

Electronic Supplementary Information

Air-activated nitrogen-doped carbon nanotube as an efficient catalyst for ethylbenzene direct dehydrogenation†

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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 prepared nitrogen-CNTs. The detailed preparation procedure was presented as follows: The CNT was finely ground with melamine (mass ratio of CNT to melamine is 1:30) in an agate mortar, the mixture was air activated in muffle at a 300 °C for desired time, and then heated up to the 750 °C and maintained at this temperature for 0.5 h in N₂ atmosphere for pyrolysis process at the certain ramp rate to obtain the final A-M-CNT material. The classical N-doped CNT (M-CNT) was prepared by the same method and conditions as those for the preparation of A-M-CNT except for removing the air activation process.

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 CuKα source ($\lambda = 1.5406 \text{ \AA}$). 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 Kα 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.

Catalytic performance measurement

The direct dehydrogenation of ethylbenzene under oxidant- and steam-free conditions, as a model 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 styrene rate 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 M-CNT and the pristine CNT as well as the industrially-used K-Fe catalysts were also measured.