Supporting Information

Comparison of CH_4 and CO_2 adsorptions onto calcite(10.4), aragonite(011)Ca and vaterite(010)CO_3 surfaces: a MD and DFT investigation

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Larger cutoff energy and denser k-point grid will generate more accurate calculation results. Generally speaking, the both parameters should be as better as possible. But on the contrary side, the better of these parameters, the more computation costs will be required. So, when setting these parameters, the computation capacity must be considered too. In order to adopt reasonable values for these computation parameters, we have conducted the convergence tests to determine these computation parameters.

1.CONVERGENCE TESTS

In the convergence tests, the dependence of lattice constants on the computation parameters

(cutoff energy and k-point grid separation) are examined for the bulk aragonite, calcite and vaterite, respectively.

1.1 Tests of Cutoff Energy. The cutoff energy is tested from 300 eV to 600 eV, and the lattice parameters are examined. The results are shown in Table S1 and Figure S1.

Table S1. Bulk calcite, aragonite and vaterite lattice constants (Å) vary with the increase of cutoff energy.

Bulk	Lattice	Cutoff energy (eV)							Deviation	Deviation
phases	parameters	300	350	400	450	500	550	600		percent
Aragonite	*a*	5.064136	5.032576	5.020010	5.018017	5.016090	5.018590	5.017971	-0.000046	0.00%
	b	8.116949	8.071630	8.043022	8.038812	8.038756	8.026043	8.037959	-0.000853	-0.01%
	c	6.014245	5.838469	5.819538	5.815541	5.817017	5.821721	5.817908	0.002367	0.04%
Calcite	*a*	5.074161	5.065608	5.053910	5.052675	5.052239	5.052333	5.052251	-0.000424	-0.01%
	c	17.800280	17.308490	17.263240	17.251030	17.250020	17.251370	17.257590	0.006556	0.04%
Vaterite	*a*	4.610356	4.570394	4.547950	4.542336	4.549481	4.553406	4.550924	0.068020	1.49%
	b	6.849513	6.691839	6.682203	6.679197	6.667999	6.666323	6.669218	0.170316	2.55%
	c	8.553916	8.520798	8.510499	8.512680	8.508940	8.506884	8.509885	0.041236	0.48%

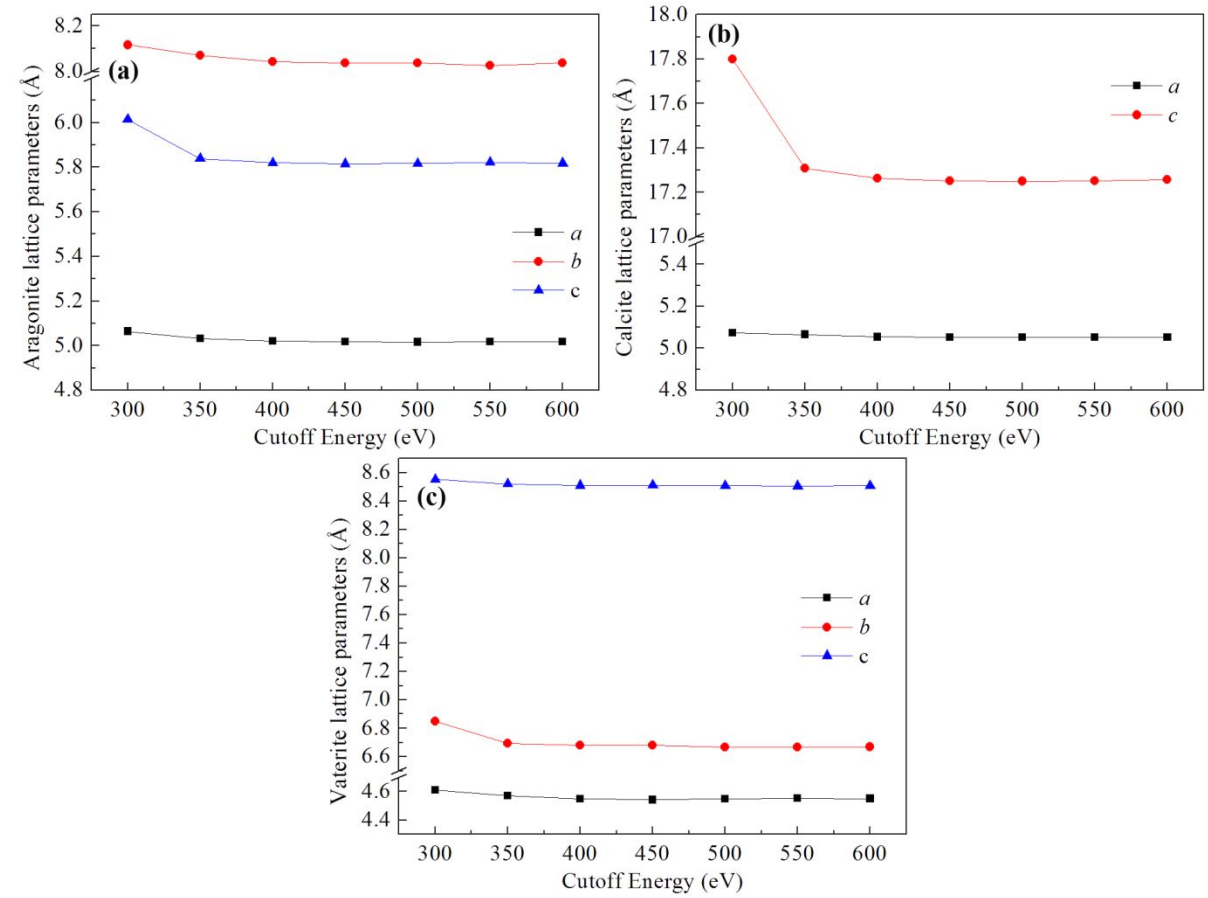

Figure S1. Convergence of bulk lattice constants with the increase of cutoff energy: (a) aragonite, (b) calcite, and (c) vaterite.

As shown in and Figure S1, the lattice parameters of bulk aragonite, calcite and vaterite are basically parallel when cutoff energy increases to 450 eV.

In Table S1, the deviation is the difference between the values calculated with cutoff energy of 450 eV and 600 eV. And deviation percent is the ratio of the difference divided by the value calculated with 600 eV cutoff energy. The largest deviations are 0.002367 Å, 0.006556 Å and 0.170316 Å for bulk aragonite, calcite and vaterite, respectively. And, the values of the largest deviation percent are 0.04%, 0.04% and 2.55% for the three phases, respectively.

As the above stated, the cutoff energy of 450 eV is enough large to ensure the DFT calculation accuracy. Hence, the 450 eV cutoff energy is adopted in this work.

1.2 Tests of k-point Grid Separation. For the Monkhorst-Pack k-point grid, a denser grid's density can generate more accurate calculation result. Generally, a dense k-point grid will indicates a smaller grid separation.

In the present work, the adsorptions of CH_4 and CO_2 on three $CaCO_3$ polymorphs are compared and emphasized. To guarantee the calculation results of adsorption systems are comparable, the grid separation should be same (or as close to each other as possible).

The grid density can be specified in several ways in CASTEP code. In our calculations, the k-point grid is set by directly specifying the grid separation as 0.03 $Å^{-1}$, and the k-point parameters in the form of "a × b × c" will be automatically generated by the computer.

In our convergence tests, the k-point grid separation are increased from 0.01 $Å^{-1}$ to 0.04 $Å^{-1}$, and the lattice parameters of three bulk phases are examined. The results are shown in Table S2 and Figure S2.

Table S2. Bulk calcite, aragonite and vaterite lattice constants (Å) vary with the increase of k-point grid separation.

Bulk phases	Lattice parameters	Cutoff energy (Å^{-1})							Deviation	Deviation percent
		0.010	0.015	0.020	0.025	0.030	0.035	0.040		
Aragonite	*a*	5.017817	5.017801	5.017927	5.017855	5.018017	5.017962	5.018015	-0.000200	0.00%
	b	8.039428	8.039839	8.039501	8.039653	8.038812	8.038968	8.039768	0.000616	0.01%
	c	5.815060	5.814324	5.815212	5.814782	5.815541	5.815510	5.813875	-0.000480	-0.01%
Calcite	*a*	5.053205	5.052474	5.052371	5.053325	5.052675	5.053274	5.052324	0.000530	0.01%
	c	17.238875	17.256290	17.256069	17.248568	17.251029	17.246849	17.250514	-0.012150	-0.07%
Vaterite	*a*	4.539226	4.545108	4.542801	4.545270	4.542336	4.541701	4.547751	-0.003110	-0.07%
	b	6.676868	6.679337	6.680462	6.678320	6.679197	6.679397	6.679060	-0.002329	-0.03%
	c	8.518261	8.510148	8.511334	8.507663	8.512680	8.510593	8.510910	0.005581	0.07%

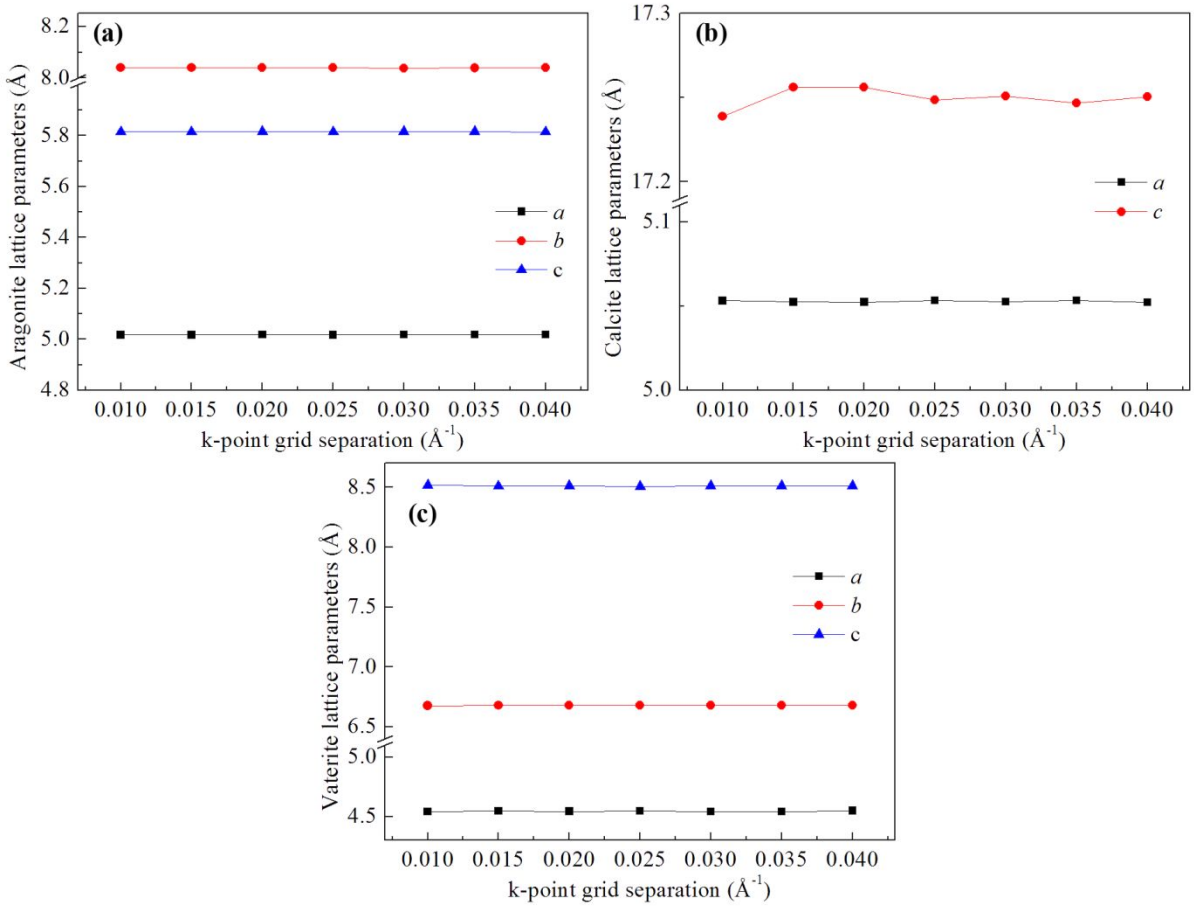

Figure S2. Convergence of bulk lattice constants with the increase of k-point grid separation: (a) aragonite, (b) calcite, and (c) vaterite.

As shown in and Figure S2, the lattice parameters of bulk aragonite, calcite and vaterite are basically parallel when k-point grid separation decreases to 0.03 Å^{-1}.

In Table S1, the deviation is the difference between the values calculated with k-point grid separation of 0.03 $Å^{-1}$ and 0.01 $Å^{-1}$. And deviation percent is the ratio of the difference divided by the value calculated with 0.01 $Å^{-1}$ k-point grid separation. The largest deviations are 0.000616 Å, 0.012150 Å and 0.005581 Å for bulk aragonite, calcite and vaterite, respectively. And, the values of the largest deviation percent are 0.01%, 0.07% and 0.07% for the three phases, respectively.

As the above stated, the k-point grid separation of 0.03 $Å^{-1}$ is reasonable to ensure the DFT calculation accuracy. Hence, the k-point grid separation 0.03 $Å^{-1}$ is adopted in this work.

2.CONCLUSIONS

The convergence tests have been conducted for the computation parameters (cutoff energy and k-point grid separation), their influences on the lattice constants of bulk aragonite, calcite and vaterite, respectively.

The results demonstrated that, the cutoff energy of 450 eV and k-point grid separation of 0.03 $Å^{-1}$ can sufficiently guarantee the DFT calculations accuracy. Hence, the cutoff energy of 450 eV and k-point grid separation of 0.03 $Å^{-1}$ are adopted in this work.

We also noticed that the cutoff energy 450 eV and k-point grid separation around 0.03 $Å^{-1}$ have been successfully implemented in the adsorption system containing calcite(10.4) surface [1], and calcium carbonate hydrates[2].

REFERENCES

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