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γ-RADIATION PRODUCED SUPPORTED METAL COMPLEX CATALYSTS

V*. DETERMINATION OF RHODIUM BY ATOMIC ABSORPTION SPECTROSCOPY

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Summary

Rhodium in polymer-supported catalysts as well as in organorhodium complexes can be determined conveniently by atomic absorption spectroscopy. Following oxidative destruction of the organic material in a mixture of concentrated sulphuric acid and hydrogen peroxide, an aqueous solution to which 2% lanthanum nitrate has been added is aspirated into an air/acetylene flame. A linear calibration graph is obtained at 343.5 nm for rhodium concentrations in the range 0—20 ppm. Standards are prepared by oxidising $[RhH(CO)(PPh_3)_3]$ in the same way as the sample. In this way interference by chloride is avoided. This interference is important when large amounts of chloride are present as in commercial rhodium trichloride in aqueous hydrochloric acid solution standards.

Introduction

We have recently described polypropylene supported rhodium(I) hydroformylation catalysts [1]. An important parameter of these is their rhodium content. A number of non-destructive methods such as X-ray fluorescence spectroscopy [2], thermal neutron activation analysis [3] and charged particle activation analysis [4] have been used to determine the metal content of supported metal complex catalysts. However all of these methods suffer from the major drawback of being subject to many interferences necessitating the often difficult task of preparing standards in the same matrix as the materials under test.

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* For Part IV see ref. 1.

To date no detailed account of the determination of rhodium in polymer-supported complexes has been given. Initially samples were sent for commercial analysis by a gravimetric method in which the sample was heated at 2000°C under a stream of hydrogen and the residue assumed to be rhodium metal. It soon became apparent that this method was overestimating the amount of rhodium present; indeed its application to the pure rhodium(I) complexes $[Rh(acac)(CO)(Ph_2PC_6H_4CH{=}CH_2\text{-}p)]$ and $[RhH(CO)(PPh_3)_3]$ for which excellent carbon, hydrogen and phosphorus microanalytical data were available gave rhodium contents about 10% high. These high values are probably due to the formation of unreactive rhodium phosphides [5].

Atomic absorption spectroscopy has been used previously to determine the rhodium content of alumina supported metallic rhodium [6,7] and platinum/rhodium [8] catalysts. Since atomic absorption spectrometers are widely available in chemical laboratories it offered an inexpensive, rapid method of analysis that might obviate the interference from phosphorus found in the gravimetric analysis.

Experimental

The support material used in the present work is polypropylene which is particularly inert and insoluble, so that its dissolution requires strongly oxidising conditions. A combination of concentrated sulphuric acid and 30% aqueous hydrogen peroxide was used [9] and gave no problems; the use of perchloric acid instead of the hydrogen peroxide is strongly discouraged [10]. Between 0.05 and 0.20 g of material was accurately weighed out and heated in concentrated sulphuric acid (10 ml) until it was thoroughly charred. Aqueous hydrogen peroxide (10 ml of 30% v/v) was added, and when effervescence had subsided, the solution was concentrated using Gorsuch's apparatus [10]. Further additions of hydrogen peroxide followed by reconcentration were repeated until a colourless solution was obtained. This was refluxed for one hour, cooled and after addition of lanthanum nitrate to give a final lanthanum concentration of 2% (w/v) made up to 100 ml using distilled water. The amount of sample used was such that the final solution contained between 10 and 20 ppm rhodium. Standard solutions were prepared by the same procedure using $[RhH(CO)(PPh_3)_3]$ as the source of rhodium. $[RhH(CO)(PPh_3)_3]$ was prepared as described in the literature [11], found: C, 71.7; H, 5.1; P. 9.9; $[RhH(CO)(PPh_3)_3]$ calc.: C, 71.9; H, 5.1; P, 10.1%.

The rhodium content was determined on a Varian AA-575 spectrometer by aspirating the samples into an oxidising air/acetylene (80/14) flame, measuring the absorbance at 343.5 nm with a spectral band pass of 0.5 nm and a lamp current of 5 mA. This gave an optimum working range of 5—25 ppm with a sensitivity of 0.15 ppm. Five standard solutions (S1—S5) were used, and they and the unknowns (U1—U*x*) were measured in the order S1—S5, U1—U*x*, U*x*—U1, S5—S1, S1—S5, U1—U*x*, U*x*—U1, S5—S1 to compensate for any instrumental drift, although drifts of more than 1% were never observed. The absorbance against rhodium concentration was linear in the range 0—20 ppm.

Results and discussion

Previous workers have shown that the determination of rhodium using both air/acetylene and nitrous oxide/acetylene is subject to a large number of interferences from a variety of cations and anions [12]. Of these sulphate [13,14] was the most serious in the present work because the destruction of polymer-supported complexes was most safely undertaken using a mixture of concentrated sulphuric acid and hydrogen peroxide. It has been suggested previously that the interference caused by sulphate ions may be negated by the addition of a releasing agent such as lanthanide ions [13,15]. When this was studied it was found that the addition of lanthanum nitrate caused a dramatic enhancement of the rhodium signal up to 1% (w/v) lanthanum nitrate, but that further addition of lanthanum nitrate had no effect on the observed signal. Accordingly 2% lanthanum nitrate was added to all samples and standards. An investigation of the efficiency of the releasing ability of lanthanum nitrate on a series of solutions of increasing sulphate concentration showed a constant absorbance up to 15% (v/v) sulphate, but that further sulphate resulted in suppression of the absorbance. Thus when 2% lanthanum nitrate is used, sulphate concentrations must not be allowed to exceed 15%. Lanthanum also prevented the suppression of the rhodium absorbance by phosphate present, formed by oxidation of the phosphine ligands. The suppression of the rhodium signal by phosphate and sulphate is believed to be due to incomplete dissociation of the rhodium compound in the flame [14]. The counteraction of this by lanthanum is reported to be due to the preferential binding of these anions by lanthanum allowing complete dissociation of the rhodium compounds [16].

Initially we attempted to use a commercially available standard solution of rhodium trichloride in dilute (3.7% v/v) hydrochloric acid containing 1000

TABLE 1

ANALYTICAL DATA FOR ORGANORHODIUM(I) COMPLEXES

Complex [a]	Rh analysis Found (calcd.) (%))	Microanalysis [b] (Found (calcd.) (%))			
		C	H	Cl	P
$[RhCl(CO)(PPh_3)_2]$	14.9	64.2	4.5	5.1	9.1
	(14.7)	(64.3)	(4.4)	(5.2)	(9.0)
$[RhCl(CO)(Ph_2PC_6H_4CH{=}CH_2\text{-}p)]$	13.3	66.0	4.5	4.9	8.2
	(13.8)	(66.3)	(4.6)	(4.8)	(8.3)
$[RhCl(CO)(Ph_2PC_6H_4CH_2CH{=}CH_2\text{-}p)_2]$	16.5	66.7	4.9	4.75	8.3
	(16.6)	(67.0)	(5.0)	(4.6)	(8.0)
$[RhCl(CO)(Ph_2PC_6H_4CH_2CH_2CH{=}CH_2\text{-}p)_2]$	14.9	67.4	5.4	4.6	7.5
	(15.3)	(67.6)	(5.3)	(4.4)	(7.75)
$[RhCl(CO)(Ph_2PC_6H_4CH_2C(CH_3){=}CH_2\text{-}p)_2]$	12.4	67.8	5.5	4.4	8.0
	(12.8)	(67.6)	(5.3)	(4.4)	(7.75)
$[Rh(acac)(CO)(Ph_2PC_6H_4CH{=}CH_2\text{-}p)]$	19.1	60.2	4.8	—	6.1
	(19.9)	(60.3)	(4.7)		(6.0)
$[Rh(nbd)(Ph_2PCH_2C(CH_3){=}CH_2)_2]^+ BF_4^-$	12.8	61.0	5.4	—	8.3
	(13.5)	(61.4)	(5.5)		(8.1)

[a] The preparations of those complexes not previously described in the literature will be given shortly.
[b] Microanalyses were performed by Elemental Microanalysis Ltd.

ppm of rhodium. Although this was made up with the appropriate amount of sulphuric acid and lanthanum nitrate, analyses were unsatisfactory. This was shown to be due to chloride ion enhancement of the rhodium signal at the relatively high levels of chloride present in the standard. Accordingly standard rhodium solutions were prepared using analytically pure [RhH(CO)(PPh$_3$)$_3$] and treating that in exactly the same way as the samples under test. [RhH(CO)(PPh$_3$)$_3$] was chosen as the standard because it is easily prepared highly pure in about 95% yield in a one-pot reaction from rhodium trichloride. It is an air stable, non-hygroscopic solid. Its solutions, following oxidative destruction showed no deterioration over a period of six months, so that fresh standards need not often be prepared.

The results obtained when the present method was used to analyse a series of rhodium complexes are shown in Table 1. All the analyses lie within ±5% of the calculated values. Thus the present method provides a simple, relatively inexpensive method for the analysis of rhodium in both rhodium complexes and in polymer supported rhodium catalysts.

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