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# Comparison of digestion methods for the determination of ruthenium in catalyst materials



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## ABSTRACT

A fusion method, an acid digestion method with a high pressure asher (HPA) and two microwave (MW)-assisted acid digestion methods were compared to investigate their suitability for the determination of Ru in catalyst materials. Ru contents in the digested samples were determined with inductively coupled plasma optical emission spectrometry (ICP-OES). Ru powder and three Ru compounds ( $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ , anhydrous  $\text{RuO}_2$  and  $\text{RuCl}_3$ ), possibly present in Ru catalysts, were digested and analyzed to compare the digestion efficiencies of the methods. Significant differences among the digestion efficiencies of the methods were observed; the fusion method having the best digestion efficiency for the compounds studied. The methods were applied for the determination of Ru in alumina- and carbon-supported catalysts. No differences among the methods were observed for these samples.

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## 1. Introduction

Ruthenium is a versatile catalyst for various chemical reactions [1]. Ru catalysts have applications, e.g. in Fischer–Tropsch synthesis and ammonia production [2]. Due to active research in the field of Ru catalysts, also the Ru contents in catalyst materials are often determined. However, according to our knowledge there are only a couple of detailed studies with the principal aim of reliable determination of Ru content in catalyst materials. For example, the determinations of Ru in catalytic materials having carbon [3–6], alumina [7,8] or silica–alumina [8] as a support material have been studied. In one of these studies a fusion method employing KOH and  $\text{KNO}_3$  was applied [6]. Traditionally, acid digestions on a hot plate have been carried out. For example concentrated HCl and mixtures of HCl and  $\text{HNO}_3$  have been used for the digestion of Ru on carbon-supported catalysts [3–5], whereas mixtures of HCl and  $\text{H}_2\text{SO}_4$  (with the addition of HF in the presence of silica) have been used for the digestion of Ru on alumina and silica–alumina supports [7,8].

It is well known that (metallic) Ru is very resistant to chemical attack [9]. Another problem encountered in Ru analytics is that oxidative conditions during the digestion stage may lead to Ru losses due to formation of volatile  $\text{RuO}_4$ . It has, for example, been found that Ru volatilizes as  $\text{RuO}_4$  from boiling nitric acid solutions

after an induction period. The length of the induction period was the shortest with the highest concentration of  $\text{HNO}_3$  [10,11]. For this reason the use of a lower amount of nitric acid compared to the *aqua regia* composition (3:1 (v/v) HCl– $\text{HNO}_3$ ) in Ru digestions has been recommended [3,12]. When the HCl to  $\text{HNO}_3$  ratio of 6:1 was used to digest carbon-supported Pt–Ru catalysts in open vessels on a hot plate, slightly higher recoveries and a little more reproducible results compared to *aqua regia* digestion were obtained [3]. On the other hand, Scaccia and Goszczynska [5] obtained similar results when they compared *aqua regia* and hydrochloric acid digestion in the determination of Ru in carbon-supported Pt–Ru catalysts.

Nowadays sample preparation in closed vessels (e.g. microwave-assisted digestion) is strongly favored over open vessel digestions due to the many advantages gained (e.g. digestion times are shortened and a smaller amount of corrosive acid vapors is liberated). Digestions in closed vessels with different acid mixtures have been applied in determinations of low concentrations of Ru and other platinum group elements, e.g. in geological and environmental materials [13–17].

Measurements of the Ru contents in digested catalyst samples have been done by using spectrophotometry [3,4,6], atomic absorption spectrometry (AAS) [5,6,8] and inductively coupled plasma optical emission spectrometry (ICP-OES) [7]. Also X-ray fluorescence spectroscopy (XRF) as a non-destructive analytical method, not requiring sample digestion, is a possible choice for the determination of Ru in catalyst materials. However, a large sample mass (~15 g) is usually needed in XRF analysis. In the

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development stage of catalyst materials the sample masses available for analytical determination may be more than ten-fold lower, thus excluding the use of XRF. The lack of suitable calibration materials may also represent a problem in XRF technique.

In this study different digestion methods for the determination of Ru in catalyst materials were investigated. The aim of this study was to achieve a complete Ru digestion with no losses. The Ru contents in the digested samples were determined with the ICP-OES technique. A fusion method with KOH–KNO<sub>3</sub> mixture and acid digestion methods with various HCl–HNO<sub>3</sub> mixtures were applied for the digestions of Ru in different catalyst materials. Previously these reagent mixtures had been applied for the determination of Ru only in carbon-supported catalysts [3–6]. The effect of experimental variables in microwave (MW)- and high pressure asher (HPA)-assisted acid digestions was tested in order to find the most suitable digestion conditions for Ru catalysts. The use of both MW- and HPA-assisted digestions created the opportunity to use large variations in digestion temperatures and times when studying the effects of these variables. Since no clear information was available on the dissolution properties of Ru from different Ru compounds present in the catalyst materials, the digestion efficiencies of the methods were evaluated by digesting metallic Ru powder as well as selected Ru compounds (RuO<sub>2</sub>·xH<sub>2</sub>O, anhydrous RuO<sub>2</sub> and RuCl<sub>3</sub>).

## 2. Experimental

### 2.1. Instrumentation

A PerkinElmer Optima 5300 DV ICP-OES (PerkinElmer Inc., Waltham, MA, USA) was used to determine Ru (240.272 nm). The ICP-OES instrument was equipped with an AS-93plus auto-sampler, a Rytton double-pass Scott-type spray chamber and a Gem Tip Cross-flow pneumatic nebulizer. The instrumental parameters for ICP-OES were as follows: RF power 1.3 kW, nebulizer gas flow 0.8 L min<sup>-1</sup>, auxiliary gas flow 0.2 L min<sup>-1</sup>, plasma gas flow 15 L min<sup>-1</sup> and sample uptake rate 1.5 ml min<sup>-1</sup>. Normal resolution and axial mode of viewing were used in the measurements.

An HPA-S (Anton Paar GmbH, Graz, Austria) high-pressure asher with 90 ml quartz vessels and a CEM MARS 5X microwave oven (CEM Corp., Matthews, NC, USA) equipped with XP-1500 plus high pressure Teflon<sup>®</sup> TFM vessels (CEM Corp., 100 ml, maximum pressure 10 MPa and temperature 300 °C) were used in the acid digestions of the samples. The microwave oven was operated in a temperature-controlled mode. A programmable muffle furnace L5/11/B170 (Nabertherm GmbH, Lilienthal, Germany) was used for sample digestions with the fusion method.

### 2.2. Reagents and catalyst samples

Ultrapure water was purified with a Millipore Gradient (Millipore Corp., Billerica, MA, USA) water purification system. A commercial stock solution containing 1000 mg L<sup>-1</sup> Ru in 10% HCl (VWR BDH Prolabo) was used for calibration of the ICP-OES. HCl (37–38%, J.T. Baker, Baker Analyzed), HNO<sub>3</sub> (65%, J.T. Baker, p.a.), HF (40%, Merck, p.a.), H<sub>2</sub>O<sub>2</sub> (30%, J.T. Baker, Baker Analyzed), KNO<sub>3</sub> (Merck, p.a.), KOH (Merck, p.a.) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Riedel-de Haën, p.a.) were used in the sample digestions. Ru powder (99.9%, –325 mesh, Alfa Aesar) and the following Ru compounds: RuO<sub>2</sub>·xH<sub>2</sub>O (99.99%, Ru 54–58%, Alfa Aesar), anhydrous RuO<sub>2</sub> (99.95%, Ru min. 75.2%, Alfa Aesar) and anhydrous RuCl<sub>3</sub> (99.5%, Merck) were used to compare the digestion efficiencies of the digestion methods.

Three commercially available alumina-supported Ru catalysts and one commercially available carbon-supported Ru catalyst were analyzed in this study. The catalysts were 0.5% Ru on 3 mm

alumina tablets (Alfa Aesar), 2% Ru on 1/8 in. alumina pellets (Alfa Aesar), 5% Ru on alumina (Aldrich) and 5% Ru on carbon powder (Engelhard). Ru contents of these catalysts are not certified. For the method comparison purposes a sub-sample was taken from each of the catalyst samples and ground prior to analysis, in order to ensure the homogeneity of samples. These sub-samples may, however, not be representative of the original Ru content of the analyzed catalysts. Sample homogenization was accomplished by using an agate mortar for 5% Ru on alumina and 5% Ru on carbon or using a ring rolling mill (Siebtechnik) for 2% Ru on alumina pellets and 0.5% Ru on alumina tablets. The samples were analyzed without drying.

### 2.3. Microwave digestion methods

Catalyst samples of 50–100 mg, or 5–10 mg of Ru powder or the Ru compounds were carefully weighed into the microwave digestion vessels. Digestions were carried out using two HCl–HNO<sub>3</sub> mixtures, either 6:1 (v/v) or 3:1 (v/v, *aqua regia*). For the digestions, 9 ml of HCl and 1.5 ml of HNO<sub>3</sub> or 7.5 ml of HCl and 2.5 ml of HNO<sub>3</sub> were added to the digestion vessels. The vessels were closed and the samples were digested in the microwave oven with a two-stage program (stage 1 – heating to 180 °C at 15 min; stage 2 – holding at 180 °C for 10 min). The solutions were carefully allowed to cool to room temperature prior to opening the vessels. The solutions were transferred to volumetric flasks and diluted to 50 ml with water. The samples were further diluted and their HCl concentration was adjusted to 2% (v/v) prior to the ICP-OES determination. If an undigested residue was present in the samples (e.g. in the case of carbon-supported catalysts), the residue was allowed to settle on the bottom of the vessel prior to the dilution.

### 2.4. High-pressure asher (HPA) digestion

For the HPA digestion 50–100 mg of the catalyst samples, or 5–10 mg of Ru powder and the Ru compounds were carefully weighed into the 90 ml quartz vessels. 6 ml of HCl and 1 ml of HNO<sub>3</sub> were added, the vessels were closed, set in the heating block and inserted into the pressure vessel of the HPA. The system was pressurized with nitrogen to 100 bar and a three-stage digestion program was run (program: stage 1 – rapid heating to 100 °C; stage 2 – heating from 100 °C to 300 °C at 30 min; stage 3 – holding at 300 °C for 180 min). After cool-down and depressurizing steps the samples were diluted to 50 ml with water in the quartz vessels. The solutions were further diluted and their HCl concentration was adjusted to 2% (v/v) prior to the ICP-OES determination. If an undigested residue was present in the samples, the residue was allowed to settle on the bottom of the vessel prior to the dilution.

### 2.5. Digestion by a fusion method

The fusion method was adapted from the article written by Taddia and Sternini [6]. 50–100 mg of the catalyst samples or 5–15 mg of Ru powder or the Ru compounds were weighed to nickel crucibles. Carbon-supported catalysts were ashed in their crucibles by inserting them into a preheated muffle furnace (200 °C) and by heating the furnace to 450 °C in 2 h. Other samples were directly moved to the next stage, where 0.38 g KOH and 0.65 g KNO<sub>3</sub> were added to the crucibles and mixed with the samples. The crucibles were covered by lids and inserted into a cold muffle furnace. The furnace was heated to 450 °C in 60 min and the temperature was further held at 450 °C for 60 min. After cooling down overnight (approximately to 30 °C), 50 mg of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added to stabilize the formed Ru compounds (mainly RuO<sub>4</sub><sup>2-</sup>) and the melts were

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