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Properties of methane and carbon adsorbed at the interface between molten NaBr and Ni(111)

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Abstract

Electronic structure calculations and constant temperature *ab initio* molecular dynamics simulations were used to study the molten NaBr-Ni(111) interface. The presence of molten NaBr has a pronounced effect on the Ni(111) surface. For instance, the Na⁺ and Br⁻ ion concentrations are increased at the interface and Bader charge analysis shows that negative charge is transferred from Br⁻ ions at the interface to the Ni(111) surface. The molten NaBr also destabilizes dissociated methane (*CH + 3H*) adsorbed at the NaBr-Ni(111) interface compared to dissociated methane adsorbed on Ni(111) without NaBr. Carbon dimers (*C₂) at the NaBr-Ni(111) interface are found to be kinetically and thermodynamically unstable and dissociate into carbon atoms. Furthermore, carbon atoms initially placed at the NaBr-Ni(111) interface or on the bare Ni(111) surface quickly diffuse into the Ni(111) slab. The molten NaBr increase the stability of atomic carbon in the subsurface region. Nickel nanoparticles would be excellent catalysts for methane pyrolysis if they did not rapidly coke. One goal of this study was therefore to investigate whether a molten salt would hinder or remove coke from the Ni(111) surface. Molten NaBr may help keep the Ni(111) surface clean of carbon and catalytically active by favoring subsurface carbon. It is however

questionable whether subsurface carbon is desirable, as it has been reported that dissolved carbon precipitates out of the nickel particles as carbon whiskers that block the catalyst bed.

Keywords: Pyrolysis, molten salt, nickel catalyst, methane activation, carbon formation, interfaces, *ab initio* molecular dynamics

1. Introduction and Background

Numerous papers have discussed the possibility of replacing carbon-based fuels with hydrogen to avoid CO₂ generation. Currently the most widely practiced method of hydrogen production is steam reforming of methane or petroleum-based feedstocks. Unfortunately, to produce 50 million tons of hydrogen this method coproduces 300 million tons of CO₂. This is not satisfactory if one intends to use hydrogen in a CO₂-free economy. A possible alternative is hydrogen production by methane pyrolysis (reaction eq 1).

In gas phase methane pyrolysis takes place at high temperature, with slow rate and it is used only if the goal is to make high quality carbon black. To perform the reaction efficiently one must have a catalyst. Unfortunately, the conventional solid, heterogeneous catalysts (e.g. Ni nanoparticles supported on alumina) are deactivated by the carbon produced in the reaction.¹⁻³ The literature recommends that the catalyst should be reactivated by burning the coke, but this produces CO₂ defeating the goal of having a CO₂ free process.

A possible solution is to use a molten catalyst in a bubble column or a carbon catalyst in a fluidized bed.⁴⁻²³ In a bubble column containing the molten catalyst the pyrolysis reaction takes place in a bubble traveling upward through the liquid. The carbon produced by pyrolysis is carried

with the bubble and deposited on the surface of the melt. If the melt density is higher than that of carbon (in most cases it is) the carbon floats on the surface of the melt and can be removed by skimming. In this process each new bubble is in contact with a clean liquid-catalyst surface and coking is no longer a problem. This arrangement requires that the liquid in the bubble column is a good catalyst. Recently, it has been shown that molten Ni-Bi,²⁴ molten Cu-Bi,²⁵ molten MnCl₂-KCl,²⁶ and molten tellurium²⁷ are all good catalysts for methane pyrolysis at ~1000°C.

In this article we explore another paradigm. Clean Ni nanoparticles are highly active for methane pyrolysis, but they coke very rapidly and lose their activity. Ni nanoparticles alone are therefore not good catalysts for methane pyrolysis. The question we ask here is whether a suspension of Ni nanoparticles in a molten salt might be a good catalyst which does not coke. This might happen if the salt adheres to the surface more readily than the carbon or if the carbon atom formed by pyrolysis prefers to be in the salt rather than the salt-Ni interface. To answer this question, we use *ab initio* molecular dynamics (AIMD) and density functional theory (DFT) to simulate the properties of the interface between molten NaBr and a Ni(111) slab. We choose NaBr, because it is a simple alkali halide salt and because we hope that the interactions between Br⁻ and the Ni(111) surface have intermediate strength such that surface adsorbates are destabilized without the surface being poisoned by the anions. First, we examine the NaBr-Ni(111) interface and calculate the effect of the salt on the Ni(111) surface. In particular, we look at how the concentration of the ions depends on the distance from the surface and how the electron charge is redistributed when NaBr and Ni(111) interact with each other. The analysis shows that there is an increased concentration of both Na⁺ and Br⁻ ions at the interface and that negative charge is transferred from the Br⁻ ions at the interface to the Ni(111) surface.

We further investigate the stability of methane, dissociated methane, carbon atom(s), and carbon dimers at the NaBr-Ni(111) interface. We find that placing a methane molecule at the NaBr-Ni(111) interface leads to dissolution of methane into the salt. However, moving the CH₄ molecule from gas phase into the salt is still energetically uphill and we therefore expect a very low methane solubility in the salt. Dissociated methane (*CH + 3H*) adsorbed at NaBr-Ni(111) interface is more stable than molecular methane dissolved in the NaBr salt, but less stable than dissociated methane on a bare Ni(111) surface. The presence of NaBr therefore destabilizes dissociated methane adsorbed on the Ni(111) surface and restrict access to the surface because of its low methane solubility. However, we do not believe this rule out using solid Ni particles suspended in NaBr melt as a methane pyrolysis catalyst. This is because the adsorbed dissociated methane is more stable than dissociated methane adsorbed on other known methane pyrolysis catalyst and because a rising bubble containing methane will come in contact with the Ni particles so it is not necessary that methane is soluble in the melt.

Carbon atoms that start at the NaBr-Ni(111) interface is found to migrate rapidly into the subsurface of the Ni(111) slab. Given a choice between the metal and the salt the carbon atom prefers to go into the metal. We have also examined the behavior of a C₂ dimer species placed at the metal-salt interface. The C₂ species dissociates rapidly, and the atoms formed by dissociation also migrate into the bulk.

It has been reported²⁸ that Ni surfaces stay catalytically active for C-H bond breaking as long as carbon dissolves into the Ni metal rather than accumulating on the Ni surface. Placing Ni nanoparticles in molten salt could therefore help keep the Ni(111) surface clean of carbon and catalytically active. The solubility of carbon in Ni nanoparticles is likely substantial, as nickel carbide has been reported to be thermodynamically stable above 510°C (although the structure and

composition of the nickel carbide is not known).²⁹⁻³⁰ Unfortunately, the study [28] also states that dissolved carbon is not desirable, because the carbon eventually precipitates out of the nickel particles as carbon whiskers that block the catalytic bed.

2. Methods

2.1. Density Functional Theory and Molecular Dynamic Simulations. In our simulations, we model a molten NaBr film (20NaBr units) supported on a Ni(111) slab; thus, liquid NaBr has one NaBr-Ni(111) interface and one vacuum-NaBr interface. The Ni slab consists of a 4×4 rectangular Ni(111) surface cell and a thickness of three atomic layers where the bottom layer is fixed. The NaBr-Ni(111) system is investigated using AIMD simulations, implemented in the VASP computational package³¹⁻³⁴ and using the Nosé thermostat to sample the NVT ensemble.³⁵⁻³⁶ The motion of the atoms is treated classically, and 1 fs time steps are used to solve the Nosé equations of motion. The Nosé thermostat was set to keep the temperature around 1300 K. The energy in these simulations is obtained by DFT, using a plane wave basis set with 350 eV energy cutoff, and a $(2 \times 2 \times 1)$ Monkhorst–Pack k -point grid to sample reciprocal space. For the Bader³⁷⁻⁴⁰ charge analysis performed in this study we used a plane wave basis set with 400 eV energy cutoff, and a $(4 \times 4 \times 1)$ Monkhorst–Pack k -point grid. The PBE functional⁴¹ and D3 van der Waals correction⁴² were used to approximate the exchange-correlation effects. The calculations use the projector augmented-wave method⁴³⁻⁴⁴ and include ten valence electrons for Ni atoms, one valence electron for Na atoms, seven valence electrons for Br atom, four valence electrons for carbon, and one valence electron for hydrogen. The remaining electrons in the atoms are treated with the frozen core approximation. Spin polarized calculations were performed for all systems; the spin charge

density difference on Ni atoms range between 0.6 to 0.7 e (note Ni is known to be a ferromagnetic metal). We did not observe any spin on Na, Br, C, and H atoms.

The mean internal energy in constant temperature AIMD is given by

$$\langle E \rangle_t = \frac{1}{t-t_0} \int_{t_0}^t E(\tau) d\tau \quad (2)$$

where $E(\tau)$ is the total internal energy at time τ . Since the system is held at constant temperature, the total energy fluctuates as time evolves. The simulation prior to the time t_0 is used to equilibrate the system and is not included in the average energy. The t_0 values (Table 1) are chosen such that any transient in the internal energy is removed. The AIMD simulations are subsequent sampled for $t-t_0$ (Table 1) to converge the mean internal energies.

Table 1: t_0 and $t-t_0$ values for the discussed AIMD simulations. The t_0 values are chosen to remove any transients in the internal energies and presumably bring the system to a state that is independent of the initial positions and momenta (equilibrated).

<i>Systems</i>	<i>t_0 (ps)</i>	<i>$t-t_0$ (ps)</i>
20NaBr(<i>l</i>)/Ni(111)	6	26
CH ₄ (salt) + 20NaBr(<i>l</i>)/Ni(111)	4	23
3H* + *CH + 20NaBr(<i>l</i>)/Ni(111)	8	16
C* + 20NaBr(<i>l</i>)/Ni(111)	6	28
C(salt) + 20NaBr(<i>l</i>)/Ni(111)	4	27
C(vacuum-salt) + 20NaBr(<i>l</i>)/Ni(111)	4	23
*C ₂ + 20NaBr(<i>l</i>)/Ni(111)	3	17
2C* + 20NaBr(<i>l</i>)/Ni(111)	7	17
Ni(111)	7	17

C* + Ni(111)	14	15
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Reaction energies (ΔE) of carbon atom(s) formation, carbon dimer formation, molecular methane adsorption, and dissociated methane adsorption in 20NaBr(*l*)/Ni(111) are calculated as internal energy differences and referenced to methane and hydrogen molecules in the gas phase. For example, the reaction energy of forming atomic carbon, ΔE^*_{C} , is given by eq 3, where $\langle E^*_{\text{C}+20\text{NaBr}/\text{Ni}(111)} \rangle_t$ is the mean internal energy of a carbon atom adsorbed at the 20NaBr(*l*)/Ni(111) interface, $\langle E_{\text{H}_2(\text{g})} \rangle_t$ is the mean energy of a hydrogen molecule in the gas phase, $\langle E_{20\text{NaBr}/\text{Ni}(111)} \rangle_t$ is the mean energy of 20NaBr(*l*)/Ni(111) without any adsorbates, and $\langle E_{\text{CH}_4(\text{g})} \rangle_t$ is the mean energy of methane in the gas phase.

$$\Delta E^*_{\text{C}} = \langle E^*_{\text{C}+20\text{NaBr}/\text{Ni}(111)} \rangle_t + 2\langle E_{\text{H}_2(\text{g})} \rangle_t - \langle E_{20\text{NaBr}/\text{Ni}(111)} \rangle_t - \langle E_{\text{CH}_4(\text{g})} \rangle_t \quad (3)$$

The energies of the gas phase molecules (CH₄ and H₂) are calculated⁴⁵ with the center of mass of the molecule fixed, while the molecule can rotate and vibrate. Thus, the calculations contain the electronic, classical vibrational, and classical rotational energy of the molecule in vacuum. Subsequently, the translational energy ($3/2 k_{\text{B}}T$ where k_{B} is Boltzmann constant) is added to the energy of the gas phase molecule.

The presented AIMD simulations are computational demanding and necessitated the use of relative short simulation times, 350 eV energy cutoff, and (2×2×1) k-point grid. Longer simulations, higher energy cutoff, and more k-points would improve the accuracy of our simulations, however, the conclusions presented in this paper are based on energy differences of at least 0.35 eV, which we believe is larger than the possible errors from the choice of

computational parameters (The 0.35 eV energy difference is encountered when we compare *C adsorbed on Ni(111) with and without the NaBr film).

3. Results and Discussion

3.1. Structure of the molten NaBr-Ni(111) system. We first analyze the atomic density in the molten NaBr film as a function height above the Ni(111) surface. The following procedure was applied; the molten NaBr film was divided into a number of imaginary strips defined by planes parallel to the surface. We count the number $n(Na; z_\alpha, t)$ of Na atoms and the number $n(Br; z_\alpha, t)$ of Br atoms, present at time t , in the strip α , whose center is located at z_α . The mean number of Na atoms at a distance z_α from the surface is then given by eq 4. A similar formula is used to calculate $\langle n(Br; z_\alpha) \rangle$.

$$\langle n(Na; z_\alpha) \rangle = \frac{1}{t-t_0} \int_{t_0}^t n(Na; z_\alpha, \tau) d\tau \quad (4)$$

Figure 1a shows how the concentration of Na and Br atoms varies across the molten NaBr film. Just above the Ni(111) surface there is an excess of both Na^+ and Br^- ions, but with more Na^+ . This can also be seen in the movie shown in Figure S1 in the Supporting Information (SI), where the Na^+ (and to a lesser extend Br^-) ions tend to spend more time near the Ni atoms. The ions, however, are not bound to the surface and they move towards and away from the Ni atoms at the surface over time. Slightly further from the surface (~ 4 Å), Br^- ions have higher concentration than Na^+ to compensate for the higher concentration of Na^+ ions than Br^- ions at the interface. The oscillation in Na^+ and Br^- ion concentration continues to ~ 10 Å from the Ni(111) surface. Similar cation-anion interface segregations and concentration oscillations away from the surface have been observed for other molten salt-solid interfaces, namely $LiCl(l)/MgO(s)^{46}$ and $KCl(l)/CdSe(s)^{47}$ interface systems.

The structure of a liquid is usually characterized by radial pair-distribution functions, $g_{AB}(r)$, which are defined by

$$P_{AB}(r)dr = 4\pi r^2 g_{AB}(r) \rho_{tot} dr \quad (5)$$

$P_{AB}(r)dr$ is the probability of finding an atom B at a distance between r and $r + dr$ from A, and ρ_{tot} is the total atomic density. Figure 1b shows radial distribution functions for 20NaBr(*l*)/Ni(111). The Na–Br nearest neighbor distance peaks at 2.84 Å and the nearest Na–Na, and Br–Br distances peak at 4.13 Å, and 4.38 Å, respectively. Integration of the Na–Br radial distribution function for distances < 4.5 Å shows that every atom has an average of ~ 5.0 nearest neighbors.

Figure 1. (a) The average concentration of Na⁺ and Br⁻ ions, as a function of height above the Ni(111) surface. (b) Radial distribution function versus distance for Na⁺ and Br⁻ ions.

3.2. Bader charge variations in NaBr-Ni(111). In this section we analyze how the atomic Bader charges vary over time and how the Bader charges depend on distance to the Ni(111) surface.

Figure 2a shows the time evolution of the average Bader charge on Na and Br, as well as the net Bader charge in the Ni slab (48Ni). The average Bader charge on Br and Na is $-0.8 e$ and $+0.8 e$, respectively and these average values barely change over time. However, some charge transfer does take place between the salt and the Ni slab, such that the net charge in the slab is around $-0.5 e$.

We further analyze the Bader charges as a function of distance to the Ni(111) surface by plotting every individual atomic Bader charge as a function of height (Figure 2b). Here it is seen that Br^- ions at the NaBr-Ni(111) interface are less negatively charged than Br^- ions further out. The missing negative charge is transferred to the surface atoms of the Ni slab and, to much lesser extent, to Na^+ ions at the NaBr-Ni(111) interface. The charge transfer from Br^- to the Ni slab is likely due to interactions between the Br^- ions and the Ni surface that are covalent in nature (Na^+ ions do not seem to interact covalently with the Ni surface). As the ions get further from the surface, the Bader charge becomes constant.

Figure 2. (a) Time evolution of the net Bader charge on the Ni slab (48Ni), as well as the average Bader charge on Na^+ and Br^- ions during the 20NaBr(*l*)/Ni(111) AIMD run. (b) Bader charges on every atom at all analyzed points in time plotted as a function of height.

3.3. Molecular and dissociated methane at the NaBr-Ni(111) interface. Figure 3a shows a snapshot of molecular methane in the NaBr(*l*)/Ni(111) system. The methane molecule was initially placed at the NaBr(*l*)-Ni(111) interface, but the molecule dissolves into the salt after ~ 7 ps, (Figure S2 in the SI contains a movie of the entire simulation). We observe that the dissolution process is accompanied by the formation of a cavity in the NaBr molten salt around the methane molecule. Inside the cavity the methane molecule rotates almost freely. Since formation of the cavity increases the distances between the ions and weakens the electrostatic interactions, the solvation energy of methane in the salt becomes unfavorable compared to gas phase methane (+1.26 eV, Table 2). Similar cavity formation has already been observed around ethane, ethylene, and O_2 molecules situated at a molten LiCl-MgO interface.⁴⁶ In the LiCl-MgO system, the cavities were located at the LiCl-MgO interface, whereas we observe that the methane molecule together with the cavity is situated away from the Ni surface inside the molten NaBr film. This indicates that it

is more favorable to disrupt ionic interactions in the molten NaBr salt than to disrupt NaBr-Ni interactions at the interface.

Figure 3. (a) Snapshot of a methane molecule that was initially placed at the NaBr-Ni(111) interface, but dissolved in salt after ~ 7 ps of AIMD simulations. The solvation energy is +1.26 eV. (b) Snapshot of dissociated methane ($3\text{H}^* + ^*\text{CH}$) at the interface of NaBr-Ni(111) after 18 ps of AIMD simulations. In the figures, Ni atoms, Na and Br ions, are shown by green, blue and pink, respectively, while carbon and hydrogens are shown by red and gray, respectively.

We also study dissociated methane ($3\text{H}^* + ^*\text{CH}$) adsorbed on the NaBr-Ni(111) interface (Figure 3b) and compare the energy to the energy of methane in the gas phase (Table 2). We note that we initially inserted $\text{H}^* + ^*\text{CH}_3$ at the interface of NaBr-Ni(111), but after ~ 4 ps of AIMD simulations $^*\text{CH}_3$ dissociates and form $^*\text{CH}$; apparently $3\text{H}^* + ^*\text{CH}$ does not undergo further reaction within the time of the AIMD simulation. It has previously been found that breaking the C-H bond in $^*\text{CH}$

on Ni(111) has a higher activation energy than breaking any of the former C-H bonds (i.e. the ones in $^*\text{CH}_4$, $^*\text{CH}_3$, and $^*\text{CH}_2$).⁴⁸ Dissociative methane adsorption in the form of 3H^* and $^*\text{CH}$ at the $20\text{NaBr}(l)/\text{Ni}(111)$ interface is uphill and the internal adsorption energy is calculated to be +0.72 eV. Interestingly, the dissociative methane adsorption energy of $\text{H}^* + ^*\text{CH}_3$ and $3\text{H}^* + ^*\text{CH}$ on Ni(111) without salt is -0.39 eV and -0.64 eV, respectively (obtained by geometry optimized DFT calculations instead of AIMD). The destabilization of the adsorption energy for dissociated methane ($3\text{H}^* + ^*\text{CH}$) in the presence of molten salt is likely due to competitive adsorption at the interface, where $^*\text{CH}$ and 3H^* displaces NaBr from the surface leading to energy cost. Similar destabilization of adsorption energies have been observed for HCl adsorption at a water- $\text{TiO}_2(110)$ interface⁴⁹ and for N_2 adsorption at the interface between NaCl and small Ru clusters.⁵⁰ Even though the dissociated methane is significantly destabilized by the molten NaBr, the adsorption energy is still significantly more stable than the methane solvation energy in the molten NaBr film (1.26 eV) and dissociative methane adsorption ($\text{H}^* + ^*\text{CH}_3$) on a molten Cu-Bi surface (1.78 eV) recently studied by us,⁵¹ where we also found that the Cu-Bi alloy is very active for methane pyrolysis. This indicate that the presence of the molten NaBr film will lower the rate of methane activation (C-H bond breaking) on the Ni(111) surface, but probably not below what is required for high methane pyrolysis activity.

Table 2: Internal reaction energies for molecular methane and dissociated methane initially placed at the NaBr-Ni(111) interface compared to gas phase methane. Molecular methane diffuses into the salt, while dissociated methane ($3\text{H}^* + ^*\text{CH}$) prefers to stay at the NaBr-Ni(111) interface.

<i>Reactions</i>	<i>ΔE (eV)</i>
$\text{CH}_4(\text{g}) + 20\text{NaBr}(l)/\text{Ni}(111) \rightarrow \text{CH}_4(\text{salt}) + 20\text{NaBr}(l)/\text{Ni}(111)$	1.26

$\text{CH}_4(\text{g}) + 20\text{NaBr}(\text{l})/\text{Ni}(111) \rightarrow 3\text{H}^* + \text{*CH} + 20\text{NaBr}(\text{l})/\text{Ni}(111)$	0.72
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3.4. Single carbon atom at Ni(111), in NaBr, and at vacuum-NaBr. We also computed the stability of a single carbon atom at different positions in the NaBr-Ni(111) system. We use eq 3 to compare the energy of the atomic carbon and hydrogen gas to that of methane. The carbon atom is placed at the NaBr-Ni(111) interface (C^*), in the salt ($\text{C}(\text{salt})$), and at the interface between salt and vacuum ($\text{C}(\text{vacuum-salt})$). Interestingly, we observe that the C^* carbon atom initially placed at the NaBr-Ni(111) interface, diffuses into the Ni slab after 5ps of simulation time and remains situated between the first and second Ni layer for the rest of the simulation (we discuss diffusion into the Ni slab in section 3.6.). The reaction energies to form atomic carbon are summarized in Table 3. The reaction energies show that the C^* species in the Ni slab is by far the most stable carbon species with $\text{C}(\text{salt})$ being 5.73 eV less stable and $\text{C}(\text{vacuum-salt})$ being 5.39 eV less stable. Thus, for studying a carbon dimer and two separate carbon atoms, we only focus on the NaBr-Ni(111) interface and the Ni slab. The internal reaction energy cost to form the C^* species in the Ni slab and $2\text{H}_2(\text{g})$ from $\text{CH}_4(\text{g})$ is 1.64 eV. The energy cost may seem large, but note that at 1300 K the entropy gain ($-\text{T}\Delta\text{S}^0$) of forming $2\text{H}_2(\text{g})$ and solid carbon (graphite), while consume one $\text{CH}_4(\text{g})$ is -1.50 eV (<https://janaf.nist.gov>).

Table 3: Internal reaction energies for methane pyrolysis on 20NaBr/Ni (111), where the carbon atom is placed at the NaBr-Ni(111) interface but diffuses into the Ni slab (C^*), is placed in the molten salt ($\text{C}(\text{salt})$), or is placed at the vacuum-NaBr interface ($\text{C}(\text{vacuum-salt})$).

<i>Reactions</i>	ΔE (eV)
$\text{CH}_4(\text{g}) + 20\text{NaBr}(\text{l})/\text{Ni}(111) \rightarrow \text{C}^* + 20\text{NaBr}(\text{l})/\text{Ni}(111) + 2\text{H}_2(\text{g})$	1.64

$\text{CH}_4(g) + 20\text{NaBr}(l)/\text{Ni}(111) \rightarrow \text{C}(\text{salt}) + 20\text{NaBr}(l)/\text{Ni}(111) + 2\text{H}_2(g)$	7.37
$\text{CH}_4(g) + 20\text{NaBr}(l)/\text{Ni}(111) \rightarrow \text{C}(\text{vacuum-salt}) + 20\text{NaBr}(l)/\text{Ni}(111) + 2\text{H}_2(g)$	7.03

3.5. Carbon dimer and carbon atoms at Ni(111). In order to estimate the affinity for carbon atoms to agglomerate, we initialize a carbon dimer (C_2^*) at the $20\text{NaBr}(l)/\text{Ni}(111)$ interface and compare the dimer to two separate carbon atoms (2C^*) also initially placed at the $20\text{NaBr}(l)/\text{Ni}(111)$ interface. The carbon-carbon distances as a function of time for both the carbon dimer and the two separate carbon atoms are shown in Figure 4. The carbon-carbon bond distance in the carbon dimer vibrates between 1.4 Å-1.5 Å, for the first 20 ps of simulation time, however, the carbon dimer then dissociates and the distance increases to more than 3 Å (Figure 4a). Oppositely, the two separate carbon atoms never get closer than 2.4 Å and do not form a chemical bond at any point in time (Figure 4b). The atomic configuration for the carbon dimer at the interface after 5 ps and 25 ps of AIMD simulation time is shown in Figure 5. After 5 ps the carbon dimer is clearly visible and adsorbed on the Ni(111) surface, whereas, after 25 ps, the carbon dimer has dissociated into two separate carbon atoms. Furthermore, we see that the carbon atoms from the carbon dimer have moved into the Ni slab and are now situated between the first and second layer. The two separate carbon atoms also migrate into the Ni slab during their AIMD simulation.

Figure 4. Distance between the two carbon atoms for (a) carbon dimer and (b) two separate carbon atoms. The carbon dimer dissociates after 20 ps, whereas the two carbon atoms do not get close enough to form a bond.

Figure 5. Atomic configuration of the $*C_2 + 20NaBr(l)/Ni(111)$ interface (i.e. the carbon dimer simulation) after 5 ps and 25 ps. The carbon dimer dissociates and diffuses into the Ni slab over

time. In the figure Ni atoms are shown in green, while Na and Br ions are shown in blue and pink, respectively.

Table 4 compares the energy of the carbon dimer ($*C_2$) to that of two separate carbon atoms ($2C^*$). Since the carbon dimer dissociates into two separate carbon atoms after 20 ps, the energy sampling is only conducted for the part of the simulation where the carbon dimer is intact. The energy of the two separate carbon atoms is 0.86 eV more stable than the energy of the carbon dimer. Based on this energy difference and the observed carbon dimer dissociation, we conclude that carbon atoms prefer to stay separated rather than agglomerating into dimers. Finally, we note that the energy of two carbon atoms at the NaBr(*l*)/Ni(111) interface (3.45 eV) is only slightly higher than twice the energy of a single carbon atom at the NaBr(*l*)/Ni(111) interface (2×1.64 eV). The small difference likely corresponds to a repulsion that occur between the two carbon atoms.

Table 4: Internal reaction energies for methane pyrolysis to form carbon dimer and two separate carbon atoms initially placed at the 20NaBr(*l*)/Ni(111) interface.

<i>Reactions</i>	ΔE (eV)
$2CH_4(g) + 20NaBr(l)/Ni(111) \rightarrow *C_2 + 20NaBr(l)/Ni(111) + 4H_2(g)$	4.31
$2CH_4(g) + 20NaBr(l)/Ni(111) \rightarrow 2C^* + 20NaBr(l)/Ni(111) + 4H_2(g)$	3.45

3.6. Diffusion of carbon atoms and carbon dimer into the Ni slab. As expected from the energy analysis in section 3.4, we never observe that carbon atoms diffuse from the Ni surface into the molten salt as this movement comes with a very high energy cost. However, when the molecular dynamics trajectories of the single carbon atom and carbon dimer are monitored, they show that the carbon species diffuse into the Ni slab. Figure 6 shows the height of the single carbon atom

and the carbon dimer with respect to the top Ni layer over time. The adsorbed carbon species jump from the Ni(111) surface to a location in between the first and second Ni layer after ~ 5 ps for the single carbon atom (Figure 6a) and after ~ 8 ps for the carbon dimer (Figure 6b). Since the carbon dimer doesn't dissociate into two separate carbon atoms until 20 ps, both the single carbon and the carbon dimer species are able to diffuse into the Ni slab. The carbon species never jump to a location between the second and third Ni layer and we speculate that the frozen third Ni layer prevents this from happening.

Figure 6. (a) Distance over time between the single carbon atom and the top Ni layer. (b)

Distances over time between the two carbon atoms (C_1 and C_2) in the carbon dimer and the top Ni layer.

3.7. Effect of molten NaBr on the stability of carbon in the Ni slab. Finally, we estimate the effect of the NaBr melt on the stability of the single carbon atom when it is situated inside the Ni slab. We therefore compare the energy of forming the C^* species and $2H_2(g)$ from $CH_4(g)$ without and with the $20NaBr(l)$ film. The reaction energy to form C^* in the Ni(111) slab without the molten NaBr film is 1.99 eV (Figure 7a), whereas the reaction energy to form C^* in the Ni(111) slab with

the NaBr film is 1.63 eV (Table 3, Figure 7b). In both cases, the carbon atom was initially placed on the Ni(111) surface, but diffuses into Ni slab (even without the molten NaBr film). The energy difference suggests that the presence of the molten salt stabilizes the internal energy of carbon in the Ni subsurface region. The molten NaBr is therefore unlikely to prevent the Ni catalyst from coking or from being converted to a carbide.

Figure 7. Cumulative mean internal energies as a function of elapsed time for (a) $2H_2(g) + C^*$ in Ni(111) and $CH_4(g) + Ni(111)$ without adsorbates. (b) $2H_2(g) + C^*$ in $20NaBr(l)/Ni(111)$ and $CH_4(g) + 20NaBr(l)/Ni(111)$ without adsorbates. The reference states ($CH_4(g) + Ni(111)$ and $CH_4(g) + 20NaBr(l)/Ni(111)$) without adsorbates.

$\text{CH}_4(\text{g}) + 20\text{NaBr}(\text{l})/\text{Ni}(111)$ are set to 0 eV after the full simulation time. The reaction energies are 1.99 eV in (a) and 1.63 eV in (b).

4. Summary and Conclusions

The presence of the molten NaBr film influences the properties of the Ni(111) surface in several interesting ways. Bader charge analysis shows that negative charge is transferred from Br^- ions at the NaBr-Ni(111) interface to the Ni(111) slab. The net charge in the Ni slab is found to be $\sim -0.5 e$. With regard to methane pyrolysis, methane solvated in the NaBr film is less stable than gas phase methane. Additionally, dissociated methane adsorbed at the NaBr-Ni(111) interface is less stable than dissociated methane adsorbed on Ni(111) without NaBr. However, this may not be a problem, as both situations are more stable than dissociated methane adsorbed on molten Cu-Bi alloys, which are known to be active for methane pyrolysis. Carbon atoms at the NaBr-Ni(111) interface are unlikely to agglomerate, since carbon dimers are thermodynamically and kinetically unstable. Carbon atoms placed at the at the NaBr-Ni(111) interface do not stay at the interface, but diffuse into the Ni slab. The stability of carbon atoms in the subsurface region of the Ni(111) slab is increased by the presence of molten NaBr.

We had hoped that the molten NaBr would wash carbon of the Ni(111) surface, for instance by dissolving the carbon in the molten salt, but our study shows that this does not happen. Instead, the molten NaBr may help keep the Ni(111) surface free of carbon and catalytically active by stabilizing subsurface carbon. The dissolved carbon will eventually precipitate out of the nickel particles and form solid carbon. The behavior of that carbon will determine whether dissolving carbon in the nickel particles is a desirable way to remove coke.

Supporting Information

Movie of the 20NaBr(*l*)/Ni(111) trajectory showing the movement of Na⁺ and Br⁻ ions above the Ni(111) surface; movie of the CH₄(salt) + 20NaBr(*l*)/Ni(111) trajectory showing the dissolution of methane into the salt; movie of the *C₂ + 20NaBr(*l*)/Ni(111) trajectory showing diffusion of *C₂ into Ni(111) and subsequent dissociation into 2C*; cumulative mean internal energy plots as a function of elapsed time for molecular methane and dissociated methane initially placed at the NaBr-Ni(111) interface, compared to gas phase methane; cumulative mean internal energy plot of methane pyrolysis on 20NaBr/Ni (111) as a function of elapsed time, where the carbon atom is placed at the NaBr-Ni(111) interface, in the molten salt, or at the vacuum-NaBr interface; cumulative mean internal energy plot of methane pyrolysis as a function of elapsed time to form carbon dimer and two separate carbon atoms initially placed at the NaBr-Ni(111) interface.

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