



Preparation and Characterization of Chloride-Free Alumina-Supported Platinum Catalysts

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ABSTRACT

Supported precious metal catalysts are extensively used as efficient catalysts. This kind of catalysts, particularly chloride-free catalysts, synthesized using organoplatinum compounds as precursors has attracted immense research interest compared to their parent metals due to their unique physico-chemical properties. The main objective of this research is to prepare and characterize the chloride-free alumina-supported platinum catalysts. An organometallic compound of ammonium bisoxalatoplatinate(II) hydrate was used to prepare unsupported and alumina supported platinum catalysts. A series method including IR, XRD, SEM, TEM, EDA, and XPS was used to characterize samples. The research shows that ammonium bisoxalatoplatinate(II) hydrate could be synthesized and used to prepare unsupported and alumina supported platinum free of chloride impurities.

Keywords: Catalysts, Platinum, Chloride-free, XPS.

INTRODUCTION

Organometallic compounds are widely used as catalyst precursor.^{1,2} A combination of impregnation of the support with a solution containing the appropriate organometallic species and heat treatment can yield metal and/or metal oxide particles uniformly distributed over the surface of the support. Unfortunately since multi-step reaction pathways are frequently involved, the preparation of particular organometallic precursor is often time consuming. A second problem is that chloride containing species are typically the most easy-prepared organometallics.³ Thus it is possible

that chloride will be present in of the resulting catalysts.⁴ Chloride ions have been reported to be absorbed on, and hence block, the active site of metal catalysts.⁴⁻⁷ As such chloride ions can inhibit a number of metal catalyzed reactions.⁸ Removing such chlorides can be both difficult and time consuming since requires additional processing.

Potassium bisoxalatometallate complexes are simple chloride-free compounds. Potassium bisoxalatoplatinate(II) is well known and easy to be prepared.⁹ This complex can be thermally decomposed at relatively low temperatures to the metal and/or metal oxide, and it is ideal precursors



for the formation of chloride-free catalysts.^{1,10} The high solubility in aqueous solutions suggests it may be straight forward to deposit this compound onto high surface area supports. After heat treated, the metal and/or metal oxide crystallites dispersed over the surface of the support will be obtained.

The presence of K as a product of heat treatment of potassium bisoxalatoplatinate(II) was confirmed.^{11,12} In general potassium is not believed enhance the catalytic activity of Pt, and there is some evidences that potassium acts as inhibitor. Fortunately the K species could be removed by washing the heat treated samples with water. However, washing heat treated $K_2Pt(ox)_2 \cdot 2H_2O$ with water failed to remove all the potassium since in this case the insoluble oxide was formed.^{13,14}

The structural studies of $K_2Pt(ox)_2 \cdot 2H_2O$ demonstrate the presence of discrete $Pt(ox)_2^{2-}$ and therefore it should be possible to replace potassium with ammonium cation.^{15,16} The advantages should be realized by avoiding the use of K. Since the ammonium cation will be oxidized during heat treatment, subsequent washing of the Pt product should be unnecessary. This research is to establish if chloride-free Pt catalysts could be prepared using complex of the type $(NH_4)_2Pt(ox)_2 \cdot 2H_2O$.

EXPERIMENTAL AND METHOD

Ammonium bisoxalatoplatinate(II) $(NH_4)_2Pt(ox)_2 \cdot 2H_2O$ was prepared using a modification of the method described by Schlutz *et al.*, for $Co_{0.83}Pt(ox)_2 \cdot 6H_2O$.¹⁷ An excess of 1 M HCl was added to $Ag_2Pt(ox)_2$ (5 g, 0.008 mol) suspended in 100 mL of water. The resulting AgCl precipitate, coagulated by heating the solution, was removed by filtration to yield a clear yellow solution of $H_2Pt(ox)_2$. $(NH_4)_2(ox)$ (2 g, 0.016 mol) dissolved in 20 mL of water was added to the filtrate and the resulting yellow solution was re-filtered and allowed to stand, in air, at room temperature for 2 weeks. The solution slowly turned blue and deposited yellow needle-shaped crystals of the desired product. These were collected and washed successively with cold water, alcohol and acetone and finally air dried.

The preparation of alumina supported $(NH_4)_2Pt(ox)_2 \cdot 2H_2O$ was achieved by dissolving

$(NH_4)_2Pt(ox)_2 \cdot 2H_2O$ (0.4964 g, 0.0013 mol) in 25 mL of hot water containing a suspension of Al_2O_3 (2.549 g, 0.025 mol). The volume of the solution was then reduced to about 5 mL by heating rapidly and stirred solution at near boiling point. After cooling to room temperature, the yellow solid was collected and successively washed with cold water, alcohol and acetone and finally air dried. Samples were heat treated in a muffle furnace for four hours at 950°C and 1100°C for unsupported and supported samples, respectively.

Infrared (IR) spectra were recorded on a Biorad FTS-40 spectrophotometer between 400 to 4000 cm^{-1} . Powder X-ray diffraction (XRD) patterns of the samples were collected using $CuK\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) peaks, observed at 2θ range between 5° to 90° with step size of 0.01° per second, and recorded on a Siemens D5000 diffractometer operating the DIFFRAC 500 software. Scanning electron micrographs (SEM) were collected using a JEOL JSM-6000F microscope, while transmission electron microscopy (TEM) studies were performed on a Phillips CM12 microscope. Energy dispersive analysis (EDA) were performed with an EDAX PV9900 system on a Phillips 505 scanning electron microscope. X-ray photoelectron spectra (XPS) were recorded on a Kratos XSAM 800 spectrometer.

RESULTS AND DISCUSSIONS

Untreated unsupported and alumina supported $(NH_4)_2Pt(ox)_2 \cdot 2H_2O$ have been synthesized, and characterized using some methods. Comparison of the infrared spectra of alumina, untreated unsupported and alumina supported $(NH_4)_2Pt(ox)_2 \cdot 2H_2O$, suggests that $(NH_4)_2Pt(ox)_2 \cdot 2H_2O$ can be deposited onto alumina without any decomposition. It is clear from the infrared spectra that the structure of the three materials is different to each other. The broad and strong bands at the region 2800-3700 cm^{-1} of infrared spectra of the $(NH_4)_2Pt(ox)_2 \cdot 2H_2O$ sample feature the characteristic of NH_4^+ group and water, belong to $(NH_4)_2Pt(ox)_2 \cdot 2H_2O$ complex (Fig. 1.), as described in smectite and illite,¹⁸ NH_4^+ ion in zeolitic materials,¹⁹ and NH_4^+ -smectite nanocomposites.²⁰

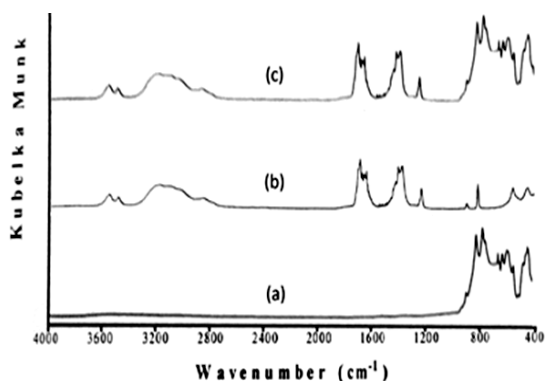


Fig. 1. The IR spectra of (a) alumina, (b) untreated unsupported, and (c) alumina supported $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$

Scanning electron microscopy (SEM) was employed to study the morphology of the samples. Electron micrographs of $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$ is shown in Fig. 2.a. The complex forms needles being about 35 μm long. In this case there is no evidence for any minority phases. Electron micrograph of alumina supported $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$ is given in Fig. 2.b. The particle size of supported material is considerable smaller than the unsupported material. In this case well dispersed crystallites of oxalate complex is present on the surface the alumina particles. Chloride was not observed in the EDA of the sample studied (Figure 2.b).

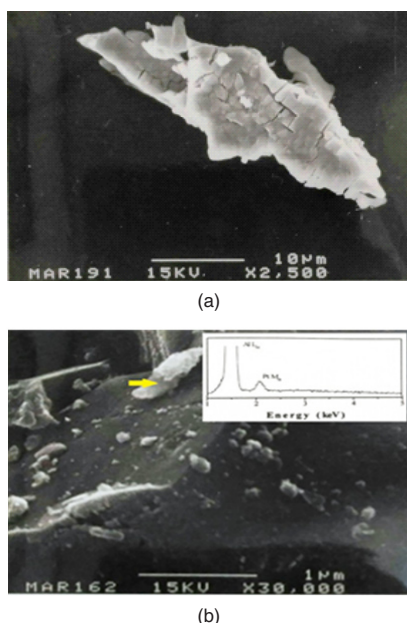


Fig. 2. Electron micrographs of (a) unsupported, (b) and alumina supported $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$. An arrow points toward $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$ on the surface of alumina. The EDA spectra (b) indicates the presence of the main metals i.e. Al and Pt in the alumina supported $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$ sample

The XRD measurement confirms that the structure of the NH_4^+ salts of $\text{Pt}(\text{ox})_2^{2-}$ is retained when it is deposited onto alumina (Fig. 3). The diffraction pattern of the complex did not show any lines, except these due to alumina. There is noticeable changes in the relative intensities of the Bragg reflections in the pattern of $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$, however this is believed to be a result preferential growth of the complex on the support.

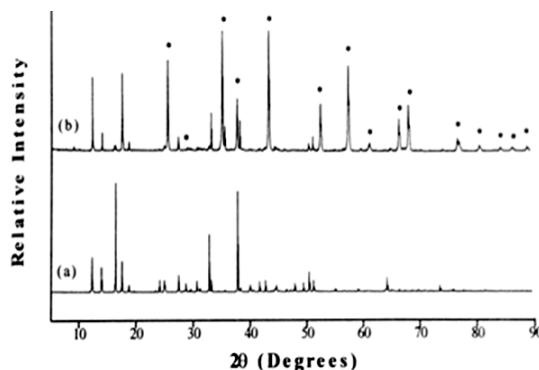


Fig. 3. XRD patterns of (a) unsupported and (b) alumina supported $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$. Lines marked (*) are due to alumina

The XRD patterns of the decomposition products of alumina supported $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$ formed at different temperatures are given in Fig. 4. Heat treatment at 400°C produces Pt metal. Heating the sample at temperatures between 500°C to 1100°C results in crystallization of Pt. The Pt is stable even after heating to 1100°C. Unfortunately, the limitation of heat treatment unsupported sample causes the XRD pattern unable to collect.

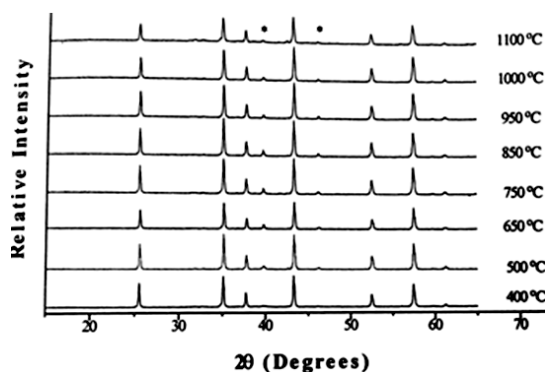


Fig. 4. XRD patterns of heat treatment products of alumina supported $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$. Lines marked (*) are due to Pt.²¹

SEM and EDA were also employed to characterized heat treated unsupported and alumina supported $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$. The SEM and EDA of the samples are shown in Fig. 5 and 6, respectively.

The electron micrographs of $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$ heated at 400°C produces spherical crystallites sizes about $0.1 \mu\text{m}$ diameter which then collapsed after further heating at 550°C forming rounded particles sized about 30 nm diameter. Upon additional heating of the samples at 650°C , the particle grew, forming a smooth honey-comb like structure. EDA on various heat treated samples shows that the only element present was Pt.²¹

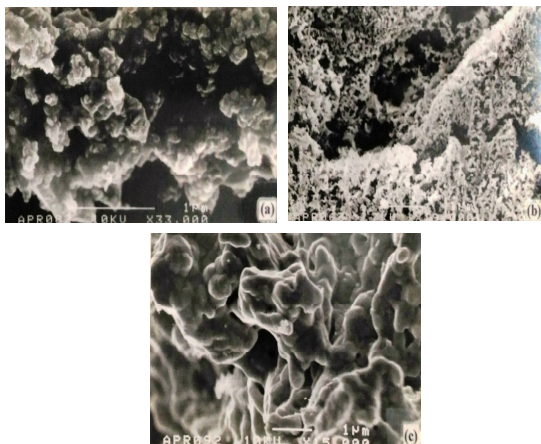


Fig. 5. Electron micrographs of unsupported $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$ after heating at 400°C (a), 550°C (b), and 650°C (c) for 4 hours

SEM and EDA spectra of heat treated alumina supported $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$ are shown in Fig. 7 and 8. The electron micrographs of the material heated from 400 to 700°C showed a range of poorly formed crystallites to be present, whilst heating at higher temperature produces more crystalline materials of various size from 50 to 300 nm on the surface of alumina support. In comparison to the unsupported materials, it is apparent that the net-like particles did not persist on the surface of support. This is presumably has implications for sintering or reactions of the particles with the surface of support.

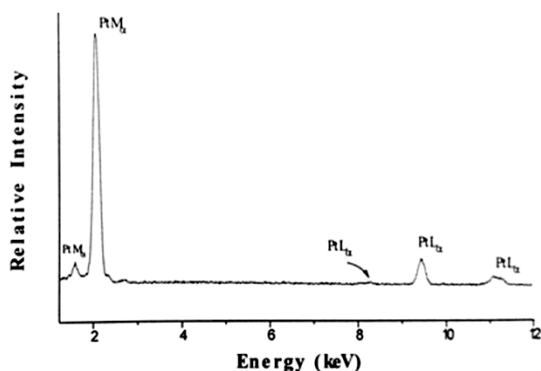


Fig. 6. EDA spectra of unsupported $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$ after heating at 550°C for 4 hours



Fig. 7. Electron micrographs of alumina supported $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$ after heating at 400°C for 4 hours

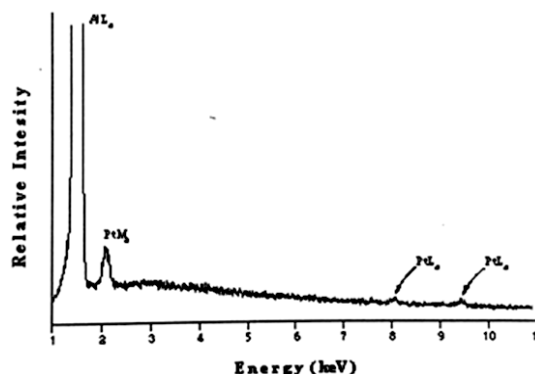


Fig. 8. EDA spectra of alumina supported $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$ after heating at 950°C for 4 hours

TEM was used in order to characterize any small particles that may form on the surface of heat treated alumina supported materials. For the Pt complex a range of particle sizes were observed and the precise size of the crystallites depended on the heating conditions. For example, the heat treating the alumina supported platinum complex at 600°C produces particles with size ranging from 15 to 37 nm , which is somewhat bigger size than that found by Ivanova,²¹ distributed over the alumina support (Fig. 9), as confirmed by EDA spectra (Fig. 10) and XRD measurement (Figure 4).

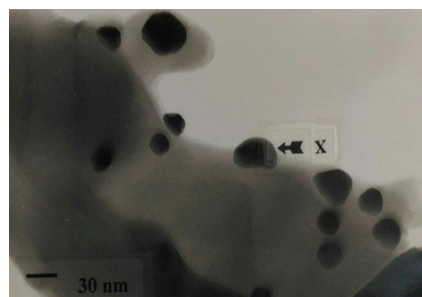


Fig. 9. TEM of heat treated alumina supported $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$ at 600°C .

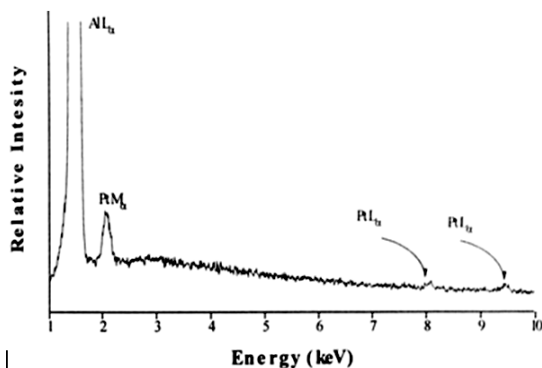


Fig. 10. EDA spectra of a particle X on the alumina support

The surface composition on the heat treated alumina supported sample was studied by XPS. The survey spectra on the alumina supported sample after heating at 400°C for 4 h was collected (Fig. 11). The spectra are dominated by strong Al and O signals from alumina support; all other lines observed are as expected. No lines due to Cl were observed.

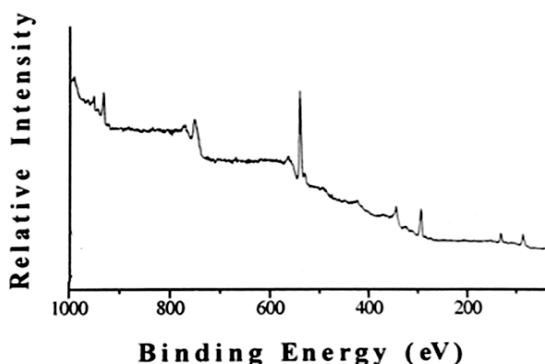


Fig. 11. XPS survey spectra of alumina supported $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$ after heating at 400°C and water washing. The BE value on the graphs have not been corrected for charging effect

Partial overlap of the Pt 4f and Al 2p lines complicates the analysis of the Pt 4f spectra (Fig. 12). Peak fitting analysis suggest a single Pt species is present with Pt 4f_{7/2} BE of 70.9 eV indicating Pt(0).²² The spectra provided no evidences for the presence of any Pt oxides.

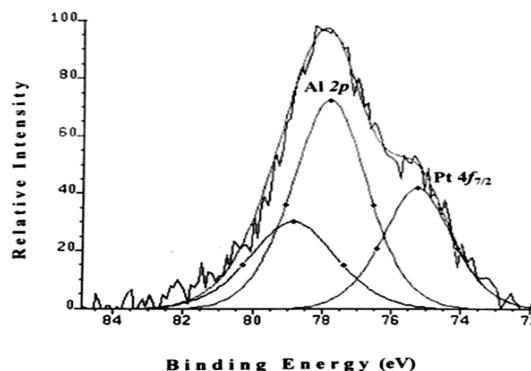


Fig. 12. Pt 4f spectra of alumina supported $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$ after heated at 950°C. The BE value on the graphs have not been corrected for charging effects of 2.8 eV

CONCLUSION

A series of IR, XRD, SEM, TEM, EDA and XPS studies showed that $(\text{NH}_4)_2\text{Pt}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$ can be prepared and can be used to prepare unsupported and alumina supported Pt free of chloride impurities.

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