KINETICS AND CATALYSIS

Concepts involved in the demonstration:

- Catalysis
- The effect of a catalyst on reaction rate
- Heterogeneous catalysis
- Homogeneous catalysis
- Gas phase reactions
- Intermediate species

Skills

- Making qualitative observations
- Experimental design

Catalysts are substances that have the ability to speed up a chemical reaction. A catalyst can be used over and over with no apparent loss to the catalyst; although in reality there is some loss due to secondary reactions. There are two basic types of catalysts. Homogeneous catalysis involves the use of a catalyst that is in the same phase as the reacting species. Heterogeneous catalysis involves the use of a catalyst that exists in a different phase from that of the reacting species. These two different types of catalysis are depicted in these demonstrations. In the catalytic reaction of potassium sodium tartrate with hydrogen peroxide, the cobalt chloride catalyst is in the same phase as the reactants. The students can see the progress of the reaction via the formation of the green activated complex. The students will also observe how the catalyst is regenerated by the reappearance of the pink cobalt (II) chloride color. In the catalytic oxidation of methanol, the platinum is a heterogeneous catalyst, where the platinum is in a solid state and catalyzes the oxidation of the methanol vapors. This reaction repeats itself as long as the methanol is not consumed and the platinum is left in the flask.

THE REPEATING "EXPLODING" FLASK A DEMONSTRATION OF HETEROGENEOUS CATALYSIS

Background

Heterogeneous catalysis is discussed in many general chemistry textbooks, but few students get to see this type of reaction. This demonstration can be used to illustrate heterogeneous catalysis and thermochemistry. Metals such as platinum, palladium and nickel can catalyze vapor phase reactions. In particular, they can catalyze the oxidation of alcohols. The explosion is actually a regular "bang" that accompanies the reaction with a period of 20 to 90 seconds. The loudness of the bang and length of the period depend on the type of metal, the alcohol and the size of the flask used. The explosion is due to the exothermic combustion of the alcohol vapor in the flask being ignited by the red hot metal, which in turn is slowly heated by the exothermic oxidation of the alcohol on the surface of the metal wire coil.

The reaction for catalytic oxidation of methanol:

CH₃OH(g) + 1/2 O₂(g) ----> CH₂O(g) + H₂O(g) ΔH° = - 156.3 kJ/mol

Materials

- 500-mL Erlenmeyer flask and/or 1000-mL flask
- A metal divider (0.3 0.5 mm thickness) made of inert metal (such as galvanized iron) that is longer than the depth of the flask and wide enough to just fit through the mouth.
- A catalytic coil, such as platinum, wound with a 3 5 mm diameter loops and made from 10 -15 cm length of wire that has a thickness between 0.3
 1 mm. The wound coil should be about 2 - 4 cm in length.
- Methanol: 50 75 mL for the 500-mL flask and 100 150 mL for the 1000mL flask
- Fine inert wire (such as copper) from which to suspend the catalytic coil.

Procedure

- 1. Heat the alcohol in the flask until it begins to boil. Quickly place the metal divider into the flask.
- 2. Heat the catalytic coil in a Bunsen burner flame until red hot and then suspend it in the flask containing the methanol
- 3. The best position for the coil with respect to the alcohol surface is about halfway down the flask.
- 4. The first explosion should begin within minutes and will continue as long as the alcohol vapor remains.

Precautions

- 1. The wire holder for the catalytic coil becomes very hot and should be handled with tongs.
- 2. The flask and metal divider also get very hot during the reaction since it is exothermic. Both should be handled with care.
- 3. Sometimes the alcohol vapor ignites as the coil is lowered into the flask, and burns at the mouth of the flask. This happens when the alcohol is too hot. The flame can be quickly extinguished by placing a damp cloth over the top of the flask and smothering the flame.
- 4. A fire extinguisher should be handy in case the flask breaks.

5. It is possible to experience a build-up of formaldehyde, especially in a small room. Do not let the reaction go for a prolonged period of time.

Questions relating to the Demonstration

Heterogeneous catalysis is a very in industrial reactions. It is thought that this type of catalysis occurs by chemical absorption of the reactants onto the surface of the catalyst. In this case the methanol vapor and the oxygen gas. *Adsorption* is the attraction of molecules to a surface. In chemical adsorption the species are bound to the surface by intermolecular forces. During this process the bonds in the species are broken and this may be the basis of the catalysis. To get the students thinking about these ideas, as many of them are not aware of these concepts, the following questions could be asked.

- 1. Is this reaction occurring in the gas phase or in the liquid phase?
- 2. (a) Where is the reaction occurring?
 - (b) What observations provide evidence for this?
- 3. What role do you think that this type of catalyst plays in the chemical reaction?

References:

Rubin Battino, Dept. of Chemistry, Wright State University, Dayton OH 45435

Trevor M. Letcher, Douglas E.A. Rivett, Dept. of Chemistry of Chemistry and Biochemistry, Rhodes University, Grahamstown, 6140 South Africa

EFFECT OF A CATALYST ON THE RATE OF REACTION

In this demonstration two clear liquids are mixed together and warmed to 50°C with no noticeable change. A small amount of a third solution is added to it and almost immediately a reaction begins to occur. This is an excellent demonstration to show the effect of the catalyst. The students are able to see the intermediate species the catalyst forms as the reaction proceeds and how the catalyst is regenerated at the end of the reaction.

Materials

Reagent	Quantity for a Single Run	Stock Solution
Potassium Sodium Tartrate KNaC ₄ H ₄ O ₆ [•] 4 H ₂ O	25 g/300 mL	83.3 g/1000mL
6 % H ₂ O ₂ *	20 mL 30% per 100 mL	100 mL 30% per 500 mL
CoCl ₂ • 6 H ₂ O	1.0 g/25 mL	10 g/250 mL

*Note: Clairoxide[®] Liquid Developer, manufactured by Clairol[®], is 6% hydrogen peroxide and can be used instead of the 30% hydrogen peroxide, which is hazardous to use. Using the Clairoxide[®], which is known as 20-volume hydrogen peroxide, has an additional benefit; the students are reminded that chemistry materials are present in our everyday lives and can be found in grocery stores.

PROCEDURE

- 1. Prepare two1000-mL beakers. One will serve as a control.
- 2. In each of the two 1000-mL beakers mix 300 mL of potassium sodium tartrate solution and 100mLof the 6% hydrogen peroxide solution.
- 3. Heat to the desired temperature {50°C-70°C).
- Remove from the heat and add the catalyst (CoCl₂, solution) to one of the beakers. Place the reaction vessels in a shallow container in case of overflow. The reaction is very vigorous at higher temperatures

Discussion

The tartrate ions are oxidized by the hydrogen peroxide to CO₂ and water.

5 H₂O₂ (aq) + KNaC₄H₄O₆ (aq)
$$\rightarrow$$
 4 CO₂ (g) + NaOH (aq) + KOH (aq) + 6 H₂O(I)

Without the catalyst the evolution of CO_2 is quite slow. With the cobalt chloride solution the reaction proceeds with the rapid evolution of CO_2 . This is an excellent demonstration of the formation of an intermediate species. The color change from pink to green to pink is easy to observe and can be timed to see the effect of temperature on the reaction rate (approx 100 sec, at 50°C to 30 sec at 70°C.

When the reaction is complete (no more bubbling), the catalyst is regenerated. This is shown by the formation, once again, of the pink color, indicating the regeneration of the (pink) $CoCl_2$ catalyst. To emphasize that the catalyst has been regenerated, add a small amount of spent solution to the second 600-ml beaker, cover with a watch glass, and observe. Students will note a repeat of fairly rapid bubbling, as well as formation of new green intermediate followed by the return to the pink coloration.

HAZARDS:

- 6% hydrogen peroxide is an oxidizer and a skin and eye irritant
- 30% hydrogen peroxide is severely corrosive to the skin, eyes and respiratory tract. It is a very strong oxidant. A dangerous fire and explosion risk exists.

QUESTIONS RELATED TO THE DEMONSTRATION

This reaction is an example homogenous catalysis, which is the use of a catalyst in the same phase as the reacting species. Students should be made aware that the catalyzed reaction mechanism makes available a reaction path having an increased rate of reaction. This usually occurs by creating an alternate mechanism of lower activation energy. As the demonstration proceeds the students should be asked to make careful observations about the reaction. They should note the temperature and any evidence of a chemical reaction before the catalyst is added. They should also be making careful observations about the change in the color of the catalyst. To make them further aware of these concepts the instructor should be prompting with the following questions.

- 1. When the potassium sodium tartrate and the hydrogen peroxide are mixed, do you see any evidence of a reaction?
- 2. What color changes do you note after the cobalt (II) chloride has been added.
- 3. Is the catalyst a homogeneous or heterogeneous catalyst?
- 4. What evidence is there that an intermediate species is formed?
- 5. What role does this type of catalyst play in the chemical reaction?
- 6. What would happen if you carried out the reaction at a higher temperature? Would it speed up, slow down, or stay the same?
- 7. Try carrying out this reaction at different temperatures to see the effect of temperature on the reaction.