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Facile simultaneous defect producing and O,N-doping of carbon nanotube with unexpected catalytic performance for clean and energy-saving production of styrene†

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O,N-doped carbon nanotube with increased structural defects and enriched surface ketonic C=O groups (MN-CNT), prepared by a facile and low-cost one-step strategy, demonstrates unexpected catalytic performance in ethylbenzene direct dehydrogenation for styrene production with clean and energy-saving feature. This work paves a new avenue for preparing the other highly-efficient carbocatalysts in diverse organic transformations.

Direct dehydrogenation (DDH) of ethylbenzene has attracted considerable attention owing to the growing demand for styrene in chemical industry. The commercially available K-Fe catalyst has some disadvantages like quick deactivation due to potassium loss, unstable Fe^{3+} state, coke-deposition, besides the health injuries to human beings caused by the used Cr in this catalytic system. Moreover, the introduction of superheated steam into the feed is indispensable, and which gives the thermodynamic driving force as a heat due to its endothermic character, and shifts the chemical equilibrium to higher styrene conversion, besides inhibits quick deactivation caused by coke-deposition.[1-4] However, the used excess steam (about 2-3:1 for current technology) leads to high energy consumption.[5-7] The search for new catalyst systems with high Fe^{3+} stability and coke-tolerance in the absence of potassium or steam is highly desirable, but a large breakthrough on these issues is in an extremity although many efforts have been made throughout the world.[8-13]

From the viewpoint of sustainable development of chemical industries, the carbocatalysts are being considered as fascinating and green alternatives to Fe-based catalyst for energy-saving, clean and safe styrene production. However, current efforts have been mainly focused on carbon catalyzed oxidative dehydrogenation,[14-25] and so far rare report on oxygen- and steam-free DDH can be found.[26-29] Therefore, the development of metal-free nanocarbon catalyzed DDH is highly desirable but remains a rigorous challenge.

Recently, the direct dehydrogenation of ethylbenzene to styrene under oxygen- and steam-free conditions was firstly reported by employing nanodiamond as an efficient metal-free catalyst,[26] which depicts a fascinating prospect for clean and energy-saving styrene production via DDH reaction over robust carbocatalysts. The exciting results inspire researchers to develop carbon-based catalysts for this reaction.

It was previously demonstrated that the N-doping of carbon materials can efficiently enhance the DH reaction.[27,30] Furthermore, some nanostructured carbon materials including 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.[31-35] The further improvement in catalytic activity is essential for possible industrial production of styrene, although the great advances in this issue have been made. It was previously established that the surface ketonic C=O is the main active sites for C-H activation. Therefore, the increase in ketonic C=O amount and also the improvement in their nucleophilicity are favorable for promoting direct dehydrogenation.[26-35] The enlarged surface structural defectiveness can improve the absorbing and activating reactants, which improves the catalytic performance of carbocatalysts.[28,36,37] 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 in DDH reactions.[28,38] The pyrolysis of carbon materials with melamine or melamine-cyanuric supramolecular assembly leads to the formation of some structural defect,[27,39,40] but the defectiveness is not high enough. The further improved defect-formation is required. Therefore, in order to synthesize a highly active carbocatalyst for DDH of ethylbenzene, the development of a facile and robust one-step approach for preparation of O,N-doped carbonaceous materials with enriched surface ketonic C=O groups and structural defects by simultaneous structural

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Electronic Supplementary Information (ESI) available: Experimental details for materials preparation, characterization, and catalytic performance measurement as well as the extra XPS data. See DOI: 10.1039/x0gc00000x defects production and O,N-doping is highly desirable, but it remains a challenge.

Herein, we firstly report a facile and robust one-step strategy for fabricating the surface structural defects enriched O,N-doped CNT catalyst by the explosive decomposition of melamine nitrate (the details for the synthesis process can be seen in ESI†), through which the structural defects production and O,N-doping can be simultaneously achieved. Benefiting from the simultaneous enlargement in structural defectiveness and increase in surface ketonic groups amount as well as the improvement in nucleophilicity of C=O and basic properties of materials caused by N-doping, the as-synthesized MN-CNT demonstrates outstanding catalytic performance in DDH of ethylbenzene (1.7 and 6.9 times the steady-state styrene rate of the per gram pristine CNT and the industrially used K-Fe catalyst, respectively with 98.4% selectivity to styrene). The MN-CNT even shows 1.4 times the steady-state styrene rate of the classical N-doped CNT (M-CNT) prepared by the same pyrolysis process with similar parameters as those for preparing MN-CNT except for replacing melamine nitrate by melamine. The work opens a new horizon for preparing the other highly-efficient carbocatalysts in diverse reactions.

Figure 1 presents the HRTEM images and the magnified images of typical regions of the as-synthesized MN-CNT, M-CNT and the pristine CNT samples. As shown in Figure 1a-c, the clear surface structural defects on the CNT walls of the MN-CNT can be observed. However, the relatively perfect CNT walls on the pristine CNT can be clearly seen (Figure 1g-i). Figure 1d-f demonstrates that the Carbon nitride layer or carbon nitride fragment coated on nanotube wall of M-CNT can be formed by the pyrolysis of CNT and melamine (the presence of N can be identified by the following XPS analyses). In comparison with M-CNT, no visible Carbon nitride layer or carbon nitride fragment on MN-CNT can be observed, although the similar pyrolysis process was employed except for replacement of melamine with melamine nitrate. The structural defects production and the Carbon nitride layer or carbon nitride fragment disappearance on the as-synthesized MN-CNT may be ascribed to the explosive decomposition of melamine nitrate. Besides the established surface ketonic C=O, the increased structural defects on the developed MN-CNT catalyst can perform as active sites for DDH of ethylbenzene, and therefore allows the MN-CNT to exhibit remarkably enhanced catalytic performance.[28,38]

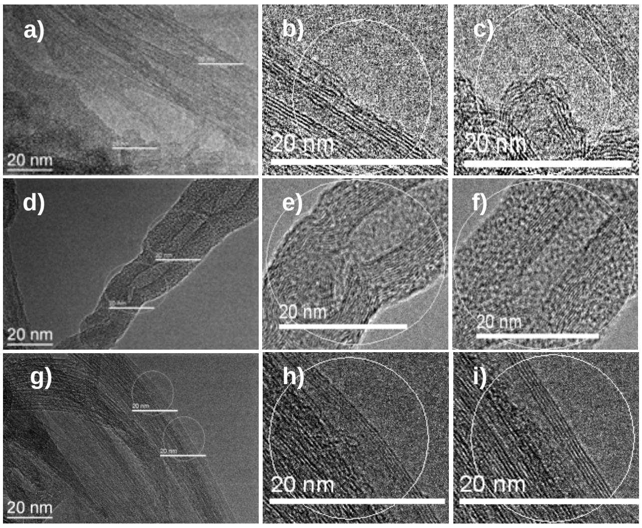

Figure 1. HRTEM images of the as-synthesized MN-CNT (a-c), M-CNT (d-f), and the pristine CNT (g-i) samples.

XRD and Raman were employed to further investigate the structural characteristics of the as-synthesized MN-CNT, M-CNT and the pristine CNT materials. From Figure 2a, the diffraction peaks corresponding to (002), (100) and (111) on the XRD patterns of the as-synthesized MN-CNT and the pristine CNT can be identified,[34] suggesting the well-formed graphitic structure. However, interestingly, no characteristic peaks towards (100) and (111) planes on the XRD pattern of M-CNT can be well resolved,[38] ascribed to the existence of thick Carbon nitride layer or the carbon nitride fragment identified by HRTEM analyses. The XRD peak towards (100) on the MN-CNT shifts from 42.6 to 43.7 ° in comparison with that of pristine CNT, suggesting the smaller interplane spacing.[32] Moreover, the broadened and weakened peak corresponding to (002) plane on M-CNT sample gives a further evidence for the existence of amorphous carbon nitride layer or with less levels of graphitization on M-CNT,[41,42] which may deteriorate catalytic activity in direct dehydrogenation by inhibiting surface active sites from ethylbenzene.[38] Raman is a quite sensitive technique for probing the surface structure.

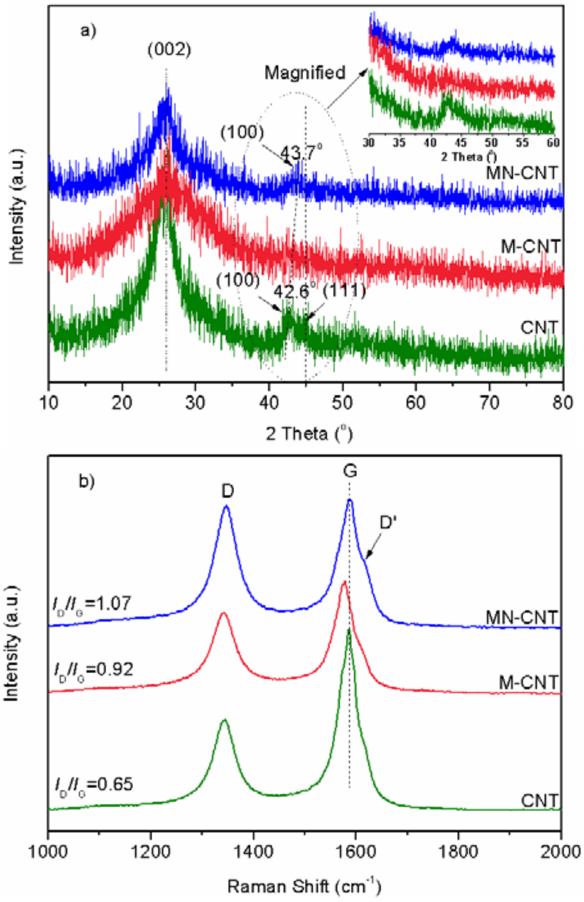

Figure 2. XRD patterns (a) and Raman spectra (b) of MN-CNT, M-CNT, and the pristine CNT samples.

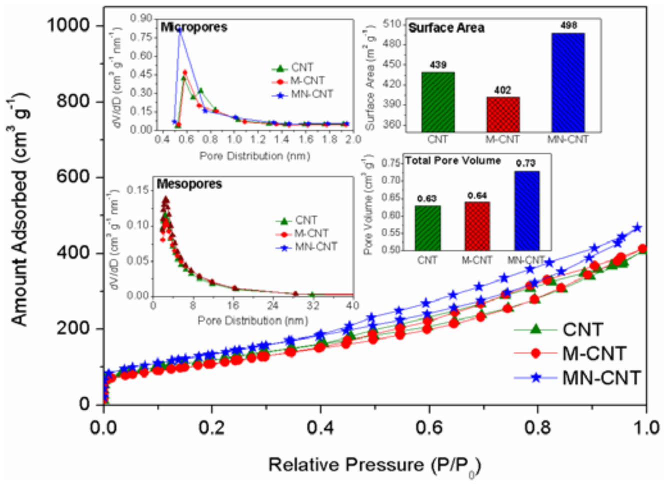

Figure 3. Nitrogen adsorption-desorption isotherms. Inset: BJH pore size distribution from desorption branch, H-K micropore distribution, surface area, and total pore volume of MN-CNT, M-CNT, and the pristine CNT samples.

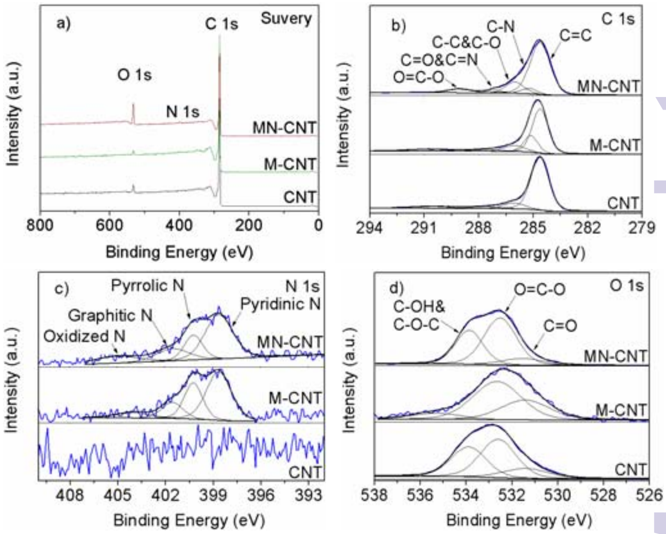

Figure 4. XPS spectra including Survey (a), C 1s (b), N 1s (c) and O 1s (d) spectra of MN-CNT, M-CNT, and the pristine CNT samples.

Therefore, the Raman analyses were further performed on the above three samples. From Figure 2b, the D (A1g mode corresponding to structural defects or disorder carbon) and G (E 2g mode corresponding to ideal graphitic carbon) modes in the range of 1000-2000 cm^{-1} can be observed on the three samples. The higher I_D/I_G for MN-CNT in comparison with that for pristine CNT is an indicator of more structural defect and lattice edge of the as-prepared hybrid composite,[43,44] but the higher I_D/I_G for M-CNT in comparison with that for pristine CNT suggests the surface disordered carbon nitride layer or carbon nitride fragment.[38] This is consistent with the results from HRTEM and XRD analyses. Moreover, the D' peak as a shoulder peak of G band on the Raman spectra of MN-CNT is a further indicator for increased structural defects,[38] in consistent with HRTEM. The enlarged structural defectiveness confirmed by HRTEM and Raman characterization renders MN-CNT to be an excellent catalyst for DDH of ethylbenzene.

The texture characteristics of the as-synthesized MN-CNT, M-CNT, and the pristine CNT were investigated by N_2 adsorption-desorption measurement. From Figure 3, the MN-CNT has much higher specific surface area and pore volume as well as more micropores than the M-CNT and the pristine CNT but with similar mesoporous size distribution, which can be ascribed to the attacking effect on CNT wall by the explosive decomposition of melamine nitrate. The higher surface area may be caused by the increased defects on MN-CNT catalyst. These features of the MN-CNT favor the DDH reaction. Moreover, the lower specific surface area of M-CNT than that of pristine CNT can be caused by the covering effect of carbon nitride layers or carbon nitride fragments on CNT walls that identified by the above HRTEM, XRD and Raman analyses. Surface chemical properties of carbocatalysts significantly affect their catalytic performance in diverse reactions including DDH.[26-34]

XPS, a sensitive and effective technique was employed to investigate the surface chemical properties of the as-synthesized MN-NT, M-CNT, and the pristine CNT samples. The XPS spectra are presented in Figure 4, and the quantitative analytical results are listed in Table S1. From Figure 4a-c and Table S1, the N incorporation into carbon matrix for both MN-CNT and M-CNT can be identified. The main side-products for the DDH of ethylbenzene are benzene and toluene resulted from the cracking of ethylbenzene, which consists with the results reported in references.[26-39] The surface phenolic hydroxyl group and/or possible COOH may promote the cracking of ethylbenzene due to its acidity, since acid sites are active for cracking reaction of hydrocarbon.[26,27,30] 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.[27,30] Moreover, the as-prepared MN-CNT has lower N content than M-CNT, ascribed to the explosive decomposition of O-containing nitrate motif in the melamine nitrate. Furthermore, from Figure 4d and Table S1, the explosive decomposition strategy of the O-containing precursor also lead to the increase in surface O content on MN-CNT. However, the coating of Carbon nitride layer leads to the decreased O content on M-CNT. The O 1s XPS spectra can be deconvoluted into three peaks with the binding energies at around 531.6, 532.4 and 533.7-535.3 eV, assigned to C=O, O=C-O and C-O-C/C-OH containing groups.[31,33,38,45] From Table 1, the contents of surface ketonic C=O groups, the main active sites for DDH reaction, on the as-synthesized MN-CNT, M-CNT, and the pristine CNT are 1.0, 0.5, and 0.65, respectively. From above, the simultaneous defect production and O,N-doping on the MN-CNT were identified.

Carbocatalyzed direct dehydrogenation of ethylbenzene under oxidant- and steam-free has been considered as a green and energy-saving approach for clean production of styrene, an industrially important chemical. Herein, the catalytic performance in ethylbenzene DDH reaction of the as-synthesized MN-CNT, M-CNT, and the pristine CNT was measured. The steady-state styrene rate and the selectivity to

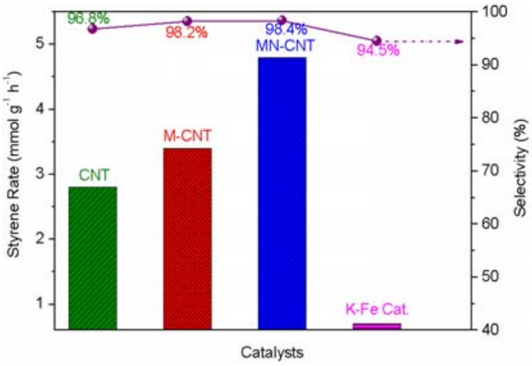

Figure 5. Styrene rate and selectivity of MN-CNT, M-CNT, the pristine CNT, and the industrially used K-Fe catalyst as a function of time on stream for oxidant- and steam-free DDH of ethylbenzene to styrene.

styrene are presented in Figure 5, and the industrially used ethylbenzene DDH K-Fe catalyst is included for comparison. The developed MN-CNT catalyst gives 4.8 mmol g^{-1} h^{-1} of steady-state styrene rate with 98.4% of high styrene selectivity. The catalytic activity of MN-CNT is remarkably higher than that of the as-synthesized M-CNT and the pristine CNT. Correlated to the characterization results, the much superior catalytic performance of MN-CNT benefits from the simultaneous enlargement in structural defectiveness and 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 and the increased specific surface area. Moreover, the removal of carbon nitride layers or carbon nitride fragments may enhance the accessibility of active sites to ethylbenzene, which also favors the DDH reaction. This is in consistent with the previously reported results.[38,40,46] The developed MN-CNT catalyst exhibits 6.9 times of steady-state styrene rate of the K-Fe catalyst, implying a bright prospect for future industrial application in clean and energy-saving production of styrene.

In summary, we present a clean and energy-saving method for styrene production by the direct dehydrogenation of ethylbenzene over novel and efficiently O,N-doped CNT catalyst. The surface structural defects enriched O,N-doped CNT catalyst was successfully prepared by a facile one-step explosive decomposition method. The developed carbocatalyst in this work exhibits a high catalytic activity towards the DDH of ethylbenzene to styrene, which benefits from the increased structural defects, enriched surface ketonic C=O group, enlarged specific surface area, as well as the improved nucleophilicity of surface ketonic C=O due to electronic enrichment and basic properties of materials caused by N-doping. The work paves a new avenue for preparing the other highly-efficient carbocatalysts in diverse organic transformations.

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Facile simultaneous defect producing and O,N-doping of carbon nanotube with unexpected catalytic performance for clean and energy-saving production of styrene†

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This work presents a facile and efficient strategy for synthesis of the structural defect-rich O,N-doped CNT catalyst with unexpected catalytic performance in direct dehydrogenation of ethylbenzene for clean and energy-saving production of styrene, ascribed to the simultaneously increase in surface ketonic group amount, enlarged structural defectiveness, increased specific surface area and pore volume as well as the improved nucleophilicity of C=O and enhanced basic properties caused by N-doping.