## **Supplementary Information for**

# Mapping the Dynamics of Methanol and Xenon Co-adsorption in SWNTs by *in situ* Continuous-flow Hyperpolarized <sup>129</sup>Xe NMR

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## **Experimental section**

#### **Sample Preparation**

SWNTs were provided by Tsinghua-Foxconn Nanotechnology Research Center (TFNRC).<sup>1</sup> SEM and TEM results showed that the SWNTs exhibited superaligned arrays with average inner diameters of 2 to 2.5 nm (Figure S2). Because the SWNTs were grown on a silicon substrate, they had no metal catalysts in the final products. Electron Spin Resonance (ESR) result (Figure S3) demonstrated that the SWNTs had a very high purity that was sufficient for NMR characterization. MCM-41 was synthesized by the method described in references 2 and 3. XRD and TEM results showed that the sample had a good crystallization with an average inner diameter of 2 nm (Figure S4).

#### In situ Continuous-flow HP <sup>129</sup>Xe NMR Experiment

Prior to the in situ HP <sup>129</sup>Xe NMR experiments, about 10 mg samples were dehydrated at 300 °C for 20 h in vacuum ( $<10^{-2}$  Pa). Also the SWNTs were not densely packed to ensure that Xe is more accessible from the outside to the inside nanotubes. As we previously reported,<sup>4-6</sup> laser-hyperpolarized <sup>129</sup>Xe was achieved with an optical pumping cell in the fringe field of spectrometer magnet and 60 W diode laser array (Coherent). A continuous flow of 1 % Xe-1 % N<sub>2</sub>-98 % He gas mixture was delivered at a rate of 150 ml/min to the rotor reactor with natural abundant CH<sub>3</sub>OH (Aldrich) bubbled with dry helium gas at a rate of 10 ml/min. One-dimensional HP <sup>129</sup>Xe MAS NMR spectra were accumulated on a Varian Infinityplus-400 spectrometer at 110.6 MHz with a  $\pi/2$  pulse width of 3  $\mu$ s, a 0.5 s recycle delay and 60 scans for SWNTs, and a 2 s recycle delay and 15 scans for MCM-41. The chemical shifts were referenced to the signal of <sup>129</sup>Xe gas. The chemical shift of the referenced <sup>129</sup>Xe gas was treated temperature independent, since its variation was within 1 ppm in the whole temperature range of the measurements because of the very low concentration of xenon. Note that the acquisition of HP <sup>129</sup>Xe NMR was under continuous-flow condition and the fresh HP <sup>129</sup>Xe would completely exchange with the adsorbed <sup>129</sup>Xe in the nanochannels in the time range of 0.2 s, thus the signal intensity of HP <sup>129</sup>Xe was independent of recycle delay time. Blank experiments of four different recycle delay times from 0.05 to 8 s have been performed at 20 °C before the *in situ* NMR experiments (Figure S10). It showed that a recycle delay of 0.5 s was sufficient for our experiments and it was hence used in this work. In our *in situ* NMR setup,

mass spectroscopy (MS) was connected with the NMR probe to detect the exhaust gas concentration (Figure S1).

#### **Computational Methods**

Grand Canonical Monte Carlo (GCMC) method was used to study the co-adsorption of Xe and CH<sub>3</sub>OH in confined nanochannels. Two unidimensional pore systems including (10, 10) SWNT and zeolite with the framework structure of VFI were investigated. The structure of Si-VFI was optimized with the DMol3 program<sup>7</sup> after replacing all of Al, P with Si atoms, using a PW91 correlation functional and the DNP basis set.<sup>8</sup> The pore diameter of the zeolite was approximately 1.5 nm, similar to that of the (10, 10) nanotube. Periodic boundary conditions were exerted in all three dimensions and the frameworks were assumed to be rigid in the simulation. The box used for CNT was 33.814 × 33.814 × 24.595Å, and  $37.95 \times 37.95 \times 24.312Å$  for VFI-zeolite. The adsorption isotherms of Xe and Xe-methanol systems at 253K were carried out by the Sorption module of Materials Studio. For both systems, the equilibration steps were set to 500,000 and the production steps were set to 1,500,000.

The Xe NMR chemical shift was calculated by the GIAO method <sup>9,10</sup> and reported in ppm relative to the free Xe molecule. Density functional theory with the B3LYP hybrid functional method<sup>11-14</sup> and standard DZVP basis sets<sup>15</sup> were employed here. The calculated resonance of <sup>129</sup>Xe NMR in Xe-Xe system is very similar to that reported in the literature,<sup>16</sup> which means the method used here can obtain reasonable results. Counterpoise (CP) correction was applied to reduce the basis set superposition error (BSSE),<sup>17</sup> which is important not only for interaction energies but also for molecular electronic properties. All of the calculations were performed using Gaussian09.<sup>18</sup>



Figure S1. Sketch of the experimental setup for *in situ* continuous-flow MAS NMR study.



**Figure S2.** Scanning Electron Microscope (SEM) (left) and High Resolution Transmission Electron Microscope (HRTEM) (right) graphs of SWNTs. SEM image was obtained on a FEI Quanta 200F field emission scanning microscope working at an acceleration voltage of 20 kV. HRTEM was performed on a FEI F30 microscope operated at an acceleration voltage of 200 kV.

SWNT



**Figure S3.** Electron Spin Resonance (ESR) spectrum of SWNTs sample. ESR was carried out on a Bruker EMX spectrometer at 77 K. A microwave frequency of 9.813 GHz and a power of 30 mW were used.



**Figure S4.** (a) X-ray diffraction (XRD) pattern and (b) Transmission Electron Microscope (TEM) image of MCM-41. XRD was performed on a Rigaku D/Max 2500 diffractometer with a Cu Kα radiation source. TEM was carried out on a FEI Tencnai G<sup>2</sup> Spirit at an acceleration voltage of 120 kV.



**Figure S5.** (a) *In situ* HP <sup>129</sup>Xe MAS NMR spectra recorded as a function of time, with a time resolution of 30 s per spectrum during adsorption and desorption of methanol in MCM-41 nanochannels at 0 °C; (b) Time variation in relative peak intensities of <sup>129</sup>Xe in nanochannels and in gas phase. The solid lines were normalized experimental data, described in the text and the dashed lines are the best fits to the data of <sup>129</sup>Xe nanochannels.



**Figure S6.** (a) *In situ* HP <sup>129</sup>Xe MAS NMR spectra recorded as a function of time, with a time resolution of 30 s per spectrum during adsorption and desorption of methanol in MCM-41 nanochannels at 20 °C; (b) Time variation in relative peak intensities of <sup>129</sup>Xe in nanochannels and in gas phase. The solid lines were normalized experimental data, described in the text and the dashed lines are the best fits to the data of <sup>129</sup>Xe nanochannels.



**Figure S7.** (a) *In situ* HP <sup>129</sup>Xe MAS NMR spectra recorded as a function of time, with a time resolution of 30 s per spectrum during adsorption and desorption of methanol in SWNTs nanochannels at 0 °C; (b) Time variation in relative peak intensities of <sup>129</sup>Xe in nanochannels and in gas phase. The solid lines were normalized experimental data, described in the text and the dashed lines are the best fits to the data of <sup>129</sup>Xe nanochannels.



**Figure S8.** (a) *In situ* HP <sup>129</sup>Xe MAS NMR spectra recorded as a function of time, with a time resolution of 30 s per spectrum during adsorption and desorption of methanol in SWNTs nanochannels at 20 °C; (b) Time variation in relative peak intensities of <sup>129</sup>Xe in nanochannels and in gas phase. The solid lines were normalized experimental data, described

in the text and the dashed lines are the best fits to the data of <sup>129</sup>Xe nanochannels.



**Figure S9.** MS spectra recorded time variation in signal intensities of methanol and Xe in exhaust gases of SWNTs and MCM-41. nanochannels and in gas phase.



**Figure S10.** (a) HP <sup>129</sup>Xe MAS NMR spectra recorded at various recycle delay times of MCM-41; (b) HP <sup>129</sup>Xe MAS NMR spectra recorded at various recycle delay times of SWNTs. The acquisition scans were both 16.

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