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FOUR-REACTOR APPARATUS FOR CHROMATOGRAPHIC STUDIES OF CATALYSTS AND SORBENTS

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SUMMARY

A general purpose, four-microreactor apparatus was constructed, which includes three sections (A, B and C) of six-way valves, four in each section. Each section of valves plays a separate role: the valves in section A serve for introducing reactants into an individual reactor or a gas chromatograph by the pulse technique, those in section B serve for linking the four microreactors to the apparatus, and those in section C make possible the introduction of reaction mixtures into the chromatograph when the reactor is in operation being fed continuously with substrates.

INTRODUCTION

The idea of using microreactor systems for testing catalytic activity has existed for almost 30 years. Probably the first known microreactor system in an apparatus with radiometric attachments was that constructed by Kokes *et al.*[1]. The application of two six-way valves by Ettre and Brenner[2] made it possible to link microreactors to gas chromatographic analysers. Three possible operating systems of the Ettre and Brenner microreactor with six-way valves were adopted in Perkin-Elmer chromatographs[3]. The Ettre and Brenner system[3] is widely used, but nevertheless microreactor systems are often original constructions and so far not many papers have appeared that are directed specifically to such systems[4–7]. Normally the microreactors used are mostly simple attachments to chromatographic analysers. Their simplicity imposes some limitations, so that construction or adaptation of an additional attachment is necessary.

The microreactor system constructed by Śmigiel and Siedlecki[8] is an example of a significant development in this field. By application of three six-way valves, the system can be easily adapted for continuous or pulse introduction of substrates into the reaction zone. However, this system cannot be used for the continuous introduction of multi-component mixtures, and does not permit the controlling of linear increases in temperature. Therefore some measurements, *e.g.*, chemisorption or acidic site strength distribution by thermal desorption of ammonia, cannot be made. As the

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Śmigiel and Siedlecki microreactor assembly contains only a single microreactor, any change in operating conditions set for individual experiments must be time consuming.

As known devices have disadvantageous features and their applicability is significantly limited, an attempt was made to construct a prototype system of wide applicability for sorption measurements or catalytic studies.

CONSTRUCTION

In order to reduce interstage times, *e.g.*, sample preparation time and preheating time, the microreactor assembly involves several parallel reactor paths connected in series or in parallel to the carrier gas path of the chromatograph. In the present assembly, four microreactors were installed. It seemed logical to join together several research systems that have previously been applied separately.

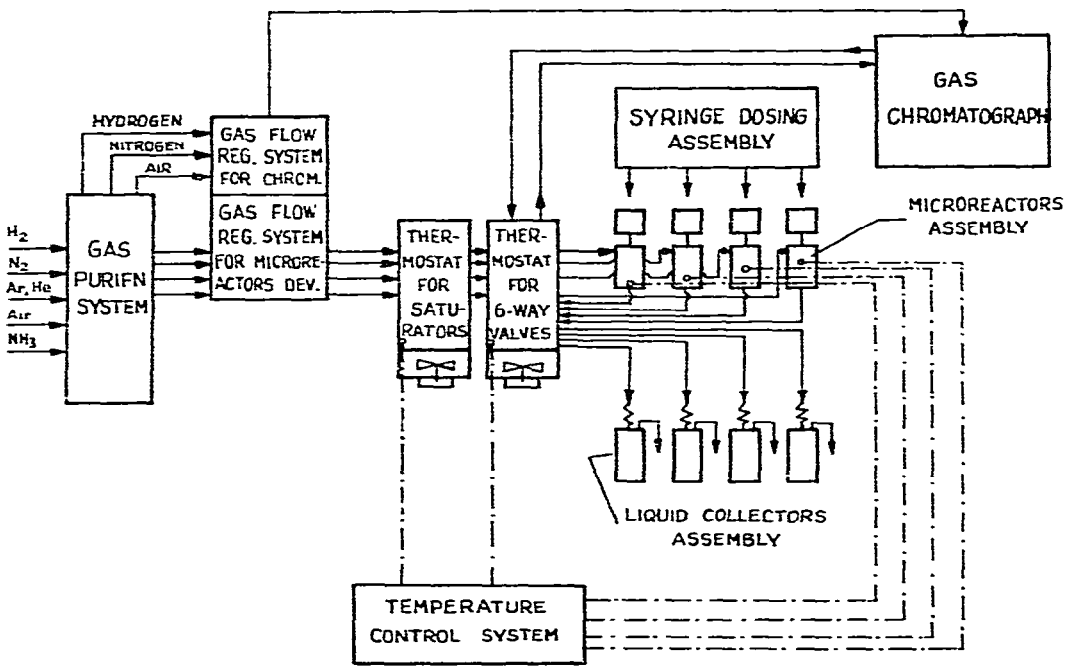

Fig. 1. General diagram of the four-microreactor apparatus with connected assemblies.

Fig. 1 shows the apparatus, including the following four systems:

(1) Gas purification system. This system contains reactors for catalytic deoxygenation of gases, and adsorbers for drying and purification.

(2) Gas jet flow control unit. This consists of eight flow regulators. Four of them are used for controlling jets of gas flowing through the microreactors, and the remainder are used for the preparation of mixtures of carrier gas with jets of the adsorbate. The jet control units consist of a high-precision regulating valve, an accurate manometer (calibrated in units of jet) and a capillary.

(3) Electronic system. This system includes temperature regulators for isothermal runs and a programming unit for control of for linear temperature increases.

(4) Syringe system. The continuous dosing of substrates is carried out with four glass syringes (1–100 ml). The syringe plungers are moved by a special servomechanism that provides uniform motion of all the syringe plungers. The servomechanism is driven by an electric motor through a planetary gear so that the speed of the plungers can be regulated over a wide range.

The microreactor apparatus consists of the following assemblies: thermostat for the four independent vapour saturators; thermostat for the system of six-way valves controlling jets of gases and vapours; four thermostats for the microreactors; and reaction product collectors.

All parts of the apparatus subject to the action of corrosive substances are made of resistant materials, *i.e.*, stainless steel, glass or PTFE.

The six-way valve assembly and the vapour dosers are placed in the thermostat with an imposed air circulation. The temperature of the thermostat can be controlled up to 473°K.

All of the pipe conduits (tubing) have small diameters and are heated with independent temperature regulation up to 573°K. Each microreactor is equipped with a membrane doser for pulse introduction of samples by a microsyringe or syringe assembly for continuous controlled feeding.

The realization of the idea of a four-microreactor assembly was facilitated by the elaboration of an original integrated multi-way valve system permitting mutual connection of four microreactors so that it is possible to carry out experiments continuously or consecutively in each microreactor. Various methods can be applied for catalytic activity testing or investigation of surface properties. The four-microreactor assembly permits independent operation of each microreactor under different conditions of temperature, catalyst load and reactant gas flow-rate. The construction of the device also makes possible the direct analysis of reaction products through the application of dosing loops in each microreactor path. Any of the four microreactors can be connected (by moving the valve lever) directly to the carrier gas path (Fig. 2).

As the apparatus contains microreactors of various sizes and shapes suitable for different methods of testing and is equipped with independent temperature control units, it is possible to measure ammonia adsorption and desorption on acidic centres of catalysts. The construction is a compact one and is adapted for connection with typical gas chromatographic analysers. For practical (manual) reasons, the temperature and the gas stream control units are separated from the system and placed on external control boards.

Test substances (reactants) can be contacted with a catalyst or a sorbent in many ways: continuous dosing may be carried out by saturation of an inert or reactant gas with vapours of substances kept in a vapour doser thermostat; pulse dosing may be effected by releasing the test substances from dosing loops or by using a microsyringe. If a doubt arises as to whether it is possible to prepare a homogeneous reaction mixture by saturating the carrier gas with vapours from the vapour dosers or when the substrate is a complex mixture of compounds, to provide continuous dosing at a fixed catalyst load range, the apparatus is equipped with a syringe dosing system and cut-off valves between the vapour dosers and each microreactor path.

The shape and size of the microreactors used in the apparatus can be ac-

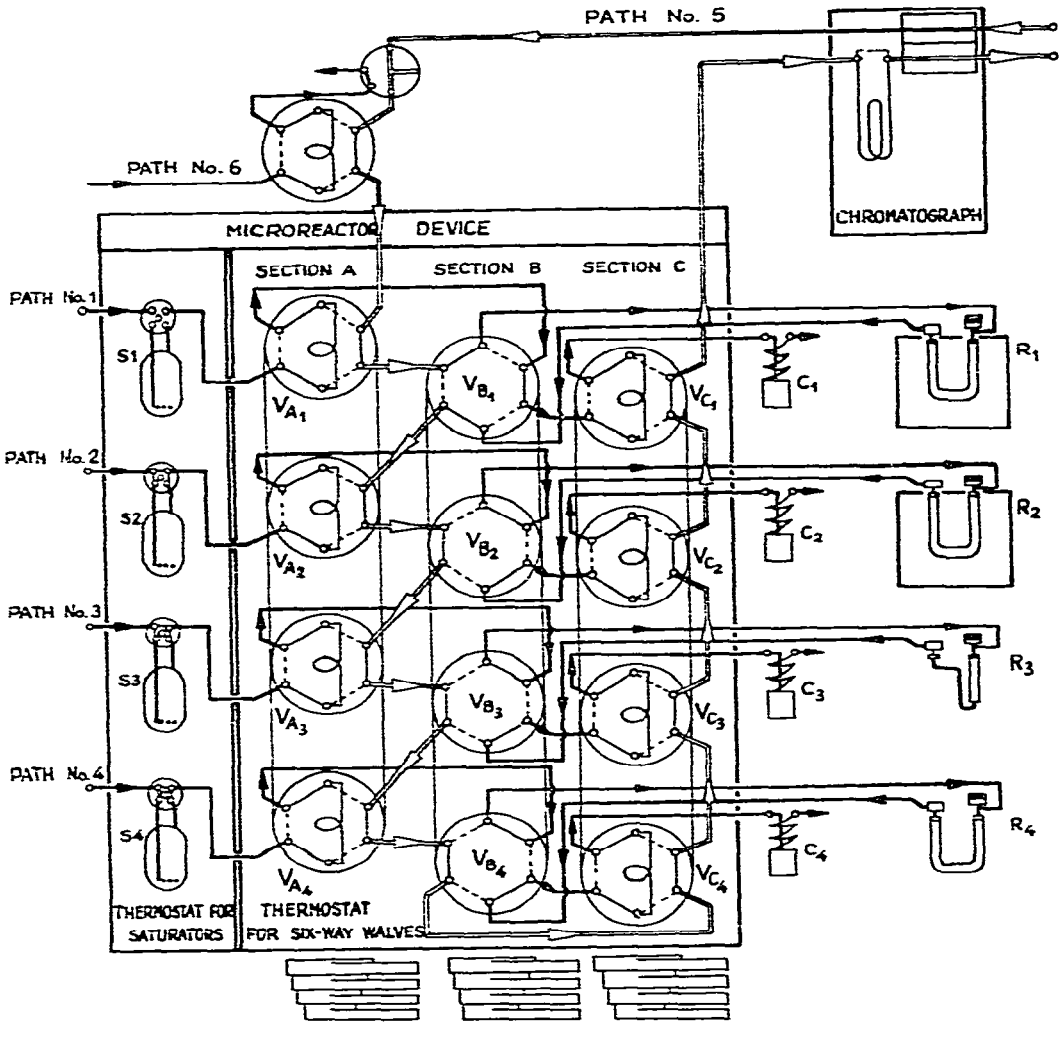

Fig. 2. Diagram of flow jets in the four-microreactor apparatus. V_{A_n}, V_{B_n}, V_{C_n} = six-way valves; C_n = collectors of liquid samples; R_n = reactors.

commodated by typical Dewar vessels, and the apparatus can therefore also be used for thermal desorption measurements.

OPERATION

Although the construction of the apparatus is complex, the operation of the system can be illustrated by an appropriate connection of the twelve two-position six-way valves (Fig. 2). It is obvious that this flow-sheet cannot illustrate all of the combinations and the potential of the apparatus for directing and controlling jets of gases or vapours. The solid lines within the area of a valve in Fig. 2 correspond to one of the two possible routes for gas and/or vapour jets. The broken lines denote routes

of jets when the valve lever is placed in the other position. Such a change of the gas jets is usually carried out during reaction product sampling or for the preparation of the apparatus for an another set of experiments.

In Fig. 2 three sections of valves can be distinguished. The valves in sections A and C (V_{A_1}–V_{A_4} and V_{C_1}–V_{C_4}) work as dosing valves, as they are equipped with capillary dosing loops. The capillary dosing loops can be replaced with a number of another sets of various internal volumes. To the valves in section B, the four microreactors R_1–R_4 are connected instead of dosing loops.

A stream of reacting gas is divided into the four working paths and flows to the regulating system. Each of the four jets from the regulating system flows through an appropriate directing valve into one of the saturators, or directly into the system of six-way valves in section A. Depending on the position of the valve levers, each of the four jets may flow independently through the corresponding capillary dosing loop or directly to the corresponding directing valve in section B, just omitting the loop. Now, depending on the position of the lever of the valve in section B, the jets may flow through the microreactors R_1–R_4, or omitting the microreactors they may flow through parallel conduits to the corresponding dosing valves in section C. The parallel jets flow from outside the microreactors through or omitting the dosing loops into the collecting condensers for the reaction products. The valves in sections A and B are connected to each other with the carrier gas conduit of the chromatograph according to the sequence V_{A_1}–V_{B_1}–V_{A_2}–...–V_{B_4}. Next, the carrier gas conduit connects the valves in section C according to the sequence V_{C_4}–V_{C_3}–V_{C_2}–V_{C_1}. The carrier gas from section C is directed to the gas chromatograph.

The above connection of the valves permits the dosing loop or microreactor to be introduced into the stream of the carrier gas. Before the entry of the carrier gas into the apparatus, additional multi-way valves are installed. The additional six-way valve serves for pulse introduction of gaseous adsorbates (*i.e.*, ammonia), and the five-way valve serves for the continuous introduction of the adsorbates into the stream of carrier gas. The four-way valve with an empty microreactor installed in the carrier gas (or a mixture of the carrier gas with an adsorbate) line is used for measuring the specific surface area of catalysts or adsorbents.

The potential of the apparatus can be illustrated by the example of testing the acidity of a catalyst by continuous thermal desorption of ammonia[5].

To start the experiment, the catalyst studied, with a fixed size of grains, is placed in the U-shaped (R_4 type, Fig. 2) microreactors. The levers of the valves in each section (A, B, C) are positioned as shown in Fig. 2, path No. 4 (V_{A_4}–V_{B_4}–V_{C_4}). Then the samples are degassed in streams of argon passing in parallel through the microreactors. The temperature is controlled at a constant level by the microreactor thermostats. The carrier gas path (path No. 5) is illustrated in Fig. 2. Ammonia (path No. 6) may be introduced into the carrier gas path either in a pulsed manner with the additional six-way valve, or continuously using the five-way valve. Introducing ammonia into the microreactor (R_4) filled with the catalyst being studied is continued until the chromatograph recorder reaches a constant and stable level. Then the lever of the valve (V_{B_4}) is moved and the microreactor is switched into the stream of the carrier gas. Now the stream of gases flows as shown by the broken lines in Fig. 2. As a result of changing the position of the V_{B_4} the recorder pointer suddenly drops to the zero line and, after sorption equilibrium has been reached, the recorder pointer de-

flects again to a level defined by the sorption equilibrium. On cutting off the ammonia supply at a constant temperature, the thermal desorption of the adsorbed ammonia begins. On switching on the linear temperature increase programme, controlled thermal desorption of the chemisorbed ammonia is attained.

By carrying on experiments using, *e.g.*, path No. 4, it is possible to save time in preparing the remainder of the samples in microreactors R_1, R_2 and R_3, replacing catalysts, degassing, etc., simultaneously. These operations do not affect the experiment in progress in microreactor R_4 connected to the carrier gas path and the chromatograph. After the experiment carried out in microreactor R_4 has been completed, the V_{B_4} valve lever is set back to the starting position, and then any other microreactor ready for next experiment may be used in series.

This prototype apparatus has been checked in a wide variety of laboratory applications. At present, it is used extensively mainly for testing catalytic activity and acidity and for sorption studies in progress in our laboratory.

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