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NOTES

An Experimental Study of Cyclic Operation of a Benzene Hydrogenation Reactor[1]

In a recent review on cyclic operation of chemical reactors, Silveston (*1*) has cataloged a wide variety of reaction systems to show that the behavior of a reactor under cyclic feeding operation has a definite pattern. Attempts have been made to model the observed phenomenon, for example, in CO oxidation (*2*), and to extrapolate the findings. Although several theories have been proposed to explain the reactor behavior under cyclic operation, it appears that the response of the catalyst particle is an important factor. The object of the present study is to determine whether any nexus exists between the instantaneous exit conversion and the particle temperature in hydrogenation of benzene. This reaction has not previously been studied in this context. Experiments have been carried out in a Berty reactor using a single catalyst particle.

Figure 1 shows the experimental setup used in the present study. It essentially consists of a stainless-steel internal recycle reactor (*3*) heated by a furnace with automatic temperature control. The reactor has two thermocouples to measure the inlet and outlet temperatures. A 6 × 6-mm cylindrical Ni/alumina catalyst particle (Ni = 41.7% w/w) is placed inside the reactor in such a way that one thermocouple measures the temperature at the center of the particle by piercing it and the other measures the bulk temperature. The catalyst particle is rigidly held in position inside the reactor by the thermocouple itself. In addition, the setup consists of a preheater, a condenser, and a feeding arrangement for gas and liquid.

The catalyst particle is reduced *in situ* at 673 K and 1 MPa for about 30 h using 99.9% pure hydrogen. After the reduction is completed, the pressure is raised to 2 MPa and the heating rate is reduced such that the bulk temperature is maintained at about 445 K. The impeller speed is adjusted such that there is no difference between the particle and bulk temperatures. Preheated benzene is then passed at a rate of 0.225 mol/h such that the molar ratio of benzene to hydrogen is maintained at 1 : 4. With the introduction of benzene, the particle temperature increases and eventually stabilizes at about 453 K, while the bulk temperature remains constant at 445 K. Cyclic feeding operation is then started with precisely set periodic regularity. In a given run only one of the two reactants is subjected to cyclic feeding operation while the flow of the other is not disturbed. The feeding is in square pulses with on-time equal to off-time and the magnitude equal to the steady-state value. The cyclic feeding strategy is illustrated in Fig. 2. The particle temperature and the outlet benzene conversion are continuously monitored maintaining the bulk temperature. The benzene conversion is obtained by gas chromatography.

Figure 3 is a consolidated plot of the experimental data. Instantaneous exit conversion of benzene (Fig. 3a) and the corresponding catalyst particle temperature (Fig. 3b) are shown as a function of the number of completed cycles for two different cycle periods: 20 and 60 min. The results are given for a few representative cycles at the end of *n* cycles, where *n* is about 5 to 8 in each experiment.

The average particle temperature in exothermic catalytic reactions is usually higher than that in the bulk. Hydrogenation of benzene is a moderately exothermic reaction

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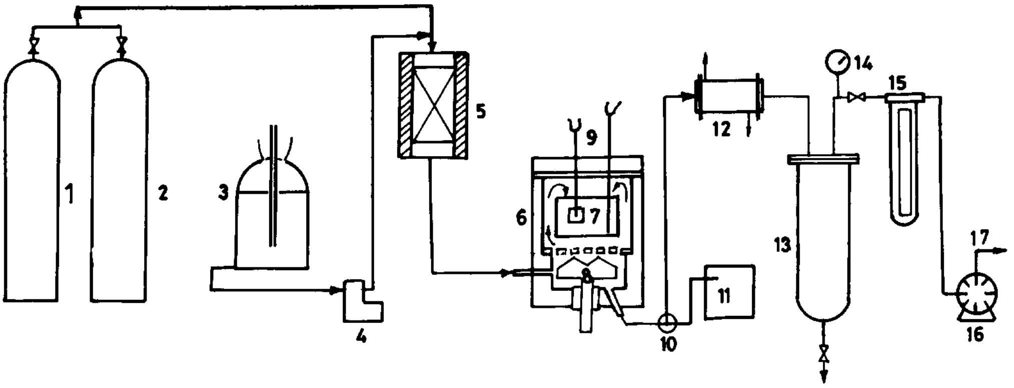

FIG. 1. Experimental assembly. (1) Hydrogen gas cylinder, (2) nitrogen gas cylinder, (3) benzene storage vessel, (4) metering pump, (5) vaporizer, (6) reactor, (7) catalyst particle, (8) impeller, (9) thermocouples, (10) three-way valve, (11) gas chromatograph, (12) cooler, (13) gas–liquid separator, (14) pressure gauge, (15) flow meter, (16) gas meter, (17) vent.

with a standard heat of reaction of −208 kJ/mol (*4*). Thus, an increase in the particle temperature is to be expected under normal conditions. An examination of Fig. 3 reveals some interesting points. Cyclic feeding has in general led to an output behavior that is also cyclic. The effect of the cycle period on the instantaneous benzene conversion is similar to that on the particle temperature. The effect of changing the identity of the cycled reactant from benzene to hydrogen on the general pattern of the observed particle temperature or conversion seems to be influenced by the cycle period. The behavior in the absence of feed cycling is intermediate between those for high and low cycle periods. It may be noted that irrespective of the identity of the reactant under cyclic feeding, the lower period has produced higher temperature, and hydrogen cycling at the lower cycle period has resulted in a greater magnitude of change from the stable steady-state temperature. Further, higher particle temperature has generally led to higher conversion.

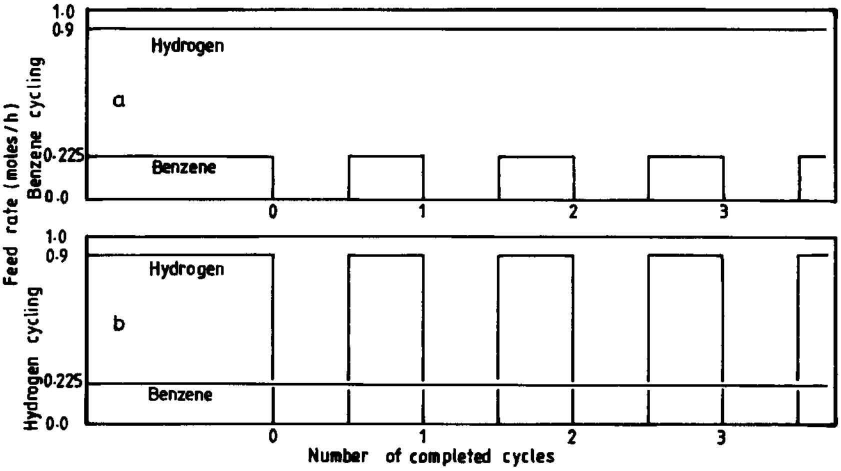

FIG. 2. Cyclic feeding strategy: (a) benzene cycling and (b) hydrogen cycling.

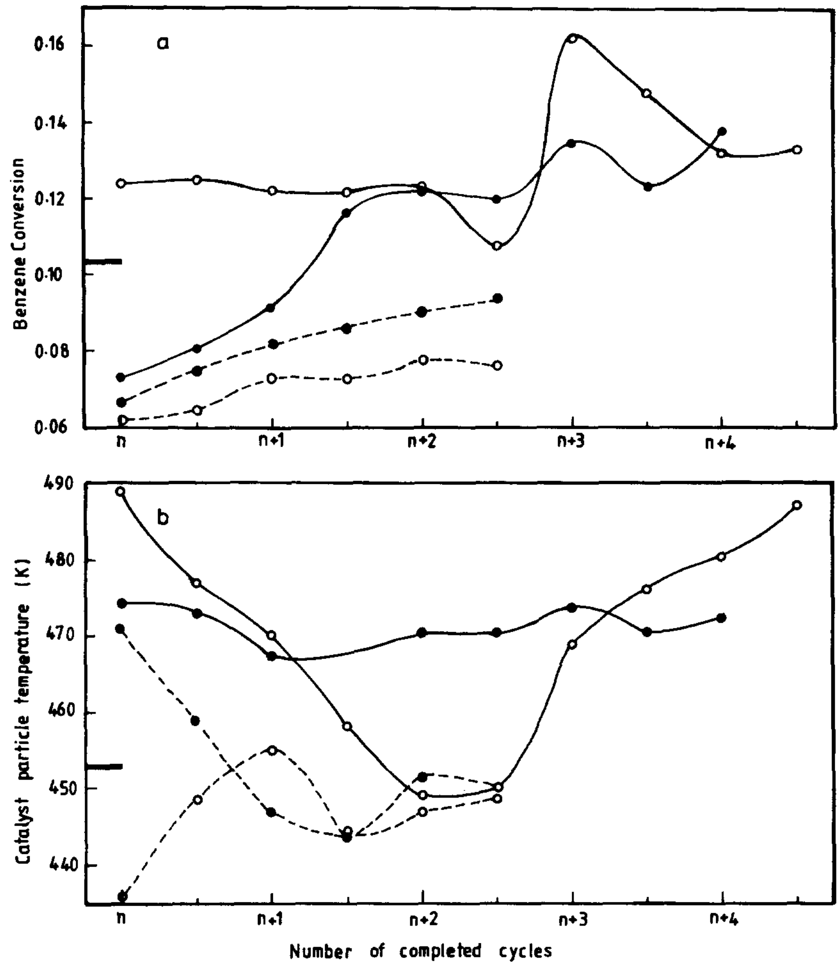

FIG. 3. (a) Benzene conversion and (b) catalyst particle temperature vs number of completed cycles. (○) Hydrogen cycling, (●) benzene cycling. (—) 20-min feed cycle; (---) 60-min feed cycle; (▬) steady state; *n* is about 5 to 8 in each case.

The rise in the particle temperature depends primarily on three factors: (i) heat generated within the particle due to reaction exothermicity; (ii) heat conducted by the particle away from the reaction zone; and (iii) heat convected away from the particle due to flow around it. Among them, (i) and (ii) are not likely to be affected by any change in the feeding pattern directly, whereas the convective heat transfer rate reflects any feeding variation more or less instantaneously. Furthermore, the catalyst particle would still be rich in the reactant concentration, even after its feeding is temporarily stopped during the first half of a cycle, and the reaction continues to occur as long as the reactant is present. It is therefore obvious that cyclic feeding can cause a substantial change in the overall heat balance between the particle and bulk by affecting mainly the heat carried away from the particle. In short, the particle temperature is expected to increase when the feed is stopped and to decrease when the feed is restarted in a cyclic feeding operation. However, the hold-up in a single catalyst particle would be very small, and when the feeding is stopped for too long a period, the concentration change in the bulk may induce a reversal of the diffusion process in the particle to quench the reaction altogether. Thus, with a large cycle period, the catalyst particle may cool below the reaction sustaining temperature. Further, the operation tends to be aperiodic for small cycle periods. Since the cyclic feeding has in fact shown improvement in conversion, it is reasonable to suggest that an optimum cycle period exists to obtain the best performance. In a recent paper, Prairie and Bailey (*5*) have reported that this is true in the case of hydrogenation of ethylene. In the absence of any data on the particle temperature, they attributed the improved performance to a shift in the chemisorption equilibrium caused by repeated change in the molar ratio of the reactants as a result of the cyclic feeding. While this is indeed true, it must be emphasized that chemisorption equilibrium is dependent more strongly on temperature. In benzene hydrogenation also chemisorption plays a crucial role in the kinetics by shifting the equilibrium between reactive and nonreactive benzene species (*6*), and the observed higher particle temperature indicates that a temperature-induced shift in chemisorption equilibrium may be responsible for a better conversion in cyclic feeding.

This work leads to the following conclusions:

1. Improved performance in the cyclic operation of a benzene hydrogenation reactor is closely related to the higher particle temperature achieved during such an operation.

2. The higher particle temperature itself may be due to a change in the net heat transfer rate between the particle and the bulk caused by the cyclic feeding.

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A. SUDHAKAR RAO
K. B. S. PRASAD[2]

Coal Division
Indian Institute of Chemical Technology
Hyderabad 500007
India

M. BHAGAVANTHA RAO

Department of Chemical Technology
Osmania University
Hyderabad 500007
India

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[2] To whom correspondence should be addressed.