THERMAL PROPERTIES OF RHODIUM(III) CHLORIDE
Rhodium content determination

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Abstract

Thermal decomposition of rhodium(III) chloride under inert, oxidative and reductive gas atmospheres was investigated in order to determine its thermal properties. Stoichiometries of the reactions occurring during heating are described. It is suggested that the chemical formula of soluble rhodium(III) chloride should be presented as $RhCl_3 \cdot \frac{1}{2}HCl \cdot xH_2O$. Cold crystallisation of anhydrous rhodium(III) chloride at a temperature of about 500°C was established. The procedure for quantitative determination of volatile matter (water and hydrochloric acid) content and rhodium content by thermogravimetry is given and discussed. The repeatability and reproducibility of the method are estimated.

Keywords: DSC, rhodium(III) chloride, rhodium content determination, TG, TG-DTA

Introduction

So-called hydrated or soluble rhodium(III) chloride is a rhodium derivative of the most important practical application. It is commonly used as a raw material for the manufacture of other rhodium compounds, in particular its complex compounds (applied mainly as precursors of homogeneous catalysts in organic synthesis, e.g. oxo synthesis [1]) or for modification of sensors and catalysts for afterburning of combustion gases [2, 3]. Soluble rhodium(III) chloride is obtained in thermal evaporation of rhodium(III) hexachloric acid solution in hydrochloric acid [4]. Its chemical formula is usually presented as: $RhCl_3 \cdot aq$ or $RhCl_3 \cdot xH_2O$, where x=2, 2.5, 3 or even 4 – depending on supplier. Thus, commercially available hydrated (soluble) rhodium(III) chlorides differ in rhodium content, which varies from approx. 36.5 to above 42% (*m/m*). The content of rhodium in soluble rhodium(III) chloride can be determined by different means; AAS, XRF, MS, ICP-AES, ETV-ICP-MS, coulometry or colorimetry methods have been described [5–8].

In the present study rhodium(III) chloride has been investigated with the use of thermal analysis methods (TG, TG-DTA, DSC) in order to determine its thermal properties

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and enable elaboration of procedure for quantitative analysis of rhodium, which could be used for routine application in quality control.

Experimental

The different lots of commercial samples of pure soluble rhodium(III) chloride from Fluka AG with rhodium content of about 40% (m/m) and soluble rhodium(III) chlorides manufactured in the Institute of Heavy Organic Synthesis, with similar rhodium content, have been the subject of the present investigation.

The thermal analysis has been conducted using the TA-2, TG-50/TA4000 or TGA/SDTA-851^e/STAR^e Mettler Toledo thermobalances and DSC-25/TA4000 or DSC-822^e/STAR^e Mettler Toledo differential scanning calorimeters.

Samples of about 30 or 10 mg were used for TG and DSC respectively. Cylindrical Pt crucibles were applied for TG and standard Al ones with perforated lid for DSC. Flow rate of purge gases was equal to 100 mL min^{-1}.

Results and discussion

Thermal properties of rhodium(III) chloride

Non-isothermal heating of soluble rhodium(III) chloride, $RhCl_3 \cdot xH_2O$ in air or an inert gas atmosphere causes initially its dehydration leading to anhydrous rhodium(III) chloride form, which is then decomposed into metallic rhodium in inert gas [9] or into rhodium(III) oxide in air [10]. TG curves, illustrating the above reactions obtained in the study presented are shown in Fig. 1 (curves 1 and 2).
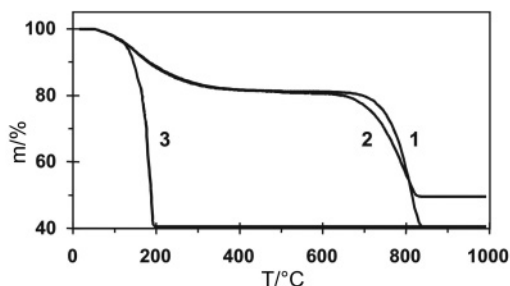

Fig. 1 TG curves of soluble rhodium(III) chloride in nitrogen (curve 1), air (curve 2) and hydrogen (curve 3) atmospheres at the heating rate of β=24°C min^{-1}

According to Walewski *et al*. [10], isothermal heating of soluble rhodium(III) chloride in mild temperature conditions (110°C) in air, causes its partial dehydration, leading to monohydrate rhodium(III) chloride, which is stable at this temperature and only at a higher temperature (about 230°C) is fully dehydrated, giving anhydrous rhodium(III) chloride.

However, in the present study, it was found that the elemental composition of the sample with constant mass, obtained by heating of soluble rhodium(III) chloride at 110°C for 24 h (w_{Rh}=45.2%, w_{Cl}=54.5%), does not correspond to formula $RhCl_3 \cdot H_2O$, but rather to the hypothetical $RhCl_3 \cdot \frac{1}{2}HCl$. The hypothesis on the formation of $RhCl_3 \cdot \frac{1}{2}HCl$ (rather than $RhCl_3 \cdot H_2O$) has been verified by determination of the content of hydrochloric acid in the products of partial dehydration of soluble rhodium(III) chloride by means of titration with sodium hydroxide. The degree of dehydration of the prepared samples was measured by thermogravimetry, as:

$$a = \frac{\Delta m_{500}}{\Delta m_{500}(0)} \tag{1}$$

where Δm_{500} means mass loss up to a temperature of 500°C for the partially dehydrated sample, and $\Delta m_{500}(0)$ for initial soluble rhodium(III) chloride.

Table 1 Results of investigation of dried rhodium(III) chloride samples

Preparation		TG, N_2, β=24°C min^{-1}		Titration	Result
Conditions (β=12°C min^{-1})	$-\Delta m$/%	$\dfrac{-\Delta m_{500}/\%}{m_s}$	α/%	w_{HCl}% (m/m)	$\dfrac{m_{HCl}/\%}{m_{500}}$
–	0	17.38	0	6.30	7.62
110°C, 1 h	3.7	13.71	21.1	6.73	7.80
110°C, 2 h	6.0	11.37	34.6	6.84	7.72
110°C, 10 h	9.5	7.92	54.4	7.04	7.65
140°C, 1 h	10.4	6.98	59.8	6.32	6.80
160°C, 1 h	12.1	5.31	69.5	4.94	5.22
180°C, 1 h	13.4	3.98	77.1	3.80	3.96
200°C, 1 h	14.7	2.76	84.1	2.14	2.20
220°C, 1 h	17.4	0.08	99.5	0	0

The results of investigations (Table 1) indicate that heated (dried), at temperature of 110°C, soluble rhodium(III) chloride completely loses water, and not hydrochloric acid, which content is at approx. 0.5 mol (HCl)/mol ($RhCl_3$). Taking into account this finding chemical formula of soluble rhodium(III) chloride should be, in author opinion, presented as $RhCl_3 \cdot \frac{1}{2}HCl \cdot xH_2O$. Further 'drying' (in higher temperature) causes removal of hydrochloric acid that leads to the formation of anhydrous rhodium(III) chloride – non-soluble in water. However, contrary to the conclusions reported in the work [10] it has been found in the present study by XRD method, that anhydrous rhodium(III) chloride obtained after dehydration and hydrochloric acid removal is amorphous, and it becomes crystalline only after heating to a temperature of approx. 500–550°C. Thus the exothermic effect observed while it is heated in air or nitrogen at a temperature of approx. 500°C (Fig. 2), should refer rather to a cold

crystallisation of metastable amorphous $RhCl_3$ phase, than to its polymorphous transition, as suggested in [10].
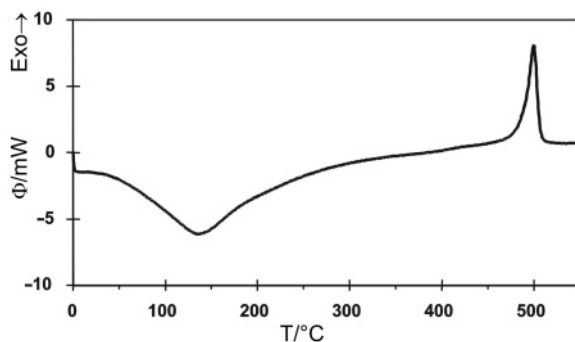

Fig. 2 DSC curve of soluble rhodium(III) chloride; air, $\beta=12°C\ min^{-1}$

With further temperature increase crystalline $RhCl_3$ undergoes thermal decomposition in an inert gas atmosphere or thermo-oxidative decomposition in the air (Fig. 1, curves 1 and 2, respectively) according to the following reactions:

$$RhCl_3 \xrightarrow{(N_2)} Rh + 1.5Cl_2 \tag{2}$$

$$2RhCl_3 \xrightarrow{(air)} Rh_2O_3 + 3Cl_2 \tag{3}$$

Non-isothermic heating of soluble rhodium(III) chloride in reducing atmosphere (hydrogen) causes one-step mass loss in the temperature range of ~25–200°C (Fig. 1, curve 3) according to the following stoichiometry:

$$RhCl_3 \cdot 0.5HCl \cdot xH_2O \xrightarrow{(H_2)} Rh + xH_2O + 3.5HCl \tag{4}$$
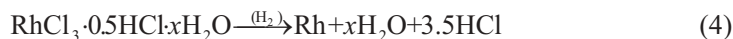
Procedure for thermogravimetric determination of rhodium content

Stoichiometries of the reactions (2)–(4) may constitute the basis for quantitative determination of rhodium content in rhodium(III) chloride: $RhCl_3 \cdot aq$ or $RhCl_3$. In order to obtain appropriate analytical signals enabling such determination it is sufficient to perform
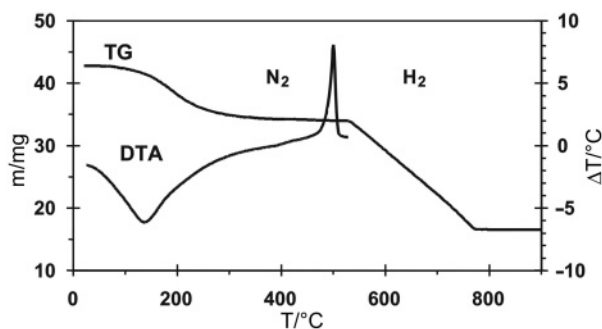

Fig. 3 TG and DTA curves of soluble rhodium(III) chloride, heating rate $\beta=24°C\ min^{-1}$ in nitrogen up to 520°C and in hydrogen (3% H_2 in N_2) above this temperature

thermogravimetric measurement of the tested rhodium(III) chloride with a constant heating rate, to a temperature of 900°C in nitrogen or air atmosphere, or to a temperature of 250°C in a hydrogen atmosphere. However, the result of analysis is more reliable when TG, or preferably TG-DTA measurement is performed at constant heating rate (to a temperature of 900°C), in nitrogen at the beginning, and then from the temperature of 520°C in hydrogen – Fig. 3. Then, at a temperature of up to 500°C drying of soluble rhodium(III) chloride occurs according to the following stoichiometry:

$$RhCl_3 \cdot 0.5HCl \cdot xH_2O \xrightarrow{(N_2)} RhCl_3 + 0.5HCl + xH_2O \qquad (5)$$
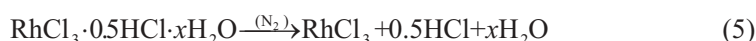
Successively, cold crystallisation of the formed anhydrous rhodium(III) chloride takes place, and, after hydrogen is fed, thermal reduction of anhydrous rhodium(III) chloride follows the stoichiometry:

$$RhCl_3 \xrightarrow{(H_2)} Rh + 3HCl \qquad (6)$$

The TG curve of soluble rhodium(III) chloride recorded in such conditions enables determination of the total content of volatile matter (H_2O+HCl), w_v:

$$w_v = \frac{-\Delta m_{500}}{m_s} \qquad (7)$$

and content of rhodium occurring (at temperature ~500°C) in the form of $RhCl_3$, w_{Rh}:

$$w_{Rh} = 0.9675 \frac{-\Delta m_{500}^{800}}{m_s} \qquad (8)$$

The presence of the exothermic effect (DTA curve) at a temperature of 500°C qualitatively confirms that the sample tested contains soluble rhodium(III) chloride. The equality:

$$W_{Rh}(a) = w_{Rh}(b) = w_{Rh}(c) \qquad (9)$$

indicates the high purity of the rhodium(III) chloride tested, where

$$w_{Rh}(a) = 0.4917 \frac{m_{500}}{m_s}$$

is the rhodium content, calculated with the assumption that the dry matter of the sample, m_{500} is anhydrous $RhCl_3$;

$$w_{Rh}(b) = 0.9675 \frac{-\Delta m_{500}^{800}}{m_s}$$

rhodium content, calculated with the assumption that the Δm_{500}^{800} mass loss corresponds to the stoichiometry of the reaction (6);

$$w_{Rh}(c) = \frac{m_{800}}{m_s}$$

rhodium content, calculated with the assumption that the final mass, m_{800} is metallic rhodium.

If the rhodium chloride tested does not meet the parameter of high purity, i.e., when a substantial difference of $w_{Rh}(a)$, $w_{Rh}(b)$ and $w_{Rh}(c)$ occurs, complementary investigations using other methods are required for the proper determination of rhodium content and/or the performing of its speciation.

Example

For a high analytical grade soluble rhodium(III) chloride from Fluka, the following values have been obtained: $w_{Rh}(a)$=40.57 , $w_{Rh}(b)$=39.98, $w_{Rh}(c)$=41.20% (*m/m*), as means of 9 determinations. Such findings testify that the tested sample contains ~1.2% (*m/m*) of a ballast substance, other than rhodium(III) chloride. Because the rhodium content determined by AAS method as the mean of 10 determination is equal to 41.23% (*m/m*) with standard deviation of 0.53% (*m/m*), the metallic rhodium is recognised as the main pollutant of the sample and its content is estimated as ~1.2% (*m/m*).

Conclusions

Standard deviations of the above described thermogravimetric method for determination of volatiles and rhodium contents in soluble rhodium(III) chloride basing on 10 consecutive measurements, performed for the same average laboratory sample are equal to: $s(w_v)$=0.18% (*m/m*) and $s(w_{Rh})$=0.15% (*m/m*). These values illustrate repeatability of the method. Standard deviations of the method estimated basing on differences between two parallel determinations of the samples in routine tests [11] (quality control of numerous preparations of soluble rhodium(III) chloride over more than two years) are equal to: $s^*(w_v)$=0.26% (*m/m*) and $s^*(w_{Rh})$=0.22% (*m/m*). These values characterise long-term reproducibility of the method in the conditions at the author's laboratory. Considering the absolute character of the method they also describe its accuracy.

Because of its simplicity, precision and accuracy the method is safely applicable for routine use in quality control. The possibility of full recovery of rhodium is its additional advantage, as rhodium has a very high market value.

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