Supporting Information for

Effect of Ag and Pd Promotion on CH₄ Selectivity in Fe(100) Fischer-Tröpsch Catalysis

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1. Adsorbate energy vs. binding energy

Binding energies describe the energy cost of binding one gas-phase adsorbate molecule to the surface, whereby adsorption energies reflect this cost plus the additional consideration of the cost of an adsorbate interacting with its periodic image. These interactions occur through two primary mechanisms: 1) wavefunction overlap between neighboring adsorbates, and 2) non-local electrostatic interactions (dipole-dipole). The difference in calculation stems from the size of the cell used to describe the adsorbate: for calculating binding energies, a 20-Å box was used to represent an isolated gas-phase adsorbate; in calculating adsorption energies, the actual unit cell was utilized (approximately 5.6 Å \times 5.6 Å \times 22 Å), stripped of all atoms less the adsorbate. Though adsorption energies more accurately depict the reaction as modeled, binding energies will be more appropriate when comparing to the cluster-derived data, as there were no periodic interactions to consider in the cluster model.

2. Climbing-Image Nudged Elastic Band Transition State Searching

The nudged elastic band (NEB) method is used to search for first order-saddle points along the minimum energy pathway. Unlike other methods, the CI-NEB approach circumvents many pitfalls of an often difficult task of transition state searching by chaining a set of images together, and then allowing the highest energy image to search up "climb" to the transition state. A general overview of the process can be found in the wonderfully useful forums of Professor Graeme Henkelman: http://theory.cm.utexas.edu/henkelman/

Here, VASP optimized structures and energies were obtained for the following scenarios:

Initial State (IS)	Final State (FS)
$CH_{3}^{*} + H^{*}$	$CH_4(g)$
$CH_{3}^{*} + C^{*}$	$C_2H_3^*$

where * denotes a surface-bound species. These geometries are input as the IS and FS geometries into

the Henkelman group VTST tool nebmake.pl (for usage, see here:

http://theory.cm.utexas.edu/vtsttools/scripts.html)

Five additional images are extrapolated from the two optimized endpoints. These are fed into an NEB initial run, set at low tolerance and gentle optimization to set the search in motion. A general INCAR file is provided here, with variable fields marked in RED.

Line	General:
1	SYSTEM = [NAME OF SYSTEM]
2	ISTART = 0
3	ICHARG = 2
4	PREC = ACCURATE
5	ALGO = FAST
6	LREAL = Auto
7	LWAVE = .False.
8	LCHARG = .False.
9	ISPIN = 2
10	VOSKOWN = 1
11	LORBIT = 11
12	LDAU = .True.
13	LDAUTYPE = 1
14	IMAGES = 5
15	SPRING = -5
16	LCLIMB = .True.
17	
18	Electronic Relaxation:
19	ENCUT = 350
20	ISMEAR = 1
21	EDIFF = 1E-6
22	SIGMA = 0.1
23	ISIF = 0
24	EDIFFG = -0.025
25	
26	Ionic Relaxation:
27	IBRION = 1
28	NSW = 200
29	NPAR = 4
30	POTIM = 0.1

Line 1: unique system name

Line 16: The tag LCLIMB = .true. was only added after a preliminary run and evaluation of progress. Once satisfied that the geometries and energies were chemically reasonable, the climbing image algorithm was activated.

Line 19: The kinetic energy cutoff was set to 300 eV for the first run, and 350 eV for all subsequent runs. Coincidentally, the k-point mesh was set to 3x3x1 for run 1, and to 6x6x1 for all runs thereafter via the KPOINTS file.

Line 21: Global break condition for the electronic SC loop, set to stop if the total free energy change and eigenvalue energy change between two steps fall below 1 x 10^{-5} eV (first run) and 1 x 10^{-6} eV all runs thereafter.

Line 24: Break condition for the ionic loop, set to stop if all forces fall below 0.5 eV/Å (runs 1 & 2), 0.1 eV/Å (all runs up to and including penultimate), 0.05 eV/Å (final run).

Line 27: The force based optimizers IBRION = 1 and 3, or the quasi-Newton and quick-min methods, respectively, are preferred for NEB calculations.

Line 30: If an initial optimization is too aggressive (initial forces are high), the time step can be adjusted here (try 0.01) for several iterations (20-30) to achieve a stabilized configuration.

3.Validation of cluster-model results: Adsorption Geometries

A comparison of adsorbate binding preference over the periodic (slab) model (this study) and cluster model (previous study) can serve as a preliminary validation of adsorbate-surface behavior. A detailed account of all adsorbate binding geometries for both slab and cluster models is provided in the Supporting Information table S1. Generally speaking, adsorbates optimized closer to the surface of the slab model when compared to the cluster model. This was attributed to the greater spacing between Fe surface atoms on the (100) face described in the periodic calculation. For the cluster approach, severe under coordination of perimeter atoms induced a partial collapse of the surface structure when optimized, leading to atomic spacings closer to the more densely-packed Fe(111) face than the

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Fe(100); thus, adsorbates in this study were less exposed to steric and Pauli repulsion allowing for greater penetration into the space directly above the surface. Surface height increased with increasing hydrogenation of carbon, as the surface-carbon bond became weaker (longer). Naturally, CH_4 had the highest average height above surface, as it was only weakly physisorbed to the surface on all systems. Adsorbates with a single carbon (CH, CH_2 , CH_3) or with two carbons excluding ethylene and acetylene (C_2H , C_2H_3) achieved optimizations closer to the surface, as this "bare" carbon was able to penetrate into the surface space above the 4-fold hollow (Fig. S1.a). Acetylene and ethylene, however, adsorbed parallel to the surface; thus, penetration was limited by adsorbate size (Fig. S1.b); consequently, their adsorption geometries were 0.6-0.7 Å higher above surface than their aforementioned two-carbon counterparts.

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Figure S1. Various adsorbate binding geometries, profile view (top-view inset). a) C (left) and C_2H_3 (right) had deeper surface penetration by the surface-directed carbon. b) Acetylene (left) and ethylene (right) showing two bonding schemes in the Fe(100) four-fold hollow. c) Methyl adsorbed in the top position on both slab (left) and cluster (right) models. d) Increased surface spacing on the slab (left) forces ethylene into the less favorable π -binding mode. di σ -binding observed on the cluster model (right).

When contrasting models, adsorption geometries were most similar for CH₃ binding, as it tended to prefer top/bridge-binding, making it less susceptible to differences in surface geometry (Fig.

S1.c). Interestingly, the cluster model produced a CH_3 adsorption geometry closer to that predicted elsewhere (1.66 Å),⁵¹ suggesting that cluster models may adequately describe top-binding and bridgebinding phenomena. The apparent shortcomings of the cluster model in hollow binding phenomena may be attributed to spacing issues, absence of a sub-layer, or as observed in the following discussion, over/underestimation of surface back-donation, where applicable to the bonding mechanism. These effects are naturally less pronounced over top site binding, perhaps explaining the increased accuracy of cluster models to describe such phenomena.

C-H bond lengths were influenced by adsorbate height, as adsorbates closer to the surface experienced a greater activation of the C-H bond leading to greater C-H bond lengths for the slab model. Two species of particular interest to chain growth are ethylene and acetylene, as these species have been shown to lie low to the surface and are further stabilized by the Dewar-Chatt-Duncanson (DCD) mechanism.⁵² This additional stabilization is often offered as an explanation to the negative deviation of C2 species in the Anderson-Schulz-Flory FT product distribution.⁵³ While C₂H₄ preferred the bridge-site in the cluster model, the greater spacing in the Fe(100) surface described in this study allowed C₂H₄ to settle into the 4-fold hollow (Fig SI.d). Adsorption activated the C-C bond, and an extension of the bond length relative to the gas phase value (C-C 1.336 Å)⁵⁴ was attributed to the aforementioned DCD mechanism. Here we predict a C-C bond length over pure Fe (1.509 Å) closer to that observed elsewhere (between 1.45 and 1.50 Å).²⁵ For C_2H_2 , activation of the C-C bond was similar over both models, despite showing bridge and hollow binding preference for the cluster and slab models (1.365 Å and 1.392 Å, respectively). These are in good agreement with theoretical values determined for C-C stretching over bridge and hollow adsorption on Pd(100) (1.32 Å and 1.39 Å, respectively).⁵⁵ Clotet et al. used clusters of different sizes to examine acetylene adsorption over Cu(100) and Pd(100).⁵⁶ Though they were able to produce vibrational data in good agreement with

experiment, adsorption geometries were accurate for Pd(100) and not Cu(100). Naturally, vibrational effects are locally dominated and can be adequately described by clusters. As back-donation originates in the metal *d*-band, this effect can be improved by increasing the cluster size, as suggested by Bagus *et al.*,⁵⁷ or through the implementation of plane-wave models.

Ag and Pd promotion generally increased activation of the C-C bond in the slab model. It is apparent that promotion had a more noticeable effect on bonding geometries for adsorbates that aligned parallel to the surface, suggesting that the promoter plays a larger role in the mechanism of charge transfer (i.e., back-donation). This is an effect that was not widely observed in the cluster model.

	Cluster model					Slab model						
adsorbate	system	ht. ^a	С-Н г	C-C r	M-M r^b	ht. ^a	С-Н г	C-C r	M-M r^b	Δ M-M r^c	%d12 ^d	%d23 ^e
С	Fe	1.088			2.573	0.333			2.774	-2.29	17.53	-8.27
	FeAg	1.149			2.524	0.255			2.857	-0.31	11.84	-5.10
	FePd	1.146			2.545	0.256			2.829	-0.46	-5.77	4.43
СН	Fe	1.307	1.094		2.574	0.591	1.110		2.845	0.21	6.42	-2.47
	FeAg	1.327	1.092		2.527	0.493	1.110		2.916	1.74	3.39	1.99
	Fe-Pd	1.331	1.093		2.545	0.546	1.109		2.886	1.55	-7.08	3.10
CH_2	Fe	1.425	1.108		2.529	0.651	1.135		2.894	1.94	12.60	-3.14
	Fe-Ag	1.847 (top)	1.091		N/A	0.705	1.13		2.964	3.42	3.21	-3.28
	Fe-Pd	1.515	1.106		2.527	0.690	1.137		2.941	3.48	-5.05	-0.11
CH ₃	Fe	1.804	1.106		2.534	1.829	1.106		2.803	-1.27	5.33	-2.85
	Fe-Ag	1.917	1.102		2.581	1.686	1.107		2.809	-2.01	8.21	-1.34
	Fe-Pd	1.785	1.105		2.545	1.709	1.107		2.804	-1.34	-3.93	1.34
CH_4	Fe					2.653	1.096		2.839	0.00	-0.13	0.49
	Fe-Ag					2.687	1.096		2.866	-0.93	5.93	-3.07
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TABLE S1. Adsorption geometries over cluster-surface analogs and plane-wave slab models. All lengths reported in Å.

	Fe-Pd					2.513	1.096		2.858	0.56	-7.38	5.62
C_2H	Fe	1.37	1.08	1.31	2.534	0.648	1.088	1.368	2.841	0.07	11.16	-3.13
	Fe-Ag	1.293	1.08	1.323	2.562	0.532	1.086	1.359	2.93	2.23	10.36	-1.49
	Fe-Pd	1.403	1.078	1.298	2.545	0.589	1.089	1.355	2.92	2.74	-4.27	3.19
C_2H_2	Fe	1.707	1.091	1.365	2.534	1.211	1.107	1.392	2.758	-2.85	23.89	-6.44
	Fe-Ag	1.836	1.090	1.357	2.545	1.229	1.106	1.385	2.862	-0.14	11.52	0.27
	Fe-Pd	1.69	1.09	1.361	2.545	1.223	1.106	1.388	2.863	0.74	-5.10	5.34
C_2H_3	Fe	1.315	1.099	1.49	2.527	0.624	1.104	1.545	2.784	-1.94	9.46	-1.51
	Fe-Ag	1.369	1.097	1.503	2.527	0.585	1.103	1.545	2.902	1.26	9.22	-1.32
	Fe-Pd	1.407	1.097	1.501	2.527	0.631	1.104	1.541	2.873	1.09	-6.50	3.04
C_2H_4	Fe	1.889	1.1	1.526	2.531	1.577	1.111	1.509	2.734	-3.70	12.24	-4.41
	Fe-Ag	1.85	1.101	1.532	2.527	1.700	1.028	1.451	2.851	-0.52	14.60	-4.32
	Fe-Pd	1.779	1.098	1.542	2.547	1.605	1.112	1.483	2.788	-1.90	-4.41	2.33

^{*a*} Height measured as the vertical distance from the averaged height of atoms involved in adsorption to the lowest adsorbate atom.

^b M-M *r* measured as the average bond length between atoms involved in adsorption.

^c Δ M-M r measured as the percent change of M-M r relative to the average bond length of atoms on the clean surface.

 d %d12 calculated as the percent change between the interlayer spacing between rows 1 and 2 in the adsorbate/slab system relative to the row 1 - row 2 spacing of the clean slab.

 e^{-6} %d23 calculated as the percent change between the interlayer spacing between rows 2 and 3 in the adsorbate/slab system relative to the row 2 - row 3 spacing of the clean slab.