Supporting Information

Syngas segregation induced by confinement in carbon nanotubes: a combined first-principles and Monte-Carlo study

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Choice of the basis set in first principles calculations of the binding energies of H₂ and CO

The size of the cluster model and basis set chosen for this study were determined by comparing the binding energies of H₂ on a planar graphite layer with those obtained by the more accurate MP2/aug-cc-PVTZ method.^{S1,S2} Adsorption of H₂ at the same orientation was considered at distances of 3.0 and 3.1 Å from the graphite surface, as in earlier studies.^{S1, S2} Similar cluster models $C_{16}H_{10}$ and $C_{24}H_{12}$ were used to model the graphite layer. Binding energy is defined as $E_b^{graphite} = E^{graphite-molecule}$. E^{graphite}- $E^{molecule}$. Figure S1 shows that both 6-311++g (2d, p) and 6-311++g (2d, 2p) basis sets (without BSSE correction) give reasonable binding energies of -0.071 and -0.072 eV, respectively, compared to the reference value (-0.064 eV) reported earlier.^{S1} In comparison, a basis set larger than 6-311g (d, p) containing additional diffusion functions leads to a much higher binding energy is -0.0418 eV using the 6-311++g (2d, p) basis set and the $C_{16}H_{10}$ model and -0.0490 eV on the cluster $C_{24}H_{12}$. Both values are much smaller than the reference value. Therefore, we chose the 6-311++g (2d, p) basis set without the BSSE correction and the $C_{16}H_{10}$ cluster in the following calculations as an optimum compromise considering the computational time and accuracy.



Figure S1. Binding energy of H_2 on a planar graphite layer as a function of the size of basis sets using the MP2 method without BSSE correction. The squares and circles represent the H_2 binding energies obtained with the model $C_{16}H_{10}$, while the triangles and diamonds represent those with the model $C_{24}H_{12}$. H_2 molecules are placed at a distance of 3.0 Å and 3.1 Å from the center of H_2 to the center of a hexagonal carbon ring of the CNT surface, respectively. The dashed line corresponds to the reference value of -0.064 eV for H_2 adsorbed on the cluster model $C_{24}H_{12}$ at an equilibrium distance of 3.0 Å reported by Ferre-Vilaplana.^{S1}

model	ϵ_{CS}/k_B	σ_{CS}	ϵ_{OS}/k_B	$\sigma_{\rm OS}$	ϵ_{HS}/k_B	σ_{HS}	
	(K)	(Å)	(K)	(Å)	(K)	(Å)	
2LJ	35.5 ⁸³	3.39	42.0 ^{S3}	3.14	32.2 ^b	3.18	
3LJ	19.3 ^a	3.36	47.2 ^a	3.01	32.2 ^b	3.18	

Table S1. Cross-interaction LJ parameters for H₂-graphite and CO-graphite

The subscript "s" stands for the interactions between graphite C-C; ^{*a*} and ^{*b*} indicate potential parameters for CO-graphite and H-graphite interactions calculated using the Lorentz-Berthelot rules. ^{S4}

model	ε _C /k _B (K)	σ _C (Å)	ε _O /k _B (K)	σ ₀ (Å)	ε _H /k _B (K)	σ _H (Å)	ε _s /k _b (K)	σ _s (Å)
2LJ	39.9 ^{\$5}	3.39	61.6 ⁸⁵	2.89	36.7	2.89	28.2	3.35
3LJ	13.2 ^{\$4}	3.83	80.1 ^{S4}	3.12	36.7	2.89	28.2	3.35

Table S2. LJ potential parameters for interactions between H₂-H₂, CO-CO and graphite C-C

The subscript "s" stands for the interactions between graphite C-C.

Table S3. LJ potential parameters for H₂ and CO molecules interacting with a (7, 7) CNT

model	Exterior (7, 7)						Interior (7, 7)					
	ε _{CS} /k _B (K)	σ _{cs} (Å)	ε _{OS} /k _B (K)	σ _{os} (Å)	ε _{HS} /k _B (K)	σ _{HS} (Å)	ε _{CS} /k _B (K)	σ _{cs} (Å)	ε _{OS} /k _B (K)	σ _{os} (Å)	ε _{HS} /k _B (K)	σ _{HS} (Å)
2LJ	30.1	3.39	35.6	3.14	29.7	3.18	41.5	3.39	49.1	3.14	43.5	3.18

The subscript "s" stands for the interactions between CNT C-C.

Table S4. LJ potential parameters for H₂ and CO molecules interacting with a (15, 15) CNT

model	Exterior (15, 15)						Interior (15, 15)					
	ε _{CS} /k _B (K)	σ _{CS} (Å)	ε _{OS} /k _B (K)	σ _{os} (Å)	ε _{HS} /k _B (K)	σ _{HS} (Å)	ε _{CS} /k _B (K)	σ _{CS} (Å)	ε _{OS} /k _B (K)	σ _{os} (Å)	ε _{HS} /k _B (K)	σ _{HS} (Å)
2LJ	33.0	3.39	39.1	3.14	31.4	3.18	40.1	3.39	47.4	3.14	33.8	3.18

The subscript "s" stands for the interactions between CNT C-C.



Comparisons of the interactions of H₂ and CO on (10, 10) CNT using different methods

Figure S2. The potential energy surfaces (PES, U_i) of (a) H_2 ; and (b) CO on the $C_{16}H_{10}$ cluster model of (10, 10) CNT calculated using the parameters of a planar graphite layer for both the interior and exterior CNT surfaces (LJ_e, Table S1), and the potential parameters from 2LJ and 3LJ models (Table 1 of the manuscript), in comparison with those obtained from MP2 binding energy (BE) curves. LJ designates a Lennard-Jones potential. Although the interaction energies differ using different methods, the interior binding energies are always higher than the exterior ones. However, compared to the LJ_e and 3LJ models, the PES from the 2LJ model was much closer to that from ab-initio binding energy curves.

The influence of the interior (13, 13) potentials on the interactions of molecules-interior (10, 10) surface

This analysis was carried out by comparing the potential energy surfaces (defined by U_i in Equation 3) of H₂ on the cluster models of the (10, 10) SWNT and the (10, 10)-(13, 13) DWNT, respectively. As shown in Figure S3, the minima of the interaction energy for H₂ adsorption on the interior of (10, 10)-(13, 13) DWNT (DWNT^{int}) is approximately 11.8% larger than that on the (10, 10) SWNT interior (SWNT^{int}), and the one on the DWNT^{ext} is about 18.2% larger than on the SWNT^{ext}. Thus, the potentials of the (13, 13)^{int} can be considered to affect only slightly the

interactions of the inside H_2 with the $(10, 10)^{int}$. Similarly, the effect of the potentials of the $(10, 10)^{ext}$ on the interactions of the outside H_2 with the $(13, 13)^{ext}$ can also be neglected.



Figure S3. The potential energy surfaces (PES) of H_2 on the interior and exterior of CNTs calculated using the potential parameters from a 2LJ model. The (10, 10) SWNT and (13, 13)/ (10, 10) DWNT were modeled with $C_{16}H_{10}$ and $C_{32}H_{20}$ fragments, respectively.



Figure S4. The MP2 binding energy curves for (a) H_2 ; (b) CO on different sites of a (10, 10) CNT surface as a function of the distance from the center of the adsorbed molecule to the CNT surface.

Differential electron density of molecule-CNT



Figure S5. (a) The electrostatic potential of a (7, 7) CNT. The red lines parallel to the electrostatic potential (ESP) axis represent the CNT walls. The blue lines with arrows indicate the direction of the induced electron shift. Contour plots of the change in electron density for (b) H₂ adsorbed on site A of the exterior (10, 10) surface at a distance of 7 Å; (c) and (d) CO adsorbed on the most stable site B of the interior and exterior (10, 10) surfaces, respectively. The area of the plot in (b) is 280 Bohr² and in (c)-(d) 196 Bohr².

Figure S6. The MP2 binding energy curves for (a) H_2 ; and (b) CO adsorbed on the most stable sites of (7, 7), (10, 10) and (15, 15) CNTs.

Figure S7. Concentrations of CO and H_2 molecules inside and outside of a (10, 10)-(13, 13) DWNT as a function of pressure obtained with the potential parameters from (a) 3LJ model; and (b) graphite for both the interior and exterior surfaces. The insert figure shows the ratio of CO/H₂ inside the CNT (filled squares) in comparison to the ratio in the gas phase (the dashed line).

Figure S8. Local concentrations of CO and H_2 molecules inside and outside of CNTs with different diameters as a function of pressure.

References

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