DETERMINATION OF PALLADIUM IN HYDROGENATION CATALYSTS BY HR-CS FAAS METHOD

Miroslava Smrčová[1)], Dagmar Remeteiová[1)]*
[1)] *Technical University of Košice, Faculty of Metallurgy*, *Košice, Slovakia*

[*]Corresponding author: *e-mail: miroslava.smrcova@tuke.sk, Tel.: +421 55 602 2323, Department of Chemistry, Faculty of Metallurgy, Technical University of Košice, Letná 9, 04200 Košice, Slovakia*

Abstract

Present paper deals with analytical control of hydrogenation supported catalysts (Pd/AC) composition using high-resolution continuum source atomic absorption spectrometry with flame atomization (HR-CS FAAS). Catalysts were prepared with expected 3 wt. % Pd content by the simple technique of deposition − reduction of palladium in a basic environment. Formaldehyde was applied as the reduction agent. The working conditions (gas flow and burner height) for determination of the catalytically active component in the prepared Pd/AC catalysts were found. Prior to the analysis by HR-CS FAAS method Pd/AC was subjected to microwave (MW) assisted digestion in the environment of strong oxidizing acids. Appropriate digestion time of 15 min and temperature of 200 °C had been also experimentally obtained.

Keywords: platinum-group, porous material, MW assisted digestion, HR-CS FAAS

1 Introduction

Catalytic hydrogenation represents one of the most used reduction methods and belongs to the group of heterogeneous catalytic processes [1], [2]. Substrates acting in this type of chemical reaction are generally unsaturated hydrocarbons, aromatic rings, nitro compounds, carbonyl compounds, azides and derivatives of carboxylic acids [3]. In the process of catalytic hydrogenation it is necessary to use a suitable catalyst, because in the case of its absence the chemical reaction does not take place at all [1]. In practice the supported catalysts of platinum-group metals (Pd, Pt, Ru, Rh) are the most frequently used [1], [4], [5]. Commonly used supports are porous materials such as activated carbon, carbon nanotubes and nanofibers, oxides of aluminium, iron, silicon or alkaline earth metal [6][10]. The basic requirement for a suitable catalyst support is its high porosity ensuring high specific surface area (SSA) [11] where the interactions of hydrogenated compound molecules and chemisorption of hydrogen occur. This results in a favourable transition state and reorganization of bonds [1]. In addition to high porosity, the catalyst support should possess also other important physical characteristics such as density, pore size and mechanical strength. From this point of view activated carbon is often used for supported catalysts preparation, because of its chemical inertness, thermal stability, specific surface area (500 – 1200 m^2 g^{-1}) and financial availability [11]-[13].

Because of the close relation between nature and content of the active phase of supported catalysts and their activity in a particular type of chemical reaction, there is a need to find suitable methods for determination of their elemental composition [14]. High-resolution

continuum source atomic absorption spectrometry (HR-CS AAS) represents a revolution in the field of elemental analysis. Modern HR-CS AAS spectrometer, ContrAA 700, brings very significant improvements in comparison with traditional line source devices [15], [16]. The optical system of the spectrometer comprises only one continuum source of radiation – xenon short-arc lamp. A high-resolution double echelle monochromator with synchronized moving prism and grating allows to achieve a resolution of 2 pm in the range of 190 – 900 nm. All spectral lines, resonance, as well as secondary lines are available at any time. Switching from one wavelength to another is carried out in few seconds. The monochromator is stabilized by incorporating neon lamp. The correct setting of the desired wavelength is achieved by calibration of the monochromator for spectral lines of neon [17]. A linear CCD array detector contains 588 pixels, 200 of which are used for monitoring of the analytical signal and background correction. Other pixels are used for correction of the lamp intensity fluctuations [18], [19]. Photodetector with low noise provides high sensitivity, resolution and the ability to determine the intensity of the resonance spectral lines and spectral lines in the area within 1 nm. Background correction is performed simultaneously with the measurement of an analytical signal [20]. Molecular interferences originating from the sample and also spectral interferences are automatically removed from the spectrum by applying correction models containing interfering spectra of the given molecules and elements [17].

The amount of advantages characterizing this method creates an indisputable argument for its successful use in heterogeneous catalysis. The limit of detection at the ppm ($\mu g \; g^{-1}$) level makes the HR-CS FAAS method suitable for the determination of the catalytically active component after the catalyst digestion. The high efficiency of the digestion can be achieved by applying a MW energy, which ensures rapid heat generation directly inside the sample. A further advantage is a significant reduction of time needed to sample digestion, as well as reducing the amount of used reagents [21]-[26].

The aim of the presented research is to find the most suitable conditions (time and temperature) for the MW assisted digestion of the prepared Pd/AC catalyst and also for determination of the catalytically active component – Pd by HR-CS FAAS method (gas flow and burner height). We respect the International System of Units in general, but for practical purposes, we have used expressions of time in minutes, temperature in Celsius degrees and length (rather height) in millimetres.

2 Experimental materials and methods
2.1 Preparation of Pd/AC catalyst samples

Activated carbon (AC) (NORIT® SX PLUS, Norit Americans Inc., USA) with SSA 1100 $m^2 \; g^{-1}$ (declared by the producer) was used as the support material for Pd catalyst preparation. Palladium chloride (SIGMA-ALDRICH Co. LLC., USA) was dissolved in the sodium chloride solution (Lachema, Czech Republic) to formation of $Na_2[PdCl_4]$ complex. AC was mixed in sodium carbonate solution (2.5 wt. %) and palladium complex was added dropwise at 45 °C. After heating the reaction mixture up to 95 °C, the formaldehyde solution (Mach Chemicals, Czech Republic) was added dropwise. The mixture was held 1 h at 95 °C and then it was filtrated, rinsed with sodium carbonate solution (0.2 wt. %) and dried to 40 – 60 % wetness. All used chemicals were of analytical grade.

2.2 MW assisted digestion of Pd/AC catalyst

Experiments were performed in the laboratory microwave oven Ethos One (Milestone Systems Italia Srl., Italy) that ensures uniform distribution of microwave radiation. The selected power of 500 W was dynamically controlled by the immediate requirements of the Pd/AC digestion reaction. The digestion agent was a mixture of 5 cm^3 HNO$_3$ (conc.) (Analytika, Czech Republic) and 2 cm^3 HCl (conc.) (Analytika, Czech Republic). The most suitable conditions for digestion (temperature and time) had been previously experimentally observed. The digestion efficiency at different experimental conditions was controlled by determination of the catalytically active component – Pd by HR-CS FAAS method. The digestion time varied between 15 – 25 min in discrete mode with step size of 5 min/step and the temperature in the range of 160 – 220 °C with step size of 20 °C/step. Temperature inside the digestion vessel was measured by built-in sensor and the internal space of the microwave oven was monitored by the integrated video camera.

Each experiment was performed with two parallel weighed samples. After completion of the digestion reaction it was necessary to separate the solid phase from the solution containing the catalytically active component. This step was aimed at finding a suitable separation method. Centrifugation using the universal centrifuge CN-3100 (MRC Ltd., Israel) and filtration were compared. In applying the centrifugation, the mixture was transferred to a centrifuge vial with 20 cm^3 of demineralized water and centrifuged at 3600 RPM for 20 min. Subsequently, the supernatant was casted, the solid residue washed with 25 cm^3 of demineralized water and re-centrifuged for 20 min at unchanged speed. When applying the filtration, the solid residue was also washed with 25 cm^3 of demineralized water. After the separation process, the volume of each sample was supplemented to 500 cm^3 so the content of catalytically active component in the solution was in the range of the calibration.

2.3 Determination of Pd content by HR-CS FAAS method

Determination of the active component of the catalyst was carried out after its MW assisted digestion by HR-CS FAAS method using the primary spectral line of Pd with the wavelength of 244.791 nm. The measurements were performed on the HR-CS AAS spectrometer ContrAA 700 (Analytik Jena AG, Germany), which was operated by software ASpect CS. The most suitable working conditions of analysis (gas flow and burner height) prior to the calibration of signals had been experimentally determined using a calibration solution with the highest Pd content − 10 ppm. Calibration solutions were prepared by diluting standard solution of Pd (SIGMA-ALDRICH Co. LLC., USA) in HNO$_3$ (0.32 mol dm^{-3}). The diluent agent was solution of 1 wt. % HCl (Analytika, Czech Republic).

3   Results and discussion

3.1 Finding the most suitable conditions of analysis by HR-CS FAAS method

In order to find the most suitable working conditions for determination of the catalytically active component in the prepared samples so-called "automatic optimization" mode was used. In implementing the "automatic optimization" gas flow and burner height are altered simultaneously to achieve the highest absorbance signal at a given analyte content in the solution. The process of working conditions "optimization" is shown in **Fig. 1** (software output). The experimental conditions recommended by the manufacturer of ContrAA 700 and found by us are presented in **Table 1**.
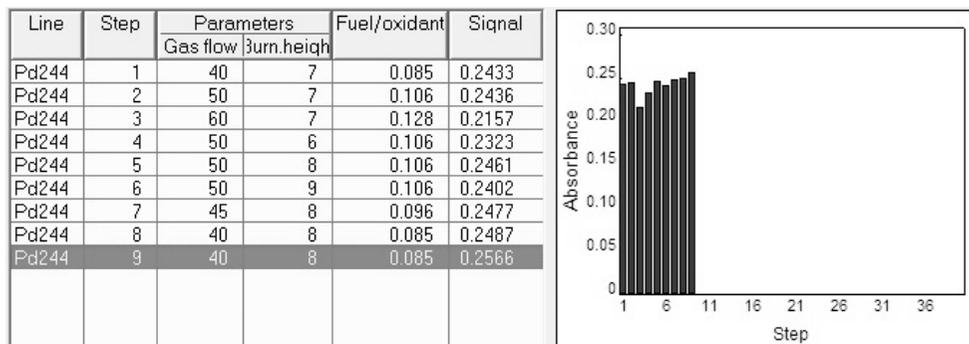
Fig. 1   Finding the most suitable conditions for the determination of Pd content by HR-CS FAAS

Table 1 Recommended and found experimental conditions for the determination of Pd content

Experimental condition	Recommended	Found
Gas flow/dm^3 h^{-1}	40	40
Burner height/mm	7	8

As shown in **Table 1**, the difference between the manufacturer's recommended working conditions and found is minimal. The above-described "optimization" was performed immediately prior to each analysis, but the found values remained mostly constant.

3.2 Calibration of signals

After finding the most suitable experimental conditions of analysis the calibration of signals was performed. Calibration solutions were prepared in an environment of 1 wt. % HCl. The working range of the calibration was to 10 ppm Pd content. According to the actual parameters the appropriate calibration model – linear or non-linear was selected. The calibration of signals, as well as "optimization" of working conditions was realized prior to each determination of Pd content. In **Fig. 2** (software output) is shown a non-linear calibration model, which had better parameters compared to the linear model.
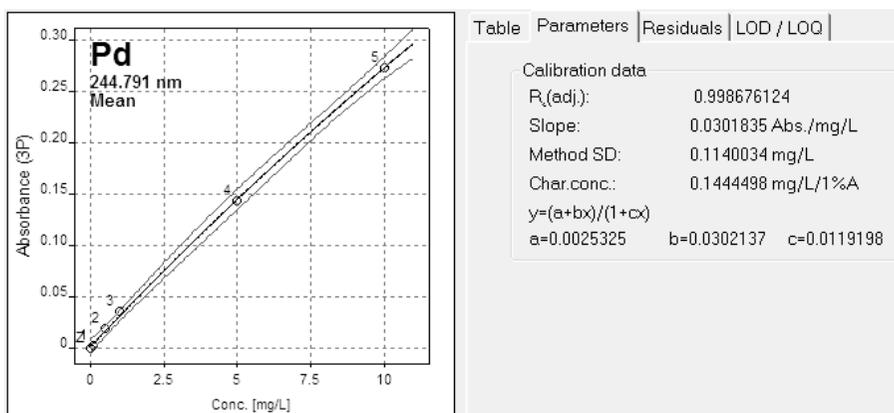
Fig. 2   A non-linear calibration model for the determination of Pd content

3.3 Finding the most suitable conditions for MW assisted digestion of Pd/AC
Preliminary experiments were focused on finding the appropriate time for the acid digestion of Pd/AC catalyst at the selected temperature of 200 °C. This temperature value is recommended for digestion of the samples based on AC by the manufacturer of microwave oven Ethos One. The individual conditions of digestion at power of 500 W are shown in **Table 2**. In this case the power does not present parameter influencing the digestion efficiency. Setting its value depends on the current requirements of the reaction and the number of actually used digestion vessels.

Table 2 Conditions of MW assisted digestion of Pd/AC at 200 °C

Experiment	Weighed sample*/g	Step 1 time/min	Step 2 time/min	Step 3
E1	0.2003	15	15	cooling to 76 °C
E2	0.2000	20	20	cooling to 76 °C
E3	0.2000	25	25	cooling to 76 °C

* dry matter content 80.12 wt. %

Measured Pd contents in $\mu g\ g^{-1}$ after experiments E1 – E3 as an average of ten repeated measurements of two parallel determinations are graphically shown in **Fig. 3**.
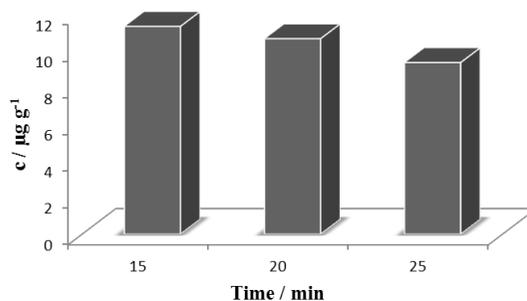
Fig. 3   Pd content at different times of MW assisted digestion of Pd/AC at 200 °C

The more objective information represents the value of Pd content expressed in wt. % (commercially used expression of the content) calculated with respect to the weighed sample of the catalyst (**Table 3**).

Table 3 Pd content (wt. %) in the samples after MW assisted digestion of Pd/AC at 200 °C

Experiment	Pd content in catalyst/wt. %
E1	2.27
E2	2.13
E3	1.87

The extending of the digestion time caused decrease of digestion efficiency, which may be due to the back-sorption of Pd on support particles or to the formation of agglomerates of undecomposed support particles after prolonged the period of MW radiation exposure and thereby occurs "trapping" of Pd.

After centrifugation of the mixture from digestion there were ultrafine particles of the solid residue created, which were difficult separated from the solution even after repeated centrifugation. For this reason, other separation method – filtration was tested. The filter material was a filter paper KA 3 (PAPIRNA Perstejn, Czech Republic) with high filtration speed. The following experiments were performed in parallel with the application of both separation techniques − centrifugation and filtration before determination of the catalytically active component content.

The next step represented finding the most suitable temperature for MW assisted digestion of Pd/AC catalyst at the selected time of 15 min, where there was reached the most efficient digestion (experiment E1). The conditions of individual experiments with an unchanged power of MW system – 500 W are presented in **Table 4**.

Table 4 Conditions of MW assisted digestion of Pd/AC at the time of 15 min

Experiment	Weighed sample*/g	Step 1 t/°C	Step 2 t/°C	Step 3
E4	0.2000	160	160	
E5	0.2000	180	180	cooling to 76 °C
E6	0.2000	200	200	
E7	0.2000	220	220	

* dry matter content 80.12 wt. %

From the graphic representation of measured Pd content values (**Fig. 4**) it is evident that filtration is more appropriate separation method, because in each experiment were achieved higher contents of the analyte than when applied centrifugation. This fact may be due to incomplete washing of the solid residue. The need for multiple repeated washing and re-centrifugation increases the time of experiment.
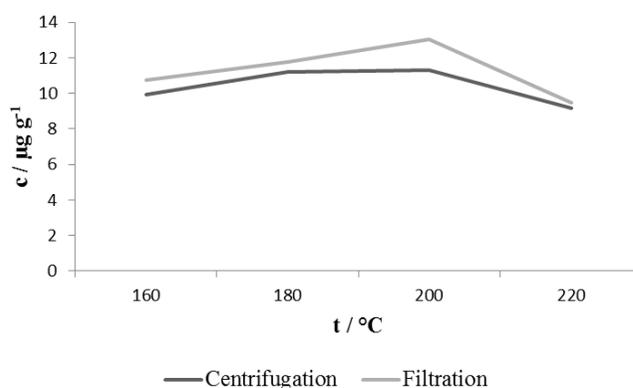
Fig. 4   Pd content at different temperatures of MW assisted digestion of Pd/AC at the time of 15 min

The resulting values of Pd content after digestion at various temperatures and after application of filtration (F) and centrifugation (C) were analogously calculated with respect to the weighed sample of the catalyst and are summarized in **Table 5**.

Table 5 Pd content (wt. %) in the samples after MW assisted digestion of Pd/AC at the time of 15 min

Experiment	Pd content in catalyst/wt. % F / C
E4	2.15 / 1.99
E5	2.36 / 2.24
E6	2.62 / 2.27
E7	1.90 / 1.84

The digestion of Pd/AC at the found most suitable conditions (15 min, 200 °C) was performed also at abbreviated "rise time", that is the time to reach the desired digestion temperature. The selected period of 10 min was not sufficient, resulting in a decrease of active component content in the obtained solutions (9.99 and 9.51 for filtration and centrifugation, respectively).
To verify the appropriate digestion temperature MW assisted digestion of another Pd/AC catalyst (expected content of Pd 3 wt. %) was performed. The conditions of individual experiments were identical as in the case of experiments E5 – E7 and are listed in **Table 6**.

Table 6 Conditions of verifying MW assisted digestion of Pd/AC at the time of 15 min

Experiment	Weighed sample/g	Step 1 t/°C	Step 2 t/°C	Step 3
E8	0.2000	180	180	
E9	0.2000	200	200	cooling to 76 °C
E10	0.2000	220	220	

The graphical presentation of the active component content at different digestion temperatures is shown in **Fig. 5**. The temperature of 200 °C was confirmed to be the most suitable for the MW assisted digestion of the prepared catalysts. It is obvious again that there was higher Pd content in the solutions after filtration compared with the solutions after centrifugation.
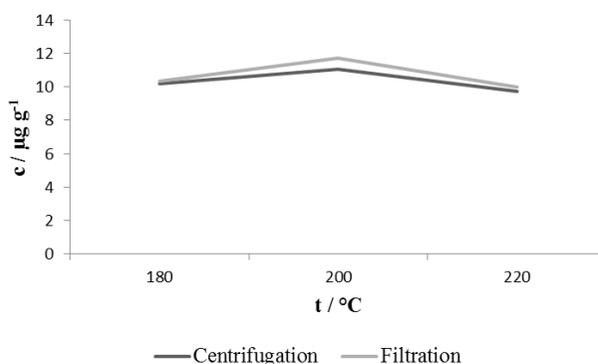
Fig. 5   Pd content at different temperatures of verifying MW assisted digestion of Pd/AC at the time of 15 min

The resulting Pd contents after verifying MW assisted digestion are presented in **Table 7** from which it is apparent that increasing of temperature may also cause a similar effect as in the case of extended time.

Table 7 Pd content (wt. %) in the samples after verifying MW assisted digestion of Pd/AC at the time of 15 min

Experiment	Pd content in catalyst/wt. % F / C
E8	2.59 / 2.54
E9	2.93 / 2.77
E10	2.50 / 2.44

4   Conclusions

The most suitable conditions for MW assisted digestion of Pd/AC catalyst and for HR-CS FAAS analysis of the catalytically active component were studied in this work. Based on the performed experiments, the following conclusions can be stated:

- A.   The most suitable working conditions for MW assisted digestion of Pd/AC catalyst are as follows: time of 15 min and temperature of 200 °C.
- B.   The results have shown that prolongation of the digestion time and increase of the temperature cause decrease of digestion efficiency, because of Pd back-sorption on support particles or the formation of agglomerates of undecomposed support particles resulting in "trapping" of Pd.
- C.   The use of MW assisted digestion is in regard of the relatively low reagents amount, as well as of the short reaction time in full compliance with the principles of "Green chemistry", which represents the modern trend not only in the industry but also in the chemical laboratory practice.
- D.   HR-CS FAAS method is unambiguously appropriate for determination of the catalytically active component content in the solution after digestion of the catalyst.
- E.   The most suitable working conditions for the determination of Pd content by HR-CS FAAS method are 40 $dm^3 h^{-1}$ gas flow and 8 mm burner height.
- F.   A difference between the theoretical active component content and the actually determined can be probably caused by the applied methodological approach of sample preparation.

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