Design of 2D materials for selective adsorption: a comparison between Monte Carlo simulations and direct numerical integration

Electronic Supplementary Information (ESI)

1. Effect of box size

The number of molecules in each simulation depended on the pressure and pore width, and varied between 10 and 1603. We selected an area that would ensure that no less than 10 molecules were present at the lowest pressure studied (10 kPa).

We carried out a size effect analysis for two different areas: 6 nm x 6 nm (small size) and 12 nm x 12 nm (large size). The results (see Figure S1 and Figure S2) were comparable, so we used 12 nm x 12 nm and did not investigated further the size effect.

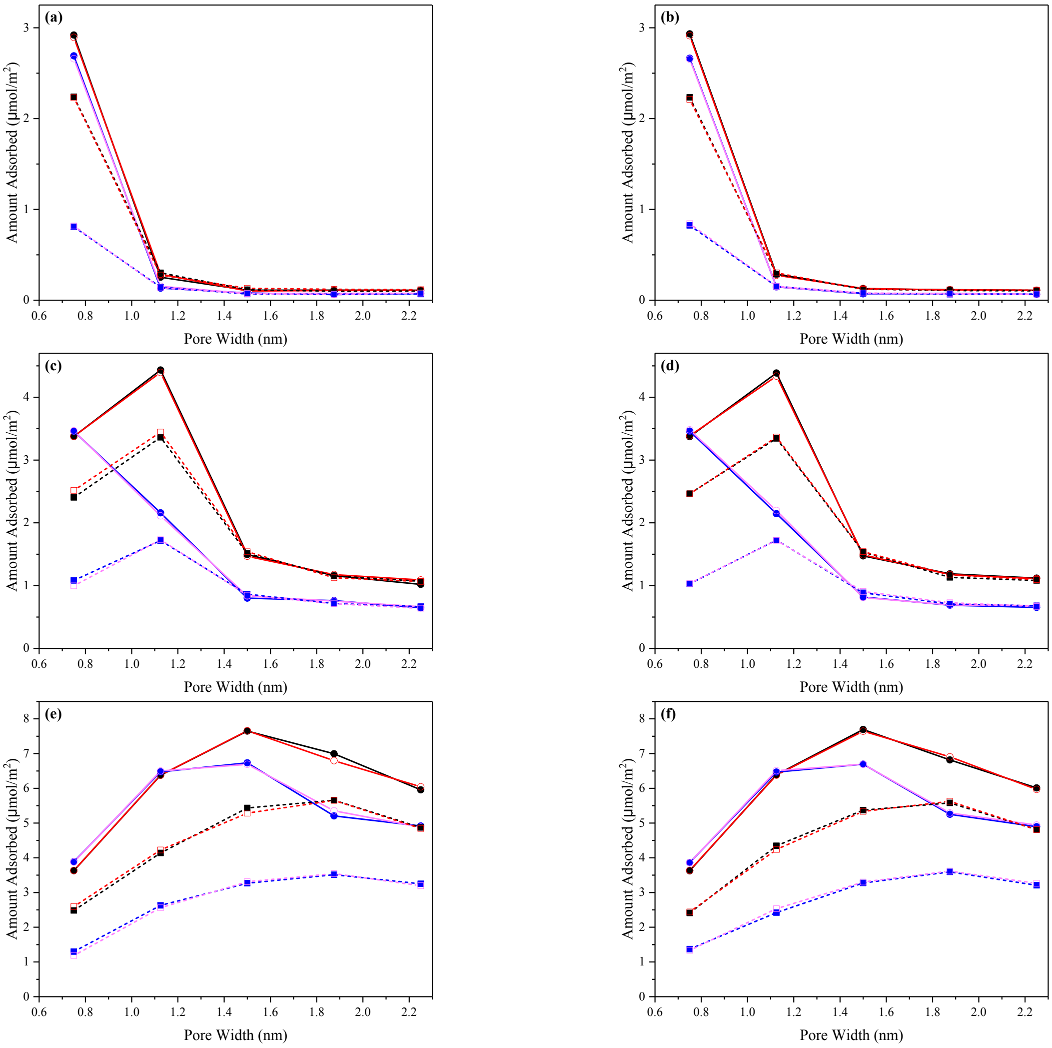

Figure S1 Comparison of amount adsorbed of ethane and ethylene in five different slit pore sizes between two different areas (a) small size at 10 kPa, (b) large size at 10 kPa, (c) small size at 100 kPa, (d) large size at 100 kPa, (e) small size at 1000 kPa and (f) large size at 1000 kPa. Solid symbols (black for ethane and blue for ethylene) represent models where electrostatic contributions are ignored and open symbols (red for ethane and pink for ethylene) represent models where electrostatic contributions are considered. Solid lines with circle symbols are for pure component simulations, whereas dashed lines with square symbols are for simulations of mixtures with a bulk equimolar composition.

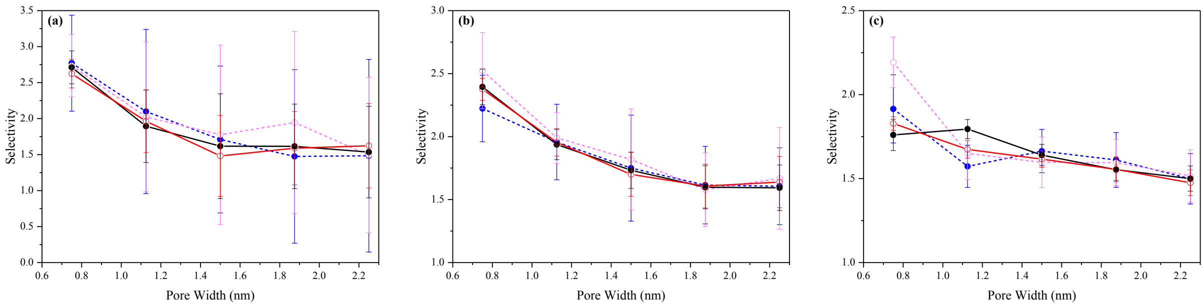

Figure S2 Selectivity based on simulations of ethane/ethylene mixture with a bulk equimolar composition in five different slit pore sizes at (a) 10 kPa, (b) 100 kPa and (c) 1000 kPa and 298 K. Solid symbols (black for ethane and blue for ethylene) represent models where electrostatic contributions are ignored and open symbols (red for ethane and pink for ethylene) represent models where electrostatic contributions are considered. Solid lines are for simulations in large size, whereas dashed lines are for simulations in small size.

We do not consider that at the conditions we studied there would be any significant size effect once proper statistics can be obtained as we do not see the formation of ordered phases that can become frustrated if the box size is not commensurate with the natural periodicity of the adsorbed phase. For studies where hexatic or solid phases are formed inside the pores, it would be important to assess more carefully the size effects.

2. Effect of pore size on loading

Figure 4 in the main manuscript shows peaks in loadings for specific pore sizes at a given pressure. The peak at 0.7 nm can be easily understood looking at the potential energy curves (see Figure S3) using the 10-4-3 potential. The lowest value of the solid-fluid interactions is in the centre of the pore, for pores of 0.7 nm (approximately). In smaller pores repulsions with the wall start to be important, and the minimum is pushed to higher energies. In larger pores there is no significant overlap of the attractive contributions of both walls, making the minimum of the potential energy higher. At low pressures, like 10 kPa, the amount adsorbed will be proportional to the potential energy between the solid and the adsorbed molecules, and the stronger the interaction the more molecules will be adsorbed.

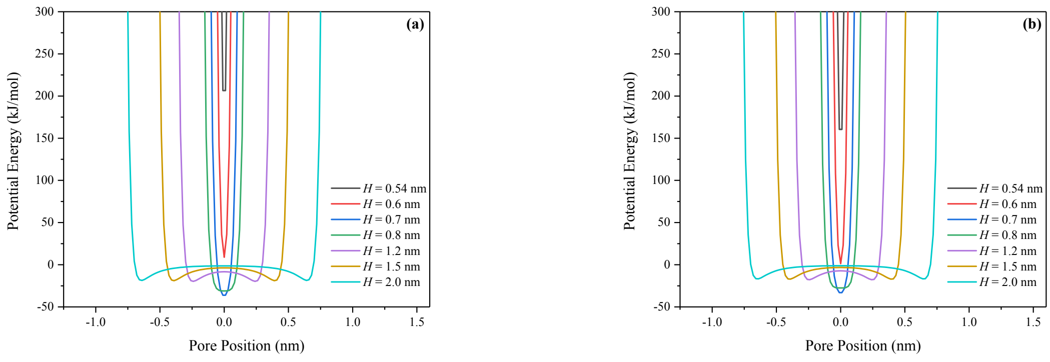

Figure S3 Potential energy of (a) ethane and (b) ethylene in different slit pore sizes at 298 K. The origin in the *x*-axis represents the pore centre.

At higher pressures the amount adsorbed starts to be a contribution of the solid-fluid and fluid-fluid interactions. The peaks are formed based on the ability of the molecules to pack at a given pore width. If the pore width is commensurate with the molecule size, they will pack efficiently, but if it is not, there will be unoccupied spaces that will result in a reduction in the amount adsorbed.

3. Density profiles

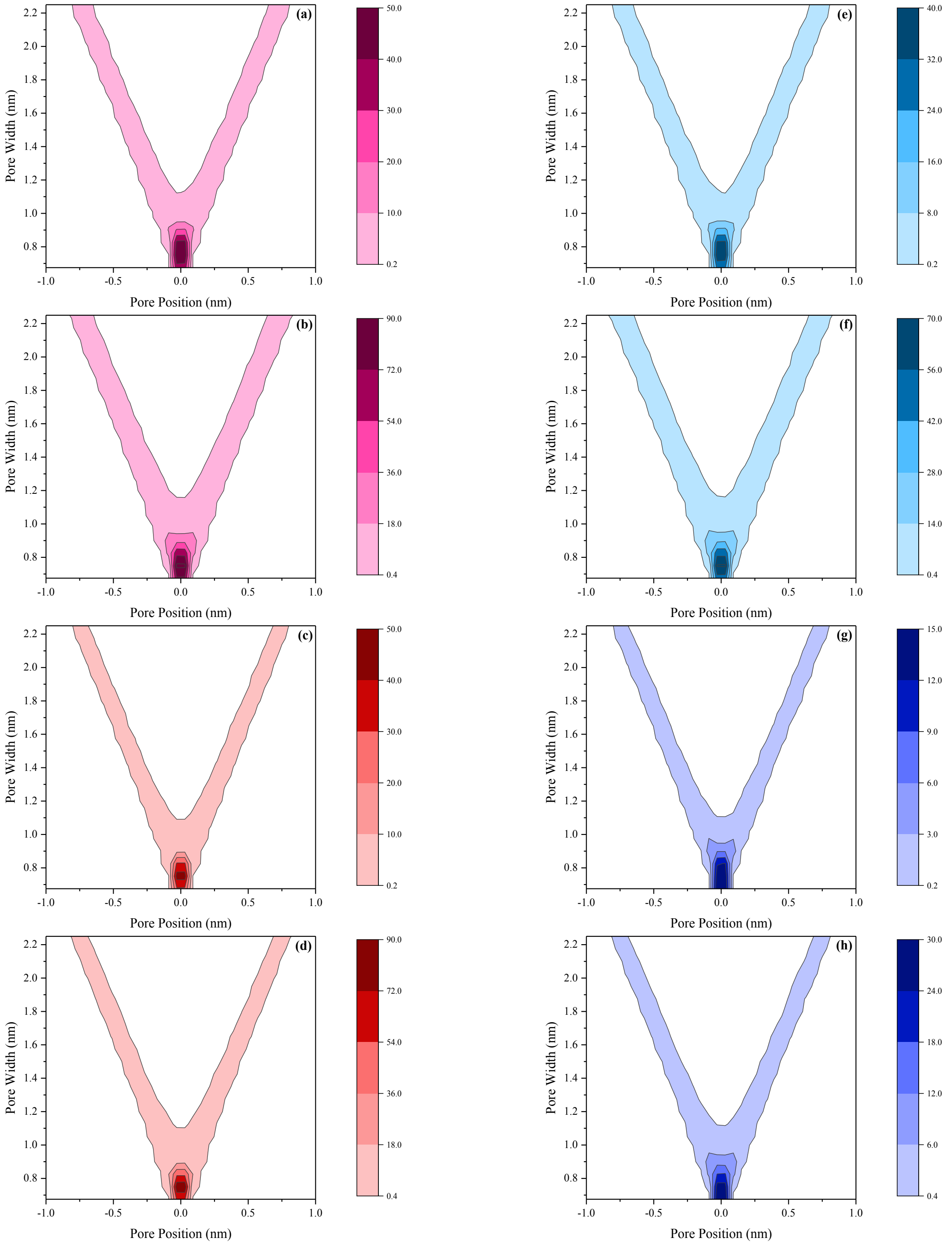

Figure S4 Density profiles (kmol/m^3) for CH_3 groups and CH_2 groups, and the centre of mass in the carbon slit pores at 10 kPa and 298 K: (a) M-pure C_2H_6; (b) CH_3-pure C_2H_6; (c) M-pure C_2H_4; (d) CH_2-pure C_2H_4; (e) M-C_2H_6 in mixture; (f) CH_3-C_2H_6 in mixture; (g) M-C_2H_4 in mixture; (h) CH_2-C_2H_4 in mixture. The origin in the *x*-axis represents the pore centre.

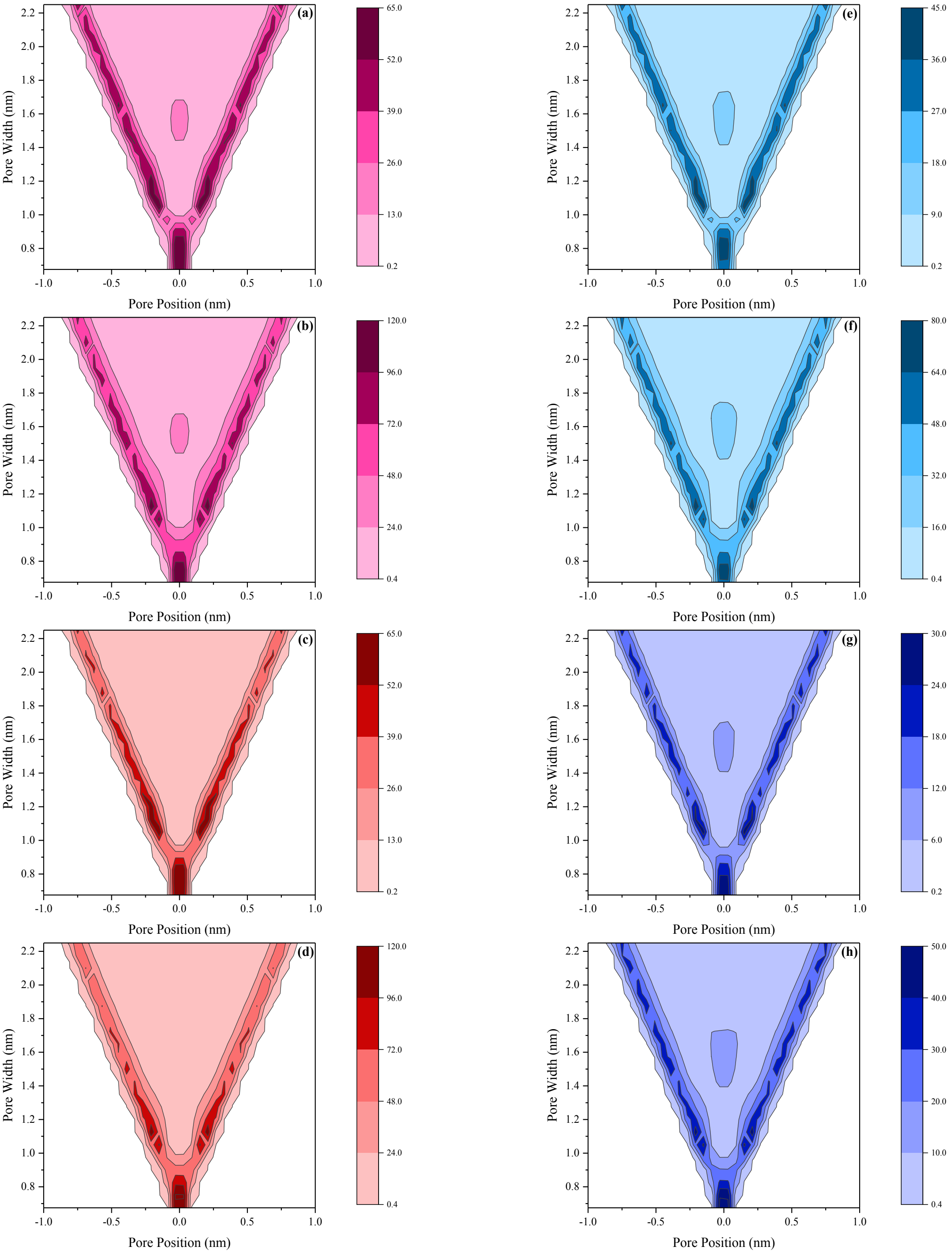

Figure S5 Density profiles (kmol/m^3) for CH_3 groups and CH_2 groups, and the centre of mass in the carbon slit pores at 1000 kPa and 298 K: (a) M-pure C_2H_6; (b) CH_3-pure C_2H_6; (c) M-pure C_2H_4; (d) CH_2-pure C_2H_4; (e) M-C_2H_6 in mixture; (f) CH_3-C_2H_6 in mixture; (g) M-C_2H_4 in mixture; (h) CH_2-C_2H_4 in mixture. The origin in the *x*-axis represents the pore centre.

4. Orientation profiles

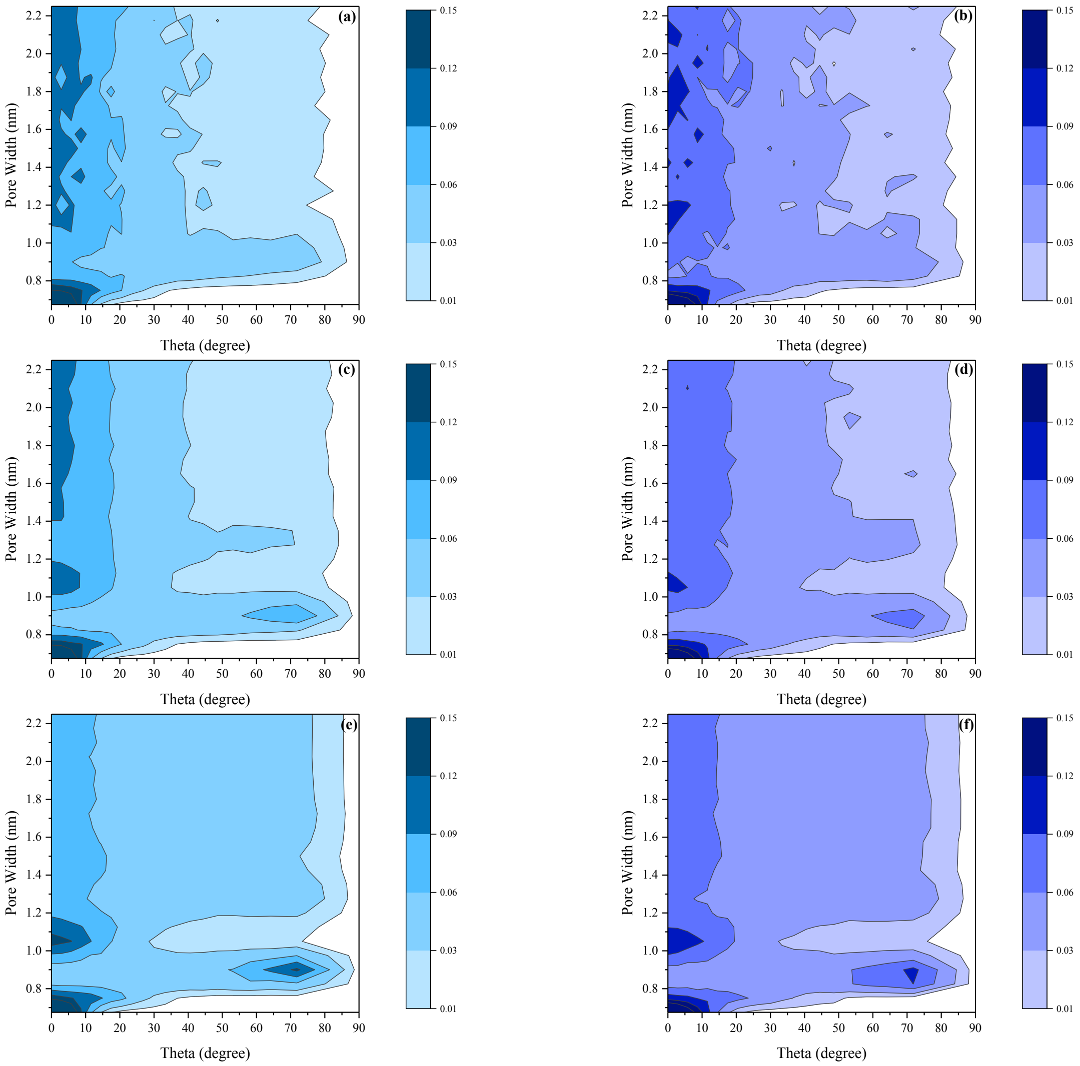

Figure S6 Orientation profiles for C_2H_6 and C_2H_4 in mixture simulations in the carbon slit pores at 298 K (a) C_2H_6 at 10 kPa; (b) C_2H_4 at 10 kPa; (c) C_2H_6 at 100 kPa; (d) C_2H_4 at 100 kPa; (e) C_2H_6 at 1000 kPa and (f) C_2H_4 at 1000 kPa.

5. Minimum energy configuration

The calculated positions (distance to the wall) and orientations of an adsorbed gas molecule at the minimum potential energy configuration are presented in Figure S7. In narrow pores, the minimum energy is obtained when the molecules are at the centre of the pores, while in large pores, the minimum energy converges to molecules at a distance of 0.355 nm from the wall for ethane adsorption and 0.351 nm for ethylene adsorption. In larger pore sizes, the distance of the ethylene molecule to the wall is always smaller than that of the ethane molecule, because ethylene is smaller than ethane, and can get closer to the wall. Both ethane and ethylene are preferentially adsorbed in a perfectly parallel orientation ($\theta = 0^{\circ}$) to achieve a minimum energy configuration. A minimum energy configuration with molecules perpendicular to the wall would only be achieved at the exact pore size where the distance between the two minima in the potential energy is the same as the bond length.

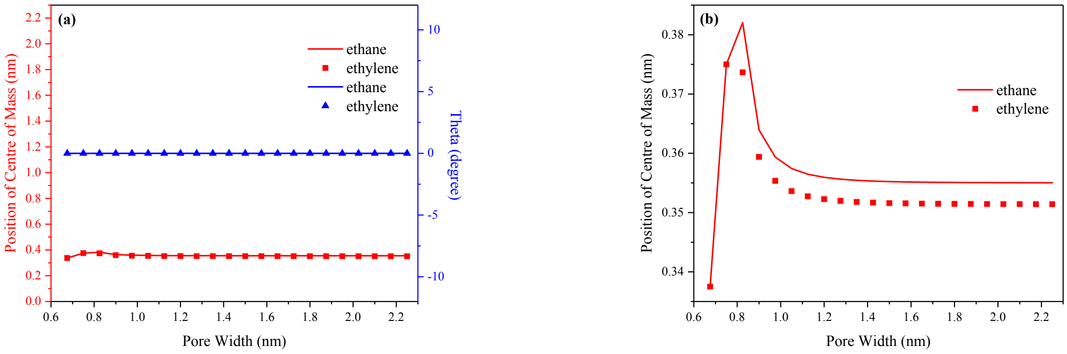

Figure S7 Position (red) and orientation (blue) of the centre of mass of ethane and ethylene at the minimum energy and 298 K.

The potential energy (see Figure S8) between ethane and the solid surface is always higher than that between ethylene and the solid surface at minimum energy configuration. Therefore, carbon slit walls always have a preference towards ethane over ethylene regardless of pore size. The selectivity can be then predicted based on the energy difference in Figure S8 using equation (16) as shown in Figure 8. When the pore size is large enough, the potential energy for both ethane and ethylene adsorption converges, so the selectivity tends to approximately 2.0.

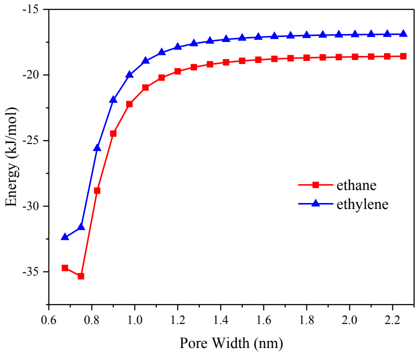

Figure S8 Potential energy for ethane and ethylene adsorption at the minimum energy and 298 K.

6. Direct numerical integration

The potential energy calculated from equation (4) and Boltzmann factor in the integral kernel of equation (13) for an ethane or ethylene molecule inside a slit pore can be obtained for all positions and orientations inside the pore, which are then used in equation (15) to calculate the selectivity. A graphical representation of the potential energy and the Boltzmann factor are shown in Figure S9 for H = 0.900 nm (2.4 σ_{ethane}). Similar results have been obtained of other pore sizes (not shown).

For H = 0.900 nm, the minimum energy for ethane adsorption is –24.44 kJ/mol when the adsorbed molecules are parallel to the solid walls ($\theta = 0^\circ$) and locate in a distance of 0.364 nm from the solid walls (i.e. the distance between the ethane molecule and the pore's centre is 0.086 nm). For ethylene adsorption, a minimum energy of –21.92 kJ/mol is found when the molecules also align parallel to the walls ($\theta = 0^\circ$), but with a distance of 0.359 nm to the solid walls (i.e. the distance between the ethylene molecule and the pore's centre is 0.091 nm). These energy values are similar to those when adsorbed molecules site exactly in the pore centre and in a perpendicular orientation to the wall, ca. –24.35 kJ/mol for ethane adsorption and –21.32 kJ/mol for ethylene adsorption, where a local minima is observed. Therefore, at a finite temperature, it is expected that the molecules will be found in both, parallel and perpendicular orientations. Then, calculating the selectivity using equation (16) would overestimate the actual value, while equation (15) would provide a more realistic estimation.

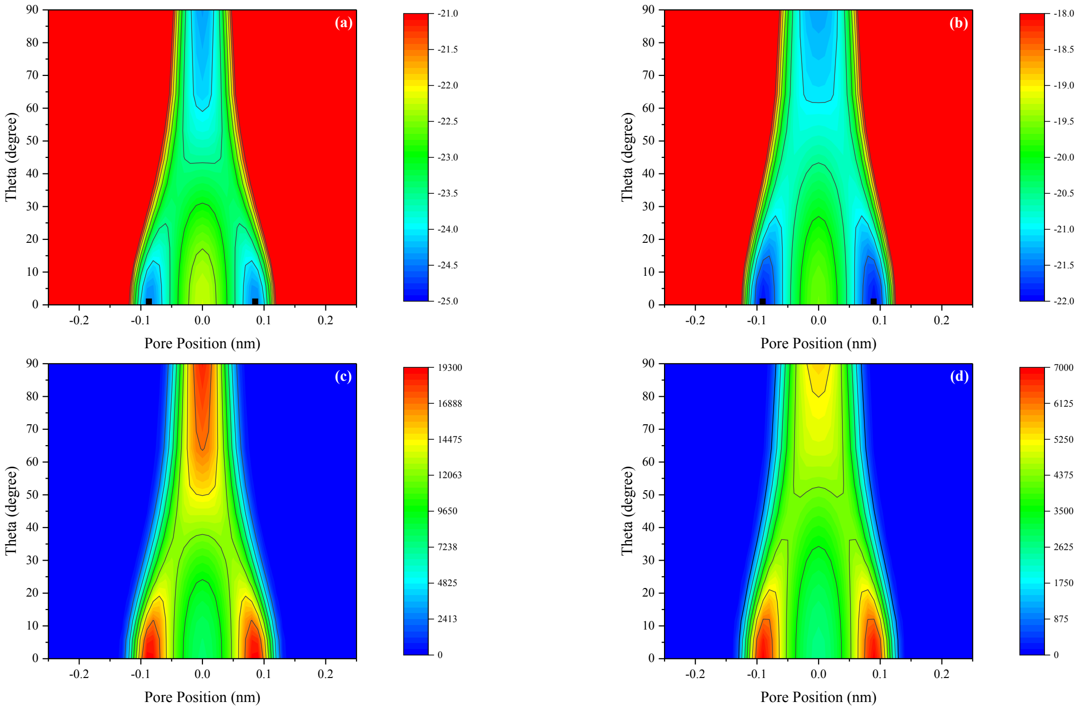

Figure S9 Potential energy profiles (kJ/mol) for (a) ethane and (b) ethylene and Boltzmann factors of (c) ethane and (d) ethylene in a pore size of H = 0.900 nm and at 298 K. Black symbols represent the position and orientation of the centre of mass at the minimum energy configuration (–24.44 kJ/mol for C_2H_6 and –21.92 kJ/mol for C_2H_4). The origin in the x-axis represents the pore centre.