TABLE 2. RESULTS OF CORRELATION TESTING
(45 data points from this study)

Correlation	Average Absolute Deviation, %	Average Error %
Larkins et al. (1961)	57.9	−57.9
Turpin and Huntington (1967)	62.2	−62.2
Otake and Okada (1953)	30.3	−30.2
Charpentier and Favier (1975)	14.3	− 9.4
Clements (1978)	10.4	0.6

SUMMARY

1. Both the gas and liquid flow rates and liquid viscosity, as well as the packing size, are seen to have a significant (± 50 percent) effect on the dynamic liquid holdup in a packed column.

2. The gas density and viscosity appear to have a less strong (± 20 percent) influence on dynamic liquid holdup.

3. The holdup correlation of Charpentier and Favier (1975) and the capillary flow model of Clements (1978) appear to represent the data for viscous liquids in beds of small catalyst packings well.

ACKNOWLEDGMENTS

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NOTATION

a_t = total external surface area of particles, $cm^2/(cm^3$ of empty tube)
D_p = effective particle diameter, cm
g = absolute acceleration of gravity, cm/sec^2
G = superficial gas flow rate, gm/cm^2sec
Ga = Galileo number $D_p^3 g\rho^2/\mu^2$
L = superficial liquid flow rate, gm/cm^2sec
$\Delta P/Z$ = pressure drop per unit length, atm/m
Re = Reynolds number, D_pG/μ_G, D_pL/μ_L
U_L, U_G = velocity of liquid and gas, respectively, cm/sec
We = Weber number, $U_G^2D_p\rho_G$

Greek Letters

β_{nc} = dynamic holdup, (cm^3 of liquid)/(cm^3 of bed)
ϵ = bed void fraction
δ_L, δ_G = predicted single-phase pressure drops for gas and liquid, respectively, atm/cm
μ_L, μ_G = liquid and gas phase viscosity, cp
ρ_L, ρ_G = liquid and gas phase density, gm/cc
χ = $[(\Delta P/Z)_1/(\Delta P/Z)_g]^{\frac{1}{2}}$
σ = surface tension, dyne/cm

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Transient Behavior of Fresh and Fouled Nickel Hydrogenation Catalyst

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The unsteady-state characteristics of catalytic reactors must be understood in order to design control systems, to investigate stability, and to determine whether to operate the reactor in a steady-state or cyclic mode. To this end, experimental studies have been conducted of the transient behavior of acetylene hydrogenation reactions, the overall stoichiometry of which may be written

$$C_2H_2 + H_2 \rightarrow C_2H_4$$
$$C_2H_4 + H_2 \rightarrow C_2H_6.$$

EXPERIMENTAL MATERIALS AND METHODS

A commercial nickel catalyst, Girdler G87RS, was employed in these investigations. It contains 43% nickel by weight on a refractory support, with a surface area of $3.4 \times 10^4\ m^2kg^{-1}$. Prior to use, the catalyst was crushed and screened to a size range 0.84-1.2 mm, after which the pellets were pretreated for 24 h in a 5% (wt) solution of $Na_2S_2O_3$ (Komiyama and Inoue 1968). Before each experiment, the catalyst was activated in the reactor in a hydrogen stream at 477 K for 6 h.

All experiments were conducted in a spinning-basket catalytic CSTR. The feed flow rates of hydrogen and nitrogen were switched with a timer and solenoid valves, and effluent hydro-

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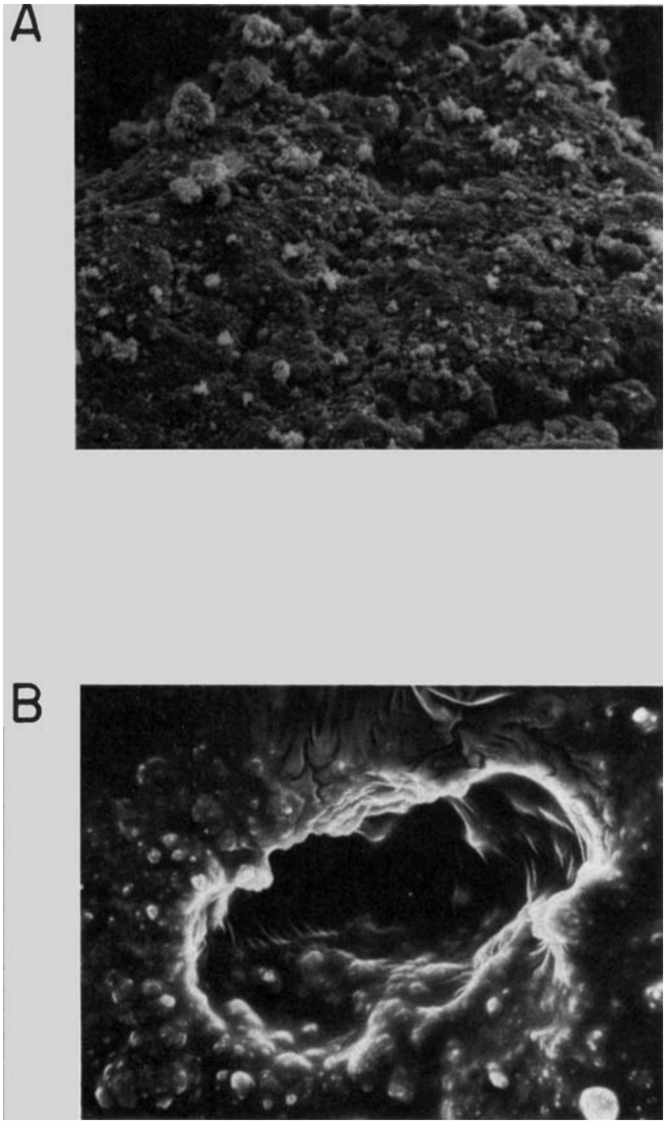

Figure 1. Scanning electron microphotographs of (A) fresh catalyst (x900) and (B) fouled catalyst (x900).

carbon composition was monitored using both an infrared spectrophotometer and gas chromatography. Additional details on the experimental apparatus may be found in Bilimoria and Bailey (1978). Experimental conditions employed in this work are identical to those reported previously (temperature = 439K, pressure = 108.2 kNm^{-2}, reactor mean residence time = 66 s (constant), basket/impeller rotation rate = 104.7 rad s^{-1}, acetylene feed rate = 0.5 cm^3s^{-1}, total feed rate = 5 cm^3s^{-1}).

The transient behavior of the reactor was studied for fresh and for fouled catalysts. In step increase experiments, the reactor was first operated at steady state with a feed hydrogen flow of 0.25 cm^3s^{-1}. At a time designated zero, this flow was switched to 1.625 cm^3s^{-1}, and the effluent composition was monitored during the transition to the new steady state. An analogous but reversed procedure was employed for the step decrease experiments. For all experiments, the nitrogen feed flow rate was adjusted such that the sum of feed hydrogen and nitrogen flows was 4.5 cm^3s^{-1} at all times.

RESULTS

During an extended series of experiments, a liquid residue was produced which coated the reactor internals and fouled the catalysts. The existence and nature of this fouling is clearly illustrated in the scanning electron microphotographs in Figure 1. The barren, sharply defined features of the fresh catalyst contrast markedly with the nearly fluid appearance of a fouled macropore.

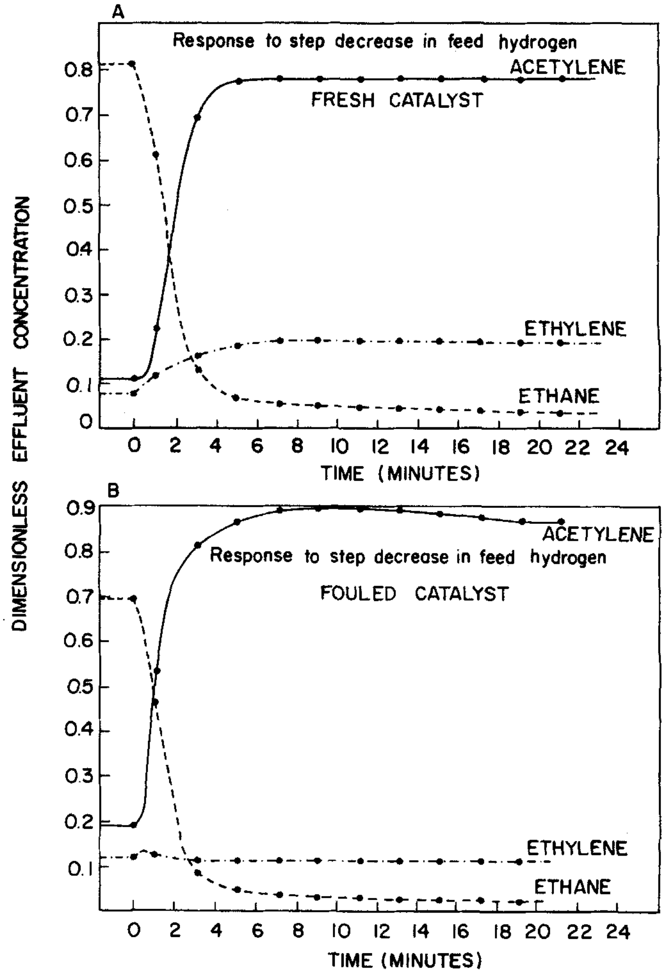

Figure 2. Responses of the catalytic CSTR to a step decrease in feed hydrogen flow for (A) fresh and (B) fouled catalyst. (dimensionless concentration of component i = (concentration of component i)/(feed acetylene concentration)).

Step decrease results for fresh and fouled catalysts are shown in Figure 2. Data points on this and the succeeding figure denote chromatographic measurements; intermediate values were obtained from the IR data. With fresh catalyst, all trajectories are monotonic and the time scale for reaching the low hydrogen steady-state is about 10 min. On the other hand, the fouled catalyst reponse involves a brief excursion of ethylene concentration and a broad, protracted overshoot in acetylene concentration. Here approximately 20 min. are required to attain steady state.

Even more unusual behavior was observed in feed hydrogen step increase experiments (Figure 3). For fresh catalyst, ethylene exhibits a wrong-way response. Overshoots are present in the acetylene and ethane transients. In the studies with fouled catalyst, a single undershoot-overshoot cycle is seen for acetylene, ethylene again has a positive excursion after the step, and very little overshoot is seen in ethane concentration. The time to achieve steady state is approximately 10 min. in both cases.

DISCUSSION

The experimental system contains less than 75 s of mixing and hydraulic lags, and relaxation times for diffusion and conduction within the rotating catalyst beds are estimated to be of the order of 1 and 25s, respectively. Therefore, if the reactor may be regarded as pseudohomogeneous, the time required to switch from one steady-state to another should be no greater than 3.5-5

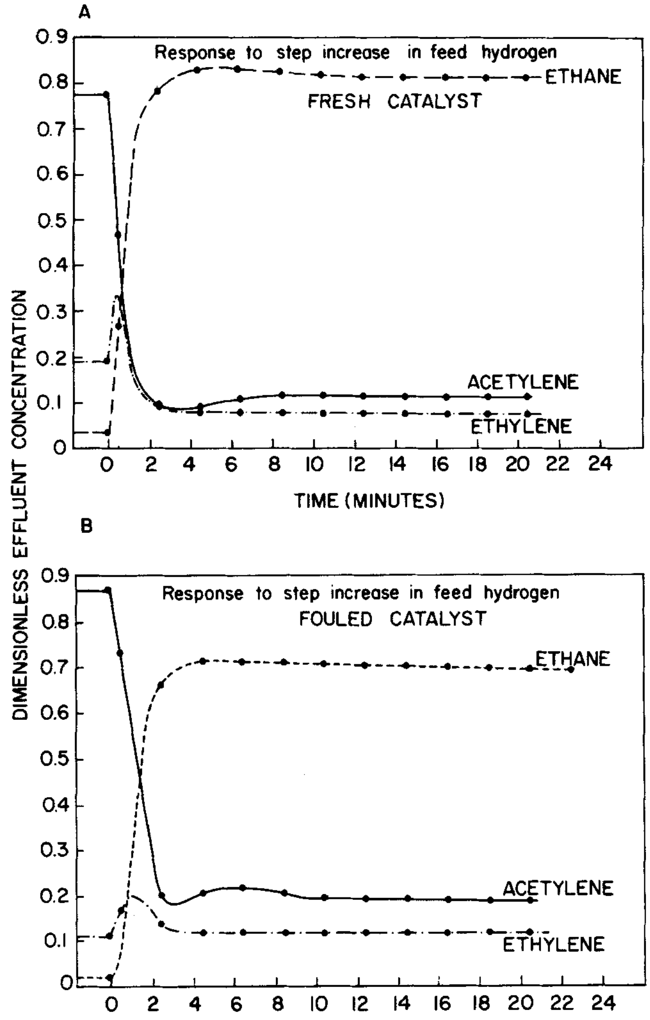

Figure 3. Step increase transients for (A) fresh and (B) fouled catalyst (dimensionless concentrations defined as in Figure 2).

min. The longer transients seen here for fresh catalyst must therefore be caused by slow interactions with and/or reactions on the catalyst surface.

Fouling profoundly alters the dynamic behavior of the reactor, changing both the trajectory shapes and, in the case of the step-down experiment, the time required to achieve steady state. The asymmetric response pattern for fresh catalyst (slower step up, faster step down) is reversed for fouled catalyst.

This work adds to two important themes in the recent literature. First, slow events on the catalyst surface can in some cases dominate reactor transient behavior (Sheintuch and Schmitz 1977). Careful consideration of the possible existence of these features is critical in analyses of catalytic reactor dynamics: the quasi-steady state approximation for surface species should be invoked with care and not casually assumed to be valid. Secondly, it appears that the complex effects of fouling on reactor transients shown above cannot be explained mathematically simply by introduction of scaling factors which multiply the overall rates of the two hydrogenation reactions. In this event, the influences of fouling are impossible to represent using separable kinetics (Butt and Bilimoria 1978, Butt et al. 1978), and a more complex representation of fouling is required for reactor modeling and analysis. Further research along these lines is in progress.

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Gas Phase Ozonation of Aliphatic Sulfur Compounds

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Odors are typically classified as nuisance air pollution problems rather than health hazards. Traditionally, sources of non-toxic odors have been restricted by law to special geographical zones, based on prevailing winds and population growth patterns. This approach follows the widely held concept that the best solution to pollution is dilution. But population growth and air dilution patterns are not always predictable. Moreover, scientific evidence suggests that adverse synergistic effects may result, when pollutants are dispersed into the ecosystem. Hence, present political trends encourage abatement or curtailing of gaseous emissions. Failure to do so may invite civil suits and/or government intervention. Thus, the growing technology for treating gas streams to remove non-toxic odors as well as toxic constituents.

The first step in dealing with odor pollution is always identifying the causative agent or agents. This is followed by an hypothesis on how it is generated, and corrective procedures

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