The Sabatier principle illustrated by catalytic H_2O_2 decomposition on metal surfaces

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Abstract

Heterogeneous catalysis is evermore important in today's industry. Hence, it is important to introduce students to this field and its tools. Here a new way of introducing one of these tools - the Sabatier principle - via a lab-exercise is presented. A volcano plot is constructed for the well-known heterogeneous H_2O_2 catalytic decomposition reaction on various metal foils. The volcano plots the activity per catalyst surface area versus the computationally calculated binding energy of OH groups on the catalysts. The OH group is identified as the only surface intermediate in an intuitive reaction mechanism and hence it is the relevant reactivity parameter. From the calculated binding energies and the reaction mechanism the volcano peak position is inferred. This work is most relevant to introductory levels of chemistry both in advanced high school classes, and initial levels of university.

Heterogeneous catalysis has gained ever more attention and importance. As students venture into the field of chemistry it is highly important to introduce them to the possibilities and principles of heterogeneous catalysis as early as possible to motivate them to pursue this field.

This work presents a possible approach to do so at an introductory level. It is the purpose to introduce students to the advantages of combining a theoretical model with experiments in order to get an improved understanding of the differences in catalytic activity of relevant materials via the Sabatier principle. Furthermore, this approach gives the students hands-on lab experience in a simple and fun experiment; which can be interpreted qualitatively by use of the periodic table and quantitatively by computational simulations.

Catalysis is usually divided into heterogeneous and homogeneous catalysis. For both cases it applies, per definition, that the catalyst must not be consumed during the reaction. In the following we focus only on heterogeneous catalysis. The active part of an industrial heterogeneous catalyst is most commonly a solid surface of a metal or a metal oxide. The surface offers a low barrier energy path from reactants to products by binding reactants and reaction intermediates and also avoids the problem of the unlikely three-body interactions in the gas phase. The best catalytic surfaces for a given reaction will have a reactivity that is a compromise of the binding energy. On one hand the binding energy of the reactants to the surface must be strong enough, so that they can react into the reaction intermediates. However, on the other hand the binding must not be too strong preventing the products leaving the surface; and make room for more reactions to take place. This is in essence the Sabatier principle (1). The optimal catalyst surface will be a trade-off between binding the reagents to the surface and not binding any of the reaction intermediates stronger than the desorbed product. The principle explains why a so-called volcano curve is most often obtained when plotting catalytic activity vs. surface reactivity. It is important to note the distinction between activity and reactivity. The activity is a measure for how fast the catalytic reaction occurs on the surface and must therefore always be measured per surface area (also called the specific rate). If not the activity of a foil and a powder catalyst would differ for the same material, which they clearly should not. The reactivity on the contrary is a measure of the inherent reactivity of the surface towards adsorbing molecules. The reactivity can be quantified by the binding energy between the surface and a reaction intermediate that is central to the catalytic reaction. The obtained volcano curves can be very helpful in the design of optimized catalysts. If similar materials are compared the qualitative relative surface reactivity can be obtained from the periodic table of the elements. Pure transition metals are for instance often used as catalysts and for these the reactivity decreases when going from the left to the right in the periods. However, if different surfaces are taken into account, *e.g.*, both metals and metal oxides, computational chemistry is of paramount importance as it offers a fast way of calculating the binding energy of conceivable reaction intermediates, relevant to the reaction, on a variety of surfaces.

In the following we will use these principles to get a volcano curve for the familiar classroom experiment of catalytic hydrogen peroxide decomposition reaction using *e.g.* MnO_2 and potato or liver enzymes (2) via equation (1).

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g), \qquad (1)$$
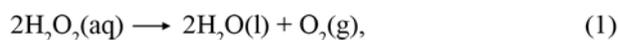
A classroom exercise in finding the reaction kinetics of this reaction has previously been reported in this journal (3) and could very well be combined with the one described here. In order to apply theoretical calculations to this reaction we have to devise a likely reaction path, but more on this later.

Theoretical and experimental work

This section will describe the basis for the theoretical binding energy calculations as well as the experimental procedure for measuring the activity of H_2O_2 decomposition for different surfaces.

Theoretical calculations

Computer simulations offer a way to calculate binding energies of molecules on surfaces. The ground state energy and electronic structure, for a given surface or molecule, can be obtained using Density Functional Theory (DFT) (see further in (1,4)). It is a quantum mechanical method, where the interactions between electrons and nuclei are accurately accounted for. The input is just the atomic structure of the system, meaning the atomic numbers and the position of the atoms in space. The output is the ground state energy. Binding energies can be calculated by comparing energies *e.g.* of a system containing a molecule bound to a surface with the energy of the same system where the molecule is separated from the surface. The binding energies of OH, (a relevant reaction intermediate in H_2O_2 decomposition) on different surfaces, obtained by DFT calculations, are given in table 1. The obtained free energies are converted to conditions at 298 K, by taking entropy into account, and the reference point of liquid water, and oxygen gas, and the bare catalyst surface at standard conditions - as described in the literature (5).

Here, we have supplied a description of the computational method, this level of introduction may be omitted if the students are at an introductory level. This is especially true for high school students who may gain just as much from the exercise if the calculations are viewed as mere tabulated values.

Catalyst	Binding energy kJ/mol	Measured activity mol O_2 /(m^2 s)
Ni	-42.45	0.00457
Cu	-7.72	0.00271
Pt	36.66	0.0319
Ag	63.68	0.0123
Au	162.09	0.0104
TiO_2	324.52	0.00191

Table 1: Binding energies of OH groups on relevant metals and metal oxides as obtained form DFT calculations.
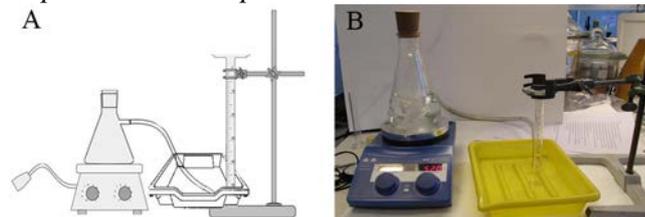
Experimental setup

Figure 1: (A) Schematic illustration of the experimental setup, and (B) photograph of experimental setup. To the left the reaction flask on the stirrer is shown with the solution containing KOH, H_2O_2, a magnetic stir bar, and the catalyst. The flask is fitted with a tight fitting rubber stopper and a hose. The hose leads the gasses to the upturned volumetric measuring cylinder. The cylinder is filled with water and placed upside down in the water tray without allowing air to enter. When the H_2O_2 is added, and the flask corked, and the volume of oxygen gas read off as a function of time.

To measure the catalytic activity of some of the surfaces where the binding energy of OH was calculated, representative foils of metals are chosen. Here, we test a titanium metal foil (Sigma-Aldrich) with a spontaneously formed surface oxide layer, gold (Goodfellow), platinum

(Goodfellow), nickel (Goodfellow) and copper (Goodfellow) foils and a silver wire (Sigma-Aldrich). All foils where of >99% purity, and cut into pieces around 1x2 cm (1 mm diameter silver wire of 5 cm length was used) the exact geometry does not effect the experiment. Here, one piece of each was used, except for platinum where two small pieces making 0.7 cm^2 were used. Expenses to materials may be cut by only testing nickel and titanium foils and for instance a piece of gold or silver jewelry (as regular as possible to ease the surface area estimation). NB the silver jewelry should not be left in the solution for extended periods of time as the surface may slowly dissolve. As mentioned later on, powders of the material can also be used, but it requires that the specific surface area of the powder is known. Preparation time for this experiment is 30-45 min and each experiment takes 20-30 min. Data processing amounts to around 10-20 min per sample. We emphasize that students need not measure the leveling off observed in the insert of figure 2.

A reaction solution of 250 mL 0.1 M KOH and the foil to be tested were placed in a suction flask fitted with a rubber stopper, a magnetic stir bar, and a hose going to an upturned 10 mL measuring cylinder (see figure 1), filled with water, in a water bath. The cylinder is filled completely to the brim with water and a hand is placed over it to seal it, and then it is turned upside down. The hand is gently removed once the opening of the cylinder is completely immersed in the water bath. Should a few bubbles make their way into the cylinder this does not effect the measurements. When the experiment is initiated 10 mL 30 % H_2O_2, is added and the rubber stopper is fitted simultaneously. The timer is started just as the bubbles fill the cylinder to the first volume mark; this is done to eliminate the effect of possible bubbles already present in the cylinder. It is only the volume of evolved oxygen that is measured since water from the reaction condensate when bubbling through the water bath.

To get the catalytic activity the evolved oxygen in mole per area of foil is plotted as a function of time to give curves like figure 2 (see appended spreadsheet for an example of the calculations). As we have defined earlier the true activity is the evolved oxygen per surface area per time, which is equal to the initial slope of the curve (see figure 2). Here, we implicitly assume that the roughness of the foils and wire are the same for all the metals; meaning that the geometric/macroscopic area represent the true surface area. This is commented upon later. The volcano may now be plotted as this activity on a logarithmic scale versus the OH binding energy (reactivity of the surface) see figure 5.
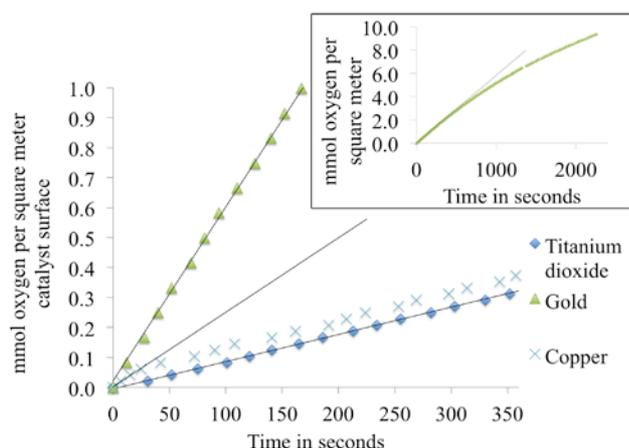

Figure 2: Amount of substance of oxygen evolved per area of metal foil as a function of time exemplified by titanium, copper, and gold. The initial slope of the reaction is the activity used to compare the catalysts. The curve is nearly linear at first and then drops off a bit as the H_2O_2 is used up (see insert). This is the reason that the activity is only measured initially where there is plenty of H_2O_2 so that the only limit to reaction is the properties of the surfaces. The reduced rate for copper after approximately 30 seconds is not due to lack of reagent but most likely the formation of an ill-defined surface oxide. This oxide, though not easily modeled to obtain OH binding energies, is

expected to have a higher binding energy. This is common for all metals when oxidized. Limiting the amount of gas, which is collected to the first linear part of the reaction, removes the need to identify the linear part and makes the data treatment easier.

Hazards

The H_2O_2 solution is an oxidizer and should be handled with care. KOH is a base and should also be handled with care. Standard laboratory practice such as the use of gloves and goggles is necessary.

Results and interpretation

$$H_2O_2(aq) + 2* \longrightarrow 2OH* \qquad \text{(E) to (A)}$$
$$2OH* + H_2O_2(aq) \longrightarrow 2H_2O* + O_2(g) \qquad \text{(B) to (D)}$$
$$2H_2O* \longrightarrow 2H_2O(l) + 2* \qquad \text{(D) to (E)}$$
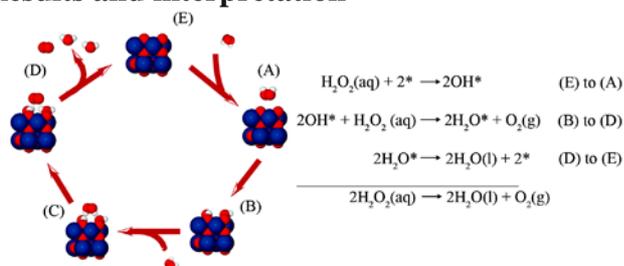$$\overline{2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)}$$

Figure 3: Schematic interpretation of the reaction model proposed in this work for the H_2O_2 decomposition. The catalytic cycle is exemplified by the reaction on a TiO_2 surface. Ti is in blue, O in red and H in white. The model shows that a H_2O_2 molecule is adsorbed onto a clean surface (A) and split in two OH groups bound to the surface (B). Subsequently another H_2O_2 molecule comes in and donates two H atoms to the OH on the surface (C). This results in two water molecules on the surface and an oxygen molecule (D). These all desorb to leave the clean surface for a new reaction (E).

A reaction mechanism is needed to find a relevant binding energy to calculate. Here we suggest a simple intuitive reaction mechanism shown in figure 3 (and the animated movie in the supplementary information). We assume that H_2O_2 adsorb on the catalytic surface to make two OH groups, which next react with one more H_2O_2; transferring two H atoms from the second reactant to the two adsorbed OH species leaving O_2 and two water molecules on the surface. They subsequently desorb and diffuse into the surrounding solvent and the surface is ready for another reaction. This is called a catalytic cycle. The calculated binding energies of the OH group on various surfaces tabulated earlier may then be used together with the measured activity to plot the volcano in figure 5. We use the activity in the form of moles of oxygen evolved per second per square meter of catalyst; this allows for the direct comparison of powders and foils. It is advised that this point is made to the students and a discussion on how to optimize surface area is taken. As illustrated in the appended spreadsheet carefully done experiments on silver wires and powders agree within the first two decimals. It is strongly encouraged that, if specific surface areas of silver powders are obtainable from the manufacturer or by using a nitrogen adsorption instrument (BET analysis), the students be allowed to try with both silver samples. Note, that a measuring cylinder of 250 mL is necessary for only 30 mg silver powder as the rate is so fast. The powder we used from Sigma-Aldrich (cat-nr 327085) was measured by BET to have a surface area of 0.61 m^2/g. This offers a memorable opportunity to visualize the effect of increased surface area.

A crucial point must be made before contemplating the volcano plot in detail. If the free energy of each of the above given steps of the reaction pathway is plotted a three step curve is obtained. If the energy of the reaction is considered figuratively as a ball rolling down from the high initial energy to the low product energy state; then it follows that the ball will only roll downhill. In figure 4 this will prevent the ball from rolling up the TiO_2 path and also down the copper path because it would then have to pass an uphill stretch. In terms of the Sabatier principle this is interpreted, as the binding of the intermediate OH being too weak on the TiO_2 and too strong on the copper. One may

then state that the energy of OH on the surface must lie in between the energy of the bare surface plus two free H_2O_2 molecules and the bare surface plus a free oxygen and two free water molecules. In figure 5 these limits are illustrated as shaded regions at which the energy of the bound OH groups become unfavorable. It is worth noting that faded boundaries imply that we cannot view this as a rigid rule for activity; but more as a constraint for the optimal catalysts.
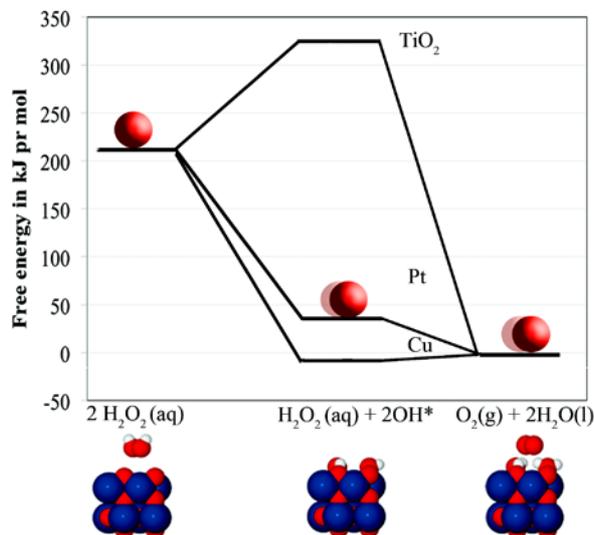

Figure 4: Energy diagram with balls rolling. For TiO_2 the surface binds OH too weakly and nothing happens as the ball cannot roll uphill. In the case of platinum the OH energy is just right and the ball rolls spontaneously to the product energy level. For copper the OH binding energy is too strong and the OH sticks to the surface, which is symbolized by the ball getting trapped in the valley. These three cases illustrate the window of opportunity, as any surface with an OH binding energy within the initial and final energy will catalyze the reaction. Underneath each step of the energy diagram the situation on the surface is illustrated with the TiO_2 surface.

From the volcano plot in figure 5 one can see that the relative activities predicted by our model corresponds well with the observed activities. That is, the metals that bind OH too strongly are poor catalysts and thus lie on the left side of the volcano. These metals are inherently unstable in an oxidizing environment; indeed these metals will form oxides after prolonged reaction and indeed very fast in the case of copper. Hence, OH adsorbs and reacts irreversibly with the metals; this will alter the metallic surface during the reaction. This leads to another crucial point: If the surface changes significantly so will the binding energy and false conclusions may be drawn. At the same time one notices that the right side of the volcano, that is the weak hydroxide binding surfaces, are stable surfaces. It is advised that the students are encouraged to see the parallel to everyday life. A suitable question relates to the behavior of gold jewelry in contrast to for instance a copper pot. Noting that the frequency of these items needing polishing, is inversely related to their stability should provide food for thought. At the top of the volcano, *i.e.* within the window of opportunity, platinum, silver and gold are located. These are by far the best catalysts for the decomposition reaction; remembering the classic classroom experiments (2) manganese dioxide, with a binding energy of 106.1 kJ/mol also falls in the window of opportunity.
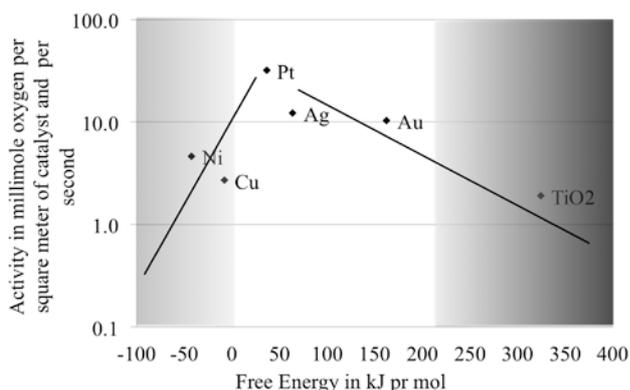
Figure 5: Volcano curve of reactivity, in millimole oxygen evolved per second and square meter catalyst surface area (on a logarithmic scale), as a function of OH binding energy. From this it is seen that the reactivity of Cu, and TiO_2 are low as predicted by the model. This effect is due to the too strong and too weak OH binding to Cu and TiO_2, respectively. It is furthermore seen that the surfaces that fall inside the window of opportunity are far more active than the ones that do not. The window of opportunity is found and explained in figure 4.

So far we have indicated that the model seems to correlate quite well with the actual reaction pathway; this is not sufficient proof that the reaction happens as our models states. However, it is hard to imagine any reaction mechanism where the reaction intermediates does not bind to the surface via oxygen like OH which means that the OH binding energy is always a good measure of the surface reactivity. An important aspect of the volcano curve is that it is a good tool to screen for other possible catalysts.

Typical data as obtained by students are shown in figure 6A; the data are plotted as obtained in the appended spreadsheet, *i.e.* not corrected for differences in surface area. Students were instructed to obtain measurements up to a given volume, previously determined by the instructor for the applied amount of catalyst, so that only the linear part is obtained. In the performed exercise student data fell around 40 % away from the data presented in figure 5; this must be attributed to a non-identified constant error such as faulty equipment (a hose was found to be slightly leak), or possibly chemical preparation (concentration of KOH stock solution). This is suspected, as the student volcano curve seen in figure 6B is a vertical displacement of the one in figure 5. Copper is seen to fall with a large scatter (up to 90 % of the data presented here) in the student exercise so it might be advantageous to omit this for consistency purposes. These issues with reproducing the data demonstrate the strength of the exercise. Even an unfortunate error does not affect the idea of these experiments as it does not affect the trend in the Sabatier plot.
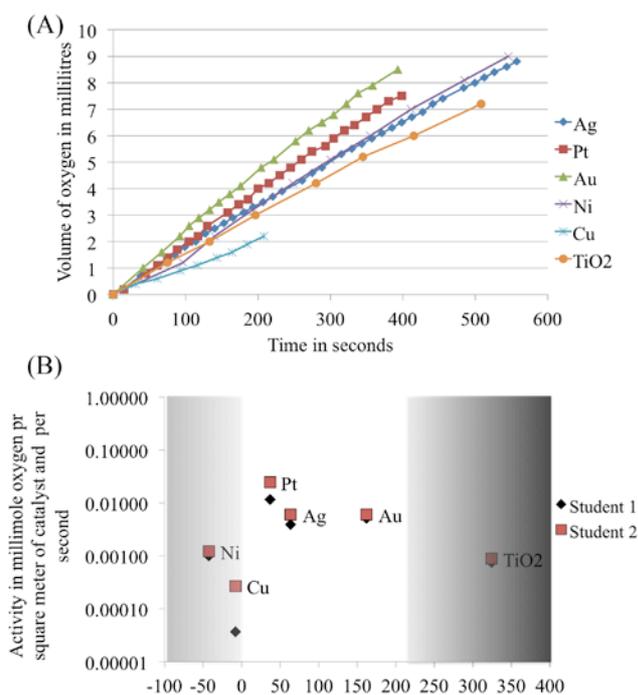
Figure 6: (A) Typical data collected by students as volume of oxygen versus time; note that the volume of gas is not normalized to surface area as this is the data as obtained by the students. (B) The Sabatier plot as obtained from two different students, the excellent agreement for most point is clearly seen. Copper deviates probably due to the formation of a surface oxide.

Conclusion

This lab experiment is instructive because (i) the students get hands-on laboratory experience. (ii) The concept of surface area becomes nicely illustrated when using metal foils. (iii) The process shows how powerful a tool DFT-calculations may be for predicting reactivity for a given reaction. (iv) It shows that a model solely guided by chemical common sense may predict reactivity. (v) Procedures such as the one demonstrated here are used widely in academia as well as in the industry to predict why catalysts deactivate or to find new catalyst candidates (6). (vi) High-school students are capable of performing the experiments and the level of introduction of the calculated quantities may be varied to fit the student's level. Furthermore, more experienced students may be introduced in greater extent to the calculations to give them better challenges. Here we have chosen an intermediate level.

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