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COMMNUICATION

Pd/CNT-SiC monolith as a robust catalyst for Suzuki coupling reaction

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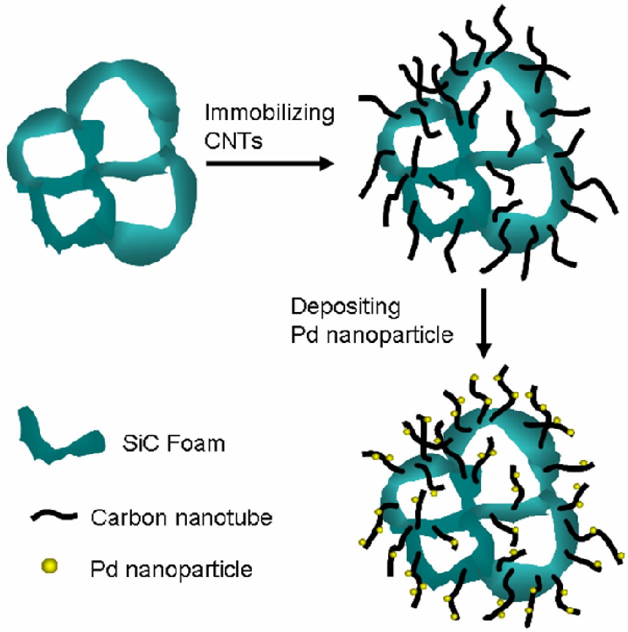
A novel Pd/CNT-SiC monolith catalyst has been prepared by a simple two-step approach. The as-synthesized Pd/CNT-SiC monolith afforded high activity and stability for the suzuki coupling reactions. In particular, it can be easily separated from reaction mixtures, showing its potential application in liquid phase reaction.

Palladium (Pd) catalyst have been used in chemical industry due to their unique physical and chemical properties.[1-3] However, Pd nanoparticles can easily aggregate limiting their applications.[4] Considerable efforts have been made to overcome this issue by depositing Pd nanoparticles on various solid supports, such as silica, zeolite, alumina, metal oxide, carbon, polymer and some composite materials.[5-12] Among the solid supports, active carbon (AC) is usually used owing to its high specific surface area and strong resistance to acid. Unfortunately, the presence of high microporosity in AC hampers the diffusion of reactants. And AC has low mechanical strength and contains impurity resulting in the risk of its stability.[13] Recently, carbon nanotubes (CNTs) have displayed potential application as catalyst support, in virtue of their large surface area, strong metal-support interactions and no microporosity, which can benefit for the mass transfer and catalytic activity in liquid phase reaction.[14-15] Up to now, commercial CNTs have been prepared in the form of fine powder by chemical vapor deposition (CVD) methods.[16-17] However, the CNT powder is easily aggregated and difficult to be separated from the liquid reaction mixtures. Therefore, it is desirable to design CNTs into larger objects. Compressing CNT powder into pellets with various sizes and strength is difficult to be carried out in industrial scale. Besides, the compaction of CNTs may destroy their intrinsical structure. Growing CNTs or CNFs on structured supports (such as cordierite,[18] commerical SiO_2 spheres,[19] Ni foam,[20] carbon aerogel[21]) as monoliths can provide a more practical route to address these problems, and the monolithic materials supported nanoparticles catalyst would be easily separated and reused in catalytic reactions. Among the structured supports, silicon carbide (SiC) with high mechanical strength, good thermal conductivity and chemical inertness, has been an attractive candidate in recent researches. For example, zeolite coated on the SiC support working as a monolith shows high activity and stable ability in benzoylation reaction in liquid phase.[22] SiC foam coated with nitrogen-doped CNTs exhibit high activities of selective oxidation of H_2S.[23] A carbide derived carbon (CDC) layer produced on SiC surface has been proved to be a good catalyst support of loading Pd/TiO_2 catalyst for hydrogenation of 4-carboxybenzaldehyde.[24]

In this paper, we have developed a facile two-step method to produce Pd/CNT-SiC monolith. A CNT layer is completely coated on SiC foam and Pd nanoparticles with high density are uniformly dispersed on the CNT surface. The as-prepared Pd/CNT-SiC monolith exhibits remarkably higher catalytic stability, activity and recycling ability in suzuki cross-coupling reaction, comparing with that of the commercial CNTs supported Pd catalyst. This new monolithic catalyst will be quite useful in liquid phase reaction.



Scheme 1. The preparation process of Pd/CNT-SiC monolith.

Scheme 1 shows the schematic illustration of the synthesis of Pd/CNT-SiC monolith. The detailed information of preparing process was given in support information. The prepared route contains two major steps: firstly, immobilizing CNTs on SiC foam is proceed by a traditional CVD method,[25] and the treatment with concentrated HNO_3 is following given to functionalize CNTs with oxygen groups and remove the residual Fe nanoparticles in the CNT-SiC support; then, palladium salt is dispersed on the surface of CNT-SiC support by the wetness impregnation method and reduced by H_2 at 300 °C.

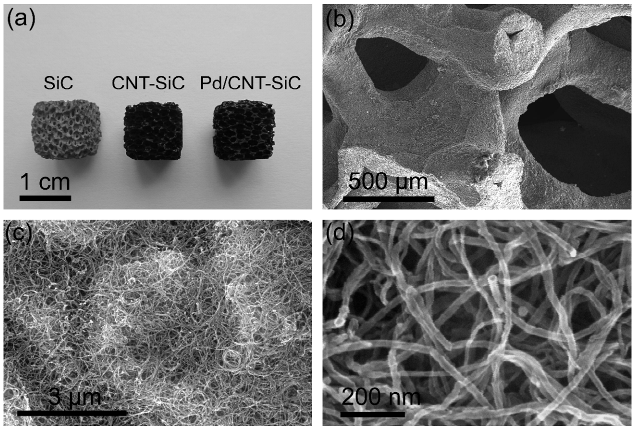


Figure 1. (a) Photograph of SiC, CNT-SiC and Pd/CNT-SiC monolith. (b-d) SEM images of Pd/CNT-SiC monolith.

The photograph of SiC, CNT-SiC and Pd/CNT-SiC monolith is shown in Figure 1a, it can be seen that the Pd/CNT-SiC monolith still maintain the same honeycomb structure with that of the initial SiC foam. Scanning electron microscopy (SEM) images displayed in Figure S1 show that SiC foam is composed of SiC skeleton with millimeter-scaled pores. Figure 1b presents the porous structure of the Pd/CNT-SiC monolith, which can be observed that there is no pore blockage in the monolith after the growth of CNT layer. SEM image of the Pd/CNT-SiC monolith, as shown in Figure 1c, displays that the CNTs are uniformly coated onto the SiC matrix after treating the monolith by concentrated HNO_3 and loading Pd nanoparticles. Figure 1d shows that the grown CNTs are entangled with each other and the average diameter of is around 20 nm.

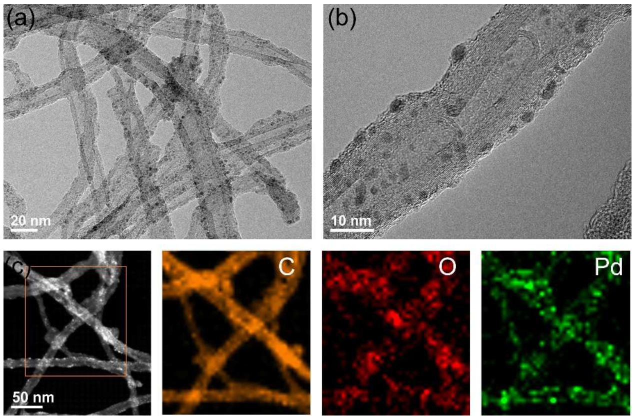


Figure 2. (a) TEM and (b) HRTEM images of Pd/CNT-SiC monolith. (c) STEM-EDX elemental maps of Pd/CNT-SiC monolith.

Transmission electron microscopy (TEM) is employed to further analyze the detailed structure of the Pd/CNT-SiC monolith. As seen in Figure 2a, the produced CNTs have a narrow distribution of diameter. Meanwhile, we can see that many black dots corresponding to the Pd nanoparticles are well distributed on the CNT surface. High-resolution TEM (HRTEM) image (Figure 2b) reveals that some defects can be observed on the outer surface of CNTs due to the oxidation by the concentrated HNO_3 solution. Meanwhile, we can also find that the Pd nanoparticles with the size range around 2.7 nm are uniformly located on the CNT surface. The STEM image and EDX elemental mapping (Figure 2c and Figure S2) further reveal that Pd nanoparticles with high density are evenly dispersed on CNT surface. Moreover, concentrated oxygen elements on the surface of CNTs are also detected by the EDX-mapping. These defects and functionalities can distinguishly promote the dispersion of Pd nanoparticles on the CNT surface.[26] The SEM and TEM results indicated that we developed a facile two-step method to prepare Pd/CNT-SiC monolith catalyst.

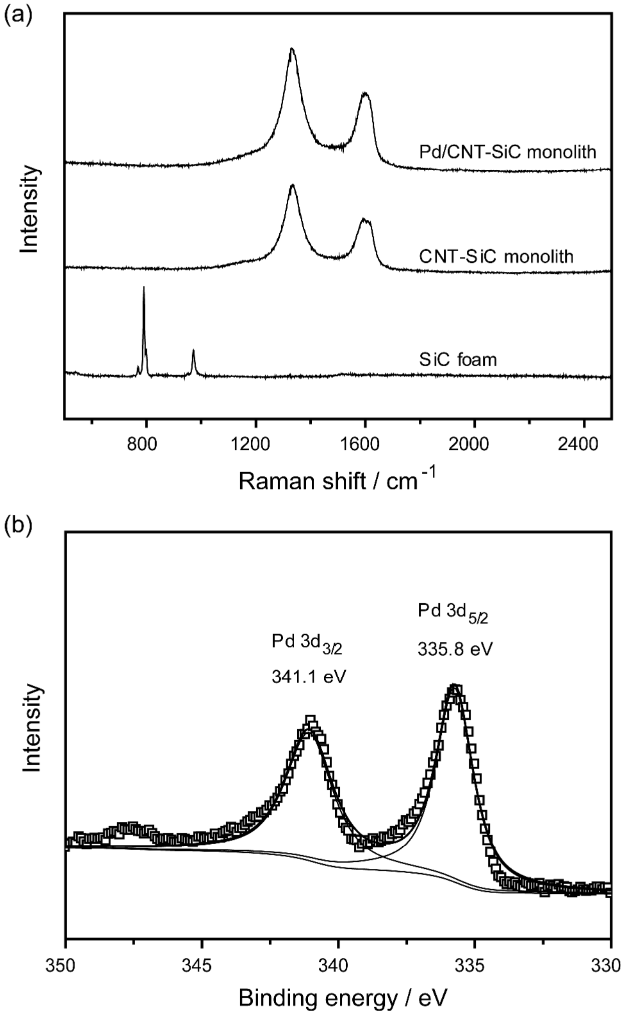


Figure 3. (a) Raman spectra of SiC foam, CNT-SiC monolith and Pd/CNT-SiC monolith. (b) XPS Pd 3d spectrum of Pd/CNT-SiC monolith.

Raman spectra of SiC foam, CNT-SiC monolith and Pd/CNT-SiC monolith are shown in Figure 3a. SiC foam has the characteristic SiC peak at 790 cm^{-1} but no obvious D peak (1336 cm^{-1}) and G peak (1597 cm^{-1}) of carbon are founded. However, after the growth of CNTs on SiC foam and the following purification, the strong D band and G band are observed, because of the shielding effect of obtained CNT layer. The Raman quantitative results of CNT-SiC monolith give the high I_D/I_G value (around 2.5, area intensity ratio),[27] indicating some defects on CNTs, which are also benefit for the high dispersion of palladium on CNT surface. After deposition of palladium nanoparticels on the CNT-SiC monolith, the strong Raman band in the Pd/CNT-SiC monolith is still observed and its fitting results give the similar I_D/I_G value (about 2.3).

X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical state of palladium particles on the CNT-SiC monolith. The XPS Pd 3d spectrum of Pd/CNT-SiC monolith is displayed in Figure 3b, which is fitted with two peaks at 335.8 eV (Pd $3d_{5/2}$) and 341.1 eV (Pd $3d_{3/2}$). These binding energy values can be attributed to the Pd (0) state,[11,28] indicating that the Pd species on the surface of CNT-SiC monolith is metallic Pd and no PdO exists in the Pd/CNT-SiC monolith. Figure S3 gives the survey spectrum of Pd/CNT-SiC monolith. The strong signal of O 1s further confirms that the surface of CNTs has a large number of oxygen functional groups, which consist with the EDX-mapping results.

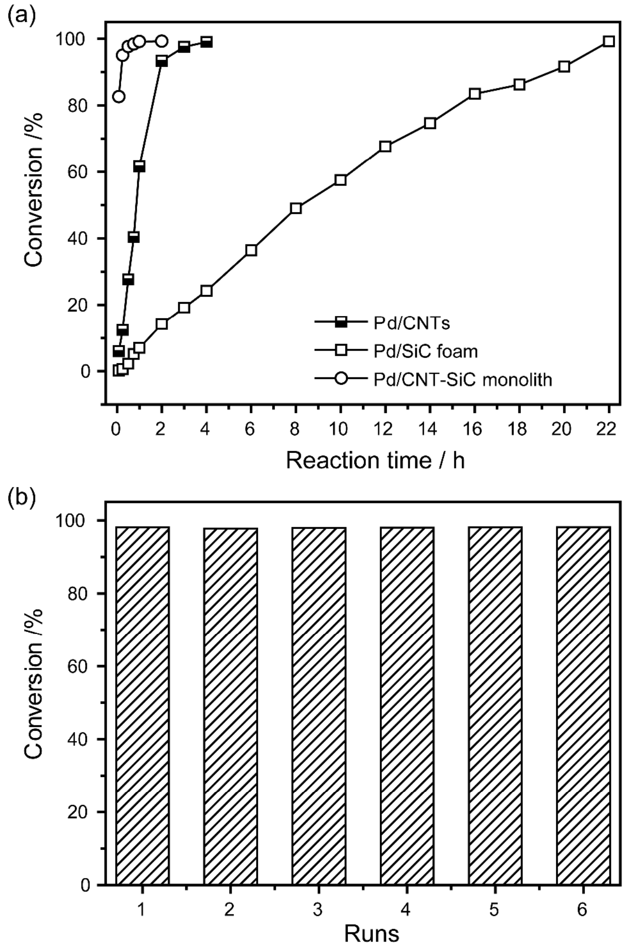


Figure 4. (a) Conversion of iodobenzene in Suzuki coupling reaction for Pd/CNT-SiC monolith, Pd/CNTs and Pd/SiC foam catalysts. (b) Conversion on recycling of the Pd/CNT-SiC monolith after 60 min. Reaction condition: 60 °C, iodobenzene (5 mmol), phenylboronic acid (10 mmol), K_3PO_4 (20 mmol), 20 ml C_2H_5OH, 5 ml H_2O, 600 mg catalysts (0.05 wt% Pd). TOF of Pd/CNT-SiC monolith: 1800 h^{-1}.

The Suzuki cross-coupling reaction of iodobenzene and phenylboronic acid was used to evaluate the catalytic performance of Pd/CNT-SiC monolith. The reaction was carried out by using ethanol and water as the solvent, and K_3PO_4 as the base. Figure 4a shows the catalytic performance of Pd/CNT-SiC monolith along the time in the Suzuki reaction at 60 °C. For a comparison, the catalytic performances of Pd/CNTs and Pd/SiC foam are also given in Figure 4a. Through the results, we can see that after 5 min reaction, the conversion of Pd/CNT-SiC monolith was up to 83%, indicating that the monolithic catalyst is active for this reaction. And after 60 min, the conversion of Pd/CNT-SiC monolith reaches nearly 100%, while just 62% and 7% conversions are observed for the Pd/CNTs and Pd/SiC foam, respectively. The TOF of Pd/CNT-SiC monolith is 1800 h^{-1}, which is higher than these of Pd/CNTs (439 h^{-1}) and Pd/SiC foam (80 h^{-1}). As we known, the surface area of SiC foam is quite low and its surface is chemical inert.[29-30] Generally, it is difficult to directly support the metal nanoparticles on the SiC foam.[24] A CNT layer coating on SiC foam can remarkly enhance the surface area of SiC foam, and is benefit for loading the Pd nanoparticels on CNT-SiC monolith, which could result in the higher activity of Pd/CNT-SiC monolith than that of Pd/SiC foam. From the TEM results, we can also obtain that the average size of Pd nanoparticles in Pd/CNT-SiC monolith is 2.7 nm, while that in Pd/CNTs catalyst is 4.3 nm. Therefore, comparing with the Pd/CNTs catalyst, one possible reason for the higher activity over Pd/CNT-SiC monolith could be the Pd nanoparticles with smaller sizes evenly dispersed on the monolith as shown in Figure 2a; the other possible reason is that the use of Pd/CNT-SiC monolith can avoid the aggregation of CNT powders in the reaction and the millimeter pores in the SiC foam can also facilitate the mass transfer, promoting the access of reactants to the supported Pd nanoparticles.

To investigate the stability of Pd/CNT-SiC monolithic catalyst, a series of recycling experiments for the Suzuki coupling of iodobenzene and phenylboronic acid were conducted. As shown in Figure 4b, the catalytic activity almost did not reduce even after the reuse of 6 times. The high stability and excellent reusability of the catalyst should result from the strong interaction between the Pd nanoparticles and CNTs, and the novel structure of SiC support.

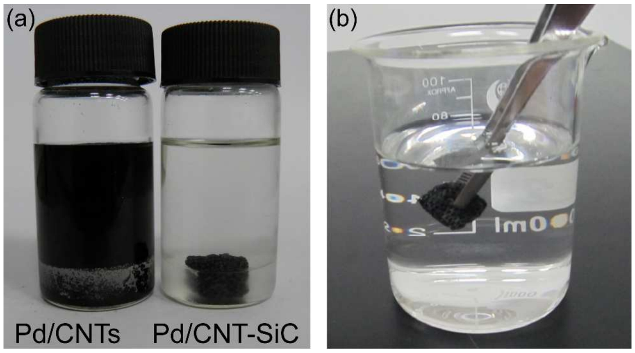


Figure 5. (a) The photograph of Pd/CNTs and Pd/CNT-SiC monolith after the catalytic reaction. (b) The washing process of the Pd/CNT-SiC monolith.

The photograph of reaction solutions for the Pd/CNTs powder and Pd/CNT-SiC monolith catalysts after Suzuki reaction are shown in Figure 5a, respectively. From this image, we can see that the Pd/CNTs powder is completely mixed into the reaction solution. It is well known that the isolation of powder catalysts is difficult in practical applications and usually adopts the additional filtration. However, in the case of Pd/CNT-SiC monolith catalyst, the reaction solution is quite clear without black catalysts. Meanwhile, the monolithic catalyst can be quickly separated by just taken out from the reaction mixture, and washed by a simple process (Figure 5b). The as-prepared Pd/CNT-SiC monolith catalyst is more easily recovered after the catalytic reaction, compared with that of the commercial CNT powder supported Pd catalyst.

In summary, we have presented a robust and facile method to prepare a Pd/CNT-SiC monolith catalyst. The as-synthesized Pd/CNTs-SiC monolith features a uniform CNTs catalyst layer coating on the porous SiC foam and highly dispersed Pd nanoparticles on the CNTs surface. Comparing with that of the commercial CNTs supported Pd catalyst, a higher catalytic activity of the obtained Pd/CNT-SiC monolith is demonstrated in the suzuki cross-coupling reaction. In particular, the Pd/CNT-SiC monolith could be more easily separated and recovered from reaction solutions, indicating good potential for industrial applications. This new method may offer more opportunities for developing powerful and reusable catalysts for green organic synthesis.

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† Electronic Supplementary Information (ESI) available: [The detailed synthesis condition, characterization, catalytic measurement and SEM images]. See DOI: 10.1039/b000000x/

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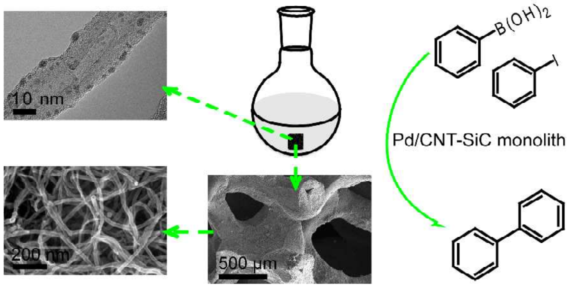

A Pd/CNT-SiC monolith prepared by a simple two-step method exhibits robust catalytic activity and recycling ability in Suzuki coupling reactions.