The Scientific Method and its Application toward the Development of Heterogeneous Alkene Epoxidation Catalysts from Tripodal Titanium Silsesquioxane Complexes

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What is the scientific method?

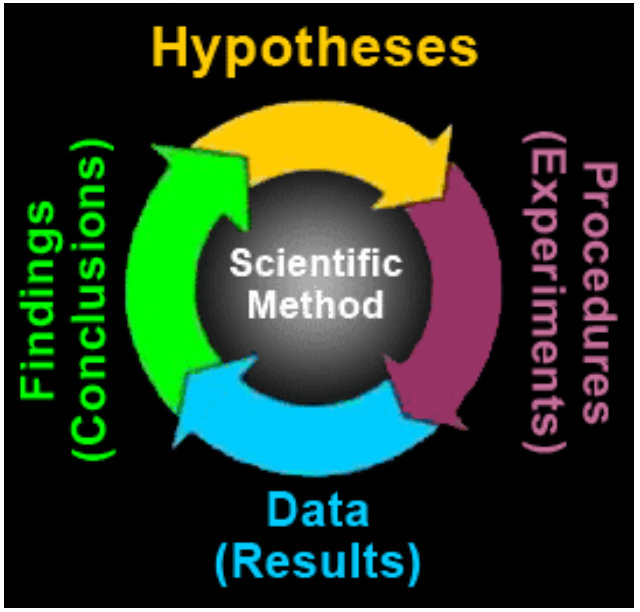
- A systematic way to:

• ask and answer questions

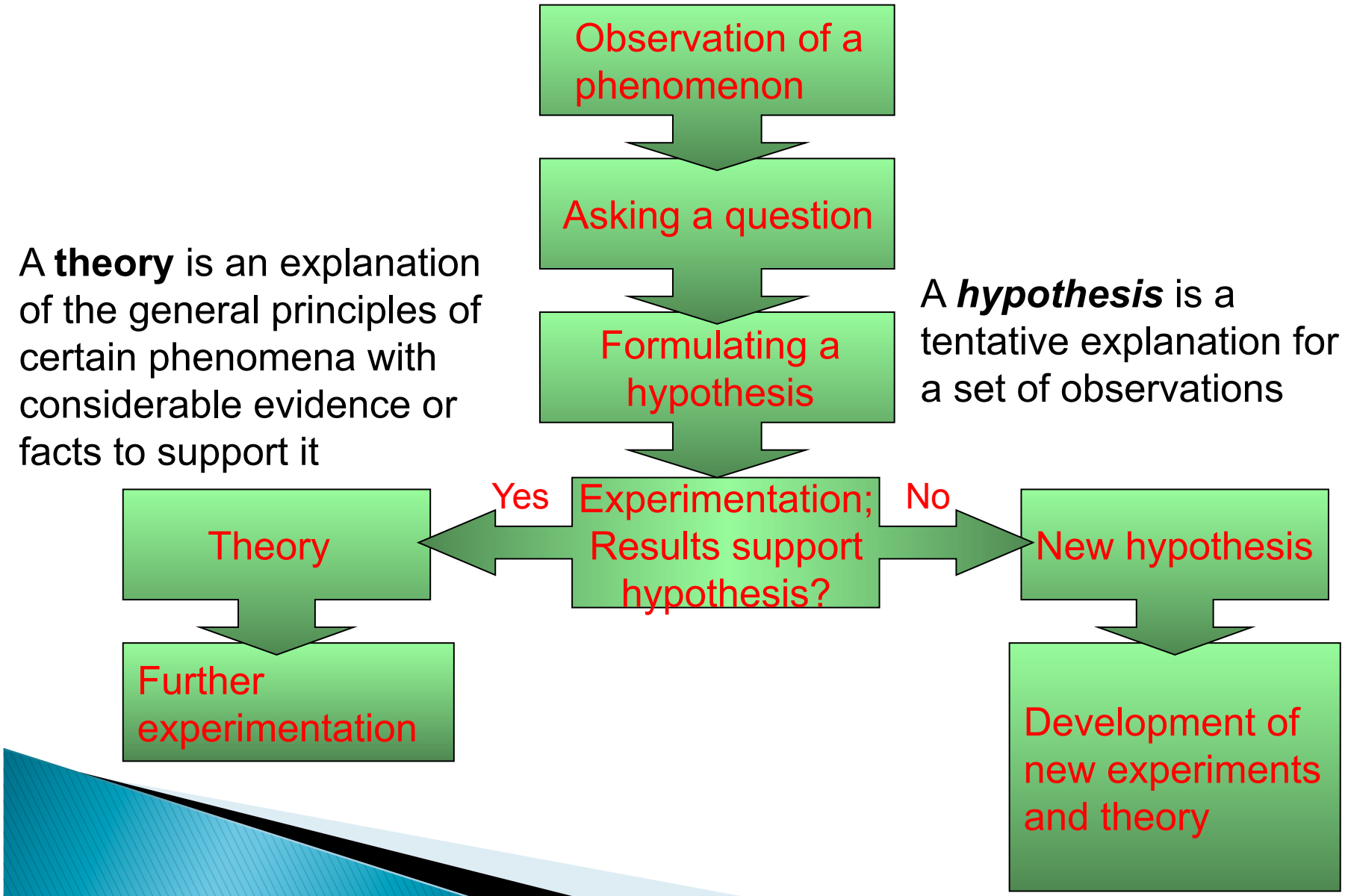
• develop rational explanations

• understand cause and effect

• focus on the question at hand



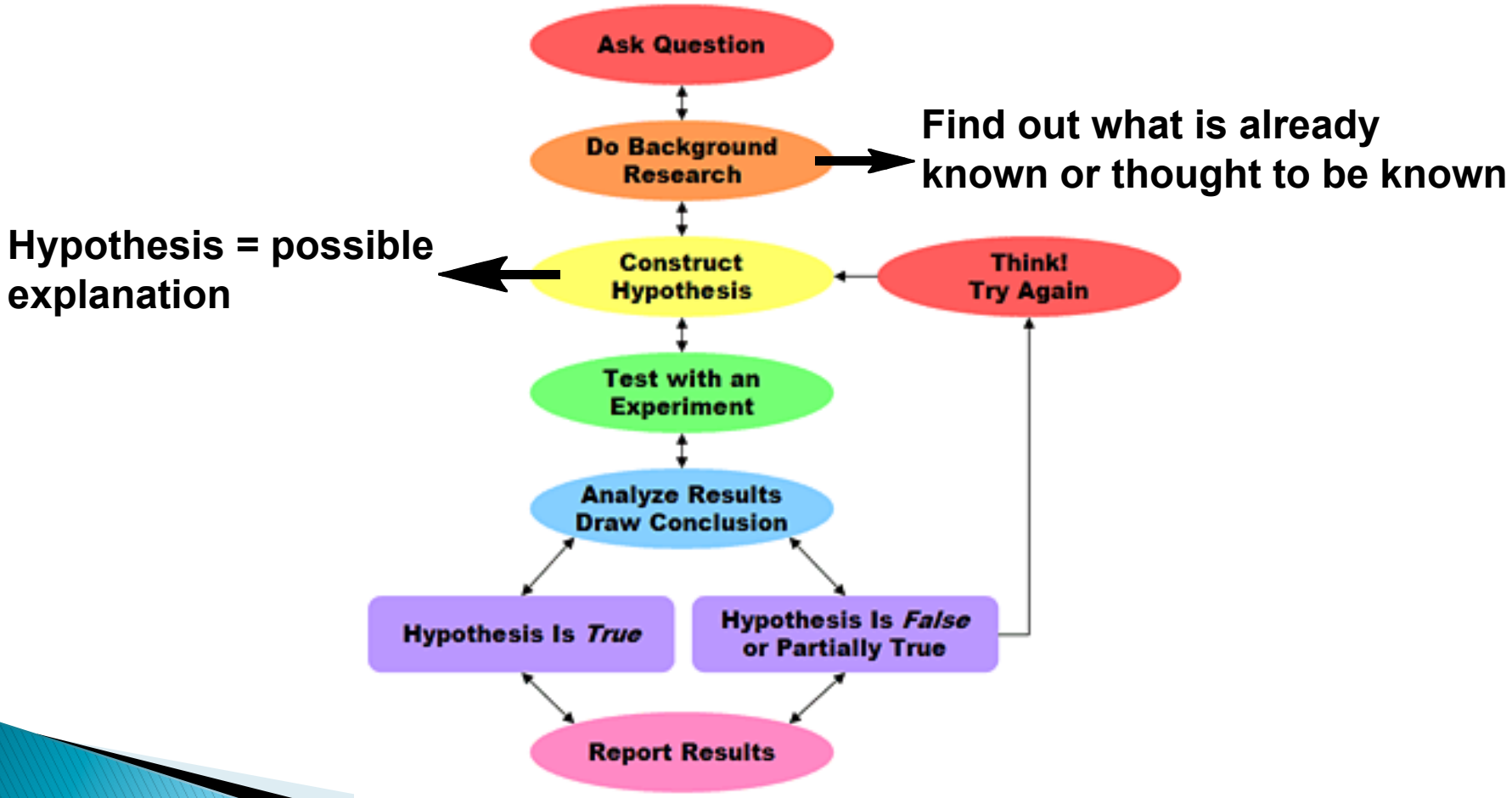
The **scientific method** involves several steps



A **theory** is an explanation of the general principles of certain phenomena with considerable evidence or facts to support it

A ***hypothesis*** is a tentative explanation for a set of observations

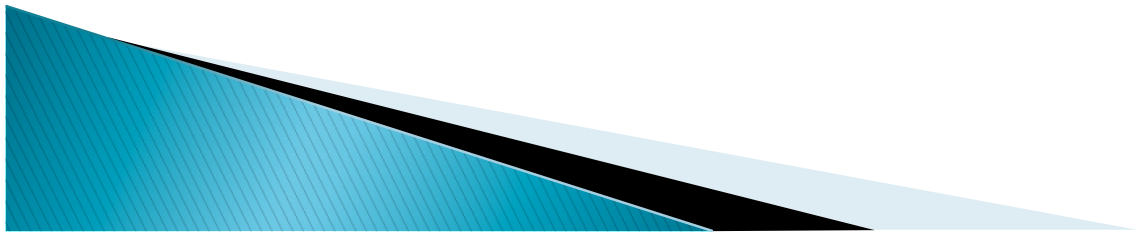
The scientific method – an iterative process that involves not being afraid to step back and rethink your hypothesis



http://www.sciencebuddies.org/science-fair-projects/project_scientific_method.shtml

Which of the following is/are not correct about a hypothesis? It is

1. a fact
2. a tentative explanation for an observation
3. subject to experimentation
4. not the same as a theory
5. not always correct



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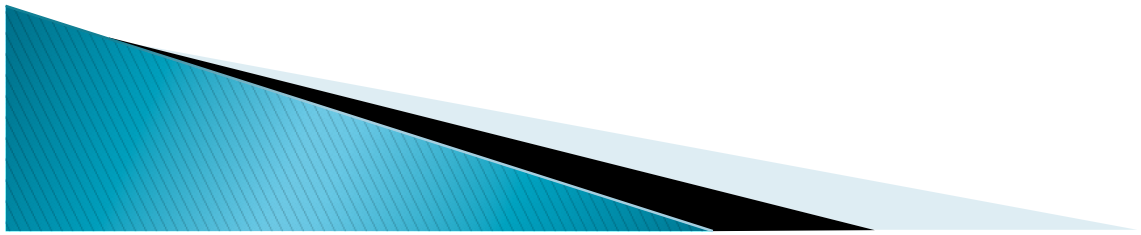
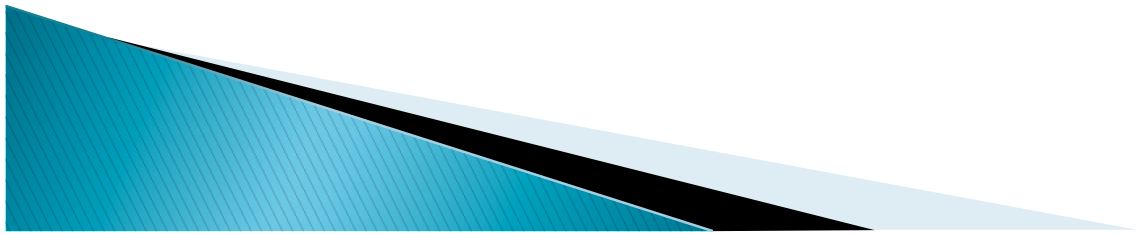


"Beethoven's contribution to music would have been much greater if he had been married." This statement is an example of

1. a theory
2. a hypothesis
3. a fact
4. a law
5. an observation



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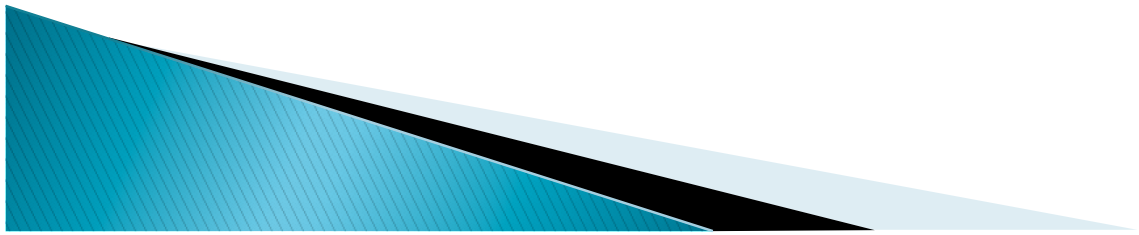
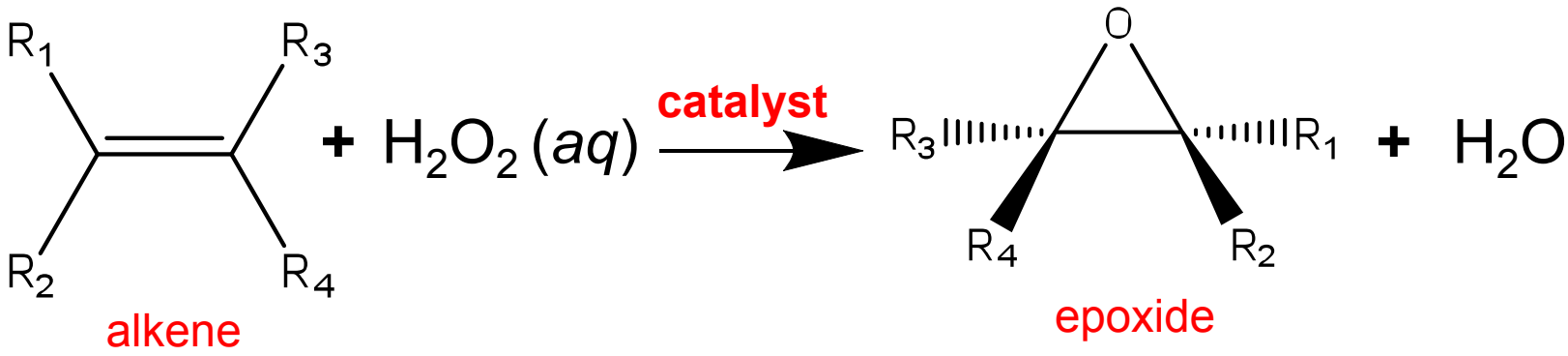


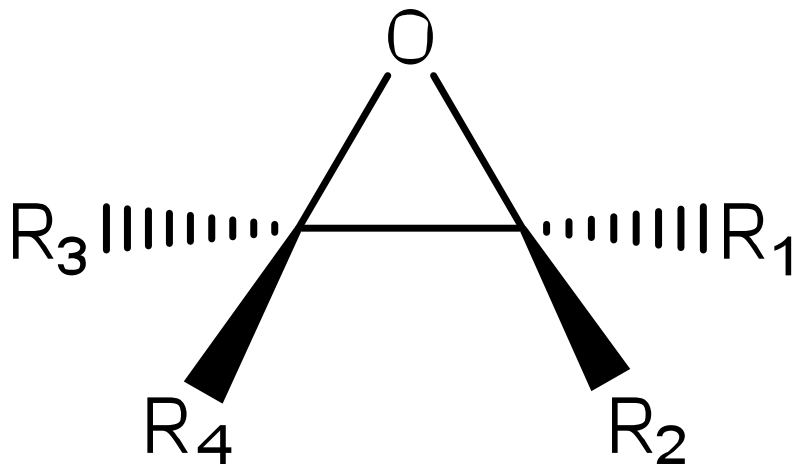
To begin our work, we asked the question: How do we develop a catalyst for the conversion of alkenes into epoxides that uses cheap aqueous hydrogen peroxide as oxidant and is tolerant of water, which is released in the reaction?



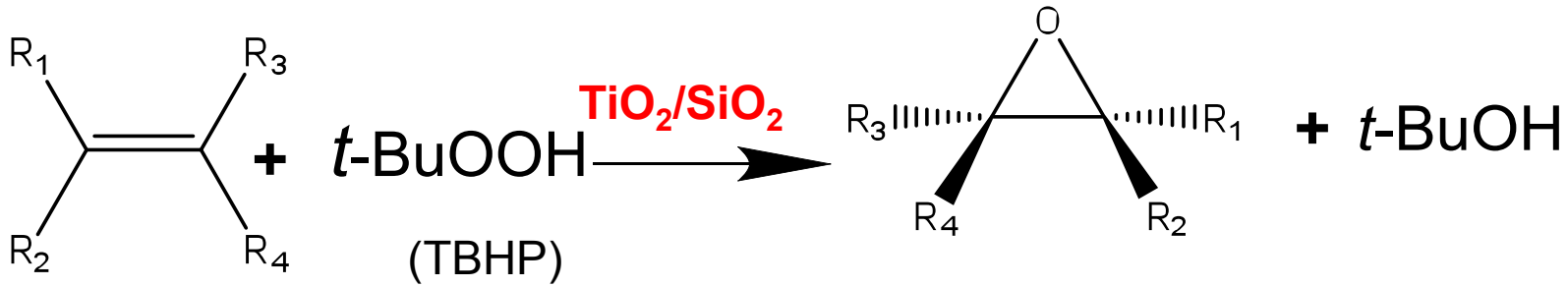
A catalyst can speed up a chemical reaction that may otherwise be too slow to be useful and/or may allow us to form more of our desired product (i.e. impart selectivity) in chemical reactions

Why are epoxides important?

- They are:
  - highly strained cyclic ethers
  - highly reactive
  - useful industrial building blocks –polyester fibers, anti-freeze, polyurethane, etc.

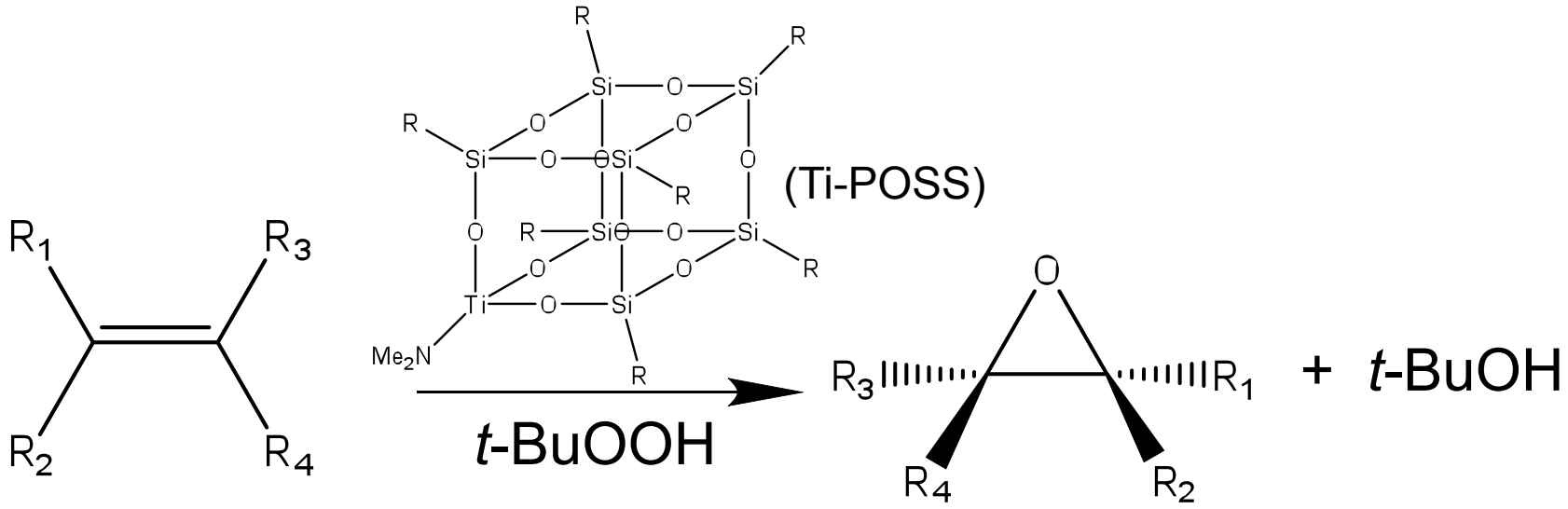


Background research: Titanium-containing heterogeneous catalysts, such as TiO_2/SiO_2, with alkyl hydroperoxides (ROOH), such as *t*-butyl hydroperoxide (TBHP) as oxidant, have been used in olefin epoxidation



- *A heterogeneous catalyst does not dissolve (is insoluble) in the reaction medium while a homogeneous catalyst dissolves (is soluble) in the reaction medium.*
- *The oxidant supplies the oxygen atom required for epoxide formation from the alkene*

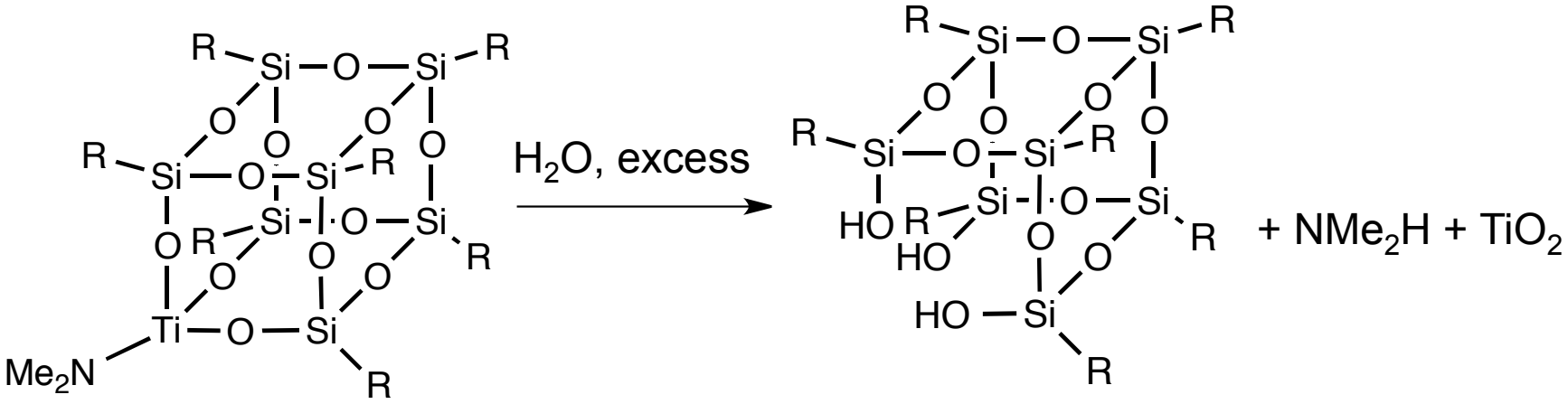
Background research: Tripodal Ti silsesquioxane (Ti-POSS) complexes appear to be among the most active and selective of all known catalysts for olefin epoxidation reactions using alkyl hydroperoxides, such as TBHP, as oxidant



Typically >97% epoxide selectivity for simple alkenes

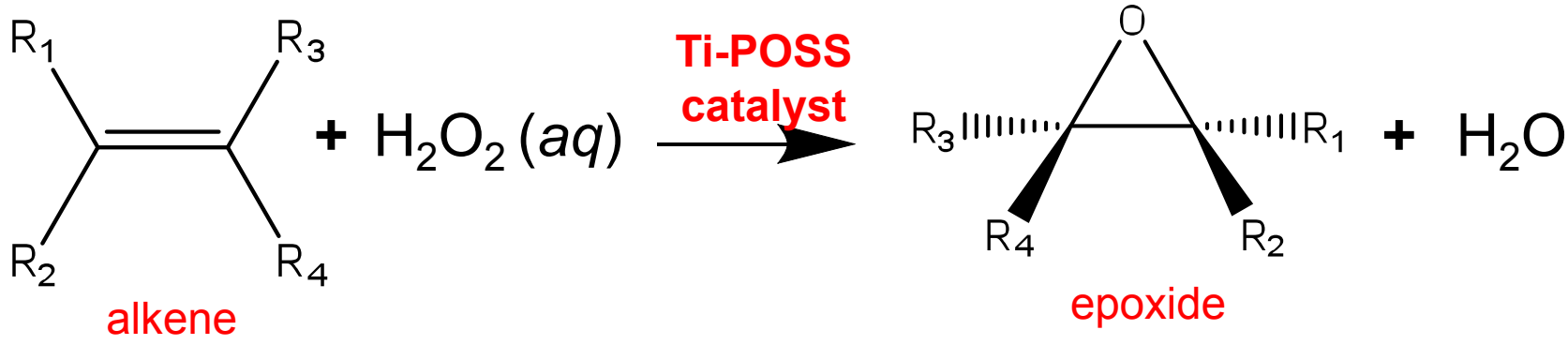
Background research: With aqueous H_2O_2 as oxidant, Ti-POSS catalysts are deactivated (destroyed) due to hydrolysis by the water produced

Hydrolysis reaction:



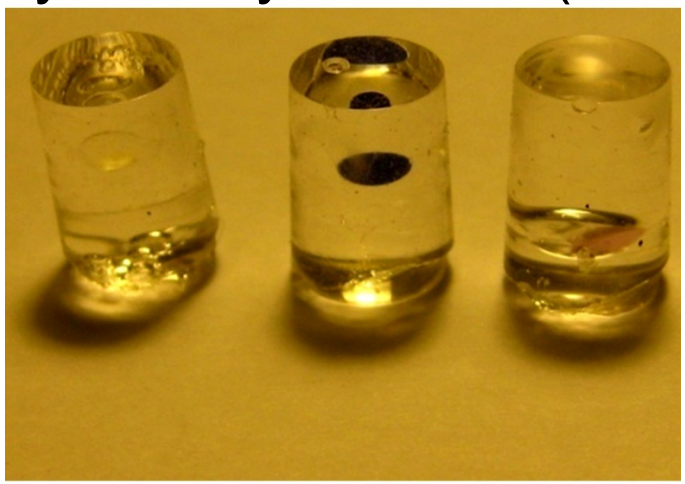
Ti-POSS reaction with water results in Ti leaching (loss) from the active catalysts

Our question: How do we develop a catalyst for the conversion of alkenes into epoxides that uses cheap aqueous hydrogen peroxide as oxidant and is tolerant of water, which is released in the reaction?



Hypothesis: enclosing Ti-POSS catalysts in a hydrophobic (water-excluding) environment would keep water out while allowing in the alkene and H_2O_2; thus, permitting alkene epoxidation to occur

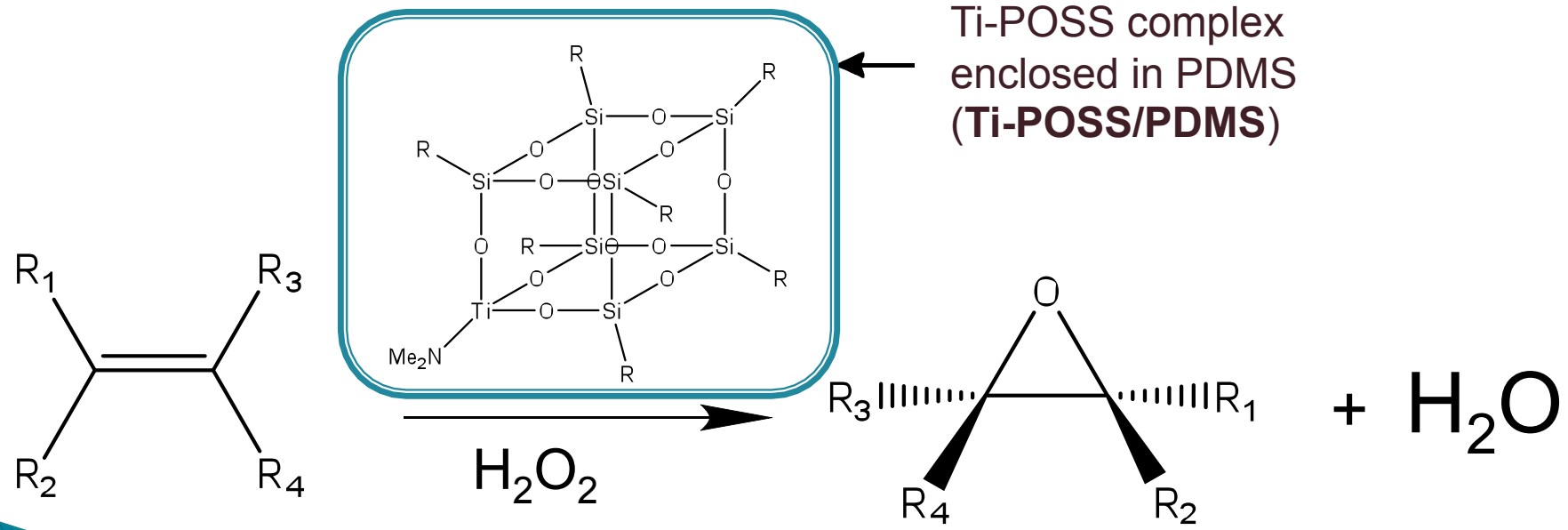
Use polydimethylsiloxane (PDMS) membrane!



- PDMS is a hydrophobic elastomer
- PDMS has been used with other oxidation catalysts

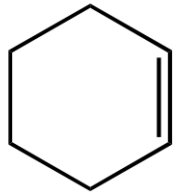
http://www.uta.edu/ee/NanoBioLab/research.htm

Hypothesis: By enclosing Ti-POSS catalysts in a hydrophobic environment, we can achieve high epoxidation selectivity and conversion while using aqueous H_2O_2 as oxidant



Test with experiments:

(cyclohexene = *c*-C_6H_{10})



(0.5 mmol)

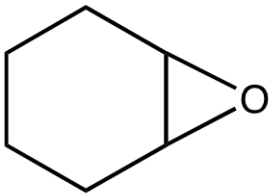
+ H_2O_2 (aq)

(30 wt %)

(0.5 mmol)

Immobilized catalyst
(2 mol % Ti)

60˚ C, 40 h
MeCN



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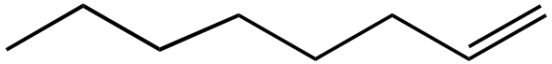


(1-octene = 1-C_8H_{14})

(0.5 mmol)

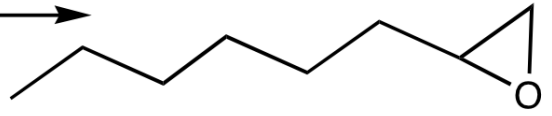
+ H_2O_2 (aq)

(30 wt %)

(0.5 mmol)

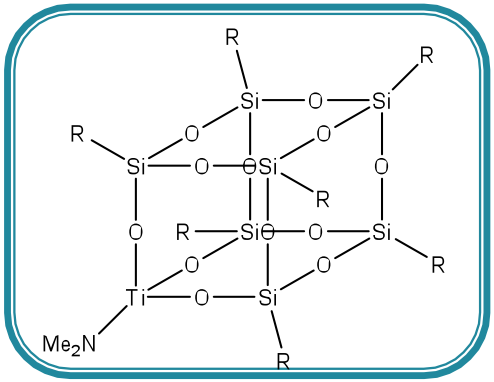
Immobilized catalyst (2 mol % Ti)

60˚ C, 40 h
MeCN



(3)

Immobilized catalyst =



1, R = *i*-C_4H_9

Test with experiments:

Catalyst	Substrate	Conversion (%)	Epoxide Selectivity (%)	H_2O_2 efficiency (%)
1	1-octene	95	99	98
1	Cyclohexene	88	99	98
TS-1	1-hexene	15	100	64

0.01mmol Ti, 0.5 mmol alkene, 0.5 mmol H_2O_2 , 5 mL MeCN, 60 °C, 40h

In agreement with our hypothesis, Ti-POSS/PDMS catalyst **1** showed high epoxide selectivity, H_2O_2 efficiency, and activity in alkene epoxidations using aqueous H_2O_2 as oxidant. It even outperformed TS-1, a very useful epoxidation catalyst.

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The high H_2O_2 efficiency of **1** can be attributed to the uniformly hydrophobic (water-excluding) environment provided around the Ti-POSS by the PDMS membrane, which we presume results in low local water concentrations, and higher [alkene]:[H_2O_2] ratios at the Ti center

Results obtained for 1-octene epoxidation with **1**/PDMS and aqueous H_2O_2 will be the same in any solvent since the PDMS membrane would exclude water as before. This statement represents

1. a fact
2. a hypothesis
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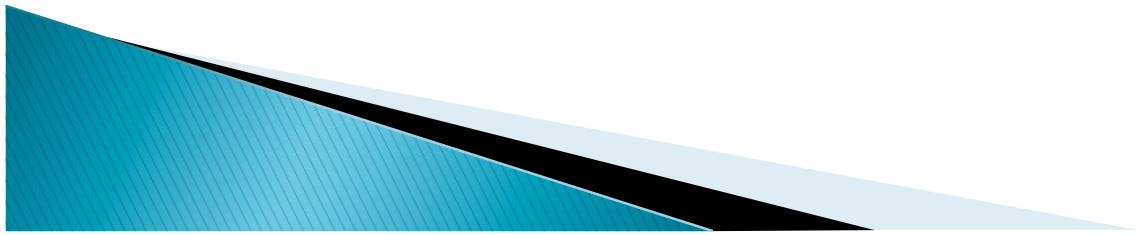

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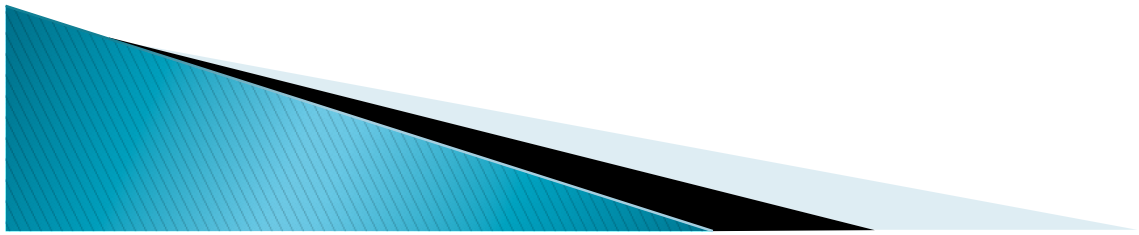
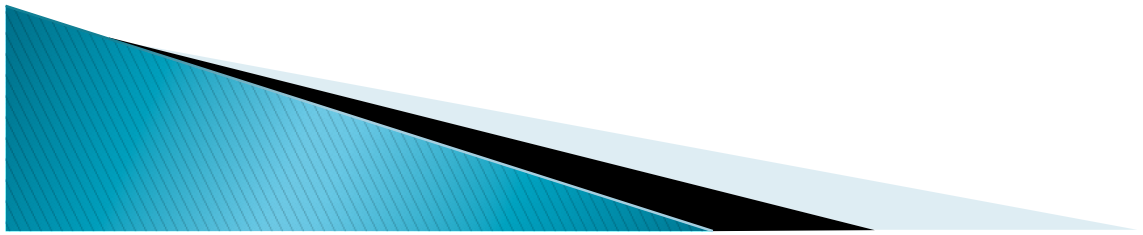


Which of the following statements is/are true?

1. A hypothesis should be tested by experiment
2. Experiments can provide support for a hypothesis
3. Experiments can disprove a hypothesis
4. A hypothesis can be improved through experimentation
5. All of the above



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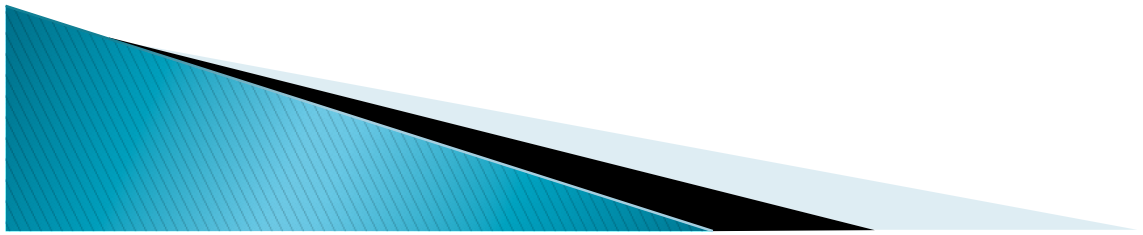
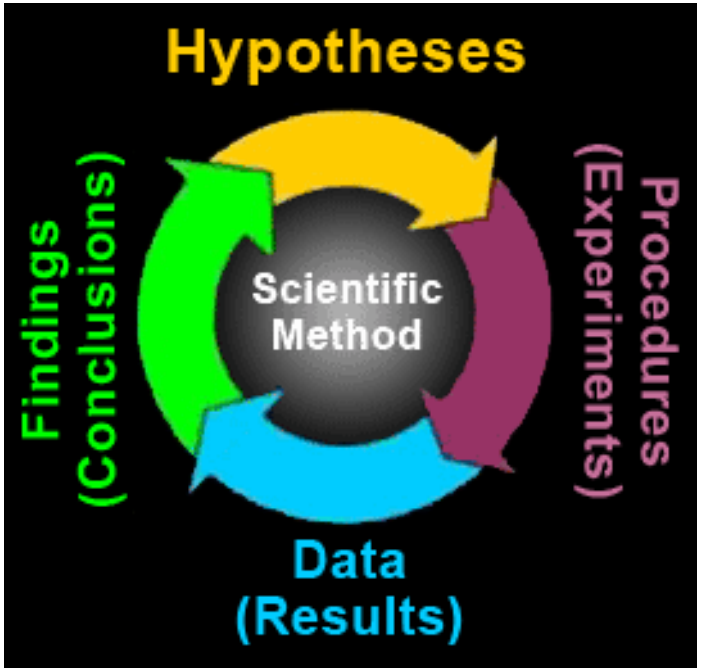


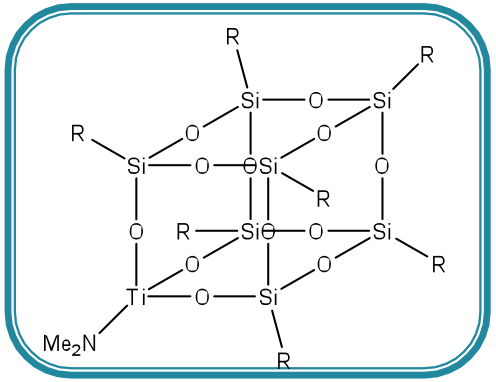
Conclusion

- The scientific method is a systematic way of asking and answering questions
- It is iterative process that involves not being afraid to step back and rethink the original hypothesis
- Using the scientific method, we were successful in developing Ti-POSS catalysts that use aqueous H_2O_2 as the oxidant



http://mccarthyi.edu.glogster.com/mrsmacscitoolz/

Our studies showed that **1/PDMS** maintained its 1-octene epoxidation efficiency for 5 reuses in acetonitrile. However, **1/PDMS** contains the Ti-POSS complex physically trapped in PDMS membrane so the complex would eventually leak out of the membrane as the membrane swells over time in solution.



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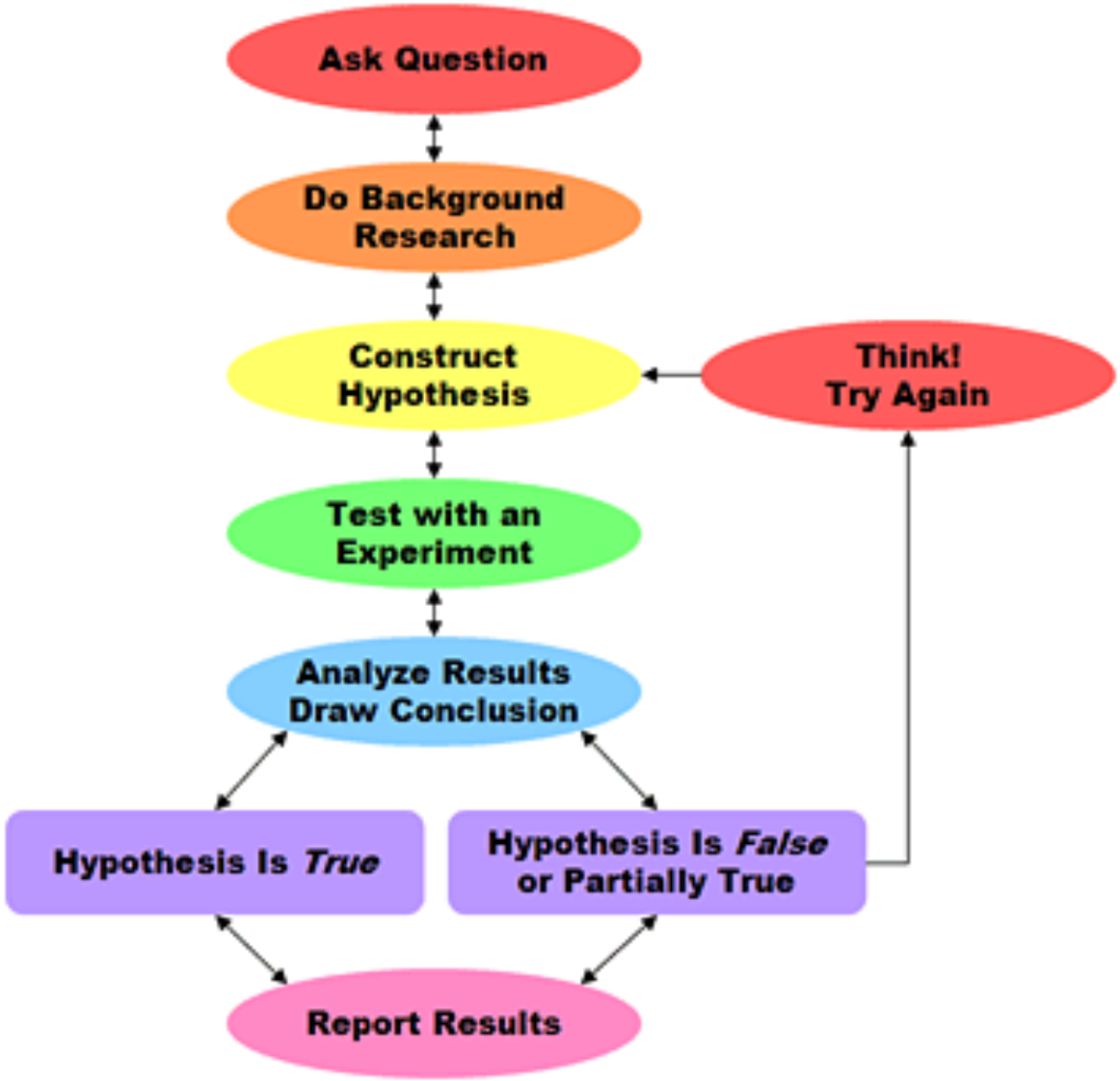
New Question: How do we improve reusability of the catalysts while maintaining their high activity, epoxide selectivity, and H_2O_2 efficiency?

We'll apply the scientific method!



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Come back and see what we come up with!