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LETTERS TO THE EDITORS

Benzene Hydrogenation Over a Pd/Al_2O_3 Catalyst

Disagreement has arisen in the literature concerning metal–support interactions in the hydrogenation of benzene over supported catalysts. Recently, Sancier (*1*) used a slug reactor to study this reaction over a Pd/Al_2O_3 catalyst. He proposed an apparent metal–support interaction which allowed benzene to react with spilled-over hydrogen on the alumina surface in addition to the usual reaction occurring on the Pd surface. However, Aben *et al.* (*2*) used a steady-state flow reactor to conduct a thorough study of benzene hydrogenation over Ni, Pt, and Pd supported on a variety of refractory oxides. In contrast to Sancier, they found the rate of hydrogenation to be proportional to the metal surface area and independent of the support involved.

In this study we have resolved this conflict by reproducing the catalyst prepared by Sancier and studying the benzene hydrogenation reaction using a differential flow reactor.

EXPERIMENTAL METHODS

The hydrogenation reaction was conducted in a steady-state flow reactor usually operating under differential conditions. The reactor has been described previously (*3*). A Perkin–Elmer 154 gas chromatograph with a Carbowax 20 column was employed to separate benzene and cyclohexane.

The alumina was prepared by Kaiser Aluminum and Chemical Corporation by the same procedure as the sample obtained by Sancier. This allowed us to reproduce the catalyst system studied in (*1*). The catalyst sample, 2.1 wt % Pd/Al_2O_3, was prepared by impregnating alumina with a $(NH_4)_2PdCl_4$ solution. Before impregnation, the alumina was ground and sieved with the 80/150 cut being retained for this study. After impregnation, the alumina was dried in an oven at 120°C then heated in flowing hydrogen at 400°C for 4 hr. The catalyst charge was prepared by mixing together the desired quantities of 2.1% Pd/Al_2O_3 and the diluent Al_2O_3 in the same manner as Sancier, i.e., the two components were gently rolled together until a uniform mixture was obtained. In all but two runs, the total catalyst charge was constant at 0.5 g.

Using the method described by Aben (*4*), a typical high-vacuum gas adsorption system was employed to determine the number of Pd surface atoms (Pd_s) by hydrogen chemisorption.

The catalyst samples were pretreated *in situ* at 200°C for 2 hr under flowing hydrogen, which was purified by passage through a Deoxo unit followed by a molecular sieve trap. The catalyst was then cooled to a reaction temperature of 150°C. All runs were conducted at a hydrogen pressure of 1 atm and a flow rate of 25 ml STP H_2/min. A Sage syringe pump was used to provide a constant benzene flow of 4.0×10^{-3} ml/min through a preheater to the reactor. The benzene (B&A, reagent grade) was used without further purification. These conditions were similar to those used by Sancier except for the addition of the hydrogen purifier.

RESULTS AND DISCUSSION

Hydrogen chemisorption measurements showed the presence of 8.13 μmole of Pd_s/g of catalyst. This corresponds to an approxi-

TABLE 1

T = 150°C; H_2 pressure = 1 atm; H_2/benzene = 20.

Sample	Dilution ($g\ Al_2O_3$: $g\ Pd/Al_2O_3$)	Amt of Pd/Al_2O_3 (g)	Total amt of catalyst bed (g)	Av conv. (mole %)	σ (%)	Turnover no. $\left(\frac{\text{molecules benzene}}{\text{sec} \cdot Pd_s}\right)$	Comments
1	0:1	0.2000	0.5000	3.60	0.54	0.017 ± 0.003	Mixed with 0.30 g of quartz
2	0:1	0.5010	0.5010	23.0	3.29	0.043 ± 0.006	
3	0:1	0.2005	0.2005	10.5	0.60	0.049 ± 0.003	
4	0:1	0.0445	0.0445	1.27	0.22	0.027 ± 0.005	
5	9:1	0.0503	0.5003	1.11	0.095	0.020 ± 0.002	
6	9:1	0.0503	0.5006	1.10	0.20	0.020 ± 0.004	Al_2O_3 pretreated @ 400°C for 4 hr
7	90:1	0.0055	0.4999	0.130	0.025	0.022 ± 0.004	
8	206:1	0.0023	0.4995	0.047	0.004	0.019 ± 0.002	
9	227:1	0.0022	0.4994	0.052	0.012	0.022 ± 0.005	

mate Pd dispersion of 4%. Using this value, turnover numbers [molecules of benzene reacted/(Pd_s·sec)] were calculated for each run. The catalyst systems studied and the resulting turnover numbers along with their standard deviations (σ) are given in Table 1. All conversions were calculated by multiplying each peak area by the appropriate response factor and subtracting out the small cyclohexane impurity (0.02 mole %) in the benzene feed.

In agreement with Aben *et al.* (*2*), we found that the reaction was zero order in benzene concentration. For each run, conversions were constant within experimental error over the 2–4 hr period required to obtain 5–7 conversion measurements. Pretreatment of the diluent alumina at 400°C under flowing hydrogen had no effect on conversion (Run 6).

Although hydrogen spillover has been shown to participate in certain catalytic reactions (*5*, *6*), it does not play a role in this reaction. The independence of turnover number from catalyst dilution is readily apparent in Fig. 1. For the undiluted Pd/Al_2O_3 catalyst, high conversions were obtained when the reactor was not operating differentially (Runs 2 and 3). The hydrogenation of benzene is exothermic and Runs 2 and 3 appear to reflect the effect of temperature gradients within the catalyst bed. When differential rates are obtained, temperature gradients within the bed are reduced to a negligible level. Within the regime of low conversions, the rate is proportional only to the Pd surface area thus verifying the results of Aben and co-workers (*2*).

Unfortunately, we cannot estimate turnover numbers from Sancier's data since Pd surface areas were not measured in his study. However, using the rate equation and data determined by Aben to calculate the rate of reaction at 150°C, we predict a turnover number of 0.052. This value is in good agreement with our value of 0.021 and provides a further indication of the consistency of our data with that of Aben and co-workers.

We feel that the data of Sancier reflect primarily the limitations of slug reactors. These limitations have been discussed by others (*7*–*9*); and there is agreement that kinetics of zero-order reactions such as this one should not be studied by the use of slug reactors. However, two additional comments seem appropriate at this time and they may explain the behavior of the data in (*1*). First, the usage of unpurified hydrogen by Sancier is unacceptable to us, particularly when such small quantities of Pd are involved. In the highly diluted samples less than 0.1 μmole of Pd_s is present if a reasonable Pd dispersion of 10% is assumed. Schlatter and Boudart (*10*) have proposed that alumina may act as a scavenger for impurities. The role of the dil-

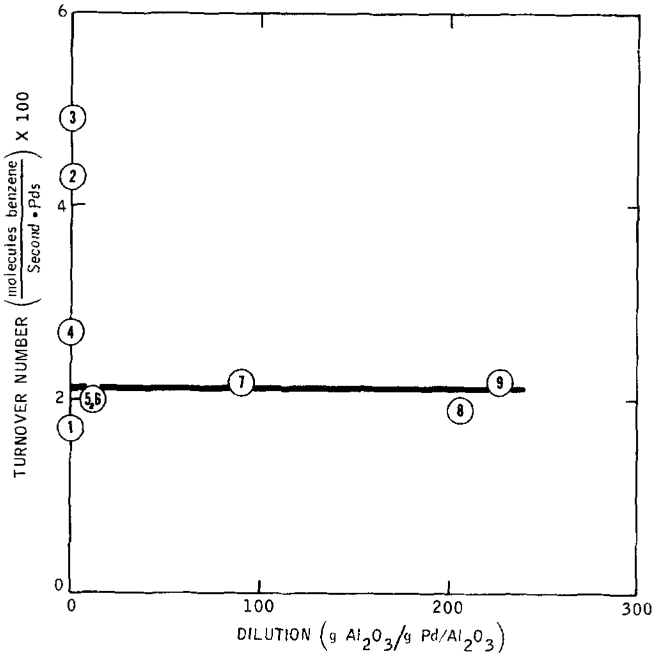

Fig. 1. The independence of specific activity from catalyst dilution.

uent alumina may then be that of adsorbing impurities from the hydrogen. If so, an increase in available alumina surface area should provide greater protection against these impurities and result in the behavior obtained by Sancier. Secondly, Germain *et al.* (*11*), showed that benzene hydrogenation on Ni surfaces is inhibited by the product, cyclohexane. Similarly, the rate on Pd may be inhibited by significant amounts of cyclohexane produced under conditions of high conversion as was the case in (*1*). At such high conversions (up to 69%), Sancier did indeed find his lowest normalized conversions. Product inhibition would be negligible at low conversions. Therefore, the apparent rate enhancement seen by Sancier at high catalyst dilutions instead may be rate inhibition at low dilutions.

References

1. Sancier, K. M., *J. Catal.* **20,** 106 (1971).

2. Aben, P. C., Platteeuw, J. C., and Stouthamer, B., *Recl. Trav. Chim. Pays-Bas.* **89,** 449 (1970).

3. Sinfelt, J. H., *J. Phys. Chem.* **68,** 344 (1964).

4. Aben, P. C., *J. Catal.* **10,** 224 (1968).

5. Boudart, M., Vannice, M. A., and Benson, J. E., *Z. Phys. Chem. N.F.* **64,** 171 (1969).

6. Vannice, M. A., and Neikam, W. C., *J. Catal.* **20,** 260 (1971).

7. Bassett, D. W., and Habgood, H. W., *J. Phys. Chem.* **64,** 769 (1960).

8. Gaziev, G. A., Filinovskii, V. Yu, Yanovskii, M. I., *Kinet. Katal.* **4,** 688 (1963).

9. Bett, J. A. S., and Hall, W. K., *J. Catal.* **10,** 105 (1968).

10. Schlatter, J. C., and Boudart, M., unpublished data.

11. Germain, J. E., Maurel, R., Bourgeois, Y., and Sinn, R., *J. Chim. Phys. Physicochim. Biol.* **60,** 1219 (1963).

M. A. Vannice*

Corporate Research Laboratories
Esso Research and Engineering Company
Linden, New Jersey 07036

W. C. Neikam

Sun Oil Company
Marcus Hook, Pennsylvania 19061

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* To whom queries concerning this letter should be sent.