

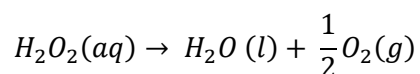
IB Chemistry Internal Assessment

Research Question: How do different catalysts affect the rate of hydrogen peroxide oxidation, according to their reducing potentials?

1. Introduction

Redox reactions are huge contributors to industrial processes nowadays, and their kinetics have always interested me in a particular way. A redox reaction involves the processes of reduction and oxidation, which have three main ways of defining them, in terms of electron transfer, oxygen and hydrogen addition, and oxidation states. For the purpose of this investigation, reduction will be described as the process in which the oxidation state decreases and oxidation as the process of increasing the oxidation state. In a redox reaction, the species that is being reduced is called the oxidizing agent, while the species undergoing oxidation is called the reducing agent. However, some substances have both the capacity to oxidize and reduce themselves (Ed Vitz, 2020). A common example is hydrogen peroxide.

The decomposition of hydrogen peroxide is widely used in the industry.



As it is a great oxidizing agent (Sergey Bylikin, 2014), in acidic or medium alkaline conditions, it has multiple applications. These include the bleaching of mechanical pulps with metal catalysts (Brown, 1993), in cosmetics as a bleaching hair product, and in medicine, as it increases the whiteness of teeth (Top ten industrial applications of Hydrogen Peroxide, 2017). However, H_2O_2 also acts as a reducing agent when reacted with powerful oxidizing agents. Transition metals are known for being good catalysts and oxidizing agents, due to their multiple oxidation states. When combined with hydrogen peroxide, some of these compounds can act as oxidizers, reducing themselves.

This paper aims to compare four powerful oxidizing agents and their effectiveness on oxidizing hydrogen peroxide. By comparing the time of each reaction, they can be ranked based on their oxidizing abilities. Two of the most common catalysts in organic chemistry are potassium dichromate ($K_2Cr_2O_7$) and potassium permanganate ($KMnO_4$) and therefore they are powerful oxidizing agents chosen for this experiment. Recent literature (Annamaria Russo Sorge, 2012) points to manganese-based catalysts as the most promising alternative to metallic catalysts in the decomposition of H_2O_2 . Therefore manganese (IV) oxide (MnO_2) has been largely investigated as a good catalyst for this specific reaction. The last catalyst is

iron (III) chloride ($FeCl_3$), as the mechanisms of the Fenton-like reagent ($Fe(III)/H_2O_2$) have been the subject of numerous studies (Joseph de laet, 2006) and the catalyst is widely used for this decomposition. Except for manganese dioxide, which was used as a solid, they were dissolved into equimolar solutions, aiming for more uniform reactions.

For further analysis of the oxidizing agents, their reduction potentials were also taken into account to formulate a hypothesis. Reduction potentials or standard electrode potentials are a way of measuring how easily a substance loses electrons. In the chemistry IB Data Booklet (Chemistry Data Booklet, 2016 4th edition) there is a table of standard electrode potentials from Lithium to Fluorine. The more negative the E^o value, the better reducing agent the chemical species is (Clark, 2013). According to this table, at 298K and in ascending order of reducing potentials, the compounds can be organized as MnO_2 , $FeCl_3$, $K_2Cr_2O_7$, $KMnO_4$. Therefore, a hypothesis states that the strength of the oxidizing agents on the reaction with hydrogen peroxide should follow the same order, potassium permanganate being the fastest to reduce H_2O_2 , followed by potassium dichromate, then iron (III) chloride, and finally manganese dioxide. This investigation will compare the data obtained on the experiment with the Data Booklet values of reduction potentials and comment on any discrepancy.

Terminology

For the purpose of better understanding, oxidizing agents will be defined as ‘a reactant that removes electrons from other reactants during a redox reaction’ (Helmesntine, 2020). By this definition, the four substances are effectively acting as oxidizers in the reaction, being an active part of the reaction. However, as shown by multiple sources (Anthony Plauck, 2016) it is common to refer to the oxidizing agents that take part in the decomposition of hydrogen peroxide as catalysts. The definition of a catalyst is a substance that is not consumed by the chemical reaction and increases the rate of reaction by providing an alternative pathway (Helmenstine, 2020). However, researchers still refer to the ‘catalytic decomposition of H_2O_2 ’ as they increase the rate of the reaction but take part in the redox reaction, reducing themselves.

2. Investigation

2.1 Variables

Independent variable	Dependent variable	Controlled variables
Oxidizing agents	The time of the reaction	The concentration of the oxidizing agents and H_2O_2 ; the room temperature; the scale used

The independent variable is the choice of oxidizing agent because, to find the most effective at increasing the rate of reaction, all four compounds must be used. To increase the reliability of the results each oxidizing agent was given 5 trials, all measured at the same standard conditions.

The dependent variable is the time of reaction which was measured based on the bubbling observed. For this investigation, the reaction was given as over after 5 minutes, even though they might not have reached completion yet and may have entered an equilibrium state. The fizzling marked the end of the reaction, so when it remained constant, the reaction was given as completed.

The controlled variables were the concentration of hydrogen peroxide, which remained the same for all trials, and the concentration of the liquid catalysts. Room temperature was kept constant throughout the experiment. As the whole experiment was made in one day, there were no sudden temperature variations due to weather change. The third controlled variable was the scale, the same for every measurement, avoiding discrepancies.

3. Methodology

3.1 Apparatus

1. Four 500mL volumetric flasks with respective lids
2. 125mL Erlenmeyer flask
3. 250mL beaker
4. Five 50mL beakers
5. 100mL beaker
6. 20mL graduated glass pipette
7. Plastic pipette
8. A large tray to catch any spills
9. A metal spatula
10. A glass stirring rod
11. Scale of 3 significant figures
12. Cellphone timer

3.2 Photograph of set-up



Figure 1 and 2: Two photographs were taken by my iPhone: the photo on the left shows the solution of hydrogen peroxide on the 500cm³ volumetric flask; the photo on the right shows the solution of the three liquid catalysts in 500cm³ volumetric flasks.

4. Risk Assessment

Safety Considerations: Due to the current pandemic of the Covid-19 virus, some extra safety precautions had to be considered. The laboratory had a limited capacity of 3 students and a teacher at a time, to follow social distancing guidelines. Masks were mandatory inside the school and no eating or drinking was allowed, to avoid the spread of the virus.

H_2O_2 is a powerful bleaching agent and causes skin irritation, eye damage and may be harmful when swallowed. Therefore, to ensure safety while performing the experiment, latex gloves and masks were used during the investigation. All catalysts are powerful oxidizing agents, so they are dangerous for human contact. Potassium permanganate can severely irritate and burn the skin and eyes when in contact with them. Potassium dichromate and iron (III) chloride can cause skin irritation, eye burns and it is corrosive. Potassium dichromate is especially toxic for the lungs, as it is carcinogenic and must be dealt with carefully. Breathing iron (III) chloride can irritate the nose, throat, and lungs causing difficulty in breathing (Program, 1986). Manganese (IV) dioxide is a strong oxidizer and contact with other material may cause a fire. It is also harmful if inhaled or swallowed (Fisher, 1998).

Ethical Considerations: There were no ethical considerations to be taken into account.

Environmental Considerations: After every trial, all substances were separated for proper further disposal by an external waste management company. This was done to prevent any intoxication by the substances.

5. Experimental Procedure

The hydrogen peroxide concentration of the flask used was 30%. After some research, it was observed that similar experiments were made using higher concentrations (CLEAPSS, 2019), however, the concentration of hydrogen peroxide in this experiment was decreased to 10% aiming for slower and less vigorous reactions, allowing for greater ease of execution of the experiment and its measurements. Since the flask with H_2O_2 had a concentration of 30%, it needed dilution. Therefore, as stated below, this was the step-by-step for the experiment:

1. Using the dilution formula, find the volume of H_2O_2 needed for the whole experiment.
2. Prepare a 10% concentration solution of H_2O_2 . Using a 10mL graduated glass pipette, add 142.8 mL of 30% hydrogen peroxide into a 500mL volumetric flask. Add water to the same flask until the 500mL mark. This will be the amount of H_2O_2 used for the whole experiment.
3. With a spatula, measure 0.5g of MnO_2 and put in a 50mL beaker on top of the scale.
4. With a spatula, add 11.38g of $KMnO_4$ and $FeCl_3$ to two different 50mL beaker on top of the scale. For $K_2Cr_2O_7$, the amount must be doubled, so 21.18g was measured on the scale.
5. Add a small amount of water to the 50mL beakers containing the catalysts' powder. Stir it with a glass stirring rod.
6. To prepare the solution of 0.287 mol L^{-1} pour the oxidizing agents' solution into a 500mL volumetric flask. Add water until the 500mL mark. Close the flask with a proper lid. Repeat this for the three liquid compounds.
7. For the reaction, using a volumetric 10mL glass pipette, add 20mL of H_2O_2 into a 50mL beaker, and set it aside.
8. With a different volumetric glass pipette, add 20mL of the oxidizing agent into a 50mL beaker.
9. Place a large tray on the table and pour the hydrogen peroxide into a 125 cm^3 Erlenmeyer flask inside the tray. Add the catalyst to the flask where the reaction will occur. In the case of manganese dioxide, add the powder to the Erlenmeyer flask.
10. Immediately start the timer and accompany the reaction observing the bubbles. When the bubbling is very reduced or constant, stop the timer.
11. Discard the finished reaction in a barrel for chemical residues. Repeat this process for every oxidizing agent 5 times to reduce the impact of random error and allow for the collection of more data.

6. Raw Data

Trials	MnO_2	$K_2Cr_2O_7$	$KMnO_4$	$FeCl_3$
1 st (s)	300	95	26	105
2 nd (s)	341	104	28	113
3 rd (s)	344	91	18	115
4 th (s)	314	103	25	116
5 th (s)	249	87	24	123
Average time	309.6	96	24.2	114.4

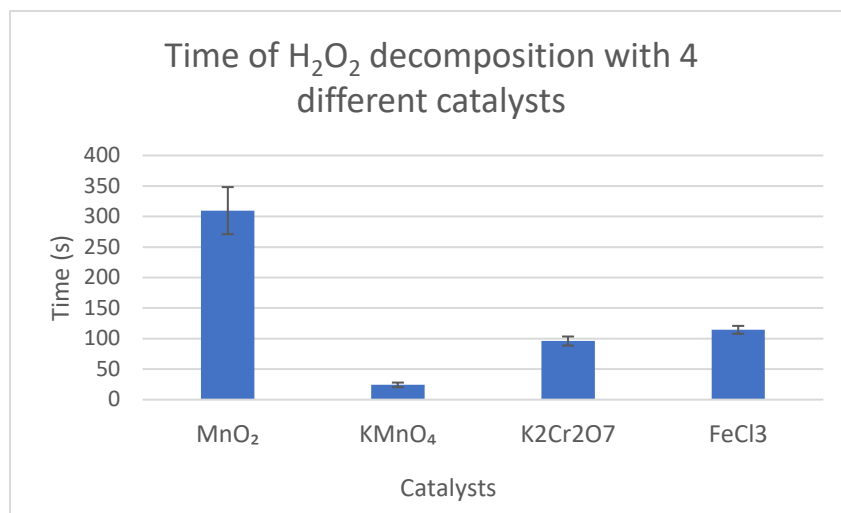
Table 1: a raw data table showing the time in seconds until each reaction came to completion

Qualitative observations:

1. Effervescence could be observed on the reaction involving MnO_2 . The color of the solution remained black as the solid oxide.
2. The reaction of potassium dichromate turns into a brownish color when added to hydrogen peroxide and it forms a brown foam on top. After about 15 seconds, the reaction turns into a red color. It takes about 10 seconds from the start of the reaction to start fizzling and creating bubbles.
3. The reaction including potassium permanganate turns brown/black almost instantaneously. It is a quick reaction, and it releases a lot of $O_2(g)$ at once.
4. The color of the iron (III) chloride reaction turns from pale yellow to a brownish color. Additionally, an evolution of gas can be observed. After approximately 30 seconds it returns to its original color when the effervescence stops.

7. Processed Data

From the data table of the experimental procedure, Graph 1 was plotted:

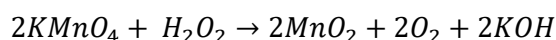


Graph 1: A graph made in Excel from the average time (s) against and the catalysts

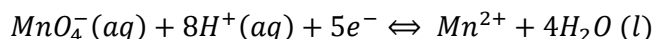
8. Results and Discussion

When the oxidizers are gathered and compared closely, MnO_2 can be noticed as the slowest to decompose hydrogen peroxide. Potassium dichromate and iron (III) chloride are in the same range of the 90s to 120s while $KMnO_4$ has shown to be the fastest oxidizer of them all. Keeping in mind all reagents concentrations were the same so they had the same amount of mols, the comparison between them is on a molar perspective.

Potassium permanganate ($KMnO_4$) is a strong oxidizing agent and it has shown to be the most effective for this reaction. It reacts with hydrogen peroxide according to the reaction below:



The half-equation for the reduction of the permanganate ion is expressed below



The oxidation state of the manganese atom on the chemical species $KMnO_4$ changes from +7 to +4, undergoing reduction. At the same time, the oxygen atoms in hydrogen peroxide oxidate to a higher oxidation state, from -1 to 0. Potassium permanganate contains manganese ions on its highest oxidation state (+7) which increases the electronegativity of the elements (Rahman, 2013) and makes it a good oxidizing agent. As the oxidation state of the manganese atom increases, so does the strength of the oxidant (Bodner Research Web, s.d.).

The reducing potential for the permanganate ion is stated on the Data Booklet as +1.51V. It is very positive, the second most powerful oxidant on the table, after fluorine. This means that the ion has a high tendency

to gain electrons from a new species, in this case, H_2O_2 . Therefore, it increases substantially the rate of reaction, being able to oxidize hydrogen peroxide in a small interval of time.

Potassium dichromate ($K_2Cr_2O_7$) was the second quickest reagent to oxidize hydrogen peroxide. When compared with potassium permanganate, $K_2Cr_2O_7$ is milder. In organic chemistry, dichromate ions convert primary alcohols into aldehydes, or carboxylic acids when heated under reflux (Sergey Bylikin, 2014). In contrast, potassium permanganate converts alcohols into carboxylic acids directly. Under acidic conditions, this reaction is expected to form Cr_2O_3 , which makes the solution turn into a deep blue color. After a while, it is expected that the color fades and becomes a pale green-blue (Royal Society of Chemistry, s.d.). However, as shown in the Qualitative Observations section, this experiment did not possibly form chromium (*III*) ions because the solution had a brown-red coloration after the reaction. The reason for this is the neutral pH of the reaction, without the addition of aqueous HCl for example. As well as potassium permanganate and other catalysts, potassium dichromate has different oxidizing power in acid or alkali conditions. This is an anomaly, and it provides some field for research under what was formed during this experiment in particular.

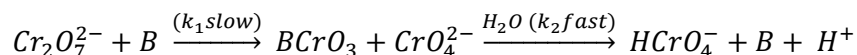
Following the brown-red color of the product obtained, some viable explanations for the reaction of dichromate with hydrogen peroxide were raised. KCr_3O_8 is an unstable tetra peroxo species that contains Cr (+*V*) atoms. It is obtained when potassium dichromate and 30% hydrogen peroxide react under alkaline conditions, forming a red-brown solution, such as the one observed in this investigation (Haxhillazi, 1973). However, with further research, it was discarded, as this compound requires a high concentrated H_2O_2 , unlike the 10% peroxide used in the experiment.

Another possible product of the curious reaction between $K_2Cr_2O_7$ and hydrogen peroxide was Chromic acid (H_2CrO_4). It has a dark red color (Chemical Book, 2017), very close to the product obtained in this experiment. Nonetheless, chromic acid still requires an acidic condition, such as the addition of $H_2SO_4(aq)$ to be produced, therefore this possibility was inviable.

The third possibility is the compound chromium trioxide, with the molecular formula CrO_3 . According to Kings Chem Guide 3rd edition ‘chromium trioxide could be obtained from potassium dichromate, however, due to poor solubility, the synthesis is more complicated’ (Ledgard, 2014). This compound is dark red to brown colored and the most interesting about it is the presence of chromium(*VI*). If chromium trioxide was formed in the reaction of $K_2Cr_2O_7$ and H_2O_2 , it means the oxidizing agent did not undergo reduction, as chromium remains with the same Nox¹ as before. This implies that hydrogen peroxide did the redox reaction

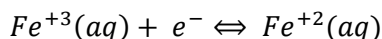
¹ Nox = Oxidation Number

by itself, undergoing disproportionation². As reported by an article of the University of Otago (Nicola E. Brasch, 1994), dichromate ions undergo hydrolysis, and chromium trioxide is an intermediate. This occurs according to the Perlmutter-Hayman (Berta Perlmutter-Hayman, 1966) suggested reaction mechanism below:



The B reagent has been tested (M. Adegboyega Olatunji, 1987) but not yet established. Perlmutter-Hayman suggested the equation and the reverse reaction of $HCrO_4^-$ with oxyanions to give $BCrO_3$ products is well established. If the dichromate ions did undergo hydrolysis with the water present on the solution, this could be a suitable explanation for the observed color change from orange to a red-brownish solution of $HCrO_4^-$ ion.

The third most efficient oxidizer for the reaction was iron (III) chloride ($FeCl_3$). Iron (III) chloride oxidizes hydrogen peroxide at practically the same rate as potassium dichromate. Due to its high selectivity (Paulina Pedziwiatr, 2018) for hydrogen peroxide given the stereo mechanism of the reaction, it is said to be a good oxidizing agent for the decomposition of H_2O_2 . At higher concentrations, iron is an effective decomposition catalyst, with sometimes the addition of ferric or ferrous ions. The iron-catalyzed decomposition of hydrogen peroxide has been studied thoroughly under acidic conditions since the discovery by Fenton³ that ‘a mixture of a ferrous salt and hydrogen peroxide possessed potent oxidizing properties absent in the separate reagents’ (Brown, 1993). Therefore, $Fe(III)$ ions are knowingly good oxidizing agents and with acidic conditions, their abilities would be enhanced. $Fe(III)$ catalytically decomposes hydrogen peroxide into O_2 and H_2O . For the reaction of iron (III) chloride with hydrogen peroxide, the oxidizing agent half-equation is:



It has a reducing potential of +0.77V, according to the Data Booklet.

Finally, there is manganese dioxide (MnO_2). Manganese dioxide is widely used in industry due to its redox capabilities. It is also a major contributor in industrial processes as a catalyst because it is generally easier to separate large quantities of products from heterogeneous catalysts such as MnO_2 than catalysts in the

² Disproportionation reaction is when the same species undergo both oxidation and reduction at the same time. Hydrogen peroxide has a tendency to decompose due to the nature of its unstable peroxide bond. (Bedka, 2018)

³ Developed in the 1890s by Henry John Hostman Fenton, the now called ‘Fenton’s reagent’ is a solution of hydrogen peroxide with ferrous ions (typically bonded to sulfate ions) in which the ions act as catalysts. It is used to oxidize contaminants or waste waters. (Fenton's Reagent, 2020)

same phase of the product (Sergey Bylikin, 2014). On the graph, it shows that MnO_2 has the slowest oxidizing ability, possibly because it is a powder. The physical state of the oxidant influences the kinetics of the reaction, so it was expected that it took longer to react, due to the tighter bonds between the atoms. ‘Also, some active basic metal oxide components do not interact strongly with the different oxide functionalities present on oxide supports and, consequently, do not disperse very well to form nanocrystalline phases’ (Wachs, 2005). Besides that, because the reagent is a powder, it was difficult to make sure all of it was transferred without any spill. The effervescence of the reaction also could have spilled some powder out of the beaker and onto the tray, decreasing the reacting molecules of the sample (Dolhun, 2014).

According to the Chemistry Data Booklet, the half-equation of Manganese ions as oxidizing agent is



The reduction value is negative, showing that the ion is a better reducing agent than an oxidizer.

9. Uncertainty

Measuring equipment inherently carries uncertainties with it, which must be determined (SD34Science). Essentially, measurement uncertainty is ‘an estimated range of values that your measurement result could confidently be within’ (Hogan, 2019). Its importance in chemistry includes the reliability of the experiment when compared to a literature value. In this experiment, the random error (also called human error) includes the reaction time of an average human, as a timer was used. According to a study carried out by Thompson *et al.* the mean reaction time for an average human to detect visual stimuli is approximately 180 – 200ms (P D Thompson, 1992). The uncertainties of the instruments are stated in the table below:

Mass	Volumetric Glassware	Beakers and Flasks
- Digital Scale: $0.5g \pm 0.001g$	- Graduated glass 10mL pipette: $142.8mL \pm 0.5mL$	- 500mL Volumetric flasks: $500mL \pm 25mL$ - 125cm ³ Erlenmeyer flask: $125mL \pm 6.25mL$ - 50mL Beaker: $20mL \pm 2.5mL$

Uncertainty of H_2O_2

The uncertainty of hydrogen peroxide is $142.8mL \pm 0.5mL$, which is one of the graduated glass pipettes used to measure the volume prepared for the experiment.

Uncertainty of liquid oxidizing agents

$$m(un) = 0.5g \pm 0.001g \qquad \%m(un) = \frac{100\% \times 0.001g}{0.5g} \rightarrow 0.2\%$$

$$m(un) = 0.5g \pm 0.2\%$$

$$C(un) = n(un) + v(un) \qquad v(un) = \frac{100\% \times 25mL}{500mL} \rightarrow 5\%$$

$$C(un) = 0.2\% + 5\% \rightarrow 5.2\%$$

$$C = 0.287mol L^{-1} \pm 5.2\% \rightarrow 0.287 mol L^{-1} \pm 0.015$$

Therefore, the concentration of these compounds ranges from 0.272 to 0.302 $mol L^{-1}$.

Uncertainty of the solid oxidizer

$$m = 0.5g \pm 0.001g$$

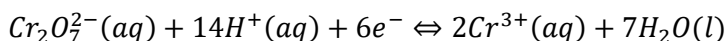
$$m = 0.5g \pm 0.2\%$$

Since it was used in the solid-state, its concentration is constant and the mass ranges from 0.499g to 0.501g.

10. Limitations of the investigation

This experiment had some limitations:

1. All the reactions were made under inert pH conditions, which could have influenced the time each catalyst took to catalyze the reaction. As pointed out before, some catalysts (such as potassium dichromate) are improved oxidizing agents when they are reacted under acidic conditions. According to the half-equation of dichromate



It contains protons on the left side, as one of the reagents, showing the need for the low pH for reduction to occur. The experiment in this investigation did not form Chromium (III) ions, which troubled the comparison of reduction potentials. Without the presence of a low pH, the efficiency of this catalyst could have decreased, which influences how it is compared to another catalyst that does not necessarily need an acidic environment to decompose hydrogen peroxide.

2. As with any experiment using a cellphone timer, it has uncertainties inherent to it. My reaction time could have been greater because I had to do two things at once, add the reagents to the Erlenmeyer flask and start the timer at the same time. I believe though, that repeating this step so many times could have influenced my reaction time as it did not remain constant for all the trials. Having a

partner to divide experimental tasks would perhaps bring more efficiency to avoid errors in multitasking.

3. When dealing with the heterogeneous catalyst, it was difficult to ensure that all the solid was properly transferred at the same time. In some trials, even though I poured the powder inside the flask, a little amount remained inside the beaker. This could have happened because after many trials the beaker could have been wet inside, which made the powder stick to it and not fully react. A way to improve that would be using a different dry beaker every time, to make sure there were no water particles inside it.

11. Conclusion

The best catalyst for this reaction was successfully found to be potassium permanganate ($KMnO_4$). It took the least time to decompose hydrogen peroxide, because of its excellent oxidizing abilities. The aim of this paper, which was to conduct the experiment and analytically compare the efficiency of each catalyst, was sustained. Potassium permanganate has been part of many studies with hydrogen peroxide, due to its 'highly efficient redox reaction' (Ying Sun, 2019) under acidic conditions.

Regarding the hypothesis 'The strength of the oxidizing agents on the reaction with hydrogen peroxide should follow the same order of their reduction potentials' it was confirmed to a certain extent. The investigation showed that all catalysts followed the same increasing order of efficiency in catalysis and of electrode potentials. The relationship between the ability to catalyze and reduction potential is directly proportional. Potassium permanganate had a potential of $+1.51V$ and presented the highest ability to decompose hydrogen peroxide. Following the rank, potassium dichromate has a reduction potential of $+1.36V$ and even though it did not form Cr^{3+} ions, it was the second most powerful oxidizer. Additionally, it provided room for improvement and research on the mechanisms that could have influenced the product of this specific reaction. Iron (III) chloride has an electrode potential of $+0.77V$ which places it in the third place, as the experimental data shows. At last manganese dioxide has a reduction potential of $E^o = -1.18V$, a negative value and the smallest of them all. This is reflected in its catalyzing abilities, which took the longest above all.

Given the uncertainties of the experiment, which were presumably low, the investigation is considered a success. However, further research could be made under the specific pH conditions that each catalyst is normally used in industry so that their catalyzing ability can be improved. Lastly, the rate of reaction of the uncatalyzed decomposition could also be mentioned in a further paper, to give more room for comparison and analysis of the results.

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