supported by the U. S. Atomic Energy Commission.

REFERENCES

1. SMITH, R. L., NARO, P. A., AND SILVESTRY, A. J., *J. Catal.* **20**, (1971).
2. CSICSERY, S. M., AND HOUSTON, R., (private communication).
3. SCHMIDT, L. D., AND LUSS, D., *J. Catal.* **22**, 269 (1971).
4. MCCAROLL, J. J., EDMONDS, T., AND PITKETHLY, R. C. *Nature (London)* **223**, 1260 (1969).
5. KAPLAN, R., (private communication).
6. DELAMARE, F., AND RHEAD, G. E., *Surface Sci.* **28**, 267 (1971).
7. HONDROS, E. D., AND MCLEAN, M., "Structure et Proprietes des Surfaces des Solides 1969." Ed. du Centre Natl. de la Recherches Scientifique, 1970.
8. ROBERTSON, W. M., AND SHEWMON, P. G., *Trans. AIME* **224**, 804 (1962).
9. WINTERBOTTOM, W. L., *in* "Surfaces and Interfaces" (J. J. Burke *et al.*, Eds.). Syracuse Univ. Press, Syracuse, 1967.
10. GOODMAN, R. M., AND SOMORJAI, G. A., *J. Chem. Phys.* **52**, 6325 (1970).
11. HERRING, C., *in* "Structure and Properties of Solid Surfaces" (R. Gomer and C. S. Smith, Eds.). Univ. of Chicago Press, Chicago, 1953.
12. LANG, B., JOYNER, R. W., AND SOMORJAI, G. A., *Surface Sci.* **30**, 440 (1972).
13. BOUDART, M., *Advan. Catal.* **20**, 153 (1969).
14. BOUDART, M., ALDAG, A. W., PTAK, L. D., AND BENSON, J. E., *J. Catal.* **11**, 35 (1968).
15. SOMORJAI, G. A., *Catal. Rev.* (in press).

G. A. SOMORJAI

Inorganic Research Division, Lawrence Berkeley Laboratory, and Department of Chemistry
University of California, Berkeley
Berkeley, California 94720
Received February 22, 1972

Interparticle Hydrogen Migration on Pd–Al_2O_3 Catalysts for Benzene Hydrogenation?

A variety of catalytic systems are reported to be influenced by hydrogen migration or hydrogen spillover (*1–6*). Boudart, Vannice and Benson have reported the ease with which WO_3 is reduced when physically contacted with platinum black after water had been preadsorbed on the mixture (*3*). It is believed that water provides an interface between the mechanically mixed platinum black and WO_3 particles. Dissociated hydrogen then migrates from platinum particles to WO_3 particles and hence room temperature reduction of WO_3 occurs. Such migration phenomena are potentially important both in understanding surface catalytic behavior and in the preparation and practical use of catalysts.

A recent study by Sancier (*6*), using a pulsed reactor system for the hydrogenation of benzene on a Pd–Al_2O_3 catalyst, shows an increase in specific activity when the catalyst bed is diluted with inert Al_2O_3. These results were interpreted as being caused by interparticle hydrogen migration or spillover. This interpretation has been questioned by Vannice and Neikam (*7*), who collected data on a comparable catalyst under steady state conditions. Steady state runs showed no evidence that spillover occurs. Hence, dilution of the Pd–Al_2O_3 catalyst bed with inert Al_2O_3 only enhances productivity in the pulsed reactor system. In his rebuttal, Sancier (*8*) stated that ". . . the conditions employed in the pulsed reactor are particularly suitable for the detection of 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." The catalytic surface which contacts a benzene pulse could very well differ from the catalytic surface which develops under steady state conditions. Hydrogen spillover involving interparticle migration could be too slow to contribute appreciably to the steady state hydrogenation rate. Although the data of Vannice and Neikam is of practical significance, it does not rule out spillover as an explanation for Sancier's results. Vannice and Neikam do make an important point when they suggest that Sancier's data may reflect the limitations of pulsed reactor systems.

The purpose of this study was to make comparisons between steady state and pulsed catalyst behavior on the same catalyst specimen and to see if a more comprehensive examination of the catalyst under pulsed conditions still indicated spillover or merely showed behavior characteristic of pulsed reactor systems.

The 2.2% $Pd-Al_2O_3$ catalyst was prepared and activated as described by Sancier (*6*), who supplied the alumina used in this study. Palladium chloride was obtained from Fisher Scientific. The hydrogen supply (electrolytic grade from National Cylinder Gas) was passed through a deoxo-mole sieve drier unit before use. Benzene was Mallinckrodt AR reagent grade. A hydrogen stream was saturated with benzene at various temperatures to introduce the desired amount of benzene into the reactor system. A variety of valve and reactor configurations (Fig. 1) were used so that both pulsed and steady state studies could be done on the same catalyst specimen. Switching from one mode of operation to the other was instantaneous. Carle micro-volume valves, the detector and auxiliary attachments, were mounted inside an oven which was heated, when necessary, to avoid condensation of reactants or products in various parts of the system. The usual placing of the chromatographic column in series with the reactor for pulsed operation was avoided, as shown in Fig. 1. The detector served the dual purpose of monitoring peak shapes as well as showing when all of the pulse had passed through the detector and into a 25-cm³ delay loop. Before the pulse emerged from the delay loop, the switch position was changed to transfer the pulse to the glc helium stream for chromatographic analysis. For steady state operation the 25-cm³ delay loop was replaced with a smaller sample loop (~0.5 cm³) for routine analyses. A Hewlett-Packard Model 5753 chromatograph, using a 10-ft, 17% silicone 703 chromosorb P column operated at 100°C, was used to analyze product mixtures. Catalyst samples were pretreated in stainless steel reactors for at least 2 hr at 200°C with flowing hydrogen before the temperature was lowered to 150°C for the run.

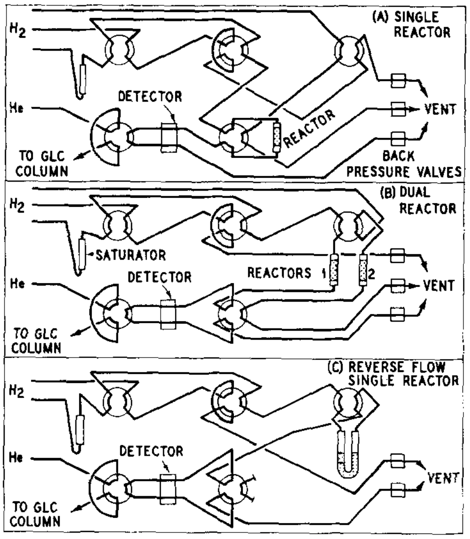

FIG. 1. Valve switching and sampling configurations for operating reactor(s) under steady state or pulsed mode.

An essential key for even a qualitative interpretation of pulsed reactor data involves knowing the reaction order. If the reaction is first-order with respect to benzene, interpretational problems are minimized while zero, fractional, or second-order reactions are difficult to evaluate (*9*). The rate of a zero-order reaction under steady state conditions is independent of reactant concentration or pressure; and conversion (x) is inversely proportional to the initial reactant pressure $(P_B)_0$:

$$x = [kRT/(P_B)_0](m/F),$$

where m is the mass of catalyst, T is temperature, and F is gas flow-rate through the catalyst bed. Pulsed, zero-order sys-

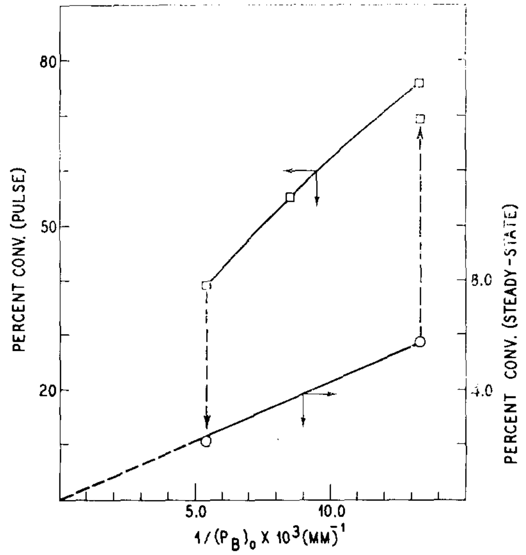

FIG. 2. The effect of benzene partial pressure on conversion. ⊡ Pulsed; ⊙ Steady state.

tems are not so easily defined although conversion should be inversely proportional to some function of the reactant pressure. Any characteristic of the catalyst, catalyst bed, reactor, or flow system which causes a pulse to broaden either before or during passage through the catalyst bed should have an effect on conversion. When two pulses containing the same quantity of reactant but differing in shape are carried through a catalyst bed under otherwise identical conditions, the broadest pulse will maintain contact with any given catalyst surface for the longest period of time. Hence, for a zero-order reaction, conversion should be increased by any means which tends to cause the pulse to broaden before or during passage through the bed.

The hydrogenation of benzene on Pd–Al_2O_3 catalysts is reported to be zero-order (with respect to benzene) under steady state conditions (*7*, *10*). No indication of order was given for pulsed reactor operation (*6*) and it does not necessarily follow that the two are identical. To obtain at least a qualitative indication of the (pulsed) order with respect to benzene, the reactor system shown in Fig. 1a was used. Both pulsed and steady state behavior were examined. Hydrogen saturated with benzene was passed through a 0.23-cm^3 pulsing loop. The partial pressure of benzene in the 0.23-cm^3 loop was controlled by selecting the appropriate saturator temperature. For this series of runs, the pulse size or volume was constant and the partial pressure of benzene was varied. Figures 2 and 3 show the effect which the initial partial pressure of benzene, in the pulsing loop, has on conversion. Although this method is admittedly crude, it does show that the reaction is zero or near zero-order with respect to benzene and that interpretation of pulsed reactor results will not be simple for this reaction.

Since the reaction order is near zero any significant broadening of pulses before or during contact with the catalyst bed should increase conversion at constant flow. To

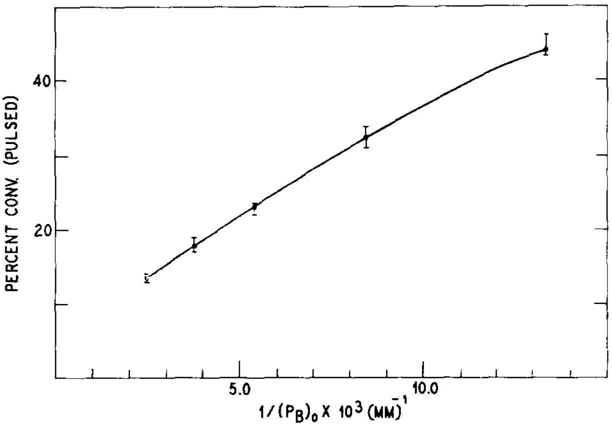

FIG. 3. The effect of benzene partial pressure on conversion.

check on this behavior the dual reactor arrangement shown in Fig. 1b was used where both pulse shape and conversion could be monitored simultaneously. In reactor 1, a 100-mg sample of catalyst was suspended in a quartz chip bed. Quartz chips were used to reduce reactor volume and to hold the catalyst in place. In reactor 2, a physically mixed sample of 100 mg of catalyst plus 900 mg of alumina diluent was also suspended in a quartz chip bed. Both samples were heated to 200°C for 8 hr in hydrogen before the runs were made at 150°C. The idea was to examine both samples under identical conditions to ascertain the real effect which alumina diluent has on activity under both pulsed and steady state modes of operation. The results are shown in Fig. 4. The level of conversion in the alumina-diluted catalyst bed was always higher than in the undiluted bed; and the pulses out of the diluted bed were always broader than those which came from the undiluted catalyst bed. Under steady state conditions both catalyst beds had comparable activity with the diluted bed being slightly, although perhaps not significantly, less active. The additional bed length caused by dilution with alumina has a marked effect on pulse shapes. Even a slight chromatographic effect (some separation of cyclohexane from benzene) was noted for the longer bed. These results coupled with a near-zero reaction order leave the hydrogen spillover explanation open to serious question.

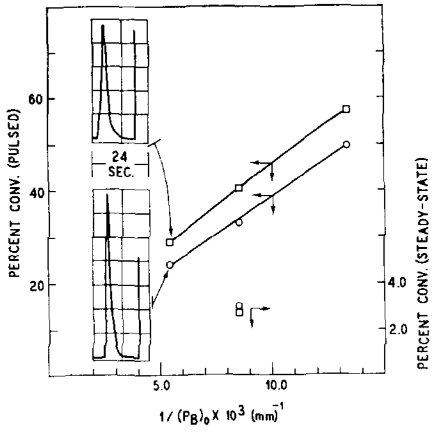

FIG. 4. The effect of catalyst bed dilution on pulse shape and conversion. ⊡: 100 mg of Pd–Al_2O_3 plus 900 mg of Al_2O_3; ⊙: 100 mg of Pd–Al_2O_3.

The next step was to investigate catalyst behavior when the catalyst and the alumina were not in contact. The reactor system used is shown in Fig. 1c. A 100-mg catalyst sample was separated by a thin layer of 80–200 mesh quartz chips from 900 mg of alumina diluent. The Carle valve shown just above the reactor in Fig. 1c was used to reverse the flow through the reactor. Thus, a pulse could be sent in either direction through the catalyst bed. With the catalyst and the alumina separated, the possibilities for interparticle hydrogen migration were removed and any differences in conversion as a function of flow direction would require an alternate explanation. The data in Table 1 shows the pulsed behavior to be very dependent on flow direction. Much higher levels of conversion were always obtained when pulses were first broadened by passage through the alumina bed before contact with the catalyst bed.

TABLE 1
THE EFFECT OF FLOW DIRECTION ON CONVERSION IN A SEPARATED BED OF CATALYST AND ALUMINA[a]

Mode of operation	H_2 Flow (ml/min)	Percent conversion and run sequence: 100 mg Catalyst 900 mg Alumina	Percent conversion and run sequence: 900 mg Alumina 100 mg Catalyst
Pulsed	70	50.9	79.2
Pulsed		48.5	
Steady state	68	5.8	5.3
Pulsed	35	79.4	~99
Pulsed	144	41.5	63.2
Pulsed	70	50.2	

[a] $(P_B)_0 = 75$ mm; $T = 150°C$; and $P = 1$ atm.

To aid in ruling out the alumina as a poison scavenger, an alternate method of broadening pulses was employed. This consisted of using an empty 10-cm^3 reactor in series with the catalyst containing reactor as shown in Fig. 5. The remainder of the valve system in Fig. 1c was used as shown.

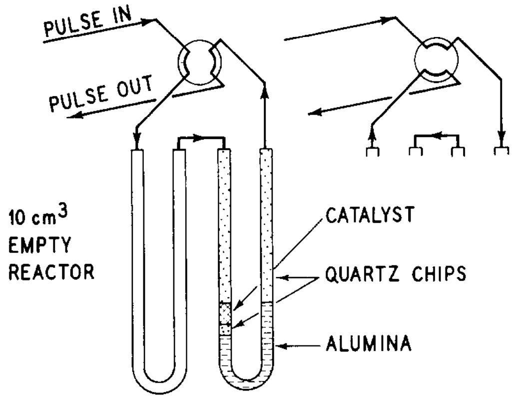

FIG. 5. System for studying the empty tube effect on conversion.

The data in Table 2 shows that when the empty reactor is located downstream from the catalyst bed, no significant change in conversion is noted. However, when the pulse must first pass through the 10-cm^3 empty reactor before contacting the catalyst bed, a very significant increase in conversion is noted. The empty reactor is almost as effective in increasing conversion as is a 900 mg sample of alumina. Although this empty reactor effect does not rule out the possibility of some poison scavenging by alumina, it does suggest that perhaps any pulse-broadening method will have a very marked effect on conversion. Poison scavenging, if it occurs, appears to be of secondary importance.

TABLE 2

EMPTY TUBE EFFECT ON CONVERSION UNDER PULSED REACTOR CONDITIONS

Flow sequence	Percent conversion and run sequence
→ Catalyst → Al_2O_3	44.4 ↓
→ Al_2O_3 → Catalyst	64.8 ↓
→ Al_2O_3 → Catalyst → ET[a]	65.8 ↓ 66.0
→ ET → Catalyst → Al_2O_3	63.0 ↗

[a] ET: 10-cm^3 empty tube placed in series with the catalyst bed.

The higher steady state activity of this catalyst compared to the one used by Vannice and Neikam (*7*) seems to arise from an increase in Pd dispersion (12%) and a large turnover number (0.09–0.11 molecules of benzene reacted per surface Pd atom per second). There appears to be no meaningful way to compare the activity of this catalyst with that used by Sancier (*6*).

It is concluded that if hydrogen spillover effects (i.e., interparticle migration) really exist for this reaction system, such effects must certainly be masked by the limitations of studying a zero or near zero-order reaction under pulsed reactor conditions.

ACKNOWLEDGMENTS

Special thanks are due Dr. K. M. Sancier for providing the alumina support and Mr. J. D. Chance for his assistance in building and operating the reactor system.

REFERENCES

1. ROBELL, A. J., BALLOU, E., AND BOUDART, M., *J. Phys. Chem.* **68**, 2748 (1964).
2. BENSON, J. E., KOHN, H. W., AND BOUDART, M., *J. Catal.* **5**, 307 (1966).
3. BOUDART, M., VANNICE, M. A., AND BENSON, J. E., *Z. Phys. Chem. Neve Folge* **64**, 171 (1969).
4. SINFELT, J. H., AND LUCCHESI, P. J., *J. Amer. Chem. Soc.* **85**, 3365 (1963).
5. VANNICE, M. A., AND NEIKAM, W. C., *J. Catal.* **20**, 260 (1971).
6. SANCIER, K. M., *J. Catal.* **20**, 106 (1971).
7. VANNICE, M. A., AND NEIKAM, W. C., *J. Catal.* **23**, 401 (1971).
8. SANCIER, K. M., *J. Catal.* **23**, 404 (1971).
9. BASSETT, D. W., AND HABGOOD, H. W., *J. Phys. Chem.* **64**, 769 (1960).
10. ABEN, P. C., PLATTEEUW, J. C., AND STOUTHAMER, B., *Rec. Trav. Chim. Pays-Bas* **89**, 449 (1970).

A. J. MOFFAT

Phillips Petroleum Company
Bartlesville, Oklahoma 74004
Received March 21, 1972