JOURNAL OF CATALYSIS 52, 45–49 (1978)

Catalytic Hydrogenation of Cyclohexene

I. Vapor-Phase Reaction on Supported Platinum

E. SEGAL, R. J. MADON, AND M. BOUDART[1]

Department of Chemical Engineering, Stanford University, Stanford, California 94305

Received August 2, 1977; revised November 11, 1977

The reaction rates for the vapor-phase hydrogenation of cyclohexene over Pt/SiO_2 between 273 and 313 K are reported. The reaction is zero order with respect to cyclohexene. The reaction order with respect to hydrogen is 0.8 at low hydrogen pressures and temperatures and close to 0.5 at higher hydrogen pressures and temperatures. The shift in kinetics is explained by a Horiuti–Polanyi (1934, *Trans. Faraday Soc.* **30**, 1164) mechanism, in which adsorption of hydrogen is equilibrated at high temperatures and pressures but becomes essentially irreversible at low temperatures and pressures. The reaction is structure insensitive as its rate does not change when Pt dispersion changes from 14 to 100%.

INTRODUCTION

Since the pioneering research of Sabatier and Ipatieff, the catalytic hydrogenation of alkenes has been the subject of a great amount of experimental work. Much information concerning the mechanism of hydrogenation has been accumulated due to the kinetic studies of hydrogenation, deuteration, and isotopic exchange with saturated hydrocarbons (*1–4*). For cycloalkenes, most of the kinetic investigations were performed in solution (*5*). In this paper we report the results of a kinetic study of the vapor-phase hydrogenation of cyclohexene over platinum catalysts supported on silica gel.

EXPERIMENTAL

The kinetic measurements were carried out in a batch recirculation system described in an earlier paper (*6*). To recirculate the gas mixture over the catalyst a stainless steel welded bellows pump was used (*7*). The standard value of the flow rate was 2.3 dm^3/min. The volume of the recirculation loop was 2.39 dm^3. At suitable time intervals 23-cm^3 samples were withdrawn for chromatographic analysis.

The cyclohexene (chromatoquality reagent, 99.7 + mol%; Matheson, Coleman and Bell) was passed at room temperature through a transitional alumina column, preheated in flowing helium at 400°C, subjected to several freeze–pump–thaw cycles to remove oxygen, and stored in a previously evacuated bulb attached to the gas manifold. The hydrogen or deuterium was purified by diffusion through a Milton–Roy palladium thimble. Helium which was used as a diluent, was passed through a glass coil cooled with liquid nitrogen before being introduced into the system.

The catalysts used in this work were 60/200-mesh Pt/SiO_2 samples; their compositions and Pt dispersions, determined according to the method of Benson and

---

[1] To whom correspondence should be sent.

0021-9517/78/0521-0045$02.00/0

Boudart (*8*), are listed in Table 1. The first four samples prepared according to the method of Benesi *et al.* (*9*) were donated by Dr. H. A. Benesi. They were prereduced at 400°C and stored in air prior to use. The preparation and pretreatment of the 37 and 1.1% Pt/SiO_2 catalysts made in our laboratory has been described elsewhere (*10*).

The standard pretreatment for the catalyst consisted of a 2-hr evacuation followed by a 1-hr hydrogen purge at room temperature. The amount of catalyst used for a run varied between 5 and 20 mg. The reactant gas introduced into the recirculation loop contained 12.7 Torr of cyclohexene, 76.2 Torr of hydrogen, and 749.3 Torr of helium. These partial pressures together with a working temperature of 295 K are called *standard conditions* in the discussion below.

Chromatographic analysis was carried out with a Varian–Aerograph A-90-P chromatograph equipped with a column of 30% dibutylphthalate on Chromosorb P. Only hydrogen, cyclohexane, and cyclohexene were detected in the sampled effluent.

RESULTS

All kinetic data are collected in Table 2. No observable deactivation occurred from run to run. All runs were zero order with respect to cyclohexene so that rates expressed as turnover numbers N were simply calculated from values of Pt dispersion and from the slopes of straight lines in plots of amount of cyclohexane vs time. Rates were unaltered when cyclohexane was introduced into the reactant mixture.

TABLE 1

Turnover Numbers N at Standard Conditions for Vapor-Phase Hydrogenation of Cyclohexene

Platinum (wt%)	Dispersion (%)	N (s^{-1})
0.53	56	2.67
0.38	100	2.64
1.50	100	2.73
2.30	62	2.75
3.70	14	2.53
1.10	100	2.72

TABLE 2

Values of the Turnover Numbers (N) at Different Temperatures and Pressures[a]
Catalyst: 0.53% Pt/SiO_2
Dispersion = 56%

H_2 (Torr)	N (s^{-1})	H_2 (Torr)	N (s^{-1})
T = 273 K		T = 303 K	
76.2	0.94	38.0	2.69
114.3	1.11	76.2	4.34
152.4	1.53	101.6	4.44
228.6	1.99	152.4	5.83
304.8	2.40	228.6	7.05
381.0	3.23	254.0	7.39
457.2	3.64	381.0	9.52
584.2	4.87	508.0	10.83
		660.4	12.30
		749.3	12.50
		825.5	12.96
		876.3	13.10
T = 295 K		T = 313 K	
38.0	1.55	38.0	3.52
76.2	2.65	76.2	5.50
116.8	3.43	152.2	8.82
152.4	4.14	228.6	8.97, 12.80[b]
203.2	5.57	254.0	12.00
254.0	6.54	304.8	13.70
330.2	7.11	381.0	15.73
406.4	8.98, 8.13[b]	482.6	19.66
558.8	9.11, 8.97, 9.40[b]		
688.3	10.04		
825.5	10.80, 10.94[b]		
892.0	11.09, 10.65		

[a] Catalyst: 0.53% Pt/SiO_2; dispersion = 56%.

[b] Separate runs.

Values of N for two values of the recirculation rate below the standard value (1.2 dm^3/min) and above it (3.4 dm^3/min) were 2.67 and 2.87 s^{-1}. Thus the recirculation rate had no influence on the reaction rate. Values of N for catalysts with 0.53 and 2.3% Pt were 2.67 and 2.78 s^{-2}, respectively. The absence of any depen-

TABLE 3

Values of the Reaction Order with Respect to Hydrogen at Different Hydrogen Pressures and Temperatures

Temperature (K)	Pressure range (Torr)	Reaction order n with respect to hydrogen
273	76.2–584.2	0.82
295	38 –250	0.78
	250 –892	0.48
303	38 –876.3	0.51
313	38 –482.6	0.57[a]

[a] Value corrected according to Boudart and Madon (*12*).

dence of N on recirculation rate and Pt content at almost identical values of Pt dispersion are convincing tests that the reaction was carried out in the kinetic regime (*11*, *12*).

The data of Table 2 were plotted to determine the reaction order with respect to hydrogen. At 273 K, the partial pressure of H_2 was varied from 76.2 to 584.2 Torr and the order was observed to be 0.82. The results at 295 K, where the partial pressure of hydrogen was varied from 38 to 892 Torr, yielded two values of the order of reaction with respect to hydrogen. For the values of hydrogen pressure lower than 250 Torr, the reaction order is 0.78, whereas for the higher pressures one obtains 0.48. At 303 K the value of the reaction order with respect to hydrogen obtained in the same way for all the pressure values is 0.51, while at 313 K one obtains 0.65. This change in reaction order with respect to hydrogen could be ascribed either to the interaction of transport phenomena at high hydrogen pressure and temperatures as turnover numbers are relatively high (*13*) or to some change in the kinetic parameters as the hydrogen pressure and the temperature are increased. By means of the Koros–Nowak criterion (*11*, *12*) for 295 K, $P_{C_6H_{10}} = 12.7$ Torr and $P_{H_2} = 825.5$ Torr, it was confirmed that the reaction was still carried out in the kinetic regime as N values for the 0.53% Pt/SiO_2 and 2.3% Pt/SiO_2 catalysts were 10.94 and 9.60 s^{-1}, respectively. In addition, N values determined under the same conditions for two samples of the 0.53% Pt/SiO_2 catalyst with different granulations (60/200 mesh and 150/200 mesh) were identical within experimental error: 10.91 s^{-1}. Taking into account these results we conclude that neither mass nor heat transfer is responsible for the observed change in the values of the reaction order with respect to hydrogen, at least under such conditions.

At 313 K and 254 Torr of hydrogen pressure, the values of N for the 0.53% Pt/SiO_2 and 2.3% Pt/SiO_2 catalysts were 12.0 and 9.3 s^{-1}, respectively, and hence diffusion seems to be influencing the reaction. For such conditions the value of the reaction order with respect to hydrogen, corrected according to Boudart and Madon (*12*), is 0.57.

For clarity, values of the reaction order with respect to hydrogen at different temperatures and hydrogen pressures are collected in Table 3.

The value of the activation energy corresponding to the standard value of hydrogen pressure (76.2 Torr) was 8 kcal mol^{-1}, whereas at higher hydrogen pressures (825.5 Torr) we obtained 6.7 kcal mol^{-1}. When deuterium was used instead of H_2, N at standard conditions was 2.02 s^{-1}.

DISCUSSION

According to the data of Table 1, the hydrogenation of cyclohexene on platinum appears to be a structure-insensitive reaction (*14*), as N stays the same when the particle size of the metal is changed within a critical region, from below 1 nm to above 5 nm, corresponding to platinum dispersion from 100 down to 14%. In addition, these data, and other data mentioned under Results, show that the kinetic work, with the exception of the data at the higher temperature, is exempt from distortions due to heat or mass transfer, poisoning or contacting, because the turnover number measured at fixed conditions does not change with platinum loading of the catalyst as the percentage of metal is varied by a factor of 7.

Hence, the order of reaction n with respect to hydrogen and its changes with temperature and pressure shown in Table 3 seem real and deserve an explanation. According to Table 3, n approaches 0.5 at high temperatures and pressures while it seems to tend toward unity at low temperatures and pressures. These are the observed trends.

A simple explanation is based on the sequence of elementary steps initially proposed by Polanyi and Horiuti (*15*):

$$H_2 + 2* \rightleftarrows 2H*, \qquad (1)$$

$$R + 2* \rightleftarrows *R*, \qquad (2)$$

$$*R* + H* \rightleftarrows RH* + 2*, \qquad (3)$$

$$RH* + H* \rightarrow RH_2 + 2*, \qquad (4)$$

where R and $*R*$ denote cycloalkene in the vapor phase and in the adsorbed state, respectively. $RH*$ stands for the usual half-hydrogenated monoadsorbed intermediate, and RH_2 represents the hydrogenated product. Step (1) is considered to be in quasiequilibrium, with equilibrium constant K_1, at high temperatures and pressures, but becomes essentially irreversible, with a rate constant k_1, at low temperatures and pressures. In other words, in the presence of alkenes at low temperatures and pressures the reverse of step (1) may be considered negligible. Similar observations have been cited by Erkeleus *et al.* (*16*) and Eley (*17*). Steps (2) and (3) are postulated to be in quasiequilibrium at all times and step (4) is written as an irreversible elementary process with rate constant k_4. But the main assumption is that the half-hydrogenated monoadsorbed intermediate is the most abundant species intermediate (masi) with surface concentration $(RH*)$ and that there exists only a small *constant* amount of free sites located inbetween the bulky hydrocarbon adsorbed species, where hydrogen is dissociatively adsorbed as $H*$ at low surface coverage. Our assumption is expressed by the relation: $(RH*) \gg (*R*), (H*), (*)$.

The total concentration of sites (L),

$$(L) = (RH*) + (*R*) + (*) + (H*)$$

may then be written as

$$(L) \approx (RH*) \approx (RH*) + (*). \qquad (5)$$

When step (1) is in quasiequilibrium, we can write

$$(H*) = K_1^{\frac{1}{2}}(H_2)^{\frac{1}{2}}(*) = K^{\frac{1}{2}}(H_2)^{\frac{1}{2}}, \qquad (6)$$

where the constant concentration of free interstitial sites $(*)$ has been absorbed in the equilibrium $K_1^{\frac{1}{2}}(*) = K^{\frac{1}{2}}$.

Now, at low pressures and temperatures,

$$r = r_1 = \tfrac{1}{2}zk_1(*)^2(L)^{-1}(H_2) = k(H_2), \qquad (7)$$

where z is the number of sites surrounding a given site and $\frac{1}{2}z(*)/(L)$ is the probability that any of the surrounding sites, for a dual-site adsorption, are free. The latter may be absorbed in k_1 so that $\frac{1}{2}z(*)^2(L)^{-1}k_1 = k$.

By contrast, at high pressures and temperatures,

$$r = r_4 = k_4(H*)(RH*) = k'(H_2)^{\frac{1}{2}}, \qquad (8)$$

where $k' = k_4K^{\frac{1}{2}}(L)$. Thus, in principle, the trends reported in Table 1 can be explained in a rather simple manner.

The form of the rate expression does not depend on whether the olefin is σ diadsorbed or π bonded onto a single site, but it requires dissociative adsorption of hydrogen on two sites.

From the Results section it is seen that, at standard conditions, the ratio of hydrogenation to deuteration is 1.32. Maxted and Moon (*18*) observed that the ratio of the rates of adsorption of hydrogen (protium) and deuterium on Pt black at 18°C was 1.4–1.5. Though the analogy is not too convincing, due to the fact that our Pt surfaces are covered with hydrocarbon species unlike those of Maxted and Moon and that the deuteration was carried out only at one temperature, it is nevertheless interesting as it does show a hydrogen isotope effect close to that observed in the present work. While all the kinetic results reported here are rather straightforward, the main novel conclusion of the work is that the vapor-phase catalytic hydrogenation of cyclohexene over platinum is structure insensitive. The same observation in the liquid phase on platinum, as well as in the vapor and liquid phases on palladium, will be reported in subsequent papers of this series.

ACKNOWLEDGMENTS

One of us (E. S.) was able to carry out this investigation during a leave of absence from the University of Bucharest. The work was supported in part by Exxon Research and Engineering Co.

REFERENCES

1. Bond G. C., "Catalysis by Metals," Chaps. 9, 11. Academic Press, London and New York, 1962.
2. Bond, G. C., and Wells, P. B., *Advan. Catal. Relat. Subj.* **15**, 91 (1965).
3. Meyer, E. F., and Kemball, C., *J. Catal.* **4**, 711 (1965).
4. Schrage, K., and Burwell, R. L., Jr., *J. Amer. Chem. Soc.* **88**, 4555 (1966).
5. Hussey, S., Keulks, G. W., Nowack, G. P., and Baker, R. H., *J. Org. Chem.* **33**, 610 (1968).
6. Schlatter, J. C., and Boudart, M., *J. Catal.* **24**, 482 (1972).
7. Hanson, F., and Benson, J. E., *J. Catal.* **31**, 471 (1973).
8. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 704 (1965).
9. Benesi, H. A., Curtis, R. M., and Studer, H. P., *J. Catal.* **10**, 328 (1968).
10. Madon, R. J., Ph.D. Dissertation, Stanford University, Stanford, Calif., 1973.
11. Koros, R. M., and Nowak, E. J., *Chem. Eng. Sci.* **22**, 470 (1964).
12. Boudart, M., and Madon, R. J., to be submitted.
13. Boudart, M., *AIChE J.* **18**, 465 (1972).
14. Boudart, M., *Advan. Catal. Relat. Subj.* **20**, 153 (1969).
15. Polanyi, M., and Horiuti, J., *Trans. Faraday Soc.* **30**, 1164 (1934).
16. Erkeleus, J., Galwey, A. K., and Kemball, C., *Proc. Roy. Soc. Ser. A* **260**, 273 (1961).
17. Eley, D. D., "Catalysis" (P. H. Emmett, Ed.), Vol. 3. Reinhold, New York, 1955.
18. Maxted, E. B., and Moon, C. H., *J. Chem. Soc.*, 1542 (1936).