CHEMISTRY LETTERS, pp. 1391-1394, 1990.

Chloro Complex of Ruthenium (Ⅲ) with Trioctylmethylammonium Chloride and Its Thermal Decomposition

Hiroshi WATANABE,* Hiroaki UTSUYAMA, and Shinji SAHARA
Department of Applied Chemistry, Faculty of Engineering,
Shizuoka University, Hamamatsu 432

The chloro complex of ruthenium (Ⅲ) with TOMAC, and its thermal decomposition behavior have been investigated. The complex exists in a polymeric chloro complex bridged with hydroxyl groups. Further, the thermal decomposition process of the complex was proposed.

Recently, ruthenium has been noted because it exhibits excellent utility as a catalyst. Recovery of ruthenium from scraps has been diligently attempted, and the solvent extraction technique is expected to be one of the recovery methods.[1] In this paper, in order to obtain the fundamental information for the recovery of ruthenium, Ru (Ⅲ) chloro complex with trioctylmethylammonium chloride (TOMAC, $R_3R'NCl$), formed by solvent extraction, and its thermal decomposition were investigated.

Ru (Ⅲ) chloro complex: The chloro complex of Ru (Ⅲ) with TOMAC was prepared as follows: 0.01 mol dm^{-3} TOMAC in benzene was shaken for 10 min at 20 ℃ with the aqueous solution containing 0.141 g dm^{-3} $RuCl_3$ in 2 mol dm^{-3} HCl; the organic phase was shaken again with a fresh aqueous solution ; then the same operation was repeated 10 times to load until ruthenium saturated the organic phase; the organic phase was separated from the aqueous phase by centrifuging; the metal concentration in the organic phase was determined by atomic absorption spectrophotometry, the chloride concentration by Volhard's method, and water content by Karl Fischer's method; the organic phase was heated in vacuo (40 ℃/1 mmHg) to isolate the complex. The resulting complex was subjected to purifying by column chromatography, but the complex immediately decomposed, because of being unstable, so that it wasn't examined with elemental analysis. Hence in the following experiments the complex was used without further purification.

The molar ratio $[R_3R'N]/[Ru]/[Cl]/[H_2O]$ in the organic phase saturated with ruthenium was found to be 0.95 : 1 : 2.2 : 0.48; it can be approximated to 1 : 1 : 2 : 0.5. Accordingly, it is presumed that the stoichiometric composition of the complex is $R_3R'NRu(OH)_2Cl_2 \cdot 0.5H_2O$.

The complex isolated from the organic phase was examined by infrared spectroscopy with the paste method (Fig. 2). In the spectrum of the complex, in addition to absorption bands for the alkyl groups of the complex,[2] an absorption band assigned to ν OH appeared at 3460 cm^{-1}. Furthermore, absorption bands due to ν Ru-OH vibration appeared at 1070 and 1020 cm^{-1}; ν Ru-O-Ru vibration at 890, 860, and 795 cm^{-1}; and δ RuO_2 vibration at 485 and 462 cm^{-1};[3] an absorption band at 320 cm^{-1} is assigned to ν Ru-Cl vibration.[4] Therefore, it is inferred that the complex exists in a polymeric chloro complex bridged with hydroxl groups.

Thermal decomposition of Ru (Ⅲ) chloro complex: Thermogravimetry (TG) and differential thermal analysis (DTA) of the complex were examined under atmospheres of nitrogen and air. The heating rate and flow rate were 5 ℃ min^{-1} and 50 cm^3 min^{-1}, respectively. The residues derived from the complex by heating up to the required temperature and holding for 1 min were examined by infrared spectroscopy and X-ray diffraction.

The DTA and TG curves of Ru (Ⅲ) chloro complex with TOMAC are shown in Fig. 1. The DTA curve under an atmosphere of nitrogen (Fig. 1(a)) exhibited endothermic reactions at 45, 150, 220, and 280 ℃. The TG curve revealed a loss in weight of 4.8% at 195 ℃, followed by weight-loss of 27.1 and 44.1% and 195-220 and 220-290 ℃, respectively, and the final loss in weight of 84.7%. Therefore, the DTA curve of the complex is explained as follows: the endothermic reaction at 150 ℃ due to the release of water molecules adhering to the complex and dissociation of polymer; the endothermic reaction at 220 ℃ corresponds to the release as hydrogen chloride and methyl chloride of chlorine atoms co-ordinated to the ruthenium,[5] and the endothermic reaction at 280 ℃ is due to the cracking of alkyl groups by the extractant ; then Ru (Ⅲ) is reduced to metallic ruthenium. While the DTA curve under an atmosphere of air (Fig. 1(b)) exhibited endothermic reactions at 45, 150, and 220 ℃, and a large exothermic reaction at 350-450 ℃ based on combustion of cracked alkyl groups. The TG curve revealed the loss in weight of 26.6, 40.6, and 14.6% in the ranges of 195-220, 220-290, and 280-440 ℃, respectively; after that

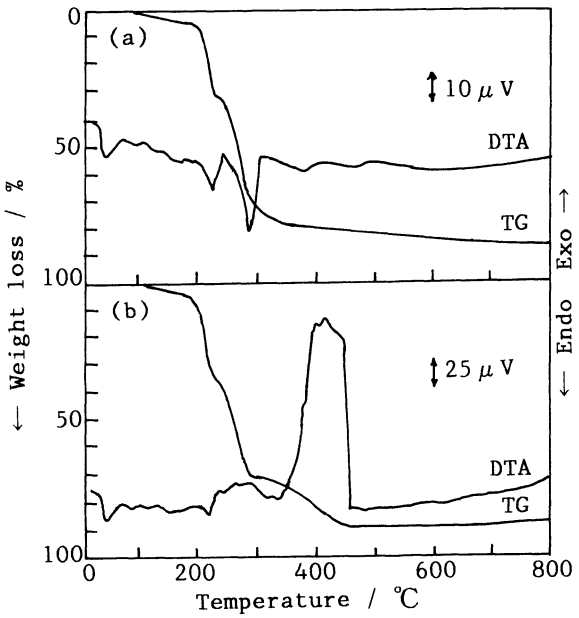

Fig. 1. TG and DTA curves for Ru (Ⅲ) chloro complex with TOMAC under atmospheres of nitrogen (a) and air (b).

it exhibited increase in weight with re-oxidation of ruthenium and showed a final loss in weight of 81.8%, indicating formation of RuO_2. it is also supposed that the endothermic reaction of the DTA curve under both atmospheres below 100 ℃ due to melting of the complex because the TG curve corresponding to the endotherm did not show the loss in weight.

Since infrared spectral patterns of the thermal decomposition products under atmosphere of nitrogen and air resembled one another, only the infrared results under an atmosphere of air were illustrated in Fig. 2. The spectrum on heating at 100 ℃ resembles that of the complex, but on heating at 150 ℃, the ν OH absorption band decreased in intensity compared with that for the complex, the ν Ru-Cl band was split, and the absorption bands based on the ν Ru-O-Ru decreased in intensity. On heating at 200 ℃ an absorption band assigned to an unsaturated hydrocarbon appeared at 1920 cm^{-1}. Further ν Ru-Cl and ν Ru-OH absorption bands also decreased in intensity. On heating at 250 ℃ each band assigned to alkyl groups remarkably decreased in intensity, and all bands based on ruthenium-oxygen bonds and ν Ru-Cl absorption bands disappear, and the complex completely decomposes on heating at 300 ℃. These resuluts of infrared spectroscopy correspond to the results of TG and DTA.

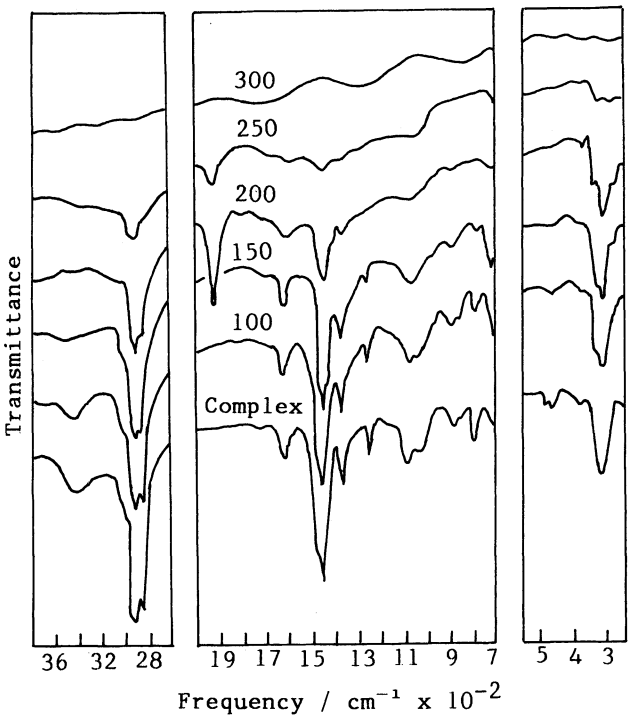

Fig. 2. Infrared spectra of Ru (Ⅲ) chloro complex with TOMAC and its thermal decomposition products under an atmosphere of air (Numerals on curves are heating temperature, ℃).

The thermal decomposition products of the complex obtained on heating over 500 ℃ were examined by X-ray diffraction. The X-ray diffraction diagrams under atmospheres of nitrogen and air are shown in Fig. 3(a) and (b), respectively. From Fig. 3(a), on heating at 500 ℃ the diffraction peaks are not clear. However, on heating at 600 ℃, the diffraction patterns (△) of metallic ruthenium appeared in d(A)=2.07(101), 2.16(002), 2.37(100) etc., and then they increase in intensity with the rise in temperature. On the other hand from Fig. 3(b), the diffraction patterns under an atmosphere of air are different from that of an atmosphere of nitrogen. On heating at 500 ℃ the diffraction patterns(○) of ruthenium oxide

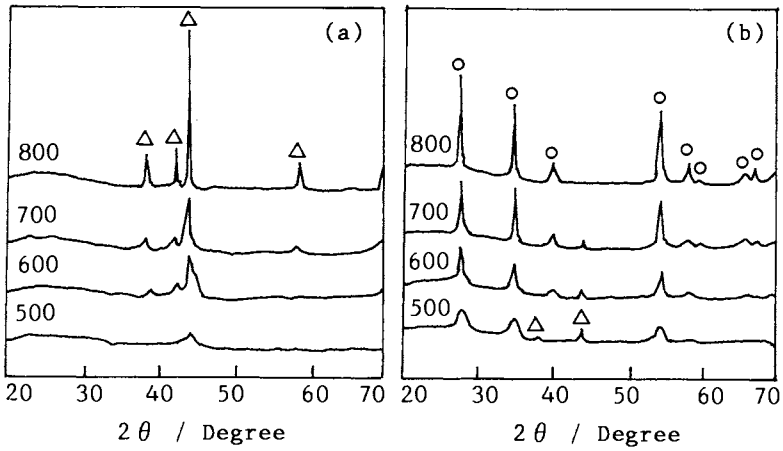

Fig. 3. X-Ray diffraction patterns of the thermal decomposition products of Ru (Ⅲ) chloro complex with TOMAC under atmospheres of nitrogen (a) and air (b) (Numerals on curves are heating temperature, ℃. △ and ○ denote Ru and RuO_2, respectively).

appeared in d(A)=1.68(211), 2.54(101), 3.16(110) etc. in addition to those of metallic ruthenium. However, since the diffraction lines of the ruthenium oxide are broad, it is deduced that the crystal degree is low. The diffraction patterns of the ruthenium oxide increase in intensity, and line shapes become sharp with rising temperature. On heating at 800 ℃ the diffraction patterns of metallic ruthenium disappeared, and ruthenium oxide was completely formed. These results also indicate that by heating under an atmosphere of air after Ru (Ⅲ) has been reduced to metallic ruthenium, RuO_2 is formed by re-oxidation. Consequently, the following process is proposed for the thermal decomposition of Ru (Ⅲ) chloro complex with TOMAC:

$$(R_3R'NRu(OH)_2Cl_2)_n\cdot n/2H_2O \xrightarrow[80\text{-}195\ ℃]{-H_2O,\ \text{Dissociation}} R_3R'NRuOCl_2 \xrightarrow[195\text{-}]{-Cl,\ \text{Cracking}}$$

$$\xrightarrow[300\ ℃]{\text{and Reduction}} Ru + (Ru_2O_3)^{6)} \begin{cases} \xrightarrow[300\text{-}800\ ℃,\ \text{in air}]{\text{Oxidation}} Ru + RuO_2 \xrightarrow[800\ ℃\ \leqq]{\text{Oxidation}} RuO_2 \\ \xrightarrow[300\ ℃\ \leqq,\ \text{in } N_2 \text{ gas}]{\text{Reduction}} Ru \end{cases}$$

We wish to thank N.E.Chem.Cat.Inc. for the sample of $RuCl_3\cdot nH_2O$.

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(Received May 17, 1990)