Electronic Supplemental Materials

Decomposition of Methyl Species on a Ni(211) surface: Investigations of the Electric Field Influence

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1. Geometric Structure Information

We examined the electronic structures of the hydrogen or hydrocarbon species on Ni(211) with and without an external electric field. Table 1S summarizes the bond lengths of the isolated H and CH_x species on Ni(211) in the presence and in the absence of an electric field (atom labels are referred to in Fig. 2 of the manuscript). For the isolated hydrogen or carbon species, the external field didn't significantly change the bond lengths between H and Ni or between C and Ni, which correlates well since the adsorption energies of the C and H species were not greatly affected by the presence of an electric field. For the CH group, the C-Ni bond lengths were slightly longer with a negative electric field as compared to when it is absent, resulting in a weaker CH molecule adsorption energy. On the other hand, with a positive electric field, the C-Ni bond lengths didn't significantly change, and accordingly, the CH molecule adsorption energy was also not significantly altered by a positive electric field.

Table 1S. Summary of the bond lengths of the H and CH_x species (x=0~3) when adsorbed on a Ni(211) surface in the presence and absence of an external electric field.

Species	Field	H Ni ₁	H Ni ₂	H Ni ₃	Species	Field	C Ni ₂	C Ni ₄	C Ni ₅	C Ni ₆	
-	(V/Å)	(Å)	(Å)	(Å)	-	(V/Å)	(Å)	(Å)	(Å)	(Å)	
Н	1.0	1.695	1.695	1.733	С	1.0	1.823	1.823	1.843	1.843	
	0	1.694	1.694	1.744		0	1.821	1.822	1.846	1.846	
	-1.0	1.694	1.695	1.766		-1.0	1.822	1.822	1.847	1.847	
СН	Field	C_Ni ₂		C_Ni ₄		C_Ni ₅	C_Ni ₆		0	С-Н	
	(V/Å)	(Å)		(Å)		(Å)		(Å)		(Å)	
	1.0	1.943		1.944		1.947		1.947		1.106	
	0	1.940		1.941		1.947		1.947		1.109	
	-1.0	1.938		1.938		1.951		1.952		1.109	
CH ₂	Field	C_Ni ₁		C_Ni ₂		C_Ni ₃	C_H ₁		C	C-H ₂	
	(V/Å)	(Å)		(Å)		(Å)		(Å)		(Å)	
	1.0	1.899		1.917		1.970		1.160		1.103	
	0	1.894		1.925		1.973	1.162		1.	1.101	
	-1.0	1.890		1.934		1.989	1.165		1.102		
CH ₃	Field	C_Ni ₁		C_Ni ₂		C_H_1	C-H ₂		C	C-H ₃	
	(V/Å)	(Å)		(Å)		(Å)	(Å)		((Å)	
	1.0 1.990 2		2.056	5	1.102		1.101	1.	1.141		
	0	1.990		2.066		1.101		1.100		1.143	
	-1.0	1.997		2.095		1.102		1.101		1.143	

For both the CH₂ and CH₃ species, we found that the bond lengths between the C atom and the bonded Ni atoms significantly decreased after applying a positive electric field, leading to the stronger interactions between the adsorbate and the Ni surface atoms. This resulted in stronger CH_2 and CH_3 molecule adsorption energies with a positive electric field than the scenarios without an electric field. On the other hand, when we applied a negative electric field the C-Ni bond lengths increased, and consequently resulted in weaker CH_2 and CH_3 molecule adsorption energies. As a result, the effect of an electric field on the bond lengths of the H and CH_x species (x=0~3) correlates quite well with the electric field's influence on the adsorption energies of the H and CH_x species.

2. Projected Density of States

In order to better understand the effect an external electric field has on the adsorption energy of the hydrogen or hydrocarbon species, we further examined the density of states (DOS) of the CH_x species on both the Ni(111) and Ni(211) surface in the presence and absence of an external electric field.

In the manuscript, we presented the projected DOS of the C_{2p} and H_{1s} orbitals for the adsorption of a CH₃ molecule on both the Ni(111) and Ni(211) surface in the presence and absence of an electric field. The peaks below the Fermi level of the C_{2p} and H_{1s} orbitals shifted closer to the Fermi energy and had more interaction with the d band of the bonded Ni atoms, leading to a greater adsorption energy than when such a field is absent. However, a negative electric field had an opposite effect. Here, an analysis of the DOS for the bonded Ni_{3d} orbital is given in Fig. 1S. We found that the effect of the electric field on the DOS of the Ni_{3d} orbital in the energy range of -5 to 5 eV is negligible. However, in the energy range from -10 to -5 eV, the peaks of the Ni_{3d} orbital, which is the result of the interaction between the CH₃ molecule and the bonded Ni atoms, changed slightly when a positive or a negative electric field is applied. These peaks of the d band of the Ni atom shifted closer to the Fermi level and had more interactions with the adsorbates when a positive electric field is applied than the scenarios when the field was negative or absent. Again, these results correlate quite well with the fact that CH₃ binds more strongly in the presence of a positive electric field.



Fig. 1S. The projected DOS of the bonded Ni_{3d} orbital when a CH_3 molecule is adsorbed at the most stable site with and without the presence of an electric field. The energies refer to the Fermi energy, indicated by the vertical black dotted line.

In addition to the above work, we also investigated the effect of the electric field on the projected DOS of the H_{1s} and C_{2p} orbitals for a CH_2 molecule on both the Ni(211) and Ni(111) surface (Fig. 2S). We found that the peaks of the H_{1s} and C_{2p} orbitals below the Fermi level had the same trends as the CH_3 species did: the projected DOS peaks of the H_{1s} and C_{2p} orbitals shifted closer to the Fermi energy with a positive electric field and shifted further away from the Fermi energy with a negative electric field. As a result, the H_{1s} and C_{2p} orbitals had more interactions with the d band of the corresponding Ni atoms and the CH_2 molecule was more strongly adsorbed on both the Ni(111) and Ni(211) surface with a positive electric field as compared to when a negative field is present or in its absence. On the other hand, when we applied a negative electric field, the peaks of the H_{1s} and C_{2p} orbitals shifted further away from the Fermi energy and had less interaction with the d band of the Ni surface. For the Ni_{3d} orbital (Fig. 3S), the peaks between -5 to 5 eV overlapped each other with and without the presence of a field. This is the same situation as the adsorption of CH_3 on Ni surfaces. However, the corresponding Ni_{3d} orbital was slightly altered by the presence of a field for energies below -5 eV, as was the case for the adsorption of CH_3 on the Ni surfaces.



Fig. 2S. The effect of an electric field on the projected DOS of the H_{1s} (a) and C_{2p} (b) orbitals for a CH₂ molecule adsorbed at its most stable site. The energies are relative to the Fermi energy, indicated by the vertical black dotted line.



Fig. 3S. The effect of an external electric field on the projected DOS of the Ni_{3d} orbital for a CH_2 molecule adsorbed at its most stable site. The energies are relative to the Fermi energy, indicated by the vertical black dotted line.

The DOS of the H_{1s} , C_{2p} and Ni_{3d} orbitals for two scenarios are given in Fig. 4S and Fig. 5S. The first scenario is the CH molecule adsorbed at the S4 hollow site on the Ni(211) surface, and the second scenario is the CH molecule adsorbed and at the fcc site on the Ni(111) surface. For a CH molecule on the Ni(211) surface, the peaks of the H_{1s} , C_{2p} and Ni_{3d} orbitals almost overlap each other in the presence and absence of an external electric field. However, the bond

lengths of the CH molecule (see Table S1) changed slightly in the presence of an external electric field, leading to different adsorption energies of the CH species on the Ni(211) surface. On the other hand, for the CH molecule on Ni(111), the peak shift trends of the H_{1s} , C_{2p} and Ni_{3d} orbitals are similar to those of CH₂ and CH₃ molecules in which the peaks of the H_{1s} and C_{2p} orbital shifted closer to the Fermi level with a positive electric field and shifted further away from the Fermi energy with a negative electric field. As a result, the changes in the adsorption energy of the CH species on the Ni(111) surface also had the same trends as the adsorption of the CH₂ and the CH₃ molecule had a stronger adsorption energy with a positive electric field and a weaker adsorption energy with a negative electric field.



Fig. 4S. The effect of an electric field on the DOS of the H_{1s} (a) and C_{2p} (b) orbitals for the CH molecule adsorbed at its most stable site. The energies are relative to the Fermi energy, indicated by the vertical black dotted line.



Fig. 5S. The effect of the electric field on the projected DOS of the Ni_{3d} orbital for a CH molecule adsorbed the most stable site on both the Ni(111) and Ni(211) surface. The energies are relative to the Fermi energy, indicated by the vertical black dotted line.

For the C and H species adsorbed on the Ni(211) and Ni(111) surfaces, the projected density of states on the H_{1s} , C_{2p} orbitals and the d band of the corresponding Ni atoms are given in Fig. 6S and Fig. 7S. The effect of the electric field on the peaks of the H_{1s} , C_{2p} and Ni_{3d} orbitals is negligible. However, the bond lengths of the C and H species changed slightly in the presence of an external electric field (see Table 1S), leading to different C and H adsorption energies on the Ni surfaces.



Fig. 6S. The projected DOS of the C_{2p} orbital (a) and the bonded Ni_{3d} orbital (b) for a C molecule adsorbed at its most stable site in the presence of and the absence of an external electric field. The energies are relative refer to the Fermi energy, indicated by the vertical black dotted line.



Fig. 7S. The effect of an electric field on the projected DOS of the H_{1s} (a) orbital and the bonded Ni_{3d} orbital (b) for a H molecule adsorbed at its most stable site. The energies are relative to the Fermi energy, indicated by the vertical black dotted line.