Teacher's Preparatory Guide

Lab 1: Nanocatalysts Clean Your Car Emissions

Purpose: This lab is part 1 of a 2- (optional 3-) part series of inquiry-driven labs designed to help students understand reactions and the research involved in a catalytic converter. In this lab, students will be introduced to catalytic converters and understand the difficulties encountered by researchers in creating nanoparticles of consistent size and shape. Specifically, students will create alginate-MnO_2 catalytic spheres and cylinders and relate them to nanoparticles used in catalytic converters. Then, students can calculate the percent yield to rate their level of consistency. Lab 2 uses the structures made in this lab.

Level: High School (Environmental Science, Chemistry)

Time required: One 45-minute class period, or half of a 90-minute block period

Teacher Background: Cars have a catalytic converter between the engine and the muffler. Catalytic converters convert harmful emissions of nitrogen oxides, hydrocarbons, and carbon monoxide to more benign gases like nitrogen, oxygen, and carbon dioxide. An image of the location of the catalytic converter is found at http://auto.howstuffworks.com/catalytic-converter.htm.

Recently, lots of catalytic converters are being stolen! Why? These pollution-reducing devices contain small amounts of platinum and other precious metals whose price has skyrocketed in changing economic times. In 2003, platinum traded for $600 per troy ounce (~31 g) and now it is over $2000 per troy ounce.

Scientists are looking for other metals to replace or reduce the amount of platinum and other precious metals in the catalytic converter. Gold is cheaper than platinum and rhodium that are currently in use; gold can play a role in the oxidation of harmful emissions. However, gold has to be converted to nanoscale size particles in order to be effective in this process. Gold nanoparticles encased in spheres of titanium or cerium oxide have the ability to form a monolayer of nanoparticles on the special coating atop the ceramic framework of a converter. This extra coating is needed because without it, gold nanoparticles would fuse (sinter) and become ineffective as catalysts at the high temperatures produced in a gasoline engine.

Catalysts in the nanoscale range are important because of the greater surface area afforded by nanoparticles. Surface area is known to increase with decreasing particle size (increased surface area to volume ratio) and reaction rates are, in turn, related to surface area. With greater surface area, there is more area with which the chemical agents can react. Nanoparticles allow for greater surface area and therefore faster reactions.

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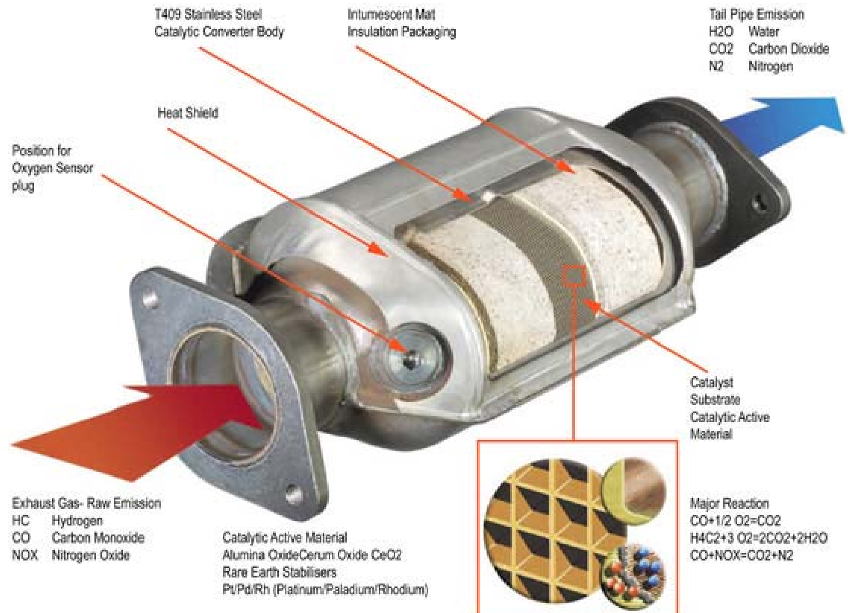
Nanoscale catalysts, called *nanocatalysts*, are applied as metallic coatings on a ceramic structure that looks like a honeycomb. Some of these coatings also contain ceramic beads (image above). The design exposes the maximum amount of surface area to the emission stream released from the engine. There is a reduction process that releases oxygen ($2NO \rightarrow N_2 + O_2$ and $2NO_2 \rightarrow N_2 + 2O_2$), and an oxidation process that consumes oxygen as carbon monoxide and hydrocarbons produce carbon dioxide and water ($2CO + O_2 \rightarrow 2CO_2$).



http://www2.warwick.ac.uk/fac/sci/physics/research/condensedmatt/nmr/members/postgraduates/greg/cat.jpg

The catalyst in this lab is manganese dioxide contained in alginate spheres that are created when a mixture of 2% sodium alginate, glass, and MnO_2 is dropped into 5% calcium chloride solution. The calcium ions replace the sodium ions and change the flexible alginate chains to form a gelatinous network structure.

The catalytic reaction is immediately visible as MnO_2-alginate beads rise to the surface, releasing oxygen as the hydrogen peroxide decomposes. Students will track the rate of reaction by counting the bubbling that occurs in a certain time period and/or track the volume of gas that is produced in a given amount of time by collecting the gas in a graduated cylinder using water displacement.

The chemical equation for this redox reaction is:

$$2H_2O_2 \rightarrow O_2 + 2H_2O$$

Manganese dioxide is a catalyst that lowers the activation energy of the reaction and facilitates the formation of the products of the reaction through oxidation and reduction. The alginate/glass structures containing the catalyst allow the students to visualize the oxygen gas released as the reaction occurs. There are many possibilities for students to design inquiry-based investigations to examine the connections between catalysts and reactant by manipulating variables such as substrate concentration, manganese dioxide concentration, and surface area are involved in the contact between the catalyst and the reactant.

Materials for each group of 2–4 students:

- 3% H_2O_2
- 30 ml alginate/manganese dioxide/glass powder solution (see Resource section)
- 30 ml 5% $CaCl_2$ solution
- 30 ml medicine cup (for alginate mixture)
- 50 ml small plastic container
- glass stirring rod
- plastic syringe or 1ml dropping pipette
- 3-inch square household plastic screen or cheesecloth

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- Vernier calipers (for measuring alginate structures)
- 100 mm diameter petri dish
- hand lens or stereomicroscope
- tap water
- paper towels

Safety Information: Do not breathe the glass powder. Note: Students do not directly work with the glass powder, rather, the glass powder is mixed with the alginate and manganese dioxide first, before given to the students. Manganese dioxide is a strong oxidant and is moderately toxic by ingestion. Hydrogen peroxide 3% solution is a topical antiseptic and should not be splashed into the eyes or applied over large areas of the body. Calcium chloride solution (5%) can dry skin, so flush any spills on the skin with water. Material Safety Data Sheets (MSDS) for all of these chemicals should be available in the lab.

Advance Preparation:

- PREPARATION OF ALGINATE/MnO_2/GLASS POWDER SOLUTION
  To prepare 300 ml of 2% alginate solution, add 6 grams of alginate to 300 ml of water. Mix in a blender for 30 seconds (or until all of the powder is dissolved), and heat in the microwave for 1 to 2 minutes until the mixture starts to boil. The alginate may be stored in the refrigerator if made the day before the lab; otherwise, be sure the mixture is cool before adding 5 grams of MnO_2 and 90 grams of glass powder. The mixture should be stirred with a glass rod. Alternate methods for preparing the alginate solution may be found in the *Teachers Guide* to the Microbial Lava Lamp Classroom Activity at http://www.csun.edu/~hcbio029.

Teaching Strategies: One day before introducing the inquiry activity, the teacher can bring in a "Microbial Lava Lamp" (www.csun.edu/~hcbio029/lavalamp/Lava_Lamp_Teachers.pdf). This is optional, but worth it. The presence of this device as anticipatory set in the classroom should pique curiosity about the alginate beads as they float to the top, and drop as they release carbon dioxide. *Do not answer any specific questions about the microbial lava lamp at this point.*

Instructional Procedure: Lab 1

Microbial Lava Lamp

Time	Instruction	Reasoning
5 min	Introduce catalytic converter theft issue; teacher directed discussion of what a catalytic converter does and why people steal them.	Precious metals are getting more expensive; catalytic converters carry out oxidation reduction of emissions from gasoline and diesel engines.
15 min	In groups of 2–4, students create alginate spheres and cylinders in calcium chloride, wash in H_2O; discuss briefly why the alginate changes state.	Visually observe the alginate change phase from a sol to a gel. Students use the scientific method by changing factors that influence size and shape.
5 min	Cleanup; sort structures into similar size and shape.	Students prepare for tomorrow's activity.
5 min	Students use hand lenses or dissecting	Visually observe the oxygen bubbles form

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	microscopes to see the alginate structures reacting with H_2O_2.	at the surface of the alginate particles.
5 min	Ask groups (and then the class): "How can we quantify the reaction rate of this chemical reaction?"	Oxidation and reduction in this reaction: $2H_2O_2 \rightarrow O_2 + 2H_2O$ Note: Only oxygen release can realistically be quantified.
15 min	*Homework:* Students complete analysis & conclusions.	Students reinforce math skills and relate the activity to real-world application.

Guided Dialogue Before beginning the lab, review the meaning of these terms:

Catalyst *A substance that is used to increase the reaction rate of a chemical reaction but does not become part of the end products. The catalyst provides a different pathway or mechanism that makes bond making, bond breaking or electron exchange occur more rapidly. It lowers the activation energy needed for the reaction to proceed (see the "reaction energy diagram" in Wikipedia).*

Heterogeneous catalyst *The catalyst (solids) and the reactants (gases) are in different phases. Catalytic converters have heterogenous catalysts that adsorb reactant gases on the ceramic surface that is coated with platinum, rhodium, and palladium.*

Homogenous catalysts *Catalysts in the same physical phase as the reactants (e.g., enzymes and substrates).*

Nanoparticles *Particles that are 1–100 nm in size; a nanometer (nm) is 1 x 10^{-9} (one-billionth) of a meter.*

Oxidation *Loss of electrons (in this reaction, oxygen in hydrogen peroxide is both oxidized $H_2O_2 \rightarrow H_2O$ and reduced $H_2O_2 \rightarrow O_2$).*

Reduction *Gain of electrons. In the overall reaction $H_2O_2 \rightarrow H_20 + O_2$, H_2O_2 reduces to O_2.*

Alginate *A reversible hydrocolloid that can exist in two different states: the sol form has greater flexibility and straight chain polymers; the gel form has many crosslinks and is a semisolid.*

Ask students questions to provoke thought and review what they already know. For example:

1. Why are people stealing catalytic converters? *The precious metals that coat the surface of the converter have greatly increased in value.*
2. What is the difference between emissions from your car's engine and the exhaust? *The emissions come directly from the engine and they are processed by the catalytic converter to both oxidize and reduce emissions and turn them into less harmful forms when they leave the tailpipe of the car as exhaust.*
3. What are the gases that are found in car exhaust? *carbon dioxide, nitrogen, water vapor, nitrogen oxides, and some carbon monoxide*
4. What are the common emissions produced by running a car engine? *carbon dioxide, carbon monoxide, nitrogen oxides, and hydrocarbons*
5. What specific metals or minerals are commonly used in automotive catalytic converters? *platinum, rhodium, and palladium*
6. How large do you think the metallic particles are that are found in the ceramic coating of the catalytic converter? *These are metallic nanoparticles, ranging in size from 2–200 nm.*
7. Why use nanoparticles? *They provide a greater surface area than larger particles allowing for more area on which the reaction can take place.*

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Directions to the Activity

Name:______________________________Date:______________Class:_______________

Student Worksheet (with Answers)

Catalytic Conversions: Guided Inquiry

Safety

Avoid splashing hydrogen peroxide into the eyes or onto other areas of the body. Any spills of calcium chloride on the skin should be immediately flushed with water.

Introduction

Catalysts are in the news! The most valuable part of your car that thieves want to steal is your catalytic converter. Inside a catalytic converter are nanoparticles, which are 10 times smaller than the hair on the eye of a bee. A nanoparticle is on the scale of 1- 100 nanometers. One nanometer is 1×10^{-9} meters. Catalysts in the nanoscale range are important because of the greater surface area afforded by nanoparticles. Surface area is known to increase with decreasing particle size (increased surface area to volume ratio) and reaction rates are, in turn, related to surface area. With greater surface area, there is more area with which the chemical agents can react. Nanoparticles allow for greater surface area and therefore faster reactions. Since these particles are so small, researchers are working to get control over their size and shape. Why are size and shape important?

Materials

- 10 ml of alginate-glass MnO_2 mixture
- 30 ml 5% $CaCl_2$ solution
- 3% H_2O_2 solution
- glass stirring rod
- plastic syringe or 1 ml dropping pipette
- petri dish (100mm diameter)
- Vernier caliper
- hand lens or stereomicroscope
- 3" plastic screen or cheesecloth
- tap water
- paper towel
- blank data table (sphere)
- blank data table (cylinder)

Question

What will affect the size and shape of the "nanoparticles" that you will be creating?

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Make a Prediction:

Example prediction: The physical methods used, such as where in relation to the surface of the solution is the alginate mixture released and how long the pipette is squeezed. The alginate mixture will clump in spheres if dropped from above the cup and form cylinders if released from the dropper under the surface of the solution.

Procedure

1. Fill the small plastic cup with $CaCl_2$ solution.
2. Using a plastic syringe or pipette, add drops of the alginate mixture, one at a time, to the solution. Many factors affect the size and shape of the structures. Experiment to discover how to make consistently sized spheres and consistently sized cylinders. You can take a closer look at the alginate structures by using the screen provided to remove them from the solution and to rinse them in water.
3. Once you feel that you understand how to create structures that are of consistent sizes and shapes, use the screen to remove the "practice" structures from your solution. Now try to create 10 spheres similar in size.
4. Remove the alginate structures from the $CaCl_2$ solution using the screen, and rinse them with water.
5. Use the calipers to measure and record the diameter of each of the spheres in the table below.
6. Now, place the alginate structures into a petri dish half filled with 3% hydrogen peroxide. Then look at the structures in the dish under greater magnification. Record a description of what you now see (on the table for observations) and identify questions to ask.
7. Repeat steps 3–6, creating cylinders instead. In step 5, also measure and record the length of each of the cylinders in the table below.
8. Return the structures made to the $CaCl_2$ solution; you will use them in the next activity.

Record Your Observations

Use the tables below and on the next page to record the measurements and observations you have made.

Sphere	1	2	3	4	5	6	7	8	9	10
Diameter										

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(mm)										

Cylinder	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Diameter (mm)										
Length (mm)										

Alginate structures in H_2O_2	**Observations under magnification: What else do you observe? Sketch and describe.**
Bubbles appear on surface of structures.	*Gas bubbles are seen forming and leaving the surface of the structures; small bubbles fuse into larger ones before they escape. There are more bubbles on the cylinders than on the spheres.*

Analyze the Results

1. Show how you calculated the percentage of alginate structures that were the same size. Show all of your work on a separate page.
2. What factors were controlled in this reaction? *temperature, volume of peroxide, volume of reaction container, mass of alginate structures*________________________________

   ____

Draw Conclusions

1. How successful was your group in making alginate structures that are the same size? Justify your success through the percentage of structures that were the same size and shape. *Example answer: We were able to get 85% of the spheres the same size and 68 % of the cylinders the same size.*____________________________________

   ____
2. What factors affected your ability to be consistent?

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Example answer: whether I squeezed the pipette above or below the water, how quickly I squeezed, how long I squeezed the pipette, how much alginate was in the pipette

3. Nanoparticles are structures that cannot be seen by an optical microscope. They are too small to be seen within the range of visible light. There are instruments that allow us to image them based on forces at the atomic scale. Nanoparticles are much, much smaller than the structures you made today. What problems may researchers run into when trying to create a batch of nanoparticles that are all the same size and shape?

   Example answer: The chemical and physical methods of creating the nanoparticles might result in variations in size and shape. An electron microscope is needed to see and measure the particles.

During the Lab:
Ask students to describe what is happening to the alginate mixture: *It is changing from a sol to a gel.*
Ask students to describe, specifically, what happens for the sol to change into a gel. *Alginate is a polymer that comes from kelp. Sodium alginate is water-soluble and it consists of long, flexible chains. Calcium replaces the sodium in the alginate when it comes in contact with calcium chloride. The sol changes to a huge cross-linked network structure called a gel.*

Left: What students will see when alginate/manganese dioxide surface reacts with hydrogen peroxide.

Cleanup: Have students remove alginate structures from the solution and rinse in tap water, using the plastic screen or cheesecloth provided. Then, have students sort their structures into

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groups of similar size and shape and put them in a petri dish that is labeled with the names of people in their group.

Going Further: Students who have a good grasp of the content of the lab can be further challenged with this question:
Today you experimented with size as a variable. Predict how you think size and shape may affect the rate of a reaction? *The greater the surface area of the catalyst, the faster the rate of the reaction; small spheres of the same total mass have greater total surface area and hence a faster rate of reaction.*

Assessment:
Guided Inquiry
The students will each turn in their completed worksheets at the end of the lab. Teachers should look for:
- ability to perform scientific skills (10 points)
- accuracy in collecting and recording the data (20 points)
- accuracy in stating observations (10 points)
- accuracy in analyzing the results and drawing conclusions, including showing work on how the percentage was calculated and the accuracy of those calculations (10 points)

Independent Inquiry
Possible rubric: Students receive 16 points for completing each challenge (48 points total):
- completing a challenge (3 points)
- recording measurements in a table (3 points)
- showing work on how the percentage was calculated (5 points)
- accuracy on calculations (5 points)

Extra points for challenge 2 only:
- achieving 100% consistency with size and shape (2 points)

Resources: You may wish to use these resources either as background or as a resource for students to use in their inquiry-based design:
- An example of an article that tells about the increase of thefts for catalytic converters: (SB Independent article www.wpi.edu/About/History/Profiles/catalytic.html).
- The Microbial Lava Lamp: Teachers Guide and Student Guide (pdf), By Dr. Paul Tomasek, California State University, Northridge,.. Information on sources of materials is also available at this site. http://www.csun.edu/~hcbio029/.
- How Catalytic Converters Work - http://auto.howstuffworks.com/catalytic-converter.htm
- Wikipedia Catalytic Converters - http://en.wikipedia.org/wiki/Catalytic_converter

Microbial Lava Lamp

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Source	Items
Grocery or hardware store	• cheesecloth or plastic screen
Local pharmacy or grocery stores	• 3% hydrogen peroxide • medicine cups • plastic cups & containers
http://willpowder.net/ and also scientific suppliers http://www.flinnsci.com/store/Scripts/ck_prodList.asp	• alginate
Potters Industries Inc. PO Box 840, Valley Forge, PA 19482-0840 (610) 651-4700	• Spheriglass glass powder
Sunnyside Sea Farms, 475 Kellogg Way, Goleta, CA (805) 964-5844 http://www.seafarms.com	• alginate • calcium chloride
Fisher Scientific **(or other scientific suppliers such as Sargent-Welch)** http://www.fishersci.com	• manganese dioxide powder (30 ml) • calcium chloride (30 ml) • Vernier calipers • 100 mm petri dishes • dropping pipettes • glass stirring rod • plastic syringes • hand lens or stereomicroscope

National Science Education Standards (Grades 9–12)
Content Standard A: Science as Inquiry

- Abilities necessary to do scientific inquiry
- Understandings about scientific inquiry

Content Standard B: Physical Science

- Structure and properties of matter
- Chemical reactions

Content Standard E: Science and Technology

- Abilities of technological design
- Understandings about science and technology

California Science Education Standards (Grades 9–12)
Chemistry, Content Standard 6: Solutions

a. Students know the definitions of *solute* and *solvent*.

Chemistry, Content Standard 8: Reaction Rates

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a. Students know the rate of reaction is the decrease in concentration of reactants or the increase in concentration of products with time.
b. Students know how reaction rates depend on such factors as concentration, temperature, and pressure.
c. Students know the role a catalyst plays in increasing the reaction rate.
d. Students know the definition and role of activation energy in a chemical reaction.

Investigation and Experimentation, Content Standard 1

a. Select and use appropriate tools and technology to perform tests, collect data, analyze relationships, and display data.
b. Identify and communicate sources of unavoidable experimental error.
c. Identify possible reasons for inconsistent results, such as sources of error or uncontrolled conditions.
d. Formulate explanations by using logic and evidence.
g. Recognize the usefulness and limitations of models and theories as scientific representations of reality.
j. Recognize the issues of statistical variability and the need for controlled tests.
l. Analyze situations and solve problems that require combining and applying concepts from more than one area of science.
m. Investigate a science-based societal issue by researching the literature, analyzing data, and communicating the findings.

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