

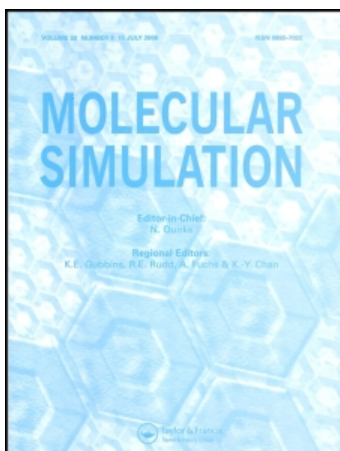
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Molecular Simulation

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title-content=t713644482>

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First Published: September 2008

To cite this Article Liu, Bin, Lusk, Mark T., Ely, James F., van Duin, Adri C. T. and Goddard III, William A. (2008) 'Reactive molecular dynamics force field for the dissociation of light hydrocarbons on Ni(111)', *Molecular Simulation*, 34:10, 967 — 972

To link to this Article: DOI: 10.1080/08927020802178609

URL: <http://dx.doi.org/10.1080/08927020802178609>

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Reactive molecular dynamics force field for the dissociation of light hydrocarbons on Ni(111)

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(Received 31 January 2008; final version received 3 May 2008)

The dissociation of small hydrocarbon molecules on Ni(111) surfaces is investigated using the Materials Studio[®] density functional theory code DMol³. The energetic barriers for these dissociations were obtained via linear/quadratic synchronous transit analysis. This kinetics information comprises a first principles database for hydrocarbon surface chemistry. The set was used to fit a new reactive molecular dynamics force field which was subsequently applied to consider the rate of finite temperature methane dissociation on Ni(111). In addition, the force field was used to estimate the degree of its transferability to hydrocarbons that are distinct from but structurally similar to those used to generate it.

Keywords: density functional theory; DMol³; hydrocarbons; dissociation rate; ReaxFF; molecular dynamics

1. Introduction

Hydrocarbon bond breaking is typically the rate limiting step in heterogeneous catalysis involving hydrocarbons and is a part of many industrially important processes including steam reforming, cracking and electrochemical oxidation in solid-oxide fuel cells [1–5]. A quantitative grasp of molecular interactions continues to be an experimental challenge to catalytic chemists, and these efforts are increasingly aided by computational interrogations at both the atomistic and the meso-scale levels.

Of particular interest in this work is the use of *ab initio* data sets to fit empirical potentials to be subsequently used in reactive force field molecular dynamics (MD) models – a methodology which has been successfully carried out for many years [6–10]. One such MD code, ReaxFF, is designed to be particularly transferable, and van Duin et al. [11] reported success in the structural predictions of a range of hydrocarbon molecules. ReaxFF force fields have also been developed for boron/nitrogen/hydrogen systems [12], silicon/silica systems [13] and for transition metal complexes [14].

ReaxFF force fields with demonstrated predictive strength were developed for H/C/Ni systems by separately fitting to *ab initio* data for a set of hydrocarbon molecules [11], atomic Ni-all carbon systems [15] and binding energies of hydrocarbons on small Ni clusters. However, because the predictive accuracy of empirical force fields tends to diminish as the structures diverge from those used to fit the parameters, there is a utility in creating force fields that are optimised to particular classes of interactions.

The physical setting that motivated such an optimised set of MD parameters is methane decomposition on Ni(111).

The generic force field was used to quantify the rate of dissociation under conditions of constant volume and species number with the temperature fixed at 1250 K to mimic the fuel cell operating conditions [16]. Although, this is somewhat higher than the range of interest in the fuel cell operations, which motivated this work, it allowed better statistics to be gathered on hydrocarbon decomposition. The dissociation barrier was first estimated to be 205 kJ/mol by carrying out a single constrained MD dissociation event in which hydrocarbon dissociation was forced through a prescribed reaction path. As detailed below, such a high barrier would indicate that dissociation occurs only very slowly. A finite temperature simulation was subsequently carried out on a system consisted of 30 methane molecules above a periodic five-layer 5 × 6 Ni slab for 400 ps, and no dissociation of CH₄ was observed – consistent with the high reaction barrier estimate.

The results of the generic ReaxFF simulations were then compared with theoretical predictions using classical reaction rate theory as governed by:

$$\frac{d[\text{CH}_4]_{\text{ads}}}{dt} = k_{\text{dis.ads.}}[\text{CH}_4]. \quad (1)$$

Here $[\text{CH}_4]_{\text{ads}}$, is the surface density of the adsorbed CH₄ molecule (in mol/m²), the number of CH₄ molecules on the surface, $[\text{CH}_4]$ is the gas phase density (in mol/m³), which can be estimated by dividing the number of CH₄ molecules in the simulation by the volume, and $k_{\text{dis.ads.}}$ is the effective rate constant (m/s). According to the kinetics parameters reported by Burghgraef et al. [17] the rate constant for methane dissociation on nickel is 1.05×10^{-6} m/s

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at 1250 K. This implies that the dissociation probability should be 4.2×10^{-6} during each 400 ps interval at 1250 K. However, this rate estimate is almost certainly too low because the activation energy (200.2 kJ/mol) that was adopted by Burghgraef et al. is much greater than the experimental value of $(52.7 \pm 5.0 \text{ kJ/mol})$; [18]). It therefore makes sense that the dissociation rate of predicted using the generic ReaxFF parameter set is too low since it has essentially the same reaction barrier.

To improve the theoretical estimate for the rate constant, we performed a density functional theory (DFT) [19] transition state theory analysis that resulted in a much lower barrier of 81.9 kJ/mol. By replacing the Burghgraef activation energy with this value, we obtained an improved estimate of 0.3 dissociation events per 400 ps.

In order to gain additional confidence in the rate of dissociation, Deutschmann's microkinetic modelling approach [20–21] was used to obtain a second estimate for the dissociation rate of CH₄. This methodology assumes that the rate constant is the product of the rate of surface collisions and the probability that such collisions result in a reaction – i.e. the sticking coefficient. The sticking coefficient is 8×10^{-3} using Deutschmann's mechanism [20]. Assuming, that the rate of CH₄ dissociation on surfaces is much greater than that for adsorption, the overall dissociation rate constant for the gas phase is then given by:

$$k = \frac{\gamma}{(\Gamma_{\text{tot}})^m} \sqrt{\frac{RT}{2\pi W}} \quad (2)$$

Here, γ is the sticking coefficient, Γ_{tot} is the adsorption site density ($2.6 \times 10^{-9} \text{ mol/cm}^2$) and W is the molecular weight (0.016 kg/mol). Consistent with the reactant being in the gas phase, the exponent parameter m is taken to be zero. The resulting value of rate constant, k , is then 2.57 m/s at 1250 K which corresponds to 10 dissociation events every 400 ps.

The two theoretical estimates for the rate of methane decomposition are quite different (0.3 and 2.57 m/s) but both suggest that the generic ReaxFF force field set underpredicts the reaction rate. This, combined with the high value of dissociation barrier measured, has motivated the use DFT to construct a data set specifically targeting the interactions of light hydrocarbons with Ni(111) surfaces. The information was applied to generate a force field intended to be especially accurate at predicting hydrocarbon decomposition on nickel surfaces. Specifically, a training set was populated with the dissociation energies and barriers for H₂, CH₄, C₂H₆ and C₃H₈ on Ni(111). The reactive force field code was then used to consider methane dissociation rates at finite temperatures. The new force field is intended to be of use in considering the dissociation of a range of structurally similar hydrocarbons. To assess this capability, the force field was fitted

without taking advantage of the data for the heaviest two hydrocarbons and a comparison was then made of the energy barriers offered these molecules as estimated by DFT and predicted by ReaxFF.

2. Methods

The DMol³ DFT code [22–23] provided within Materials Studio[®] 4.0 was used to perform all the electronic structure calculations. A norm conserving, spin unrestricted, semi-core pseudopotential [24] approach was employed with electron exchange and correlation accounted for using the Perdew–Wang generalised gradient approximation [25].

A five-layer, 3×3 , periodic slab was chosen to represent Ni(111) for adsorbates with the bottom two layers frozen with bulk lattice spacing. A 9 Å vacuum space was placed above the surface to avoid interference from neighbouring images. A $2 \times 2 \times 1$ Monkhorst–Pack k -point mesh [26] was used to sample the Brillouin zone of the unit cell. Linear/quadratic synchronous transit (LST/QST) analysis was employed to identify transition states [27].

Target parameters in the ReaxFF force field were fit to the training set based on a successive one-parameter search to reproduce the energy corresponding to each configuration from DFT theory [28]. The training proceeded iteratively until convergence was achieved.

Constant temperature (NVT)-MD was used in the validation studies of the force field. Simulations were performed with a velocity Verlet [29] approach with a time step of 0.25 fs. A Berendsen [30] thermostat with a temperature-damping constant of 250 fs was used to control the system temperature. In addition, constrained MD was occasionally used to obtain comparative adsorption/desorption barriers and reaction energies for single CH₄, C₂H₆ and C₃H₈ molecules. The method forces selected atoms to move towards or away from each other in order to more carefully study their interactions.

3. Results and discussion

3.1 Quantum chemistry calculations

Binding energies were calculated for H, CH₃, C₂H₅ and C₃H₇ on Ni(111) sites and are listed in Table 1, where t_1 ,

Table 1. Binding energies (in kJ/mol) for H, CH₃, C₂H₅ and C₃H₇ on Ni(111) sites.

Site	H	CH ₃	C ₂ H ₅	C ₃ H ₇
t_1	–245	–203	–177	–120
b_2	–273	–199	–157	–120
c_3	–283	–219	–162	–119

Table 2. Dissociation energies and barriers for H₂, CH₄, C₂H₆ and C₃H₈.

Adsorbate	Dissociation energy (kJ/mol)	Dissociation barrier (kJ/mol)
H ₂	-82	2
CH ₄	-122	82
C ₂ H ₆	-45	84
C ₃ H ₈	-40	60

Only primary dissociation is considered for the hydrocarbons.

b_2 and c_3 refer to atop, bridge and 3-fold sites, respectively. Both H and CH₃ favour the high symmetry 3-fold site, whereas the bulkier C₂H₅ and C₃H₇ fragments favour the t_1 site due to steric effects. As indicated in the table, binding energy is weakened by steric effect as well. The dissociation energies and dissociation barriers for H₂, CH₄, C₂H₆ and C₃H₈ are displayed in Table 2.

3.2 Force field development

With the intent of developing force fields tailored to hydrocarbon dissociation on Ni(111), only H₂ and CH₄ data were used to fit the force fields in order to test the transferability of the force field in capturing the dissociation of the heavier C₂H₆ and C₃H₈ molecules. Force field parameters with respect to the Ni atom, Ni-H/C bonds and various H-C-Ni valence angles were

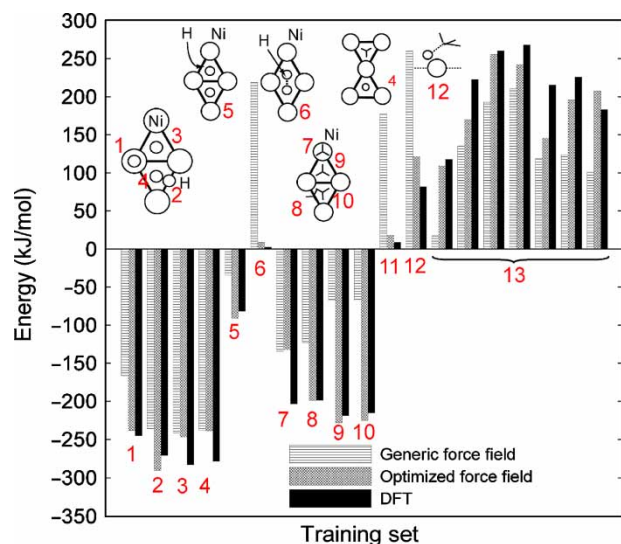


Figure 1. The fitting of ReaxFF parameters against DFT results and comparison with the old force field: 1–4: H binding at atop, bridge, 3-fold hcp and 3-fold fcc sites on Ni(111); 5: dissociation energy for H₂; 6: dissociation barrier for H₂; 7–10: CH₃ binding at atop, bridge, 3-fold hcp and 3-fold fcc sites on Ni(111); 11: dissociation energy for CH₄; 12: dissociation barrier for CH₄; and 13: the interpolated geometries between 11 and 12.

chosen to be the fitting target. The training set consisted of the H atom and CH₃ binding at t_1 , b_2 and c_3 sites and the dissociation energies of H₂, CH₄ and dissociation barriers of H₂, CH₄. This data was supplemented with energies associated with intermediate geometries generated from the LST/QST algorithm. The fitting results are compared with DFT data in Figure 1.

As indicated in Figure 1, the generic force field underestimates the H₂ dissociation energy and severely overestimates its dissociation barrier. Both problems are corrected in the new fit. In addition, the lack of observed CH₄ dissociation on Ni(111) can now be explained using Figure 1; the dissociation energy and barrier were simply overestimated, and this has also been improved in the new parameter set.

The transferability of the new force fields to C₂H₆ and C₃H₈ dissociation is examined in Figure 2. The positive results suggest that this parameter set may be transferable to a range of structurally similar alkane molecules.

3.3 Reactive molecular dynamics application

The new force fields were subsequently applied to consider finite temperature dissociation events. Figure 3(a–e) displays the MD-generated energy profiles for the dissociative adsorptions of H₂, CH₄, C₂H₆ and C₃H₈. The simulations were performed at a temperature of 5 K

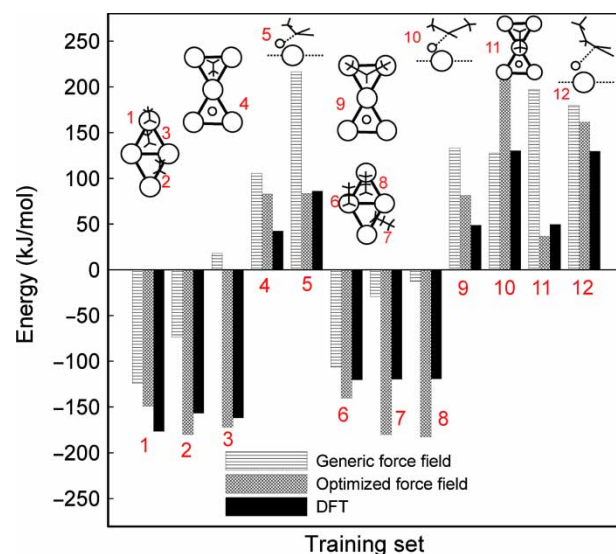


Figure 2. Comparison between the new and old force field on C₂H₆ and C₃H₈ that is not part of training to demonstrate force field transferability: 1–3: C₂H₅ binding at atop, bridge and 3-fold hcp sites on Ni(111); 4: dissociation energy for C₂H₆; 5: dissociation barrier for C₂H₆; 6–8: C₃H₇ binding at atop, bridge and 3-fold hcp sites on Ni(111); 9: dissociation for secondary C–H bond of C₃H₈; 10: dissociation barrier for secondary C–H bond of C₃H₈; and 11: dissociation energy for primary C–H bond of C₃H₈; 12: dissociation barrier for primary C–H of C₃H₈.

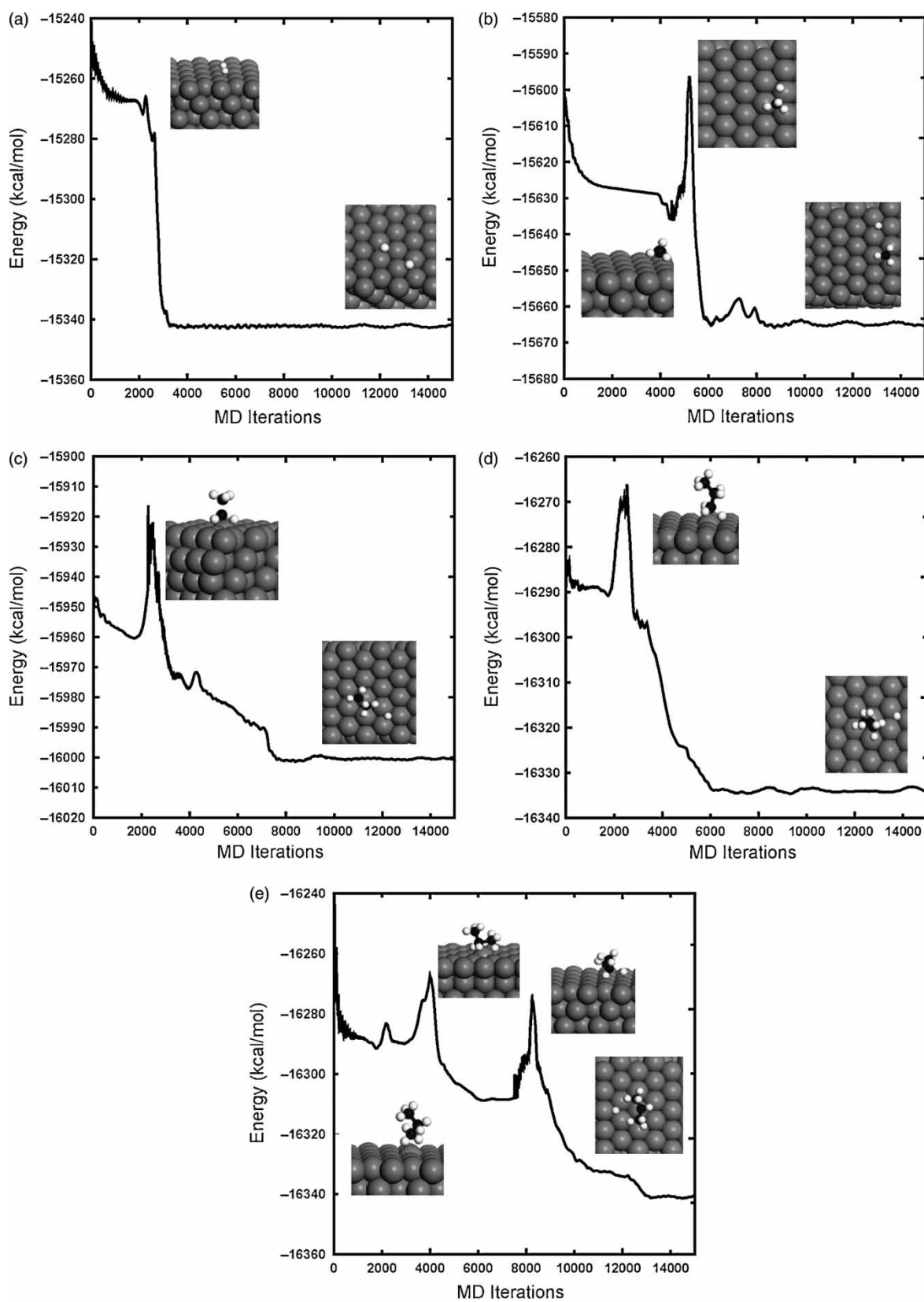


Figure 3. Energy profiles for dissociation: (A) H_2 ; (B) CH_4 ; (C) C_2H_6 ; (D) C_3H_8 primary C-H bond and (E) C_3H_8 secondary C-H bond.

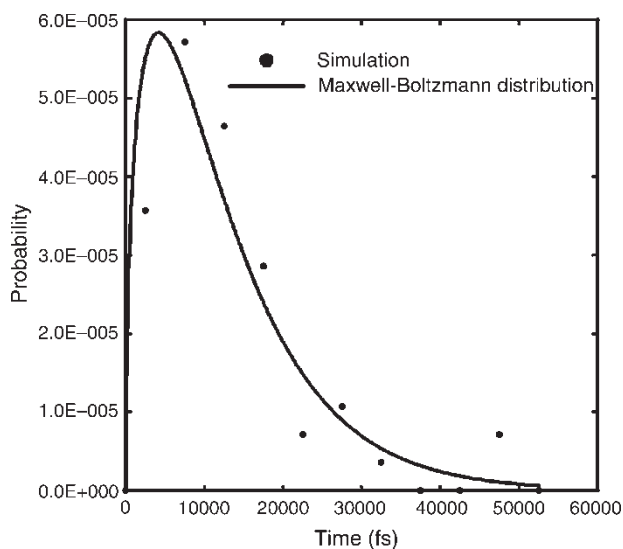


Figure 4. A the fit of simulation time histogram to the Maxwell-Boltzmann model expressed in terms of dissociation time.

since the intent was to reproduce the dissociations kinetics through *guided* pathways. The inset pictures illustrate the configurations corresponding to each state. Both the profiles and configurations show reasonable behaviour for these small hydrocarbons above Ni(111) and are consistent with the *ab initio* data.

Conventional NVT-MD was then used to study the rate of CH₄ dissociation on Ni(111). The simulation was constructed by assigning a random initial position and velocity to one CH₄ molecule followed by a measurement of the time required for dissociation. This was repeated 51 times with a resulting distribution reasonably fit (Figure 4) by the distribution expressed in Equation (3):

$$f(t) = 3t_{\text{mean}}^{-3/2} \sqrt{\frac{3t}{2\pi}} e^{-\frac{3t}{2t_{\text{mean}}}}. \quad (3)$$

This was derived by first assuming that the kinetic energy of the molecules exhibits a Maxwell-Boltzmann distribution. A second assumption was then made that the dissociation time is proportional to the kinetic energy of the molecule. Finally, the distribution was normalised with the exponent expressed in terms of the mean of the distribution, $t_{\text{mean}} = 13.07$ ps. The distribution was then used to determine a rate constant of $k = 270$ m/s – higher than the estimates from classical reaction rate theory (0.3 m/s) and the method based on sticking coefficients (2.6 m/s). These single-molecule simulations were stopped immediately following dissociation under the assumption that the initial velocities, positions orientations evenly sample the configuration space. The resulting high rate constant prompted a second approach in which a single simulation was run for over 155 ps with 30 methane

molecules. A much lower rate constant of 12.9 m/s was obtained and is thought to more accurately reflect the physical setting.

4. Conclusions

A new reactive force field set has been developed that is optimised for the dissociation of small hydrocarbon molecules on Ni(111). The addition of a DFT data set tailored for such interactions resulted in an observed rate of methane decomposition that is higher (12.9 m/s) than either of the estimates derived using experimental data (0.3 and 2.6 m/s). The fitting procedure revealed shortcomings of the generic H/C/Ni force field set – specifically positive dissociation energies (endothermic) and over-estimated dissociation barriers. Although, the new training was limited to only H₂ and CH₄ dissociation on Ni(111), good reaction barrier agreement between ReaxFF predictions and DFT analysis was obtained for C₂H₆ and C₃H₈ as well – an indication of force field transferability to similarly structured molecules. The newly developed force field still overpredicts the binding energies of H–Ni, C–Ni pairs and this will be addressed in future optimisation work.

Acknowledgements

This work was partially supported by the US Department of Energy, Office of Science, Grant DE-ER9542165.

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