Construction and Use of the Gas Reaction Catalyst Tube*[*]

As shown in the figures, the experimental apparatus consists of a 60 mL syringe containing the gaseous reactants connected to a gas phase catalyst tube containing elemental palladium on a ceramic support. The other end of the catalyst tube is connected to another 60 mL syringe where the products will be collected. This second picture shows our homemade catalyst tube in more detail.

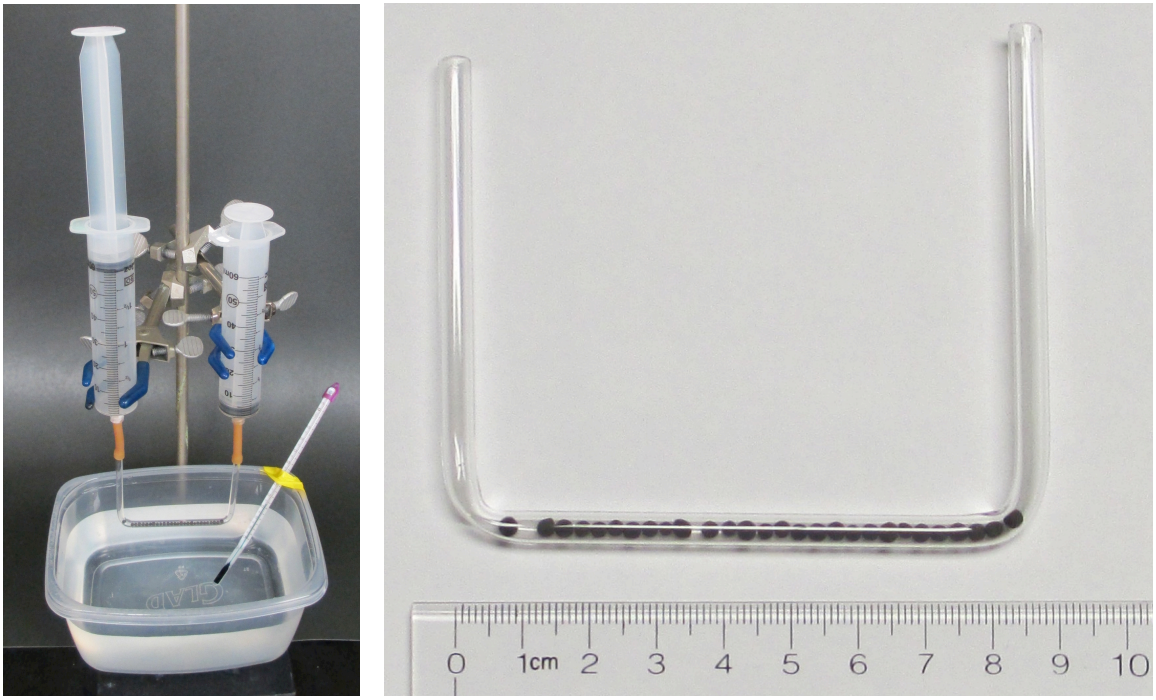

Figure. Experimental set up of catalyst, reactants and product syringes.

A 25-cm length of borosilicate glass tubing, 6 mm OD, is fire-polished on one end until the opening becomes slightly constricted. A 90º angle is formed in the tubing approximately 8 cm from one end with an oxygen/natural gas torch. If the bend slightly constricts the inside diameter, that can serve the useful purpose of preventing the Pd beads from escaping. At this point, the tubing should have the shape of the letter "L". We will next place Pd-coated alumina beads into the tubing via the longer arm of the "L".

A disposable wide-step plastic transfer pipet can be formed into a funnel by cutting off the stem so that it can be slipped over the "L"-shaped glass tubing. The top half of the bulb can be cut off to create the funnel. Wearing gloves, beads of 0.5% Pd

[*] From the Supplemental Material provided in our article: Heterogeneous catalysis: The Horiuti-Polanyi mechanism and alkene hydrogenation. Bruce Mattson*, Wendy Foster, Jaclyn Greimann, Trisha Hoette, Nhu Le, Anne Mirich, Shanna Wankum, Ann Cabri, Claire Reichenbacher, and Erika Schwanke, ***Journal of Chemical Education,*** **2013**, **90** (5), 613–619.

on alumina are dropped, one-at-a-time, into the tube. In our experience, the larger beads do not fit in the tube. After the beads inside the glass tube extend a length of 4 – 8 cm, the second 90^{o} bend can be formed. Again, a slight constriction prevents the escape of the Pd beads. The second end of the U-shaped tube is fire-polished. Allow 30 minutes to construct the catalyst tube. The catalyst tube can be used indefinitely.

Volume and residence time

Using a separate empty tube, the internal volume of our catalyst tube was established to be 0.1 mL per cm in an empty tube. This was done by filling the glass tube with water, measuring the mass and length of the water in the tube. Mass is converted to volume. The catalyst tube shown above has 8 cm of beads. Knowing these values can be useful in that the reaction only takes place when the gas mixture is in the presence of the catalyst. If 60 mL are passed in 30 s, the rate is 2 mL/s. Given that 0.8 mL gas mixture can be in the presence of the catalyst at any point in time. This gives an average residence time of 0.8 mL/ 2 mL s^{-1} = 0.4 s.

Moles of catalyst

The tube pictured contains 0.61 g of 0.5% Pd on alumina, which equals 3.0 mg Pd or 2.9 X 10^{-5} mol Pd. This amount of catalyst cost $1.42.

Working air-free

Syringes and the catalyst tube are purged of air with argon. This is done by connecting the syringe to the argon tank equipped with a regulator valve with a needle valve for fine flow control. Latex tubing connects the needle valve to a bubbler. The bubbler is filled to a depth of 3 cm above the opening of the inside tube with mineral oil; this provides a pressure maximum. The tubing to the argon source and the tubing to the equipment (syringes, catalyst tube) are connected to the horizontal T-part of the bubbler; the side arm is left open to the air. An alternative bubbler device can be made with glass tubing, a T-connector, a large test tube and a 2-holed stopper. As a technique, one should keep an eye on the bubbler and always maintain positive pressure. As long as bubbles are present, argon pressure is positive. If argon is being withdrawn too fast (as would happen if the plunger of a syringe were pulled out too fast), the bubbles would stop and the mineral oil would climb inside the inner tube of the bubbler. This indicates negative pressure in the system and should be avoided.

The argon purge of syringes follows the sequence: The syringe with plunger fully inserted is connected to the argon source tubing, the syringe is filled with argon by withdrawing the plunger to the 60 mL mark, the tubing is disconnected, the argon is discharged into the air by pushing the plunger fully inward, the argon source tubing is reconnected and the process is repeated at least two more times. When not in use, syringes are kept capped. If argon is not available, nitrogen also works.

Tubing

Short pieces (4 cm) of latex tubing are used to connect syringes to each other and to the catalyst tube. Similar pieces are used for drying tubes. A syringe filled with argon is used to purge the connecting tubes of air just prior to use in connections.

Pretreatment of the Catalyst

Prior to each experiment, the catalyst tube must be prepared to minimize the presence of water, oxygen and residual substances from previous experiments. With a stream of argon flowing through the glass catalyst tube, the catalyst tube is heated over a Bunsen burner flame for a period of 3 minutes with constant motion to prevent hot spots. The catalyst tube is allowed to cool to room temperature with argon flowing. The catalyst tube is then connected to two syringes that were previously purged of air with argon. Short pieces (4 cm) of latex tubing are used to connect syringes to each other and to the catalyst tube. The treated catalyst tube can be stored by connecting it to two argon-purged syringes. This creates a closed system under argon.

Preparation of the Drying Tube

If gases are prepared by using one of our in-syringe methods, it may be useful to dry the gases before using them. This is true if the product gases are to be analyzed by mass spectroscopy or NMR spectroscopy, but is generally unnecessary if product analysis is being done by qualitative chemical tests. The drying tube is constructed from a 5 cm length of 1/8-in latex tubing. A tiny cotton plug (from an ordinary cotton ball) is inserted into one end using a plastic pipet as a poker. About 0.5 g of a drying agent is then added to the tube, followed by another cotton plug. We have used either anhydrous, granular Na_2SO_4 or anhydrous, powdered $MgSO_4$. Drying tubes are prepared fresh for every experiment.

Materials

Fisher, Flinn and Educational Innovations sell all of the items needed. Fisher has the best prices for syringes bought in boxes of 30. Flinn and Educational Innovations are excellent sources of syringe caps and latex tubing.

Reagent	Vendor (used for example only)	Product number and price (2012)
60 mL plastic syringes	Fisher Scientific	13-689-8; $60.65 for 30; $213.62 for 4 pks x 30
Syringe caps	Flinn Educational Innovations Fisher	AP8958; ten-pack, $2.40; GAS-160, ten-pack, $2.95 14-823-31 case of 50 $64.31
Latex tubing, 1/8-inch (3.175 mm) ID	Flinn Educational Innovations	AP2076; 10-ft, $7.15; GAS-220, 5-ft, $5.95

Experimental procedure

In a typical reaction, volume stoichiometry dictates a reasonable mixture. For example, equal volumes (30 mL) of each of alkene and H_2(g) would be used for a hydrogenation reaction (and 30 mL of product gas would be expected). Volumes are measured out in individual argon-flushed syringes and then combined into one of the syringes using a 4 cm latex connecting tube. The reactant syringe is attached to one end of the catalyst using a latex tube. The entire volume is passed through the catalyst tube submerged in a water (or ice) bath over the course of 30 seconds, for example. The reactants are passed in a smooth, continuous motion. Products are collected in another 60 mL syringe attached to the other side of the catalyst tube.

Preparation of samples using Gas Chromatography - Mass Spectometry

Approximately 10 µL of product is needed for this analysis. The injection syringe is flushed with at least one volume of sample gas and discharged before obtaining a sample for injection. The needle of the 10 µL syringe is directed through the opening in the 60 mL syringe. The large syringe is held with the opening upright if the gas sample is heavier-than-air, such as butane, or with the opening downward for lighter-than-air gases such as methane. The GC-MS is set to mild conditions, only reaching 40ºC in the oven and as low of an ionization energy as possible to minimize fragmentation.

Preparation and analysis of samples using ^{1}H-NMR

An NMR tube is filled to the appropriate level with deuterochloroform. A thin-stem plastic transfer pipette is stretched to form a long, very thin capillary. The bulb and unstretched ends are cut off, leaving only the capillary portion. The tubing is inserted into the 60 mL syringe containing the product gases to be analyzed. Teflon tape is wrapped around the opening of the syringe and the capillary tube to form a gas-tight seal. The other end of the capillary tube is inserted to the bottom of $CDCl_3$ in the NMR tube. In ten 1 mL increments, the product gas is slowly passed through the solvent forming a stream of small bubbles. After each increment, the NMR tube is capped, and shaken to dissolve product gas above the surface of the solvent. This process is repeated ten times. Some gases such as butane are very soluble and such an elaborate procedure can be simplified considerably.