

Supporting information:

Enhancing chemical reactions in a confined hydrophobic environment: a NMR study of benzene hydroxylation in carbon nanotubes

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Experimental Section

Material synthesis. DWNTs have been synthesized and purified following a reported procedure ^[1] i.e. refluxing in nitric acid, oxidation in static air, followed by annealing at 1400 °C in an ultra-high vacuum system. The purified DWNTs have opened caps. The inner diameter falls in a range of 1.0-1.5 nm and the outer diameter 1.5-2.0 nm.

Re@DWNT was prepared by exposing evacuated DWNTs (10^{-3} Pa at 400 °C) to $\text{Re}(\text{CH}_3)_3\text{O}_3$ vapor. The mixture was kept at 100 °C for 48 h before exposure to anhydrous ethanol in Ar. Then it was treated with ethanol and deionized water to remove Re species on the outer walls, followed by drying under ambient condition. Re/AC was prepared by dispersing AC (Alfa Aesar carbon black acetylene 50% compressed 039724) in ethanol under ultrasonication, followed by addition of an anhydrous ethanol solution of $\text{Re}(\text{CH}_3)_3\text{O}_3$ dropwise, evaporation of solvent and the same drying procedure as Re@DWNT.

Characterization. Transmission electron microscopy (TEM) measurements were carried out on a FEI Tecnai G2 microscope operated at an accelerating voltage of 120 kv. The samples were ultrasonically suspended in ethanol and placed onto a carbon film supported over a copper grid.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) showed Re loading of 8.4wt% in Re@DWNT, 8.0wt% in Re/DWNT, and 1.1wt% in Re@DWNT-2 and Re/AC.

Prior to NMR study, they were dehydrated at 450 °C for 16 h. 12 μL $^{13}\text{C}_6\text{H}_6$ (Sigma-Aldrich, 99 atom% ^{13}C) was sealed in a capillary, which was inserted into 5 mm MAS NMR rotor containing 60 mg DWNTs. All NMR spectra were collected on Varian Infinityplus-400 spectrometer. The chemical shifts of ^{13}C NMR spectra were referenced to adamantane with the up-field methine peak at 29.5 ppm. The NMR measurement parameters used for dynamic monitoring of the intensity change and quantitative analysis were summarized in Table S1.

Table S1. The NMR measurement parameters

| | MAS | Rotor | Pulse angle | Pulse width | Recycle delay |
|-----------------------|---------|-------|-------------|-------------------|---------------|
| dynamic monitoring | 2.5 KHz | 5 mm | $\pi/2$ | 4.5 μs | 1 s |
| Quantitative analysis | 8 KHz | 5 mm | $\pi/4$ | 2.5 μs | 30 s |

Table S2. Spin–lattice relaxation time (T1) measured for benzene and acetic acid.

| | Ben _{in} | Ben _{out} | Ac _{in} | Ac _{out} |
|----|-------------------|--------------------|------------------|-------------------|
| T1 | 145 ms | 207 ms | 185 ms | 5.9 s |

Catalytic hydroxylation of benzene. Catalytic hydroxylation of benzene to phenol was carried out in a 50 ml stainless steel reactor with 1 ml benzene, 8 ml 75%(v/v) acetic acid aqueous solution, 1 ml 30% H_2O_2 , 100 mg catalyst and 80 °C for 5 h. The products were cooled down in ice-water overnight before analysis by GC (Agilent 7890 equipped with an Innowax column and a FID detector).

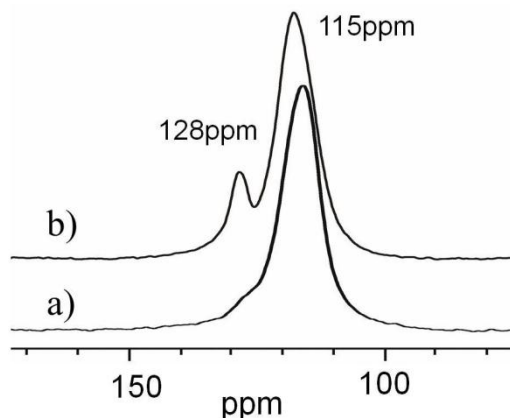


Figure S1. ^{13}C NMR spectra (a) for adsorption of benzene, which has been allowed sufficient time for stabilization following the experiments in Figure 2. (b) In order to confirm the assignment of the 115 ppm signal, we have carried out the following experiments: The rotor is opened and the outside signal at 128 ppm signal disappears, which is likely attributed to evaporation of benzene out of the rotor. Then more benzene is added directly into the rotor, leading to reappearing of the 128 ppm signal while the 115 ppm peak remains almost unchanged in this spectrum. Therefore, the 115 ppm signal can be safely attributed to benzene inside DWNTs.

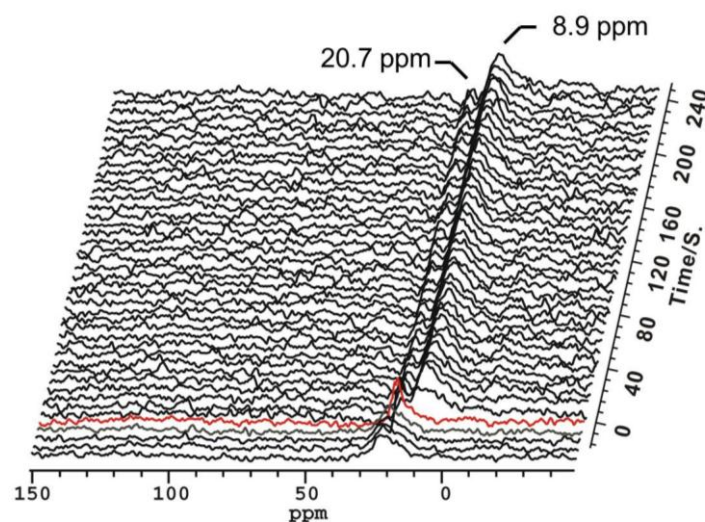


Figure S2: ^{13}C MAS NMR spectra upon exposure of DWNTs to acetic acid at room temperature. The 20.7 ppm signal is attributed to the outside acetic acid while the 8.9 ppm to the inside acetic acid.

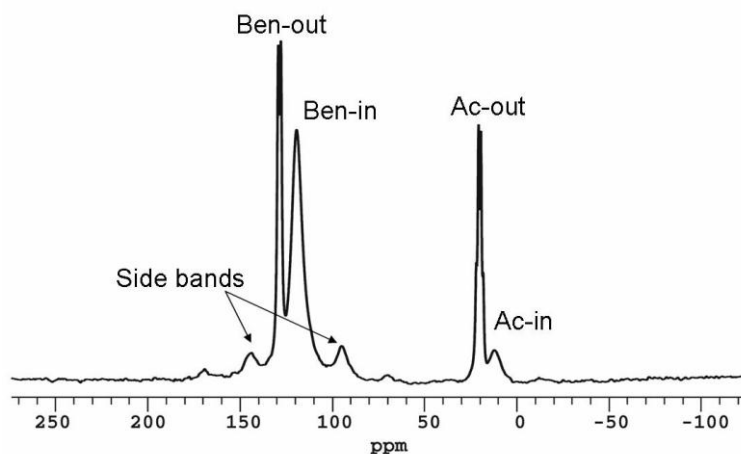


Figure S3. ^{13}C solid NMR spectrum recorded following the experiments in Figure 2. The relaxation delay in the pulse sequence has been allowed for 30 s for quantitative analysis of the relative concentration of benzene and acetic acid inside and outside of DWNTs. The integral peak area of benzene is divided by six because of six labeled ^{13}C atoms, while there is only one ^{13}C atom in acetic acid. The area of the side bands for the inside benzene signal is also included while the side bands for the outside signal are negligible. By estimating the total area of the benzene signals (including the inside and outside signals) and that of the acetic acid signals, one can obtain the molar ratio of benzene to acetic acid in the bulk, $\text{Ben}_{\text{bulk}}/\text{Ac}_{\text{bulk}}$ to be 1.11.

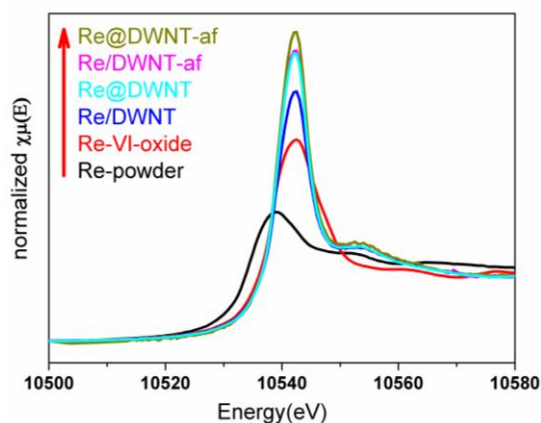


Figure S4 Re L3 edge XANES spectra of Re@DWNT, Re/DWNT, Re@DWNT-af (Re@DWNT after benzene hydroxylation) and Re/DWNT-af (Re/DWNT after reaction) XANES was performed at the BL14W1 beamline of the Shanghai Synchronic Radiation Facility (SSRF). All the XANES spectra were taken using a

constant scan step of 0.2 eV through the edge region. Energy calibration was performed with Re powder. The results show that the valence state is similar for the inside and outside Re species.

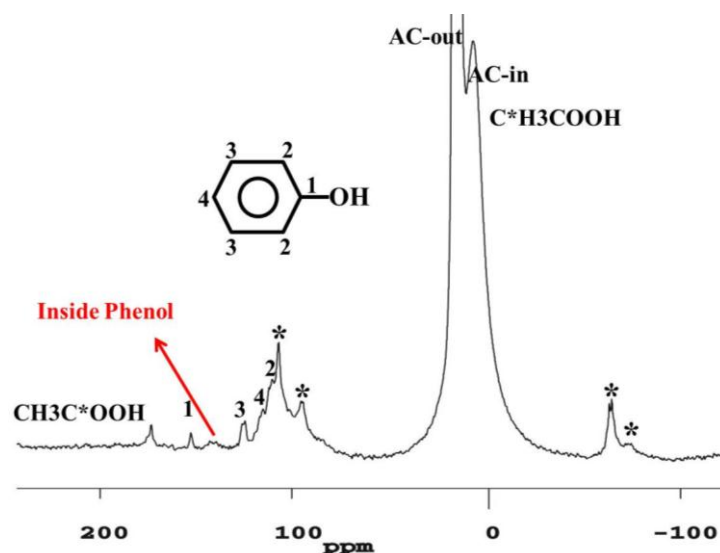


Figure S5. ^{13}C NMR spectra upon exposing DWNTs to phenol dissolved in a small amount of acetic acid (3.1 mg ^{13}C labeled phenol in 40 μL acetic acid, 20 mg DWNTs). The inside signal for phenol can be identified at 146.0 ppm, marked with a red arrow, which is shifted up-field by about 10 ppm with respect to the corresponding outside signal, in agreement with a series of other molecules such as methanol, benzene and acetic acid. In addition, three other peaks are observed in the range of 110-130 ppm corresponding to the outside phenol (115.5 ppm–2# C, 121.1 ppm–4# C, 129.8 ppm–3# C).

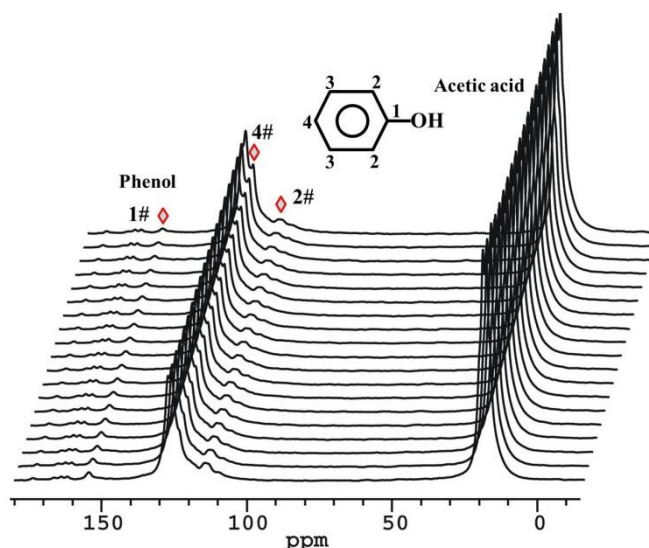


Figure S6. In situ ^{13}C MAS NMR spectra taken during benzene hydroxylation over Re@DWNTs with marked signals corresponding to phenol on the outside of DWNTs. Reaction conditions: 80 °C, 5 μL $^{13}\text{C}_6\text{H}_6$, 30 μL acetic acid (methyl labeled by ^{13}C), and 10 μL H_2O_2 (30%), 20 mg Re@DWNTs. Each spectrum was collected within 16.06 min without dwelling time. The spin rate of the rotor is 8 kHz. It can be seen that the outside phenol signal has already appeared in the first spectrum during the reaction, further confirming that phenol prefers to stay on the outside of DWNTs although we do not observe the transport process.

References:

- [1] H. Yu, Q. Zhang, Q. F. Zhang, Q. X. Wang, G. Q. Ning, G. H. Luo and F. Wei, *Carbon* 2006, **44**, 1706-1712.