Supplementary Materials

Activation Energy Calculations for Formamide–TiO_2 and Formamide–Pt Interactions in the Presence of Water

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We have simulated formamide, water–formamide, and water–ethanol mixtures (the 50–50 % solution) of ρ = 0.7–1.0 g/cm^3.

The MD simulation results for the formamide(f)+water(w) and ethanol(e)+water(w) solutions and surface interactions, which are summarized below, are shown for $\rho \approx 0.8$ g/cm^3 = 50%(f)+50%(w) (1152 formamide and 1152 water molecules). The MD simulation results of the formamide(f) solution and surface interactions, which are also summarized below, are shown for $\rho \approx 1.0$ g/cm^3 = 100%(f) (2304 formamide molecules).

The bulk TiO_2 (anatase) phase was defined by the unit cell lattice vectors of the following lengths: $a_0 = b_0 = 3.785$ Å and $c_0 = 9.514$ Å. As the adsorbing surface, we have composed in total four layers of 420 TiO_2 molecules (5040 = 1680 (Ti) + 3360 (O) atoms).

The bulk Pt_4 (platinum) phase was defined by the unit cell lattice vectors of the following lengths: $a_0 = b_0 = c_0 = 3.923$ Å. As the adsorbing surface, we have composed in total four layers of 784 Pt_4 molecules (3136 (Pt) atoms).

The corresponding system sizes and molecular composition of 50-50% formamide-water and ethanol-water solutions and their densities are specified in Table **2**.

Table 2. The Geometry Details and Molecular Composition of the Simulated Models

System size	*X*, Å	*Y*, Å	*Z*, Å	ρ, g/cm^3	Ewald Parameters (k_1, k_2, k_3)
$(TiO_2)_{5040}(CH_3NO)_{13824}$	56.77	52.99	73.06	1.06	22, 22, 22
$(Pt)_{3136}(CH_3NO)_{13824}$	54.99	54.99	69.22	1.06	22, 22, 28
$(TiO_2)_{5040}(H_2O)_{3456}(CH_3NO)_{6912}$	56.77	52.99	73.06	0.74	22, 22, 30
$(Pt)_{3136}(H_2O)_{3456}(CH_3NO)_{6912}$	54.99	54.99	69.22	0.74	22, 22, 28
$(TiO_2)_{5040}(C_2H_5OH)_{20736}$	56.77	52.99	72.56	1.09	22, 22, 30
$(Pt)_{3136}(C_2H_5OH)_{20736}$	54.92	54.92	69.22	1.09	22, 22, 28
$(TiO_2)_{5040}(H_2O)_{3456}(C_2H_5OH)_{10368}$	56.77	52.99	72.56	0.76	22, 22, 30
$(Pt)_{3136}(H_2O)_{3456}(C_2H_5OH)_{10368}$	54.92	54.92	69.22	0.76	22, 22, 28

A classical molecular dynamics study was performed using the DL_POLY_4.03.3 [28] general-purpose code. The NVT ensemble at T = 300 K in conjunction with a Nosé-Hoover thermostat with the three dimensional Ewald summation and the Verlet leapfrog scheme were employed. To calculate electrostatic forces, the Ewald sum was used; the automatic optimization parameter was $f = 1.0 \cdot 10^{-4}$; and the convergence parameter was 0.24375 Å^{-1}. The integration time step of the dynamic equations of motion was 1 fs. All simulations were periodic in three dimensions.

For the formamide molecule, the force field parameters were choosen from the DL_FIELD database [29], which, in their turn, had been taken from the CHARMM package [30].

The detailed formamide and ethanol potential and force field topology (chemical, angular, and dihedral bond parameters, atomic charges, etc.) are described below in Tables **3-5**.

Table 3. Intermolecular Lennard-Jones (LJ) Parameters for the Ethanol and Formamide Interactions with the TiO_2 and Pt Surfaces and Water Molecules. The Geometry of the Ethanol, Formamide, and Water Molecules is Shown Separately

LJ-parameters for FM			LJ-parameters for ETH		
Group	**ε, kcal/mol**	**σ, Å**	**Group**	**ε, kcal/mol**	**σ, Å**
N–N	0.2000	3.2963	C1–C1	0.1200	3.3000
N–H	0.0959	1.8482	C1–C2	0.1200	3.3000
N–C	0.1183	3.4300	C2–C2	0.1200	3.3000
N–Hf	0.0663	2.8241	C1–H1	0.0000	2.5400
N–O	0.1549	3.1627	C2–H1	0.0000	2.5400
N–OW	0.1744	3.2234	C1–Oe	0.1550	3.0800
N–Ti	0.7010	4.1310	H1–H1	0.0000	1.7800
C–C	0.0700	3.5636	H1–Oe	0.0000	2.3200
C–H	0.0567	1.9818	H1–OW	0.0000	2.3200
C–O	0.0917	3.2963	Oe–Oe	0.2000	2.8500
C–OW	0.1032	3.3571	C2–Oe	0.1550	3.0800
C–Ti	7.2630	4.1340	C1–Pt	0.9400	2.9000
Of–Of	0.1200	3.0291	C2–Pt	0.9400	2.9000
Of–H	0.0743	1.7145	Oe–Pt	0.9200	2.7000
Of–Hf	0.0514	2.6905	C1–OW	0.1360	3.4300
Of–Ti	7.7253	2.3431	C2–OW	0.1360	3.4300
Of–O	0.2278	3.1306	Oe–OW	0.1760	3.2000
Of–OW	0.2278	3.1306	OW–OW	0.1521	3.1650
Hf–Hf	0.0220	2.3520	C1–He	0.0000	2.5400
Hf–H	0.0318	1.3760	C2–He	0.0000	2.5400
Hf–OW	0.0578	2.7513	Oe–He	0.0000	2.3200
H–H	0.046	0.400	H1–He	0.0000	1.7800
H–OW	0.0836	1.7753	He–He	0.0000	1.7800
H–HW	0.0460	0.4000	OW–Pt	0.9200	2.7000
C–Pt	0.9400	2.9000	OW–Ti	7.7253	2.3431
Of–Pt	0.9200	2.7000	OW–O	0.2278	3.1306
N–Pt	1.7687	3.0615	Oe–O	0.2278	3.1306
OW–OW	0.1521	3.1206	Oe–Ti	7.7253	2.3431
HW–HW	0.0460	0.4000	C1–O	0.0917	3.2963
OW–HW	0.0836	1.7753	C2–O	0.0917	3.2963
OW–Ti	7.7253	2.3431	Ti–C1	7.2630	4.1340
OW–O	0.2278	3.1306	Ti–C2	7.2630	4.1340

Table 3. Contd.....

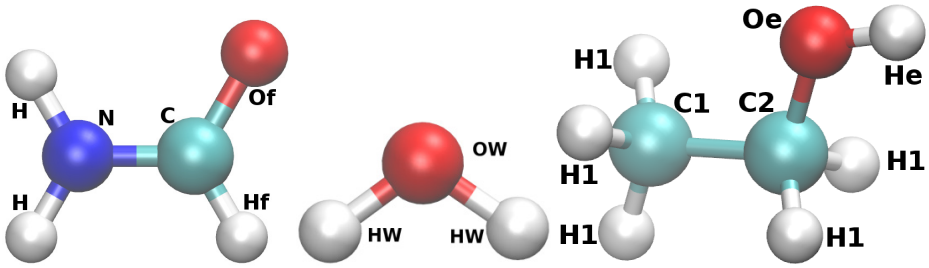
LJ-parameters for FM			LJ-parameters for ETH		
Group	**ε, kcal/mol**	**σ, Å**	**Group**	**ε, kcal/mol**	**σ, Å**
					

Table 4. The Atomic Masses and Effective Partial Charges of Formamide, Ethanol, Surfaces, and Water

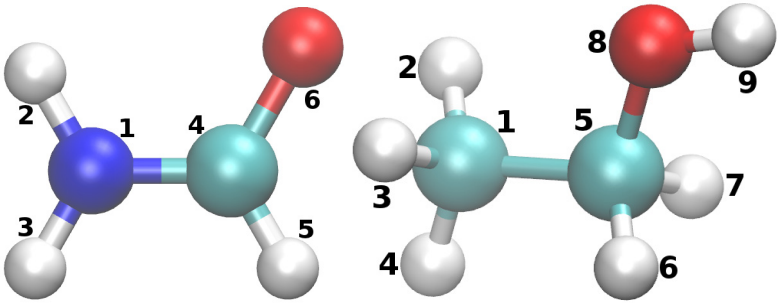
Atom	m/m_e, a.m.u.	q/e, proton charge	Atom	m/m_e, a.m.u.	q/e, proton charge
N (1)	14.0067	–0.69	C1 (1)	12.0110	–0.27
H (2.3)	1.00797	+0.35	C2 (5)	12.011	+0.05
C (4)	12.011	+0.42	H1 (2.3.4.6.7)	1.00797	+0.09
Hf (5)	1.00797	+0.08	Oe (8)	15.9994	–0.66
Of (6)	15.9994	–0.51	He (9)	1.00797	+0.43
Ti	47.867	+2.2	Pt	195.084	+0.00
O	15.9994	–1.1	HW	1.00797	+0.41
			OW	15.9996	–0.82
					

Table 5. The Potential Force Field Parameters Used for Formamide and Ethanol Molecules

Harmonic bond potential: $K(r_{ij} - r_0)^2/2$						
Bond	***K*, Å·kcal/mol**	r_0, **Å**		**Bond**	***K*, Å·kcal/mol**	r_0, **Å**
1–2	960.00	1.00		1–5	222.00	1.52
1–4	860.00	1.36		1–2	309.00	1.11
4–6	1300.00	1.23		5–6	309.00	1.11
4–5	634.26	1.10		5–8	428.00	1.42
1–6	100.00	2.37		8–9	545.00	0.94
1–5	100.00	1.98		1–3	309.00	1.11
1–3	960.00	1.00		1–4	309.00	1.11
				5–7	309.00	1.11
Lennard-Jones bond potential: $4\varepsilon((\sigma/r_{ij})^{12} - (1/r_{ij})^6)$						
Bond	ε, **kcal/mol**	σ, **Å**				
2–6	0.0743	1.4473				
2–5	0.0318	1.3760				
3–6	0.0743	1.4473				
3–5	0.0318	1.3760				
Angular potential: $K(\theta_{ijk} - \theta_0)^2/2$						
Group	***K*, Å·kcal/(mol·rad^2)**	θ_0, °		**Group**	***K*, Å·kcal/(mol·rad^2)**	θ_0, °
2–1–3	46	120		2–1–3	35.5	109.44
2–1–4	100	120		6–5–7	35.5	120.00
1–4–6	150	122		2–1–5	34.6	109.46
1–4–5	88	111		1–5–8	75.7	109.00
6–4–5	88	122		1–5–6	34.6	108.89
2–1–4	46	120		5–8–9	57.5	109.50
3–1–4	100	120		6–5–8	45.9	108.89
Dihedral potential: $K[1 + \cos(m\varphi_{ijkn} - \delta)]$				$K(\varphi_{ijkn} - \varphi_0)^2/2$		
Group	***K*, kcal/mol**	δ, °	m	**Group**	***K*, kcal/mol**	φ_0, °
2–1–4–6	1.4	180	2	2–1–5–8	0.16	180
2–1–4–5	1.4	180	2	2–1–5–6	0.16	–60
3–1–4–6	1.4	180	2	6–5–8–9	0.14	–60
3–1–4–5	1.4	180	2	1–5–8–9	1.3	180
				2–1–5–7	0.16	60
				3–1–5–6	0.16	180
				3–1–5–7	0.16	–60
				3–1–5–8	0.16	60

For the anatase surface, the force fields as reported by Kavathekar *et al*. [31] and Guillot *et al*. [32] were used. For the TiO_2 surface, the potential parameters were developed by Matsui and Akaogi [33]. The metallic substrate used was cubic Pt, which has the formula Pt_4. It was arranged in 8 layers numbering a total of 3136 atoms. The lattice constant was a = 3.923 Å. All the pa-

rameters of platinum were taken from EIM databases and dataset website supported by the Russian Foundation for Basic Research [34]. (Table **6**) represents the Buckingham (buck) potential parameters of the TiO_2 surface [33] and Sutton and Chen (SC or st-ch) potential parameters of the Pt surface [35].

Table 6. The Force Field Potentials and Parameters for TiO_2 and Pt Surfaces

Buckingham potential for TiO_2: $A_{ij}\exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6$				
i-j	A_{ij}, kcal/mol	ρ_{ij}, Å	C_{ij},Å^6 kcal/mol	
Ti–Ti	717647.4	0.154	121.067	
Ti–O	391049.1	0.194	290.331	
O–O	271716.3	0.234	696.888	
Quartic tethering potential parameters for TiO_2 and Pt : $kr^2/2 + k'r^3/3 + k''r^4/4$				
k, kcal/(mol·Å^2)		*k',* kcal/(mol·Å^2)		*k'',* kcal/(mol·Å^2)
0.4		0.0		0.4
Sutton-Chen potential parameters for Pt: $\varepsilon\left[\sum_{i=1}^{i}(a/r_{ij})^N/2 - C\sqrt{\sum_{i=1}^{i}(a/r_{ij})^M}\right]$				
ε, kcal/mol	*a*, Å	*N*	*M*	*C*
0.4	3.92	11.0	7.0	71.336

For water, an SPC rigid body model was used [36–38]. The water bond angles and lengths were not constrained; the water potential parameters are also shown in (Table **3**).

The van der Waals (vdW) interactions between the solutions (formamide–water and ethanol–water) and surfaces (TiO_2 and Pt) were represented by the Lennard--Jones (LJ) potential. The pair potential parameters from [39] was used for the Pt–N interaction. The cross-interaction parameters for formamide–water, ethanol–water, and surfaces (TiO_2 and Pt) are shown in (Tables **3**).

A parallel Shake algorithm expressed in terms of the domain decomposition strategy for constraining the rigid and other chemical bonds was used [28]. The MD simulations were realized in the temperature range of 250 K to 400 K with a step of 25 K.

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