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Catalytic Pressure–Pulse Microreactor

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A pressure-pulse microreactor was designed to withstand pressures up to 70 atm. The reactor was attached to a gas chromatograph. A convenient procedure was developed for analyzing on the same column components ranging from ethane to those boiling up to 300°, and a method was worked out which made it possible to carry out microscale preparative separation of the individual compounds emerging from the reactor.

I. Introduction

With the development of a microcatalytic reactor and the pulse technique by Emmett and co-workers (*1*, *2*) a powerful experimental tool has been added for carrying out research in catalysis. The reactors originally developed were intended for work at atmospheric pressure. The present paper describes a microreactor suitable for pressures up to 70 atm; however, even higher pressures could be used.

The main difficulty associated with the design of a pressure microreactor connected to a gas chromatograph is of an analytical nature. The reaction product emerges from the reactor unevenly, because of gradual evaporation of liquid reactants and axial back-mixing of the gaseous product. This situation is further aggravated by the use of superatmospheric pressures. This phenomenon could be partially prevented by the use of narrow capillarys for the reactor which would force the reactants to travel through the reactor with a more uniform velocity. The use of such tubes, however, would not cancel the adverse effect of pressure and furthermore this system would not be too adaptable for catalytic studies, since, e.g., good mixing is mandatory when hydrogen is employed as a reactant and as a carrier gas and for that reason the use of relatively large diameter reactors is necessary. This requirement, however, creates conditions unfavorable for chromatographic analysis and for that reason a modified chromatographic analytical procedure was developed.

It was the authors' aim to build a reactor using commercially available parts, and therefore an extensive use was made of Swagelok parts and of standard stainless steel tubings and fittings.

The difficulty of injecting small amounts of samples, usually of 1 to 10 μliter into the microreactor in a reproducible way under pressure, was resolved by the use of a 50-μliter capacity microsyringe with a Teflon-tipped plunger (Type 1705N, Hamilton Company, Inc., Whittier, California). A modified inlet port was also designed to prevent leakage of the injected sample through the rubber septum. Injections against pressures of 100 atm were possible.

II. Apparatus

The reactor assembly (Fig. 1a,b) consisted of (a) microreactor placed in a furnace and joined to an inlet and outlet fitting, both surrounded with heated metal

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discs; (b) gas chromatograph attached directly to the microreactor; (c) temperature control panel; (d) gauges for measuring gas flow and pressures; (e) conventional gas purification units.

carrier gas was thus able to pass through this line to the annular space formed between the sleeve and the male part of the reducer, and then through the 1/32-inch hole down into the reactor tube. The con-

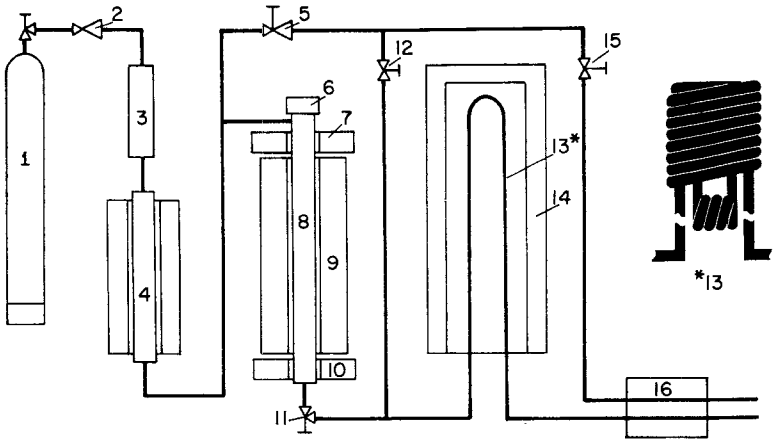

FIG. 1. Flow sheet of the microreactor assembly: 1, hydrogen tank; 2, pressure regulator; 3, deoxo unit; 4, dryer; 5, pressure regulator; 6, reactor inlet port; 7, inlet block heater; 8, reactor; 9, reactor heater; 10, outlet block heater; 11, flow control valve (reactor); 12, flow control valve (chromatograph); 13, chromatographic column; 14, column heater; 15, flow control valve (detector); 16, detector cell.

1. Microreactor. The microreactor was constructed from stainless steel tubing, 150 mm long. Two different sizes of reactors have been built; the larger one was made from 3/8-inch OD tubing and the smaller one from 1/4-inch OD tubing, both having a wall thickness of 0.8 mm.

The inlet part (Fig. 2) of the reactor was fabricated from a Swagelok reducer especially constructed for this purpose (Crawford Fitting Company, Cleveland, Ohio). A 1/16-inch diameter hole was drilled in the center along its axis. A section of the upper part of the reducer was made smaller in diameter and a 1/32-inch diameter hole was drilled in it, perpendicular to its axis. A tightly fitting sleeve was slipped over this end of the reducer and welded to it at both ends. The top weld was machined off on a lathe in order to leave a smooth surface and the top part of the sleeve was threaded to fit the rubber septum retaining nut. The 1/8-inch OD gas inlet was inserted in the hole, drilled previously in the sleeve, and welded. The nection between the reactor and the inlet was made of standard Swagelok parts.

A stainless steel septum holder disc, the inside of which was slightly conical, was screwed to the top part of the inlet. A small air jet was directed to the top in order to prevent melting of the silicone rubber disc.

The outlet (Fig. 3, left) consisted of a standard Swagelok reducing union, the smaller size end, 1/8-inch inside diameter was connected to the inlet port of the chromatograph through a precision valve and a transfer line.

For both sizes of the reactor an alternate outlet was also constructed (Fig. 3, right), consisting of a Swagelok "Tee" which made possible the use of an internal thermocouple. The thermocouple well consisted of thin-walled 1/8-inch OD tubing, closed at one end.

2. Heating section. The furnace for the reactor was constructed from two semicircular heating elements (50 000 series, Lindberg Hevi-Duty, Watertown, Wiscon-

sin) surrounded by an asbestos cement insulation and by an outside cover made from thin stainless steel sheet. The two halves of the furnace were connected by hinges. Thin-walled ⅛-inch OD and about

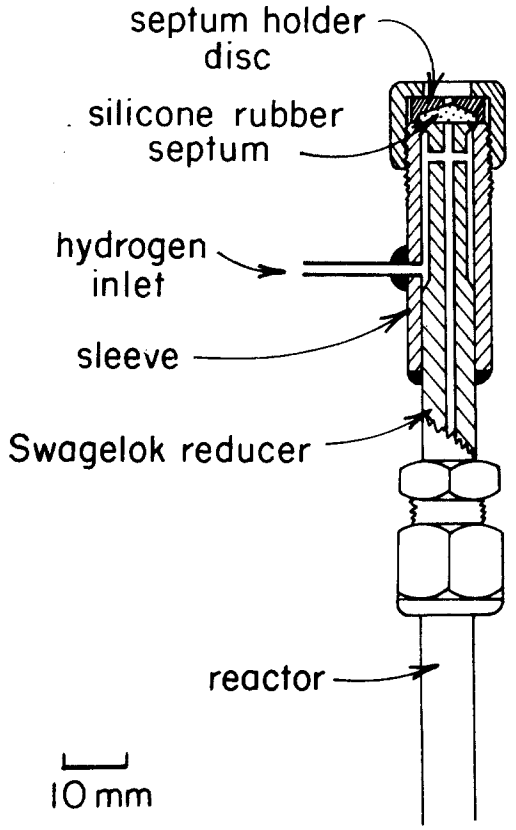

FIG. 2. Inlet port design.

120 mm long stainless steel tubing was attached close to the inside wall of one of the heating elements. The tubing acted as a thermowell to accommodate the thermocouple for the furnace temperature controller.

The inlet and outlet heating blocks were machined from stainless steel discs with holes in the center to fit the inlet and outlet sections of the reactor. Both heating blocks contained wells for the 700-W cartridge heaters (Watlaw Firerod Heater, Kelburn Engineering Company, Chicago, Illinois) and separate holes for the thermocouples for the measurements of block temperatures. For more convenient assembling of the reactor, the inlet heating block was split into halves held together with two bolts and the outlet block contained a slot reaching to the center hole. Both heating blocks were surrounded by a thin hard asbestos ring, machined to fit tightly.

The precision valve (Whitey Research Tool Company, Oakland, California) and the transfer line leading to the inlet part of the chromatograph were heated by means of a tape heater in order to prevent the condensation of the reaction products emerging from the reactor. The stem of the valve was kept cool by a small air jet to prevent melting of the plastic gland packing.

3. Gas chromatograph. An F&M Model 300 programmed temperature gas chromatograph (F&M Scientific Corporation, Avondale, Pennsylvania) was used. An ⅛-inch Swagelok "Tee" was inserted in the line connecting the carrier gas manual flow control valve and the injection port, as close as possible to the latter. The microreactor was joined to the third port of the "Tee." This arrangement makes it possible to vary the contact times of the reaction by changing the amount of carrier gas passing through the reactor, but by maintaining constant the total gas flow going through the chromatograph. The above arrangement allows also the normal use of the original injection port.

4. Controls. The temperatures of the reactor assembly were controlled manually from a panel with built-in powerstat variable autotransformers (The Superior Electric Company, Bristol, Connecticut) except for the reactor furnace which was controlled by means of an on–off temperature controller, Honeywell Brown Pyr-o-vane (Honeywell, Philadelphia, Pennsylvania). In order to make the reactor temperature more stable and avoid excessive temperature cycling common with this type of controllers an autotransformer was used to preset the temperature to a value slightly higher than desired; the temperature controller was connected parallel to a resistance and regulated only about 20% of the total heating current, making pos-

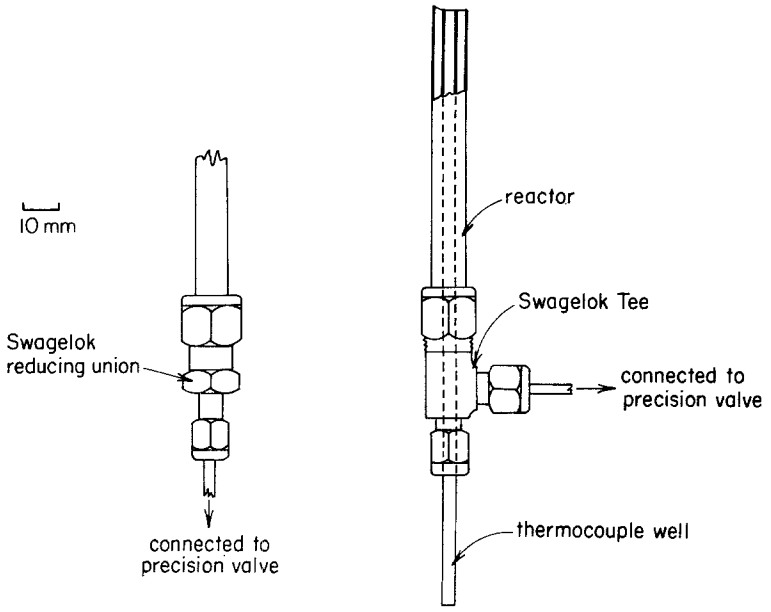

FIG. 3. Outlet port design.

sible hereby a very stable reactor temperature.

Temperatures were measured using a portable temperature potentiometer (Cat. No. 8692, Leeds & Northrup Co., Philadelphia, Pennsylvania) with iron-constantan thermocouples.

The flow of the carrier gas through the reactor was controlled manually by means of the precision valve and was measured with a soap-bubble gas flow meter at the outlet of the chromatograph.

The pressure in the reactor was controlled by means of a pressure-reducing valve (Harris Calorific Company, Cleveland, Ohio) mounted on the carrier gas cylinder. A second pressure-reducing valve of the same type was connected to the carrier gas inlet of the chromatograph and was used to provide gas to the reference side of the detector cell, and when experiments with varying contact times were made, to the outlet of the microreactor. This was accomplished by passing the gas through the original carrier gas flow control valve and Swagelok ⅛-inch "Tee."

III. Analytical Procedure

Reaction products resulting from the injection of a sample and subsequent reaction in a microreactor usually do not emerge from the reactor as a gas plug but assume a Gaussian-type distribution. This effect is even more pronounced when working under pressure, as in the present case, and this phenomenon makes chromatographic separation of the reaction products difficult or impossible. To overcome this difficulty a trapping technique was developed which allows collection in the first few centimeters of the filled chromatographic column all the reaction products resulting from the injection. This technique gave excellent resolution and even improved the separation of components as compared with the standard procedure for chromatographic analysis.

The trapping was carried out at liquid nitrogen temperature. In order to make this possible, the first length of the packed chromatographic column, about 30 cm was wound into a small coil with two to four turns, having a diameter of about 30 mm (Fig. 1, [13]). This coil was immersed in liquid nitrogen, contained in a small Dewar flask, prior to the injection of the sample to the reactor. After the injection several minutes were needed to trap all the reaction products; then the small Dewar flask containing the liquid nitrogen

was removed, and a certain period of time, which was established experimentally, was allowed for this section of the column to warm up. This took place through heat exchange with the surrounding air at room temperature, therefore no attempt was made to control the rate of this natural temperature programming. The rest of the column was kept at room temperature during this step. During this time hydrocarbon gases evaporated and came out from the column with excellent resolution. After this period, the temperature programming was applied for the whole column and the compounds having higher boiling points were driven off in the known manner.

Comparative analytical runs with mixtures of hydrocarbon gases showed that when using the same column at room temperature no separation of these compounds could be obtained at all. The improved separating power of the column, using the low-temperature trapping, can be ascribed to a "natural" exchange between the coil and the surrounding air at room temperature after the removal of the cooling bath.

The trapping technique increased not only the separating efficiency of chromatographic columns but increased their capacity at the same time too. So it was possible to connect microcatalytic reactions with preparative gas chromatography in injecting, e.g., several hundred microliters of starting material in 10–50-μliter portions into the microreactor while maintaining the trapping section at liquid nitrogen temperature. After having finished the injections the separation procedure was carried out as described above. Reactor products consisting of as many as 12 compounds resulting from repeated injections of a total of 500 μliters of starting material could be preparatively separated in one chromatographic run on a ¼-inch diameter chromatographic column provided with a trapping section.

IV. Conclusion

The pressure microreactor with the trapping procedure can be used for microcatalytic investigations in the known manner. The split stream carrier gas technique permits variation of the contact times of catalytic reactions. The time required for a complete experiment varies from 15 to 40 min, depending on the molecular weight distribution of the reaction product.

Material balances made on experiments ranging from nearly zero to nearly 100% conversion showed the reproducibility to be 100± 1.5% in relation to the internal reference compound injected. With due care deviations can be reduced to ±0.4%.

The assembly and the procedure described are suitable not only for the study of the kinetics and mechanisms of catalytic and thermal reactions, but also for the quantitative study of reactions of solid substances with gases or liquids, such as occur during the pretreatment and regeneration of catalysts.

References

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