

Further Remarks on Benzene Hydrogenation Over a Pd/Al₂O₃ Catalyst

Vannice and Neikam (1) have attempted to compare their experimental data on benzene hydrogenation over a Pd/Al₂O₃ catalyst in a flow reactor with our results obtained in a pulse reactor (2) and to draw some conclusion concerning hydrogen spillover. For quantitative comparison the specific activity of each of the catalysts used is required. Subsequent to publication of the data in Ref. (2), the surface area of our catalysts has been determined by CO sorption (3) and found to be 0.44 m²/g, which on the basis of 1.2×10^{15} Pd_s surface sites/cm² yields 8.8 μmoles of Pd_s/g of catalyst, a value comparable to that obtained by H₂ sorption for the catalyst employed in Ref. (1).

A lower limit of the specific zero-order rate constant [turnover number = molecules/(sec. Pd_s)] can now be estimated from our results on the basis of the fraction of the benzene molecules converted, the flow rate through the reactor, and the reactor volume. We recognize that for kinetic analysis of a zero-order reaction, sorption equilibrium needs to be maintained during the course of the pulse experiment (4). Examination of the pulse shapes of the GC signals due to reactant and product indicate that this requirement appeared to be satisfied in our experiment. Furthermore, the possibility of increased benzene loss due to adsorption on the alumina was examined. Experiments demonstrated that the areas of the GC signals of benzene agreed within ±1% for pulses coming in contact with alumina or bypassing the reactor containing the alumina.

The values of k_0 so calculated from the pulse reactor data are shown in Table 1 along with some of the original data from Ref. (2). In the above calculation of k_0 , we are using a corrected value of 1.4×10^{18} benzene molecules in the pulse aliquot rather than the incorrect value 2×10^{15}

used in Ref. (1). Note that the values of k_0 are larger by at least a factor of 50 than those obtained in the differential flow reactor (1). In view of the similar degree of catalyst dispersion, as manifested by the surface area measurements, one may conclude that the catalyst shows much higher activity in the pulse experiments. Furthermore, the gradual increase of k_0 with alumina dilution (Table 1, Runs 1 to 9) is consistent with our earlier conclusions concerning surface diffusion.

The suggestion has been made (5) that the results of the pulse experiment approximates a first-order action with respect to benzene. To explore such a possibility we have computed the first-order rate constant k_1 [(Pd sites·sec)⁻¹] as summarized in Table 1. Again we note an increase in k_1 on dilution with alumina as might be expected to result from hydrogen migration. This effect is particularly evident from the data in which alumina is added as a diluent to a given mass of Pd/Al₂O₃ catalyst (comparison of runs 1 and 3, 2 and 4, 5 and 6, Table 1).

We question the suggestion (1) that in the pulse reactor the alumina diluent acted as a trap for the removal of impurities from the hydrogen stream. The hydrogen used (Matheson prepurified grade, 99.95% minimum purity) flowed continuously over the catalyst for many hours in a given experiment without any decrease in catalytic activity. Furthermore, the much higher specific activity of the catalyst in the pulse reactor contraindicates such a poisoning effect. Rather we conclude that the conditions employed in the pulse reactor are particularly suitable for the detection of the surface migration phenomenon because the catalyst, the support, and the diluent have ample time to become populated with chemisorbed hydrogen preceding the arrival of the benzene pulse. Further examination

TABLE 1
REACTION RATE CONSTANTS FOR HYDROGENATION OF BENZENE ON MIXTURE OF Pd/Al₂O₃ AND Al₂O₃
Pulse reactor at 150°C.

Run	Mass (mg)		Benzene hydrogenated (vol %)	Reaction rate constants	
	Pd/Al ₂ O ₃	Al ₂ O ₃		k_0 ($\frac{\text{molecules}}{\text{sec} \cdot \text{Pd}_s}$)	k_1 [(Pd _s · sec) ⁻¹ × 10 ¹⁸]
1	100	0	45	1.0	1.1
2	55	0	33	1.4	1.3
3	100	900	69	1.5	2.1
4	50	950	40	1.7	1.8
5	25	475	22	1.9	1.8
6	25	975	25	2.2	2.0
7	5	995	7.4	3.0	2.8
8	1.5	1000	2.2	3.3	2.8
9	0	1000	Nil	—	—

of the kinetics of benzene hydrogenation in a pulse reactor is indicated.

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