In situ thermolysis of Pt-carbonyl complex to form supported clean Pt nanoclusters with enhanced catalytic performance

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ABSTRACT Clean Pt nanoclusters with a diameter of 1.0–2.4 nm, supported on reduced graphene oxide (rGO) nanosheets, were successfully synthesized by simple *in situ* thermolysis of a Pt-carbonyl complex. The supported Pt nanoclusters are in an electron-deficient state because of the electron transfer between the nanoclusters and the rGO sheets. The as-prepared Pt-1 nm/rGO shows high catalytic activity for the 100% selective hydrogenation of nitrobenzene, with the turnover frequency (TOF) reaching 975.4 h⁻¹ at 25°C and 1 atm. This number is higher than the previously reported value for the heterogeneously catalyzed hydrogenation of nitrobenzene. The proposed process follows a direct hydrogenation mechanism, as is revealed by the analyses of the intermediate products. This work presents a facile and effective synthetic approach for achieving highly efficient nanocatalysts, and can be extended to obtain other metal catalysts with ultra-small sizes and excellent performance.

Keywords: hydrogenation, nanoclusters, reduced graphene oxide, platinum, catalyst

INTRODUCTION

Aniline (AN), an important chemical raw material, is mainly used in the organic chemicals industry, e.g., in the synthesis of resins, dyes, and pharmaceuticals. AN is typically prepared by the hydrogenation of nitrobenzene (NB) in the liquid or vapor phase, and the latter is usually performed at 473 K over copper-based catalysts [1], which often suffers from low selectivity and poison resistance [2]. Noble metal (such as Pd, Pt, Ru) catalysts have been developed and demonstrated to show good performance in the hydrogenation of NB in the liquid-phase [3–6]. In such

systems, harsh reaction conditions, e.g., higher system temperature and pressure are commonly required [7–11]. Other issues associated with the toxic organic solvents and poor selectivity of the catalyst also exist. Furthermore, undesirable by-products, such as nitrosobenzene (NSB), *N*-phenylhydroxylamine (PHA) and azoxybenzene (AOB) are inevitably produced [12,13]. Therefore, it is highly desirable to develop green catalysts that simultaneously possess high activity and selectivity at room temperature and atmospheric pressure.

Carbon materials, particularly graphene and carbon nanotubes, which have the same sp² hybridization state, are promising candidates for the development of high-performance catalysts because of their unique structures with a large specific surface area [14–18]. Liu and co-workers [19] prepared Pt NPs supported on multiwall carbon nanotubes (MWCNTs), which exhibited excellent activity for the solvent-free hydrogenation of NB to AN at a pressure of 2.0 MPa. Nie *et al.* [20] used Pt/reduced graphene oxide (rGO) nanocomposites as the catalysts for the hydrogenation of nitroarenes, which showed higher catalytic activity than Pt/CNTs at 1.0 MPa. Nevertheless, these catalytic systems are not efficient enough and require harsh conditions.

Pt nanoparticles (NPs) are known to be effective and environmentally friendly catalysts, and have attracted tremendous attention in the past few decades. They are frequently employed to catalyze a wide range of oxidation and hydrogenation reactions [21–24]. Unfortunately, the low abundance of platinum in nature and high cost restricts its widespread application. A significant enhancement in

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the catalytic efficiency and recycle durability of platinum is of paramount importance in reducing its use. Nanoclusters with a high volume/surface ratio and quantum effect have been proven to be efficient catalysts in various useful reactions. To date, several synthetic approaches have been developed to fabricate these small nanoparticles, including solution-phase reduction, gas-phase synthesis, and the ligand-assisted approach [25–29]. However, the fabrication of small nanoparticles is still challenging because of their severe aggregation, wide size distribution, low output, and low activity. Furthermore, these methods involve poor control of the particle size distribution.

In this work, we presented a detailed study on *in situ* formed Pt nanoclusters on rGO by thermally decarbonylating their carbonyl compounds. The sizes of the Pt nanoclusters can be easily controlled by fine tuning the reaction conditions. The effect of the cluster size on the catalytic performance for NB hydrogenation was systematically investigated. The results indicated that the Pt-1 nm/rGO nanocatalysts exhibited the highest catalytic performance, including a high conversion ratio, excellent selectivity, and good durability under ambient conditions (25°C, 1 atm).

EXPERIMENTAL SECTION

Materials

$\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was purchased from Shanghai Aladdin Chemistry Co. Ltd, China. CH_3COONa , graphite powder, H_2O_2 , and H_2SO_4 were purchased from the Sinopharm Chemical Reagent Co. Ltd. Methanol and isopropanol were purchased from Xilong Chemical Co. Ltd. CO and N_2 were purchased from Qingdao Tianyuan Gas Co. Ltd., and KMnO_4 was obtained from Beijing Chemical Reagent. All the reagents were analytical grade and used as received.

Preparation of graphene oxide

Graphene oxide (GO) was synthesized via a modified Hummer's method [30]. In a typical procedure, graphite (1 g) and concentrated sulfuric acid (23 mL) were mixed in a 250-mL round-bottom flask, placed in an ice-water bath, and stirred for 15 min. Then, KMnO_4 (3 g) was slowly added into the suspension and stirred for 1 h. The flask was transferred into an oil bath at 35°C and stirring was continued for an additional 30 min, then 46 mL deionized water was added slowly. The solution was incubated at 98°C for 15 min. Once the reaction was completed, 140 mL of deionized water and H_2O_2 (10 mL, 30%) were added to remove the excess KMnO_4 and stirred for 40 min. Finally, the resulting suspension was filtered and washed with 5% HCl aqueous solution and H_2O_2 until the solution pH was ~7.

Finally, the GO solution was lyophilized and GO powder was obtained.

Preparation of Pt-carbonyl complex/GO

Briefly, 0.0372 g of $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (3.8 mmol), 0.0728 g (27.9 mmol) of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, and 10 mL of methanol were sequentially added to a 50-mL three-neck flask. The flask was purged with highly pure nitrogen for 30 min. Thereafter, the system was placed in a CO atmosphere, and the temperature was raised to 40°C. After reaction for 24 h, the solution turned chartreuse in color. Then, the desired amount of GO was added and the mixture was stirred for an additional 12 h.

Preparation of Pt/rGO nanocatalysts of different sizes

Pt clusters with controlled sizes loaded on rGO were prepared by removing the carbonyl group of the Pt-carbonyl complex over the temperature range of 150–200°C at different reaction times under a gentle flow of nitrogen gas. For example, Pt-1.0 nm/rGO could be prepared by decarbonylating at 150°C for 1 h; Pt-1.4 nm/rGO was obtained at 2 h; Pt-1.7 nm/rGO was prepared after reaction at 200°C for 2 h; and Pt-2.4 nm/rGO was obtained at 4 h. Finally, the as-prepared catalysts were separated by filtration and washed with ethanol and deionized water until no Cl^- ions could be detected.

Characterization

The crystalline phase of the as-prepared samples was characterized by powder X-ray diffraction (XRD) using a Philips X' Pert diffractometer with Cu-K α radiation ($\lambda = 0.15418$ nm). The chemical state and composition of the products were analyzed using X-ray photoelectron spectroscopy (XPS, ESCALab250). Transmission electron microscopy (TEM) was performed using a JEM2100UHR transmission microscope equipped with an energy dispersive spectroscopy (EDS) detector (EDAX, JEOL, Japan). Infrared spectra were obtained using an IR spectrometer (Thermo-Nicole, NEXUS, USA). Raman spectra were recorded on a Raman spectrometer (DXR Microscope). Gas chromatography (GC) analysis was performed using an Agilent 3420A GC equipped with a KB-5 column and an FID detector.

Catalytic performance evaluation

In a typical procedure, 1.0 mmol of the NB was dissolved in 6 mL of isopropanol and mixed with 1.0 mg of the as-prepared nanocatalysts under 1 atm H_2 at 25°C. The reaction mixture was stirred at 900 rpm at room temperature. After the reaction was complete, the mixture was separated

by centrifugation, and the products were examined by gas chromatography (SP-3420A) with a 30 m capillary column (KB-5) using a flame ionization detector. The used catalysts were washed with isopropanol and collected at room temperature for performing the subsequent reactions.

RESULTS AND DISCUSSION

TEM images of Pt-1.0 nm/rGO with a loading of 40 wt.% Pt are shown in Fig. 1. The actual loading of Pt was determined by inductively coupled plasma mass spectrometry to be 39.1 wt.%. The images clearly illustrate that the Pt clusters are homogeneously dispersed on the surface of the rGO sheets and have an average size of 1.0 nm with a narrow size distribution (Fig. 1a). The results indicate that rGO acts as an efficient support for the dispersion of uniform-sized Pt nanoclusters. The selected area electron diffraction (SAED) pattern in the inset of Fig. 1a further confirms the polycrystalline nature of Pt. Fig. 1b displays the HRTEM image of the Pt clusters dispersed on the rGO. The *d*-spacing of ~0.226 nm corresponds to the (111) plane of the face-centered cubic Pt, indicating that the clusters are

well crystallized. High-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) imaging and the corresponding EDS mapping in Fig. 1c–e further show the good dispersion of Pt at a high loading on the rGO surface and the homogeneous distribution of elemental Pt and C. The formation process of Pt clusters is proposed as follows. The precursor $[\text{Pt}_3(\text{CO})_6]_5^{2-}$ (Fig. S1) clusters possess a trigonal prism framework at low temperature [31]. Increasing the temperature, the compound clusters begin to convert to a larger cluster bounded by linear C=O groups. The resulting carbonyl groups can be further desorbed by evacuation at 150°C, leading to the formation of Pt nanoclusters. Furthermore, as shown in Fig. S2, all the absorption bands of Pt/rGO belong to rGO, revealing a clean surface of the nanoclusters. XRD was used to examine the crystalline structure of GO and Pt/rGO (Fig. S3). It is noted that a sharp diffraction peak appears at 10.8° for pure GO, which is ascribed to the (002) plane of the graphene sheets of a few layers. After the formation of supported nanocatalysts, a new diffraction peak appeared at about 25°, implying the existence of stacking structures of

Figure 1 TEM image (a) and corresponding HRTEM image (b) of the Pt-1.0 nm/rGO nanocatalysts with 40 wt.% of Pt. The insets in (a) show the Pt particle size distribution and the SAED pattern. (c–e) HAADF-STEM image and the corresponding EDS mapping of C and Pt.

rGO [32]. Two characteristic diffraction peaks of (111) and (200) (JCPDS card 01-087-0642) are very broad, implying very small sizes of the sample.

Fig. 2 shows the representative TEM images and the corresponding particle size distributions of the Pt/rGO catalysts. Highly dispersed Pt nanoclusters smaller than 3 nm were observed. The particle sizes seem uniform, and large particles are seldom detected. Statistical analysis of the particle size was performed by measuring ~100 Pt nanoparticles, which yielded the histograms shown in Fig. 2b, d, f. It can be seen that the average size of the Pt nanoparticles is in the range of 1.4–2.4 nm at a temperature of 150–200°C after different reaction times. The higher the

temperature and the longer the reaction time, the larger is the size of the obtained Pt nanoparticles. In addition, the size of the Pt nanoparticles on carbon supports is often related to the loading; that is, a higher loading usually results in the formation of larger Pt particles. In the case of Pt/rGO with different sizes, the size of the Pt nanoparticles remains small despite the higher loading, which can be attributed to the strong anchoring effect of the oxygen-containing functional groups of the rGO.

The chemical composition and oxidation state of the as-prepared Pt-1 nm/rGO samples were identified by XPS (Fig. 3). The survey spectrum (Fig. 3a) shows the presence of carbon, oxygen, and platinum elements in the sample.

Figure 2 TEM images and size distributions of Pt/rGO obtained under different conditions: (a, b) Pt-1.4 nm/rGO with 40 wt.% of Pt; (c, d) Pt-1.7 nm/rGO with 40 wt.% of Pt; (e, f) Pt-2.4 nm/rGO with 40 wt.% of Pt.

Figure 3 XPS of Pt-1 nm/rGO: (a) survey spectrum, (b) C 1s region, (c) Pt 4f region for Pt-1 nm/rGO. (d) Raman spectra of GO (1) and Pt-1 nm/rGO (2).

Fig. 3b shows the high-resolution spectrum of C 1s, where four different carbon bonding states can be observed. The peak at 284.6 eV was ascribed to the C–C bond, whereas the signals at ~286.4, 287.8, and 289.0 eV were attributed to the C–OH, C=O, and O–C=O configurations, respectively [33]. Compared to the typical high-level oxidation state in GO, the product exhibited a sharp decrease in intensity, showing a significant loss of oxygen after thermal treatment. Fig. 3c shows the core-level XPS spectra of the Pt 4f region of the Pt/rGO catalysts. The binding energy of the Pt 4f_{7/2} is 71.9 eV, with a shift of 1.2 eV as compared to the binding energy of the standard metallic state (70.7 eV) [34]. The peaks at 72.6 (Pt 4f_{7/2}) and 76.0 eV (Pt 4f_{5/2}) can be assigned to Pt²⁺, owing to the oxygen linkages between the interfaces of the Pt clusters and the rGO, and the formation of oxide layers on the Pt surface. The shift suggests that the electron transfer may occur between the Pt nanoclusters and the oxygen of rGO. The high electronegativity of oxygen reduces the electron density of the Pt atoms and leads to electron-deficient states of the Pt nanoparticles in the Pt/rGO catalyst. For the Pt/rGO catalyst, about 88.5% of the Pt exists in the metallic state and 11.5% exists as Pt–O–C.

In order to understand the conformational changes of carbon during the reaction, Raman spectra of GO and Pt/rGO catalysts were obtained (Fig. 3d). The D band at ~1350 cm⁻¹ for GO and rGO is attributed to the disorder induced features caused by lattice defects. The G band at ~1587 cm⁻¹ represents the in-plane vibration of symmetric sp² C–C bonds [35]. Compared to the case of GO, the D/G intensity ratio (I_D/I_G) in the Pt/rGO composites shows a slight increase (0.90 vs. 0.99), which is indicative of a decrease in the average size of the sp² domains [36]. The results confirm the reduction of GO by removing the carbonyl groups.

The catalytic performance of the obtained supported Pt nanoclusters was evaluated by the selective hydrogenation of NB at 25°C under 1 atm H₂. The results show nearly 100% yield of AN for the Pt/rGO nanocatalysts. To demonstrate the impact of the supports, the Pt-free rGO and pure Pt NPs (1 mg) were separately used to catalyze this reaction within 2 h. The yield of AN was 0% and 8.18%, respectively (Fig. 4a), demonstrating that the supports play an essential role in boosting the catalytic performance. Then, the Pt-1.0 nm/rGO nanocatalysts with different loadings were used to catalyze the reaction. With the increased quantity of Pt, the

Figure 4 (a) Catalytic performance comparison of NB hydrogenation over the different catalysts in 2 h. (b) Catalytic performance comparison over Pt-1.0 nm/rGO nanocatalysts with different Pt loadings in 2 h.

conversion and selectivity of hydrogenation of NB also increased. The catalyst with 40 wt.% Pt exhibits the best performance, associated with the complete conversion of NB and 100% selectivity of AN within 2 h (Fig. 4b).

We also investigated the influence of the Pt cluster size on the catalytic activity. Fig. 5 shows a comparison of the hydrogenation conversion of NB catalyzed by Pt/rGO nanocatalysts with 40 wt.% Pt and different Pt cluster sizes. It was observed that Pt-1 nm/rGO achieved a 100% conversion ratio of NB to AN in 30 min together with a selectivity of 100%. The turnover frequency (TOF) of Pt-1 nm/rGO (TOF: mol number of NB transformed per mol per h) reaches 975.4 h^{-1} . This value is higher than the previously reported data for heterogeneously catalyzed dehydrogenation of NB [8,37,38]. The conversion ratio is 81.55%, 36.85%, and 4.92% over Pt-1.4 nm/rGO, Pt-1.7 nm/rGO, and Pt-2.4 nm/rGO within the same reaction period, respectively; the corresponding TOFs are 796.5, 359.4, and 4.8 h^{-1} . The conversion ratio on the Pt-1 nm/rGO sample is approximately 3 times higher than that on the Pt-1.7 nm/rGO, and over hundred fold higher than that on Pt-2.4

Figure 5 Conversion of NB during hydrogenation reactions (a) and the corresponding catalytic activity catalyzed by Pt/rGO nanocatalysts with 40 wt.% Pt and different Pt cluster sizes in 2 h (b). (1) Pt-1 nm/rGO, (2) Pt-1.4 nm/rGO, (3) Pt-1.7 nm/rGO, (4) Pt-2.4 nm/rGO.

nm/rGO. Even after the reaction was continued for 2 h, the yield of AN was only 82.2% and 12.0% over Pt-1.7 nm/rGO and Pt-2.4 nm/rGO, respectively. Apparently, the Pt cluster size has a strong influence on its catalytic activity for the hydrogenation of NB, which is in accordance with previous reports [39].

The enhancement in the NB hydrogenation can be summarized as three advantages of Pt/rGO: (1) the high dispersion of small Pt nanoclusters on the surface of rGO could provide rich active sites for the hydrogenation reaction, which not only improves the adsorption probability of the reactant molecules but also shortens the residence time of the reaction species, thus preventing over-hydrogenation [40]. (2) The Pt nanoclusters in the Pt/rGO catalysts provide an electron-deficient state, which is favorable for the adsorption of H_2 [41]. As a result, more hydride ions are produced and the catalytic performance of the Pt/rGO catalysts is enhanced. (3) The supported Pt nanoclusters were very “clean” because of the surfactant-free formation process (Fig. S2), allowing high catalytic activity in NB hydrogenation.

In order to ascertain the catalytic reaction pathway, we analyzed the products obtained at different times. Fig. 6a shows the products of NB hydrogenation over the Pt-1 nm/rGO nanocatalyst as the reaction proceeded. The results show that the intermediates only consist of NSB and PHA, and no other products are detected in the measurable range. The possible mechanism for AN formation from NB is shown in Fig. 6b [42]. One route for AN production is that the NB is transformed into NSB and PHA successively in the hydrogen atmosphere, whose hydrogenation results in the formation of AN. The other route directly reduces NB to PHA without the production of intermediates. Owing to the rapid transformation of NB to AN, and the relatively strong adsorption of NSB and PHA onto the surface of Pt/rGO, it is reasonable that the recombination of NSB and PHA over the catalysts was restrained, inhibiting the production of azoxybenzene or hydrazobenzene [43]. In addition, it is interesting that the concentration of NSB is higher than that of PHA in the reaction process, which also confirms the direct hydrogenation pathway.

Figure 6 (a) Reaction product profile of the NB hydrogenation over Pt-1 nm/rGO catalysts under mild conditions; (b) proposed reaction pathway for the hydrogenation of NB over Pt/rGO catalysts.

Figure 7 (a) Stability tests of the Pt-1 nm/rGO catalysts for hydrogenation of NB; (b, c) XRD and TEM image of the collected Pt-1 nm/rGO nanocatalysts after 6 cycles.

For practical applications, the stability of a catalyst is also very important. A series of hydrogenation reactions with the recovered catalysts were performed. After the catalytic reaction was complete, the catalysts were collected by centrifugation and reused in the subsequent reactions. Because of the inevitable catalyst loss in the collection process, six cycles were performed. The results indicated that the conversion of NB remains at 92% even after six cycles (Fig. 7). Moreover, the morphology and microstructure of the used catalysts did not change significantly (Fig. 7b, c), implying its high stability.

CONCLUSIONS

In conclusion, a simple method was developed to prepare supported Pt nanoclusters with controlled sizes by thermal decomposition of the Pt carbonyl anions. The factors that affect the performance, such as dispersion and size of Pt clusters, were studied in detail for the catalytic hydrogenation of NB at room temperature under atmospheric conditions. The results indicate that 1 nm Pt clusters dispersed on the rGO exhibit the highest activity. It only takes 30 min to achieve 100% conversion and selectivity, and the TOF with respect to NB conversion is as high as 975.4 h^{-1} . The origin of the high activity could be attributed to the synergistic effect of Pt clusters and rGO. Besides the support effect, the ultra-small size and the clean surface of the Pt clusters also contributed to the activity. The intermediate product analyses suggest the reaction pathway for the conversion of NB to AN follows a direct conversion route. It is expected that the specific synthetic approach can provide a promising avenue for the preparation of other metal-based heterogeneous nanocatalysts with unique sizes and excellent performance.

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原位热解羰基铂制备性能优越的负载型铂纳米团簇

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摘要 本文以羰基铂为前驱体,采用简便的原位热解方法,成功地合成了负载在还原氧化石墨烯(rGO)纳米片上的直径为1.0–2.4 nm的清洁Pt纳米团簇. 由于Pt纳米团簇和rGO片之间的电子转移,所制备的负载Pt纳米团簇处于缺电子状态. 在25°C、1 atm下,制备的Pt纳米团簇-1 nm/rGO催化剂的硝基苯选择性加氢的转换频率(TOF)达到975.4 h⁻¹. 这个数值是目前硝基苯的非均相催化氢化所报道的活性最高值. 此外,根据中间产物分析,Pt-1 nm/rGO催化硝基苯加氢的机理是直接氢化. 这项工作在构筑高效催化剂方面提供了一个简单有效的途径,并且可以进一步扩展制备其他具有超小尺寸和卓越性能的金属催化剂.