

Electronic Supplementary Information

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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Experimental Section

Materials preparation

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: Based on the reference,¹⁻⁴ the melamine nitrate (MN) was prepared. Then the CNT was finely ground with MN in an agate mortar (1:30 mass ratio), and then heated up to the 750 °C in N₂ atmosphere for pyrolysis process at the ramp rate of 5 °C min⁻¹ to obtain the final MN-CNT sample. Replaced MN by melamine (1:30), the classical N-doped CNT was prepared and denoted as M-CNT.

Materials 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 CuK α source ($\lambda = 1.5406 \text{ \AA}$). Field emission scanning electron microscope (FESEM) experiments were performed on JEOL JSM-5600LV SEM/EDX instrument. 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 K α 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 °C. The specific surface areas were calculated by the BET method as well as the micropore and mesopore size distributions were calculated from desorption branch of the isotherm by H-K and BJH model, respectively.

Catalytic performance measurement

The oxidant- and steam-free direct dehydrogenation of ethylbenzene was performed over the developed catalyst and the experimental details are as follows: the reaction was performed at 550 °C for 20 hours in a stainless steel, fixed bed flow reactor (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 °C and kept for 30 min in Ar for pretreating catalyst. After the system was cooled down to 550 °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 °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 m×0.32 mm×0.25 μm, and FID detector. The resulting carbon balance was above 100±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 the pristine ND, and the industrially-used K-Fe catalysts were also measured.

References

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

Samples	N ^a (%)	N-1 ^b (%)	N-2 ^b (%)	N-3 ^b (%)	N-4 ^b (%)	O ^a (%)	C=O (%)	C-OH/ CO-C (%)	O=C-O (%)
MN-CNT	0.8	51.2	19.3	16.6	12.9	9.9	10.5	34.1	55.4
M-CNT	1.8	50.1	27.9	14.2	7.8	1.6	31.2	10.0	58.8
CNT	0	-	-	-	-	4.1	15.8	36.4	47.8

^aThe N and O atom content measured by XPS analysis. ^bPercentage 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.