

# Universal Brønsted-Evans-Polanyi Relations for C-C, C-O, C-N, N-O, N-N, and O-O Dissociation Reactions

Shengguang Wang<sup>a</sup>, Burcin Temel<sup>b</sup>, Juan Shen<sup>a</sup>, Glenn Jones<sup>a</sup>, Lars Grabow<sup>a</sup>,  
Felix Studt<sup>a,c</sup>, Thomas Bligaard<sup>a</sup>, Frank Abild-Pedersen<sup>a,c</sup>, Claus H. Christensen<sup>b</sup>,  
Jens K. Nørskov<sup>a,c,d\*</sup>

<sup>a</sup>*Center for Atomic-scale Materials Design, Department of Physics, Technical University  
of Denmark, DK-2800 Kgs. Lyngby, Denmark*

<sup>b</sup>*Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs. Lyngby, Denmark*

<sup>c</sup>*Center for Interface Science and Catalysis  
SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California  
94025, USA*

<sup>d</sup>*Department of Chemical Engineering  
Stanford University, Stanford, CA 94305, USA*

## Abstract

It is shown that for all the essential bond forming and bond breaking reactions on metal surfaces, the reactivity of the metal surface correlates linearly with the reaction energy in a single universal relation. Such correlations provide an easy way of establishing trends in reactivity among the different transition metals.

**Keywords** Density Functional Theory – Stepped surfaces – Coupling reactions – Bond breaking reactions – BEP relations – Scaling relations

To bridge the gap between macroscopic properties of a catalyst, such as turn-over rates and selectivity and the microscopic properties obtained from electronic structure methods based on density functional theory (DFT), an in depth understanding of the underlying thermodynamics and kinetics of the corresponding metal surfaces is needed. Today, DFT has reached a level of sophistication where it can be used to describe complete catalytic reactions and hence provide an insight that pinpoints to the origin of the catalytic activity and selectivity.<sup>1,2,3,4,5,6</sup> However, extensive DFT calculations that eventually lead to this understanding are still computationally demanding. A simplification that connects the reactivity and selectivity of a catalytic surface to one or few descriptors is therefore extremely useful. Such a simplification, e.g. the Brønsted-Evans-Polanyi (BEP) relations, is able to show that the transition state energy of a reaction is linearly depending on the reaction energy.<sup>7,8,9,10,11,12</sup>

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\* Corresponding author

Herein, we investigate the transition state energies of a large number of essential bond breaking and forming reactions that play a key role in the catalytic transformation of a large fraction of base chemicals. The transition state energies investigated include C-C, C-O, C-N, N-O, N-N, and O-O coupling and have been calculated on different stepped surfaces of transition metals such as Co, Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, and Au.

For a dissociation reaction ( $AB \rightarrow A+B$ ), the transition state energy ( $E_{ts}$ ) is calculated by Equation (1), in which  $E_{ts/slab}$ ,  $E_{slab}$  and  $E_{gas}$  are the total energies of the slab with transition states, the clean slab, and the gas phase molecules relevant for the reactions, respectively. The dissociative adsorption energy ( $E_{diss}$ ) is calculated by Equation (2), in which  $E_{A/slab}$  and  $E_{B/slab}$  are the total energies of the slab with adsorbates A and B, respectively.

$$(1) \quad E_{ts} = E_{ts/slab} - E_{slab} - E_{gas}$$

$$(2) \quad E_{diss} = E_{A/slab} + E_{B/slab} - 2E_{slab} - E_{gas}$$

All calculations were performed using the DACAPO plane-wave pseudo potential DFT code.<sup>13</sup> Ionic cores were described by ultrasoft pseudopotentials<sup>14</sup>, and the Kohn-Sham one-electron valence states were expanded in a basis of plane wave functions with a cut-off energy up to 340 eV. For most adsorption systems, the surface Brillouin zone was sampled using a Monkhorst-Pack grid of size  $4 \times 4 \times 1$ , while  $2 \times 3 \times 1$  was used for  $O_2$ , and  $8 \times 6 \times 1$  was used for  $N_2$  and  $NO$  as a test of the parameters. The self-consistent electron density was determined by iterative diagonalization of the Kohn-Sham Hamiltonian. A Fermi distribution for the population of the Kohn-Sham states ( $k_B T = 0.1$  eV), and Pulay mixing of the resulting electronic density was used. All total energies were extrapolated to  $k_B T = 0$  eV. Model surfaces of the face-centered cubic crystal (fcc{211}) were used to represent the step sites, which was found to be the important active site for a number of catalytic reactions.<sup>15,16,17,18</sup> A  $(1 \times 2)$  cell with 10 atomic layers in the (211) direction corresponding to 3 layers in the closepacked (111) direction was used to model the adsorbate-metal structures. The atoms in the bottom 7 layers of the slab were fixed to their bulk positions, while the atoms in the top 3 layers were allowed to relaxation during the calculations.

Based on these energies a universal linear relation (known as BEP relation) between the transition state energies ( $E_{ts}$ ) and the reaction energies ( $\Delta E_{diss}$ ) is observed as shown in Figure 1.

Importantly, all of the herein investigated transition state energies fall on the same line in a zeroth order approximation. Given the large number of different dissociation reactions that have been addressed in this paper, this universal linear relation provides a powerful tool in estimating essentially all transition state energies. Equation (3) shows the linear BEP relation, where  $\gamma$  is the slope and  $\xi$  is the intercept of the linear relationship between the transition state energies and the reaction energies.

$$(3) \quad E_{ts} = \gamma \cdot \Delta E_{diss} + \xi$$

The linear relationship originates from the close similarity between the transition state geometries and the final state geometries.<sup>9,11</sup> Such similar geometries suggest that the slope  $\gamma$  of the BEP relations should be a little less than or very close to one. This is clearly the case for the breaking of very strong bonds since such bonds have to be stretched very far from equilibrium to sufficiently mix with the surface states. Hence, moving away from the linear behavior requires much weaker bonds or metals that mix more strongly with the activated complexes. A closer inspection of the  $\gamma$  and  $\xi$  parameters for the dissociation reactions, as shown in Table 1, therefore reveals that there are differences between the reactions considered here.

As argued, the accuracy of the linear BEP relations will depend strongly on the adsorbate and the range of metals studied. For the metals considered herein, the mixing of the transition state with the surface is very similar to that of the final state and hence the transition state energies taken relative to relevant gas phase species will scale with the final state energies. In Table 1 the parameters  $\gamma$  and  $\xi$  obtained from the best linear fit to the calculated data are shown. As expected, the slopes are very close to but slightly smaller than one for most reactions. There are a few exceptions, for example  $O_2$  splitting with a slope as low as 0.58. The lower slope of the BEP-relation for  $O_2$  originates from the transition state for this reaction being slightly less final-state-like than the C-C, C-O, C-N, N-N, and N-O bonds studied in this letter. If we use the over-all universal relation to estimate the transition state energies for the  $O_2$  dissociation, the mean absolute error (based on the limited data studied here) is 0.54 eV. This is of course slightly larger than the linear regression to the  $O_2$  dissociation points alone. It is, however, not so large that it renders the universal prediction useless. For very weak or very strong adsorption the discrepancy grows due to the fine-structure in slopes, and typically it is preferable to use the BEP relation specific to a given reaction rather than the universal line, if one has the specific relation at hand. The error by not doing so, however, is rather limited, as suggested by the surprisingly low mean absolute error on the universal BEP-relation.

The universal BEP relation is useful for establishing overall trends of dissociation reactions in a zeroth order approximation. A better description, however, is achieved, once BEP relations for the reactions in question are established for each reaction specifically and hence  $\gamma$  and  $\xi$  are determined over a range of transition-metal surfaces. This becomes important for the splitting of weak bonds where  $\gamma$  and  $\xi$  deviate substantially from the universal BEP line.

The identification of the universal BEP relation is extremely useful for an understanding of catalytic reactions and their intrinsic activity and selectivity that changes substantially over the range of transition-metal catalysts. It gives an easy way of understanding trends among transition-metal surfaces regarding the formation and breaking of bonds. This, combined with the recently established scaling relations between hydrogen containing adsorbates on transition-metal surfaces<sup>19</sup> allows for a fast zeroth order description of kinetics and thermodynamics of reactions over the whole range of transition-metal

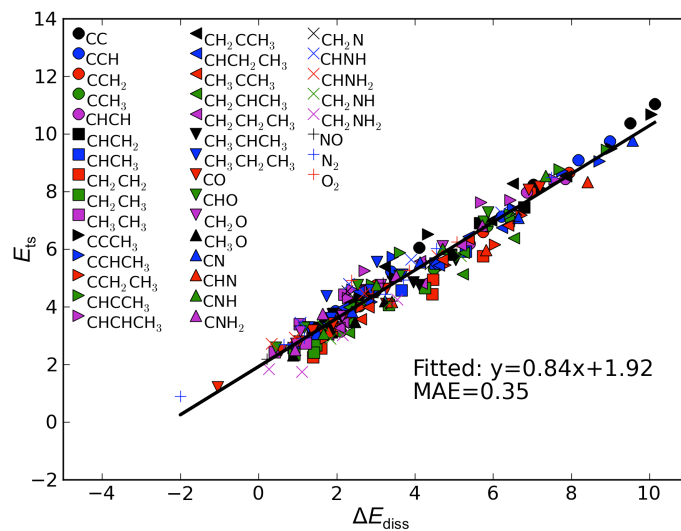
surfaces. Hence, it becomes easy to establish trends for reactions allowing a first screening for new catalytic materials by means of few simple descriptors.<sup>6,20,21,22,23</sup>

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		CH <sub>x</sub> -CH <sub>y</sub>			CH <sub>x</sub> -CH <sub>y-1</sub> CH <sub>3</sub>			CH <sub>x</sub> -O			CH <sub>x</sub> -NH <sub>y-1</sub>		
x	y	γ	ξ	MAE	γ	ξ	MAE	γ	ξ	MAE	γ	ξ	MAE
0	0	0.88	2.13	0.11	-	-	-	0.83	1.59	0.13	-	-	-
0	1	0.84	2.13	0.12	0.80	2.48	0.25	-	-	-	0.80	1.99	0.16
0	2	0.88	1.71	0.17	0.79	2.34	0.30	-	-	-	0.94	1.66	0.13
0	3	0.87	1.50	0.15	0.79	1.68	0.15	-	-	-	0.85	2.03	0.19
1	1	0.82	2.08	0.19	0.79	2.47	0.25	0.83	2.32	0.15	0.79	1.58	0.14
1	2	0.79	2.18	0.12	0.76	2.87	0.24	-	-	-	0.72	2.87	0.13
1	3	0.76	1.93	0.08	0.71	2.41	0.19	-	-	-	0.74	2.39	0.07
2	1	-	-	-	0.82	2.36	0.32	0.87	2.00	0.12	0.76	2.29	0.29
2	2	0.75	1.42	0.19	0.68	1.94	0.28	-	-	-	0.76	1.77	0.21
2	3	0.73	1.56	0.09	0.91	1.44	0.15	-	-	-	0.80	1.30	0.22
3	1	-	-	-	0.82	1.74	0.17	0.77	1.68	0.06	-	-	-
3	2	-	-	-	0.62	2.37	0.11	-	-	-	-	-	-
3	3	0.94	2.05	0.23	0.81	2.48	0.38	-	-	-	-	-	-
All		0.87	1.74	0.34	0.82	2.04	0.38	0.87	1.86	0.25	0.81	1.95	0.39
		CH <sub>x</sub> -CO			N <sub>2</sub>			NO			O <sub>2</sub>		
x	y	γ	ξ	MAE	γ	ξ	MAE	γ	ξ	MAE	γ	ξ	MAE
0	-	0.77	2.31	0.28	0.81	2.17	0.23	0.78	2.01	0.17	0.58	3.16	0.26
1	-	0.85	2.05	0.29	-	-	-	-	-	-	-	-	-
2	-	0.62	2.73	0.21	-	-	-	-	-	-	-	-	-
3	-	0.75	1.82	0.23	-	-	-	-	-	-	-	-	-
All		0.81	2.03	0.34	-	-	-	-	-	-	-	-	-

**Table 1** Linear scaling parameters  $\gamma$  and  $\xi$  for the different coupling reactions. For each individual line the mean absolute error (MAE) is shown. All energies used to obtain the lines are referenced to CH<sub>4</sub>, H<sub>2</sub>, H<sub>2</sub>O, and NH<sub>3</sub>.



**Figure 1.** Universal Brønsted–Evans–Polanyi relationship between transition state energies for a number of coupling reactions and their dissociative chemisorption energies on a variety of transition metal surfaces. All calculations have been performed on stepped surfaces for a range of different metals. The energies are taken relative to the gas phase energies of CH<sub>4</sub>, H<sub>2</sub>O, NH<sub>3</sub>, and H<sub>2</sub>.

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