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A Spectroscopic Flow Reactor For *in Situ* Studies of Heterogeneous Catalysts at Elevated Pressure and Temperature by Means of IR Transmission Spectroscopy

INTRODUCTION

Experimental investigations of the surface reactions and the nature of absorbed species have advanced the fundamental understanding of heterogeneous catalysis. One of the techniques is infrared transmissions spectroscopy and involves the spectroscopic analysis of a thin slab of the solid catalyst during or after contact with the reactants. The present state of the art enables spectroscopic analysis of gas–solid interactions at temperatures of 600°C and pressures of 8 MPa (*1*).

In this note an experimental facility is described which advances these operating conditions in the following manner:

—The pressure is at the same level as previously established for homogeneous catalyst systems, viz., 60 MPa at 450°C (*2*);

—in addition to gas–solid catalyst interactions the reactions between liquids (with or without dissolved gas) and solid catalysts can be monitored *in situ*.

The latter requirement demands a much smaller optical path length than the same for gas systems; this introduces some particular design problems.

The system described in this paper is primarily developed for the study of olefin hydroformylation by means of transition metal carbonyl catalysts immobilized on cross-linked polystyrene; the catalyst-inaction can be monitored under flow conditions of the reactants at elevated temperature and pressure.

Description of the Reaction System

The heart of the reaction system is the Spectroscopic Flow Reactor (SFR), the design of which will be discussed in one of the following sections.

The SFR is connected upstream with a reactant mix tank where reactants, viz., olefin and synthesis gas ($CO–H_2$) are dissolved under pressure in an inert solvent (e.g., n-heptane). The mix tank, solution transfer line, and the SFR are controlled at the same reaction temperature and pressure. The maximum values of those parameters is set by the operating limit of the SFR. The solution flows continuously from mix tank through the SFR where the reactions at the catalyst surface are monitored. The flow rate is adjustable by a flow control needle valve downstream of the SFR; this simultaneously reduces the pressure to ambient. Thus, the residence time of the solution in the SFR can be varied from seconds to fractions of seconds.

A surge valve is installed in the transfer line between mix tank and the SFR.

In case of a window burst in the SFR, the associated pressure drop activates the valve to close so that the solution in the mix tank is prevented from blowing out.

The design of the SFR, which is schematically illustrated in Fig. 1, is based on

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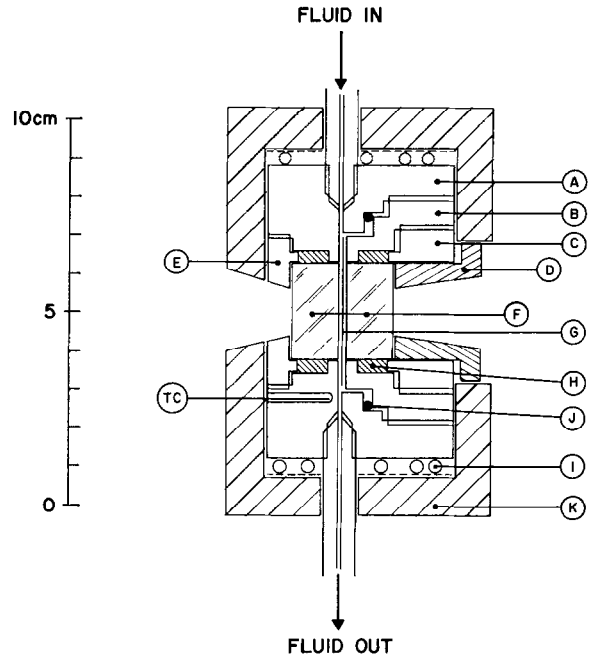

FIG. 1. Details of the spectroscopic flow reactor: A, reactor body; B, removable side of the reaction space; C, window seal compression plug; D, adjustable window support; E, window support/seal compression plug; F, optical windows; G, catalyst slab in reaction space; H, window seal; I, heating element; J, O-ring; K, thermal insulation box.

a concept which was previously reported for homogeneous systems (*2*, *3*). The reactor is made from a cylindrical slab of 304SS with an outside diameter of approximately 80 mm and a thickness of 50 mm. The catalyst disk with a thickness of approximately 0.2 mm is confined in a circular reaction space of 40 mm in diameter and 1.5 mm in width. Access to the reaction space for the solution is provided by 1-mm-diameter entrance and exit ports positioned opposite each other.

The windows, which transmit the ir radiation through the SFR are placed in the flat sides of the reaction space, with the catalyst disk in between. One side of the reaction space can be removed for easy replacing of the catalyst, without dismantling of the delicate window seals; a Kalrez O-ring (Crane Packing Company, Morton Grove, Ill.) provides the seal between the reactor body and the removable side.

The SFR is heated electrically with a 1-mm-o.d. Thermocoax heating element wrapped around the reactor. A hard asbestos cylindrical box surrounding the reactor prevents for heat losses; two circular holes in each flat face of the insulation box admit the ir radiation. The temperature is measured with a 1-mm-o.d. Thermocoax thermocouple, inserted in the reactor body.

The SFR is placed directly in the beam of a Perkin–Elmer 337 ir Spectrometer.

The window dimensions are 25 mm in diameter and 12.5 mm in thickness. They are forced on the window supports by the pressure in the reaction space. The circular hole in each support leaves a window aperture of 12.5 mm. The position of one support is adjustable by rotating inside the seal compression plug, so that the optical path length between the windows can be set at any value between approxi-

mately zero or the thickness of the catalyst disk and 3 mm.

Critical in the design is the type of window seal. It was found after trying several other configurations that a set of sealing rings compressed between the circular face of the window and the reactor body responded best to the extreme conditions of temperature and pressure.

Each set of sealing rings consists of alternating soft and hard rings of 1-mm thickness. The hard rings are made from Transite and fit with a slightly larger clearance around the window and in the reactor body than the soft rings. The soft rings are made from a PTFE composite. The set of seal rings is compressed by the seal compression plugs. This force causes a minor plastic flow of the soft rings into the clearance between the inside and outside of the hard ring and hence creates the desired seal.

The choice of PTFE composite determines the maximum operating pressure and temperature of the reactor. Plain PTFE creates an effective seal up to 190°C and 40 MPa, while Rulon–25 (obtained from Dixon Corporation, Bristol, R. I.) was effective up to 350° and 50 MPa (*1*).

An improved window seal, as described previously (*2*), increases the operating limits of Rulon to 450°C and 30 MPa of N_2 pressure or 60 MPa of heptane pressure.

The choice of window material has also a decisive influence on the maximum operating conditions of the reactor. Wider ir transmittance usually runs parallel to lower mechanical strength (*3*). For the kind of experiments envisioned, namely, hydroformylation at temperatures of around 200°C and pressures of up to 20 MPa calcium fluoride windows is an appropriate choice (*3*).

Discussion

Although the Spectroscopic Flow Reactor is originally designed for the liquid phase hydroformylation reaction, catalyzed by cobalt carbonyl immobilized on cross-linked polystyrene, its potential field of application extends to inorganic solid supports, such as silica and alumina.

Hence, the wide variety of solid catalyzed reactions at high pressures with commercial significance fall within the range of investigation with the SFR. Examples are ammonia synthesis, Fisher–Tropsch reaction, carbonylation of methanol to acetic acid, hydration of ethylene to ethanol, etc. Species adsorped at the surface of solid catalysts can now be observed directly at the temperature and pressure of the technical scale operation.

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