Asian Journal of Chemical Sciences

2(3): 1-13, 2017; Article no.AJOCS.33676
ISSN: 2456-7795

Determining the Catalytic Properties of a Material Using Relative Bond Strength

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Authors' contributions

This work was carried out in collaboration between all authors. Author MAM designed the study and wrote the first draft of the manuscript. Author GG managed the analyses of the study. Author MMA ran the computational calculation. Author WMAWMK managed the literature searches. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/AJOCS/2017/33676
Editor(s):
(1) Georgiy B. Shul'pin, Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia.
Reviewers:
(1) Alfredo Juan, Universidad Nacional del Sur, Argentina.
(2) Birsa Mihail Lucian, Alexandru Ioan Cuza University of Iasi, Romania.
Complete Peer review History: http://prh.sdiarticle3.com/review-history/19138

Original Research Article

Received 25th April 2017
Accepted 13th May 2017
Published 19th May 2017

ABSTRACT

Fuel cells are one of the most promising renewable energy sources. However, they are relatively expensive due to their use of platinum, a precious metal, as the catalyst. Much research has been conducted with the aim of optimizing fuel cell efficiency, including identifying alternative catalysts. In this study, we propose a new parameter known as relative bond strength as an indicator for the catalytic properties of a material. Relative bond strength is calculated based upon the relationship between bond length and bond strength. The results of this study provide evidence for the viability of this parameter through computational calculation involving different types of materials and cluster sizes.

Keywords: Fuel cell; catalyst; bond length; bond strength; relative bond strength; DFT; geometry optimization.

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1. INTRODUCTION

Fuel cells are one of the many sources of renewable energy available today. They can convert chemical energy into electrical energy. The reaction consists of hydrogen as a reactant and platinum as a catalyst.

However, fuel cell energy is very expensive to produce due to the high price of platinum. Platinum/Palladium are very versatile metals and commonly used as catalysts in petrochemical, pharmaceutical and fine chemical production [1]. Because of this, many efforts have been made towards optimizing the production of fuel cell energy with the goal of reducing or replacing platinum as the conventional catalyst. In Yang, et al.'s [2] 2003 study, for example, the low-cost method of preparing PtRu/C was explored. Many recent studies claimed that there is an alternative catalyst for fuel cells [3-8]. Although there are ways to differentiate between different alternative catalysts, most of these methods are time consuming and very costly.

In this study, we proposed a new parameter called relative bond strength, which can be used to determine the viability of a material to serve as a catalyst. To assess its utility, the relative bond strengths for different materials, including platinum, were calculated. We also investigated the influence of the size of the catalyst clusters on the value of the relative bond strength. If a significant correlation between (a) the relative bond strength value and the types of materials, and (b) the relative bond strength and the size of catalyst clusters can be demonstrated, it can be inferred that this parameter can be used as an indicator in the search for alternative catalysts, especially in the exploration of new and unknown material configurations.

Platinum plays an important role as a catalyst in hydrogenation [9-11]. The surface reaction of platinum has been studied extensively in past experiments [12-29]. These studies provide useful background information in the search for a cheaper, more reliable catalyst than platinum. This study represents a preliminary investigation of potential catalysts, specifically focused to the properties of bond lengths and bond strengths. Since, Platinum is a very good catalyst. Thus, our research and calculation mainly refers to platinum as the baseline for the new proposed parameter.

The concept relating bond length and bond strength was not new. In 1973, Brown and Shannon studied the relation between bond length and bond strength [30]. They found that for most diatomic molecules, except a few anion-cation pairs, the bonding force is stronger when the bond length is shorter. In 1976, Shannon discovered an anomaly in the bond-length-bond-strength (BLBS) relation of anion-cation pairs [31]. The anomaly resulted from not considering several factors such as the unit cell volume, the coordination number and the oxidation state. The BLBS relation can be generalised using Badger's rule, as follows:

$$k_e = A(R_e - B)^{-3} \qquad (1)$$

k_e: force constant

R_e: equilibrium length

A: universal constant

B: a parameter that depends on the specific row in the Periodic Table to which the diatomic molecule belongs

Cioslowski et al. [32] also tested the relation between bond length and bond strength. They found that the formula only gave an estimated value, which may not suitable in certain cases. In recent studied, Kraka et al. [33] in 2016, drawing from both experimental and theoretical results, proved that Badger's rule is not an accurate measurement of BLBS relation; however, this violation occurred in extremely rare cases. Badger's rule can still be used with a wide range of diatoms, but there are uncertainties as to whether this method can predict BLBS relations for new and unknown diatoms or molecules, especially those, which may have better catalytic properties than platinum. An example of this can be seen in Pompeo et al.'s [34] study, which shows that a strong support in catalyst will affect the behaviour of the catalyst. The new structure configuration of the support can be any kind of molecule and ranging in sizes. Subsequently, this new configuration and support of catalysts that were previously unknown cannot be confirmed as obeying Badger's rule. We expect that the newly proposed parameter will have universal properties due to its simplified measuring process and its rugged properties in dealing with different kind of molecules and structures.

Before computing the BLBS relation or the relative bond strength, it is wise to check whether a single atom of "catalyst" can lower the activation energy needed for certain reaction. Fig. 1.1, for example, shows the energy contained in the hydrogen molecule as it dissociates. Each point on the graph corresponds to the structures shown in Fig. 1.2. As the distance between hydrogen atoms increase, the energy level also increases. The difference in energy between product and reactant is around 6 eV, and the reaction is endothermic. This indicates that approximately 6 eV of energy is needed to dissociate one hydrogen molecule into two hydrogen atoms. This process is vital in fuel cell production, as the catalyst enhances the dissociation of hydrogen molecules and can thus lower the energy required for such reactions.

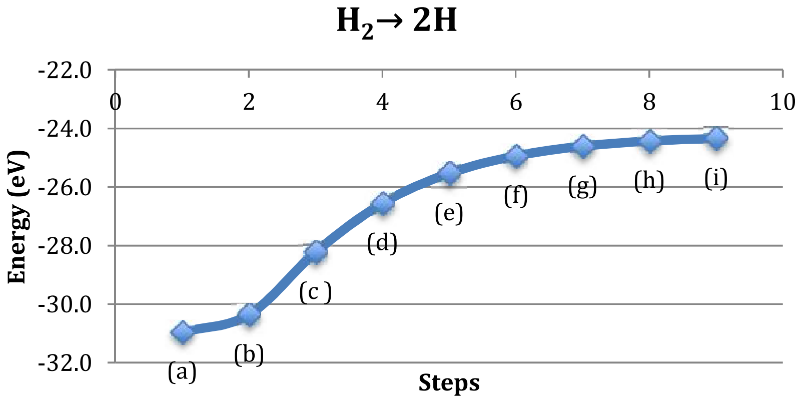
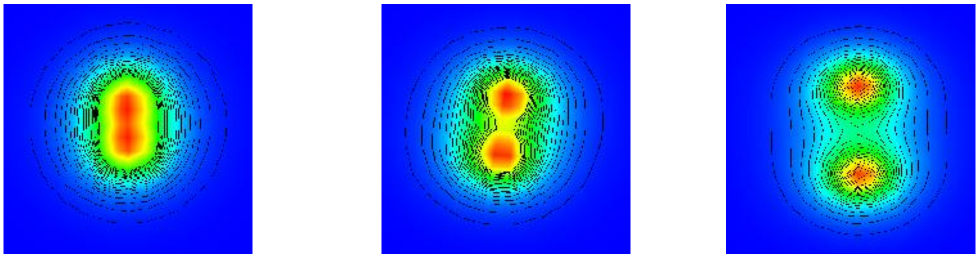
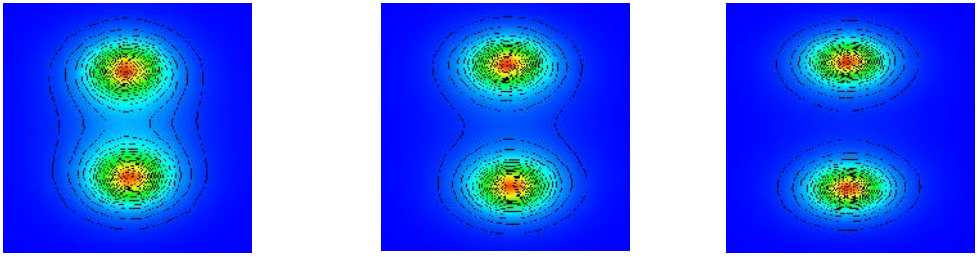


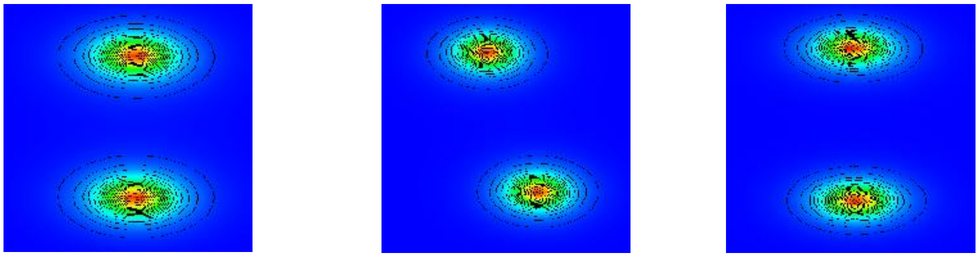
Fig. 1.1. Total energy required for hydrogen dissociation (H_2 to 2H)



(a) r = 0.768 A (b) r = 1.000 A (c) r = 1.500 A



(d) r = 2.000 A (d) r = 2.500 A (e) r = 3.000 A



(e) r = 3.500 A (f) r = 4.000 A (g) r = 4.500 A

Fig. 1.2. Contour plot of hydrogen dissociation from H_2 into 2H

A single atom of an element was introduced as a catalyst into the hydrogen dissociation reaction. Table 1.2 shows calculations of the difference between the product and reactant for each element, which produces varying amounts of energy required for hydrogen dissociation. These values show that platinum is the best catalyst overall, as it lowered the amount of energy required by the greatest amount. Likewise, carbon is not a good catalyst for hydrogen dissociation as it tends to attract the hydrogen atom and subsequently form hydrocarbon, which is evident by the higher amount of energy required (Table 1.2). From these quick calculations, its proven that even with the presence of a single atom of "catalyst", there is a visible effect on the reaction. Thus, even with diatomic structure, we believe the "effect of the catalyst" can be detected and measured.

Table 1.2. Enthalpy calculations for hydrogen dissociation in the presence of different single atom 'catalysts'

$H_2 \rightarrow 2H$
product = -24.9568 eV
reactant = -30.9540 eV
enthalpy (product - reactant) = 5.9972 eV (endothermic)

$PtH_2 \rightarrow PtH + H$
product = -751.8559 eV
reactant = -740.5172 eV
enthalpy (product - reactant) = -11.3387 eV (exothermic)

$SiH_2 \rightarrow SiH + H$
product = -133.2011 eV
reactant = -132.2948 eV
enthalpy (product - reactant) = -0.9063 eV (exothermic)

$CH_2 \rightarrow CH + H$
product = -162.7341 eV
reactant = -176.1156 eV
enthalpy (product - reactant) = 13.3815 eV (endothermic)

$TiH_2 \rightarrow Ti + H$
product = -1213.3468 eV
reactant = -1207.8180 eV
enthalpy (product - reactant) = -5.5288 eV (exothermic)

Our work has three main objectives: first, to formulate a new parameter that can help in determining the catalytic properties of a material; second, to evaluate the viability of this parameter by applying it to a wide range of potential catalytic materials; and finally, to evaluate the viability of this parameter by investigating its relationship with different catalyst cluster size.

Regarding the relationship between bond length and bond strength, Oudenhuijzen et al. [35] and Willenbockel et al. [36] both stated that the bond strength of a molecular bond could be manifested by bond length. Oudenhuijzen et al. [35] in their work categorized the Pt-H bond length in bulk into two types: strongly bonded and weakly bonded. The weaker bond has a longer bond length compared to the stronger bond. This phenomenon can be described as the Goldilocks zone for the catalytic properties; namely, a good catalyst must have the bond length within the range set by both extremes. However, it must be addressed that comparison purely on bond length is not acceptable for different materials. Thus, we introduced our new parameter, which will normalize the value so that a fair comparison can be made across different materials. Hence, the relative bond strength is proposed.

Regarding our second objective, we hypothesized that different materials will have different and unique values of relative bond strength. This hypothesis agrees with previous works [37,38]. Logically, a good catalyst will attract reactant within a specific range of values of relative bond strength. Meanwhile, a poor catalyst will attract reactant beyond this range. This is already stated by Oudenhuijzen et al. [35] in which a good catalyst will have specific Goldilocks zone of bond strengths. In this work, we shall determine the range of values of relative bond strength for a good catalyst.

Based on our third objective, we hypothesized that a good catalyst should have a stable value of relative bond strength for different cluster sizes. Allian et al. [40] have studied this stability in 2011 and their work showed that both large and small Pt clusters have quite similar reactivity [39]. In other words, a good catalyst should display small variations in the value of the relative bond strength across different cluster sizes. Nonetheless, even though stability is a good indicator, non-stability can quite profitable. For instance, a poor catalyst may show large variations in the value of relative bond strength as the cluster size varies. Thus, this variation proves that a non-catalytic material can become catalytic as their form and structure are altered. Our study showed that there are certain materials whose values of relative bond strength can be affected by the cluster sizes.

Our research in the surface study of catalysts is computational in nature. Conventional experimental studies will always promote uncertainty due to alteration of the catalyst surface [41]. Therefore, the choice of computational method in this research intends to minimize this uncertainty. The drawbacks of computational methods are compensated by the versatility in configuring the molecules under investigation.

In this paper, the concept behind the new parameter will be described in the Methodology and Theory section. The input parameter for our calculations and computational methods used will also be described in this section. Furthermore, the result and discussion will be in the Result and Discussion section. The second and third objective will be explained in detail. Finally, this paper will be concluded in the Conclusion section.

2. METHODOLOGY AND THEORY

In this section, we will describe the theoretical background of the new parameter and the computational methods employed to obtain it.

The strength of a bond is related to it length. A shorter bond length implies a greater overlap between electronic orbitals. Therefore, the bond is stronger as to overcome the repulsion force. On the other hand, a longer bond implies less overlap between electronic orbitals. Consequently, the repulsion force is less and therefore the strength of the bond is weaker.

The length of a bond may be increased or decreased through the technique of geometry optimization, which is a method to identify the molecular structure having the lowest energy, therefore being most stable [42].

The value of relative bond strength for a structure is calculated thus:

$$Relative\ bond\ strength = \frac{Original\ bond\ length\ (a)}{Optimized\ bond\ length\ (b)\ or\ (c)} \quad (2)$$

Table 2.1 lists the values for the radius obtained from Sanderson's work [43]. The bond length is the sum of the radius of element X with the radius of hydrogen. This sum is taken to be the original bond length as in equation (2). Thus, in process of creating the initial molecules before optimization, the bond length has been set to the values shown in Table 2.1. The process was performed using Avogadro, molecule editor software version 1.0.1 [44]. The results obtained via the geometry optimization method will be further discussed in the Results section.

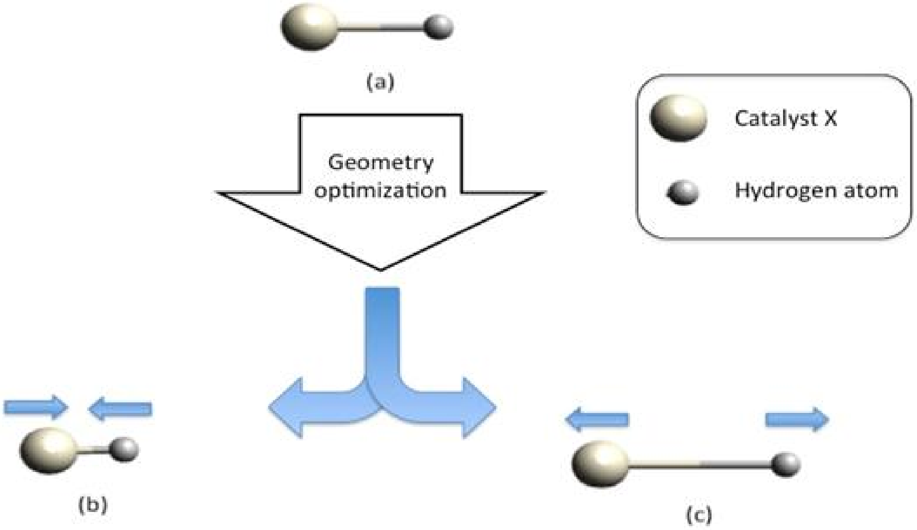


Fig. 2.1. The original configuration of structure (a) will be optimized and transformed into structure (b) or structure (c). Structure (b) shows bigger relative bond strength value compared to structure (c)

Table 2.1. Radius and bond length between elements X with a single hydrogen atom

Element X	Radius (Å)	Original bond length (Å)
Lithium, Li	1.67	2.20
Carbon, C	0.67	1.20
Nitrogen, N	0.56	1.09
Oxygen, O	0.48	1.01
Sodium, Na	1.90	2.43
Silicon, Si	1.11	1.64
Sulphur, S	0.88	1.41
Titanium, Ti	1.56	2.09
Selenium, Se	1.03	1.56
Cadmium, Cd	1.61	2.14
Platinum, Pt	1.77	2.30
Hydrogen, H	0.53	1.06

After creating the structures, the geometry optimization process will be performed using Octopus version 5.0.1 [45]. The species for the elements used is Hartwigsen-Goedecker-Hutter pseudopotentials. Since, we do not define the shape of our simulation box, by default it will be a sphere with a predetermined radius 11.00 Å and a grid spacing of 0.175 Å. The grid spacing is chosen based on a compromise between computational time and accuracy. Finally, the geometry optimization process was performed with a new algorithm, the conjugate gradient algorithm of Broyden-Fletcher-Goldfarb-Shannon (CG-BFGS) [46]. Specifically, there is an updated algorithm with a small extension to the BFGS method used in our calculation known as CG-BFGS2. As stated on the Octopus website, "The bfgs2 version of this minimizer is the most efficient version available, and is a faithful implementation of the line minimization scheme described in Fletcher, *Practical Methods of Optimization*, Algorithms 2.6.2 and 2.6.4."

A few remarks need to be stated here, in which the diatomic molecules chosen can be separated into two categories, open shell system and close shell system. For open shell system, the extra-unoccupied electron will be treated as dangling electron. This dangling electron deliberately present to which we believe will affect the calculation. This is proven by a quick calculation for OH and H_2O. The average bond length for OH and H_2O are ~1.01Å and ~0.95Å respectively. However, this difference will not affect our main objective, which is to prove the feasibility of our new proposed parameter. On the contrary, this is one of the strength of the new proposed parameter, which it can be applied to different configurations. Moreover, this dangling electron will be treated the same as the free electron in platinum metal. Thus, this will be useful to mimic the behavior of the good catalyst, platinum.

The feasibility of the new parameter of relative bond strength was evaluated by applying it to different types of materials and by determining its relationship with the cluster size. Both use the same geometry optimization method, but with differences in the preparation of the initial structure.

To test the universality of relative bond strength as a parameter across different types of materials, we built the structure for X-H and X_2-H using Avogadro. The bond length between X-H is set to the values stated in Table 2.1. Next, the geometry optimization process was applied using Octopus for each of the elements X. The optimized bond length was then measured using Avogadro. Finally, the relative bond strengths for each configuration were calculated using the original and optimized bond lengths.

To determine the influence of cluster size upon the relative bond strength, we confined our investigation to the Pt_3 cluster. Since bigger clusters have a greater range of potential structural configurations, we must find the most stable configuration before doing any bond length measurements. For a Pt_3 cluster, we found that there are three potential configurations: linear, ring and L-shaped. We applied the geometry optimization process to each potential configuration and compared the total energy of each configuration. The configuration having the lowest total energy is the most stable configuration and this was selected for subsequent bond length measurements. Next, three copies of the selected configuration were made and each of it was added a single hydrogen atom. The position of the hydrogen atom is different for each of the copied configurations, in which each file will have different platinum atom attached with the hydrogen atom (Fig. 3.2). After that, the geometry optimizations processes were applied to each of these structures. Finally, the bond length was measured and relative bond strength was calculated.

3. RESULTS AND DISCUSSION

Comparing the optimized bond length with their experimental values can validate the geometry optimization methods applied in this work (Table 3.1).

We acknowledged that most of the diatomic molecules studied do not occur naturally, except for the hydrogen molecule. This means that direct comparison with experimental data is not possible for most of them. Thus, the experimental values used for comparison are average values from different types of diatomic molecule. However, we believed that these values could still be used to gauge whether our calculation is on the right track.

Our geometry optimization method produced reasonable estimates of bond length values. The percentage difference between the optimized bond lengths with the literature values is less than 6%. The differences may due to open shell system. This has been elaborated in Methodology and Theory section. Thus, with this computational result, we believe that our geometry optimization method is acceptable. Subsequently, it's also valid for the other types of molecule.

A minimum criterion for an element to qualify as a catalyst is for it to have a relative bond strength value greater than the relative bond strength value for hydrogen molecule, which is 1.39. The stronger bond created between the elemental atom and the hydrogen atom will split the hydrogen molecule. Fig. 3.1 shows that most of the elements have a lower relative bond strength value compared to the hydrogen molecule, except for platinum and titanium. We can therefore conclude that both platinum and titanium have catalytic properties. This conclusion is supported by the fact that both elements are commonly used as catalysts.

We found that increasing the number of atoms – for instance, from single to double – will cause the relative bond strength value to fluctuate. Such fluctuations are problematic if it becomes smaller compared to the relative bond strength value for the H_2 molecule. For example, the relative bond strength value for a single atom of titanium is greater than the relative bond strength value for a hydrogen molecule. However, the relative bond strength value for a titanium molecule becomes less than the relative bond strength value for the hydrogen. This fluctuation may result from the extra stability gained when titanium forms a molecule. On the other hand, the platinum atom displays smaller fluctuation in the relative bond strength value when it forms a molecule. Thus, we concluded that the element platinum has more stability in term of catalytic properties while changing in size.

From these findings, it can be observed that two major factors play important role in influencing catalytic properties. First, the relative bond strength value of an element must be greater than the relative bond strength value for the hydrogen molecule. Second, the fluctuation in the relative bond strength values for an element as the cluster size increases reflects its stability. Therefore, a promising candidate for a good catalyst should have a relative bond strength value greater than 1.39 and its value should not fluctuate too largely as the cluster size increases.

Next, more complex molecular configurations are explored by studying a catalyst molecule containing three atoms. A platinum triatomic molecule was chosen and the influence of cluster size on the relative bond strength value for platinum was investigated. Three possible molecular configurations were chosen: linear, L-shaped and ring. All three configurations have been optimized and the total energies obtained for each molecular configuration are as (Table 3.2).

Based on Table 3.2, the total energies for each configuration are not significantly different. However, the ring structure, having the lowest total energy, was found to be the most stable compared to the others. Therefore, ring structure was chosen for further computational analysis.

Before we proceed, there is a few remarks must be made. Energy calculations using computational methods is not very precise for some molecules [50]. In his book, *Concise Physical Chemistry*, Roger stated: 'Results from some computational kinetic studies are roughly comparable to measured values, but this is a difficult field because computed activation enthalpies are very sensitive to the estimated structure of the activated complex and the rate constant is an exponential function of an *H*.' A discovery made by Miswan et al. [51] in 2017 adds weight to this statement. The results of energy calculation can be divided into two groups: in the range of hundreds and in the range of thousands. However, it still can be used to determine the most stable structure. This is because the trends for both are almost identical.

Table 3.1. Comparison between optimized bond lengths with literature values obtained from the wired chemist [47], the computational chemistry comparison and benchmark data base [48] (CCCBDB) and the Handbook of chemistry and physics 84th edition [49]

Diatomic molecule	Optimized bond length	Bond length [47]	Percentage difference	Bond length [48]	Percentage difference	Bond length [49]	Percentage difference
H-H	0.77 Å	0.74 Å [47]	3.92%	0.74 Å [48]	3.77%	0.74 Å [49]	3.77%
C-H	1.15 Å	1.09 Å [47]	5.32%	1.12 Å [48]	2.50%	1.12 Å [49]	2.50%
N-H	1.07 Å	1.01 Å [47]	5.54%	1.03 Å [48]	3.60%	1.03Å [49]	2.90%

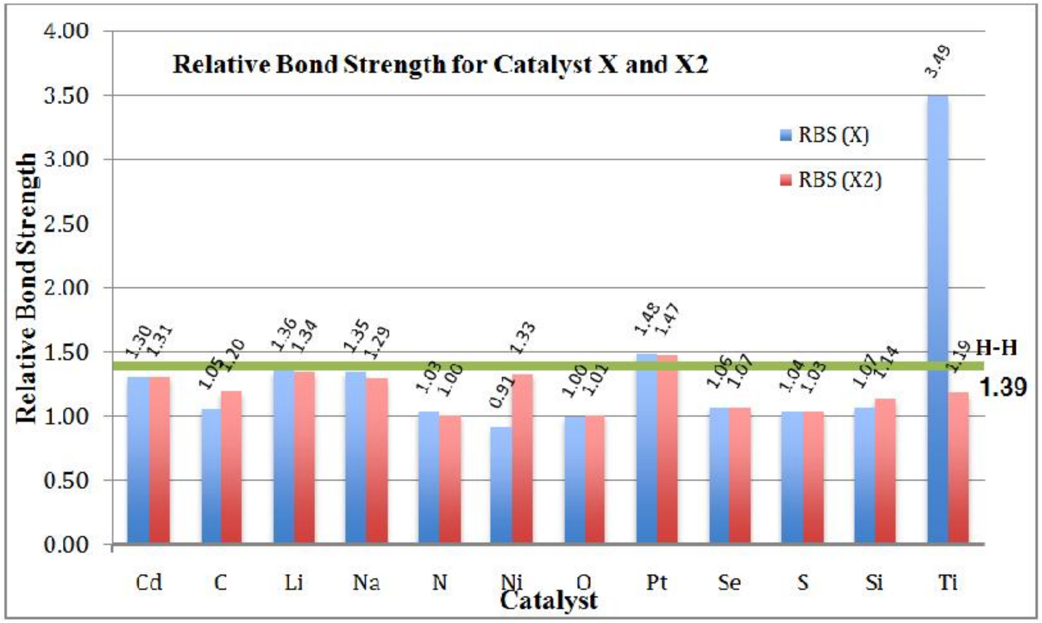


Fig. 3.1. Relative bond strength for single atom (blue) and double atom (red)

The ring configuration was copied and a hydrogen atom was attached to different platinum atoms in the ring configuration to give rise to three possible cases, as shown in Fig. 3.2(b), 3.2(c) and 3.2(d). However, the structures shown is the structures after geometry optimization. Thus, it differs from the original configuration as in Fig. 3.2(a).

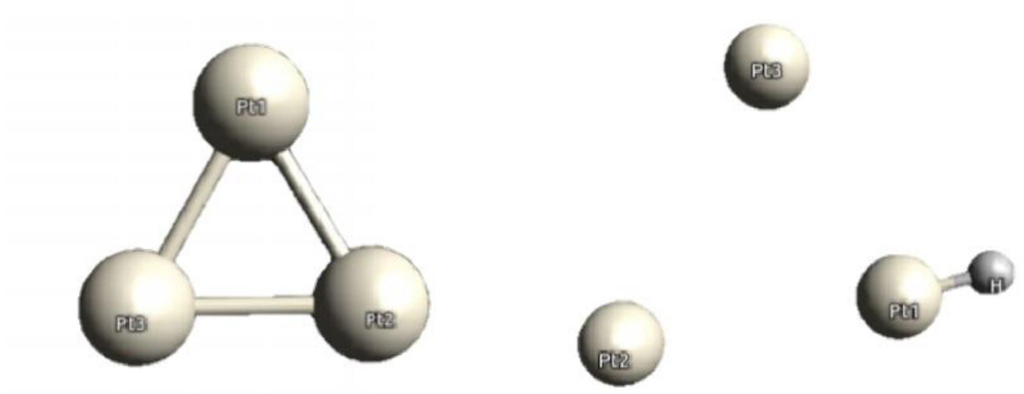
Each of the three structures (b), (c) and (d) were optimized and the bond length values for each case are shown in Table 3.3.

The case in Fig. 3.2(b) shows a deformation in the original ring structure, implying that this case is unstable. Therefore, we expect the relative bond strength value between the hydrogen atom the and first platinum atom to be less than the H_2 line.

From Fig. 3.3, we can see that the relative bond strength value for most of the Pt-H is greater than relative bond strength value for the hydrogen molecule. This shows that the relative bond strength between platinum and hydrogen is stable even for larger molecules. A good catalyst must be stable whilst undergoing reaction this criterion is coherent with the result of Allian et al. in 2011.

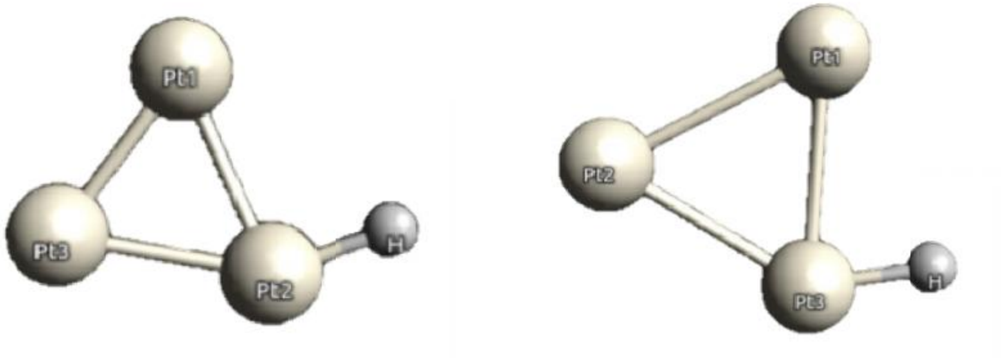
Table 3.2. Total energies for different configurations of a triatomic system

Molecular configurations	Energy (eV)
Linear	-2117.9038
L-shaped	-2132.1489
Ring	-2136.8178



(a) Ring structure

(b) The hydrogen atom attached to the first platinum atom



(c) The hydrogen atom attached to the second platinum atom

(d) The hydrogen atom attached to the third platinum atom

Fig. 3.2. The ring configuration (a) and the three different cases (b), (c) and (d) after optimization, depending on the location to which the hydrogen atom was attached to the ring structure

Table 3.3. The bond lengths between the platinum atoms for each structure in Fig. 3.2

Structures	3.2 (a)	3.2 (b)	3.2 (c)	3.2 (d)
Pt1-Pt2	2.465 Å	4.050 Å	2.657 Å	3.168 Å
Pt2-Pt3	2.459 Å	4.511 Å	2.586 Å	3.052 Å
Pt3-Pt1	2.455 Å	3.823 Å	2.467 Å	3.047 Å

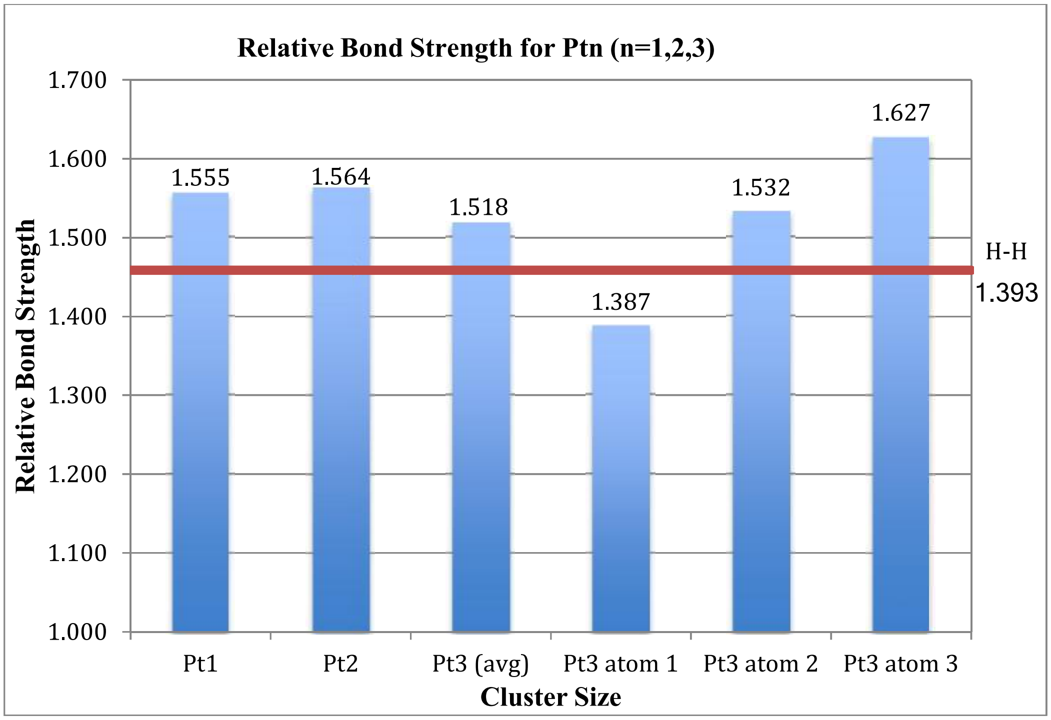


Fig. 3.3. A graph of relative bond strength values for different configurations of Pt-H molecule

The last three bars (Pt_3 atoms 1, 2 and 3) show the effect of the position of hydrogen atom in ring-structured Pt_3 cluster. The configuration in which the hydrogen atom was attached to the first platinum atom in Pt_3 ring structure has the lowest relative bond strength value. Meanwhile, the other two configurations show an opposite result, i.e. the relative bond strength values are greater than the value for a hydrogen molecule. Therefore, we infer that the “transition point” between the reactive and non-reactive behaviors of the catalyst will be influenced by the cluster size.

Oudenhuijzen et al. [35] previously studied the strong and weak attraction of a hydrogen molecule, specifically that there is a “mixed” behavior in the transition point between reactive and non-reactive behaviors for a single catalyst. The similarities between their previous work and our present work indicate that the new parameter – relative bond strength – can be reliably used for a larger cluster sizes to predict the potential reactivity of a catalyst.

4. CONCLUSION

In this research, we prove that the new proposed parameter, which is relative bond strength, can be used to determine the catalytic behavior of a material. This parameter has been proposed to fill the gap in the search of alternative catalyst especially for fuel cell. With this parameter, a new information and perspective can be obtained regarding catalytic behavior. Subsequently, reduce the time it took to test the viability of the "new catalyst".

This parameter has been tested for a various type of elements, which act as the alternative catalyst. We found that, the minimum values for relative bond strength is 1.39. This is also validating by differing the size of the cluster, in which the minimum values still hold. However, our work cannot found the maximum values for the relative bond strength. Thus, the Goldilocks zone cannot be stated. We also found that the new parameter can be used for various type and size of materials. This ruggedness will be useful in testing a new and unknown catalyst or even with the catalyst's support.

The next step to extend this research and to further test this new parameter is to find the maximum value for relative bond strength. Besides that, a much more complex catalyst can be tested to further validate this new parameter.

In conclusion, we can conclude that our objective is achieved, in which relative bond strength can be used as an indicator for catalytic properties.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Nakatsuji H, Matsuzaki Y, Yonezawa T. Abinitio theoretical study on the reactions of a hydrogen molecule with small platinum clusters: A model for chemisorption on a Pt surface. The Journal of Chemical Physics. 1988;88(9):5759-5769.
2. Yang B, Lu Q, Wang Y, Zhuang L, Lu J, Liu P, Wang R. Simple and low-cost preparation method for highly dispersed PtRu/C catalysts. Chemistry of Materials. 2003;15(18):3552-3557.
3. Zhang L, Xia Z. Mechanisms of oxygen reduction reaction on nitrogen-doped graphene for fuel cells. The Journal of Physical Chemistry C. 2011;115(22): 11170-11176.
4. Qu L, Liu Y, Baek JB, Dai L. Nitrogen-doped graphene as an efficient metal-free electrocatalyst for oxygen reduction in fuel cells. ACS Nano. 2010;4(3):1321-1326.
5. Seger B, Kamat PV. Electrocatalytically active graphene-platinum nanocomposites. The role of 2-D carbon support in PEM fuel cells. The Journal of Physical Chemistry C. 2009;113(19):7990-7995.
6. Sahiner N, Demirci S. Natural micro-granular cellulose as an alternative catalyst to metal nanoparticles for H 2 production from NaBH 4 methanolysis. Applied Catalysis B: Environmental. 2017;202: 199-206.
7. Sahiner N, Yasar AO. Imidazolium-based polymeric ionic liquid microgels as an alternative catalyst to metal catalysts for H 2 generation from methanolysis of NaBH 4. Fuel Processing Technology. 2016;152: 316-324.
8. Fukunaga H. Optimization of cathode catalyst layer of PEFC using silk-derived activated carbon by 2-step mixing method introduction. In Prime 2016/230th ECS Meeting (October 2-7, 2016). ECS; 2016.
9. Bernasek SL, Somorjai GA. Molecular beam study of the mechanism of catalyzed hydrogen–deuterium exchange on platinum single crystal surfaces. The Journal of Chemical Physics. 1975;62(8): 3149-3161.
10. Wachs IE, Madix RJ. On the H2⁾ D2 exchange on stepped platinum surfaces. Surface Science. 1976;58(2):590-596.
11. Salmeron M, Gale RJ, Somorjai GA. Molecular beam study of the H2–D2 exchange reaction on stepped platinum crystal surfaces: Dependence on reactant angle of incidence. The Journal of Chemical Physics. 1977;67(11):5324-5334.
12. Verheij LK, Hugenschmidt MB. Hydrogen adsorption on oxygen covered Pt (111). Surface Science. 1995;324(2):185-201.
13. Pasteur AT, Dixonwarren SJ, Ge Q, King DA. Dynamics of hydrogen dissociation on Pt (100)-steering, screening and thermal roughening effects. Journal of Chemical Physics. 1997;106(21):8896-8904.
14. Christmann K, Ertl G, Pignet T. Adsorption of hydrogen on a Pt (111) surface. Surface Science. 1976;54(2):365-392.
15. Christmann K, Ertl G. Interaction of hydrogen with Pt (111): The role of atomic steps. Surface Science. 1976;60(2):365-384.
16. Poelsema B, Verheij LK, Comsa G. Does the surface temperature influence the cross section of random isolated adsorbates in thermal He scattering? Surface Science. 1984;148(1):117-125.
17. Verheij LK, Hugenschmidt MB, Anton AB, Poelsema B, Comsa G. A molecular beam study of the interaction between hydrogen and the Pt (111) surface. Surface Science. 1989;210(1-2):1-26.
18. Lang B, Joyner RW, Somorjai GA. Low energy electron diffraction studies of chemisorbed gasses on stepped surfaces of platinum. Surface Science. 1972;30(2): 454-474.

19. Gebhard SC, Koel BE. Influence of potassium on the adsorption of hydrogen on platinum (III). The Journal of Physical Chemistry. 1992;96(17):7056-7063.
20. Cowin JP, Yu CF, Sibener SJ, Wharton L. HD scattering from Pt (111): Rotational excitation probabilities. The Journal of Chemical Physics. 1983;79(7):3537-3549.
21. Luntz AC, Brown JK, Williams MD. Molecular beam studies of H2 and D2 dissociative chemisorption on Pt (111). The Journal of Chemical Physics. 1990; 93(7):5240-5246.
22. Oudenhuijzen MK, van Bokhoven JA, Miller JT, Ramaker DE, Koningsberger DC. Three-site model for hydrogen adsorption on supported platinum particles: Influence of support ionicity and particle size on the hydrogen coverage. Journal of the American Chemical Society. 2005;127(5): 1530-1540.
23. Koningsberger DC, Oudenhuijzen MK, De Graaf J, Van Bokhoven JA, Ramaker DE. *In situ* X-ray absorption spectroscopy as a unique tool for obtaining information on hydrogen binding sites and electronic structure of supported Pt catalysts: Towards an understanding of the compensation relation in alkane hydrogenolysis. Journal of Catalysis. 2003;216(1):178-191.
24. Mukerjee S. Use of hybrid cathodes to reduce platinum content in high-temperature proton exchange membrane fuel cells (HT-PEMFCs). In 229th ECS Meeting (May 29-June 2, 2016). ECS; 2016.
25. Wang D, Xin HL, Hovden R, Wang H, Yu Y, Muller DA, Abruña HD. Structurally ordered intermetallic platinum–cobalt core–shell nanoparticles with enhanced activity and stability as oxygen reduction electrocatalysts. Nature Materials. 2013; 12(1):81-87.
26. Hammer B, Morikawa Y, Nørskov JK. CO chemisorption at metal surfaces and overlayers. Physical Review Letters. 1996;76(12):2141.
27. Bradshaw AM, Hoffmann FM. The chemisorption of carbon monoxide on palladium single crystal surfaces: IR spectroscopic evidence for localized site adsorption. Surface Science. 1978;72(3): 513-535.
28. Chin YHC, Buda C, Neurock M, Iglesia E. Selectivity of chemisorbed oxygen in C–H bond activation and CO oxidation and kinetic consequences for CH 4–O 2 catalysis on Pt and Rh clusters. Journal of Catalysis. 2011;283(1):10-24.
29. Koper MT, Van Santen RA, Wasileski SA, Weaver MJ. Field-dependent chemisorption of carbon monoxide and nitric oxide on platinum-group (111) surfaces Quantum chemical calculations compared with infrared spectroscopy at electrochemical and vacuum-based interfaces. The Journal of Chemical Physics. 2000;113(10):4392-4407.
30. Brown IT, Shannon RD. Empirical bond-strength–bond-length curves for oxides. Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography. 1973;29(3):266-282.
31. Shannon RT. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography. 1976;32(5):751-767.
32. Cioslowski J, Liu G, Castro RAM. Badger's rule revisited. Chemical Physics Letters. 2000;331(5):497-501.
33. Kraka E, Setiawan D, Cremer D. Re-evaluation of the bond length–bond strength rule: The stronger bond is not always the shorter bond. Journal of Computational Chemistry. 2016;37(1): 130-142.
34. Pompeo F, Santori G, Nichio NN. Hydrogen and/or syngas from steam reforming of glycerol. Study of platinum catalysts. International Journal of Hydrogen Energy. 2010;35(17):8912-8920.
35. Oudenhuijzen MK, Bitter JH, Koningsberger DC. The nature of the Pt-H bonding for strongly and weakly bonded hydrogen on platinum. An XAFS spectroscopy study of the Pt-H antibonding shape resonance and Pt-H EXAFS. The Journal of Physical Chemistry B. 2001; 105(20):4616-4622.
36. Willenbockel M, Lüftner D, Stadtmüller B, Koller G, Kumpf C, Soubatch S, Tautz FS. The interplay between interface structure, energy level alignment and chemical bonding strength at organic–metal interfaces. Physical Chemistry Chemical Physics. 2015;17(3):1530-1548.
37. Sánchez-de-Armas R, Ahlquist MS. On the nature of hydrogen bonds to platinum (II)–which interaction can predict their

strength? Physical Chemistry Chemical Physics. 2015;17(2):812-816.

38. Outka DA, Stöhr J, Jark W, Stevens P, Solomon J, Madix RJ. Orientation and bond length of molecular oxygen on Ag (110) and Pt (111): A near-edge x-ray absorption fine structure study. Physical Review B. 1987;35(8):4119.
39. Allian AD, Takanabe K, Fujdala KL, Hao X, Truex TJ, Cai J, Iglesia E. Chemisorption of CO and mechanism of CO oxidation on supported platinum nanoclusters. Journal of the American Chemical Society. 2011; 133(12):4498-4517.
40. Árnadóttir L, Stuve EM, Jónsson H. Adsorption of water monomer and clusters on platinum (111) terrace and related steps and kinks: I. Configurations, energies and hydrogen bonding. Surface Science. 2010;604(21):1978-1986.
41. Madey TE, Yates Jr JT. Electron-stimulated desorption as a tool for studies of chemisorption: A review. Journal of Vacuum Science & Technology. 1971; 8(4):525-555.
42. Reveles JU, Köster AM. Geometry optimization in density functional methods. Journal of Computational Chemistry. 2004;25(9):1109-1116.
43. Sanderson R. Chemical Bonds and Bonds Energy. Elsevier. 2012;21.
44. Marcus D. Hanwell, Donald E. Curtis, David C. Lonie, Tim Vandermeersch, Eva Zurek, Geoffrey R. Hutchison. Avogadro: An advanced semantic chemical editor, visualization, and analysis platform. Journal of Cheminformatics. 2012;4:17.
45. Andrade X, Strubbe DA, De Giovannini U, Larsen AH, Oliveira MJT, Alberdi-Rodriguez J, Varas A, Theophilou I, Helbig N, Verstraete M, Stella L, Nogueira F, Aspuru-Guzik A, Castro A, Marques MAL, Rubio A. Real-space grids and the Octopus code as tools for the development of new simulation approaches for electronic systems, Physical Chemistry Chemical Physics. 2015;17:31371-31396.
46. Štich I, Car R, Parrinello M, Baroni S. Conjugate gradient minimization of the energy functional: A new method for electronic structure calculation. Physical Review B. 1989;39(8):4997.
47. Huheey pp. A-21 to A-34; Cottrell TL. The Strengths of Chemical Bonds. 2nd ed., Butterworths, London, 1958; B. deB.Darwent, "National Standard Reference Data Series," National Bureau of Standards, No. 31, Washington, DC, 1970; S.W. Benson, J. Chem. Educ. 1965;42:502.
48. Huber KP, Herzberg G. Molecular spectra and molecular structure. IV. Constants of Diatomic Molecules, Van Nostrand Reinhold Co.; 1979.
49. Lide DR. Handbook of Chemistry and Physics (84th ed.). CRC Press; 2004.
50. Rogers DW. Concise physical chemistry. Hoboken, NJ: Wiley; 2011.
51. Miswan MA, Gopir G, Anas MM. Exploring structural properties of small carbon clusters Cn (n = 1, 2, 3) using molecular mechanics and energy minimization; 2016. DOI: 10.1063/1.4966792

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