Universal transition state scaling relations for hydrogenation and dehydrogenation reactions over transition metals

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We analyse the transition state energies for 249 hydrogenation/dehydrogenation reactions of atoms and simple molecules over close-packed and stepped surfaces and nanoparticles of transition metals using Density Functional Theory. Linear energy scaling relations are observed for the transition state structures leading to transition state scaling relations for all the investigated reactions. With a suitable choice of reference systems the transition state scaling relations form a universality class that can be approximated with one single linear relation describing the entire range of reactions over all types of surfaces and nanoclusters.
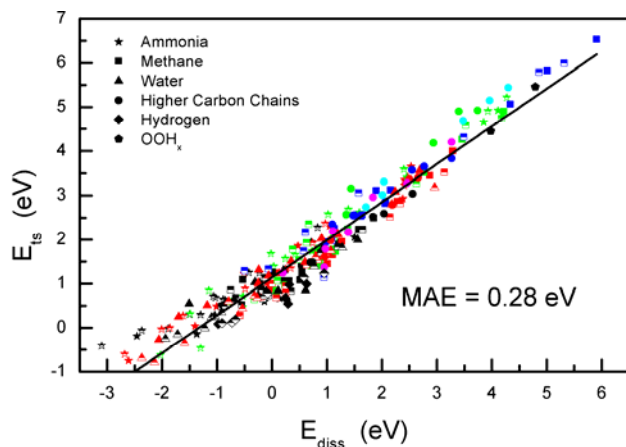
Fig. 1. Transition state energies plotted against dissociation energies with respect to energies of gas-phase CH_4, H_2O, NH_3, and H_2. The fully filled symbols refer to dissociation over close-packed surfaces, and the half-filled symbols refer to dissociation over stepped surfaces and OOH_x species have been dissociated on a M12 nanocluster. The colors represent the different hydrogen content in the molecules, where black is the first dehydrogenation step, red is the second step, green is the third step, and blue is the fourth dehydrogenation step.

1. Introduction

Linear energy relations have proven useful in simplifying the theoretical analysis of a number of catalytic reactions, thereby helping to establish an improved understanding of their underlying trends [1,2,3]. The linear energy relations in question are especially the so-called Brønsted-Evans-Polanyi (BEP) relations [4,5,6,7,8,9,10,11,12,13] describing correlations between transition states and reaction energies, and the adsorbate scaling relations [14] describing correlations between the adsorption energies of adsorbed reaction intermediates containing hydrogen with respect to either C, N, or O. More generalized, the BEP relations can be viewed as resulting from a scaling relation between reaction intermediates and transition states. By combining transition state scaling relations and adsorbate scaling relations the number of individual parameters that needs to be determined in order to describe the energetic trends underlying the kinetics of a complex catalytic reaction can be significantly reduced, and often limited to only one or very few descriptors. Good descriptors are typically adsorption energies of some of the key reactive intermediates, or combinations of these [15,16,17,18,19,20,21,22,23].

In the present paper we analyse the transition state energies for 249 dehydrogenation reactions of small hydrogen containing molecules over close-packed and stepped surfaces and nanoparticles of transition metals using Density Functional Theory (DFT). Linear energy correlations are observed for the transition state structures leading to transition state scaling relations for all the investigated reactions. Upon implementing a suitable choice of reference systems all the transition state scaling relations form a universality class [8,9] in which only one single descriptor can be used to determine the transition state for every reaction over all types of surfaces and nanoclusters.

2. Computational method

The calculations were carried out using the DACAPO plane wave Density Functional Theory code [24]. Exchange-correlation effects were described using the RPBE functional [25] with an energy cutoff of 340 eV or more. The ionic cores were described by Vanderbilt ultrasoft pseudopotentials [26]. A slab model with three (or in some cases four) close-packed atomic-layers was chosen to represent the transition metal surfaces describing the close-packed and stepped surfaces. At least one (in some cases two) top layer was fully relaxed and the rest of the metal layers were held at fixed positions. The size of surface

supercell was 2×2 for the close-packed surfaces, and supercell sizes of 1×2, 2×2, and 2×3 were used for the stepped surfaces depending on the size of the adsorbed molecules. The Brioullin zones were sampled using Monkhorst-Pack k-point meshes of 4×4×1 points or denser [27]. For the M12 nanoparticles, all the 12 atoms were fixed, while the adsorbates were allowed to relax. The calculations on the M12 nanoparticles were carried out using only the gamma-point. The transition state energies were calculated using either a bond stretching method [28] or the nudged elastic band method which can be combined with the climbing image method to precisely determine the maximum barrier [29]. The maximum coverage on the active site was one half.
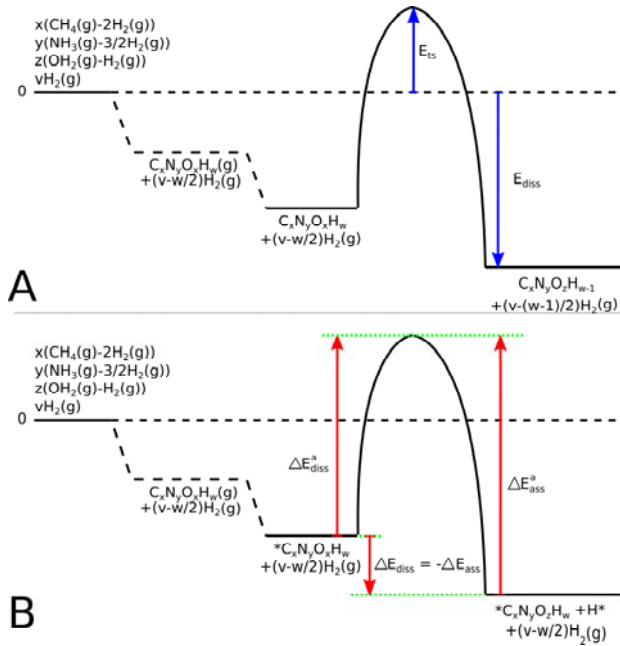
Scheme 1. The definition of energies used in this paper for the hydrogenation/dehydrogenation processes. All energies are with respect to the gas phase molecules of CH_4, NH_3, H_2O, and H_2. **Top-view. (A)** The transition state (TS) scaling relation are based upon the energies given by the two blue arrows denoted as E_{ts} for the transition state energy and E_{diss} for the final state energy. **Bottom-view. (B)** The Brønsted-Evans-Polanyi (BEP) relations use another reference energy. The BEP relations are based upon the activation barrier $\Delta E^a_{diss/ass}$ and the reaction energy $\Delta E_{diss/ass}$ as defined in the bottom panel.

3. Results and discussion

A diagram explaining the reference energy levels used in the transition state scaling relations and in the Brønsted-Evans-Polanyi (BEP) relations for the dehydrogenation/hydrogenation processes is presented in Scheme 1. The transition state scaling relations are based on the transition state energy, E_{ts}, and the final state energy E_{diss}, with respect to the gas phase species [30] CH_4, NH_3, H_2O and H_2, see Scheme 1A. Whereas the BEP relation is based on the reaction energy, ΔE_{diss}, which is the energy difference between the initial and final state, while the activation barrier, ΔE^a_{diss}, is the energy based on the difference in energy between the initial state and the transition state. This can be seen on Scheme 1B.

Figure 1 shows a universal transition state (TS) scaling relation for a series of dehydrogenation reactions over a wide range of transition metal surfaces, such as close-packed and stepped surfaces and nanoparticles. The fitted data for the transition state scaling relations for all the dehydrogenation reactions is presented in Table 1. Here the data have been arranged in categories of individual, classes, grouped and overall. The individual fit is based on only one type of reaction on one surface type, the class is based on a specific reaction on all the types of surfaces, the grouped data is for all data containing either nitrogen, carbon or oxygen, and lastly the overall fit is based on all reactions on all types of surfaces.

The mean absolute error (MAE) of the fitted line in Figure 1 is 0.28 eV. The correlation is certainly not perfect, and compared to so-called "chemically accuracy" which is typically defined as 1 kcal/mole or approximately 40 meV, the error on a prediction based on using the linear relation shown in Fig. 1 will have a typical error one order of magnitude larger. The prediction error, however, has to be seen in the light of how well a typical GGA exchange-correlation functional can describe the reaction and transition state energies. The error in currently employed exchange-correlation functionals could easily be of the same size as the error from predictions based on the transition state scaling relations. The errors in the presented relation are certainly small enough to rapidly produce a first rough estimation of activation barriers for hydrogenation/dehydrogenation reactions. The universal TS scaling relation relates the energies of transition states with final states of dehydrogenation reactions [13]. Such correlation originates from the geometrical similarity of the structures of transition states and final states [8].

Table 1. The fitted parameters of the transition state scaling relations with respect to energies of gas-phase CH_4, H_2O, NH_3, and H_2.

Reaction	Surface	Slope	Constant eV	MAE eV
$H_2O(g)+2^* \rightarrow OH^*+H^*$	Close packed	0.47±0.10	0.99±0.07	0.20
	Step	0.77±0.02	0.95±0.04	0.17
	All	0.58±0.05	0.94±0.04	0.16
$OH^*+^* \rightarrow O^*+H^*$	Close packed	0.75±0.03	1.32±0.04	0.12
	Step	0.63±0.03	0.92±0.03	0.21
	All	0.78±0.03	1.13±0.05	0.20
Water group	All	0.74±0.03	1.06±0.04	0.20
$NH_3^*+^* \rightarrow NH_2^*+H^*$	Close packed	0.57±0.09	0.95±0.11	0.24
	Step	0.69±0.05	1.45±0.07	0.14
	All	0.59±0.06	1.19±0.09	0.23
$NH_2^*+^* \rightarrow NH^*+H^*$	Close packed	0.81±0.03	1.26±0.05	0.15
	Step	0.78±0.04	1.41±0.05	0.16
	All	0.79±0.03	1.32±0.04	0.16
$NH^*+^* \rightarrow N^*+H^*$	Close packed	0.92±0.04	1.09±0.08	0.12
	Step	0.91±0.04	1.41±0.09	0.17
	All	0.87±0.03	1.34±0.07	0.19
Ammonia group	All	0.82±0.02	1.33±0.04	0.24
$CH_4(g)+2^* \rightarrow CH_3^*+H^*$	Close packed	0.67±0.11	1.04±0.10	0.19
	Step	0.64±0.09	1.01±0.07	0.19
	All	0.67±0.06	1.03±0.05	0.18
$CH_3^*+^* \rightarrow CH_2^*+H^*$	Close packed	0.92±0.05	0.80±0.08	0.11

Reaction	Surface	Slope	Constant	MAE
	Step	0.86±0.03	0.78±0.05	0.09
	All	0.89±0.03	0.79±0.05	0.11
$CH_2*+* \rightarrow CH*+H*$	Close packed	0.94±0.02	1.02±0.07	0.20
	Step	0.88±0.06	1.22±0.11	0.22
	All	0.90±0.04	1.20±0.10	0.27
$CH*+* \rightarrow C*+H*$	Close packed	1.00±0.03	0.72±0.06	0.16
	Step	0.88±0.07	1.29±0.17	0.26
	All	0.92±0.04	1.02±0.08	0.23
$C_2H_6(g)+2* \rightarrow C_2H_5*+H*$	Step	0.85±0.03	0.87±0.05	0.14
$C_2H_5*+* \rightarrow C_2H_4*+H*$	Step	0.99±0.10	0.77±0.20	0.11
$C_2H_4*+* \rightarrow C_2H_3*+H*$	Step	0.92±0.11	1.57±0.31	0.18
$C_3H_8(g)+2* \rightarrow C_3H_7*+H*$	Step	0.76±0.06	1.49±0.13	0.08
$C_3H_6*+* \rightarrow C_3H_5*+H*$	Step	1.04±0.04	1.03±0.13	0.07
Hydrocarbon group	All	0.95±0.02	0.97±0.04	0.25
$H_2(g)+2* \rightarrow 2H*$	Close packed	0.67±0.06	0.69±0.04	0.08
	Step	0.54±0.14	0.60±0.08	0.11
	All	0.61±0.07	0.65±0.04	0.10
All	**All**	**0.86±0.01**	**1.14±0.02**	**0.28**

Figure 1 collects different types of dehydrogenation reactions on transition metal surfaces and clusters. The deviation of the points comes predominantly from the difference of the structures of the reactions. As expected from Table 1, the MAE becomes smaller when we look into a certain reaction or a series of similar reactions, since the structures are more similar to each other. The MAE is typically smaller than 0.15 eV for an individual reaction over a given geometry of active surface site, as evidenced in Table 1. When looking at several reactions simultaneously or several surface geometries, the uncertainty of a prediction made from their common linear regression fit will generally increase, but in all cases stays below 0.3 eV. It is therefore useful to see Table 1 as a hierarchy of accuracy that allows treating a particular reaction more accurately if it resembles one of the specifically presented reactions, whereas the overall universal TS scaling can be used for a general hydrogen bond breaking reaction which has not been specifically treated in this study.
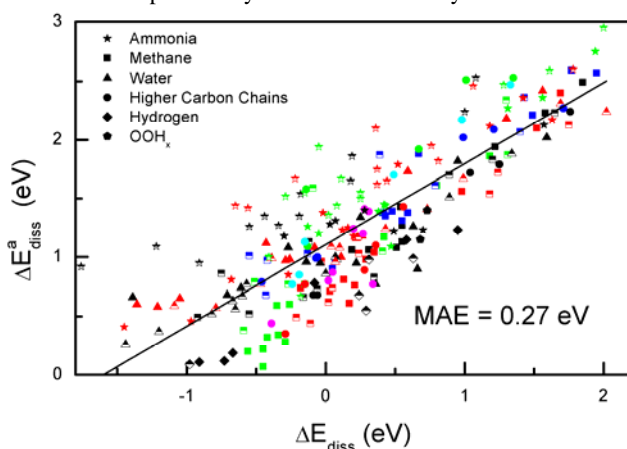

Fig. 2. Activation energies, ΔE^a_{diss}, plotted against reaction energies, ΔE_{diss}, of the dehydrogenation reactions. The fully filled symbols refer to data on close-packed surfaces, and the half filled symbols mean the data on step surfaces. The colors represent the different hydrogen content in the molecules, where black is the first dehydrogenation step, red is the second step, green is the third step and blue is the fourth dehydrogenation step.

Figure 2 shows the BEP relations of the whole set of dehydrogenation reactions. The MAE of 0.27 eV is close to that of the above-discussed universal TS scaling relation. The practical performance of these two relations with respect to estimation of activation energies should be very similar, based on the fact that their MAEs are very close. Although the universal BEP relation in Fig. 2 may at a first glance look less presentable than the universal TS scaling relation, we would like to emphasize several merits of it. The first merit of BEP relations is of course the clear trend reflected by the relations. Since activation energies and reaction energies are typical experimentally measured properties for the analysis of catalytic reactions, rather than the transition state total energies and final state total energies with respect to a gas phase reference it may also be easier to correlate theory and experiments using the BEP relations. The TS scaling relations are (in the present study) based on the structural similarities of the transition states and the final states of a reaction. Such direct similarity between states generally only holds in a limited range of surface reactivity. On the late transition metals there will be a tendency towards having late transition states, and over the early transition metals the transition states will also be earlier. The TS scaling relations (in the form presented above) will thus have a relatively larger MAE when applied to reactions over early transition metals. Therefore it makes more sense to use the TS scaling relations in the presented form for reactions over surfaces of rather similar reactivity. The BEP relations correlate the activation barrier with contributions from both initial and final states. Therefore the BEP relations tend to be valid for the catalytic reactions in a larger window of variation of the surface reactivity. The shift in similarity of the transition state structures with initial and final states thus gives rise to a slightly v-shaped distribution of errors in Figure 1, whereas the noise distribution is more homogeneous in Figure 2.

Table 2. The fitted parameters of BEP relations.

Reaction	Surface	Slope	Constant eV	MAE eV
$H_2O(g)+2* \rightarrow OH*+H*$	Close packed	0.44±0.10	1.04±0.07	0.19
	Step	0.57±0.03	1.00±0.02	0.06
	All	0.51±0.05	1.01±0.04	0.14
$OH*+* \rightarrow O*+H*$	Close packed	0.62±0.06	1.23±0.05	0.16
	Step	0.59±0.04	1.08±0.03	0.09
	All	0.59±0.04	1.15±0.03	0.17
Water group	All	0.57±0.03	1.09±0.03	0.15
$NH_3*+* \rightarrow NH_2*+H*$	Close packed	0.46±0.13	1.21±0.09	0.14
	Step	0.57±0.06	1.65±0.05	0.13
	All	0.42±0.08	1.47±0.06	0.20
$NH_2*+* \rightarrow NH*+H*$	Close packed	0.68±0.05	1.23±0.05	0.14
	Step	0.57±0.08	1.66±0.08	0.19
	All	0.68±0.06	1.41±0.06	0.21
$NH*+* \rightarrow N*+H*$	Close packed	0.79±0.09	1.13±0.09	0.11
	Step	0.74±0.11	1.45±0.09	0.19
	All	0.72±0.08	1.35±0.07	0.19

Ammonia group	All	0.61±0.04	1.43±0.04	0.23
CH$_4$(g)+2*→CH$_3$*+H*	Close packed	0.92±0.07	0.77±0.07	0.07
	Step	0.66±0.10	1.00±0.08	0.18
	All	0.72±0.06	0.96±0.06	0.16
CH$_3$*+*→CH$_2$*+H*	Close packed	0.96±0.07	0.67±0.05	0.07
	Step	0.80±0.07	0.71±0.06	0.10
	All	0.87±0.05	0.70±0.04	0.10
CH$_2$*+*→CH*+H*	Close packed	1.02±0.07	0.73±0.04	0.09
	Step	0.75±0.16	1.09±0.11	0.25
	All	0.91±0.11	0.88±0.07	0.22
CH*+*→C*+H*	Close packed	0.87±0.07	0.97±0.07	0.09
	Step	0.71±0.11	1.19±0.08	0.18
	All	0.75±0.06	1.12±0.06	0.15
C$_2$H$_6$(g)+2*→C$_2$H$_5$*+H*	Step	0.86±0.03	0.75±0.03	0.03
C$_2$H$_5$*+*→C$_2$H$_4$*+H*	Step	1.05±0.22	0.75±0.08	0.16
C$_2$H$_4$*+*→C$_2$H$_3$*+H*	Step	0.86±0.18	1.45±0.15	0.18
C$_3$H$_8$(g)+2*→C$_3$H$_7$*+H*	Step	0.76±0.06	1.11±0.06	0.09
C$_3$H$_6$*+*→C$_3$H$_5$*+H*	Step	1.04±0.07	1.13±0.05	0.08
Hydrocarbon group	All	0.84±0.04	0.94±0.03	0.21
H$_2$(g)+2*→2H*	Close packed	0.67±0.06	0.69±0.04	0.08
	Step	0.54±0.14	0.60±0.08	0.11
	All	0.61±0.07	0.65±0.04	0.10
Universal	**All**	**0.69±0.03**	**1.11±0.02**	**0.27**

The fitted parameters of separate BEP relations of the dehydrogenation reactions are listed in Table 2. It is found that the MAE becomes gradually smaller from the whole set of data to similar groups of reactions and one reaction. The reason is that the scattering caused by the difference of geometric structures has been eliminated to a large degree when only focusing on similar reactions. Hence, using parameters for a certain reaction will yield high accuracy for that or very similar reactions. The parameters for grouped reactions and the universal relation are also useful for fast calculations for preliminary and rough trends. This becomes useful when not all parameters are available or in cases where the demand for accuracy is less strict.

According to the scaling relations, the binding energies of a series of hydrogen-containing molecules are linearly correlated with the binding energies of their central atoms [14]. Figure 3 shows that the linear relations are also valid for the correlation of the transition state energies for hydrogenation/dehydrogenation reactions and binding energies of the central atoms. Furthermore, Figure 4 shows that the adsorption energies of hydrogen scale approximately with the adsorption energies of C, N, and O. The scatter increases as one move from to C to O. The linear TS scaling relations and the BEP relations are therefore both manifestations of the scaling relation between reaction intermediates and transition states with the adsorption energies of the central atoms (those atoms in contact with the surface). Because the transition state for dehydrogenation reactions are very similar over close-packed and stepped surfaces or a nanoparticle, there is no major geometrical effect for the single TS scaling relation and BEP relation for all treated hydrogenation/dehydrogenation steps, and all points fall on one line in Figure 2. For a single reaction, however, there

can be a significant electronic effect going from a close-packed surface to a more under-coordinated surface, such as a step or a nanocluster. This is a particular feature of hydrogenation/dehydrogenation reactions and somewhat different from many other bond-breaking reactions on transition metal surfaces, where steps are typically many orders of magnitude more reactive than the close-packed surfaces [10,31].
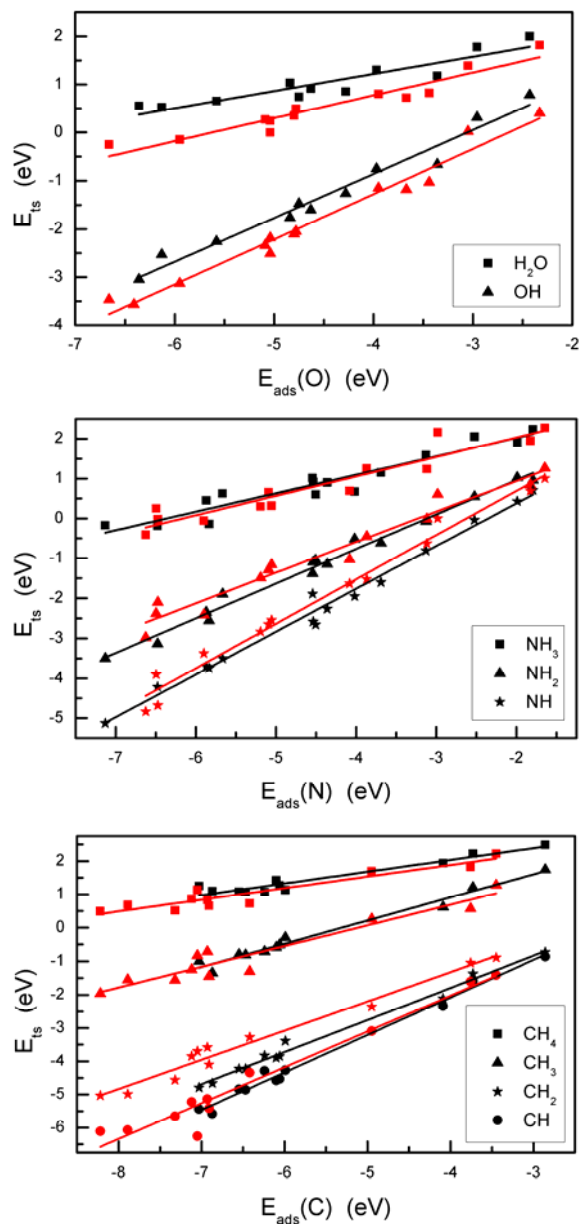

Fig. 3 The transition state energies of dehydrogenation reactions plotted against the adsorption energies of (a) O, (b) N and (c) C with respect to their gas-phase energies. The black and red colors indicate the results on close-packed and step surfaces respectively.

If we now more generally consider a transition state scaling relation to represent a general correlation between the energy of the transition state and some combination of relevant adsorption energies, then the BEP relation is one such particular choice of linear combination of the relevant

adsorption energies. One may then well ask the question: "What linear combination of relevant energies of adsorption intermediates is the best representation of a given reaction?". This question we shall attempt to address in a subsequent piece of work based on a statistical viewpoint [32].
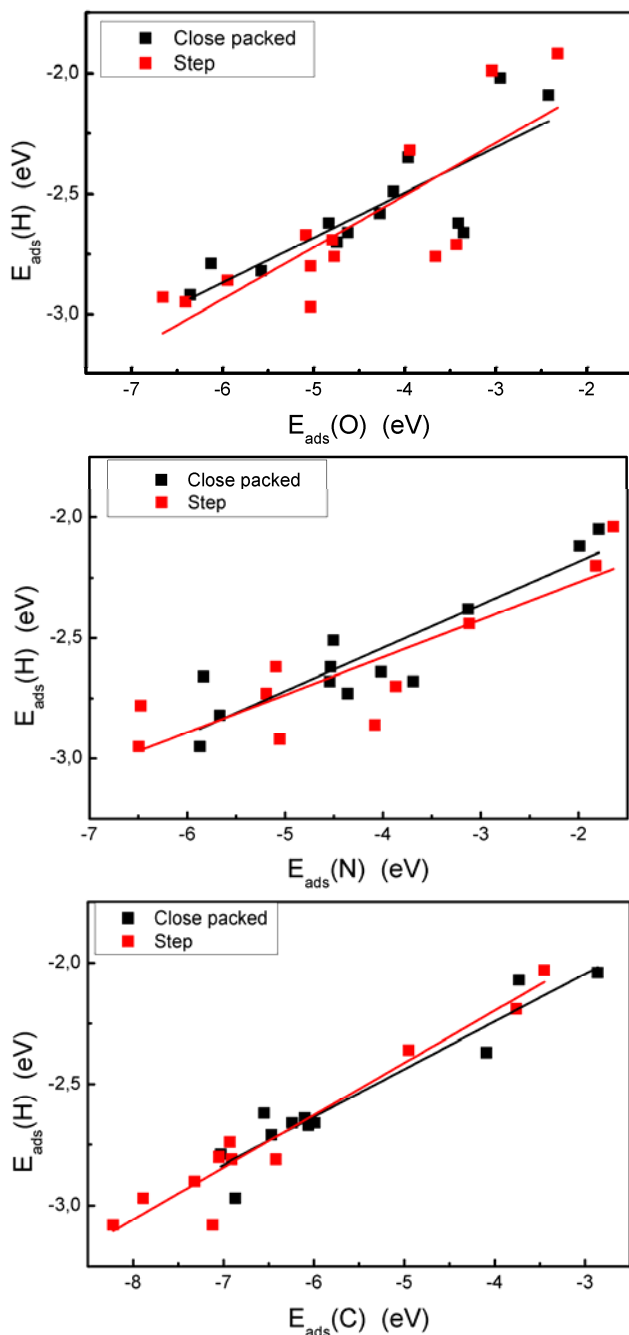

Fig. 4 The adsorption energies of H plotted against the adsorption energies of (a) O, (b) N and (c) C with respect to their gas-phase energies.

Conclusions

We have presented a universal transition state scaling relation for dehydrogenation reactions over close-packed and stepped surfaces as well as nanoparticles of transition metals. One simple relation is demonstrated to cover a very broad class of hydrogenation/dehydrogenation surface chemistry over transition metals, since all of the investigated reactions, metals, and surface geometries can be reasonably well approximated by one universal linear transition state scaling relation. This holds promise, that in the future the search for new hydrogenation catalysts may be facilitated by the fact that a first rough initial screening can be carried out based on this general linear energy relation without the need for performing full DFT calculations. Together with the adsorbate scaling relations for various reaction intermediates, the universal BEP relation for (de)hydrogenation reactions can become a tool with predictive power and give a fast and semi-accurate first hand knowledge for a number of catalytic reactions which can then subsequently be analyzed in greater detail.

Notes and references

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