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Electronic Supplementary Information

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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Experimental Section

Synthesis of the catalysts

The commercially supplied carbon nanotube (CNT) with less than 8 nm outer diameter and 10-30 length (Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, China) was washed by H₂SO₄/HNO₃ mixed aqueous solution to remove the residual metal particles. The purified CNT was used parent material to prepare N-CNTs. The detailed preparation procedure was presented as follows: the hexamethylenetetramine was dissolved into ethanol, and then a desired amount of nitric acid was added into above alcohol solution, the formed solid was recovered by filtering and the followed alcohol washing process, and therefore the hexamethylenetetramine nitrate was obtained and denoted as HN. Then the CNT was finely ground with HN in an agate mortar with the required mass ratios of HN to CNT (10:1), and then heated up to desired temperature in N₂ for pyrolysis process at the certain ramp rate to obtain the final HN-CNT sample. Replaced HN by hexamethylenetetramine, the classical N-doped CNT was prepared and denoted as H-CNT.

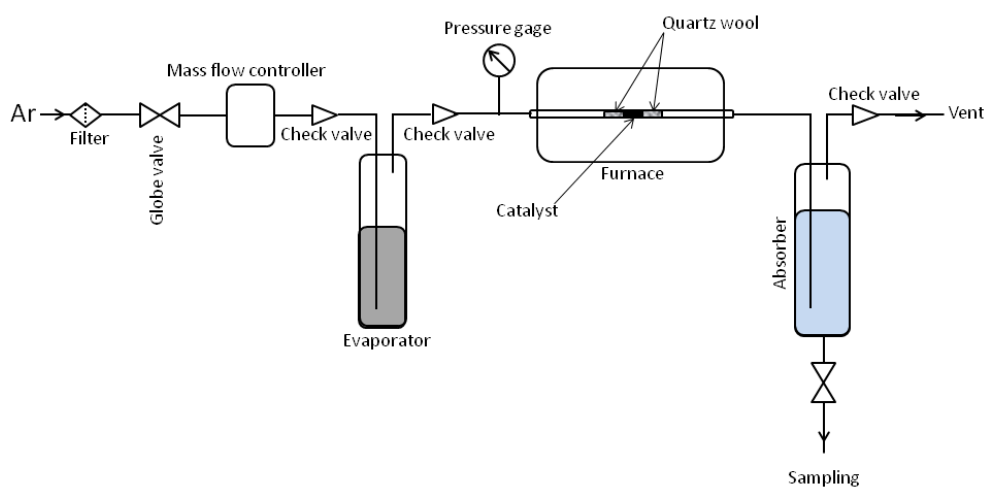
Catalysts characterization

X-ray diffraction (XRD) profiles were collected from 10 to 90° at a step width of 0.02° using Rigaku Automatic X-ray Diffractometer (D/Max 2400) equipped with a CuKα source ($\lambda = 1.5406 \text{ \AA}$). Transmission electron microscopy (TEM) images were obtained by using Tecnai F30 HRTEM instrument (FEI Corp.) at an acceleration voltage of 300 kV. The XPS spectra were carried out on an

ESCALAB 250 XPS system with a monochromatized Al Ka X-ray source (15 kV, 150 W, 500 μm , pass energy = 50 eV). Raman spectra were measured using a laser with an excitation wavelength of 532 nm at room temperature on a Thermo Scientific DXR Raman microscope. Nitrogen adsorption and desorption isotherms were determined on a Beishide apparatus of model 3H-2000PS1 system at $-196\text{ }^{\circ}\text{C}$. The specific surface areas were calculated by the BET method as well as the micropore and mesopore size distributions were calculated from adsorption branch of the isotherm by H-K and BJH model, respectively.

Catalytic performance measurement

Direct dehydrogenation of ethylbenzene was performed over the developed HN-CNT catalyst and the experimental details are as follows: the reaction was performed at $550\text{ }^{\circ}\text{C}$ for 20 hours in a stainless steel, fixed bed flow reactor (Scheme S1, 6 mm O.D.). 25 mg catalyst was loaded at the centre of the reactor with two quartz wool plugs at its two sides. The system was heated to $600\text{ }^{\circ}\text{C}$ and kept for 30 min in Ar for pretreating catalyst. After the system was cooled down to $550\text{ }^{\circ}\text{C}$ and kept for 10 min, the feed containing 2.8% ethylbenzene with a flow rate 10 ml min^{-1} and Ar as balance was then fed into the reactor from a saturator kept at $40\text{ }^{\circ}\text{C}$. The effluent from the reactor was condensed in two traps containing certain amount of ethanol connected in a series. The condensed material was cooled externally in an ice water bath. Quantitative analysis of the collected reaction products (ethylbenzene, styrene, toluene, and benzene) was performed on a FULI 9790 II GC equipped with HP-5 column, $30\text{ m}\times 0.32\text{ mm}\times 0.25\text{ }\mu\text{m}$, and FID detector. The resulting carbon balance was above $100\pm 4\%$ in all reactions. The steady-state styrene rate (20 h of time on stream) and selectivity of styrene are employed as the evaluation standard for the catalytic performance of the fabricated catalysts. The styrene rate is calculated as the formed styrene molar amount per g catalyst per hour, and the selectivity of styrene is denoted as the percentage of the desired styrene to the total products including the desired styrene and the by-products that containing benzene and toluene. For comparison, the catalytic properties of H-CNT and the pristine CNT, as well as the industrially-used K-Fe catalysts were also measured.



Scheme S1 schematic illustration of the reactor.

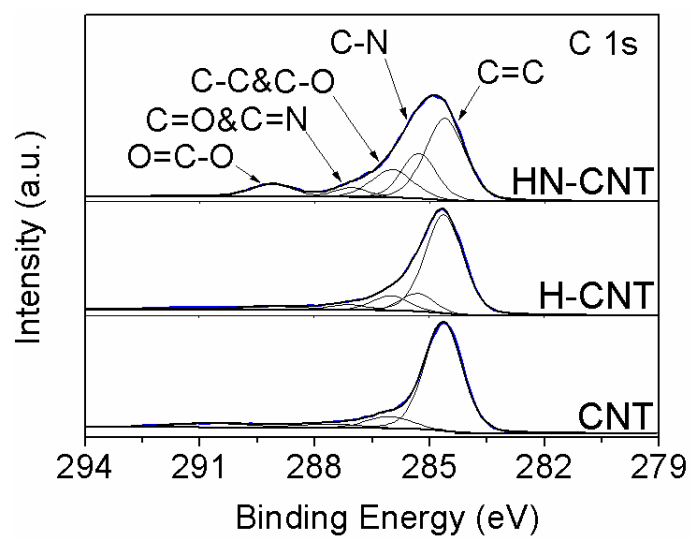


Fig. S1 XPS C 1s spectra of HN-CNT, H-CNT, and the pristine CNT samples.

Table S1 The relative integrated intensity of deconvoluted N 1s and O 1s XPS spectra for HN-CNT, H-CNT, and pristine CNT samples.

Sample	N ^a (%)	N-1 ^b (%)	N-2 ^b (%)	N-3 ^b (%)	N-4 ^b (%)	O ^c (%)	C=O (%)	C-OH/C-O (%)	O=C-O (%)
CNT	0	-	-	-	-	4.1	15.8	36.4	47.8
H-CNT	3.3	47.2	21.9	23.4	7.5	3.2	18.7	56.7	24.6
HN-CNT	1.3	40.5	27.6	23.1	8.8	13.7	6.9	40.3	52.8

^a The surface N content of the materials from XPS. ^b Percentage of various nitrogen species occupying in the total N content; N-1, N-2, N-3, and N-4 are denoted as pyridinic N, pyrrolic N, graphitic N, and oxidized N, respectively. ^c O atom molar percentage on the material surface from XPS analysis.