MASTER

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"Mechanistic Study of Catalytic Methanol Synthesis"

Submitted by: Harold H. Kung
Dept. of Chemical Engineering
Northwestern University
Evanston, IL 60201

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Project Objective:

Methanol is being considered as a likely candidate for fuel and starting raw material for chemicals in the future. The latter is already in practice to a certain extent particularly in the production of formaldehyde and acetic acid. The former has shown promise with the Mobil process that converts methanol into gasoline in a one step catalytic process. Because of its importance, it is of interest to understand the mechanism of the catalytic methanol production.

Currently methanol is synthesized from H_2 and CO with the latter being derived from oxidation of natural gas. This will probably still be the future process even if natural gas is to be replaced by coal. While the mechanistic aspects of the synthesis reaction might appear to be rather straight forward, it has been studied only very crudely, presumably due to the high pressure requirement. With the development of the Cu-Zn oxide catalyst, operating pressures as low as 50 atm. have been reported. The objective of this project is to develop a technique that can yield mechanistic information of such processes under the high pressure conditions. The central idea of the technique is based on the well-developed technique of temperature programmed desorption/reaction spectroscopy (TPDR). To accommodate the requirement of in situ detection, modification of TPDR is made such that the gas atmosphere will always be that of the reactant mixture. Suitable isotopic chemicals will have to be used to differentiate the desorbed molecules from the carrier gas.

Progress to-date:

In the last six months since the commencement of the grant, a graduate student, Mr. S. Y. Liu who finished his MS in Chemical Engineering in October has been recruited to work actively on this project as his PhD thesis research. Most of the effort has been on the design and on the actual construction of the

high pressure apparatus. A schematic of the apparatus is shown in Fig. 1. Essentially, it consists of three sections. The first section is for the reactant feed and purification. The CO feed is known to be a problem in many catalytic studies because of the relatively high concentration of metal carbonyl from the gas cylinders. Our experience suggests that these carbonyls can be decomposed by heating to about 250°C. Furthermore purchasing CO gas stored in aluminum tanks also provides noticeable improvement. The purification section will be located as close to the reactor as possible as shown in the diagram. Another feature of this section is the use of packed beds and multiple metering valves in every gas line. These are found useful in maintaining a steady gas flow rate in the system by providing a sizable pressure drop. Otherwise the on-off action of the back pressure regulator would cause fluctuation in the flow rate.

The second section is the reactor a more detailed drawing of which is shown in Fig. 2. The special feature of it is that it is housed in stainless steel protection shell which is purged with nitrogen. We feel that this is important because the reactor undergoes temperature cycles which would make leaking or failure of the connections there more likely than in other places.

The third section is for detection. We want to detect the products emerging from the reactor as soon as possible. Thus the opening to the mass spectrometer is situated near the outlet of the reactor. The major difficulty here is the necessary reduction of pressure from 20 or 30 atm down to 10^{-5} torr pressure for the mass spectrometer chamber. We intend to accomplish this by differential pumping. Essentially the gas from the reactor outlet will be leaked into a chamber pumped by a 4 in diffusion pump (see Figure 3). The gas in this chamber is then leaked into the mass spectrometer chamber which is pumped by an ion pump.

Between the reactor and the first chamber, and between the first and second chamber is a copper wall of about 2 in. thick with a 0.005 in. hole in it. Our calculation shows that the pressure in the first chamber can be as low as 10^{-2} - 10^{-3} torr. We have located a local company that can make such a small hole in the copper block for about \$100 each and we shall be sending our copper blocks to them very soon.

All of the major equipment needed, such as the mass spectrometer, the pumps, the back pressure regulators, and the flow meters have arrived. We are in the process of connecting the pieces together. We anticipate that initial tests on the apparatus can be performed in about two months.

Fig. 1

Fig 2

- 1) Conductors $\frac{3}{4}$ " Hex $\frac{1}{4}$ " NPT
- 2) Thermocouple $\frac{9}{16}$ " Hex $\frac{1}{8}$ " NPT
- 3) Tube connections $\frac{9}{16}$ " Hex $\frac{1}{4}$ " O.D.

top

bottom

Assemble reactor, section by section,
from top to bottom and
~~down~~ disassemble in reverse
order, from bottom to top.

Liu/Kung

Fig. 3