Thermochimica Acta 625 (2016) 56–64

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

# Preparation of palladium impregnated alumina adsorbents: Thermal and neutron activation analysis

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ARTICLE INFO

*Article history:*
Received 11 July 2015
Received in revised form
18 November 2015
Accepted 22 November 2015
Available online 2 December 2015

*Keywords:*
Sol–gel method
TG/DSC
QMS
HMTA decomposition
FTIR

ABSTRACT

$Pd/Al_2O_3$ composite microspheres particles with high surface area were prepared sol–gel process. The decomposition of dried gel-particles was studied by TGA/DTA and FT-IR technique. TGA studies indicated that formation of palladium is marked by a broad exothermic peak with a loss of water and oxidation of trapped HMTA/Urea nitrate mixture. The main decomposition reaction took place in the temperature range of 660–1250 K in helium and relatively lower temperature of 400 K to 1250 K in oxygen. Optical microscopy indicated that the distribution of palladium is uniform. SEM studies on silver coated particle indicated that there was surface erosion of some gel spheres while in few of them micro cracks were seen at high resolution. Content of the palladium was determined using Neutron Activation Analysis (NAA). Decomposition at various temperatures was studied using Residual gas analyser and decomposition species were identified using quadrupole mass analyser.



## 1. Introduction

The hydrogen–palladium system has been the subject of much study, both experimentally [1] and computationally [2,3]. Palladium is well-known for its selectivity and activity in hydrogenation reactions. Hydrogen readily dissociates on palladium surfaces. In addition hydrogen atoms diffuse into the subsurface layers of the metal to form palladium hydride. Thus, the gas phase hydrogen molecules and the adsorbed surface atoms are in equilibrium and, further, the hydrogen atoms adsorbed on the surface are in equilibrium with the absorbed subsurface hydrogen atoms that form palladium hydride within the metal lattice [4,5]. Palladium hydrogen system does not exhibit a stable compound but form nonstoichiometric compound at atmospheric pressure [6]. This instability in the system coupled to isotopic effect forms a useful method for the separation of hydrogen isotopes [7]. Pd-based composite inorganic membranes have been synthesized which possess high thermal and mechanical stability and have sufficient hydrogen permeability and 100% hydrogen selectivity due to the unique property of hydrogen solubility in palladium and the solution–diffusion mechanism for hydrogen permeation through palladium [8]. In order to obtain materials with uniform chemical homogeneity of the palladium on nanometric dimensions, various techniques including solid state reaction process [9], sol–gel method [10–12], tape casting [13], hydrothermal treatments [14,15], thermal decomposition [16] and polymeric synthesis routes [17] have been investigated. Si–Al–Pd catalysts were prepared using direct hydrothermal synthesis and impregnation. They found that the catalyst prepared by direct hydrothermal synthesis had higher activity and that the introduction of aluminum effectively enhanced palladium dispersion. Therefore, it is a tendency to load Pd nanoparticles into a Si–Al composite materials with high pore volume and specific surface area through a in situ method [18]. We have synthesized Palladium distributed alumina particles via sol–gel route using nitrates and HMTA urea solution for gelation process. Detailed kinetics for the solid state decomposition of hydroxides leading to formation of palladium doped alumina formation has been worked out. Palladium is also a wonder element for the adsorption of many gases manly hydrogen. It is used in many forms as a hydrogenation catalyst in industry [19]. Increasing use of palladium in industries has resulted in widespread environment concern [20,21]. Many analytical techniques have been used for the determination of palladium in many matrices, biological, environment and geological samples [23,24]. Most of these methods use tedious chemical treatment on sample involving complexation and co-precipitation procedures and can be

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http://dx.doi.org/10.1016/j.tca.2015.11.016
0040-6031/

avoided in Instrumental neutron activation analysis [25,26]. Instrumental Neutron Activation Analysis (INAA) on the other hand offers a simple procedure and need no pre treatment chemical procedure as necessary in radiochemical neutron activation analysis. Thus, INAA was adopted by us to determine the amount of palladium in palladium dispersed alumina particles prepared in the laboratory. The main goal of this paper was to standardise a procedure to prepare palladium doped porous alumina microsphere with uniform distribution of palladium. The goal was achieved by adopting a sol–gel process with a programmed heat treatment procedure. The novelty of the method is to trap the palladium at molecular levels into a hydro Gel. The uniformly palladium doped alumina particles are obtained by de hydration and decomposition of gel forming components. The thermal process was studied and also reported in the paper. The practical implication is the availability of high surface area adsorbent particles as a column packing material. The micro porous alumina when used as a column packing material allows smooth fluid flow (laminar) with Reynold's number <3000.

## 2. Experimental

### 2.1. Preparation of 3 M aluminum nitrate nona hydrate solution

Analytical grade $Al(NO_3)_3{\cdot}9H_2O$ was weighed so as to give a solution of concentration slightly higher than 3 M. The molarity of the solution was determined by precipitation of aluminum as aluminum hydroxide using Ammonium hydroxide solution. The precipitated $Al(OH)_3$ was weighed and concentration of $Al^{3+}$ ions determined. The molarity of the solution was adjusted to 3 M by required dilution by adding distilled water. Required amount of Palladium Ammonium Nitrate was added to the solution so as to retain the molarity of Aluminum nitrate to 3 M.

### 2.2. Preparation 3 M urea/HMTA solution

The calculated weights of analytical grade hexamethyleneteramine (HMTA) and urea crystals were dissolved in distilled water to obtain 3 M HMTA urea solution.

### 2.3. Preparation of Palladium doped $Al_2O_3$ microspheres

The internal gelation process has been developed for the preparation of soft hydroxide microspheres containing 1 mol% Palladium, which are subsequently compacted, reduced and sintered into pellets of dioxide. The flow sheet of the process is shown in Fig. 1. The gelation assembly used had a capacity to prepare 100 g of $Al_2O_3$ microspheres. The sol–gel assembly consists of an oil tank, gelation column, feed tank, washing equipments. The furnaces for drying and heat treatments were installed are kept in a separate location. The gelation column was filled with hot silicone oil. The height of the column was adjusted so as to give a total contact time of 25 s. The gelation medium was controlled within ±1 K of the set temperature. The feed solution was prepared by adding cold (271 K) cold HMTA–urea solution to the alumina solution. In the feed, total metal concentration was maintained at 1.7 M and hexamethylenetetramine (HMTA)–urea to metal mole ratio ($R$) was kept at 1.0. Droplets were prepared by forcing the feed solution to pass through the capillary by application of overhead pressure. The droplets were converted into gel particles within 20 s. on contact with hot silicone oil circulating through the column maintained at 193 K. The gel particles were subsequently transferred onto a conveyor wire mesh belt made of AISI 316 L stainless steel along with the hot oil. The gel particles were carried into the wash tank. The gel particles were first washed with carbon tetrachloride to remove the oil on the surface of the gel particles. The particles were then washed with 6% ammonium hydroxide solution to remove the residual chemicals. The dried microspheres obtained were characterized for surface morphology prior to further heat treatment. The dried microspheres were heat treated on a 100 g scale. The dried microspheres were loaded in two alumina boats and were calcined in an electrical resistance furnace. At each stage of the experiment.

### 2.4. Gelation of the aluminum nitrate solution

Desired amount of aluminum nitrate nonahydrate [$Al(NO_3)_3{\cdot}9H_2O$] was weighed so as to give a solution with a molarity slightly higher than 3 M. Palladium nitrate was prepared by the action of acitic acid on palladium acetate and was added to the resulting solution so as to give 1% molar doping relative to $Al^{3+}$ ions. The morality of $Al^{3+}$ in solution was adjusted to 3 M. The solution was cooled using ice bath and concentrated ammonia solution was added so as to adjust the ratio of $(NO_3)^-/Al^{3+}$ to 2.7. The solution was finally cooled using a chiller unit to 269 K wit constant stirring. A mixture of 3 M Ammonia and HMTA was simultaneously prepared to the same temperature. Cooled solution was mixed in required proportions with constant vigorous stirring. The gelation mixture is finally poured into hot oil bath maintained at a temperature of 278 K. Spherical ball so generated are soft. They are cooled to room temperature and then washed with tetrachloroethylene to remove oil. The spheres are then treated with 3 M ammonia to remove HMTA and other undesired chemicals from the spheres. The Soft spheres are oven dried at a temperature of 193 K with a constant hot air flow. Dried spheres were used for TGA and DTA study. Flow chart of the complete process for Pd impregnated alumina preparation is given in Fig. 1.

### 2.5. FT-IR Spectra of the dried and crushed microsphere

Few of the microspheres were crushed with potassium bromide and the mixture was homogenized. The homogenized mixture was palletized to obtain FT-IR spectra.

### 2.6. Procedure adopted calibration of thermal analyzer and to obtain TGA DTA of the sample

Few of the dried microspheres weighing approximately 20 mg were used for thermal studies. TG curves were obtained under identical experimental conditions both for calibration and sample runs. NETZSCH Model STA409PC/PGTGA/DTA unit was used. Helium gas flow rate of 30 mL $min^{-1}$ and heating rate of 5 K $min^{-1}$ were maintained while recording the mass loss as a function of time and temperature ranging from ambient to 1273 K. Before analysis of the mixture, the TG equipment was calibrated for mass and temperature scales using standard reference compounds such as calcium oxalate monohydrate, and magnesium sulphate.

### 2.7. Optical microscopy on dried and heat treated particles

Optical images of the heat treated microspheres were obtained using a conventional optical microscope equipped with a PC based tomography imaging system.

### 2.8. SEM studies on dried and heat treated particles

SEM images of the microsphere were obtained using 15 kV accelerating potential both for low 238× and high 5.10k× magnifications.

### 2.9. Gamma Ray Spectrometry

The High resolution spectrometer used in the studies was Set-Up using HPGe detector coupled to 4k MCA. The instrument was