Utrecht Journal of Chemical Research

Analysis of DFT calculated reaction energies for H2 dissociation on metal alloy surfaces

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Keywords: Hydrogen, heterogenous materials, web database, machine learning, periodic trends;

number of words: 1881

ABSTRACT: Extensive research on catalysis of hydrogen reactions on metal and metal alloy surfaces has already been performed. However, there is not yet a general model for catalyst activity and efficiency. This literature study focusses on converting the data of the 'catalysis-hub.org' online public database about the hydrogen adsorption reaction and to prepare it for machine learning. The data is processed and divided into batches of comparable datapoints that are ready to be analysed. Furthermore, this research seeks out to find periodic trends in the catalyst properties. The results show an increase in reaction energy for an increase in periodic group of the elements in the chemical composition of the catalyst. We found that the reaction energy is mainly dependent on the ratio of the elements in the chemical composition and to a lesser extent on the binding site of the hydrogen. Although the plots made in this research, are not enough to build a general model, this study shows that with the classified data a universal model for catalysis can potentially be developed.

Introduction

Hydrogen will play a vital role in the energy transition of the 21st century [1]. Therefore, tremendous amounts of studies have been performed on production and storage of this fuel. Hydrogen has the highest energy per mass of any fuel. However, its low ambient temperature density results in a low energy per unit volume [2]. Furthermore, the production of hydrogen comes with an inevitable energy loss. To surpass these issues the development of advanced storage techniques and efficient catalysts for the production is of paramount importance. Research on the adsorption energy of hydrogen on catalytic surfaces is essential to achieve this goal. Many studies have already been conducted to predict the properties of individual catalysts using density functional theory (DFT) calculations [3-4], but there is little information on how the properties of different catalysts relate to each other in reactions involving hydrogen gas. This literature study focusses on collecting as much data as possible on the hydrogen adsorption reaction on catalytic surfaces from the 'catalysis-hub.org' web-database [5] and converting the data into a format that will be useful for machine learning. The data on the hydrogen adsorption reaction originate from a number of different studies [6-15]. Additionally, with the collected data the study seeks out to find any periodic trends or correlations for the hydrogen adsorption reaction.

Methods

Data collection

The 'catalysis-hub.org' database contains information on surface reactions calculated with DFT. A key outcome of the data is the calculated reaction energy. The database uses JSON format to store the data. Using the GRAPHQL Query all data with hydrogen gas as reactant was collected. To make the data accessible for machine learning it was converted to a Microsoft excel file using 'convertcsv.com'.

Data adjustment and classification

The data was then extended by adding new parameters besides the parameters already present in the database: atomic numbers, electronegativity of the elements present in the chemical composition of the specific catalyst, number of different atoms in the chemical and surface composition, number of layers in the catalyst, surface area and the ratio of cell parameters in x- and y-direction. To create batches of compara-

ble data, the complete dataset was divided by the following classifications respectively: equation of the reaction, DFT code, DFT functional, facet, chemical composition of the catalyst and adsorption site. The division is shown in the tree diagram (appendix 1). The equations are divided by the amount of hydrogen atoms the reaction energy was calculated for. The DFT code is the program used for the calculations and the DFT functional indicates which type of function was used within the program. All calculations in the dataset used Quantum ESPRESSO 5.1 as DFTcode. In the database two names for the functional 'BEEF' are defined: 'BEEF' and 'BEEF_gbrv_600eV'. This is caused by different nomenclature from different references. The two versions were combined into one batch. The same was done for 'RPBE' and 'RPBE_400eV'. The facet contains information about the plane the catalyst was cut in for the three spacial dimensions. The division by chemical composition is based on the ratio in which the elements are present and on the kind of elements present. For example, the batch 'M_9M_3' contains information on catalysts that exist out of an alloy of two different metals with a 9 to 3 ratio. The 'M_3M_9' and 'M_9M_3' batches can be joined together, because the ratio is the same. The site contains information on where the hydrogen exactly bonds and is defined as follows: 'B' is 'Bridge', 'O' is 'Ontop', 'FCC' is 'Face centered cubic', 'H' is 'Hollow', 'T' is 'Top', 'Bt' is 'Bridge-tilt', 'Ht' is 'Hollow-tilt', 'Tt' is 'Top-tilt', 'a' indicates the first element in the chemical composition formula and 'b' the second element, 'f' is 'FCC structure' and 'h' is 'HCP structure'.'{}' indicates that no information on the site was given. For example, 'H|aaa|f' indicates 'Hollow aaa FCC', so the hydrogen binds in the hole between three atoms of the same element. The tree diagram can be read as follows: the batch for equation '0.5H2 + * -> H*', DFT code 'Quantum ESPRESSO 5.1', DFT functional 'BEEF', facet '111', chemical composition 'M_9M_3' and site 'H|aaa|f' contains 373 datapoints. Based on this classification several data batches were eventually excluded from the data. Because the hydrogen adsorption energy is investigated, any equations that contained any other molecule or atom than hydrogen were excluded. The following datapoints were excluded, because of a too small quantity of comparable data: datapoints with equation 'H2(g) + 2* -> 2H*' and facet '001' and datapoints with equation '0.5H2(g) + * -> H*' and facet '100', '211', '311', '322', '411' and 'monolayer'.

Data analysis

Thereafter, the reaction energy was plotted against the periodic group of both the first and second element in the chemical composition in 3D-plots using MATLAB R2019a. The dataset used for these plots was always within one batch to ensure the data is comparable. Also, the bucket needed to contain a large quantity of datapoints to ensure the outcome was reliable. A 3rd degree polynomial was used in both x and z direction to prevent under- or overfitting of the data.

Results

For finding periodic trends in adsorption energy of hydrogen the reaction energy, calculated with DFT, was plotted against the periodic group of the elements in the catalysts for the equation '0.5H2 + * -> H*', DFT code 'Quantum Espresso 5.1' and DFT functional 'BEEF'. To compare the influence of the ratio of the present metals in the catalyst three different data batches were used to plot: the 'H|aab|f' batch in the 'M_6M_6' chemical composition and '101' facet, the 'H|abb|f'' batch in the 'M_6M_6' chemical composition and '101' facet, the 'H|aaa|h' batch in the 'M_9M_3' chemical composition and '111' facet and the 'H|aaa|h' batch in the 'M_3M_9' chemical composition and '111' facet. The sites in the 'M_6M_6' batches are slightly different from the sites in the 'M_9M_3' and 'M_3M_9' batches. However, this is not a problem, because the datapoints are only compared within one data bucket. The 3D-plot for the 'M_9M_3' batch shows a clear increase in reaction energy with an increasing periodic group of the first element in the chemical composition (figure 1). For an increase in the periodic group of the first element in the chemical composition no significant change in the reaction energy is observed. The dependence of the reaction energy on the first element is expected, because the hydrogen binds at the hollow site between three elements of the first type. However, in the 3D-plot of the 'M_3M_9' data bucket the reaction energy is actually more dependent on the periodic group of the second element, while the binding site is still in between atoms of the first element (figure 2). This indicates that the ratio of the elements is of higher influence on the reaction energy than the binding site. To test this conclusion the 3D-plots of the 'M_6M_6' buckets can be used (figures 3 & 4). In both plots an increase in reaction energy for an increasing periodic group of both elements is observed, but as expected there are differences in the dependence of the reaction energy between the two different sites. In the plot of the 'H|aab|f' batch the reaction energy is more dependent on the periodic group of the first element. Oppositely, in the plot of the 'H|abb|f' batch the reaction energy is more dependent on the periodic group of the second element. These results show that the reaction energy is dependent on both chemical composition and binding site, but primarily on the former. In conclusion, in all plots a clear periodic trend is seen. Generally, the reaction increases for an increasing periodic group.

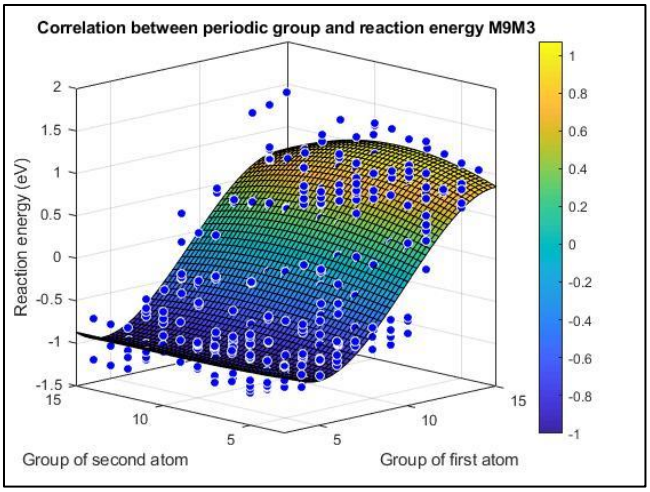

Figure 1 The reaction energy (eV) of the reactions with a catalyst with an M_9M_3 composition that were calculated with DFT, were plotted against the periodic group of both the first and the second element in the chemical composition. A third-degree polynomial in both the x and y direction was plotted through the datapoints.

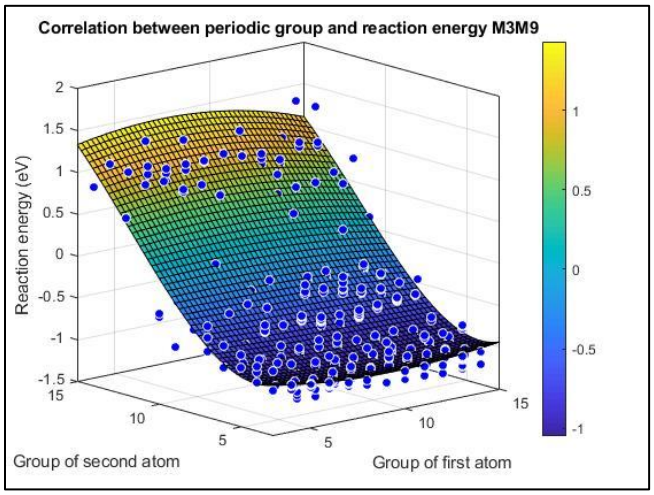

Figure 2 The reaction energy (eV) of the reactions with a catalyst with an M_3M_9 composition that were calculated with DFT, were plotted against the periodic group of both the first and the second element in the chemical composition. A third-degree polynomial in both the x and y direction was plotted through the datapoints.

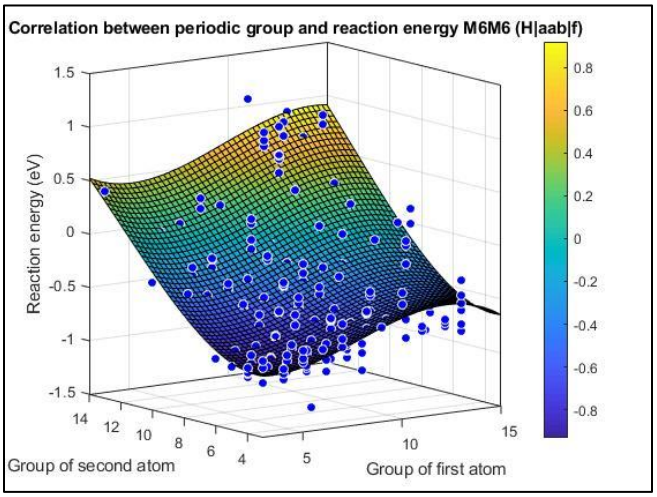

Figure 2 The reaction energy (eV) of the reactions with a catalyst with an M_6M_6 composition and an 'H|aab|f' binding site that were calculated with DFT, were plotted against the periodic group of both the first and the second element in the chemical composition. A third-degree polynomial in both the x and y direction was plotted through the datapoints.

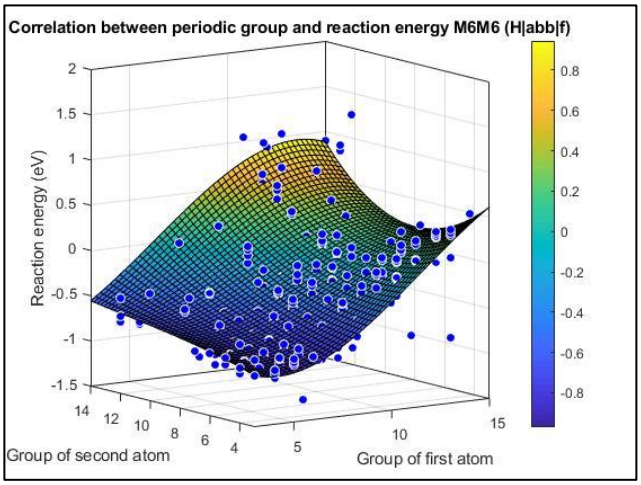

Figure 3 The reaction energy (eV) of the reactions with a catalyst with again an M_6M_6 composition but now an 'H|abb|f''binding site that were calculated with DFT, were plotted against the periodic group of both the first and second element in the chemical composition. A third-degree polynomial in both the x and y direction was plotted trough the datapoints.

Discussion and implications

This literature study is a first step in creating a general model for catalyst composition for hydrogen adsorption. By classifying and dividing the data it has been made possible to compare the chemical composition of catalyst in a constructive and efficient way. Although the plots made in this study are not yet sufficient for building a model, they do give promising perspective on finding cheaper and more productive catalysts as is shown that elements from the same periodic group give similar reaction energies. In general, 3D transition metals are significantly cheaper than 4D and 5D transition metals. Therefore, comparing reaction energies within one periodic group can potentially lead to discovery of cheaper catalysts with comparable properties. The periodic trend found in this study is in agreement with Nordlander [16], as they propose that the reaction energy increases with an increase in number of electrons in the d-orbitals. New DFT calculation results can easily be added to the right data buckets using the classification system. Machine learning will show whether it is possible to build a catalyst properties model through this system.

Conclusions

This literature study sought to classify and divide the data available on the 'catalysis-hub.org' web database to prepare it for machine learning and to find any periodic trends or correlation for the catalysis for the hydrogen adsorption reaction. The data was sorted in an orderly way to create buckets of data with comparable properties. The datapoints in such a bucket can be used for analysis. For finding periodic trends for the hydrogen adsorption reaction the reaction energy was plotted against the periodic group of the elements present in the chemical composition of the catalyst in a 3D-plot. The results showed that the reaction energy is mainly dependent on the periodic group of the element that is more abundant in the catalyst, but in a lesser way the reaction energy is also dependent on the periodic group of the element with the highest abundancy at the binding site. Furthermore, a clear periodic trend was found where the reaction energy increases with an increase in periodic group of the elements in the catalyst.

Acknowledgements

We would like to thank the Autonomous Energy Materials Discovery [AMD] Research Group - DIFFER – Dutch Institute for Fundamental Energy Research & CCER – Center for Computational Energy Research for giving us the opportunity to perform this research and Dr. Suleyman Er and Dr. Ilker Tezsevin for mentoring and supporting us during the research. We would also like to express our gratitude to the Utrecht University for providing this golden opportunity to do an internship at such a progressive institute.

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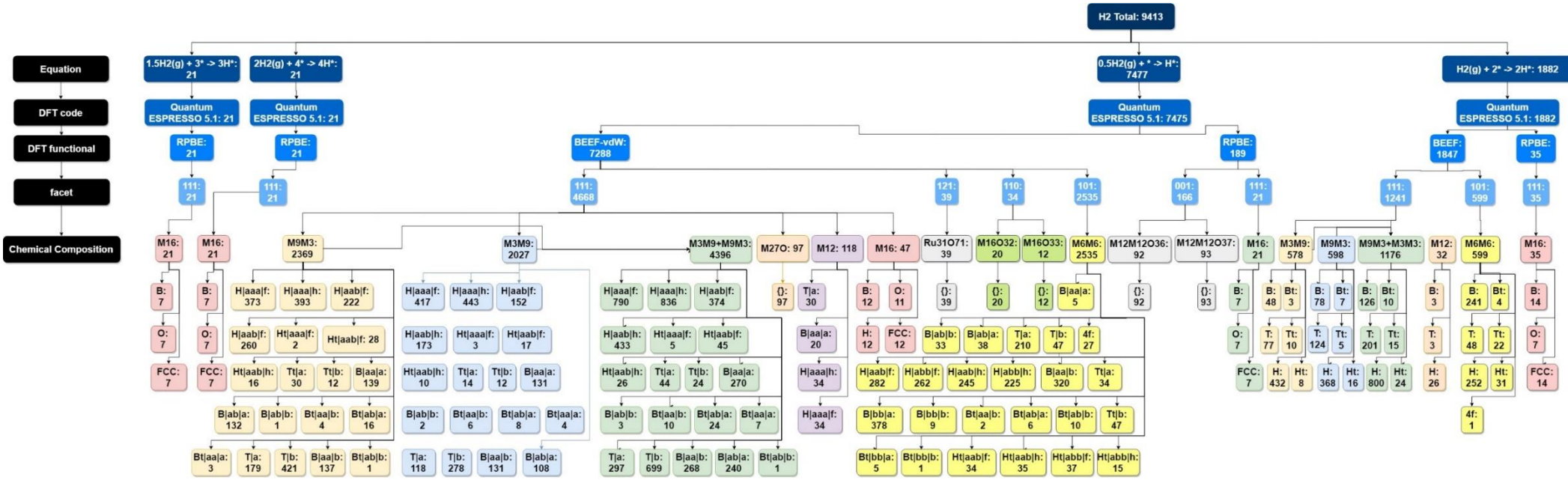

Figure 5 The tree diagram shows how the data is divided. The numbers indicate how many datapoints are in the data buckets. The division is made as follows: first is the equation of the reaction, second is the DFT code used for the calculations, third is the DFT functional that was used within the DFT code, fourth is the facet that the catalyst surface was cut in, fifth is the ratio of the elements present in the chemical composition of the catalyst and sixth is the binding site of the hydrogen on the catalytic surface. The binding sites are abbreviated to fit the image on one page. 'B' means 'binds on the bridge between two atoms', 'O' means 'binds ontop of one atom', 'FCC' is ' binds on a Face Centered Cubic crystal structure', 'H|aaa|f' means 'binds at the hollow site between three atoms of the first element in the chemical composition in an FCC structure. 'Bab|a' means 'binds on the bridge between atoms a and b but slightly closer to atom a', 'T|a' means 'binds on top of atom a', 'Tt|a' means 'binds on top of atom a but with an angle', '{}' means 'no information on the binding site was given'. All other abbreviations can be deducted from the explanation above..

Appendix 1