A NEW PROCESS TO OBTAIN PALLADIUM AS METAL POWDERS FROM SALTS: THERMODYNAMIC AND KINETIC STUDY

M. VILLICAÑA †, M.G. GARNICA-ROMO‡, J.F. PÉREZ-ROBLES§ and J.A. CORTES†

† Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, Mich., México
gromar05@yahoo.com.mx
≠ CINVESTAV-IPN. Unidad Querétaro. Querétaro, Qro., México

Abstract—In this work, a new process to obtain palladium powders from their salts by using a cementation process (in aqueous solution) through an iron electrode and a catalyst agent was studied. The process gives results that in practice can also be applied to obtain bulk metal from secondary sources. Nano and micrometric particles could be obtained from this new process. The physicochemical and morphological characteristics of these powders are heavily dependent on the method used for their production. For the Palladium test and PdCl₂ solution 0.093 M, a minimum quantity of catalyst agent was added to accelerate the reaction. In the palladium powders only small round particles were obtained, which can be easily suspended in solution. For the reaction, there is no considerable temperature dependence. Thus, the process can be carried out at room temperature resulting in considerable energy saving.

Keywords—Palladium metal powder, nanometric particles, “black” palladium powder.

I. INTRODUCTION

Palladium is obtained through complexing agents. In copper minerals there are low quantities of metals from the platinum group, mainly platinum and palladium, which are recoverable during electrolytic refining of copper from various sources or by scrap precious metals refining. The filtered extract from the platinum recovery contains palladium chloride. The latter is treated with hot ammonium hydroxide, forming, in solution, a complex called tethramminopalladium chloride (II) [Pd(NH₃)₄]Cl₂·H₂O. Adding HCl to the latter precipitates the yellow, insoluble compound dichloro-diamminopalladium PdCl₂(NH₃)₂ which is rapidly soluble in cold and diluted ammonia. This series of reactions are very efficient for producing high-purity salts, from which the metal is obtained by heat. Palladium is obtained at industry-scale, heating [Pd(NH₃)₄]Cl₂·H₂O until white-red; leaving the metal in the form of a soft powder or a sponge-like form.

Palladium chloride precipitation in the form of dimethyl-gloxima (a selective precipitant) must be done in a slightly acidic solution to avoid contamination from nickel. Palladium chloride is an orange-yellow precipitate, formula Pd[(CH₃)₂N₂O₂]₂, that transforms into the metal by calcinations (Cotton and Wilkinson, 1964; Sergueiev, 1975).

Fine and uniformly sized and shaped black palladium powders have been obtained by the Polyol process from an inorganic precursor and by chemical reduction into ethylene-glycol (Bregado and Campos, 1988; Begrado, 1989; Ferrier et al., 1985; Figlarz et al., 1989). The Mono-dispersed spherical particles (average size of 0.1 micron) are produced from hydrazine (Pd(NH₃)₃)Cl⁻ in ethylene-glycol in the temperature range of 20° C to –9° C, required by the micro-electronic industry (Pérez, 1995). The physical-chemical and morphological properties of these powders depend largely on the process used to obtain them (Contreras, 1960; Hedley and Tabachnick, 1958). The properties of these materials are generally obtainable in ultra-dispersed micrometric or submicron particle size materials. It is worth noting that the properties of these materials turn out to be very different from massive materials obtained by processes such as smelting. This is due to an increase in the solid surface, as a consequence of a high-dispersion state when in powder form (Matijevic and Hsu, 1985). There are some properties whose increases will be considerable, such as: specific surface, reactivity before and after the synthesizing process and even the system’s free energy which is formed.

This new wet process to obtain or recover metallic particles is really a catalyzed cementation process. (Pérez et al., 2001). In this process, the chemical precipitation of a metal is performed, generally from an aqueous solution of its salts, by a more electro-positive metal electrode on a shorter time-span; these potentials cannot be measured directly even though their relative values can be determined with respect to a half-cell of reference. The most frequently used is the Standard Hydrogen Electrode (SHE). Metallic salts are dissolved in water and a catalytic agent is added, which is a solid salt or a liquid. An iron electrode is then immersed in the solution. The precipitation of the metal is immediately observed on the electrode-solution interphase and the spongy precipitate is recovered by a mechanical scraper. The obtained precipitate settles, is washed abundantly with water, and is dried and weighed to quantify the reaction’s yield. The Thermodynamic, Kinetic and Activation Energy parameters are then deter-