FIRST PRINCIPLES ASSESSMENT OF BEP RELATIONS FOR STRUCTURE-DEPENDENT MICROKINETIC MODELING IN HETEROGENEOUS CATALYSIS

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Abstract

A first principles assessment of Brønsted-Evans-Polanyi (BEP)-type relations to predict chemical reactivity at different surfaces has been performed by means of periodic plane-wave Density Functional Theory (DFT) calculations. In particular, BEP has been assessed by the analysis of three dissociation reactions (CO, CH and CH_2) on (100), (110) and (111) surfaces of Rh, Pt, Ag and Cu. Our results show that BEP can correlate and predict the activation energies among the different surfaces and metals for all the reactions considered in the work, at reasonable accuracy for the exploration of complex structure-dependent reaction networks. We found that the nature of transition state can change among the surfaces in response of different trends of the binding energies among the metals/surfaces, thus strongly affecting the validity and the applicability of BEP relations in the prediction of the structure sensitivity.

Introduction

Despite the fact that the catalyst structure has been an important factor in catalysis science since the discovery of structure sensitive reactions in single crystal studies, its effect on reactivity is neglected in state-of-the-art microkinetic modelling. All the details regarding the active site (e.g., prevalent crystallographic planes, edges, corners, defects) are lumped in the concept of an abstract concept of a "free site", which is uniformly present on the catalyst surface. In reality, the catalyst is dynamic by changing its structure, shape and size in response to the different conditions in the reactor. Thus, the inclusion of such effects within the framework of microkinetic modelling, albeit extremely complex, is of outmost importance in the quest of engineering the chemical transformation at the molecular level (Salciccioli et al., 2011). This poses severe challenges for the application of hierarchical approaches, which have been successfully applied for the derivation of structure-less microkinetic models in applied catalysis. Typically, these approaches are based on a first estimation of the kinetic parameters of all the potential elementary reactions at the micro-scale is performed by employing computationally non-demanding semi-empirical methods. Therefore, the extension of the hierarchical methodology to the development of *structure-dependent microkinetic models* requires the derivation and the first-principles assessment of semi-empirical relations to predict chemical reactivity at different surfaces. At this scope, in this work, we present a detailed and explicit first-principles assessment of Brønsted-Evans-Polanyi (BEP) relations for the prediction of activation energies of elementary steps at different low-index catalyst surfaces for dissociation reactions on metal catalysts.

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Methods

The analysis has been performed according to a theory-to-theory comparison, following the approach adopted by (Maestri and Reuter, 2011). In particular, at the first-principles level, Climbing-Image-Nudge-Elastic-Band (CI-NEB) methods were employed for the detailed analysis of reaction pathways on the different surfaces using plane-wave, periodic density functional theory (PBE-DFT) by means of the Quantum Espresso code.
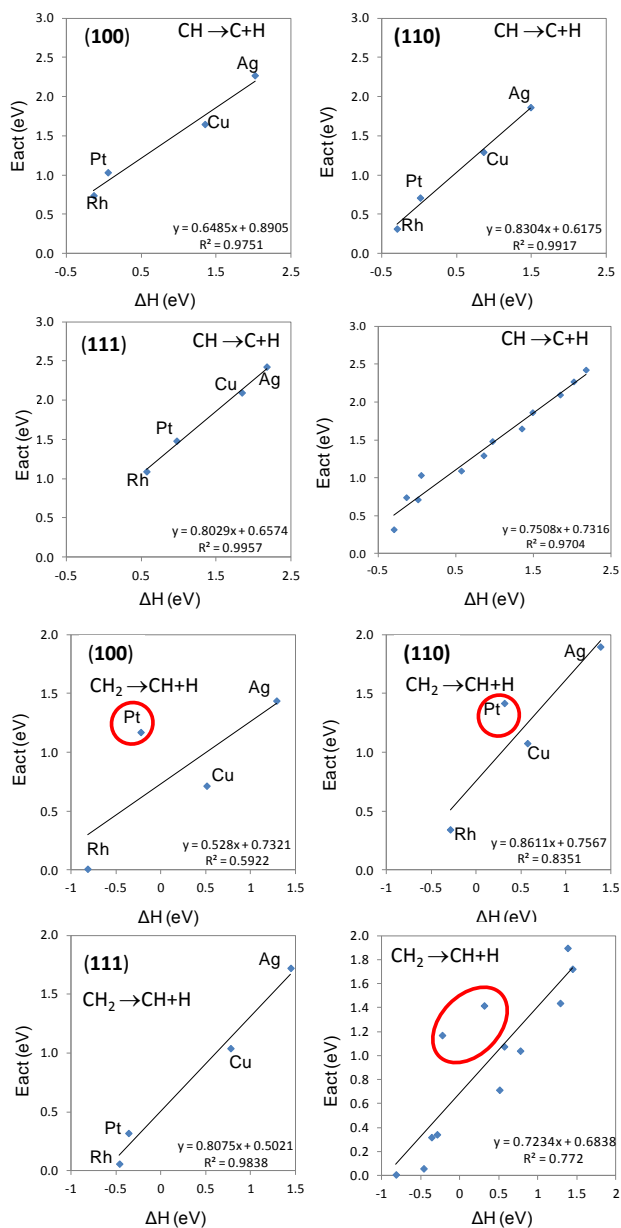
Results

Figure 1. BEP relations for CH dissociation and CH₂ dissociation on different metals and surface structures.

We have considered the dissociation reactions of CO, CH and CH₂ on (111), (110) and (100) surfaces of four different metal catalysts (Rh, Pt, Ag and Cu). The activation energy and the structure of the TS have been explicitly calculated for each reaction step on each metal for each surface at two different oxygen coverages (70 reaction pathways in total) using the CI-NEB method. We then interpreted the various activation energies, considering different possibilities of correlation for the activation

n energies. In particular:
a) same surface with respect to the different metals;
b) same metal with respect to the different surfaces;
c) all the metals with respect to all the surfaces.

Figure 1 reports the different correlations for CH and CH₂ dissociation reactions. We found that BEP relations can correlate quite well the different trends on the different surfaces and metals and thus can be used for the interpretation and prediction of activation energies on different catalyst surfaces.

The BEP relation is found to be strongly dependent on the geometry of the TS and by different trends of binding energies for reactants and products among surfaces and metals, which directly concur in establishing the character of the TS. Different interactions/geometries were indeed responsible of a change of the character of TS among the correlating variables, thus negatively affecting the BEP relation. For instance, Figure 1 shows the case of CH₂ dissociation, which presents two outliers in the BEP relations (red circles in Figure 1). Indeed, our calculations reveals that the geometry of the TS changes among the metals and surfaces and in particular the geometry on (110) and (100) Pt surfaces is different with respect to the ones on to the other 3 metals. As a result, the character of TS changes, with a direct effect on the slope of the BEP line. On the (111) surfaces, instead, the change in TS geometry is not found in our DFT calculations and consequently the BEP relation holds without any outlier. Extension to edges, corners, defects is currently on going.

Conclusions

We presented a thorough first-principles assessment of BEP relations for the prediction of structure sensitivity in elementary reactions on metal catalysts on a wide range of metals and surfaces. On the basis of these results, we show the potentiality of BEP relations for the application of hierarchical methodologies in the development of structure dependent microkinetic models.

References

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