Carbon nanotubes supported N-promoted Pd-based catalysts for acetylene hydrochlorination

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Abstract. A novel N-promoted carbon nanotubes (CNT) supported Pd catalyst (PANI/CNT-Pd) was prepared by the ultrasonic-assisted impregnation method and applied in the acetylene hydrochlorination reaction successfully. Compared with the Pd-CNT catalyst, the PANI/CNT-Pd catalyst exhibited the enhanced catalytic performance with more than 91.6% acetylene conversion and 99.6% vinyl chloride selectivity during 20 h at T = 160 °C, GHSV(C2H2) = 120 h⁻¹ and V(HCl) : V(C2H2) = 1.5. It is suggested that PANI species contained N elements have been deposited on the CNT surface and they display the critical role on the enhanced catalytic performance of PANI/CNT-Pd catalysts correlated with the less palladium loss and the carbon deposition.

1. Introduction

Due to the increasing petroleum prices and abundant coal resources in China, the coal-based acetylene hydrochlorination is the optimal chemical reaction for the manufacture of vinyl chloride monomer (VCM), which is a major raw material for polyvinyl chloride (PVC)[1]. At present, the HgCl2 supported on active carbon (AC) catalyst is widely carried out in industrial PVC production with high Hg pollutions and shortages in Hg resource, leading to severe environmental and economic problems, and it is considered that the suitable carrier is good to the reactivity promotion for acetylene hydrochlorination[19]. So many other carriers (zeolites, Al2O3, SiO2, etc) have been used for acetylene hydrochlorination as well as AC[21-23].

Carbon nanotubes (CNT) are generally considered as an extremely promising material for their high mechanical strength, large surface area, excellent electrical conductivity and good adsorption performance[24-26]. It is reported that nitrogen-doped carbon nanotubes can improve electron-transport quality and electrical properties[27-29] and CNT incorporated with conducting polymers (polyaniline, polypyrrole, etc) have been attracted much attention in a wide variety of applications such as fuel cells, catalysis, gas sensors and polymers, owing to their simple synthesis, outstanding dispersibility and environmental stability recently[27-32]. In our previous work, palladium-based catalysts with excellent activity were considered as the potential mercury-free catalysts for acetylene hydrochlorination, but non-ideal stability still needs improvements[6,16,21,30]. In this work, polyaniline (PANI) as the main nitrogen source grafted onto the surface of carbon nanotubes were prepared by chemical oxidation polymerization method and palladium supported on PANI/CNT catalysts (PANI/CNT-Pd) were achieved by the ultrasonic-assisted impregnation method, applied for acetylene hydrochlorination successfully. The catalytic performance and physicochemical properties of PANI/CNT-Pd catalysts were explored, and the possible reasons for the catalyst deactivation were discussed.

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2. Experimental

2.1. Preparation of the catalysts

PANI/CNT composites were prepared by chemical oxidation polymerization method\([30,33]\). A volume of 100 mL HCl solution (2 M) containing CNT (2.0 g) suspension was sonicated at room temperature for about 0.5 h, and then mixed with 2 mL aniline monomer (CP, N98%, 4 mL). Ferrous sulfate solution (5%, 1 mL) was added followed by the addition of ammonium persulfate (CP, N98%, 0.5 g mL\(^{-1}\)) which served as the oxidant. The reaction mixture was constantly stirred in an ice bath (temperature range of 0-5 °C) for 1 h and then reacted at room temperature for 3 h. The dark green precipitates (PANI species) were filtered and washed with distilled water/ethanol until the filtrate became colorless. After drying at 80 °C for 10 h, the PANI/CNT composites with the mass ratio of 30%, 40%, 60%, 80% PANI species were obtained and labeled as 3PANI/CNT, 4PANI/CNT, 6PANI/CNT, 8PANI/CNT, respectively.

The catalysts were all prepared by the ultrasonic-assisted impregnation method\([15,16]\). PANI/CNT composites were dried at 100 °C for 2 h for removing the adsorbed water before the H2PdCl4 solution was added dropwise to the PANI/CNT carriers (3.0 g) with continuous stirring at normal temperature. Then the mixture was impregnated with ultrasonic treatment for 1 h and stored at room temperature overnight. Finally, the obtained samples were dried at 90 °C for 10 h and recorded as PANI/CNT-Pd catalysts. The serial PANI/CNT-Pd catalysts were named in terms of the PANI/CNT carriers, which were designated as 3PANI/CNT-Pd, 4PANI/CNT-Pd, 6PANI/CNT-Pd and 8PANI/CNT-Pd, respectively. For comparison, the Pd-CNT catalyst was prepared using the similar method described above without PANI. Additionally, the Pd loading of all catalysts was kept 0.5 wt%.

2.2. Catalyst characterization

Fourier transform infrared spectrometer (FTIR) was recorded at 364 scans per spectrum at 4 cm\(^{-1}\) resolution, using EQUINOX-55 (Bruker Company, Germany) machine. The relative ingredients and microtopography of catalysts were recorded by an energy dispersive spectrometer (EDS) analyzer attached to a LEO1450VP scanning electron microscope (SEM). The real content of palladium species was detected using an inductively coupled plasma instrument (Agilent ICP-OES730). X-ray powder diffraction (XRD) data were collected on a M18XHF22-SRA diffractometer using Cu-K\(\alpha\) radiation (scanning range 2\(\theta\): 10-80\(^{\circ}\)) at 50 kV and 100 mA. Brunauer-Emmett-Teller (BET) surface areas and pore parameters were measured by Quantachrome autosorb iQ2 equipment.

2.3. Catalyst measurement

The catalytic test for acetylene hydrochlorination was carried out in a fixed bed with a 10-mm-diameter quartz microreactor operating just above atmospheric pressure. 

N2 flow (15 mL min\(^{-1}\)) via calibrated mass flow controllers in a heated glass reactor and then hydrochloride at a flow rate of 15 mL min\(^{-1}\) passed through the reactor to activate the catalyst. Hydrochloride (12.8 mL min\(^{-1}\)) and acetylene (8.5 mL min\(^{-1}\)) were fed through a mixing vessel containing catalyst (3.0 g) under the reaction conditions (T = 160 °C, a C2H2 gas hourly space velocity (GHSV) = 120 h\(^{-1}\) and VHCl: VC2H2 = 1.5). The exit gas mixture from the reactor was passed through an absorption bottle filled with sodium hydroxide solution and then analyzed for acetylene conversion and VCM selectivity by gas chromatography (GC 2010, Shimadzu).

3. Results and discussion

![FTIR spectra of CNT and Pd-based catalysts](attachment:image)

Fig.1. FTIR spectra of CNT and Pd-based catalysts

FTIR spectra of the CNT and Pd-based catalysts were presented in Fig 1. Like graphite, the FTIR spectrum of pristine CNT carrier and the Pd-CNT catalyst all had extremely low infrared absorption intensities and it is suggested that there are no obvious changes of functional groups on the Pd-CNT catalyst surface after loading Pd active components. For PANI/CNT-Pd composites, the almost identical characteristic bands situated at 1241 cm\(^{-1}\), 1295 cm\(^{-1}\), 1482 cm\(^{-1}\) and 1565 cm\(^{-1}\) were attributed to C=N stretching vibrations, stretching of C-N secondary aromatic amine, benzenoid stretching vibration, and quinoid-ring vibration\([34]\). Compared with Pd-CNT, some main bands of PANI were observed in PANI/CNT-Pd nanocomposites, though they shifted to a lower wavenumber as a result of the additional π-π conjugated interaction between the benzene ring of PANI and the graphite-structured CNT, indicating an interaction between CNT and PANI\([34]\).
Fig. 2. XRD patterns of CNT and Pd-based catalysts.

Fig. 3. SEM images of CNTs and PANI/CNT composites. (a) CNT; (b) 3PANI/CNT; (c) 6PANI/CNT; (d) 8PANI/CNT.

Table 1. Elemental composition of the catalyst record by EDS.

Table 2. The total Pd content of the Pd-CNT and 8PANI/CNT-Pd catalysts recorded by ICP.

To further explore the relative elemental compositions changes of the CNT-based composites, EDS data were performed and listed in Table 1. It was clear that all the CNT-based composites contained C and O elements belonged to the pure CNT carrier. N element was also detected in the PANI/CNT composites and PANI/CNT-Pd catalysts, attributed to the characteristic elemental of PANI polymer. Meanwhile, S species were appeared in the PANI/CNT composites and PANI/CNT-Pd catalysts for the introduced -SO3H groups onto the CNT surface after diazotization[39]. Pd and Cl elements were found in the Pd-CNT and PANI/CNT-Pd catalysts, indicating that the Pd species were loaded on the carrier surface. Compared with the fresh Pd-based catalysts, the amount of the C and Cl element were increased but the relative Pd element content was decreased in the used Pd-CNT and 8PANI/CNT-Pd catalysts, which may be resulted from the carbon deposition generation and the loss of Pd and PANI species during the reaction[30]. From ICP results (Table 2), it was further confirmed that Pd species were lost in Pd-CNT and PANI/CNT-Pd catalysts during the reaction and Pd species loss is one reason for the decreasing of catalytic activity in Pd-based/CNT catalysts (Fig. 4). Meanwhile, it was exhibited clearly that the loss ratio of Pd species in the 8PANI/CNT-Pd catalyst (22.8%) was much less than that in the Pd-CNT catalyst (50.6%), which suggested that the presence of the polyaniline layer in the Pd-based catalyst stabilize Pd species and retard Pd loss during the reaction, resulting the enhanced catalytic performance for acetylene hydrochlorination[30]. In addition, the N elements were decreased (about 9.39%) in
the used 8PANI/CNT-Pd catalyst after reaction (Table 1) and the decomposition of the polyaniline layer may be the possible reason decreased the catalyst activity (Fig 4).

**Table 3.** Porous structure parameters of the samples.

| Sample         | SBET/m² g⁻¹ | V/cm³ g⁻¹ | D/nm |
|----------------|-------------|-----------|------|
| CNT            | 133         | 0.16      | 2.69 |
| 8PANI/CNT      | 59          | 0.05      | 2.96 |
| Fresh Pd-CNT   | 128         | 0.15      | 2.68 |
| Used Pd-CNT    | 99          | 0.11      | 2.71 |
| Fresh 8PANI/CNT-Pd | 47       | 0.04      | 2.84 |
| Used 8PANI/CNT-Pd | 36        | 0.04      | 2.85 |

SBET: surface area; V: total pore volume; D: average pore diameter.

![Fig.4](https://example.com/grafico.png)

**Fig.4.** Catalytic performance of Pd-CNT and PANI/CNT-Pd catalysts. Reaction conditions: Temperature = 160 °C, C₂H₂:VCl₂ = 1.5.

BET analysis was performed and the surface area (SBET), total pore volume (V) and average pore diameter (D) of the pure CNT, the 8PANI/CNT composite and the fresh and used Pd-CNT and 8PANI/CNT-Pd catalysts were listed in Table 3. The untreated CNT has the highest surface area of 133 m² g⁻¹ and the decomposition of the polyaniline layer may be the possible reason decreased the catalyst activity (Fig 4). In summary, Pd-PANI/CNT catalysts were prepared and displayed an excellent activity and stability (more than 91.6% acetylene conversion and 99.6% vinyl chloride selectivity in 20 h) under the conditions in the acetylene hydrochlorination reaction. It is suggested that PANI...
species contained N elements have been deposited on the CNT surface and the presence of PANI has a significant influence on the catalytic activity and stability of CNT-based catalysts. This may be the existence of PANI (especially N species) to bridge the Pd species and CNT walls with the presence of Pd-N bonding and π-π bonding, which prevented Pd nanoparticles from aggregating with each other and Pd species loss, resulting in enhancing the catalytic performance. It was suggested that Pd species loss and the carbon deposition were the main reason for the PANI/CNT-Pd catalyst deactivation. In addition, it is suggested that the CNT can be a promising material to improve the catalytic performance of Pd-based catalysts for acetylene hydrochlorination reaction.

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