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Nanodiamond/CNT-SiC Monolith as a Novel Metal Free Catalyst for Ethylbenzene Direct Dehydrogenation to Styrene

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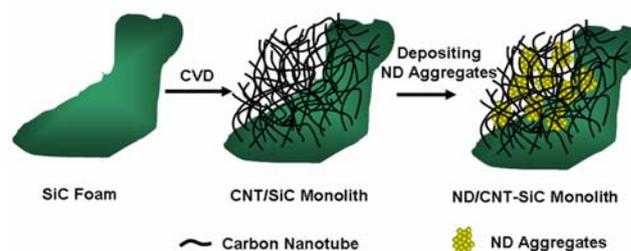
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A novel nanodiamond/CNT-SiC monolith catalyst has been prepared by a facile two-step approach. The as-synthesized monolith afforded high activity and stability for ethylbenzene direct dehydrogenation to styrene, showing its potential application as a metal free catalyst in gaseous catalytic reactions.

Nanodiamond (ND) as an important member in nanocarbons' family, has been used in the fields of drug delivery, magnetic sensor, nanocomposites, bioimaging and cellular marking, due to its unique chemical and physical properties.¹⁻⁶ Recent reports have demonstrated that the ND is a promising heterogeneous catalyst in the catalytic dehydrogenation (DH) of n-butane and ethylbenzene reactions. The outstanding catalytic performance makes ND candidates for replacing traditional metal/metal oxides catalysts in sustainable chemistry.⁷⁻⁸ Generally, most of the commercial available NDs in powder form were produced by an explosion method.⁹⁻¹⁰ The powder is highly detrimental to be used in fixed-bed reactors for industrial applications. They are prone to block the reactors, resulting in pressure drops; they are excessively difficult to handle and their suprastructural properties cannot be controlled. In order to overcome these disadvantages, it is necessary to prepare NDs into larger objects. One feasible method is direct compaction, but it can hinder the access of reactant to the active sites and may destroy the intrinsic structure of active sites during the compacting process.¹¹ The other way is loading active sites on some macroporous supports to form a monolithic catalyst.¹² Among the macroporous supports, silicon carbide (SiC) foam with high thermal conductivity and mechanical stability has been used as a monolithic support to immobilize catalysts.¹³⁻¹⁴ However, it is generally difficult to directly load the active sites on the macroporous SiC support by the traditional impregnation method, due to its low surface areas and chemical inert surface. Herein, we report a facile two-step synthesis method to produce ND/CNT-SiC monolith. We employ the macroporous SiC foam as the support, the in-situ growing carbon nanotubes (CNTs) on the SiC support as the coating layer. The commercial available ND aggregates as the active sites were supported into the CNT coating layers by a sonication-assisted impregnation method. The as-prepared ND/CNT-SiC monolith features that a CNT layer is completely coated on macroporous

SiC foam and commercial ND aggregates are uniformly embedded into the 3 dimensional (3D) CNT networks. The as-prepared ND/CNT-SiC monolith exhibits remarkably higher catalytic stability and selectivity to the ethylbenzene direct dehydrogenation reaction, comparing with that of the commercial ND powders, showing its potential application as a metal free monolithic catalyst in gaseous catalytic reactions.

Scheme 1 shows the schematic illustration of the synthesis of ND/CNT-SiC monolith. The prepared process mainly contains two steps: firstly, a 3D CNT layer was coated on SiC foam by a traditional chemical vapor deposition (CVD) method.¹⁵ Then, commercial ND aggregates were anchored into the 3D CNT networks by the sonication-assisted impregnation method. The detailed preparation process is shown in the supporting information.



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

The SEM images of as-synthesized CNT/SiC monolith with different magnifications were shown in Figure 1, and inset was the photograph of CNT/SiC monolith. It can be seen that the macroscopic porous structure of SiC (Figure 1a) was still well maintained after the growth of CNTs, comparing with that of initial SiC foam (SEM images in Figure S1), and it is black due to the deposition of CNTs. The cross-section view of CNT/SiC was shown in Figure 1b. The thickness of CNT layer grown on SiC support was about 20 μm . The enlarged SEM image in Figure 1c showed that CNTs are homogeneously coated on the surface of SiC foam. Meanwhile, the SEM image with high magnification in Figure 1d demonstrated that the CNTs grow randomly and entangled together on the SiC surface. The obtained CNTs have a narrow size distribution, and their diameter is around 20 nm. More importantly, it can be found that the CNTs grown on the

SiC surface formed a 3D networks with abundant open spaces around micrometers. All the SEM results indicated that a 3D CNT networks is successfully coated on SiC support by traditional CVD method.

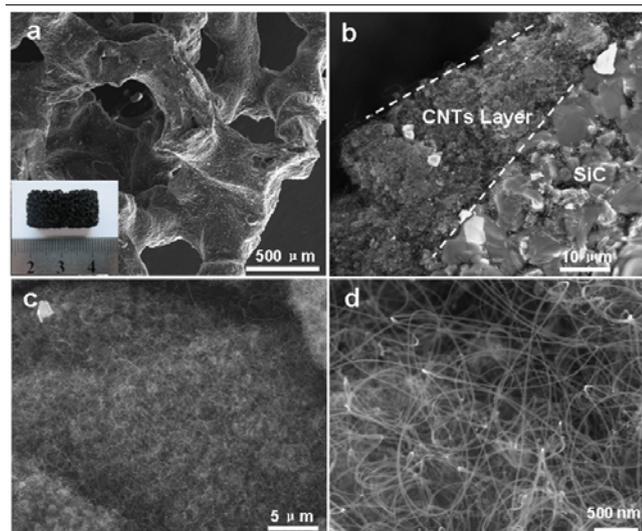


Figure 1. (a-d) SEM images of CNT/SiC monolith with different magnifications. Inset is the photograph of CNT/SiC monolith

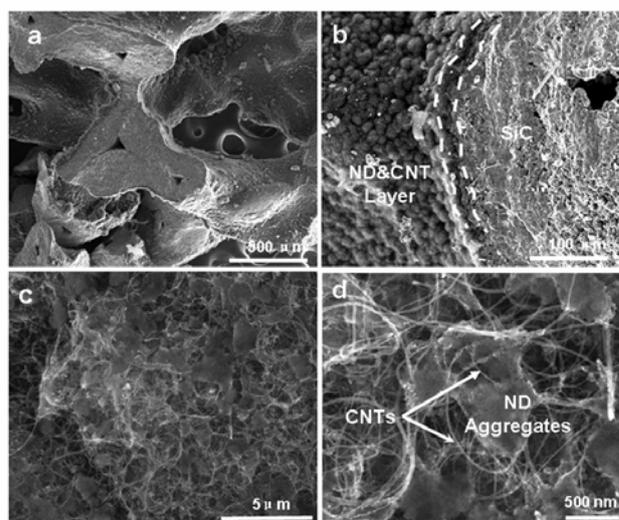


Figure 2 (a-d) SEM images of ND/CNT-SiC monolith with different magnifications. The weight loading of ND is 1.2%.

We also investigated the detailed structure of ND/CNT-SiC monolith with different ND weight loadings. The SEM images of the as-prepared monolith with 3.4% and 6.2% ND loadings are shown in Figure S4. As to the monolith with 3.4% ND loading, it can be observed that the ND aggregates are still uniformly embedded into the 3D CNT network, keeping the fish-in-net like structure as shown in Figure S3a and b. However, for the monolith with 6.2% ND loading, the CNT layer on the SiC support was completely covered by the ND aggregates, only few CNTs were exposed on the surface (Figure S4c and d).

Raman spectra of CNT/SiC and ND/CNT-SiC are displayed in Figure S5. For the CNT/SiC monolith, the strong D band and G band are observed, while no SiC peak could be found due to the shielding effect of the CNT layer. The raman quantitative results of CNT/SiC monolith give the high I_D/I_G value (about 1.3), indicating some defects on CNTs. After embedding ND aggregates into the 3D CNT networks, the strong raman bands in the ND/CNT-SiC monolith are still observed and the deconvolution results give the I_D/I_G value about 1.4.

The catalytic performances of the ND/CNT-SiC monolith (3.4% weight loading), CNT/SiC and commercial ND powders were evaluated for the direct dehydrogenation (DH) of ethylbenzene to styrene at 550 °C. The carbon balance under the present conditions is nearly 100%. The catalytic performances of all the catalysts along with reaction time are shown in Figure 3. It can be noted that the conversion of ethylbenzene over pure CNT/SiC just reached 3.8% after 14 h test, and the selectivity to styrene finally stabilized at 88.7%. However, for the ND/CNT-SiC monolith, a 19.4% ethylbenzene conversion and 98.3% selectivity to styrene are observed, which are higher than those of pure CNT/SiC catalyst and even commercial ND powders (15.1% ethylbenzene conversion and 97.1% styrene selectivity as presented in Figure 3). More importantly, we can see that the conversion of ethylbenzene over ND/CNT-SiC monolith quickly stabilized after just 7 h testing, but as to the commercial ND powders the catalytic performance can not be kept stable even after 20 h testing. The possible reasons for the better performance over ND/CNT-SiC monolith may be attributed to the high

effective surface and the short diffusion length of this hierarchical support which favors the diffusion or desorption of the reactants and the products, and the fluent heat transfer over the SiC support during the reaction.¹⁷⁻¹⁹ While, as to the commercial ND powders, the mass and heat transfer was not fluent in the reaction system, resulting in the unstable catalytic performance as displayed in Figure 3.

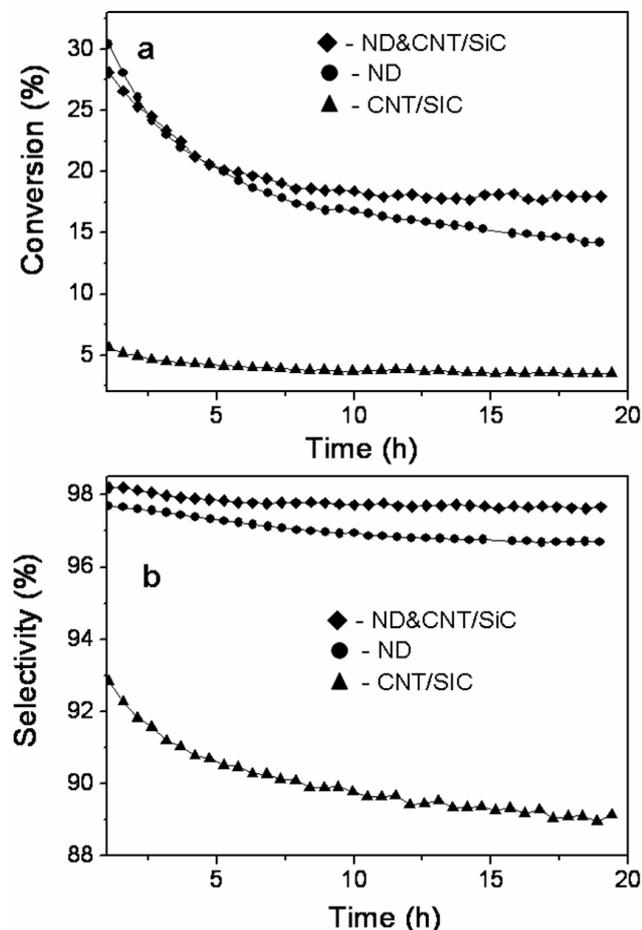


Figure 3. Catalytic performance over ND/CNT-SiC (3.4%), CNT/SiC and commercial ND powders diluted with quartz sands (3.4%). Reaction condition: 500mg, T = 550°C, Flow rate = 10 ml/min, 2.6% ethylbenzene with He balance.

Conclusion

In summary, we have demonstrated a novel two-step method for preparing a ND/CNT-SiC monolith catalyst. The as-synthesized ND/CNTs-SiC monolith catalyst features that a uniform CNT layer with 20 μm thickness was evenly coated on the porous SiC foam and the ND aggregates uniformly embedded into the 3D CNT networks, forming a fish-in-net like composites. The ND/CNT-SiC monolith shows good catalytic stability and selectivity in DH of ethylbenzene to styrene, comparing with that of CNT/SiC monolith and pure commercial ND powders, which displays its potential application as a metal free catalyst in the gaseous catalytic reactions.

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Notes and references

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