RECOVERY OF RHODIUM BY CHEMICAL VAPOR TRANSPORT MEDIATED BY GAS COMPLEXES OF THE RhCl₃-AlCl₃ SYSTEM. CHARACTERIZATION OF Rh COMPLEXES IN THE GASEOUS AND MOLTEN STATE.

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The reactions of rhodium oxide (Rh₂O₃) and/or rhodium metal with aluminum chloride (Pₐlcᵢ₃ ≤ 3atm) under a chlorine atmosphere (Pc⁻ cucumber ice 1 atm) have been studied. The formation of a Rh-Al-Cl gas complex is shown to enable the vapor transport of RhCl₃. UV/VIS spectrophotometry is used for characterizing the rhodium gas complex. A procedure for recovering rhodium metal from spent catalysts is suggested based on the vapor complexation of rhodium chloride with aluminum chloride.

INTRODUCTION

Concern for recovering precious metals (platinum, palladium and rhodium) from spent automotive catalysts has led from the beginning of the 1980's to the development of technologies for recovering these metals in USA and Canada. In the mid-80's, the annual consumption of platinum and palladium for auto-catalyst production had been estimated to around 140 and 50 tons respectively. In Europe the auto-catalysts contain principally platinum and rhodium at a ratio of 5:1 and awareness for recovering these metals from spent catalysts is increasingly growing. The total value of platinum and rhodium contained in auto-catalysts in 1994 (in Europe) was estimated to be of the order of $1.5 billion.

When considering the recovery of metals from spent catalysts the following methods merit special attention:

a) Catalyst Substrate Dissolution-Sulfuric acid digestion (Hydrometallurgical/Pyrometallurgical),
b) Leaching of Platinum Group Metals from an Insoluble Substrate-Monolithic Catalyst Processing (Hydrometallurgical/Pyrometallurgical),
c) Chlorination - calcination - leaching (Hydrometallurgical/Pyrometallurgical),
d) Plasma fusion (Pyrometallurgical),
e) "Copper collection" (Pyrometallurgical) and f) Copper and nickel smelters (Pyrometallurgical).

However, technical and economic problems of the above methods have been
identified with factors like process complexity, numerous process steps, process economics depending on by-products sales, inefficient decantation washing compared to filtration and water balance problems (insoluble substrate - monolithic catalyst process), corrosive high temperature (700°C) conditions (calcination - leaching process), high capital investment and high electrical energy cost (plasma process), alloy dissolution, long processing times (copper and nickel smelters) etc.

The present article reports a novel approach for recovering platinum and rhodium from spent catalysts. The procedure is based in combined chlorination and reaction with aluminum chloride, formation of vapor complexes and chemical vapor transport. Potential advantages of the proposed scheme can be identified with low reagent requirements (chlorine is the only reagent required), moderate operating temperatures (up to 300°C) and lack of requirements for acids, solutions or water. It will therefore not be producing waste water, spent acid or any kind of waste.

The great enhancement of the apparent volatility of inorganic metal halides in the presence of aluminum chloride is known as a phenomenon from the late '60s. Moreover, the possibility of chemical vapor transport of metal halides mediated by vapor complexes with aluminum chlorides has been examined. A large number of metal halide vapor complexes have been reported and extensive reviews of their systematics are available.

The present article is concerned with i) the reactions of rhodium metal with gaseous chlorine and of rhodium oxide with \( \text{Cl}_2(\text{g}) + \text{Al}_2\text{Cl}_6(\text{g}) \), ii) chemical vapor transport and recovery of rhodium in sealed containers and iv) spectroscopic characterisation of Rh-Al-Cl vapor complexes.

**EXPERIMENTAL**

Rhodium metal (Alldrich) has been used without further purification. Rhodium oxide (Alldrich) was dried by heating under vacuum at 200°C. High purity aluminum chloride was prepared from the corresponding Cerac/Pure Inc. reagent by repeated slow sublimations under vacuum. Chlorine gas was purchased from Matheson/Union Carbide.

Cylindrical quartz tube containers were used for studying the reactions. The Raman cells containing the melt mixtures consisted of fused silica tubing (4±0.1 mm o.d. and 2±0.1 mm i.d., ~3 cm long). Those containing vapor mixtures comprised silica tubing with 20±0.2 mm o.d., and 18±0.2 mm i.d.. Rectangular fused-silica cells of 1, 0.5 or 0.2 cm path length (Hellma, Mullheim, Germany) were used for the UV/VIS measurements of vapors and melts. Pre-weighed amounts of chemicals were transferred into clean, dry, flamed and degassed containers. Chlorine could be added in a gas-addition/vacuum line and all containers were then sealed under vacuum.
Raman spectra of vapor and molten mixtures were excited with the 514.5 and 488.0 nm lines of a Spectra Physics 164 argon-ion laser and the 647.1 and 676.4 nm lines of a Spectra Physics Stabilite 2017 krypton-ion laser. The scattered light was collected at an angle of 90° (vertical scattering plane) and analysed with a Spex 1403, 0.85 m double monochromator equipped with a -20°C cooled RCA photomultiplier and EG&G/ORTEC rate meter and photon counting electronics. The optical furnace used and the procedures for obtaining Raman spectra at high temperatures have been described in detail elsewhere.² The absorption measurements were performed with a Hittachi U-3000 spectrophotometer equipped with a high-temperature optical furnace. During the experiments the portion of the cell interrupting the optical path was at a temperature few degrees higher than the rest of the cell. This prevented condensation of solids or liquids in the optical path and permitted absorption measurements of vapors in equilibrium with condensed phases.

RESULTS AND DISCUSSION

Reaction of rhodium metal with gaseous chlorine - Synthesis of rhodium trichloride

In the literature, it is reported that rhodium trichloride is decomposed upon heating and that even in the presence of gaseous chlorine it occurs in very low concentrations in the vapor phase.⁷

For studying the reaction

\[ \text{Rh(s)} + \frac{3}{2}\text{Cl}_2(\text{g}) \rightarrow \text{RhCl}_3(\text{s}) \] ¹¹

20 mg of Rh were placed in a cylindrical quartz tube (10 mm o.d., 7.5 mm i.d., 25 cm long). Chlorine was added in excess so as to react according to reaction [I] and to create a pressure of 0.25 atm and the container was sealed under vacuum. The mixture was heated gently up to 450°C without observing any changes in the state of rhodium and in the dark yellow color of the vapour phase caused by the presence of chlorine. By overnight heating at 525°C rhodium has reacted completely giving a brown-red powdery solid and chlorine has been consumed as indicated by the decoloration of the vapors. By increasing the temperature at 900°C RhCl₃ could be sublimed yielding raspberry-red gleaming crystals.

The possibility to synthesize and vapor transport RhCl₃ was examined by studying the reaction of rhodium oxide with aluminum chloride in the absence of chlorine. Around 0.5 g Rh₂O₃ were placed in a quartz tube container (10 mm o.d., 7.5 mm i.d., 20 cm long) containing an excess of aluminum chloride. The evacuated and sealed tube was then placed in a furnace and the temperature was raised slowly (in 3-4 hours) to 250°C. Near
The chlorination was completed within a few hours and the remaining excess of $\text{Al}_2\text{Cl}_6$(g) created a pressure of ~2 atm in the tube. The dark grey $\text{Rh}_2\text{O}_3$ was thus transformed into a brown-red solid mixture ($\text{Al}_2\text{O}_3 + \text{RhCl}_3$). The tube was then placed in a tilted furnace where the lower part of the tube, containing the solids, was at 300°C and the upper part was above the melting point of aluminum chloride (around 220°C). With this thermal gradient $\text{RhCl}_3$ was vapor transported according to the following reaction:

$$\text{RhCl}_3(s) + \frac{x}{2} \text{Al}_2\text{Cl}_6(g) \rightarrow \text{RhCl}_3(\text{AlCl}_3)_x(g) \quad [3]$$

and was deposited in the form of small raspberry-red crystals at the cold part of the tube.

Attempts to establish the structural and vibrational properties of the $\text{RhCl}_3(\text{AlCl}_3)_x$ vapor complex(es) in the temperature range 300-450°C by Raman spectroscopy were unsuccessful. Laser excitation of $\text{RhCl}_3(s)$-$\text{Al}_2\text{Cl}_6(g)$ mixtures resulted to Raman scattering only due to gaseous aluminum chloride. The presence of gaseous chlorine in the cells did not create any effect apart from giving rise to the Cl(g) bands. This could be either due to low partial pressures or due to laser-induced photodissociation of the Rh-containing vapor species. Rapid cooling of the cells resulted in condensation of a white solid which presumably was $\text{AlCl}_3$.

**UV/VIS study of Rh-Al-Cl complexes**

Due to the claimed importance of chlorine presence in the thermal stability of $\text{RhCl}_3$, several samples were prepared in order to clarify whether chlorine gas has any effect in the stability of Rh-Al-Cl vapor complexes. Small amounts of $\text{RhCl}_3$ (usually 6-8 mg) were added into the optical kuvettes (V = 8.5 ml, l = 1 cm) containing an $\text{AlCl}_3$ amount which was enough to create a pressure of 3 atm at 600K and the cells were sealed with or without chlorine being present. Comparison of the spectrum which was derived after subtracting the Cl(g) spectrum from the spectrum of the $\text{RhCl}_3(s)$-$\text{Al}_2\text{Cl}_6(g)$-$\text{Cl}_2(g)$ mixture with the spectrum of the $\text{RhCl}_3(s)$-$\text{Al}_2\text{Cl}_6(g)$ mixture leads to the conclusion that: i) a band due to Rh-Al-Cl vapor complex is observed, ii) the vapor complex band is not affected by the presence of chlorine and iii) the vapor complex is not decomposed when Cl(g) is absent. The fact that the rhodium vapor complex is stable even in the absence of chlorine is considered of importance for the effective vapor transport and recovery of rhodium with the continuous flow process described below.
Figure 1 shows preliminary UV/VIS spectra of the RhCl₃(AlCl₃) gas complex at 365 and 400°C after subtraction of the Al₂Cl₆(g) spectrum. Because of the very low intensity of the 242 nm vapor complex band, the UV/VIS spectra of molten RhCl₃(s)-Al₂Cl₆(l) at 230°C were also recorded and shown in Fig. 2. The spectra in Fig. 2 exhibit a strong band at 246 nm and two weak bands at 411 and 515 nm, which are characteristic of the octahedral RhCl₆³⁺ species. The bands at 515 and 411 nm can be assigned to the Laporte forbidden 1A₁g → 1T₂g and 1A₁g → 1T₁g transitions from the ground state. Similar spectra have been observed for a solution of RhCl₆³⁺ in aqueous HCl and for a solution of RhCl₃ in the fused LiCl-KCl eutectic. To confirm the octahedral coordination of Rh(III) in fused LiCl-KCl eutectic, we have run its Raman spectrum in the temperature range 380-650°C and the spectra are shown in Fig. 3. The Raman active vibrations of the RhCl₆³⁺ octahedra span the representation

\[ \Gamma_{vib} = v₁(A₁g) + v₂(E₁g) + v₅(F₂g) \]

The bands at 295 (polarised), 275 (depolarised) and 160 (depolarised) cm⁻¹ are assigned as due to the \( v₁, v₂ \) and \( v₅ \) modes of RhCl₆³⁺ respectively. The extra band at 345 cm⁻¹ lies close to the totally symmetric stretching vibrational fundamental \( v₁(A₁g) \) and can be assigned as due to the \( 2v₂ \) overtone whose intensity is enhanced by Fermi resonance. The symmetry of the \( 2v₂(F₂g) \) overtone derives from the product \( F₂×F₂ \) and the resulting state is represented by \( A₁ + E + F₁ + F₂ \). Thus the states \( v₁ \) and \( 2v₂ \) lie close to each other and both contain the same symmetry species \( A₁ \) and can enter into Fermi resonance by repelling each other.

**Recovery of rhodium in a chemical vapor transport flow-reactor.**

Figure 4 illustrates the conceptual design of a flow-reactor for recovering rhodium by means of a chemical vapor transport based on the formation of Rh-Al-Cl vapor complexes. The apparatus consists essentially of a glass furnace (aluminum chloride evaporator) in series with a three-zone furnace and is similar to the one described in ref. 11. An inert carrier gas containing a low percentage of chlorine is passed over the AlCl₃ evaporator and the resulting N₂-Cl₂-Al₂Cl₆ gas mixture is contacted with the Rh/Rh₂O₃ containing scrap which is transformed to RhCl₃ according to reactions [1] and [2] and subsequently to RhCl₃(AlCl₃)(g) according to reaction [3]. The vapor complex is transported along the furnace, decomposed at a low temperature zone and rhodium is thus recovered in the form of RhCl₃ deposit. Studies on rhodium recovery using this flow setup are in progress.
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Figure 1. UV/VIS spectrum of RhCl₃(AlCl₃)ₓ vapors.

Figure 2. UV/VIS spectrum of the Rh-Al-CI complex in a saturated RhCl₃-Al₂Cl₆ molten mixture. The spectrum of Al₂Cl₆ is subtracted. The insert shows the bands of the visible region in magnification.
Figure 3. Raman spectra of a saturated solution of RhCl$_3$ in fused KCl-LiCl eutectic. Band assignments are based on octahedral coordination of Rh(III).

Laser wavelength, $\lambda_0 = 488.0$ nm, laser power, $w = 120$ mW; scan speed, s.s. = 24 cm$^{-1}$ min$^{-1}$; time constant, $t$, 1 s; spectral slit width, s.w.w., 6 cm$^{-1}$.

Figure 4. Schematic diagram of flow reactor for the recovery of rhodium by means of a chemical vapor transport reaction based on vapor complexation.