Electronic Supplementary Information

Interfacial CO_2-Mediated Nanoscale Oil Transport: from Impediment to Enhancement

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S1. Simulation setup and results

Table S1. The setup and results of simulations with different CO_2 adsorption density Γ_{co2}.

Case name	1A	1-1	1-2	1-3	1-4	1-5	1-6	1B
number of decane molecule	442	431	421	410	407	405	402	400
Γ_{co2} (nm^{-2})	0	1.28	2.56	3.85	4.17	4.49	4.81	5.12
Corresponding CO_2 bath pressure*	0	-	-	-	-	2.1	8.0	24.3
δ (nm)	0.06	0.15	0.23	0.32	0.34	0.36	0.38	0.39
$w_e = w - 2\delta$ (nm)	7.88	7.70	7.54	7.36	7.32	7.28	7.24	7.23
decane permeability (μD)	4.79	3.46	3.43	4.00	4.26	4.65	5.27	5.82

* estimated using the CO_2 adsorption isotherm shown in Fig. S2.

S2. Adsorption isotherm of CO_2 on calcite surfaces

We compute the adsorption isotherm of CO_2 on a calcite surface exposed to a thick decane layer. Figure S1a shows a schematic of the simulation setup. A series of simulations, in which the number of CO_2 molecules in the system are varied, are performed. The CO_2 gas density in the region away from the decane layer is recorded, and the CO_2 pressure corresponding to the recorded gas density is then computed in a separate bulk CO_2 simulation. Figure S1b shows the density profile of CO_2 and decane molecules across the system in one of the simulations. A CO_2 molecule is considered adsorbed on the calcite surface if it is located within the first CO_2 density peak (cf. Fig. S1b). Figure S2 shows the adsorption isotherm of CO_2 molecule thus computed. The saturation adsorption limit is ~5.15 nm^{-2}.

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Figure S1c compares the CO_2 density profile near a calcite surface computed in simulation based on the system shown in Fig. S1a and in simulation based on the system shown in Fig. 1 in the main text. The CO_2 adsorption density is 5.12 nm^{-2} in both simulations. The excellent agreement between the CO_2 profiles obtained from these systems confirms that the virtual graphene layer shown in Fig. 1 hardly perturb the distribution of the CO_2 adsorption layer on the calcite surface other than preventing them from leaving the interfacial zone.

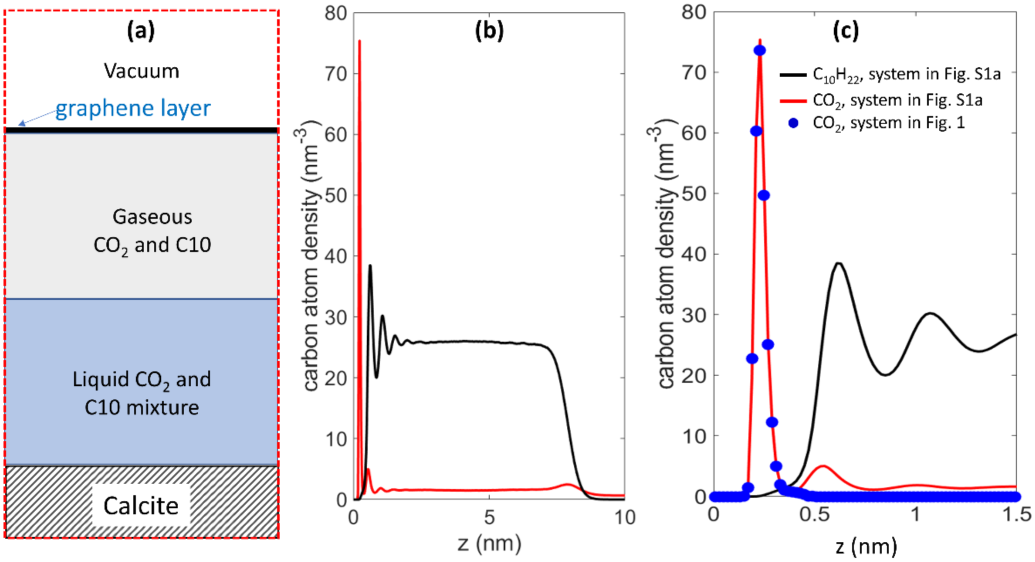

Fig. S1. (**a**) A schematic of the system used for computing the adsorption isotherm of CO_2 on a calcite surface exposed to a thick decane layer. The red dashed lines denote the fully periodic simulation box. (**b**) The CO_2 and decane density profiles in a sample case where the CO_2 density in the space above the decane layer is 0.65 ± 0.05 nm^{-3}, which corresponds to a CO_2 pressure of 24.3 bar. The density of the first CO_2 adsorption layer in both systems is 5.12 nm^{-2}. (**c**) Comparison of CO_2 density profiles near calcite surfaces obtained in system shown in (a) and in Fig. 1 in the main text, where CO_2 molecules are confined near the calcite surface using a virtual graphene plane. The density of the first CO_2 adsorption layer in both systems is 5.12 nm^{-2}.

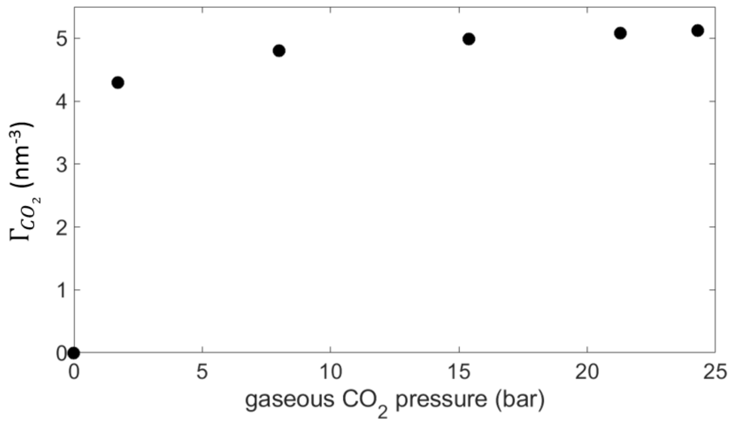

Fig. S2. The CO_2 adsorption isotherm obtained from simulations based on the system shown in Fig. S1a.

S3. Sample velocity embedding calculation results

In the velocity embedding technique, we compute the velocity profile of decane in a wide pore by (1) embedding the MD velocity profile in a near-wall region ($z \leq \Delta$) computed in a narrow pore (8 nm-wide in this work) and (2) solving the Stokes equation in the region outside of the near-wall region. This method requires the density and transport properties of fluids (here, decane and CO_2) within the near-wall region in the narrow and wide pore to be identical, which is true in this study: in the 8 nm-wide pore, the interfacial region near both pore walls do not affect each other; therefore, in any wider pores, the structure of the interfacial region is identical to that in the 8 nm-wide pore. Figure S4 shows an example of the velocity embedding result.

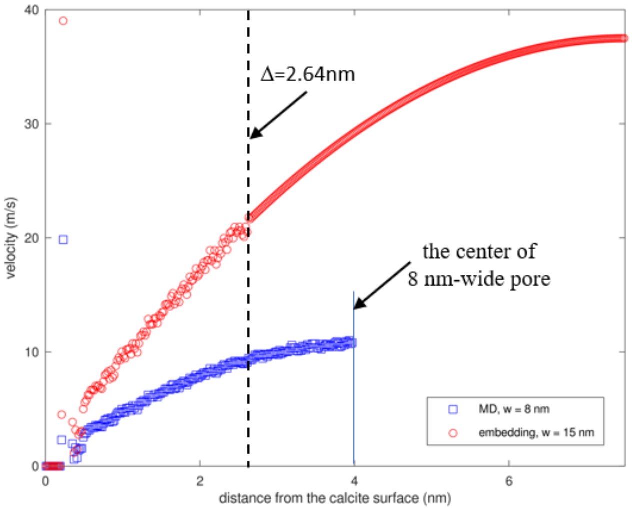

Fig. S3. The velocity profiles in a 15 nm-wide pore with $\Gamma_{co2} = 5.12\ \text{nm}^{-2}$ computed using the velocity embedding technique. Here, the velocity profile for $z \leq 2.64$ nm is embedded from the velocity profile in an 8 nm-wide pore with the same CO_2 adsorption density and that outside of this region is computed by solving the Stokes equation. Only the velocity profile in the lower half of the pore is shown because of symmetry.

S4. Distribution of interfacial decane molecules’ constituent atoms

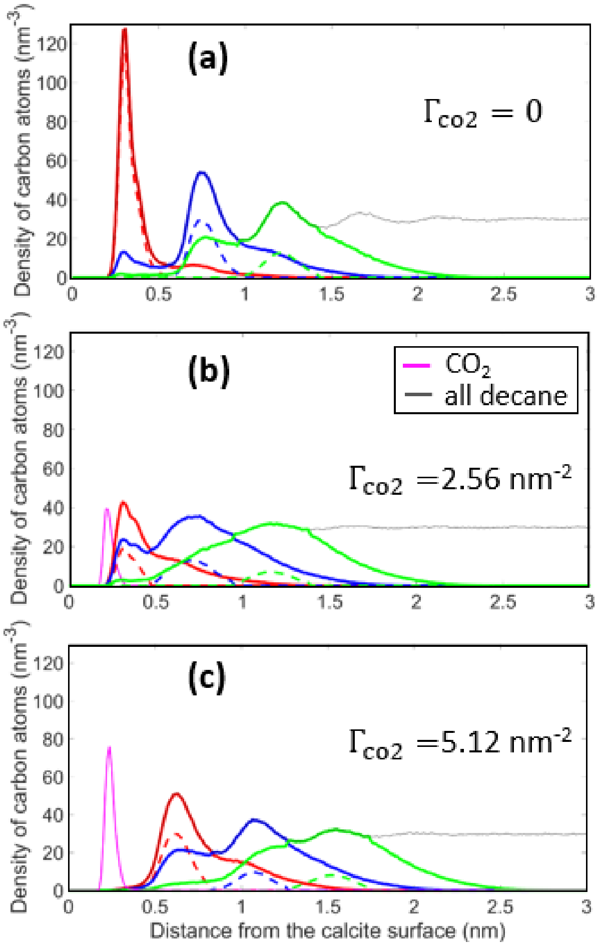

Fig. S4. Distribution of the carbon atoms of interfacial decane molecules for systems with $\Gamma_{co2} = 0$ (a), $\Gamma_{co2} = 2.56$ nm^{-2} (**b**), and $\Gamma_{co2} = 5.12$ nm^{-2} (**c**). The interfacial decane is divided into layers based on the valleys of decane carbon atom’s density profile. A decane molecule belongs to a certain interfacial layer if at least one of its carbon atoms resides in that layer (a decane molecule thus can simultaneously belong to more than one interfacial layer). In each panel, the solid red/blue/green line denotes the density of the carbon atoms of all decane molecules in the first/second/third decane layer, while the dashed red/blue/green line denotes the density of the carbon atoms of those decane molecules whose carbons *all* reside in the same layer. In (b), blue and red lines have considerable overlap with the density profile of CO_2 molecule, indicating a good mixing of the CO_2 and the interfacial decane molecules.

S5. Orientation of CO_2 molecules adsorbed on calcite surfaces

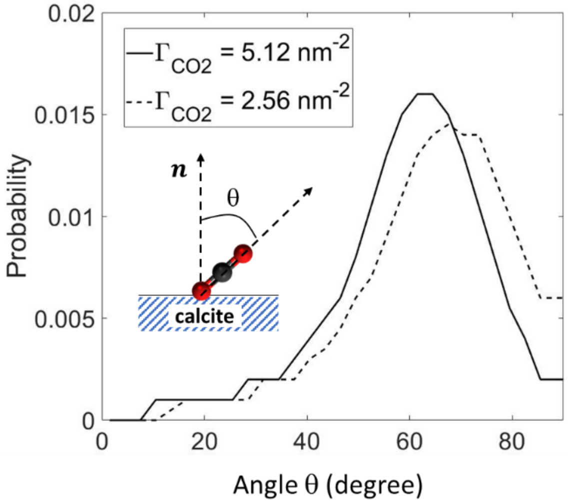

Figure S5. The distribution of the orientation angle of CO_2 molecules adsorbed on a calcite surface with respect to the surface's normal direction.