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COMMUNICATION

Increased active sites and their accessibility of N-doped carbon nanotube carbocatalyst with remarkably enhanced catalytic performance in direct dehydrogenation of ethylbenzene†

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Zhongkui Zhao*, Yitao Dai, Guifang Ge, Xinwen Guo and Guiru Wang

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This work presents an efficient and low-cost one-step strategy for simultaneously N-doping and increasing surface ketonic C=O groups and structural defects of N-doped carbon nanotube (HN-CNT) through the explosive decomposition of hexamethylenetetramine (HTA) nitrate, a low-cost N,O-containing organic compound. The as-synthesized HN-CNT demonstrates 1.64 and 2.19 times higher steady-state styrene rate with 98.5% selectivity towards styrene for direct dehydrogenation (DDH) than that of the parent CNT and the H-CNT prepared by the similar pyrolysis procedure to that for HN-CNT except for replacing HTA nitrate with HTA.

Styrene, one of the most important monomers for the synthesis of polymers and copolymers, is mostly produced by direct dehydrogenation (DDH) of ethylbenzene on the alkaline promoted iron-based catalysts.¹ The industrially used K-Fe catalyst suffers quick deactivation by coke deposition, besides huge energy consumption owing to the required excess superheated steam into the feed. Therefore, to pursue an efficient alternatives to iron-based catalysts is highly desirable, but remains a rigorous challenge. Nanocarbon materials have been demonstrated to be promising and sustainable and low-cost metal-free alternative to metal-based catalysts for organic synthesis,² hydrogen production,³ photodegradation,⁴ oxygen reduction reaction,⁵ and as counter electrode catalyst for solar cells.⁶ Nowadays, carbocatalysis has already attracted great attention, and become the foreland and hot topic in the heterogeneous catalysis.⁷

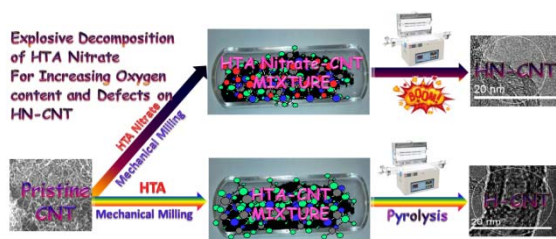
The use of carbon materials as metal-free catalysts in oxidative dehydrogenation (ODH) of ethylbenzene^{7a,7b,8} and light alkanes^{2a,2b,7a,7b,9} to produce their corresponding olefins has attracted great attention while the DDH in the absence of oxygen is only scarcely reported.¹⁰ However, the ODH process presents some serious disadvantages compared to the oxygen-free DDH namely the use of a mixture containing oxygen and hydrocarbon leading to potential safety issue and low selectivity towards styrene owing to the parallel side reactions such as combustion, besides the possible damage of

carbocatalysts since they suffer from the harsh operating conditions. The DDH is considered as a promising approach for the olefins production.^{10,11}

The DDH of ethylbenzene to styrene was firstly reported by using nanodiamond as an efficient metal-free catalyst,^{11a} which depicts a fascinating prospect for energy-saving styrene production via carbocatalysts catalyzed DDH reaction. The exciting results inspire researchers to develop carbon-based catalysts for this reaction. The great advances have been made in developing the highly efficient ethylbenzene DDH carbocatalysts.¹² It was previously demonstrated that the N-doping of carbon materials can efficiently enhance the DDH reaction.^{11b,12a} Furthermore, some nanocarbon materials like few-layer graphene decorated nanodiamond, nanodiamond/CNT-SiC, N-doped mesoporous graphene/nanodiamond, nanodiamond/carbon nitride hybrid and N-doped CNT-decorated activated carbon have demonstrated promising catalytic performance in DDH reaction of ethylbenzene.^{12b-f} However, the further improvement in activity is essential for possible industrial application, but it still remains a rigorous challenge.

It was previously established that the surface ketonic C=O is the main active sites for C-H activation.¹⁰⁻¹² Recently, it was established that, besides the ketonic C=O groups, the surface structural defects can also perform as active sites for C-H bonds activation.^{10a,13} The improvement in nucleophilicity of ketonic C=O groups by N doping benefits for promoting DDH.^{11b,12a} The pyrolysis of carbon materials with melamine can lead to the formation of some structural defect, but the defectiveness is scarce,^{11b,12a,14} the further improvement in defects is required. Moreover, the thick carbon nitride layers covered on the N-doped carbon nanotube (M-CNT) can be formed if the melamine was used as N precursor,^{13a,13b} which depresses the accessibility of active sites to reactants. We previously demonstrated that the addition of guanidine nitrate in the process of pyrolysis of melamine and the use of melamine-cyanuric acid supramolecular assembly can eliminate the compact carbon nitride layers on CNT, and also can simultaneously increase the structure defects and enrich the surface ketonic C=O groups.^{13a,13b} However, the previous reported method would consume a large amount of precious

State Key Laboratory of Fine Chemicals, Department of Catalysis Chemistry and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P.R. China. Fax: (+) 86-411-84986354; E-mail: zkzhao@dlut.edu.cn. Electronic Supplementary Information (ESI) available: Experimental details for catalyst preparation, characterization, and catalytic performance measurement and the extra characterization results. See DOI: 10.1039/x0xx00000x



Scheme 1 Schematic representations for the synthesis of HN-CNT carbocatalyst by a facile one-step approach, as well as for the synthesis of H-CNT.

guanidine and melamine-cyanuric acid. Therefore, the more efficient and low-cost strategy for fabricating N-doped CNT with increased defects and C=O is highly desirable, but it remains a challenge. The hexamethylenetetramine was demonstrated to be a good candidate as N precursor for fabricating novel mesoporous carbon nitride material.^{11b} We envision that the use of low-cost hexamethylenetetramine nitrate as N,O precursor may simultaneously increase the amount of catalytically active sites and accessibility, which in turn further improves DDH catalysis.

In this work, we firstly present a sophisticated approach for fabricating novel N-doped CNT (HN-CNT) by the explosive decomposition of the low-cost hexamethylenetetramine (HTA) nitrate, used as N,O precursor; For comparison, the H-CNT was prepared by the similar pyrolysis process under the same conditions as those for HN-CNT except for the replacement of HTA nitrate by HTA (Scheme 1). The characterization results show that the developed HN-CNT catalyst has the increased structure defects, enriched surface ketonic C=O groups, and 1.3% of surface N content (by XPS analysis) in comparison with the as-synthesized H-CNT. From Fig. 1a-c, the enlarged structural defectiveness of the HN-CNT can be clearly seen. However, the perfect CNT wall for the pristine CNT can be observed (Fig. 1g-i). Fig. 1d-f shows that the carbon nitride fragments coated on nanotube wall of H-CNT can be formed by the pyrolysis of HTA. In comparison with H-CNT, no visible carbon nitride fragment on the developed HN-CNT can be observed, although we use the similar pyrolysis conditions. The visible structural defect and the basic disappearance of carbon nitride on HN-CNT may be ascribed to

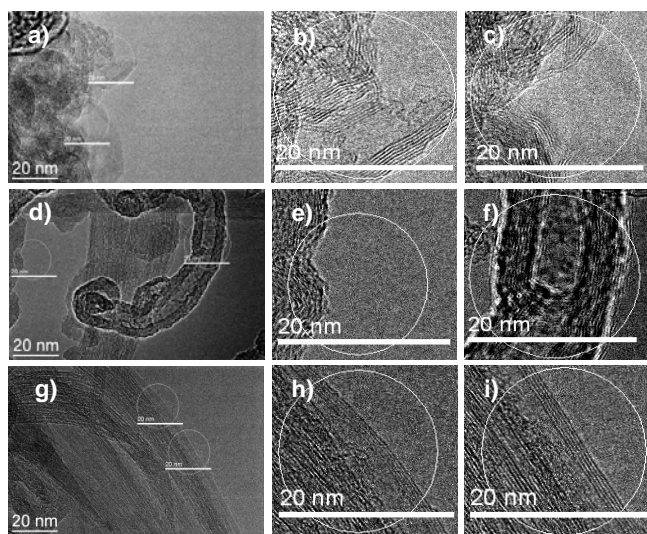


Fig. 1 HRTEM images of the HN-CNT (a-c), H-CNT (d-f), and pristine CNT (g-i) samples.

the explosive decomposition of HTA nitrate. From our previous results, the formed carbon nitride feature on the H-CNT is in different form that on M-CNT, caused by the unique structure and chemical properties of HTA Nitrate.^{13a} The increased structural defects and their accessibility allow it to exhibit outstanding DDH catalytic performance.

The texture features of the as-synthesized HN-CNT, H-CNT, and the pristine CNT were investigated by N₂ adsorption-desorption experiments. From Fig. 2a, the significantly decreased surface area and pore volume for the as-synthesized H-CNT in comparison with those for the pristine CNT can be observed, ascribed to the compact carbon nitride formed on CNT wall and the possibly blocked mouth of CNT. The formed carbon nitride fragments identified by the above HRTEM can depress the accessibility of active sites on the H-CNT, and therefore leads to poor catalytic performance. Although no visible carbon nitride fragments on HN-CNT by HRTEM, the decrease in surface area and pore volume of the HN-CNT in comparison with the pristine CNT can be observed (Fig. 2a), showing that the carbon nitride fragments cannot be completely removed from HN-CNT. Moreover, the micro- and meso-pore size distribution provides the extra evidence for the CNT mouth being blocked of the two synthesized samples. The structural characteristics of as-synthesized HN-CNT and H-CNT, and pristine CNT were further investigated by XRD and Raman techniques.

The structural characteristics of the as-synthesized N-doped CNTs (HN-CNT and H-CNT) and the pristine CNT were further investigated by XRD and Raman techniques. From Fig. 2b, towards HN-CNT, H-CNT, and pristine CNT, the diffraction

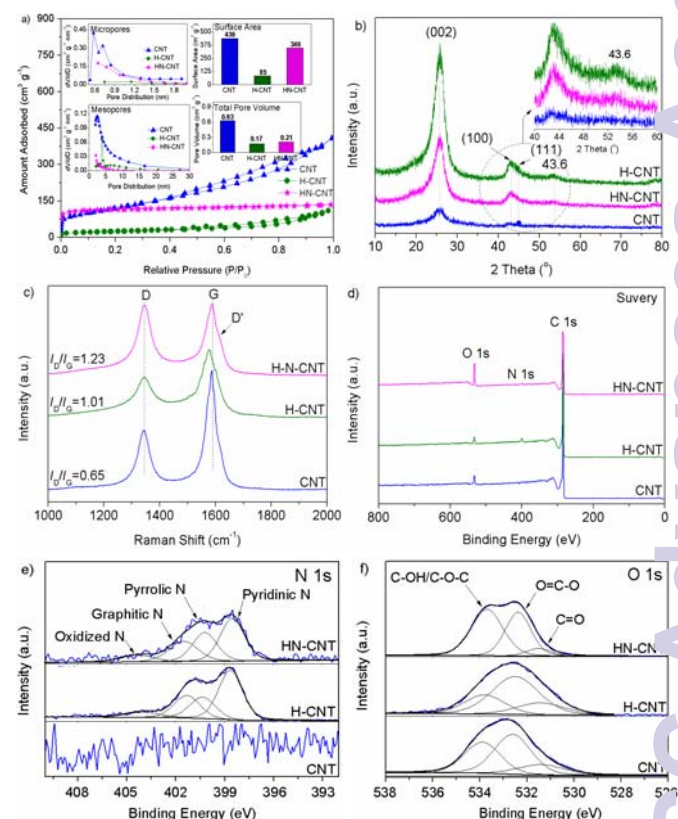


Fig. 2 Nitrogen adsorption-desorption results (a), XRD patterns (b), Raman spectra (c), XPS survey (d), N 1s (e), and O 1s (f) of HN-CNT, H-CNT, and the pristine CNT samples

peaks corresponding to (002), (100) and (111) planes can be identified, indicating the well-formed graphitic structures.^{12c-e} More interestingly, the peak at 43.6° on the XRD patterns of the as-synthesized HN-CNT and H-CNT can be observed; however, no peak at this angle on the pattern of pristine CNT can be resolved, caused by the formed carbon nitride fragments on the HN-CNT and H-CNT. The sharper and stronger peaks towards (002), (100) and (111) planes on the H-CNT in comparison those on pristine CNT imply the graphitic carbon nitride fragments, which is different from those on the M-CNT.¹⁵ The medium diffraction peaks towards (002), (100) and (111) planes for HN-CNT in comparison with those for H-CNT and pristine CNT can be seen, suggesting the partial removal of the formed carbon nitride fragments, which is consistent with the HRTEM and BET results. From Fig. 2c, we could observe that there are two main first-order Raman modes at around 1334-1337 and 1596 cm⁻¹, corresponding to A1g mode in disorder carbon or structural defect and to E 2g mode ideal graphitic carbon, respectively.¹⁶ Correlated to the HRTEM results illustrated in Fig. 1, the higher I_D/I_G for HN-CNT in comparison with that for pristine CNT is mainly caused by the more structural defects and lattice edges of the as-prepared hybrid composite,¹⁷ but the higher I_D/I_G for H-CNT in comparison with that for pristine CNT suggests the graphitic carbon nitride fragments on the material. The visible D' peak on the Raman spectroscopy of HN-CNT is a further indicator for more defects than the other two.^{13a} The enlarged structural defectiveness identified by HRTEM and Raman experiments allows HN-CNT to be an excellent DDH catalyst. Moreover, the developed HN-CNT in this work exhibits higher I_D/I_G value (1.23) in comparison with the previously reported G-M-CNT,^{13a} although the higher cost and more amount of guanidine nitrate was used. This shows the HN is more efficient and lower cost for producing structural defect, which may result in the higher catalytic performance. The better behavior of HN than guanidine nitrate might be ascribed to the different molecular structures. Further investigation would be performed to reveal why HN is more efficient for increasing structural defects on CNT in comparison with guanidine nitrate.

XPS experiments were performed to investigate the nature and coordination of the carbon, nitrogen, and oxygen in the as-synthesized N-doped CNTs and the pristine CNT, since the surface chemistry of carbon materials significantly affects their catalysis in DDH reaction.¹¹⁻¹³ From Fig. 2d and Table S1, the increased surface O content on the HN-CNT but decreased O content on H-CNT in comparison with the pristine CNT can be seen. The former is caused by the explosive decomposition of HTA nitrate; but the latter may be due to the O escaping from H-CNT in the pyrolysis process at high temperature or owing to the coating effect of compact carbon nitride fragments. From Fig. S1,2e and Table S1, the N incorporation into carbon matrix can be identified. Furthermore, the as-prepared HN-CNT has lower N content than H-CNT, ascribed to the explosive decomposition of O-containing nitrate motif in HTA nitrate. The main side-products for the DDH are benzene and toluene resulted from the cracking of ethylbenzene, which consists with the results reported in literatures.^{11,12c-e} The surface phenolic hydroxyl group and/or possible COOH may promote the cracking of ethylbenzene due to its acidity.¹⁸ The

incorporated N atom into carbon matrix can increase the electron density of carbon materials, and therefore strengthens the basic properties but weakens the acidity of the catalyst, which may result in an improvement in catalytic activity for styrene production and simultaneously compressing the benzene and toluene formation.^{12c-e} From Fig. 2d and Table S1, HTA nitrate explosive decomposition also leads to clear difference in surface N and O content and their chemical state. The O 1s XPS spectra of the three samples were deconvoluted into three peaks, assigned to C=O, O=C-O and C-O-C/C-OH containing groups, respectively (Fig. 2f and Table S1).^{13a,13b} The contents of surface ketonic C=O, main active sites for DDH reaction, on the HN-CNT, H-CNT, and pristine CNT are 0.95, 0.65, and 0.65, respectively. The higher C=O content of HN-CNT than the other two allows it to exhibit superior DDH catalytic performance.

The DDH of ethylbenzene to styrene is an industrially important catalytic process. Herein, the catalytic performance of the HN-CNT, H-CNT, and pristine CNT catalysts was tested. Fig. 3 presents the catalytic properties, and the industrially used K-Fe catalyst is also included for comparison. From the previously reported results, the catalytic activity can basically reach the steady state after the reaction runs more than 15 h. Herein, the steady-state styrene rate and selectivity at 20 h on stream was used to evaluate the catalytic performance of the as-synthesized catalysts. The developed HN-CNT catalyst gives 4.6 mmol g⁻¹ h⁻¹ of steady-state styrene rate with 98.5% of high styrene selectivity. The catalytic activity of HN-CNT is 2.19 and 1.64 times higher than that of the as-synthesized H-CNT and the pristine CNT, respectively. Moreover, from our previously reported results,^{13a,13b} although the lower surface C=O groups amount on the M-CNT prepared by pyrolysis of melamine, it exhibits higher catalytic activity than the pristine CNT, ascribed to the promoting effect of N-doping. However, the as-synthesized N-doped CNT in this work (H-CNT) by pyrolysis of HTA shows lower catalytic activity than the pristine CNT although the almost same surface ketonic C=O amount on the two samples, caused by the formed compact carbon nitride fragments on the H-CNT, whose feature is different from that on M-CNT identified by HRTEM, N₂ adsorption desorption, XRD, and Raman characterization results. Moreover, the developed HN-CNT in this work exhibits higher catalytic performance in comparison with the previously reported G-M-CNT,^{13a} ascribed to more efficiently producing structural defects by HN than guanidine nitrate identified by Raman characterization. Furthermore, the lower

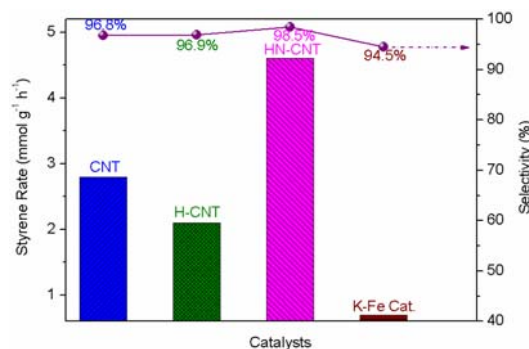


Fig. 3. Catalytic properties of HN-CNT, H-CNT, and the pristine CNT as a function of time on stream for DDH of ethylbenzene to styrene.

cost of HTA nitrate with lower usage is required to prepare HN-CNT with higher catalytic performance in comparison the previously reported guanidine nitrate, which shows the much advance in the modified CNT for DDH reaction.

Correlated to the nature of HN-CNT shown as above, the outstanding catalytic performance of the developed HN-CNT benefits from the simultaneous enlargement in structural defectiveness, the increase in surface ketonic C=O group amount as well as the improvement in nucleophilicity of surface ketonic C=O and basic properties of materials caused by N-doping. Moreover, the removal of compact carbon nitride fragments enhances the accessibility of active sites to ethylbenzene, which also benefits for the DDH reaction.^{13a,13b} Furthermore, the blocked mouth of HN-CNT identified by N₂ adsorption-desorption measurement results (very low pore volume and very fewer pores in HN-CNT) doesn't depress its catalysis in DDH reaction, suggesting the DDH reaction mainly takes place on the external surface of HN-CNT. The developed HN-CNT catalyst exhibits 6.57 times of steady-state styrene rate of the K-Fe catalyst, implying a bright future for clean, highly efficient and energy-saving industrial production of styrene under oxidant- and steam-free conditions.

Conclusion

In summary, we develop a facile and low-cost approach for synthesizing N-doped carbon nanotube catalyst with increased structural defects and enriched surface ketonic carbonyl groups through a one-step method including the explosive decomposition of hexamethylenetetramine nitrate. The as-synthesized HN-CNT carbocatalyst in this work demonstrates remarkably higher catalytic activity in direct dehydrogenation of ethylbenzene for styrene production, which benefits from the increased catalytically active sites, the increased catalytically active sites and the improved nucleophilicity of C=O and basic properties of materials caused by N-doping, as well as high accessibility of active sites to ethylbenzene owing to the removal of carbon nitride fragments. Moreover, the combination of reaction results and the N₂ adsorption-desorption measurement results suggests the DDH reaction mainly takes place on the external surface of HN-CNT. The developed facile and efficient one-step approach for simultaneously defects producing, surface C=O groups enriching, and N-doping in this work also paves a new way for the preparation of the other N-doped nanocarbon catalysts with outstanding catalytic performance in diverse transformations.

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Increased active sites and their accessibility of N-doped carbon nanotube carbocatalyst with remarkably enhanced catalytic performance in direct dehydrogenation of ethylbenzene†

Zhongkui Zhao,* Yitao Dai, Guifang Ge, Xinwen Guo and Guiru Wang

State Key Laboratory of Fine Chemicals, Department of Catalysis Chemistry and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China; E-mail: zkzhao@dlut.edu.cn

This work presents a facile, low-cost, but efficient strategy for synthesizing HN-CNT with enlarged active sites and their accessibility to reactant for direct dehydrogenation of ethylbenzene.

