Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary materials for

CO_2 activating hydrocarbon transport across nanopore throat: insights from molecular dynamics simulation

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1. The method to build model

Silica supercell: the process to build the silica supercell is given in detail as follow: firstly, the initial silica unit cell was derived from the database of the Material Studio software. Secondly, we cleave the unit cell along two perpendicular directions to obtain an orthorhombic geometry, and a schematic how to cleave is given below. By extending this orthorhombic unit cell, we could obtain desired orthorhombic silica supercell.

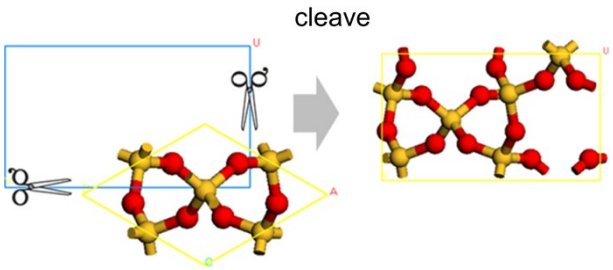

Fig. S1. The schematic to cleave the silica unit cell. Atom color codes: O, red; Si, yellow. The yellow box is periodic boundary.

Silica channel: the nanochannel model was built via three steps: First, α-quartz silica supercell with orthorhombic dimensions (xyz) of 2.5×7.1×23.0 nm^3 was constructed. Then, the corresponding atoms of nanoslit regions of supercell were removed to be as nanoslit with exposed (001) surface. The junction region connecting two nanoslits was smoothed by removing irregular atoms. Last, to reflect the realistic chemistry of fracture surface, the silica surface was hydroxylated by hydroxyl with a density of ~9.6 nm^{-2}, which is consistent with the result of crystal chemistry calculations (5.9-18.8 nm^{-2}) [1].

2. Initial models of EMD simulation

Four oil droplets composed of 100 dodecane molecules and dissolved CO_2 molecules (0, 100, 200, 300) were first built. A 2 ns equilibrium molecular dynamic simulation with NPT ensemble was conducted to achieve the reasonable oil density at a typical reservoir condition of 330 K and 20 MPa. Notably, in simulation, we keep the oil droplet having width fitting to the width of left nanoslit while the size can change along the other two directions. We place these four oil droplet inside the left nanoslit and keep the COM of these four oil droplets at the same position (Z is same). After that, the rest space of whole nanoslit including left and right sections were filled with water.

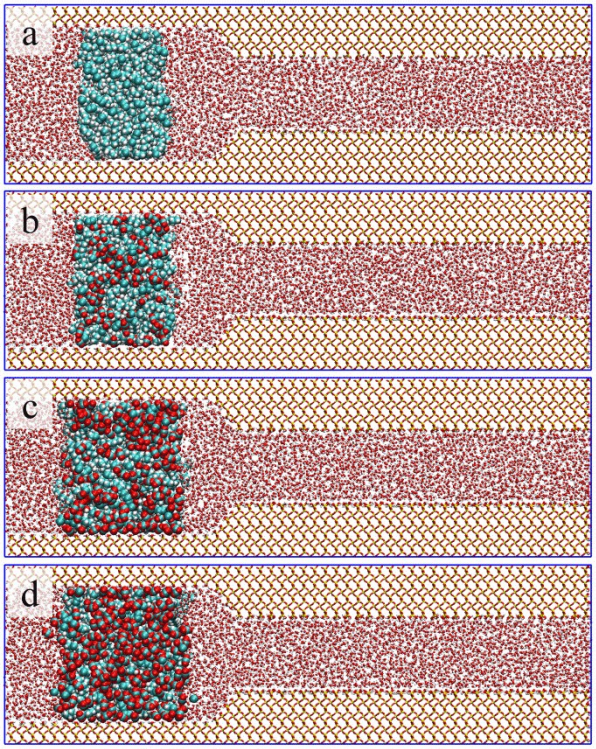

Fig. S2. Snapshots of initial system configurations of EMD: (a) 0 CO_2 molecules; (b) 100 CO_2 molecules; (c) 200 CO_2 molecules; (d) 300 CO_2 molecules. Atom color code: C, blue; O, red; H, white; Si, yellow. For clarity, dodecane and CO_2 is displaced in enlarged VDW style.

3. The detailed interaction parameter of the silica slabs, dodecane and CO_2

Table S1 Force field parameters for silica, dodecane and CO_2*

Intermolecular Interactions			
atoms	ε (Kcal/mol)	δ (Å)	q (e)
Si (quartz)	1.8405×10^{-6}	3.3020	2.100
O (Si-O-Si)	0.1553	3.1655	-1.0500
O (Si-OH)	0.1553	3.1655	-0.9500
H (Si-OH)	0	0	0.4250
C (C-H)	0.0550	3.8754	0
H (H-C)	0.0220	2.3519	0
C (O=C=O)	0.0559	2.7570	0.6512
O (O=C=O)	0.1599	3.0330	-0.3256

*The parameters were derived from ref. [2] for silica, ref. [3, 4] for dodecane and ref. [5] for CO_2.

4. The water (CO_2) contribution to resistance force change

In real displacing condition, all the fluid containing water, oil and injected CO_2 molecules will bear driving force. In our study, the resistance force change of oil droplet transport across the nanopore throat is focused. Based on our results (Fig. 3, Fig. 4a,b), the changing of conformation energy of oil droplet is substantially larger than that oil/pore interaction, meaning the conformation deformation of oil droplet is the dominating contributor to the resistance force change. In other words, the contribution coming from oil/pore interaction to resistance force change is slight. As for the water, the water molecules with high diffusion velocity don't undergo conformation deformation as it pass across the nanopore throat. Hence, only the water/pore interaction should be considered. In the whole transport process, the water/pore interaction determined by their contact area would have negligible change in comparison to the conformation energy change of oil droplet. Similarly, the CO_2 contribution to the resistance force change could also be negligible. Therefore, the results in this work should be convincing, at least in qualitative level. In order to confirm this point, another simulation using piston force was considered. The comparison (Seen Fig. S3) indicate that the water only increase the benchmark of resistance force (large force need to push large water molecules ahead), but the resistance force change as oil droplet transport across nanopore throat changes little.

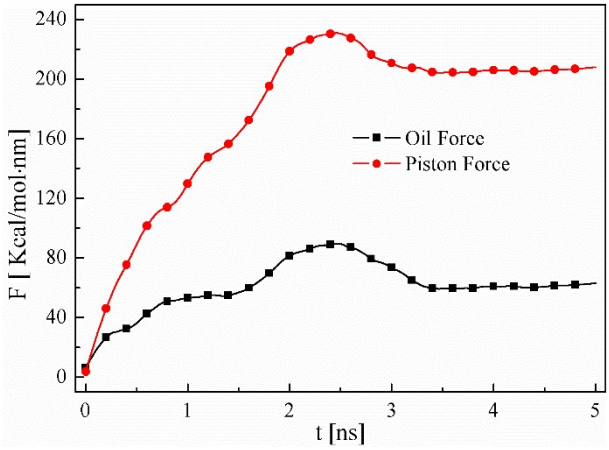

Fig. S3. The resistance force changes in our work and that using piston force pushing all fluid across nanopore throat.

5. The resistance force

As seen in Fig. 2e in main body of paper, the COM of oil droplet roughly keeps linear relationship over simulation time, meaning the oil droplet maintains nearly steady moving velocity. To realize this mobility status, the pulling force should be equal to the resistance force. In this study, the spring force is the pulling force and is calculated as depicted in Fig. 2e, thus it could be considered as resistance force.

6. Dynamic transport snapshots

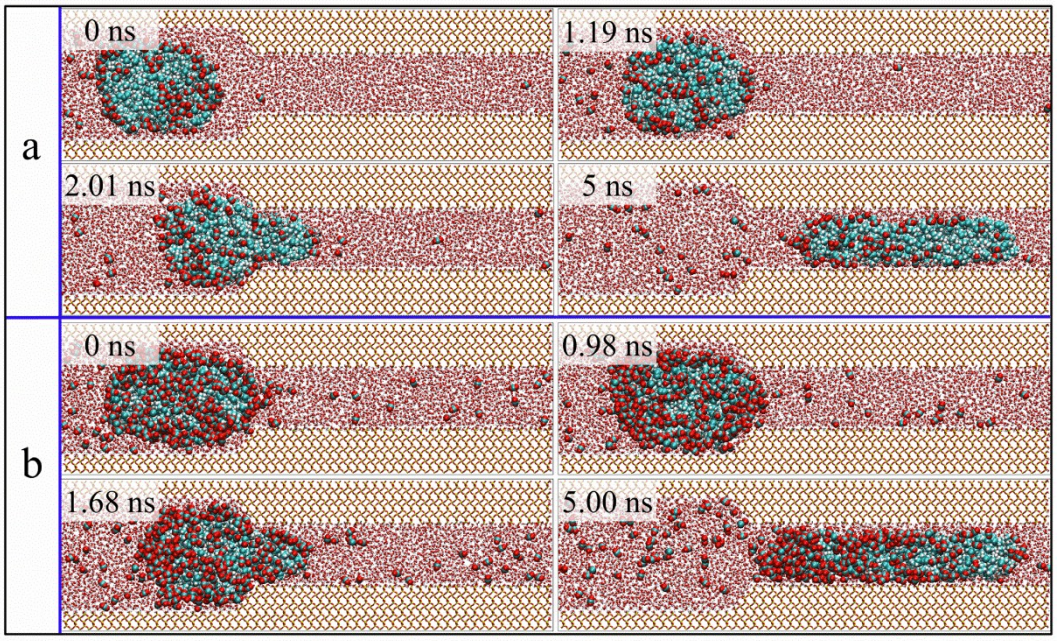

Fig. S4 Dynamic transport process of oil with CO_2: (a) 100 CO_2 molecules; (b) 300 CO_2 molecules.

7. The number changes of CO_2 molecules inside and at the surface of oil droplet

In our simulation some CO_2 molecules are found solvated in the water far from the oil droplet and has no impact on the transport behavior of oil droplet. In the systems containing different number of CO_2 molecules, only the CO_2 molecules inside the oil droplet and at the surface of oil droplet have impact on the transport behavior of oil droplet, so we calculated the changes of these CO_2 molecules during simulation (Fig. S5). As shown, the amount of these CO_2 molecules indeed increases when the added CO_2 amount increase from 100 to 300. So, our simulation results could reveal the effect of added CO_2 amount. This discussion has been added in the revised supplementary materials

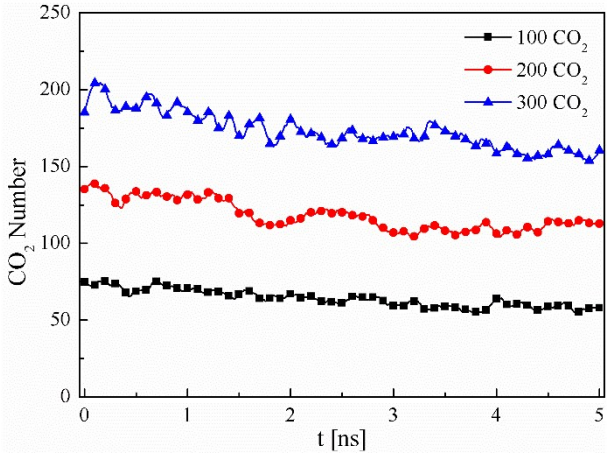

Fig. S5. The changing profile of CO_2 molecules inside the oil droplet and at the surface of oil droplet in three systems containing 100, 200, 300 CO_2 molecules.

8. The calculation method of diffusion coefficient of dodecane

To avoid the interference from spring pulling force on molecule diffusion, the process of 5 ns equilibrium molecular dynamics simulation (EMD) were selected to evaluated the diffusion coefficient of dodecane molecules in the four simulation systems. The trajectories of last 2.5 ns were used to calculate the mean-square diffusion (MSD) curve of dodecane molecules as shown in Fig. S6. The diffusion coefficient (D) was calculated by Einstein Function (1) as below [6].

$$D = \frac{1}{6}\lim_{t\to\infty}\frac{d}{dt}\sum_{i}^{n}\left\langle\left|R_i(t) - R_i(0)\right|^2\right\rangle \quad (1)$$

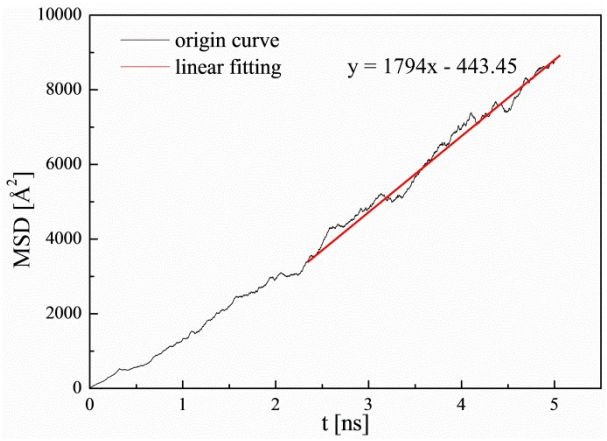

Fig. S6. Mean-square diffusion profile of dodecane molecules. Here, the system with 200 CO_2 molecules was selected as representation.

9. The calculation method of the interface tension between oil and water

The simulation box for the ternary water-CO_2-dodecane system consists of three independent phases as shown in Fig. S7. This kind of system to calculate the interface tension (IFT) was frequently used in previously Ref. [7-9] Here, the two water phases involves totally 1926 molecules, and the middle phase is the dodecane–CO_2 mixture containing 100 dodecane molecules and different numbers of CO_2 molecules (0, 100, 200, 300). Those four calculation models were firstly conducted 4 ns EMD simulation with NPT ensemble at the condition of 330 K and 20 Mpa to obtain equilibrium state. And then, 2 ns EMD simulation with NVT ensemble at the temperature of 330 K was implemented for calculating the IFT between oil and water. The IFT between oil and water was calculated using the formulation of the Gibbs interfacial tension [10]. Two interfaces in the system are both perpendicular to the z axis and parallel to the xy plane, hence the IFT is evaluated from the expression of pressure tensor [7]:

$$\gamma = -\frac{1}{2}\left(\frac{P_x + P_y}{2} - P_z\right)L_z \tag{2}$$

where $P_a = P_{aa}$ (a = x, y, z) is the diagonal elements of the pressure tensor, and L_z is the length of the simulation box in z direction.

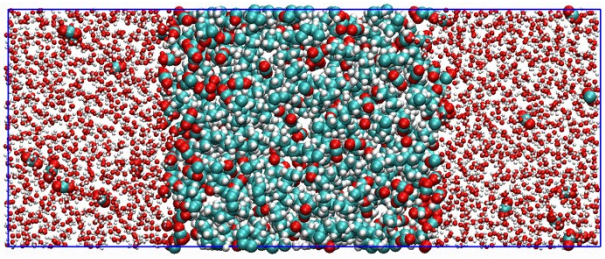

Fig. S7. The simulation box for the ternary water–CO_2–dodecane system. Here, the system with 200 CO_2 molecules was selected as representation.

10. Captions for supporting movie

Movie S1: Oil droplet transport process across the nanopore throat.

References:

[1] Koretsky CM, Sverjensky DA, Sahai N. A model of surface site types on oxide and silicate minerals based on crystal chemistry: implications for site types and densities, multi-site adsorption, surface infrared spectroscopy, and dissolution kinetics. Am. J. Sci., 1998, 298, 349-438.

[2] Cygan RT, Liang JJ, Kalinichev AG. Molecular models of hydroxide, oxyhydroxide, and clay phases and the development of a general force field. J. Phys. Chem. B 2004, 108, 1255-66.

[3] Zoete V, Cuendet MA, Grosdidier A, Michielin O. SwissParam: a fast force field generation tool for small organic molecules. J. Comput. Chem. 2011, 32, 2359-68.

[4] Vorobyov I, Anisimov VM, Greene S, Venable RM, Moser A, Pastor RW, et al. Additive and classical drude polarizable force fields for linear and cyclic ethers. J. Chem. Theory. Comput. 2007, 3, 1120-33.

[5] Harris JG, Yung KH. Carbon dioxide's liquid-vapor coexistence curve and critical properties as predicted by a simple molecular model. J. Phys. Chem. 1995, 99, 12021-4.

[6] Wang X, Liu L, Wang P, Li W, Zhang J, Yan Y. How the inhibition performance is affected by inhibitor concentration: a perspective from microscopic adsorption behavior. Ind. Eng. Chem. Res. 2014, 53, 16785-92.

[7] Liu B, Shi J, Wang M, Zhang J, Sun B, Shen Y, et al. Reduction in interfacial tension of water–oil interface by supercritical CO_2 in enhanced oil recovery processes studied with molecular dynamics simulation. J Supercrit. Fluids 2016, 111, 171-8.

[8] Zhao L, Tao L, Lin S. Molecular Dynamics Characterizations of the Supercritical CO_2-Mediated Hexane–Brine Interface. Ind. Eng. Chem. Res. 2015, 54, 2489-96.

[9] Zhao L, Lin S, Mendenhall JD, Yuet PK, Blankschtein D. Molecular dynamics investigation of the various atomic force contributions to the interfacial tension at the supercritical CO_2-water interface. J. Phys. Chem. B 2011, 115, 6076-87.

[10] de Lara LS, Michelon MF, Miranda CR. Molecular dynamics studies of fluid/oil interfaces for improved oil recovery processes. J. Phys. Chem. B 2012, 116, 14667-76.