) oxide (CeO_2), purchased from Sigma-Aldrich, were used as catalyst supports. All other chemicals were purchased from commercial sources and used without further purification.

Catalyst preparation

Au/TiO_2 (TiO_2 supported gold catalyst) and Au/CeO_2 (CeO_2 supported gold catalyst)

The gold-supported catalysts were prepared using a modification of the sol-immobilization method described elsewhere.[19] In this procedure, 1.80 mL of an aqueous solution of 2.0 wt.% polyvinyl alcohol (PVA, 36 mg) was added under intense magnetic stirring to an aqueous

solution of $HAuCl_4$ (172.5 mg, 300 mL). The metal reduction occurred after the drop-by-drop addition of 7.65 mL of $NaBH_4$ (0.1 mol L^{-1}), which turned the solution a dark purple color. The system was stirred for 30 additional minutes, after which 1.5 g of the oxide support (TiO_2 or CeO_2) was added to the sol and stirred for three hours at room temperature. After this time, the solid was separated by centrifugation (10 min at 7000 rpm) and dried at 100 ºC for 20 h. The commercial TiO_2 and CeO_2 supports have about 25 nm (information provided by the manufacturer) and the gold nanoparticles have about 3 nm.

Au-Rh/TiO_2 (TiO_2 supported gold-rhodium catalyst) and Au-Co/TiO_2 (TiO_2 supported gold-cobalt catalyst)

The same procedure described for monometallic Au catalysts was used, except for the addition of Rh and Co (1:1 Au:M mol ratio) in each of the catalysts. To synthesize AuCo sol, 40.8 mg of $HAuCl_4$ and 34.9 mg of $Co(NO_3)_2$ were added to 300 mL of deionized water. To this mixture, 1.80 mL of a 2.0 wt.% solution of 36 mg PVA was added under intense magnetic stirring. Metal reduction occurred after the drop-by-drop addition of 7.65 mL of $NaBH_4$ (0.1 mol L^{-1}). Stirring was maintained for 30 min. To synthesize AuRh sol, 34.0 mg of $HAuCl_4$ and 27.1 mg of $RhCl_3$ were added to 300 mL of deionized water. To this mixture, 1.80 mL of a solution of 2.0 wt.% PVA was added during intense magnetic stirring. Metal reduction occurred after the drop-by-drop addition of 7.65 mL of $NaBH_4$ (0.1 mol L^{-1}). Stirring was maintained for 30 min. Then, 1.5 g of the oxide support (TiO_2) was added to the sol and stirred for 3 h at room temperature. The solid was then separated by centrifugation (10 min at 7000 rpm) and dried at 100 ºC for 20 h.

Development of method for Au determination by SLS-F AAS

Supported gold catalyst slurries were prepared by adding approximately 6.0 mg of Au/TiO_2 catalyst to a 50 mL conic polypropylene volumetric flask along with 50 mL of an appropriate solvent. Deionized water, aqueous solution containing 0.1, 1.0, and 5.0% (v/v) of concentrated HNO_3, and aqueous solution containing 0.1, 1.0, and 5.0% (v/v) of *aqua regia* (freshly prepared) were the tested solvents. To improve the efficiency of the atomization process, extraction procedures using simple hand shaking and ultrasound extraction at 5, 10, 15, 30, and 45 min were evaluated.

The proportions of the sample and the solvent are also important parameters that require careful investigation, as difficulties in introducing the sample can occur, depending on the concentration of the suspension. For SLS-F AAS analysis, the best proportions were evaluated by separately adding 2, 4, 6, 8, and 10 mg of the sample to 50 mL of the appropriate solvent. All slurries were submitted to ultrasound for 30 min at room temperature and analyzed by F AAS.

Evaluation of method accuracy: decomposition of Au/TiO_2 using *aqua regia*

To evaluate the accuracy of the proposed method, the Au/TiO_2 catalyst was also analyzed by a reference method.[18] In this method, 20 mg of the gold-supported catalyst was added to a 50-mL beaker along with 5 mL of concentrated *aqua regia*. A watch glass was placed in the top of beaker, allowing the liquid to reflux. The system was heated for 3 h at 115 ºC using a heater plate. Next, the solution was transferred to a 50-mL conic polypropylene volumetric flask, and the final volume was increased to 50 mL with deionized water. Before analysis by F AAS, the solution was centrifuged for 10 min at 7000 rpm.

Results and Discussion

The majority of the solid samples submitted to elemental analysis requires conventional approaches to promote chemical decomposition prior to analysis. In the case of gold-supported catalysts, a fusion procedure or the use of high pressure and high temperature associated with the powerful acid mixture is necessary.[20] In both cases, these sample decomposition methods are time-consuming and require special attention to avoid systematic and random errors that could compromise the overall accuracy and precision of the analytical results.[21]

Slurry sampling (SLS) analysis has been proposed as a way to overcome problems associated with sample decomposition.[21] In this method, the ground sample is suspended in a solvent and the mixture is analyzed. While positive characteristics are associated with this method, some difficulties have to be carefully investigated. The proportion between the solid sample and the solvent has to be evaluated, as it can cause difficulties on sample introduction into the spectrometer. Diluted slurries can generate imprecise results due to a lack of homogeneity, while concentrated slurries can increase interference. Another difficulty is the calibration method. Calibration in aqueous medium can be used if no sample interference is observed. Otherwise, solid standards are required. An alternative that minimizes these problems is to promote the analyte extraction. In this case, the appropriate solvent and extraction procedure have to be used.

Simple shaking and ultrasound-assisted extraction were evaluated to determine the best procedure for performing

the analysis. Different solvents such as deionized water, diluted and concentrated HNO_3, and diluted and concentrated *aqua regia* were also tested to prepare the solid suspension. An in-house reference material of Au/TiO_2 catalyst containing 1.57 ± 0.08% (m/m) of Au was used. This result was obtained by using the reference method commonly adopted in Au/TiO_2 catalyst analysis.[18] In this reference method, gold was leached under treatment with concentrated *aqua regia* and heated for about three hours before analysis by F AAS. The techniques were compared using a parameter recommended by IUPAC.[22] As represented in the equation below, the recovery (R) denotes the ratio of the observed value, $V_{(obs)}$, obtained from the proposed procedure, divided by a reference value, $V_{(ref)}$:

$$R = \frac{V_{(obs)}}{V_{(ref)}} \times 100 \quad (1)$$

The slurry sampling method is the $V_{(obs)}$ and the traditional extraction method via *aqua regia* digestion was used as $V_{(ref)}$.

Influence of ultrasound radiation in slurry sampling analysis

The influence of ultrasound radiation on slurry sampling analysis was investigated. A mixture of 6.0 mg of Au/TiO_2 catalyst and 50 mL of deionized water was submitted to ultrasound for 5, 10, 15, 30, and 45 min. The results were also compared to slurries submitted to a simple hand shaking for 10 min and shaking using vortex for 10 min. The results, presented in Figure 1, show that ultrasound-assisted extraction is more efficient than extraction using simple hand shaking or vortex shaking. For the ultrasound-assisted extraction, 30 min is effective, as no further substantial changes in the recovery value were observed when a longer time period was used.

Evaluation of solvent on slurry sampling analysis

The influence of the solvent used in the preparation of the slurry and the extraction efficiency were evaluated. A mass of around 6.0 mg of Au/TiO_2 (1.57% m/m) catalyst was mixed with 50 mL of different solvents and submitted to ultrasound-assisted extraction for 30 min. The solvents used were deionized water, aqueous solution containing 0.1, 1.0, and 5.0% (v/v) of concentrated HNO_3, and aqueous solution containing 0.1, 1.0, and 5.0% (v/v) of *aqua regia* (freshly prepared). The results, shown in Table 1, indicate a recovery (R) close to 100% in all cases, except when deionized water was used as the solvent. The use of HNO_3 or *aqua regia* provides good results, even for a more diluted solution. These results indicate that the simple presence of H^+ ions in the solution promotes Au lixiviation. In this case, 0.1% (v/v) HNO_3 was the best option.

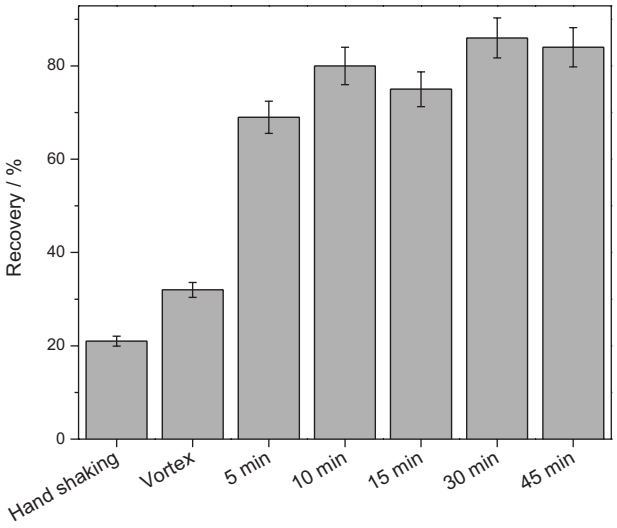

Figure 1 Influence of hand shaking, vortex shaking, and ultrasound-assisted extraction time on Au/TiO_2 (1.57%, m/m) prepared by adding 6.0 mg of Au/TiO_2 catalyst in 50 mL of deionized water. The deviation bars were calculated considering triplicates of each experiment.

Table 1. Evaluation of effect of solvent on the efficiency of Au extraction from a Au/TiO_2 (1.57% m/m) catalyst using 30 min of ultrasound-assisted extraction (n = 3)

Solvent	Recovery / %
Deionized water	83 ± 1
0.1% (v/v) HNO_3	96 ± 1
1.0% (v/v) HNO_3	96 ± 1
5.0% (v/v) HNO_3	100 ± 6
0.1% (v/v) *aqua regia*	101 ± 4
1.0% (v/v) *aqua regia*	104 ± 4
5.0% (v/v) *aqua regia*	113 ± 3

Evaluation of the slurry concentration

The main difficulty associated with direct slurry sampling analysis is finding the best proportion between the sample and the solvent (0.1% m/v HNO_3). Depending on the dilution used, interference associated with the matrix, the introduction of the sample, or an increase in heterogeneity might occur. In general, slurries that are more concentrated result in poor recoveries, due to difficulties with introduction of the slurry to F AAS. On the other hand, slurries that are less concentrated result in less precise results, probably due to the lack of homogeneity associated with a low sample mass size. For SLS-F AAS analysis, the best proportion between the sample and the solvent

(0.1% m/v HNO_3) was evaluated for analysis of a Au/TiO_2 catalyst. The slurries were prepared by adding 2, 4, 6, 8, and 10 mg of the sample to 50 mL of 0.1% m/v HNO_3. All slurries were submitted to ultrasound-assisted extraction for 30 min at room temperature. All of the experiments were performed in triplicate. The results, presented in Table 2, show that the evaluated sample mass sizes do not affect the analytical results. To check whether this result was because the analyte (Au) was extracted totally into the solvent, the slurry was centrifuged and the supernatant was analyzed. Recovery of about 10% was obtained in all supernatants, indicating that Au was not completely extracted from the catalyst matrix. Therefore, the introduction of the slurry sample (solid + supernatant) to the flame atomizer is imperative.

Table 2. Evaluation of effect of sample mass size on the efficiency of Au extraction from a Au/TiO_2 (1.57% m/m) catalyst using 30 min of ultrasound-assisted extraction and 0.1% m/v HNO_3 as solvent (n = 3)

Sample mass size / mg	Recovery / %
2	93 ± 5
4	94 ± 9
6	100 ± 3
8	88 ± 7
10	94 ± 20

Evaluation of matrix effect

Another difficulty associated with slurry sampling analysis is the matrix effect. As solid samples are introduced with no sample pre-treatment, the sample matrix can affect the atomization process, thereby changing the efficiency of the atomization. In this case, external calibration cannot be used. To check the matrix interference, a calibration curve was performed in the absence and in the presence of the solid matrix TiO_2 (Figure 2). A comparison of the slopes (b) of the calibration graphs obtained from the aqueous solution with those obtained in the presence of a solid matrix can be used to estimate the effect caused by the presence of the solid in the sample. In the absence of a matrix effect, the ratio between the slopes obtained from the aqueous solutions and the sample must be approximately 1; this condition ensures the efficiency of using aqueous reference solution for instrument calibration. The regression coefficients (r) and slopes (b) obtained from the aqueous solution were very close to those obtained from the sample containing the solid matrix. The ratio between the slopes obtained from the aqueous calibration curve and the calibration curve with solid matrix (slurry calibration) is 0.93 ± 0.11, which suggested no matrix effect. The good agreement between the two calibration curve procedures can be credited to the similar atomization mechanism of the Au in aqueous solution and in the solid sample.

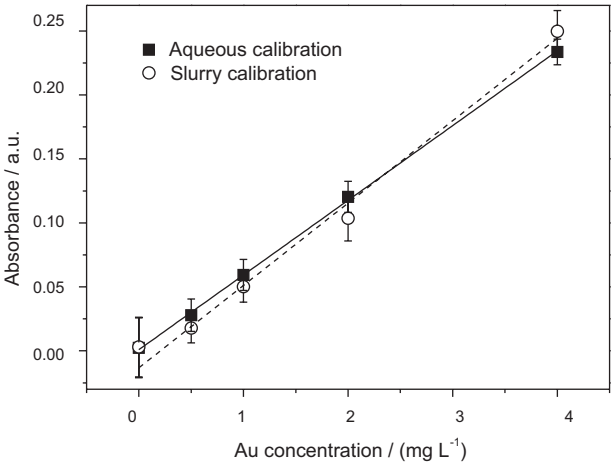

Figure 2. Calibration curves for Au determination: (■) aqueous calibration ($y = 0.0583x + 0.0012$, $r^2 = 0.9996$) and (○) slurry calibration ($y = 0.0629x - 0.0094$, $r^2 = 0.9899$).

The calculated limits of detection and quantification are LOD = 0.05 mg L^{-1} and LOQ = 0.17 mg L^{-1}. They were calculated based on the zero mass response, which is the ratio between three times the standard deviation of ten readings of the chemical modifier solution and the slope of the calibration curve adjusted to a sample mass of 6 mg.

Application of the method for analysis of other catalysts

The catalyst preparation method described in the experimental section was extended to synthesize other catalysts, using gold on a different support (Au/CeO_2) and alloys with gold and a second metal ($AuCo/TiO_2$ and $AuRh/TiO_2$). The direct slurry sampling was used to analyze the gold content in those different systems; the results are shown in Table 3. The direct slurry sampling method was compared with the reference method, wherein gold was leached under treatment with concentrated *aqua regia* and heated for about three hours before undergoing analysis by F AAS. The results are in excellent agreement using either

Table 3. Comparison between the slurry method and the decomposition method

Catalyst	Concentration by traditional method / % (m/m)	Concentration by developed method / % (m/m)	Recovery / %
$Au-Co/TiO_2$	0.76 ± 0.15	0.79 ± 0.06	104 ± 9
$Au-Rh/TiO_2$	0.40 ± 0.04	0.41 ± 0.02	102 ± 9
Au/CeO_2	1.92 ± 0.07	1.92 ± 0.05	100 ± 3

the conventional method with a digestion step or the direct slurry sampling method, regardless of whether a different solid matrix or an alloy containing a second metal was used.

Conclusions

Herein, we have studied a new analytical method for the quantification of gold in supported catalysts using slurry sampling. The method showed a high recovery percentage (100 ± 3) for the parameters developed with Au/TiO_2, the catalyst used as an in-house reference material analyzed initially using the traditional extraction method via *aqua regia* digestion. Consuming just 6.0 mg of the sample, along with 30 min of sonication and a diluted acid (0.1% HNO_3) in a final volume of 50 mL, the parameters were sufficient to determine the best conditions for the newly developed method. The slurry method allowed satisfactory results with no need for long extraction procedures. It overcomes the main drawbacks associated with sample digestion by avoiding the use of concentrated toxic reagents, minimizing sample manipulation, and consequently, reducing the risks of contamination and the sample preparation time. Moreover, different supports and bimetallic nanoparticles did not disrupt the method, at least not for catalysts synthesized by a colloidal impregnation of nanoparticles in a support using PVA as a stabilizer. The slurry sampling presented herein is efficient and offers an easier way to analyze gold catalysts, using diluted acids in a short period of time in comparison with conventional methods. This method provides an easy, fast way of analyzing the total loading of metal contained in a catalyst.

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