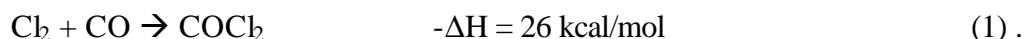


ICE – Microfluidics Module

Due Tuesday February 20

Problem 2

Economies of scale usually lead to large facilities from where chemicals are shipped. However, safety and environmental concerns could shift the current mode of operation towards smaller plants located near the intended point of application. This is particularly the case for hazardous and toxic chemical intermediates that have serious storage and shipping constraints. One such intermediate used throughout the chemical and pharmaceutical industry is phosgene (COCl_2 , carbonyl dichloride), manufactured from gaseous chlorine and carbon monoxide over activated carbon:



Phosgene is widely used as a chemical intermediate for the production of isocyanates used in polyurethane foams and in the synthesis of pharmaceuticals and pesticides. Processes using phosgene require specialized cylinder storage, environmental enclosures, pipelines, fixtures under negative pressure, and significant preventative maintenance. Moreover, phosgene is under a variety of transportation restrictions. As a consequence, most phosgene is consumed at the point of production. Off-site production often necessitates out-sourcing not only the phosgene synthesis, but also a set of sequential processing steps in order to get to a safe, transportable compound. Microchemical systems stand to provide an opportunity for flexible point-of-use manufacturing of chemicals such as phosgene. Banks of reactors can be turned on or off as needed to maintain as close to zero storage as possible. Single reactor failures would lead to extremely small chemical releases.

In this problem, you are to explore phosgene synthesis in a silicon based micropacked-bed reactor as an example of a safe on-site/on-demand production of a hazardous compound. Preliminary results have been collected by Sameer Ajmers and Matthew Losey (MIT, Chemical Engineering) with the reactor illustrated in Figure 1. The microreactor is fabricated out of single crystal silicon with standard microfabrication processes developed for integrated circuits and MEMS. The geometry is defined using photolithography and created with silicon etching. The reactor consists of a 20 mm long, 625 μm wide, 300 μm deep reaction channel (3.75 μL volume) capped by Pyrex. Figure 1b shows a scanning electron micrograph (SEM) of the inlet where flow is split among several interleaved channels (25 μm wide) that meet at the entrance of the reaction channel. Perpendicular to the inlet channels are 400 μm wide loading channels used to deliver catalyst particles to the reactor. Catalyst is loaded by placing a vacuum at the exit of the reactor and drawing in particles through the loading channels. At the outlet of the reaction chamber, a series of posts with 25 μm gaps acts as a filter to retain the catalyst

bed (Figure 1c). There are also four 325 μm wide channels perpendicular to the reaction channel along its length for holding thermocouples. Access ports for flow come from underneath at the inlet (not shown in Figure 1), the reactor exit, and at the ends of the catalyst loading channels.

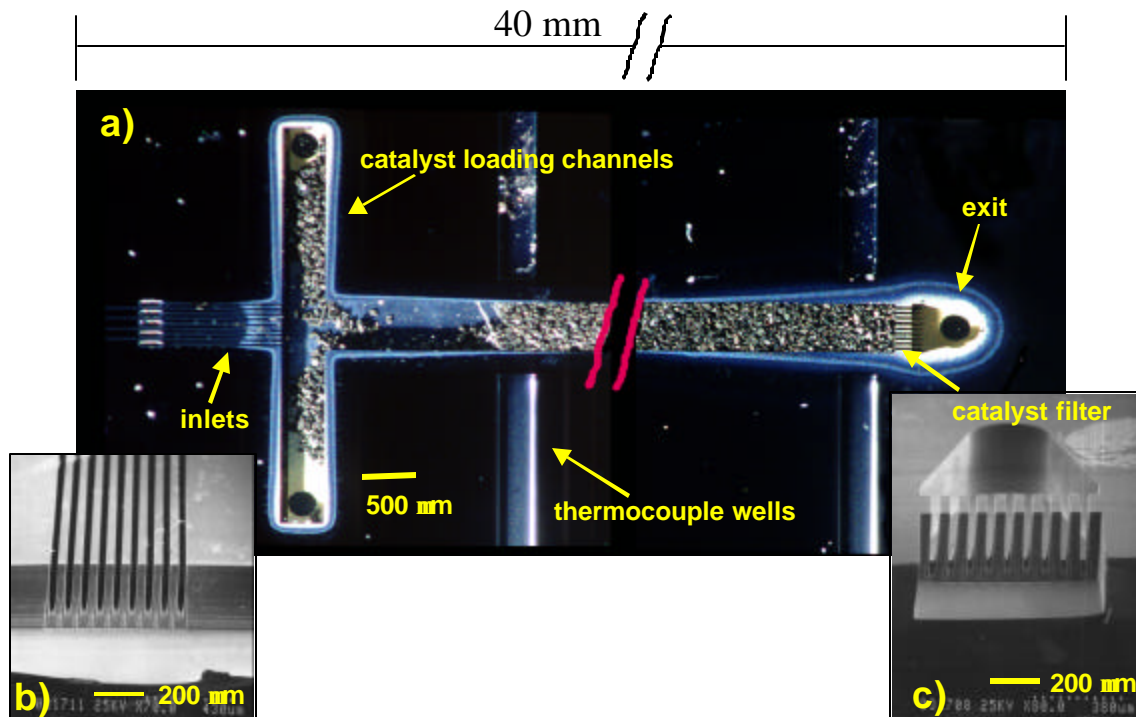


Figure 1. Microfabricated silicon packed-bed reactor. a) Top-view of reactor partially loaded with 60 μm activated carbon particles. The reactor channel is 20 mm long. The image is spliced to fit the 20 mm reaction channel by omitting the long channel mid-section. b) SEM of the 25 μm wide interleaved inlets. c) SEM of the catalyst filter structure.

The experiments were carried out with approximately 1.3 mg of 63 μm diameter activated carbon catalyst pellets. The catalyst pellets had a measured surface area of 850 m^2/g . The phosgene experiments were performed with a gas feed flowing at 4.5 sccm (Note: 1 sccm = 1 cm^3/min of gas flow measured at standard conditions: 1 atm, 0 $^\circ\text{C}$) with a 2:1 ratio of CO to C_2H_2 . The entire reactor could be considered isothermal. The exit of the reactor was fed directly into a vented exhaust hood. The absolute pressure at the inlet of the reactor was 132 KPa and was nominally atmospheric pressure at the exit. A pressure drop analysis showed that the pressure dropped linearly over the length of the catalyst packaging.

The following data were collected from the experiments:

Temperature (°C)	Conversion of chlorine
100	0.28
120	0.45
150	0.60
175	0.83

Shapatina *et al.* (*Kinetics and Catalysis*, **17** 3, 559 (1976)) describe the rate of phosgene formation by the following expression:

$$R_{rxn} = kP_{CO} \left(\frac{P_{Cl_2}}{AP_{CO} + P_{COCl_2}} \right)^{1/4}$$

where R_{rxn} = moles of phosgene produced per hour per gram of carbon catalyst,

P_i = the partial pressure of species i in atmospheres of pressure

A = equilibrium constant given by the equation: $A = 10^{\left(\frac{-1900}{T} + 3.40\right)}$,
where T is in Kelvin

k = the Arrhenius rate constant for this reaction determined in macroscopic experiments to be:

Activation energy (E_{act}) = 7.57 kcal/mol

Pre-exponential factor (A_0) = 22.6 mol/(h · m² · atm)

- (a) As a first step in the design process, the experimental conversions from the microchemical reactor are to be compared with predicted values from reactor calculations based upon the reported kinetic parameters. The reaction engineer on the design team has derived the following expression for the conversion (X) as a function of the catalyst (W).

$$\frac{dX}{dW} = \frac{kP(Y - X)}{(Y + 1 - X)F_{Cl_{20}}} \left(\frac{1 - X}{A(Y - X) + X} \right)^{1/4} \quad (6)$$

Here $F_{Cl_{20}}$ is the initial molar feed rate of Cl_2 , k is the rate constant described above, P is the pressure (which varies linearly with W), Y is the inlet ration of molar flows of CO and Cl_2 .

Derive Eqn (2) and solve it (numerically using your favorite tool, Matlab, Mapple, Excell...). Plot the predicted conversion along the length of the reactor for 175°C. Compare your predicted exit concentrations to those measured.

- (b) At what temperature is >99.5% of the Cl_2 converted to phosgene?
- (c) On the basis of your results from the above studies, design a multichannel microchemical system capable of producing 2 g/min of phosgene with >99.5% conversion of Cl_2 for use in laboratory experiments. In developing your design, you might want to consider the following questions. How many channels? What length of each channel? How should the channels be connected? If multiple, multiple-channel devices are to be used, how should they be connected to feed lines and exhaust? Will cooling be needed? How would you build the reactor(s)?