Supporting Information

Molecular Insights into Kerogen Deformation Induced by CO_2/CH_4 Sorption: Effect of Maturity and Moisture

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Table A.1

Compositions and structural parameters of kerogen units. [a]

Property	Parameter	IIA		IIC		IID	
		Experiment data	Model unit	Experiment data	Model unit	Experiment data	Model unit
Composition	H/C	1.17	1.17	0.89	0.91	0.56	0.58
	O/C	0.097	0.095	0.050	0.054	0.047	0.051
	N/C	0.029	0.024	0.021	0.021	0.021	0.023
	S/C	0.014	0.012	0.006	0.008	0.010	0.011
C group	Aromatic C (%)	40	41	54	59	72	79
	C atoms (per aromatic cluster)	12	11	19	20	20	20
	Fraction of attached aromatic C	0.43	0.46	0.30	0.28	0.24	0.28
	Protonated aromatic C (per 100 C)	13	14	17	14	28	25
O group	O in C-O groups (per 100 C)	5.0	5.2	3.5	3.7	4.7	5.1
	O in carboxylic groups (per 100 C)	1.3	1.6	0.7	0.8	0.0	0.0
	O in carbonyl groups (per 100 C)	3.4	2.8	0.8	0.8	0.0	0.0
N group	Pyrrolic (mol% of N)	52	66	65	60	62	75
	Pyridinic (mol% of N)	27	17	18	40	15	25
	Quaternary (mol% of N)	18	17	17	0	23	0
S group	Aromatic S (mol% of S)	46	67	54	50	80	100
	Aliphatic S (mol% of S)	54	33	46	50	20	0

[a] experimental data are from the work of Kelemen et al. [18].

Table A.2

Measured swelling of type II kerogen by different solvents.

Solvent	Kerogen type	Volumetric strain (%)	Reference
Pentane	II	15	[72]
Decane	II	21.6	[73]
	II	22.8	[74]
Hexadecane	II	20.4	[73]
	II	21.2	[74]
Cyclohexane	II	25	[72]
	II	27.8	[73]
	II	28.7	[74]
	II	17	[75]
Toluene	II	25	[72]
	II	35.8	[73]
	II	33.8	[74]

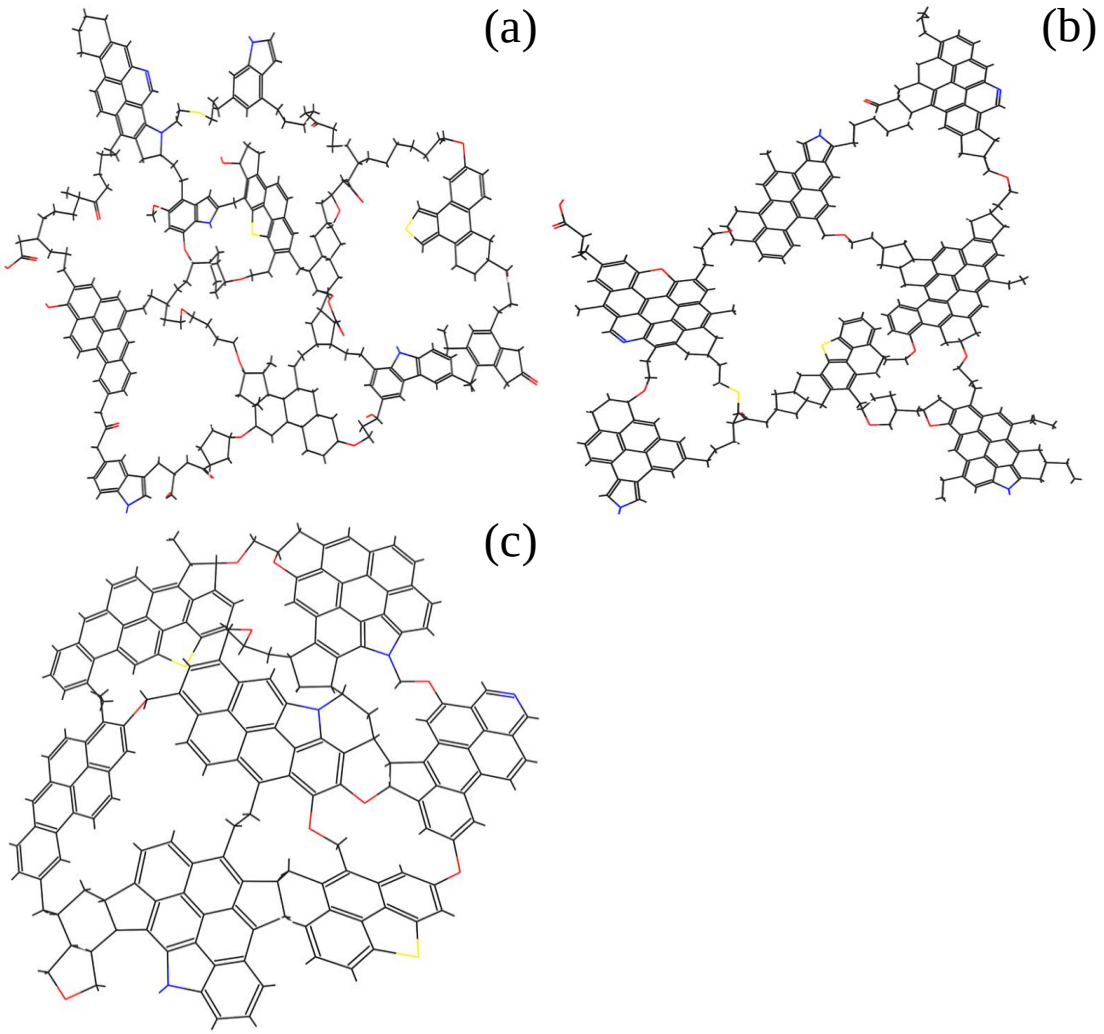

Fig.A.1. Kerogen structure units with different maturities: (a) immature kerogen (IIA) with a chemical formula of $C_{252}H_{294}O_{24}N_6S_3$; (b) kerogen in the middle of oil window (IIC) with a chemical formula of $C_{242}H_{219}O_{13}N_5S_2$; (c) postmature kerogen (IID) with a chemical formula of $C_{175}H_{102}O_9N_4S_2$. Atom representation: black for carbon atoms, red for oxygen atoms, yellow for sulfur atoms, and blue for nitrogen atoms. For clarity, hydrogen atoms are not illustrated.

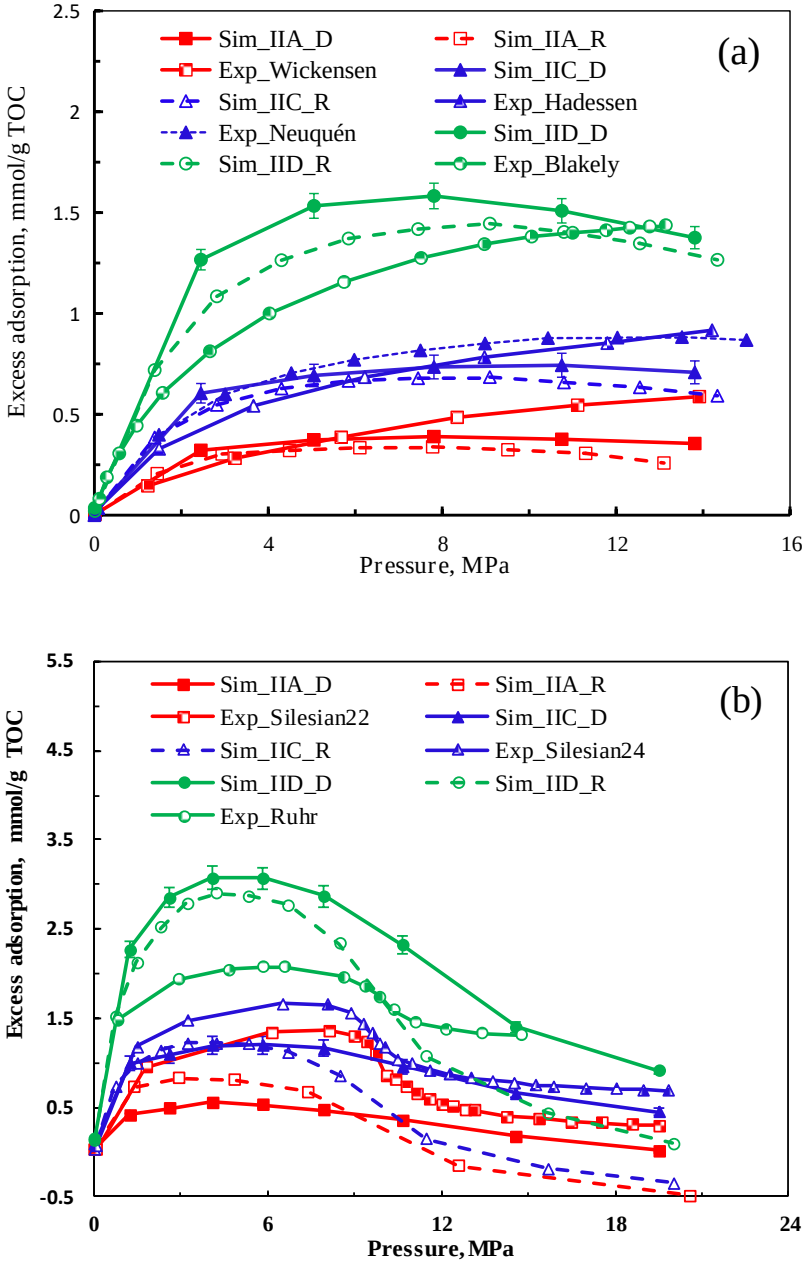

Fig.A.2. Excess adsorption isotherms of CH_4 and CO_2: (a) CH_4 at 338 K; (b) CO_2 at 318 K. D and R represent simulation results in kerogen with and without deformation, respectively. Simulation results in kerogen without deformation are from our previous work [32]. Experimental results for CH_4 are taken from Wickensen kerogen (Ro 0.53 %) [59], Hadessen kerogen (Ro 1.45 %) [59], Blakely kerogen (Ro 2.01 %) [61] and Neuquén kerogen (Ro 1.06 %) [26]. Experimental results for CO_2 are taken from Silesian coal 22 (Ro 1.2 %) [62], Silesian coal 24 (Ro 1.8 %) [62] and Ruhr coal (Ro 3.3 %) [14]. The error bars represent the standard deviations of five kerogen configurations.

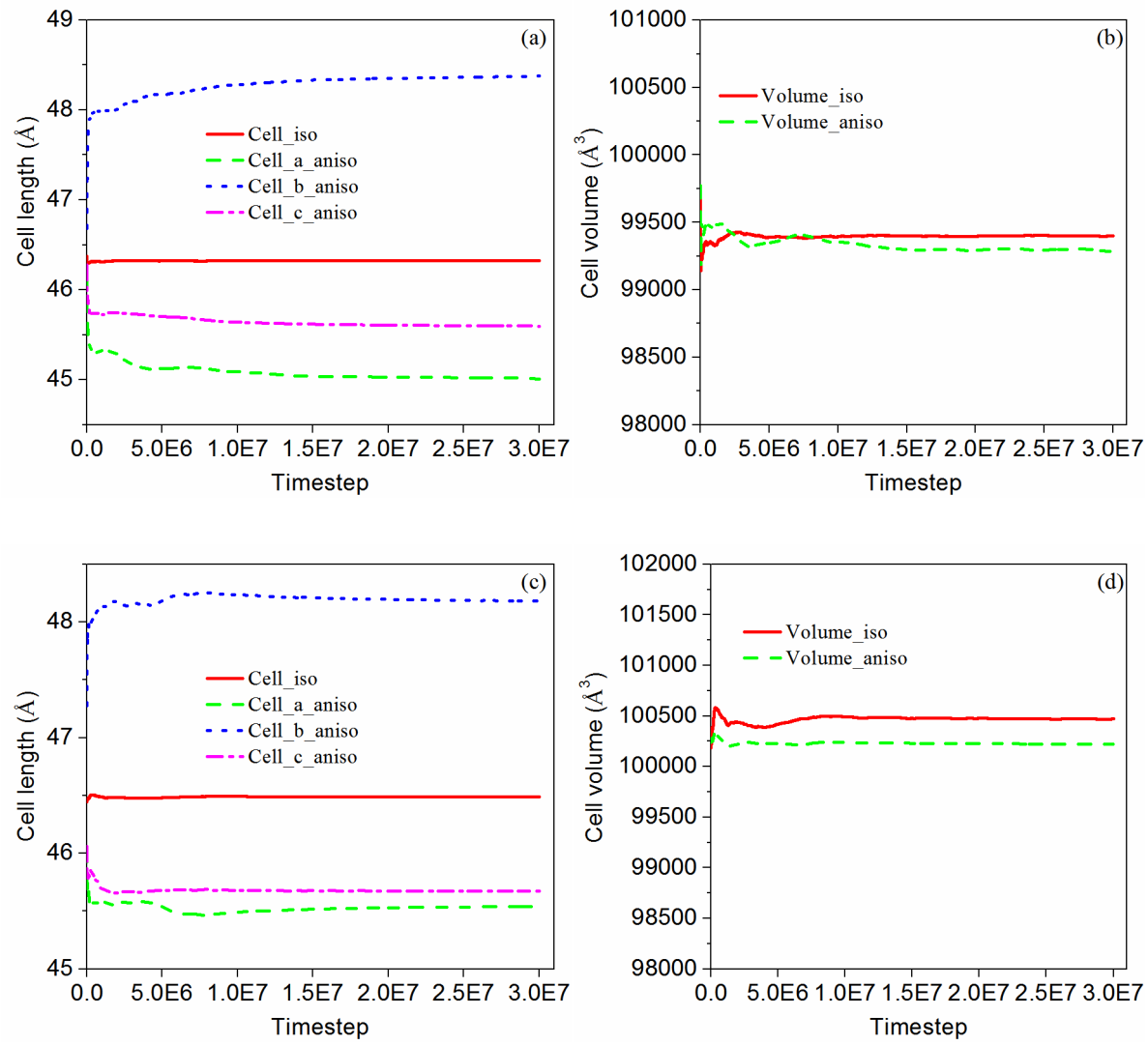

Fig.A.3. Cell length and volume of kerogen IID model with isotropic/anisotropic deformation: (a) cell length with CH_4 sorption at 338 K and 7.3 MPa ; (b) cell volume with CH_4 sorption at 338 K and 7.3 MPa; (c) cell length with CO_2 sorption at 338 K and 5 MPa; (b) cell volume with CO_2 sorption at 338 K and 5 MPa.