Reduced graphene oxide modified platinum catalysts for the oxidation of volatile organic compounds

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ABSTRACT

In this work, we report the synthesis of reduced graphene oxide (rGO) modified platinum (Pt) catalysts for decreasing the temperature of the complete conversion of benzene. The X-ray photoelectron spectroscopy (XPS) analysis reveals the presence of electron transfer between rGO and Pt, which has a significant effect on the catalytic activity. The electron transfer is also proved by Raman spectra in term of the shifting of G-band belonging to the rGO. H_2-temperature programmed reduction (H_2-TPR) results indicate that the rGO facilitates the reduction of surface oxygen over the catalyst. Moreover, increasing the concentration of rGO within a certain range has a positive influence on the catalytic activity.

1. Introduction

Graphene oxide (GO), mainly made from the exfoliation of graphite oxide instead of the oxidation of graphene, has intrinsic outstanding optical, electronic/ionic, hydrophilic, and mechanical properties, which provide a variety of potential applications in biology [1,2], catalysis [3,4], energy storage [5,6], optoelectronics devices [7,8], polymeric composites materials [9], and water purification [10].

Besides, the high surface area and a variety of oxygen-containing functional groups, e.g. hydroxyl, epoxy, aldehyde, ketone, and carboxyl render that the GO has strong oxidized ability. In addition, when the GO is reduced, the reduced graphene oxide (rGO) is formed, giving rise to plenty of broken bonds and defects to activate the oxygen. The unique chemical properties of rGO are potentially advantageous for redox catalytic reactions, especially for photo- and electro-catalysis, which almost completely occur in the liquid phase environment. Hwang et al. found that the Ni/GO could significantly enhance the evolution of hydrogen from aqueous methanol solution, and they believed that this could be attributed to the minimal electron–hole recombination resulting from the easy transfer of photogenerated electrons from the GO to the Ni in the catalysts [11]. Yang et al. revealed that Pt nanoflowers modified with rGO wrapped carbon cloth as an anode enhanced current density of cyclic voltammograms towards formic acid and methanol electrooxidation due to the excellent electron or charge transfer rate [12]. Gao et al. reported that the Pd-Au/rGO has high electrocatalytic activity and stability for the electrooxidation of methanol and ethanol in alkaline media [13]. Upon the great success for rGO in liquid phase reactions, it is definitely interesting to understand the role of rGO in gas phase catalytic reaction, such as air purification process.

In numerous problems in air pollution management, the elimination of volatile organic compounds (VOCs), which are extra harmful to human health, attracts increasing attention. Among the VOCs, benzene is one of the target compounds because of its carcinogenicity [14]. Therefore, catalytic conversion for the control of benzene becomes one of the vital issues in environmental catalysis [15,16]. So far, the high active noble metal catalysts based on Pt and Pd nanoparticles are widely used in benzene oxidation [17].

In the present work, rGO is introduced into Pt/Al_2O_3 catalyst for the catalytic oxidation of benzene. And the effect of rGO on the electron transfer, which results in an obvious improvement in the catalytic activity, is discussed.

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2. Experimental

2.1. Catalyst preparation

All chemicals used in this study were purchased from Xilong Chemical Co., Ltd. (China) and used without further purification. The water used to make all solutions was made from Millipore Milli-Q water (15 MΩ cm).

Pt catalyst was prepared by a conventional $NaBH_4$ reduction method. Firstly, 1.0 g of Al_2O_3 powder was dissolved into 150 mL of deionized water under vigorous stirring for 30 min to form a suspension. Then, a certain amount colloidal solution of GO (0.05 g L^{-1}) was diluted to 200 mL and added to the suspension. The slurry of colloidal solution with alumina powders was rapidly stirred for 90 min. Next, a 50 mL of aqueous solution of $H_2PtCl_4·6H_2O$ (26.4 mg) was added into the slurry, following by stirring for 2 h. Finally, 19.3 mg of $NaBH_4$ was dissolved in 10 mL of deionized water and added into the slurry, and the mixture was stirred for 2 h. All the experiments were all performed at room temperature. After the reaction, the sample was separated by centrifugation and washed by deionized water for three times. Then, it was dried at 80 °C overnight. The amount of the GO colloidal solutions was adjusted in order to obtain 0.1, 0.6, 1.0 wt% rGO in the catalysts.

2.2. Catalyst characterization

The specific surface area (SSA), total pore volume and average pore diameter of the catalysts were obtained by BET method from an automatic surface analyzer (Autosorb-1-C-TCD, Quantachrome Instruments, USA). Prior to measurement, each sample was pre-treated at 200 °C for 3 h to degas. A JEM 2100F transmission electron microscope (TEM, JEOL Ltd.) with an accelerating voltage of 200 kV was used to characterize the morphology of the catalysts. For the TEM measurements, a drop of the particle solution was dispensed onto a 3-mm carbon-coated copper grid, and excessive solution was removed by an absorbent paper. The sample was then dried under vacuum at room temperature.

X-ray diffraction (XRD) patterns of the catalysts were measured on an X'Pert Pro system (PANalytical) using Cu Kα (λ = 1.54 Å) radiation with scan range from 10° to 90° (2θ). Crystal phases were identified using X'pert High Score software to refer the related peaks to the standard powder diffraction in the database. Surface species of the as-prepared catalysts were determined by X-ray photoelectron spectroscopy (XPS) using an ESCALab220i-XL electron spectrometer (VG Scienta, UK) and 300W Al Kα radiation. The base pressure during the measurements was approximately 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. H_2-temperature programmed reduction (H_2-TPR) was carried out in a U-shaped quartz reactor at a gas flow of 25 mL min^{-1} (10 vol% H_2 balanced with Ar) on a Chemisorb 2720 pulse chemisorption system (Micromeritics, USA). The catalyst (30 mg, 40–60 mesh) was heated to 750 °C from room temperature at a heating rate of 10 °C min^{-1}. Raman spectrum was obtained using a Raman spectrometer (LabRAM HR800, HORIBA JobinYvon, French) equipped with a microscope, edge filters and a Peltier-cooled CCD detector. The 514.53 nm Ar-Kr ion laser (Spectra-Physics, USA) was used as excitation source in the wavenumber range of 50–2500 cm^{-1}.

2.3. Catalytic activity measurements

Performance of the catalysts was evaluated in a fixed-bed quartz microreactor with inner diameter of 6 mm. Catalysts (100 mg, 40–60 mesh) were loaded in the quartz reactor and enclosed on both sides with silica wool. The continuous flow (100 mL min^{-1}) composed of synthetic air and 100 ppm gaseous benzene was feed into the reactor, corresponding to a weight hourly space velocity (WHSV) of 60,000 mL g$_{cat}$$^{-1}$ h^{-1}. The concentration of benzene in the effluent gas was analyzed by a gas chromatograph (GC-2014, Shimadzu, Japan) equipped with a frame ionization detector (FID). The conversion of benzene was calculated from the changes in benzene concentration between the inlet and the outlet gas. Temperature was precisely controlled by a k-type thermocouple in the vicinity of the catalyst bed.

3. Results and discussion

3.1. Specific surface area, composition and structure

The XRD patterns of the Pt/Al_2O_3 catalysts decorated with rGO are shown in Fig. S1 of Supplementary Material (SM). The Al_2O_3 support is confirmed to be a mixture of α-, θ-, and δ-Al_2O_3 [18]. The effect of rGO and Pt is negligible in the XRD patterns.

The order of SSA, as shown in Table 1, is 1.0%rGO/Al_2O_3 > Al_2O_3 > 1%Pt/Al_2O_3 and 1%Pt-1.0%rGO/Al_2O_3 > 1%Pt-0.6%rGO/Al_2O_3 > 1%Pt-0.1%rGO/Al_2O_3 > 1%Pt/Al_2O_3, respectively. Therefore, the low-density and high-surface-area of rGO are helpful for improving the SSA of the catalysts. After deposition of Pt nanoparticles (NPs), the SSA of Pt/Al_2O_3 decreases within a certain degree because the density of Pt is much higher than that of the Al_2O_3 support [19]. Moreover, the effect of rGO on the total pore volume is fewer than that of Pt NPs by comparing with 1.0%rGO/Al_2O_3, Al_2O_3 and 1%Pt/Al_2O_3 owing to the density. The average pore diameters of all the catalysts are from 9.66 to 10.30 nm, lower than that of Al_2O_3 (11.44 nm), suggesting that the Pt NPs and rGO enter the pores of Al_2O_3. The nitrogen adsorption–desorption isotherms and pore-size distributions of different catalysts are shown in SM Fig. S2. The content of Pt on catalysts is from 3.16 to 3.73 wt% determined by XPS, which is a surface testing technique, instead of the designed 1 wt%. This supports that the Pt NPs are almost deposited on the surface of Al_2O_3. The vast majority of the C content is caused by the adsorption of organic carbon. Typically, the TEM images for 1%Pt/Al_2O_3 and 1%Pt-1.0%rGO/Al_2O_3 samples were shown in Fig. 1, which indicate that the Pt NPs are uniformly distributed across the surface of the catalysts. The histograms resulting from counting 250 well-separated particles (Fig. 1C and D) depicts a narrow particle size distribution with a mean particle diameter of 5.9 nm (standard derivation of 0.39 nm) for Pt in 1%Pt/Al_2O_3 and 5.7 nm (standard derivation of 0.21 nm) for Pt in 1%Pt-1.0%rGO/Al_2O_3, respectively.

3.2. X-ray photoelectron spectra

The XPS analysis of the specific catalysts is performed to determine the state and percentage of chemical species, which is beneficial to deeply understand the relationship among the different species. The binding energies of Pt 4f, C 1s and O 1s of the catalysts are shown in Fig. 2 and summarized in Table 2.

In Fig. 2A, the spectrum indicated as an asymmetric broad peak could be resolved into three peaks with binding energies at 71.56 and 74.89 eV for metallic Pt, and at 74.22 eV for Al 2p of 1%Pt/Al_2O_3, while the binding energies for 1%Pt-1.0%rGO/Al_2O_3 turns into 71.12 and 74.45 eV for metallic Pt and 74.16 eV for Al [20]. The slight shift of the binding energies to a lower value (0.44 eV) might be an evidence to show that Pt is the electronic receptors [21,22].

The C 1s XPS spectrum of rGO (Fig. 2B) can be resolved into four peaks based on the oxidation degree corresponding to carbon atoms in different functional groups: 284.78 eV for carbon in C–C and C=C, 286.32 eV for carbon in C–O, 287.17 eV for carbonyl carbon (C=O), and 288.83 eV for carboxyl carbon (O–C=O) for the sample of