

An Electronegativity Approach to Catalytic Performance

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Abstract

This article posits that there is a correlation between the electronegativity of a catalyst and the position of the same on Sabatier's volcano curve. On the premise that the electronegativity of a material dictates its reaction behaviour, on both side of the scale the least and most electronegative elements would be very reactive. However, the more stable elements, especially transition metals would behave both as electropositive and electronegative elements, hence foster catalytic activities. Furthermore, assuming that the electronegativity of compounds is the summation of the electronegativity of individual elements, then we could successfully analyse the catalytic activity of compounds and their performance on the Sabatier's scale. Based on this hypothesis, it is therefore possible for a wide range of catalysts to be produced from a synergy of transition metals thus forming ceramics, which would no doubt be cheaper and hence possibly solve the Platinum and noble metals catalyst challenges.

Keywords: Catalytic Performance, electronegativity, Sabatier's Principle, Catalysts

Introduction

Catalysts are well known for their speeding up the rate of reaction, lowering the activation energy in the reaction but are not consumed or used up in the process (Oswald, 1910). Ever since its discovery, catalysts have been widely used and about 80 – 90% of all chemical products have undergone at least one catalytic activity (Haider, 2009). Different catalysts exist and have been used extensively; however, the most used catalysts are the metals.

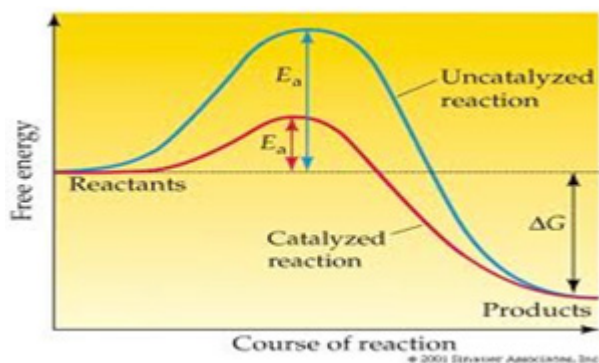


Figure 1. Catalysed and un-catalysed reactions

Generally, transition metals are the best-used catalysts. This of course has to do with their 3-d orbital electrons. In this transition metal group, good catalysts can be seen to be in the range of noble metals. The noble metals are Pt, Ru, Ra, Pd, Os, Ir, Ag, and Au. Platinum is the catalyst used in most present day electrolytic reactions. It offers some advantages over other kinds of catalysts in the noble metal class and also it is the most abundant of all noble metals. It is interesting to note that good catalysts are always noble

metals due to their high stability as they do not get involved in chemical reactions. Although in theory, they associate and dissociate with the reactants and products respectively in a chemical reaction. The maximum in which the rate of dissociation is almost equal to the rate of association is often the ideal catalyst behaviour. This is the Sabatier's principle. The limitation of these elements in supply means that their cost would always be a challenge.

Ceramic catalyst, formed from transition metals and oxides, nitrides, sulphides, and carbides, offers some quite unique advantages over some of the noble metal catalysts. Apart from being relatively cheaper than platinum catalysts due to already established infrastructure for mining these metals and steady source of these gases and metalloids, they also have good pressure drop characteristics, can operate under high temperature, light weight, low coefficient of thermal expansions, and also ability to resist corrosion and contamination especially in fuel cell where the likelihood of CO₂ poisoning degrades platinum catalysts (Gottesfield, 1990). Synergy of ceramic catalysts and noble metals has also been shown to produce good performance. From the oldest and noblest of all the, gold, Au/Fe₂O₃, Au/TiO₂ Bocuzzi (1999) Au/TiO₂, Au/ZrO₂, Au/Al₂O₃ (Grunwaldt, 1999); the most active and abundant of all; platinum ceramic catalyst synergy (Hanada et al, 2011) in which Pt/Al₂O₃ performed better than Pt/ZrO₂, and Pt/TiO₂, and one of the rarest of all, Iridium, its ceramic synergy have also been used in the production of such (Erdöhelyi, 1996). As a matter of fact, a synergy of ceramics and noble metals has been touted to be the solution to present the present challenges faced by catalysts.

Until recently, the approach for designing catalyst

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has been based on randomness, guess work, and heuristics (Callaghan 2006). This write up tries to explore the option of using the electronegativity of elements and also the synergy between ceramic catalyst and noble metals in the search for a well performing catalyst on the Sabatier's volcano plot.

Sabatier's Principle and the Search for a Catalyst:

The activities of catalysts are carried out in simple elementary steps. First reactant molecules have to adsorb on catalysts and then the product molecules would then desorb from catalysts. This process typically takes about 1 second. The principle on which the whole reaction is based on is known as the Sabatier's principle, which states that the rate of catalytic activity is a maximum when the rate of reactant absorption and the rate of desorption of product from the catalyst are equal. Hence, it means that catalytic reaction would depend on the reaction tendency of the material in question.

It can be clearly seen that the noble metals are good catalysts, and going through one of the fundamental requirement for catalysts, electronegativity of the material seems to also have a lead role, since it involves the chemical 'reaction' and 'de-reaction' of the catalyst. It is no surprise therefore to observe the trend in the electronegativity factor of these catalysts. This is because the ease of a chemical reaction depends on the ability of the reactants to donate, receive or share electrons. Thus the ease of absorption and desorption of catalysts from reactant and product molecules can be a direct consequence of this quality. Remarkably, noble metals have a stable electronegativity or a sort of neutrality between the electropositive and the electronegative elements, hence their ability to absorb and desorb as they catalyse the reaction simultaneously is almost equal. It is therefore possible to form ceramic compounds of carbides, sulphides, and oxides with transition metals whose electro negativities are within the range of 2.0-2.2 and expect a high performance catalyst.

Pauling Electronegativity Values of Compounds

Interestingly, using the Pauling electronegativity scale, all the noble metals, which are good catalysts as can be seen by their performance on the Sabatier's volcano scale, have almost the same electronegativity values. Furthermore, the closer other transition metals are to this range the better their performance on the volcano plot. A compound formed by metals with lower electronegativity and other elements, especially gases and metalloids with higher electronegativity in which the 'net' electronegativity is within the range of the noble metal's electronegativity seems to perform very much better on the Sabatier's scale.

If we assume that electro negativities of elements are

physical properties of the elements, then we can say that the electronegativity of compounds in reference to their catalytic activities would be the fractional sum of the electronegativity value of these elements. In this write up, the Pauling Electronegativity value is used as a reference without attaching much significance to the chemical character of these values.

My mathematical relationship (see eq1) may be said to hold for catalytic compounds; where ϑ_T is the electronegativity of the compound, ϑ_i is the electronegativity of individual elements, and, φ_i , is the quantity of the corresponding element in the compound.

$$\vartheta_T = \frac{\sum_i^n \vartheta_i \times \varphi_i}{\sum_i^n \varphi_i} \quad (\text{eq1})$$

And the closer the value of $\vartheta_T \approx 2.2$, the better the catalytic activity. WC would have a 'net' electronegativity of

$$\frac{1 \times \vartheta_W + 1 \times \vartheta_C}{1 + 1} = \frac{1 \times 1.7 + 1 \times 2.5}{1 + 1} = \frac{4.2}{2} = 2.1$$

The catalyst compound would no doubt produce better catalytic activity and would ascend higher in the volcano curve in comparison to others with lower 'net' electronegativity like W2C.

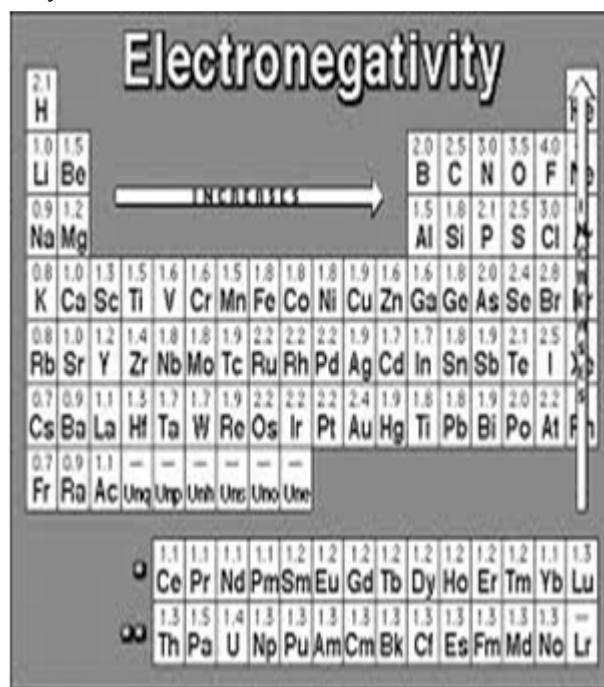


Figure 2: Pauling electronegativity scale of elements.

Volcano Plot and Sabatier's Principle

A volcano plot typically relates a kinetic parameter and a thermodynamic one. Most volcano plots are made by plotting the activation energy, or current density, which

are kinetic parameters against bond energy, or the Gibbs free energy. The maximum of the volcano plot is the point at which the rate of adsorption of reactants on catalyst just about balances the rate of desorption of the same. Of course, other factors like particle sizes, synergy pattern, etc. affect the performance of catalysts; this article intends to draw a connection between the electronegativity character and the performance of some catalyst.

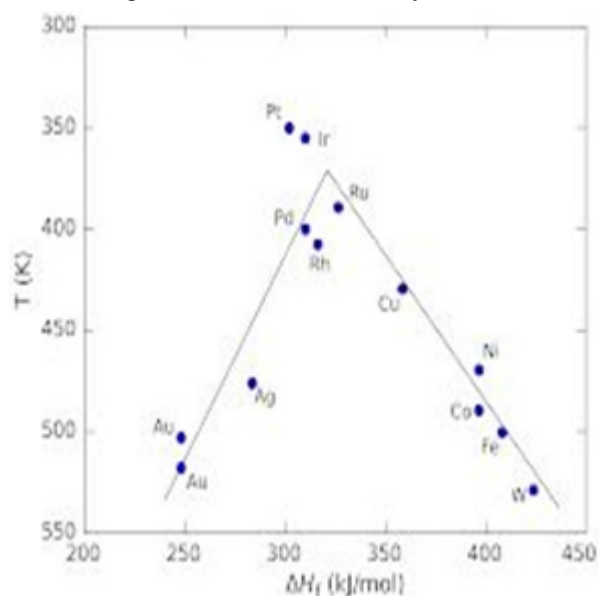


Figure 3. Noble metals and their performance on the Sabatier's scale

Observation and Postulation

From this observation, it is clear that good catalysts come from the transition elements of the periodic table, and if we look at their Pauling electronegativity, they are all close to 2.2 for the noble metals. It is therefore safe to posit that the electronegativity of elements from the transition table make them as suitable choice for being good electro-catalysts since this deals with their ability to absorb and desorb from reactants and products. Numerous studies have been done on the crystal structure of catalyst that enables easy absorption and desorption, this write up intends to introduce the view one can take to achieve good catalyst by observing their electronegativity.

A study at the transition metals show that within the region of 1.8-2.3, metals with this Pauling electronegativity exhibit an ascending performance on the Sabatier's scale. Hence, we may not be surprised to see that copper can also be adequately used as catalyst. In addition, Nickel can also be used. Iron and chromium also could be used due to their electronegativity being within the range. However, their electro negativities are not near the pinnacle of the plot which is been occupied by noble metals. The better their electro negativities (that is closer to 2.2) the more promise of a better catalytic activities. Moreover, as can be seen from Fig 2, the closer their electronegativity values are to 2.2 the better their performance on the volcano plot.

Although the noble metals have electronegativity values close to 2.2, and this can be said to be the ideal electronegativity to be able to present itself as a good catalyst, they are however not readily available. Hence, it is possible to produce affordable catalysts by taking the electro negativities of those catalysts/transition metals, which have already established mining infrastructures and some oxides, carbides, and nitrides into consideration. Other factors may have been what all these noble metals have in common and hence we can play with those variables but as can be seen from Fig 2 and Fig 3 electronegativity remains a telling property and maybe the reason for their good catalytic activity is their electronegativity.

As can be seen from these ceramic carbides in Fig 4, the closer the compound has a value closer to the 2.2 electronegativity performance the higher its rating on the volcano curve. Tungsten carbide had an 'effective' electronegativity of 2.1 and showed better performance, while Mo₂C (2.033) outperformed W₂C (1.967) most likely due to their electronegativity values which decreased also.

In some reports, like Hanedai (2011) Al₂O₃ (2.7) outperformed TiO₂ (2.833) and ZrO₂ (2.8) most likely because the electronegativity of Al₂O₃ was much closer to 2.2 than the other was and hence out performed them.

A second factor also responsible for effective performance of ceramic catalysts is based on forming a mixture of these stable electronegative compounds with a noble metal. WC had a near platinum behavior on the volcano plot by incorporating it with a layer of platinum. Using Atomic layer deposition methods, a few cycles of ceramic catalysts deposited over host noble metals had shown from literature to be able to have efficiency close to that of platinum or other noble metals.

The result presented in the figure 4 show the different performance of compounds with electro negativities close to 2.2 and how the synergy with Platinum always produced the better catalytic performance over other noble metal neighbors, then palladium, and then gold.

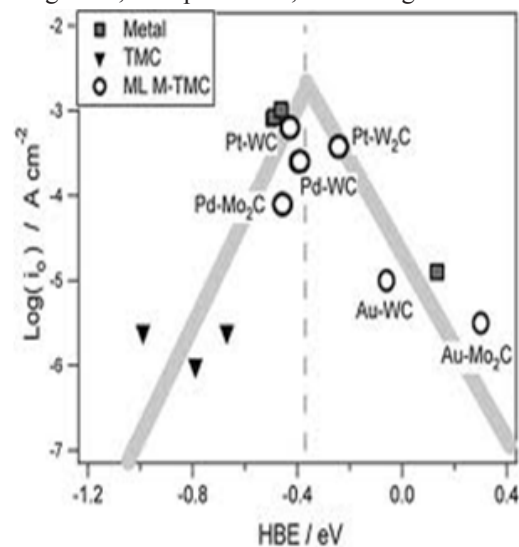


Figure 4: Performance of carbide catalysts and noble metal synergy on the Sabatier's scale.

Conclusion

The electronegativity of transition metals could be a very strong reason for their catalytic nature due to their ability to play neutral in reactions; that is ability to both adsorb and desorb from molecules. Based on this property, it is therefore possible to posit that the closer the electronegativity value of the transition metal is to that of the noble metal group of the transition metal, the better the chance of a performing catalyst. Hence, chemical compounds whose electronegativity is assumed to be the sum of the electro negativities of each element in the compound, would 'see' a near noble metal performance of these compounds.

In addition, for the same electronegativity value of a transition metal and a compound, the transition metal would be a better catalyst than the compound. A synergy of the noble metal and the ceramic increases its performance value. Hence, even after fulfilling the electronegativity condition a kind of syncretism with a noble metal like platinum and palladium would very much increase the catalytic activity as opposed to gold. Two bases to this postulation can therefore be read: First, the closer the electronegativity value of the ceramic catalyst the better its performance on the Sabatier scale. Secondly, for the same compound, the effective performance would depend on the performance of the partner noble metal.

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