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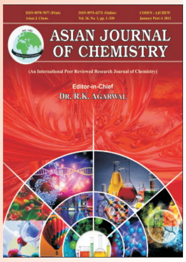

Synthesis and Thermo-chemical Profile of $[Pt(NH_3)_4]C_2O_4$ and $[Pt(NH_3)_4](OOCCH_2COO)$ as New Precursors for Supported Platinum Catalysts

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Two water-soluble complexes featuring $[Pt(NH_3)_4]^{2+}$ as a cation and common dicarboxylate (oxalate or malonate) as counter anion have been synthesized, characterized and evaluated for their thermo-chemical profile. The complexes can be easily synthesized in a yield of about 85 % from K_2PtCl_4 *via* a series of ligand substitution reactions at mild temperatures and under normal pressures. The thermolysis temperatures and products both in inert and oxidative atmosphere were determined by TG-DTA along with GC-MS. The thermolysis of $[Pt(NH_3)_4](C_2O_4)$ begins at about 220 ºC and ends at 270 ºC, forming metallic platinum, CO_2 and NH_3, whereas $[Pt(NH_3)_4](OOCCH_2COO)$ undergoes a two-phase thermolysis. The first phase corresponds to the loss of one amminia from 105 ºC, followed by the second phase, leading to complete destruction of the complex at 270 ºC. The final products are metallic platinum, CO_2, NH_3 and CH_3CONH_2. The thermolysis is caused by the intramolecular redox reaction. These unique properties render the two complexes potential as the new alternative precursors for supported platinum catalysts.

Keywords: Tetraammineplatinumoxalate, Tetraammineplatinummolonate, Thermochemical profile, Platinum catalyst.

INTRODUCTION

Supported platinum catalysts are an important kind of industrial catalysts and have been widely applied to varied chemical processes, particularly in purification of automobile exhaust[1]. Chemical wet impregnation is a conventional technique currently used for the production of supported platinum catalysts[2] and platinum compounds are necessary as the precursor of active component for this technique. There are a number of platinum compound commercially available in the market, but only a few can be employed as the precursors. These platinum precursors include H_2PtCl_6, $[Pt(NH_3)_4]Cl_2$, $[Pt(NH_3)_4](NO_3)_2$ and $(HOCH_2CH_2NH_3^+)_2Pt(OH)_6$[3-5]. As a precursor has substantial effects on the catalytic activity, the selection of the best precursor for a particular catalyst in a specific reaction can be critical[6-8]. An example is Pt/Al_2O_3 for automobile exhaust purification. The precursor for this specific application should be Cl-free and water-soluble platinum compounds such as $[Pt(NH_3)_4](NO_3)_2$ and $(HOCH_2CH_2NH_3^+)_2Pt(OH)_6$, for Cl poisons the oxidation activity of platinum[9-13]. Our recent finding that the presence of nitrate in the catalyst shortens the service life has caused concern with regard to the use of nitrate precursor $[Pt(NH_3)_4](NO_3)_2$. As a result, the choice of the suitable precursor for supported platinum catalysts, especially the catalyst used in automobile exhaust purification, is often confined to one compound $(HOCH_2CH_2NH_3^+)_2Pt(OH)_6$ which can only provide complex anions in the dipping process[14-17]. Therefore, there has been substantial need for developing new suitable platinum precursors for automobile exhaust purification catalysts. For a platinum compound to be used as a successful precursor, there are a number criteria. It should be soluble and stable in aqueous solution, does not contain harmful elements such as K, Na, Li, P, S, *etc*. and decompose cleanly on the surface of support. Of particular importance is the exclusion of Cl^- and NO_3^- as the ligand or the counter anion of the compound. In addition, the compound needs to be cost effective. Based on these requirements, two new precursors, $[Pt(NH_3)_4]C_2O_4$ and $[Pt(NH_3)_4](OOCCH_2COO)$, have been designed, synthesized and evaluated in the present paper with the intention of providing alternative precursors for supported platinum catalysts.

EXPERIMENTAL

K_2PtCl_4 was purchased from sino-platinum Corporation and other reagents are commercially available and were used without any further purification. Chemical analysis for C, H and N was performed with a Carlo-Ebra Instrument, whereas platinum was determined according to the method in USP24. Mass spectrometry studies were carried out on a VG-Autospec

Spectrometry in the FAB$^+$ mode using glycerine as matrix. FT-IR spectra were recorded in the 4000-400 cm^{-1} regions on a Perkin Elmer 880 spectrometer with KBr pellets. ^{1}H was obtained on Bruker AM-500 relative to TMS as an external standard.

Thermogravimetric and differential thermal analysis (TG-DTA) was carried out with a Netzsch STA 409 PG/PC Jupiter thermo-analytical equipment either in nitrogen atmosphere or in oxidative (20 % O_2 and 80 % N_2) atmosphere (flux rate: 40 mL/min, heating rate: 10 ºC/min, sample mass: 10-13 mg).

Gas decomposition products of the compounds were analyzed by GC-MS connected to the outlet of the thermal reactor. GC-MS analysis were performed in a gas chromatograph 2000 series equipped with a finnigan MS mass spectrometer (HP6890N/5972), using nitrogen or oxidative atmosphere as carrier gas (1 mL/min). a HP-5MS (30 m × 0.25 mm × 0.25 µm) was used as a separation column for GC. The chromatographic peaks were identified by comparison of their mass spectra with the equipment's mass spectral library.

Synthesis of *cis*-[Pt(NH_3)$_2$$I_2$]: K_2PtCl_4 (100 g, 240 mmol) was mixed at 45 ºC with KI (240 g, 6 × 240 mmol) in 500 mL H_2O for 4 h and then 14 % ammonia solution (90 mL, 1.3 × 2 × 240 mmol) was slowly added with vigorously stirring. After standing for 2 h, the resulting yellow precipitate *cis*-[Pt(NH_3)$_2$$I_2$] was collected by filtration, washed with water and ethanol and dried *in vacuo* at 65 °C. The yield was 95 % (110 g). Anal. calcd. for Pt(NH_3)$_2$$I_2$ (482.9): Pt, 40.4. found: Pt, 39.8.

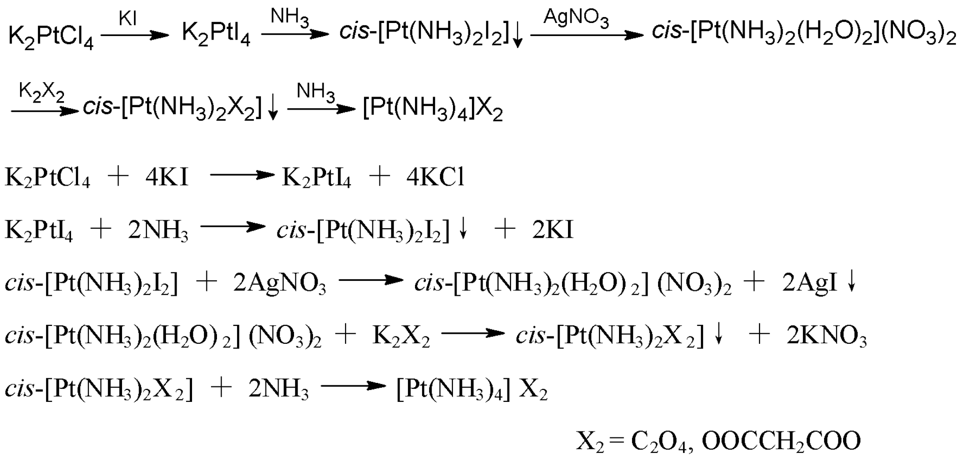
Synthesis of [Pt(NH_3)$_4$](C_2O_4): [Pt(NH_3)$_4$](C_2O_4) was synthesized by using the process described in our previous work[18] but with some improvements. Briefly, *cis*-[Pt(NH_3)$_2$$I_2$] (50 g, 103 mmol) was mixed with a 200 mL solution of silver nitrate (34.82 g, 205 mmol) and stirred at 55 ºC for about 10 h until no free silver ions could be detected by the precipitation reaction with NaCl. After AgI was filtrated off, potassium oxalate monohydrate (21 g, 114 mmol) was added to the filtrate, producing a white precipitate *cis*-[Pt(NH_3)$_2$(C_2O_4)] The precipitate was filtrated off, washed with water and dissolved in 100 mL, 14 % ammonia solution. The resulting solution was first heated in a boiling water bath to remove excessive ammonia and then transferred to a rotary evaporator. Water was evaporated under reduced pressure to produce a nearly white crystal product of [Pt(NH_3)$_4$](C_2O_4) under a reduced pressure. The product was collected and dried *in vacuo* at 60 ºC. Yield: 91 % (32.9 g). Anal. Calcd. for [Pt(NH_3)$_4$]C_2O_4 (351.1): C, 6.84; H, 3.42; N, 15.95; Pt, 55.57. Found: C, 6.80; H, 3.46; N, 15.85; Pt, 55.10. FAB$^+$-MS (m/e, RI): 352(M$^+$, 7 %), 262 (Pt(NH_3)$_4^+$, 37 %) IR (KBr, ν_{max}, cm^{-1}): 3288, 3112 (m, $\nu_{N\text{-}H}$), 1609 (vs, $\nu_{as(COO)}$), 1363 (vs, $\nu_{a(COO)}$), 1090 (s, $\nu_{C\text{-}O}$), 511(w, $\nu_{Pt\text{-}N}$). ^{1}H NMR (DMSO, ppm): 5.37 (s, ≈ 12H, 4NH_3).

Synthesis of [Pt(NH_3)$_4$](OOCCH_2COO): [Pt(NH_3)$_4$](OOCCH_2COO) was synthesized by following the procedure similar to that for [Pt(NH_3)$_4$](C_2O_4). Starting from 50 g *cis*-[Pt(NH_3)$_2$$I_2$] and with 21 g potassium malonate added, 33.1 g [Pt(NH_3)$_4$](OOCCH_2COO) was obtained and the yield was 88 %. Anal. Calcd. for [Pt(NH_3)$_4$](OOCCH_2COO) (365.1): C, 9.86; H, 3.83; N, 15.34; Pt, 53.43. Found: C, 9.73; H, 3.88; N, 15.10; Pt, 53.12. FAB$^+$-MS (m/e, RI): 262 (Pt(NH_3)$_4^+$, 93 %). IR (KBr, ν_{max}, cm^{-1}): 3264, 3012 (m, $\nu_{N\text{-}H}$), 1638-1535 (vs, $\nu_{as(COO)}$), 1431 (vs, $\nu_{a(COO)}$), 1087 (s, $\nu_{C\text{-}O}$), 510 (w, $\nu_{Pt\text{-}N}$). ^{1}H NMR (DMSO, ppm): 5.30 (s, ≈ 12H, 4NH_3), 3.16 (≈2H, CH_2(COO$^-$)$_2$).

RESULTS AND DISCUSSION

Designed complexes [Pt(NH_3)$_4$](C_2O_4) and [Pt(NH3)4] (OOCCH_2COO) can be synthesized from K_2PtCl_4 as the starting material by following the procedure illustrated in Fig. 1. K_2PtCl_4 was first converted *in situ* to K_2PtI_4 with KI and then to the insoluble intermediate *cis*-[Pt(NH_3)$_2$$I_2$] by ammonia, with a yield of up to 95 %. The coordinated iodide was removed in form of AgI from *cis*-[Pt(NH_3)$_2$$I_2$], producing a very soluble species *cis*-[Pt(NH_3)$_2$(H_2O)$_2$](NO_3)$_2$ from which *cis*-[Pt(NH_3)$_2$$X_2$] was precipitated upon the addition of K_2X_2. Substitution of X_2 coordinated to platinum with strong ammine ligand offered the final product [Pt(NH_3)$_4$]X_2 with a yield of 91 % for [Pt(NH_3)$_4$]C_2O_4 and 88 % for [Pt(NH_3)$_4$](OOCCH_2COO) calculated from *cis*-[Pt(NH_3)$_2$$I_2$]. The overall yield was 86 % and 84 %, respectively. All the synthetic conditions were mild and easy to be controlled. Platinum and silver in the waste resulting from synthetic process can be easily recovered by the conventional methods and recycled.

Both complexes were structurally characterized by chemical analysis and spectroscopic data. The content of Pt, C, N and H was in good agreement with the calculated value.



$$K_2PtCl_4 \xrightarrow{KI} K_2PtI_4 \xrightarrow{NH_3} cis\text{-}[Pt(NH_3)_2I_2]\downarrow \xrightarrow{AgNO_3} cis\text{-}[Pt(NH_3)_2(H_2O)_2](NO_3)_2$$

$$\xrightarrow{K_2X_2} cis\text{-}[Pt(NH_3)_2X_2]\downarrow \xrightarrow{NH_3} [Pt(NH_3)_4]X_2$$

$$K_2PtCl_4 + 4KI \longrightarrow K_2PtI_4 + 4KCl$$

$$K_2PtI_4 + 2NH_3 \longrightarrow cis\text{-}[Pt(NH_3)_2I_2]\downarrow + 2KI$$

$$cis\text{-}[Pt(NH_3)_2I_2] + 2AgNO_3 \longrightarrow cis\text{-}[Pt(NH_3)_2(H_2O)_2](NO_3)_2 + 2AgI\downarrow$$

$$cis\text{-}[Pt(NH_3)_2(H_2O)_2](NO_3)_2 + K_2X_2 \longrightarrow cis\text{-}[Pt(NH_3)_2X_2]\downarrow + 2KNO_3$$

$$cis\text{-}[Pt(NH_3)_2X_2] + 2NH_3 \longrightarrow [Pt(NH_3)_4]X_2$$

$$X_2 = C_2O_4,\ OOCCH_2COO$$

Fig. 1. Synthetic scheme and reactions of [Pt(NH_3)$_4$]C_2O_4 and [Pt(NH_3)$_4$](OOCCH_2COO)

The fragment ion peak corresponding to $[Pt(NH_3)_4]^{2+}$ was developed in FAB$^+$-MS spectra of the complexes. The coordination of NH_3 to Pt was confirmed by the presence of an absorption band near 510 cm^{-1}. The resonance with approximately 12 protons near 5.3 ppm in ^{1}H NMR spectra can be designated to $4NH_3$. For $[Pt(NH_3)_4](OOCCH_2COO)$, there was another resonance at 3.16 ppm due to two protons of $(OOCCH_2COO)^{2-}$. All above data show that in the molecule of two complexes, platinum(II) is coordinated by $4NH_3$, forming a bivalent coordinated cation and X_2 ions lie outside the coordinated sphere, acting as the counter anions, as shown in Fig. 2.

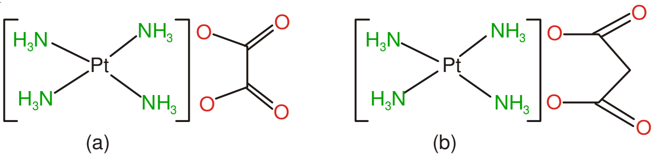


Fig. 2. Chemical structure of $[Pt(NH_3)_4]C_2O_4$ (a) and $[Pt(NH_3)_4](OOCCH_2COO)$ (b)

As ionic compounds, the complexes, similar to $[Pt(NH_3)_4](NO_3)_2$[19], have a water solubility of more than 40 g/L, sufficient for a precursors used in the manufacture of varied supported platinum catalysts and they are also stable both in the air and in aqueous solutions.

The thermal chemical behaviour of two complexes was studied by TG/DTA and the gaseous thermolysis products at 270 °C were analyzed by GC-MS. The TG-DTA curves are shown in Figs. 3 and 4 and the main products are listed in Table-1. For $[Pt(NH_3)_4](C_2O_4)$. An apparent weight loss of about 44 % was observed from 229-273 ° C with an endothermic DTA peak at 245 °C in N_2 atmosphere and from 210-253 °C with an sharp exothermic DTA peak at 252 °C in the mixture atmosphere of N_2 and O_2, corresponding to the complete decomposition of $[Pt(NH_3)_4](C_2O_4)$. The percentage of 56 % of remaining solid residue is in a good agreement with the calculated value of platinum content in $[Pt(NH_3)_4](C_2O_4)$ and the gaseous thermolysis products were determined to be CO_2 and NH_3 at 270 °C. A 2 % weight gain was found in the oxidative environment from 500-600 °C due to the partial oxidation of tiny platinum particles. The atmospheres did not have much effects on both decomposition temperatures and decomposition products in the range of 210-270 °C, implying that the thermal decomposition of $[Pt(NH_3)_4](C_2O_4)$ was the result of an intra-molecular redox reaction in which Pt(II) was reduced to Pt by oxalate, as illustrated by the following reaction.

$$[Pt(NH_3)_4]C_2O_4 \xrightarrow{210-270\ °C} Pt + NH_3 + CO_2$$

From the TG/DTA curves of $Pt(NH_3)_4](OOCCH_2COO)$, it can be seen that there was a approximately 4.5 % weight loss from 105-150 °C accompanied by an endothermic DTA peak at 132 °C. This corresponded to the loss of one NH_3 from $Pt(NH_3)_4](OOCCH_2COO)$. Above that temperature point, the TG/DTA curves are very similar to those for $[Pt(NH_3)_4](C_2O_4)$, suggesting that they had similar thermal behaviour. An apparent weight loss of about 42 % from 220-260 °C occurred with an endothermic DTA peak at 248 °C in N_2 atmosphere and an

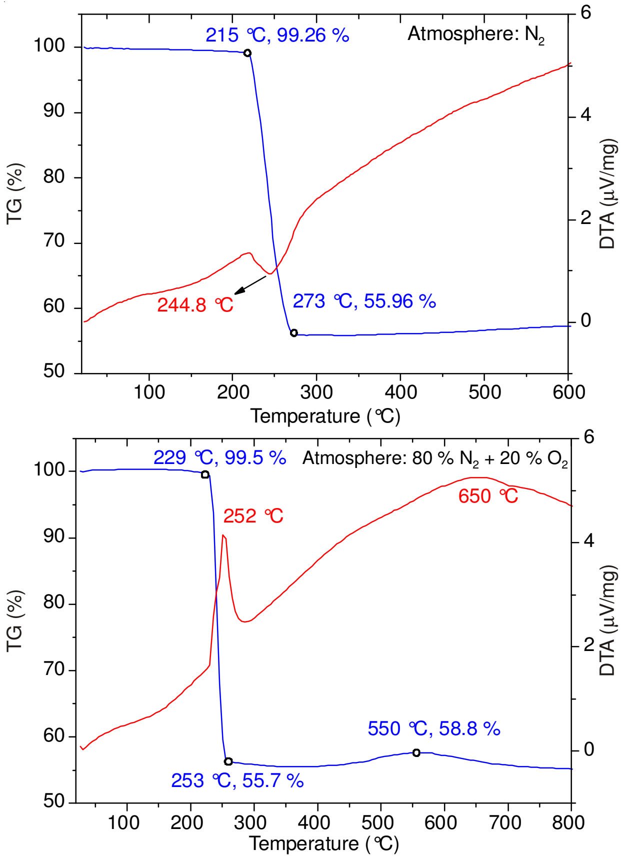


Fig. 3. TG and DTA curves of $[Pt(NH_3)_4](C_2O_4)$ in inert and in oxidative atmosphere

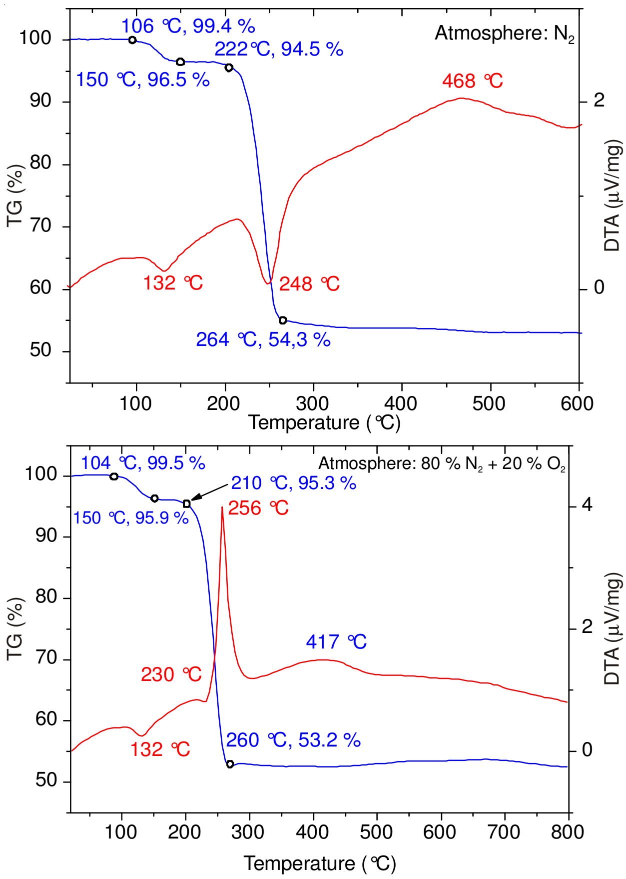


Fig. 4. TG and DTA curves of $[Pt(NH_3)_4](OOCCH_2COO)$ in inert and in oxidative atmosphere

sharp exothermic DTA peak at 256 ºC in the mixture atmosphere of N_2 and O_2, corresponding to the complete decomposition of $[Pt(NH_3)_4](OOCCH_2COO)$. The percentage of 53 % of remaining solid residue is in a good agreement with the calculated value of platinum content in $[Pt(NH_3)_4](OOCCH_2COO)$ and the gaseous thermolysis products at 270 ºC were found to be CO_2 and NH_3 and CH_3CONH_2. The third product CH_3CONH_2 was probably formed by the reaction of CH_3COOH with NH_3 in the gaseous phase. A slight weight gain because of the partial oxidation of tiny platinum particles was also observed in the oxidative environment in the range of 500-700 ºC. The thermal decomposition of $[Pt(NH_3)_4]$ $(OOCCH_2COO)$ was also caused by the intramolecular redox reaction in which Pt(II) was reduced to Pt by malonate, as illustrated by the following reaction.

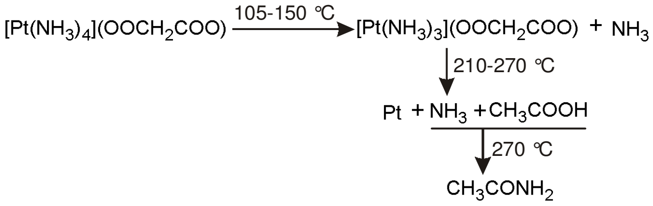


TABLE-1
MAIN GASEOUS THERMOLYSIS PRODUCTS OF THE COMPLEXES AT 270 ºC

Complex	Atmosphere	Thermolysis product
$[Pt(NH_3)_4]C_2O_4$	80 % N_2 + 20 % O_2	CO_2, NH_3
	N_2	CO_2, NH_3
$[Pt(NH_3)_4](OOCCH_2COO)$	80 % N_2 + 20 % O_2	CO_2, CH_3CONH_2, NH_3
	N_2	CO_2, CH_3CONH_2, NH_3

Conclusion

Two novel complexes $[Pt(NH_3)_4](C_2O_4)$ and $[Pt(NH_3)_4]$ $(OOCCH_2COO)$ have been developed as alternative precursors for supported platinum catalysts. The synthetic routes are very effective with an overall yield of up to 85 % and Pt-containing waste can be easily recovered by the conventional methods and recycled. All the synthetic conditions are mild and easy to be controlled, which is acceptable with respect to industrial manufacturing. The complexes have a good water-solubility, do not contain chloride or nitrate and are able to provide complex cations in the dipping process. More importantly, they undergo intra-molecular self-redox at a moderate temperature of about 270 ºC, forming metallic platinum and gaseous products: NH_3 and CO_2 from $[Pt(NH_3)_4](C_2O_4)$, CO_2 and CH_3CONH_2 and NH_3 from $[Pt(NH_3)_4](OOCCH_2COO)$, an ideal thermo-chemical profile as a precursor.

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