

# KINETICS AND CATALYSIS DEMONSTRATIONS

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**C**LASSROOM DEMONSTRATIONS ARE valuable additions to a lecture course in kinetics and catalysis. Over the last few years we have used a number of short demonstrations in class to show that catalysts can dramatically increase the rates of chemical reactions. These demonstrations are also used to show the different types of catalysts and their properties and the effects of temperature, concentration, and heat transfer on reaction rates. We have found, however, that videotapes of these demonstrations have many advantages over live demonstrations:

- Noise, odor and safety are all controlled for a videotaped demonstration
- Chemicals and solutions, which can degrade in a year, do not have to be reordered or remade each year
- Time is not spent setting up gas cylinders, beakers, hot plates, liquid nitrogen dewars, safety shields and so forth in a classroom. Setup of a VCR machine and a TV screen takes very little time
- Smaller and safer quantities of chemicals can be used. A 50 ml beaker will fill the entire TV screen when a zoom lens is used, and a white background makes color changes easily visible. Thus, a better demonstration results by videotaping a reaction in a 50 ml beaker than for a live demonstration with a 500 ml beaker
- An elevated 21-inch TV screen can be easily seen by all students in the class
- Videotaped demonstrations are guaranteed to work on the first try

Short descriptions of each of the demonstrations that we have videotaped and shown

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during the semester are presented. Because we cover a range of topics in the lectures, demonstrations are shown for acid and zeolite catalysis, solution catalysis, and supported and unsupported metal catalysis. In general, these are not new demonstrations; they have been described previously and are compiled here for easy use. The resulting videotapes are not professional quality, but they demonstrate the important points very effectively. *Note that many of these reactions are dangerous and must be done carefully in a hood and with safety glasses.*

## 1. CLOCK REACTION

This is the standard kinetics demonstration that can be used to show the effects of temperature, concentration and a catalyst on the rate of reaction [1, 2]. Fifty ml of solution A and 50 ml of solution B are combined in a 250 ml beaker. Then, 50 ml of solution C are added, and the mixture is stirred until reaction is complete, as indicated by a color change from cloudy to blue. For the solution concentrations listed below, at room temperature the blue starch complex forms after 25 s.

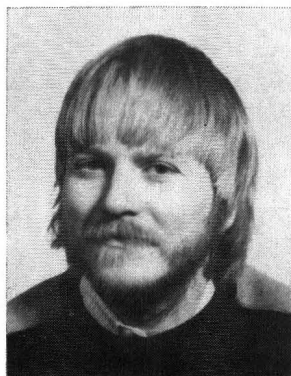
Since the reactions are not first order, reaction time is increased significantly by addition of distilled water to the mixture. Similarly, reaction time is decreased by heating above room temperature. By adding a small amount of  $\text{FeSO}_4$  solid, which acts as a catalyst [2], reaction time is decreased to 10 s.

### Solutions

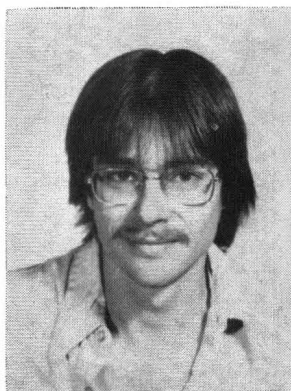
- A: 5.5 g  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  dissolved in distilled water to yield one liter of solution;
- B: 0.13 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  dissolved in distilled water to yield one liter of solution;
- C: 50 ml KI dissolved in 600 ml of 10% potato starch solution, which is then diluted with distilled water to one liter.

## 2. OSCILLATING REACTION

This demonstration, which has been called the color blind traffic light [3, 4], shows the unusual



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behavior that can occur in a complex reaction system. It is easy to prepare and is described in detail by Lefelholz [3] and Boulanger [4]. It can also be used to show the effects of temperature and concentration on reaction rates.

The following solution is prepared in 3 N  $H_2SO_4$ :

0.005 M ceric ammonium sulfate

$(Ce(NH_4)_4(SO_4)_4 \cdot 2H_2O)$  ;

0.1 M malonic acid ( $C_3H_4O_4$ ) ;

0.05 M potassium bromate ( $KBrO_3$ ).

This solution is heated with agitation to  $40^\circ C$  and about 40 drops of the redox indicator ferroin (1,10-phenanthroline ferrous sulfate complex) are added dropwise. The solution immediately begins to change color from violet to blue and back to violet, with a period of about 50 s, as the concentrations of  $Ce^{3+}$  and  $Ce^{4+}$  oscillate periodically. The ferroin changes color as the oxidation state of Ce ion changes. The color change is clearly recorded by the camera against a white background. The period of oscillation depends on the degree of agitation provided by a magnetic stirrer, and is lengthened to 72 s upon addition of about 2 ml of indicator added at once. The solution concentrations are not critical but a single portion of ferroin added at once can create a long induction period [4].

### 3. HYDROGEN OXIDATION IN AIR

Oxidation of hydrogen in air over supported metal catalysts is used to show activity differences

of metals and the increase in rates that occurs with increased surface area. This demonstration also shows how heat removal can be limiting for exothermic reactions on supported catalysts.

A half-inch diameter, vertical brass tube is used to support a wire mesh screen on which a piece of tissue paper is placed. A catalyst sample is placed on top of the tissue, and hydrogen from a gas cylinder is flowed into the bottom of the tube through a tygon tube. For 0.3 g of a 5% nickel/silica catalyst, nothing is observed. Similarly for 0.3 g of pure platinum wire, no visible indications of reaction are seen. However, when a 0.3 g sample of a 5% platinum/silica catalyst is placed on the tissue, significant reaction occurs. The heat released by the reaction heats the catalyst until it glows red, and after less than a minute the tissue paper ignites. Small quantities of catalyst and thus low flow rates of hydrogen can be used, since the camera zoom lens is used to fill the screen with the catalyst and make this demonstration visible.

### 4. HYDROGEN-OXYGEN EXPLOSION

A more dramatic demonstration of hydrogen oxidation results when the oxygen concentration is increased by using pure oxygen instead of air [5]. A 6-oz taped bottle is filled with approximately a 2:1 mixture of  $H_2$  and  $O_2$  and then sealed with a rubber stopper. The exact ratio is not critical. The stopper is then removed and approximately 0.1 g of powdered, supported platinum catalyst is dropped into the bottle from a spatula. The mixture reacts explosively, and very loudly. When a piece of white paper is taped to the back of the bottle and low background light is used, a flame is seen shooting out the top of the bottle. This demonstration shows that catalysts can dramatically increase reaction rates; the reaction is extremely slow at room temperature in the absence of a catalyst. It can also be used to show the effect of surface area since a platinum wire dropped in the bottle does not cause an explosive reaction.

Larger bottles (10 oz and 15 oz) have been used for this demonstration, but they are not safe for a classroom demonstration because the noise is almost deafening. This demonstration should be done with great care; the platinum catalyst must be completely cleaned out of the bottle before a repeat experiment is attempted.

### 5. ACID-BASE PROPERTIES OF SOLIDS

The fact that many solid oxides which are used as catalysts or catalyst supports have acidic sites

and basic sites is easily shown using indicators for powders suspended in solution. No quantitative measure of acid strength is made, but the presence of acidic and basic sites and the differences between oxides are easily shown.

A series of 250 ml beakers are each filled with 50 ml of distilled water which contains a small amount of dissolved bromothymol blue indicator. This indicator changes from yellow to blue over a pH range from 6.0 to 7.6. In our case it was yellow in distilled water. Ten to fifteen grams of a powdered oxide ( $\gamma$ -zeolite,  $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{SiO}_2$ ) are added to each beaker. Malonic acid and sodium hydroxide are also added to two beakers to show the similarity between liquid acids and bases and solid acids and bases.

The malonic acid produces no color change. The zeolite powder produces a dirty-yellow, cloudy appearance in the solution, which turns light green over a period of minutes. The silica-alumina powder does not change the color of the solution significantly. The titanium dioxide powder forms a milky suspension with the water, with a slight blue-green tinge. Alumina powder changes the solution to a deep blue-green color. Magnesia powder produces a deep blue when added. The  $\text{NaOH}$  solution turns the indicator solution a very dark blue. Two samples of powdered  $\text{SiO}_2$  were used. One caused no appreciable color change of the solution, indicating acidity, while the other sample turned the solution a dirty blue-green of intensity less than that of the  $\text{Al}_2\text{O}_3$  mixture. Differing treatment histories of these silica samples are probably the cause of this discrepancy.

The acid-base properties of most of these solids are strongly dependent on such factors as temperature, duration of heat treatment, and the amount of adsorbed water. The order of acid strength given for these solids will be different if a non-polar solvent is used instead of water [6]. Water interacts significantly with solid surfaces and can alter the acidic character. Impurities in the solids can also affect acidity. For example, aluminas are usually weakly acidic, but this can be enhanced significantly by impurities such as a chloride. Some commercial aluminas are basic, in that a suspension in water exhibits a pH above 7, which is caused by the presence of sodium.

## 6. HIGH-TEMPERATURE ZEOLITE REACTIVITY

A rare-earth exchanged x-zeolite can be used to show the properties of solid acids for hydrocarbon cracking [7]. Three and one-half grams of

paraffin wax are placed in each of two 50 ml beakers and heated with a hot plate to  $260^\circ\text{C}$ . At this temperature, the wax is a liquid. Into one beaker is dropped one gram of the zeolite powder, and into the other beaker  $\text{SiO}_2$  or  $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$  powder is added. A slight bubbling is seen for silica or  $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ , but vigorous reaction occurs almost immediately for the paraffin in contact with the zeolite. When both beakers are cooled after a few minutes of reaction, the paraffin in the zeolite-containing beaker has turned dark, while the paraffin in the other beaker has not. This demonstration is particularly convenient on videotape since it is not necessary to wait in class for the cooling to occur. Also, a rather unpleasant odor is given off by the hot wax, and 50 ml beakers minimize this. These small beakers would be difficult to see in a live demonstration, however.

## 7. LOW-TEMPERATURE ZEOLITE REACTIVITY

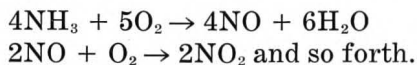
The ability of catalysts to accelerate reactions even at very low temperatures is shown by isoprene cracking below  $-146^\circ\text{C}$  [7].

Approximately 5 ml of isoprene (2-methyl-1,3-butadiene, m.p.  $-146^\circ\text{C}$ ) in a test tube are frozen by immersion in liquid  $\text{N}_2$  for about one minute. The test tube is mounted on a stand in front of a white background for good contrast, and a gram of baked zeolite powder is poured into the tube on top of the solid isoprene. As the isoprene melts and contacts the zeolite, it immediately cracks and turns a light brown color. When a powdered silica-alumina catalyst is used, the isoprene remains colorless. The color change of the zeolite-contacted isoprene is pronounced enough to be easily recorded by the camera, providing that ice, which deposits on the side of the tube after removal from the  $\text{LN}_2$  bath, is periodically wiped off. A more pronounced color change, with the formation of a black solid, occurs when two grams of baked zeolite are added to 5 ml of isoprene. Also, some spattering of the zeolite occurs. With more zeolite, a violent reaction occurs and the entire mass turns black [7].

## 8. COPPER CATALYSIS OF $\text{NH}_3$ OXIDATION AND SODIUM PEROXIDE DECOMPOSITION

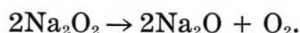
This demonstration, described by Koch [8], shows both gas-phase and liquid-phase catalysis. Copper metal is used to catalyze the oxidation of ammonia, and cupric ion catalyzes the decomposition of sodium peroxide. Ammonia is obtained from 60 ml of concentrated ammonium hydroxide

in a 250 ml flask. Four grams of sodium peroxide are slowly added and some decomposition takes place. A cone of copper (made from a circle of copper foil) of approximately one inch diameter is heated to a red glow and suspended in the flask about two inches above the liquid surface. The cone is suspended from a wire through a hole in the top of the cone. The hot copper catalyzes the oxidation of gas-phase ammonia to NO and H<sub>2</sub>O [8]:



The cone continues to glow as heat is generated by the oxidation reaction.

The generation of oxygen can also be catalyzed by the addition of 1 M copper sulfate, since cupric ion catalyzes the decomposition of sodium peroxide:



A drop of the copper sulfate solution will increase the rate of oxygen production significantly. An almost detonating mixture can be formed [8].

## 9. AMMONIA OXIDATION AND REACTOR STABILITY

An experiment that is similar to the previous one can be used to demonstrate both catalytic activity and reactor stability. Hudgins [9] described this experiment in detail, and it will be only briefly summarized here. Concentrated ammonium hydroxide solution is placed in the bottom of a 200 ml erlenmeyer flask, and a copper wire is heated to incandescence and suspended above the solution. Copper wires of different diameters (No. 12, 18, 24), were used; the smallest wire melts, and the glow of the largest wire very slowly diminishes. The No. 18 wire, however, continues to glow for some time. Hudgins [9] indicated these results for different size wires demonstrate control of a catalytic reaction by heat transfer across a film. However, it appears that the heat and mass transfer coefficients increase as the wire diameter decreases for a horizontal wire [10]. Thus, this reaction may be controlled by mass transfer.

To demonstrate reactor stability, the wire is withdrawn from the flask and then quickly replaced when the glow fades; the wire starts glowing again. A larger perturbation in temperature extinguishes the glow. This demonstration can also be used to show that transient temperatures are easily produced in catalyst particles with exothermic reactions [9]. The glowing wire shows up extremely well on videotape.

## 10. OXIDATION OF TARTARIC ACID

This is an excellent example of solution catalysis, the role of a complex as an intermediate, and the effect of temperature on reaction rate [11]. Color changes, which indicate the presence of an intermediate, are marked and show up well on the videotape when filmed against a white background.

A 0.3 M aqueous solution of potassium sodium tartrate (KNaC<sub>4</sub>H<sub>6</sub>O<sub>6</sub>·4H<sub>2</sub>O) is prepared, and 300 ml are mixed with 100 ml of 6% H<sub>2</sub>O<sub>2</sub> in a 700 ml beaker on a stirred hot plate. The tartrate solution is heated to 50°C with magnetic stirring, and 25 ml of a 0.3 M aqueous CoCl<sub>2</sub> solution is added. Immediately after addition of the cobalt, the solution is light pink. After a few-second induction period the solution changes to a dark green as a cobalt-tartrate complex is formed as an intermediate. The oxidation of tartrate is evidenced by the vigorous evolution of CO<sub>2</sub> gas. This frothing necessitates use of the large beaker. As the reaction goes to completion and gas production stops, the solution returns to its original light pink hue as the original cobalt is reformed. The total time of the reaction, as measured by this color change, is 133 s. At 60°C the induction time is markedly shorter, the reaction more vigorous, and the reaction time measured by the color change is 63 s. No reaction is observed before addition of the cobalt solution at either temperature.

## 11. CATALYST PREPARATION

The various steps in preparation of a supported nickel catalyst by impregnation were videotaped over several days, so that the preparation steps can be condensed into a few minutes of tape. This videotape shows how promoters and nickel salts are added from solution by incipient wetness, and it shows the rapid uptake of water by a porous solid. Samples of the support after various stages in the preparation are also shown in class.

## 12. ADDITIONAL DEMONSTRATIONS

Other demonstrations that may be useful include Raney nickel oxidation, to demonstrate the high reactivity of a high surface area metal, and silica gel preparation from solution.

We usually include a laboratory tour to show the equipment used for catalysis research in chemical engineering. We plan to videotape the operation of this equipment so that the class will have a better idea of its purpose and use. At present, this lab tour includes an Auger spectro-

meter, an XPS spectrometer, a static chemisorption apparatus, differential reactors with gas chromatography, a mercury porosimeter, and a temperature-programmed desorption system.

Since we also discuss bulk and surface structures and Miller indices notation, cork ball models have been used for these structures. Close-up videotapes of the various structures and of zeolite structures will allow students to study them at their leisure. The bulk structures that demonstrate Miller indice notation were prepared using templates for the different symmetries [12].

## SUMMARY

Eleven kinetics and catalysis demonstrations have been briefly described. By videotaping these demonstrations, we are able to easily use them each year in a catalysis and kinetics course. Videotaping improves the demonstrations, makes them more visible and safer, and results in better use of class time. □

## ACKNOWLEDGMENTS

We would like to thank John Ma for his help on some of these demonstrations and Professor David E. Clough for obtaining the videotaping system and encouraging us to use it.

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## REVIEW: Fluidized-Bed Processes

Continued from page 109.

The book is intended mainly for use by final-year undergraduate students or graduate students in chemical engineering. In view of its contents, however, the book should be regarded more as a reference monograph than as a classroom text. The book will also be a useful reference for researchers, development engineers, and designers in the field of fluidization technology. In fact, the book can be recommended to anyone who wishes to be initiated into the science and art of fluidized-bed chemical processes.

The book is indeed concise, containing only 222 pages. Obviously it is extremely difficult, if not impossible, to cover all aspects of fluidized-bed chemical processes in detail in a book of this size. Unfortunately, some topics of current importance are omitted. Examples are the stochastic behavior of fluidized-bed chemical processes and the performance of relatively shallow and wide fluidized bed (or the so-called horizontal fluidized bed). According to Bukur, Carem and Amundson (Chapter 11 of *Chemical Reactor Theory: A Review*, Edited by Lapidus and Amundson, Prentice-Hall, Inc., Englewood Cliffs, NJ, 1977), "It is our view that probably no deterministic model will ever describe such reactors with any precision." The horizontal flow fluidized beds have been used extensively to process solid materials because these fluidized beds tend to yield better quality and higher conversion of solid products than conventional vertical fluidized beds. □

## PROBABILISTIC ENGINEERING DESIGN: PRINCIPLES AND APPLICATIONS

by James N. Siddall

Marcel Dekker, Inc., 1983; 544 pages, \$65.00

Reviewed by Ernest J. Henley  
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Probabilistic design and risk analysis have been my 'bread and butter' research activities for the past fourteen years. It's been a lonely road: most chemical engineering academicians appear to have convinced themselves, and each other, that the path to the podium lies in double-precision, deterministic models (based, frequently, on experimental evidence as reliable as the Las Vegas gaming tables). At our shop, the required BS course in statistics has gone the way of under-