

Flame AAS Determination of Platinum, Palladium, and Rhodium in Catalysts

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INTRODUCTION

Alumina-supported Pd, Pt, and bimetallic Pt-Re catalysts have been used in a variety of industrial applications. The Pt-Re/Al₂O₃ reforming catalysts are used for upgrading low octane naphthas to high octane gasoline as well as for the production of important feedstocks for the petrochemical industry. Palladium metal is also widely used in the petroleum industry as a hydrogenation catalyst.

The ability to determine very low levels of Pt, Pd, and Rh is required when minimum amounts of these metals are necessary to retain catalytic activity. In addition, the economical recovery of these metals depends on their accurate determination. Complete determination of the noble metals can be achieved when both the metal and the support material are dissolved, employing wet chemical methods. However, classical gravimetric procedures could not easily be applied for the determination of low levels of platinum group metals, especially in spent catalysts which are usually recycled and may thus be contaminated with various metallic impurities. Different spectrophotometric techniques have been applied to the determination of platinum, palladium, and rhodium in catalysts but most of them require complete separation of platinum and palladium from the matrix prior to their determination.

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ABSTRACT

A flame atomic absorption spectrometric method is described for the determination of platinum, palladium, and rhodium in used and fresh alumina-supported and sieve catalysts. A lanthanum solution was used to eliminate chemical matrix interferences. Samples were completely dissolved in sulfuric acid and aqua regia. Overall, the method has resulted in % RSD values ranging from 1.1–5.7, 2.2–5.9, and 4.8–5.3 for Pt, Pd, and Rh, respectively; the 3 σ detection limits were 5 μ g/L Pt, 3 μ g/L Pd, and 40 μ g/L Rh.

Various atomic spectrometric techniques for the determination of platinum, palladium, and rhodium in alumina-supported catalysts have been reported. The interference of alumina was eliminated either by adding lanthanum solution (4) or using a titanium spectroscopic buffer and controlling the burner height (5) or by adding aluminum sulphate as spectroscopic buffer (10).

In the literature, no recent studies report on the determination of platinum, palladium, and rhodium in alumina-based catalysts by flame

atomic absorption spectroscopy (FAAS). In this paper, a relatively simple FAAS method is proposed that requires no separation procedure for the determination of each element in the presence of the others and the matrix. After complete dissolution of the samples, the addition of lanthanum solution was employed to eliminate matrix interferences. The method developed provides the means for an accurate determination of platinum, palladium, and rhodium in reforming catalysts.

EXPERIMENTAL

Instrumentation

For the FAAS analysis, a Perkin-Elmer® Model 403 atomic absorption spectrometer was employed. The operating parameters for Pt, Pd, and Rh are given in Table I.

For the X-ray fluorescence (XRF) analysis, the powder samples were obtained by using an X-ray wavelength dispersive spectrometer (JEOL JSDX). A tungsten X-ray tube operated at 50 kV and 30 mA was used with a LiF analyzer crystal by a plane of 220. The spectra were recorded with a scanning rate of 2 degrees/minute.

TABLE I
Operating Parameters for FAAS

Analyte	Light source	Current (mA)	Wavelength (nm)	Slit Width	Flame (nm)
Pt	HCL ^a	12.5	265.9	0.4	air - C ₂ H ₂
Pd	HCL	10	247.6	0.4	air - C ₂ H ₂
Rh	HCL	5	343.5	0.2	air - C ₂ H ₂

^a Hollow Cathode Lamp.

A Jarrell Ash® optical emission spectrograph was employed for quantitation of contamination elements.

Reagents and Standards

Palladium (980 mg/L in 5% HCl, Sigma) and platinum (1010 mg/L in 5% HCl, Sigma) stock solutions were used.

Rh solution (1000 mg/L) was prepared using $\text{RhCl}_3 \cdot 3 \text{H}_2\text{O}$ (38% Rh, Merck).

Lanthanum stock solution (10.0 g/L) was prepared by dissolving 11.85 g of La_2O_3 in 24 mL of HCl and then diluting to 1.000 L with distilled water.

Alumina stock solution (10.60 g/L) was prepared by leaching 1g $\gamma\text{-Al}_2\text{O}_3$ with 1:1 H_2SO_4 solution and then dissolving in aqua regia; the resulting solution was diluted to 50.0 mL with 1M HCl.

All other chemicals were of analytical reagent grade.

Catalyst Standards

Two synthetic active carbon-based catalysts containing platinum and platinum-palladium (prepared by Heraeus Laboratory, Hanau, West Germany) and two alumina-supported catalyst standards containing only platinum, palladium, or rhenium (Aldrich Company, Milwaukee, WI USA) were used.

Catalyst Samples

Fifteen catalyst samples were analyzed which were either only Pt or Pd or Pt-Re alumina-based or Pt-sieve, obtained from various petroleum refineries and nitric acid plants (identified in Roman numerals in Table II). These catalysts were either fresh (F), spent (S), or regenerated (R) several times. Nine of the Pt-Re, two of Pt, two of Pd-containing alumina-based, and two of Pt- and Rh-containing sieve catalyst samples were utilized. Table II lists these according to catalyst-support-

ing material and according to industries using Roman numerals.

Standard and Test Solutions

FAAS: For the individual elements, calibration solutions were prepared daily containing from 0 to 90 mg/L Pt, 0 to 30 mg/L Pd, and 0 to 50 mg/L Rh.

Test solutions containing Al at concentrations ranging from 0 to 5000 mg/L and containing fixed concentrations of 40.0 mg/L Pt and Re, 15.0 mg/L Pd was prepared for controlling Al effect. Sets of these solutions containing various concentrations of buffer (1500–5000 mg/L La) were tested. When there was no need for a buffer, water was used as the blank. Otherwise, the same concentration of buffer was added to standards, test solutions, samples, and blank.

For active carbon-based and platinum-sieve catalysts, test solutions containing 4.0 mg/L Rh, between

0 and 500 mg/L Pt, and 15.0 mg/L Pd, between 0 and 300 mg/L Pt, were prepared.

XRF: Catalyst standards of platinum, palladium, and rhenium were prepared by mixing known amounts of the promoter powders with 1g $\gamma\text{-Al}_2\text{O}_3$ powder to give a homogeneous mass. The uniformity in the distributions was checked by recording the spectra of different fractions.

Dissolution of Catalyst Samples and Standards

All catalyst materials were dried in an oven at 110°C to eliminate volatile hydrocarbons and moisture. In order to reach complete dissolution, a 1.00-g and finely ground alumina-supported catalyst sample or catalyst standard was leached with 5.0 mL of aqueous H_2SO_4 solution (1+1), and then two times with 4.0 mL of aqua regia. The aliquots were combined and diluted to 100-mL volume.

TABLE II
Composition of Catalyst Matrices Determined by XRF (w/w %)

Sample	Pt	Pd	Rh	Re	Fe	Cu	Ni	Zn
Alumina-based								
I F *	0.25 - 0.50	-	-	0.25 - 0.50	-	-	-	-
I 7R	0.13 - 0.25	-	-	0.25 - 0.50	-	-	-	-
I 9R	0.13 - 0.25	-	-	0.25 - 0.50	-	-	-	-
II F	0.25 - 0.50	-	-	-	-	-	-	-
II 7R	0.25 - 0.50	-	-	-	+	+	-	-
III S1	0.13 - 0.25	-	-	0.25 - 0.50	-	+	-	-
III S2	0.13 - 0.25	-	-	0.25 - 0.50	-	+	-	-
III S3	0.13 - 0.25	-	-	0.25 - 0.50	-	+	-	-
III S4	0.13 - 0.25	-	-	0.25 - 0.50	-	+	-	-
IV F	0.50 - 0.25	-	-	0.25 - 0.50	-	-	-	-
V F	-	< 0.13	-	-	-	-	-	-
VI F	-	< 0.13	-	-	-	-	-	-
VII S	< 0.13	-	-	< 0.25	+	+	-	-
Sieve								
I S	> 0.50	-	+	-	+	+	+	+
II S	> 0.50	-	+	-	+	+	+	+

F: Fresh, S: Spent, 7R: seven times regenerated.

+: present but values could not be determined due to lack of standards.

Accurately weighed 50.0-mg sieve-catalyst samples were leached two or three times with 3.0-mL portions of aqua regia. The insoluble contaminants obtained after filtration were dissolved by NaOH fusion. For this purpose, 10 mL of 30% NaOH solution was evaporated to near dryness in a nickel crucible. The insoluble part of the samples was added to the contents of the crucible, which was then heated in a muffle furnace at 800°C for one hour. The contents were dissolved in 100-mL water at 70–80°C and 10-mL concentrated HCl was also added for complete dissolution. The final solution was evaporated down to 50 mL.

Synthetic active carbon-based catalyst standards were heated in a muffle furnace at 600°C for two hours. Then, 3 mL of aqua regia was added and the mixture heated to near dryness. This step was repeated five times. The mixture was filtered through a blue ribbon filter paper, the residue washed three times with 3-mL portions of hot 1 M HCl solution, and the solution diluted to 50 mL.

Procedure

Platinum, palladium, and rhodium were measured by flame atomic absorption spectrometry using the sample solution directly or with suitable amounts of lanthanum buffer solution. Each calibration solution and sample solution was measured three times, water blanks were aspirated and measured after each reading.

RESULTS AND DISCUSSION

Sample Characterization

In order to characterize the catalyst matrices, XRF and OES techniques were used. Platinum and palladium concentration in all types of samples was semiquantitatively determined using XRF by comparing the peak heights in the spectra to that of the calibration

standards of platinum, palladium (0.5%, 0.25%, and 0.13%) and rhenium (0.5%, and 0.25%) catalysts (Table II). Since the sole aim was matrix characterization, only the base metals and some contamination elements were determined in the catalyst samples. Platinum and rhenium levels in spent catalysts were found to be lower than the fresh catalysts.

Besides platinum group metals, the contamination level of the elements found in spent catalysts, especially in Pt-sieve catalysts, were also determined by OES (Table III). The contamination level was higher in spent catalysts as compared to the regenerated catalysts. The aluminium and silicon values were high because they are constituents of the supporting materials.

Interferences

In the presence of large amounts of Al and Pt, the suppression of the analyte signal for Pt, Pd, and Rh was controlled by adding lanthanum to the sample and the calibration solutions. The interference effect of Al

on the platinum or palladium signal in the alumina-based catalysts, Pt on the rhodium signal in the platinum-sieve, and Pt on the palladium signal in the active carbon-based catalyst, was determined with the test solutions.

The relative enhancement is defined as the value observed, divided by the true value of the analyte signal. Thus, a relative enhancement of 1.0 shows no enhancement, 1.2 shows a 20 % enhancement, and 0.8 indicates a 20 % suppression of the analyte signal.

When no lanthanum buffer solution was added, the analyte signal decreased with increasing concentration of the matrix element. When the Al concentration reached its maximum value of 5000 mg/L (the amount supposed to be present in catalyst samples), the relative analyte signal was reduced to 0.89 and 0.85 for platinum and palladium, respectively (Figures 1 and 2). To prevent the depression in the analyte signal, 1500 mg/L La for Pt and 5000 mg/L La for Pd were used in all alumina-based sample solutions. In platinum-sieve catalysts, the platinum concentrations varying between 40–300 mg/L created an interference effect in the determination of rhodium. The use of 1500 mg/L La overcame the suppression (Figure 3). For the determination of platinum, there was no need to add a buffer solution because of the relatively low content of Rh compared to Pt in the sieve catalysts.

For the determination of palladium in active carbon-supported catalyst standards, the analyte signal became independent of the matrix containing large amounts of platinum when 1500 mg/L of La was used (Figure 4).

Evaluation

Using the established optimum conditions, the calibration curves of Pt, Pd, and Rh in the presence

TABLE III
Contamination of Elements
(% w/w) in Spent Catalysts
Determined by OES

	Wavelength (nm)	Alumina-based		
		Sieve II S	II 7R	I 7R
Cr	425.4	>1	0.02	0.02
Co	345.4	0.02	-	-
Ti	337.2	0.15	0.07	0.07
Cu	327.4	0.04	-	0.15
Mn	403.1	0.2	-	0.03
Ni	341.5	>1	0.01	-
Mg	285.2	0.04	-	-
Ca	422.7	0.1	-	-
Fe	372.0	10	0.15	~1
Si	251.6	>10	0.15	0.07
Al	396.2	0.7	>10	>10

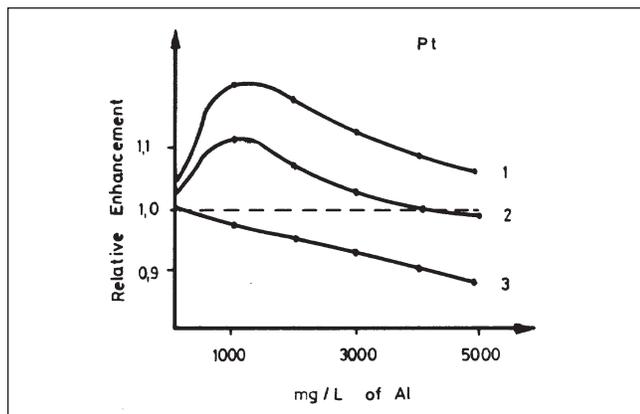


Fig. 1. Effect of Al on the determination of Pt (50.0 mg/L). 1=2500 mg/L La; 2=1500 mg/L La; 3=no buffer.

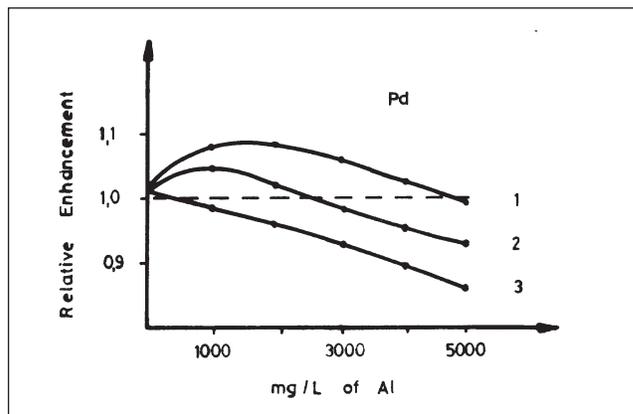


Fig. 2. Effect of Al on the determination of Pd (15.0 mg/L). 1=5000 mg/L La; 2=2500 mg/L La; 3=no buffer.

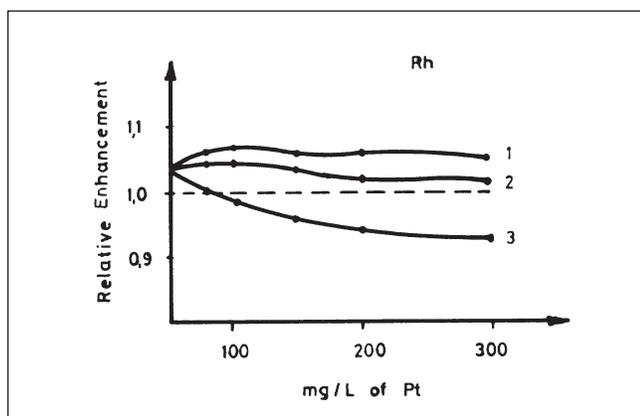


Fig. 3. Effect of Pt on the determination of Rh (4.0 mg/L). 1=2500 mg/L La; 2=1500 mg/L La; 3=no buffer.

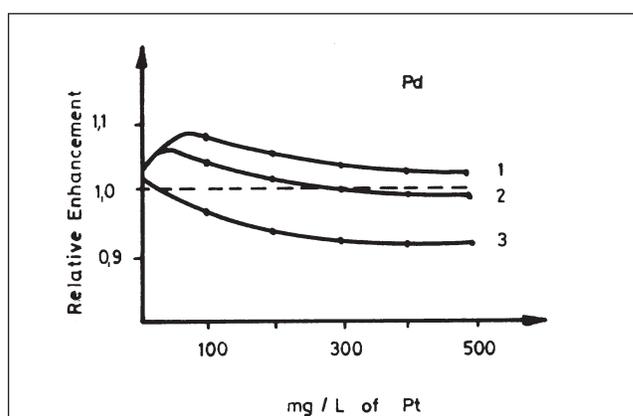


Fig. 4. Effect of Pt on the determination of Pd (15.0 mg/L). 1=2500 mg/L La; 2=1500 mg/L La; 3=no buffer.

and absence of a buffer were studied. The range of correlation coefficients for the curves of Pt, Pd and Rh were 0.993–0.997, 0.997–0.998, and 0.993–0.997, respectively ($n = 7$).

The precision of the measurement for each metal was evaluated by 10 replicate measurements of the sample solution prepared by randomly mixing 10 different sample solutions in which all of the analyte metal concentrations were in the linear range of the calibration curves. The precision data calculated as % RSD and the detection limits (DL) for Pt, Pd, and Rh are given in Table IV. The detection limit of each metal was calculated

by taking 10 replicate measurements of the blank and finding the corresponding 3σ values for concentration.

TABLE IV
Precision and Detection Limits of Pt, Pd, and Rh for the Sample Pool Solution

Element	%RSD (n=10)	DL (3σ) ($\mu\text{g/L}$)
Pt	1.4	5
Pd	1.6	3
Rh	1.9	40

The percent concentration of palladium, platinum, and rhodium in all catalyst samples are reported in Table V. The precision of the FAAS method for the analysis of catalysts calculated as %RSD ranged from 1.1–5.7% for Pt, 2.2–5.9% for Pd, and 4.8–5.3% for Rh. These figures reflect the overall precision of the method employed. The accuracy of the method given in Table VI was tested with catalyst standards having two different supporting materials. Comparison of the precision of the experimental values with the standard values of the reference materials was performed by applying the t -test at the 95% confidence level. The results showed no significant difference.

TABLE V
Pt, Pd, and Rh Concentrations in Catalysts
Determined by FAAS

Samples	x ± s, % (w/w), (n=3)		
	Pt	Pd	Rh
Alumina-based			
I F	0.318±0.005		
I 7R	0.26±0.01		
I 9R	0.248±0.005		
II F	0.346±0.006		
II 7R	0.22±0.01		
III S1	0.203±0.006		
III S2	0.196±0.006		
III S3	0.207±0.006		
III S4	0.214±0.003		
IV F	0.393±0.006		
V F	-	0.093±0.002	
VI F	-	0.034±0.002	
VII S	0.105±0.006		
Sieve			
I S	19.4±0.2		0.019±0.001
II S	4.65±0.05		0.063±0.003

TABLE VI
Results for the Standard Samples

	Pt (% w/w)		Pd (% w/w)	
	Reported ^a	Exp. ^b	Reported ^a	Exp. ^b
Alumina-based	0.5	0.54 ± 0.01	1	0.96 ± 0.04
Active carbon				
ACI			32.73	32.6 ± 0.2
ACII	58.16	57.7 ± 0.5	3.39	3.38 ± 0.03

^a Active carbon- (AC) based standards were prepared by Heraeus Laboratory

^b Experimental results are given as mean ± standard deviation, n=3. Alumina-based standards were purchased from Aldrich Company

CONCLUSION

Contrary to earlier reports (1-4), the FAAS method described is relatively simple and requires no pre-separation procedure. The addition of lanthanum makes the determination of Pt, Pd, and Rh nearly independent of matrix interferences. The precision of the method at the given % levels of Pt, Pd, and Rh in catalyst samples are comparable to the limited data available (1-4). Lower detection limits were obtained for Pd (3 mg/L) than reported in previous studies (45 and 20 mg/L) (7,9).

The method is applicable to different types of catalysts such as alumina-based, active carbon-based or sieve, which may be either spent or regenerated.

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