

LETTERS TO THE EDITORS

Comments on Sudhakar Rao *et al.* on "An Experimental Study of Cyclic Operation of a Benzene Hydrogenation Reactor"

Recently our attention was drawn to a note by Sudhakar Rao *et al.* (1) that reports two cyclic experiments and a steady-state one and concludes that periodically turning off and on the flow of either hydrogen or benzene results in an increase in benzene conversion to cyclohexane. Although there is now a large literature (2-8) documenting the possibility of conversion improvements, the data presented by the authors do not establish their claim. The authors show conversion and particle temperature measurements at what would appear to be the composition switching times. These data points are plotted against the number of completed cycles. Even though only data points taken after 5 to 8 cycles are shown, both conversion and particle temperatures vary irregularly.

Three possible explanations come to mind for these irregular variations: (1) sampling of the gas stream and the accompanying temperature measurement were not done at precisely the same time in each cycle, or (2) the cycling system had not attained a stationary cycling state in which the variation of conversion and temperature within a cycle became constant and therefore reproducible, or (3) the catalytic system is chaotic. Concerning the first explanation, most of the hydrogenation studies under composition forcing cited above were performed with cycle periods ranging from several seconds to several minutes; that is, at least one-tenth the duration of the periods used by Sudhakar Rao *et al.* (1). Under the long periods used by Sudhakar Rao *et al.*, large variations in benzene conversion would be expected because one of the re-

actants, either benzene or hydrogen, is absent from the reactor feed for half of the cycle. The authors also report a total feed rate, but not a space velocity, for their reactor. Because a Berty reactor was used, the space-time should have been about 20 s. Thus, a shift of 5 to 10 s in the sampling could account for the variations exhibited by their data. In periodic experiments, it is the time-averaged conversion and temperature rather than instantaneous values that should be compared to steady-state results. Even if sampling were to be performed precisely at the same point in the cycle, instantaneous conversions and temperatures greater than steady-state values do not necessarily imply that the time-averaged conversions and temperatures exceed the corresponding steady-state ones. The second explanation of the irregularity draws on the observation that periodic composition switching delays the attainment of a stationary state. For example, Hugo *et al.* (9) found that more than 2000 cycles were required for the cycling system to become stationary, and during this time, conversion drifted between high and low values. Their observations were made on a supported nickel catalyst, though in a CO oxidation system. The third explanation has been reported frequently in catalytic CO oxidation over platinum catalyst, even though it has not been previously reported for benzene hydrogenation.

We disagree with an important comparison made by Sudhakar Rao *et al.* (1). In their Fig. 3, they compare the behaviour of their catalytic system under different flow conditions. For example, in their hydrogen

cycling results, the time-averaged molal flows are about one-half of those used under benzene cycling. It is not surprising, therefore, that they observe differences in conversion and temperature between hydrogen and benzene cycling. Parenthetically, it may be noted that this conclusion is based on calculations with just hydrogen and benzene. Nitrogen, not mentioned in the text, is assumed not to have been a diluent in these experiments despite its appearance in the schematic of the apparatus.

We also take issue with the authors' claim (1) that their observed increased conversion is due to a change in particle temperature caused by the alteration of the heat exchange environment. Heat and mass transfer are proportional to the molecular diffusivity and conductivity. These transport properties rise rapidly with an increase in the mole fraction of hydrogen in the gas phase. According to the description of their experiments given in the note, the hydrogen concentration is greater when benzene is cycled than when H₂ is switched on and off. If transport changes are the sources of a conversion increase, particle temperatures and benzene conversion should be higher for H₂ cycling than for benzene cycling. The data at a cycle period of 20 min do not show a consistent difference. Yet it is at this very period that the authors claim to find an improvement through forcing. There is fairly

widespread agreement that improvements under composition forcing are caused by changes in the adsorbate concentrations on catalyst surfaces, leading to higher reaction rates (see, for example, Ref. (8)). Higher rates increase the heat release which in turn raises the temperature of the catalyst.

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