**Palladium nanoparticles deposited on silanized halloysite nanotubes: synthesis, characterization and enhanced catalytic property**

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Palladium (Pd) nanoparticles were deposited on the surface of halloysite nanotubes (HNTs) modified with \( \gamma \)-aminopropyltriethoxysilane (APTES) to produce Pd/NH\(_2\)-HNTs nanocomposites. The results indicated that Pd nanoparticles were densely immobilized onto NH\(_2\)-HNTs with an average diameter of \( \approx 3 \) nm. The Pd distribution on the surface of silanized HNTs showed much more uniform, and the Pd nanoparticle size became smaller compared with those directly deposited onto HNTs without silanization. Systematic characterization demonstrated that APTES were chemically bonded onto HNTs, and further confirmed the bond formation between Pd and \(-\text{NH}_2\) groups, which could ensure the firm deposit of Pd nanoparticles on the surface of silanized HNTs. The as-synthesized Pd/NH\(_2\)-HNTs exhibited an excellent catalytic activity in the liquid-phase hydrogenation of styrene to ethylbenzene with full conversion within 30 min. The mechanism of the deposit of Pd nanoparticles on silanized HNTs was also investigated.

Precious metals nanoparticles on catalyst supports have attracted considerable interest because they have been used in a number of catalysis applications, including transformation of organic\(^1\)–\(^5\) and fuel cells\(^6\)–\(^11\). Reports indicate that Pd nanoparticles are densely immobilized onto NH\(_2\)-HNTs with an average diameter of \( \approx 3 \) nm. The Pd distribution on the surface of silanized HNTs showed much more uniform, and the Pd nanoparticle size became smaller compared with those directly deposited onto HNTs without silanization. Systematic characterization demonstrated that APTES were chemically bonded onto HNTs, and further confirmed the bond formation between Pd and \(-\text{NH}_2\) groups, which could ensure the firm deposit of Pd nanoparticles on the surface of silanized HNTs. The as-synthesized Pd/NH\(_2\)-HNTs exhibited an excellent catalytic activity in the liquid-phase hydrogenation of styrene to ethylbenzene with full conversion within 30 min. The mechanism of the deposit of Pd nanoparticles on silanized HNTs was also investigated.
NH₂-HNTs nanocomposites doesn’t affect the structure of HNTs. Full range XPS spectra of samples are exhibited in Figure S1, the semiquantitative analysis of the relative atomic concentration of different elements are shown in Table S1. Si and Al are detected in both types of samples, and the concentration ratio of Si/Al is 1.46 in NH₂-HNTs, significantly higher than the value of 1.14 in HNTs, which confirms that the silane coupling agent is present in NH₂-HNTs. The Si in NH₂-HNTs partly comes from the APTES. Compared with HNTs, N 1s signal is detected in NH₂-HNTs, but the peak is not obvious especially for the sample with low APTES concentration. Those results indicate that the N species are belonging to APTES. For the Pd/NH₂-HNTs sample, a weak peak observed at 403 cm⁻¹, corresponding to (111) diffraction of palladium. Those results indicate that palladium salts have been reduced to metallic Pd, which is deposited on NH₂-HNTs as nanoparticles. The characteristic peak of palladium in Pd/NH₂-HNTs with high APTES concentration is not obvious (Figure S2), which should be due to only a partial reduction of Pd(II) to Pd(0). The crystal size of the Pd nanoparticles in Pd/NH₂-HNTs sample calculated by the Scherrer’s equation is 3 nm.

The FTIR spectra of HNTs, NH₂-HNTs and Pd/NH₂-HNTs are shown in Figure 1b. For HNTs, the peak at 3698 cm⁻¹ can be assigned to the O-H stretching vibration of the inner-surface Al-OH groups. The peak at 3622 cm⁻¹ can be ascribed to the O-H stretching vibration of the inner Al-OH groups (between the interface of the Si-O tetrahedron and the Al-O octahedron). The broad band between 1633 and 3448 cm⁻¹ arises from adsorbed water. The peak at 1037 cm⁻¹ corresponds to the in-plane stretching vibration of the Si-O network (Si-O-Si and O-Si-O). The peak at 912 cm⁻¹ is attributed to the O-H deformation vibration of inner Al-OH groups. The deformation vibration of Al-O-Si at 553 cm⁻¹ is attributed to Al-O tetrahedral sheets. The Si-O-Si deformation vibration observed at 471 cm⁻¹ is attributed to Si-O tetrahedral sheets.

After the functionalization of HNTs by APTES, the broad band at 3360 cm⁻¹ is attributed to the N-H₂ asymmetric stretching vibration. The peak at 2930 cm⁻¹ is assigned to the symmetric stretching vibration of C-H₂. The peak at 1304 cm⁻¹ shift to 1240 cm⁻¹ and 1296 cm⁻¹, respectively. These shifts of peaks in the Pd/NH₂-HNTs are associated with the formation of bonds between PVP-Pd and NH₂-HNTs.

TEM images of HNTs and Pd/NH₂-HNTs are presented in Figure 2. The white HNTs are short cylindrical hollow tubes averaging 0.7–1.5 μm in length, with an external diameter of 50–75 nm and an internal diameter of 10–30 nm (Figure 2a). After assembly with Pd nanoparticles, the characteristic tube morphology of the original minerals have been retained (Figure 2b). According to the additional EDS spectra (Figure S5a, inset), compared to those deposited on HNTs without silanization (1.0 wt.%, Figure S5c,d), more Pd nanoparticles (11.3 wt.%) are densely dispersed on the external and internal surfaces of the NH₂-HNTs (Figure S5b, Figure 2c), attributed to amino groups on the surface of NH₂-HNTs catching the metal colloidal more easily through coordinate bond, which is beneficial to the enhanced catalytic activity of Pd/NH₂-HNTs. The size of Pd nanoparticle is observed as ~ 3 nm.
(Figure 2d), which shows very nice consistency with the particle size estimated by XRD.

Figure 3a shows the $^{29}\text{Si}$ CP/MAS NMR spectra of HNTs, NH$_2$-HNTs and Pd/NH$_2$-HNTs. The spectrum of HNTs indicates an obvious peak at $-92$ ppm, assigned to the Si(O$\text{Si}$)$_3$(O$\text{Al}$) of halloysite. The spectrum of NH$_2$-HNTs and Pd/NH$_2$-HNTs displays two more resonance peaks at $-65$ ppm corresponding to tridentate, and at $-57$ ppm, attributed to bidentate. The tridentate form of Si implies that all three of the ethoxyl groups of APTES are hydrolyzed and condensed with surface hydroxyl groups of halloysite or with other hydrolyzed APTES. Observation of the bidentate form of Si means that some APTES species possess one ethoxyl (or hydroxyl) group that did not hydrolyze or condense.

Figure 3b shows the $^{13}\text{C}$ CP/MAS NMR spectra of HNTs, NH$_2$-HNTs and Pd/NH$_2$-HNTs. For HNTs, no signals are resolved by Gaussian deconvolution. For the spectra of NH$_2$-HNTs and Pd/NH$_2$-HNTs, the signal at 12.8 ppm is assigned to the carbon atoms at position Si-C in ethoxyl groups. The signal at 28.1 ppm is attributed to the carbon atoms at position C-C in the propyl groups, the intensities of corresponding signals become increased as the APTES concentration increased (Figure S6).

Figure 3c shows the Pd 3d spectra and their peak positions from the sample. Pd/NH$_2$-HNTs has photoelectron peaks corresponding to both Pd(0) and Pd(II) species. The Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ electronic states for Pd(0) are observed at 335.3 and 340.6 eV, respectively. Peaks are also detected at 337.0 and 342.3 eV, corresponding to the 3d$_{5/2}$ and 3d$_{3/2}$ electronic states, of Pd(II) species, respectively, which suggests that the reduction process led to only a partial reduction of Pd(II) to Pd(0) for Pd/NH$_2$-HNTs. As in this investigation, the atomic concentration of Pd 3d increases with increasing the atomic concentration of the N 1s (Table S1), which could be related to APTES-Pd(II) or APTES-Pd(0) complex. Figure S7a shows that Pd$^{2+}$ is not reduced until the hydrazine hydrate is added. Based on the peak integration (Figure S7b), the proportion of Pd(0)/(Pd(0) + Pd(II)) in Pd/NH$_2$-HNTs with high APTES concentration is 23.5%, lower than the Pd/NH$_2$-HNTs with low APTES concentration (31.2%), indicating that the coordination between Pd(II) and APTES makes Pd(II) difficult to be reduced.

The catalytic properties of the HNTs, Pd/HNTs and Pd/NH$_2$-HNTs are tested in the hydrogenation of styrene to ethylbenzene in an autoclave, as shown in Figure 4. It can be seen that the hydrogenation rate of Pd/NH$_2$-HNTs is higher than that of Pd/HNTs under the same reaction conditions. Correlation of the catalytic activities of the Pd nanoparticles with their distribution indicates that a higher loading content and dispersion led to higher catalytic activity (Figure S8). Our experimental findings suggest that the surface property of the NH$_2$-HNTs is beneficial to improving the dispersion and loading content, leading to a higher catalytic activity.
Discussion

The present process is schematically illustrated in Figure 5. Firstly, the surface of HNTs is functionalized with -NH₂ by APTES. The functionalized HNTs possess a large number of -NH₂ groups with positive charge, and can catch the PVP-Pd²⁺ colloidal with negative charge through coordinate bonds. Due to the bond formation between PVP-Pd²⁺ and -NH₂ groups, most of the PVP-Pd²⁺ are combined with the -NH₂ groups. Then, the addition of hydrazine hydrate could result in the formation of Pd-NH₂ complexes; meanwhile the Pd ions are reduced by hydrazine hydrate. The bond formation between Pd and -NH₂ groups could be testified.

The peak fitting program on XPS spectra of Al 2p and Si 2p is performed to detect the possible interaction between functional APTES and HNTs. The XPS spectra, together with their fitting curves, are showed in Figure 6. The content of aluminol (Al-OH) at 74.8 eV on HNTs inner surface is quite low and the aluminumoxgen (Al-O) bond is dominant in the existing forms of Al atoms. The binding energy (BE) value of Si 2p in silanol (Si-OH) is at 103.3 eV. The content of Si-OH, located at the outer side of HNTs lumens, is lower than that of siliconeoxygen (Si-O) bond (102.7 eV). When HNTs is treated with APTES, the XPS spectra of Al 2p show that the BE value of Al atom in Al-O and Al-OH are shifted to 74.6 and
75.1 eV, respectively. According to the spectra of Si 2p, the BE value of Si in Si-OH partially moves to 103.4 eV. The other part of Si-O presents at 104.9 eV. This is possibly responsible for the obvious BE shifts (Figure S9). After NH2-HNTs as being assembled by PVP-Pd, the XPS spectra of Al 2p show that the BE value of Al atom in Al-O and Al-OH is shifted to 74.4 and 74.9 eV, respectively. According to the spectra of Si 2p, the BE value of Si in Si-OH partially shifted to lower binding energies with a higher value for the full width at a half-maximum (FWHM). The BE value of Si in Si-O moves to 103.1 eV. The obviously changed BE values for Al and Si atoms may be related to coupling reaction between ethoxy groups in APTES and hydroxyls (Al-OH and Si-OH) on HNTs. The covalently bonding between APTES and HNTs is possibly responsible for the obvious BE shifts (Figure S9).

To prove that the APTES were chemically bonded onto HNTs, the O 1s spectra of the HNTs and NH2-HNTs are presented in Figure 6c. As observed in Figure 6c, the intense characteristic peak that emerged at 532.0 eV corresponds well with O 1s of HNTs binding between the Pd and -NH2 groups, and the functional groups can successfully grafted on the HNTs. To further confirm the Pd nanoparticles deposited on NH2-HNTs show a higher activity in comparison to those deposited on HNTs without silanization. Moreover, the Pd nanoparticles deposited on NH2-HNTs showed a higher activity in the liquid-phase hydrogenation of styrene to ethylbenzene.

Methods

Material preparation. Halloysite nanotubes (HNTs) were obtained from Hunan, China. All chemicals were analytical grade and used without further purification. HNTs were pretreated via emulsion dispersion, filtering, washing with distilled water, and drying for 8 h at 313 K. (1) PVP-PdCl2 was prepared as follows: 18 mg of sodium tetrachloro palladate (Na2PdCl4) was dissolved in 50 mL of methanol containing 19 mg of poly (vinyl pyrrolidone) (PVP). The solution was refluxed for 2 h until a yellowish-brown color was observed. The solution was stored in a dark bottle at 4°C for further use. (2) NH2-HNTs nanocomposites were synthesized as follows: 4 mL of APTES was dissolved in 250 mL of dry toluene. Approximately 5 g of clay powder was added, and the suspension was dispersed ultrasonically for 30 min. Evacuation pretreatment may be carried out at this stage. The suspension was then refluxed at 120°C for 20 h under constant stirring. In the refluxing system, a calcium chloride drying tube was attached to the end to ensure a dry environment. The solid phase in the resultant mixture was filtered and extensively washed six times with fresh toluene to remove the excess organosilane, then dried overnight at 120°C for further curing. (3) PVP-Pd/NH2-HNTs nanocomposites were synthesized as follows: 0.3 g PdCl2·nH2O. NH2-HNTs sample was kept in 150 mL PVP-PdCl2 solution for 12 h and was then refluxed thoroughly with distilled water and dried at room temperature. After impregnation, the color of the sample changed from white to yellow-brown. Finally, the sample was reduced by 60 mL of a 0.15 M alkaline solution (pH = 9.5) of hydrazine hydrate (N2H4·H2O), the color of the sample changed from yellowish-brown to dark-brown, suggesting the formation of metallic palladium nanoparticles on the surface.

Characterization. The crystalline phases were identified by XRD analysis using a Rigaku D/max-2500VB + 18-kW powder diffractometer with Cu Kα radiation (λ = 1.5418 Å). The data were collected in the scanning range 20 = 10–80°, with a scanning speed of 2°/min. FTIR spectra were recorded using a Nicolet 5700 spectrophotometer. TEM images were obtained using a JEOL JEM-200CX instrument equipped with an energy dispersive X-ray spectroscopy (EDS) at an accelerating voltage of 200 kV. Solid state 29Si MAS NMR measurements were recorded using a Bruker AMX400 spectrometer in a static magnetic field of 9.4 T at a resonance frequency of 79.49 MHz. X-ray photoelectron spectroscopy (XPS) analysis was performed on Thermo-Fisher Scientific K-alpha 1063 spectrometer equipped with an Al Kα monochromator X-ray source. The test chamber pressure was maintained below 10−5 mbar during spectral acquisition. The XPS binding energy (BE) was internally referenced to the C 1s peak (BE = 284.1 eV). The catalytic hydrogenation of styrene to ethylbenzene (Figure S10) was carried out in a 300 mL stainless steel autoclave equipped with a magnetically driven impeller. For each experiment, 1 mL of styrene dissolved in 200 mL of ethanol was first charged into the autoclave reactor. Once the Pd/NH2-HNTs were mixed inside the autoclave, hydrogen was introduced into the reactor to a set level, and the stirring rate was maintained at 60 rpm.

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Author contributions
H.M.Y. conceived the project and wrote the final paper. Y.Z. wrote initial drafts of the work. Y.Z. designed the experiments, synthesized and characterized the materials. X.H., Y.Z. and J.O.Y. analyzed the XPS spectra. All authors discussed the results and commented on the manuscript.

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