

Study of SWCNTs-Supported Pd and Pt Catalyst by K Filled

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In order to improve reducing property of single-walled carbon nanotubes, potassium was filled in interior of carbon nanotubes on vacuum condition. Single-walled carbon nanotubes-supported Pt and Pd catalyst was obtained when potassium filled single-walled carbon nanotubes was put in K_2PtCl_6 and $PdCl_2$ solution. The as-grown products were characterized using transmission electron microscopy, X-ray photoelectron spectroscopy techniques and mechanism of potassium filled single-walled carbon nanotubes supporting metal was researched. The results showed that potassium filled single-walled carbon nanotubes is better than the single-walled carbon nanotubes in terms of the reducing property, capacity and particle size (particles with diameters of 1 nm) of supporting metal. Potassium filled single-walled carbon nanotubes-supported Pt and Pd has good performance on distribute, tight and purity. From the research of electron transfer, electron move from potassium to the surface of single-walled carbon nanotubes. Subsequently, metal ion obtained electron was deposited on the surface of single-walled carbon nanotubes. Solution reached neutral between potassium ion and anion.

Key Words: Potassium filled, Single-walled carbon nanotubes, Supported, Metal.

INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) composed with carbon, shows good symmetry and uniqueness on structure, good intensity and perfect carrier supported with metal¹. With some reducing property and small diameter about 1 nm to 2 nm, SWCNTs can interact with metal salt to make SWCNTs composite material with supported metal³. Choi *et al.*⁴ used redox reaction with SWCNTs in the mixed solvent of water and ethanol and Au^{3+} solvent and got SWCNTs/Au, but supported metal is uneven. O'Connell *et al.*⁵ interacted SWCNTs scattered by surface active agent with $K[AuCl_4]$ and got supported even SWCNTs/Au. Lordi *et al.*⁶ oxidized the surface of SWCNTs with HNO_3 and filled much carboxyl group and deoxidized $K_2[PtCl_4]$ with glycol and SWCNTs catalytic materials. Xing and other researchers⁷ oxidized SWCNTs with HNO_3 and filled carboxyl group, used hybrid reaction with $H_2[PtCl_6]$ EC and evaporated to dryness and deoxidized with H_2 and got Pt/SWCNTs. We made good use of the reducing property of SWCNTs, by interaction of SWCNTs and K_2PtCl_6 liquor and $PdCl_2$ liquor, made successfully SWCNTs/Pt with good catalytic activity and SWCNTs/Pd with supported catalyst. However, the result showed the role of reducing property of SWCNTs is limited, especially for high valence metal ion. In order to improve reducing property of single-walled carbon nanotubes (SWCNTs), potassium was filled in interior of carbon nanotubes on vacuum condition.

Single-walled carbon nanotubes-supported Pt and Pd catalyst was obtained when potassium filled SWCNTs was put in K_2PtCl_6 and $PdCl_2$ solution. The as-grown products were characterized using transmission electron microscopy, X-ray photoelectron spectroscopy techniques and mechanism of K filled SWCNTs supporting metal was researched, which could provide applying SWCNTs with material basis and basic theory about interaction between metal or metal ion and SWCNTs and electron transfer.

EXPERIMENTAL

K@SWCNTs preparation: The preparation of SWCNTs was based on the previous reports⁸⁻¹⁰ and altered properly. The SWCNTs after purification was put in the glass tube and the glass tube was vacuumized to 1×10^{-4} Pa under 573 K to avoid the affection of water and gas. After stopping heating, the potassium metal was put in glass tube quickly and the glass tube was also vacuumized to 1×10^{-4} Pa and seal the glass tube. K@SWCNTs was got, with the K steam entered the holes in the SWCNTs after 473 K heating 48 h in hot oven and placing, then cleaning the K on the surface of SWCNTs with ethanol.

K@SWCNTs/Pt preparation: K@SWCNTs was put in aqueous solution of $K_2[PtCl_6]$ with some concentration and aqueous solution of $PdCl_2$, ultra sounded 4 h, centrifugal separation, washed 2 to 3 times with distilled water, filtered, dried and obtained K@SWCNTs/Pt and K@SWCNTs/Pd.

The synthesized samples were scattered by ultra UV observed by H-9000 TEM made by Japan Hitachi company and the states of being of the Pt and Pd in the sample were characterized by AXIS Ultra XPS energy spectrometer made by British Kratos company.

RESULTS AND DISCUSSION

TEM analysis of the samples: Fig. 1 is the TEM images of (a) K@SWCNTs/Pt and (b) K@SWCNTs/Pd that were obtained by SWCNTs supported with K interacted with 10 mmol L⁻¹ K₂PtCl₆ aqueous solution and 12 mmol L⁻¹ PdCl₂ aqueous solution. From the images, we can see that a great numbers of Pt and Pd were sinked on the surface of SWCNTs, distribution of Pt and Pd on the surface of SWCNTs was even, not rallied, the size of Pt and Pd were about 1 nm and Pt and Pd supported more, showed good sinking effect and combined with SWCNTs very tightly. This supported K could enhance the reducing property of SWCNT and when interacting with Pt and Pd salt solution, K@SWCNTs showed good reducing property, reducing much and supported much. In addition, this is the reason that the reducing speed of K@SWCNTs was quick and the crystal grew slower, which influenced the growing of the crystal in the process of reducing and sinking and made the size of supported Pt and Pd small and the K@SWCNTs became the ideal reducer and sinking carrier.

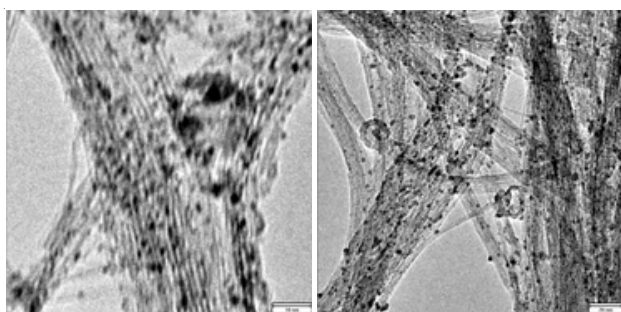


Fig. 1. TEM images of (a) K@SWCNTs/Pt and (b) K@SWCNTs/Pd

XPS analysis of K@SWCNTs/Pt: We used XPS to characterize the K@SWCNTs/Pt to know the chemical state of the supported Pt, and sophisticated fitting analysis of 4f spectrum peak of Pt in K@SWCNTs/Pt was made, which showed in the Fig. 2. Fig. 2 shows us that K@SWCNTs/Pt has two metallic

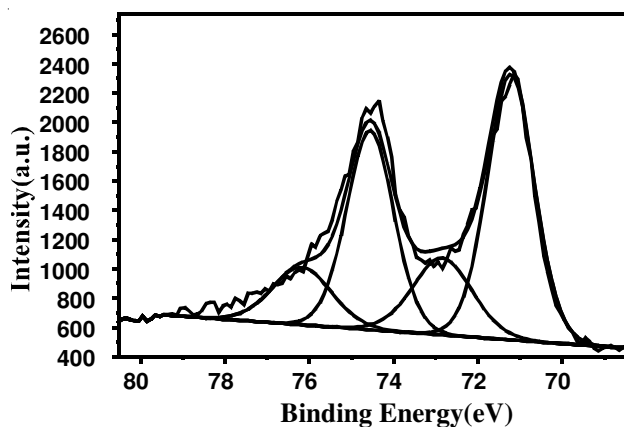


Fig. 2. XPS of K@SWCNTs/Pt

state Pt 4f_{7/2} and Pt 4f_{5/2} characteristic peak when binding energy is 71.23 eV and binding energy is 74.56 eV and its atom percentage is 73.34. The atom percentage of two characteristic peaks of oxidation state platinum Pt 4f_{7/2} and Pt 4f_{5/2} on 72.84 eV and on 76.17 eV is 26.66.

The result shows that the reducing property of K@SWCNTs/Pt is more, which could make Pt deoxidize easily from salt solution and make it support on SWCNTs. Therefore, K filled SWCNTs is the ideal reducer and sinking carrier of Pt.

XPS analysis of K@SWCNTs/Pd: Fig. 3 is the sophisticated fitting analysis of 3d spectrum peak of Pd in K@SWCNTs/Pd. Fig. 3 shows that K@SWCNTs/Pd has two metallic state Pd 3d_{5/2} and Pd 3d_{3/2} characteristic peak when binding energy of K@SWCNTs/Pd is 335.52 eV and binding energy is 340.78 eV and its atom percentage is 14.68. When binding energy is 337.51 eV and binding energy is 342.77 eV, the atom percentage of oxidation state Pd 3d_{5/2} and Pd 3d_{3/2} two characteristic peak is 85.33. Much of Pd in K@SWCNTs/Pd existed in oxidation state, because particle size of Pd on the surface of SWCNTs was small which could be oxidized easily by oxygen. Fig. 3 also shows us that the energy of K@SWCNTs/Pd could shift for greater binding energy, because supported Pd had small particle size and its decentrality was strong, and it combined with SWCNTs tightly, and small scattered Pd could interact with SWCNTs strongly.

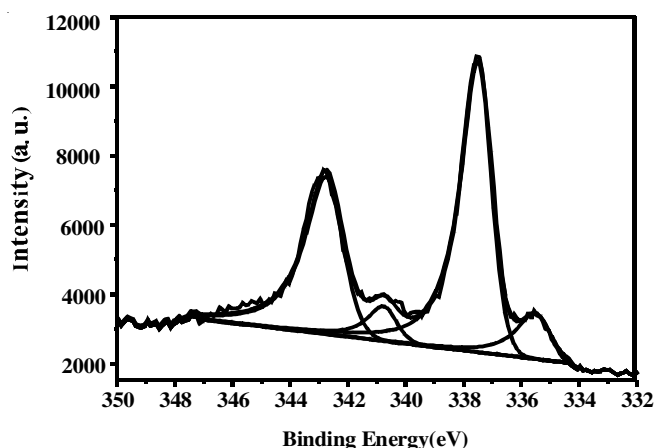


Fig. 3. XPS of K@SWCNTs/Pd

Analysis of supported metal mechanism of potassium filled SWCNTs: Fig. 4 shows that when K@SWCNTs interacted with metal ion solution, filled K would lose electron and made the electron transfer on the surface of SWCNTs, then after getting electron on the surface of SWCNTs, the metal ion in solution would be deoxidized to metal and sank on the surface of SWCNTs and K⁺ lost electron could interact with negative ion in solution and became electric neutrality. With filled K, the reducing property of SWCNTs was improved, metal ion was deoxidized radically, high valent metal ion was also deoxidized easily.

Conclusion

In order to improve reducing property of single-walled carbon nanotubes (SWCNTs), K was filled in interior of carbon nanotubes on vacuum condition. SWCNTs-supported Pt and

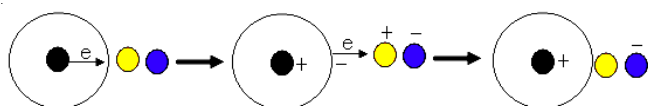


Fig. 4. Electron transfer of K@SWCNTs reducing metal

Pd catalyst was obtained when K filled SWCNTs was put in K_2PtCl_6 and $PdCl_2$ solution. The as-grown products were analyzed using transmission electron microscopy and X-ray photoelectron spectroscopy techniques. The results showed that K filled SWCNTs is better than the SWCNTs in terms of the reducing property, capacity and particle size (particles with diameters of 1 nm) of supporting metal. K filled SWCNTs - supported Pt and Pd has good performance on distribute, tight and purity. From the research of electron transfer, electron move from K to the surface of SWCNTs. Subsequently metal ion obtained electron and was deposited on the surface of SWCNTs. Solution reached neutral between K^+ and anion.

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