

# Benzene Hydrogenation over Iron. 1. Specific Activities and Kinetic Behavior over Unsupported Iron and Iron Dispersed on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Carbon, and Doped Carbon

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Specific activities for benzene hydrogenation have been measured for supported iron catalysts over a range of well-defined reaction conditions in a differential reactor. Iron surface areas based on CO chemisorption at 195 K were used to estimate particle sizes and to calculate turnover frequencies on supported iron for the first time. The turnover frequency on iron is the lowest of the group 8 metals with final values centered near  $3.5 \times 10^{-3} \text{ s}^{-1}$  at 448 K under 90 kPa H<sub>2</sub> and 7 kPa C<sub>6</sub>H<sub>6</sub>. All iron catalysts showed an activity maximum near 473 K with pressure dependencies near 3 for hydrogen and between 0 and -1 for benzene. No significant effect of crystallite size on initial TOF values was observed over a range of 2-6700 nm; however, deactivation occurred extremely rapidly on the smaller iron particles. After substantial time in the reactor, the active iron catalysts had very similar turnover frequencies at 448 K, indicating little effect of the support on specific activity; however, the highest achievable activities occurring at the activity maximum were obtained with the boron-doped carbon catalysts, which were 2-5 times more active than the other iron catalysts.

## Introduction

Benzene hydrogenation is frequently used as a model reaction for hydrogenation of aromatic hydrocarbons and it has been extensively studied over many of the group 8 metals. It is of current interest because it is the simplest reaction which might be used to study the kinetic behavior of metal catalysts for the upgrading of coal liquids by hydrogenation. Inexpensive catalysts, such as Fe, would be highly desirable; however, few studies have dealt with iron (Anderson and Kemball, 1957; Badilla-Ohlbaum et al., 1977; Beeck and Ritchie, 1950; Deberbentsev et al., 1972; Emmett and Skau, 1943; James and Moyes, 1978; Long et al., 1934; Phillips and Emmett, 1961; Schuit and van Reijen, 1958) and no kinetic studies have been reported for iron dispersed on a support.

This study was undertaken to thoroughly investigate the kinetic behavior of iron in benzene hydrogenation over a wide range of conditions in a differential reactor. Iron surface areas were measured not only so that specific activities could be determined, but also to see if very small iron crystallites possessed different catalytic properties. Finally, an emphasis was placed on the use of various carbon supports, because graphitic carbon is an electron conductor and the electronic properties of both graphitic and amorphous carbons can be altered by doping with donor or acceptor elements, such as potassium or boron, respectively. However, typical oxide supports were also utilized to disperse the iron, and unsupported iron was also studied. This paper describes and compares the catalytic properties of these iron catalysts in benzene hydrogenation.

## Experimental Section

**A. Catalyst Preparation.** The catalysts employed in this investigation are listed in Table I. All supported iron catalysts were prepared by an incipient wetness technique which employed only a quantity of an aqueous solution of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Reagent grade, Fisher Scientific) sufficient

to fill the pore volume of the support. The details of this approach are described elsewhere (Palmer and Vannice, 1980). After impregnation, the samples were oven-dried in air for 16 h at 393 K, bottled, and then stored in a desiccator. The two unsupported iron samples, ultrapure Fe<sub>2</sub>O<sub>3</sub> powder and ultrapure Fe powder (<4 ppm impurities), were obtained from Johnson Matthey Chemicals, Ltd. The Monarch 700 carbon black was heat-treated in H<sub>2</sub> at 1273 K for 12 h to remove any sulfur impurities (Vannice et al., 1981). The graphitized Monarch 700 support was prepared by heating the Monarch 700 carbon to 3073 K under N<sub>2</sub>. The iron/K-doped glassy carbon sample (3.4% Fe/K-GC) containing 0.09% K was prepared using a recipe for monolithic glassy carbons and has been described earlier (Moreno-Castilla et al., 1980). Finally, the boron-doped carbons were prepared by adding an aqueous solution of boric acid to the graphitized Monarch 700, drying at 373 K, and heating under Ar at 2073 K for 1 h (BC-11) or at 2773 K for 0.25 h (BC-12) or at 2773 K for 1 h (BC-1). The boron loadings are nominal and additional details are given in another paper which describes EPR and magnetic susceptibility properties of localized and conduction electrons in carbons (Mulay et al., to be published).

**B. X-ray Diffraction (XRD).** X-ray line broadening measurements were made on reduced samples, passivated in air, both before and after kinetic measurements. A Rigaku Model 4011 B3 diffractometer with Cu K $\alpha$  radiation was used at a scanning rate of 4° min<sup>-1</sup> over a 2 $\theta$  range of 90-20° and a rate of 1° min<sup>-1</sup> over a 2 $\theta$  range of 47-41°. The latter gave maximum sensitivity and was used to calculate Fe particle size from the  $\alpha$ -iron (110) peak at 2 $\theta$  = 44.6°. No iron oxide peaks were observed. The volume-weighted average particle size was calculated from the Scherrer equation using Warren's correction for instrumental line broadening, which was found to be 0.19° for this diffractometer in the range of 45° (Yoon, 1982).

**C. Adsorption Studies.** Hydrogen and CO chemisorption and N<sub>2</sub> and Ar BET measurements were conducted in a glass, Hg-free, adsorption system giving vacuums below 10<sup>-6</sup> torr (1.33 × 10<sup>-4</sup> Pa) with liquid N<sub>2</sub> traps.

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Table I. Description of Iron Catalysts Prepared in This Study

cat.	support	N <sub>2</sub> BET surf. area, m <sup>2</sup> g <sup>-1</sup>	amount of impregn sol cm <sup>3</sup> g of support <sup>-1</sup>	supplier of support
5.8% Fe/SiO <sub>2</sub>	Cab-O-Sil (Grade M-5)	160	2.2	Cabot Corp.
10% Fe/Al <sub>2</sub> O <sub>3</sub>	η-Al <sub>2</sub> O <sub>3</sub>	245	0.5	Exxon Res. & Eng.
5.0% Fe/C-1	Carbolac-1	950	2.5	Cabot Corp.
4.5% Fe/V3G	graphitized Vulcan 3	56	1.0	See Jung et al. (1982a)
4.8% Fe/MC	Monarch 700	206	1.0	Cabot Corp.
4.8% Fe/GMC	graphitized Monarch 700	82	1.0	---
4.8% Fe/BC-1	0.1% boron-doped GMC	110	1.0	---
5.3% Fe/BC-11	1% boron-doped GMC	92	1.2	---
5.2% Fe/BC-12	1% boron-doped GMC	87	1.0	---
3.4% Fe/K-GC	glassy carbon	350	---	---
iron powder	---	0.15 (Ar) <sup>a</sup>	---	---
Fe <sub>2</sub> O <sub>3</sub> powder	---	0.98	---	---

<sup>a</sup> Ar BET surface area.

Details of this system are given elsewhere (Palmer and Vannice, 1980). Hydrogen (Airco, 99.999%) was further purified before use by passage through a Deoxo unit (Engelhard Ind.), a 5A molecular sieve trap, and an Oxy-trap (Alltech Assoc.). Carbon monoxide (Matheson Grade, 99.99%) was passed through a molecular sieve trap held at 373 K prior to storage in 5-L bulbs. Helium (Airco, 99.9999%) was passed through a gas purifier (Alltech Assoc.), a molecular sieve trap, and an Oxytrap before use. For the BET surface area experiments, argon (Airco, 99.999%) and nitrogen (Airco, 99.995%) were used without additional purification.

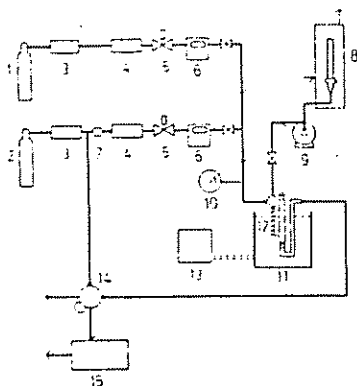
For all catalysts, the chemisorption experiments were made at 195 K using CO as the adsorbate, since CO chemisorption at 195 K has been found to be an accurate measure of iron surface area (Emmett and Brunauer, 1973; Boudart et al., 1975; Jung et al., 1982a). In some cases, hydrogen as well as CO adsorption experiments were also made at 300, 373, and 473 K. In order to determine an adsorption isotherm, six data points were typically obtained over a pressure range of 80 to 300 torr. The measurements were usually made with increasing gas pressure; however, the measurements were sometimes made in a direction of decreasing gas pressure to determine a desorption isotherm. For the first data point, it took 15 to 30 min to obtain a stable pressure reading after a sample was exposed to an adsorbate gas. The remaining data points were obtained by allowing 5 min for equilibration to occur after each pressure increase. In some cases where significant drifts in the pressure readings occurred, the equilibration time was extended until the drift disappeared or became negligible. The technique of Emmett and Brunauer (1937) was used to measure CO chemisorption. Evacuation of the sample for 2 min prior to measurement of the second isotherm removes weakly adsorbed CO, primarily from the support, and the difference between the two isotherms in the region where they become parallel, typically at pressures above 100 torr (14 kPa), is used to represent the irreversible adsorption of CO on an iron surface. To determine the H<sub>2</sub> uptake on the iron surface, the linear portion of the isotherm was extrapolated to zero pressure (Benson and Boudart, 1965).

A small amount of sample, usually about 0.3 g for supported catalysts and 4–5 g for unsupported catalysts (pure iron), was loaded in the catalyst cell, and the cell was attached to the adsorption unit. The sample was then reduced by a stepwise pretreatment procedure as follows:

(1) heat in an H<sub>2</sub> flow of 50 cm<sup>3</sup> min<sup>-1</sup> to 393 K and hold for 30 min; (2) heat to 533 K and hold for 30 min; (3) heat to 673 K and hold for 16 h. Iron-constantan thermocouples in the heating mantle and next to the catalyst were used for accurate control and measurement of temperatures which were read out on a Doric 412 A digital transducer with 0.1 K resolution. Temperature variations were less than ±2 K at all temperatures. After the reduction treatment, the temperature was lowered by 25 K, and the sample was then evacuated for 30 min. This procedure both removes hydrogen and reduces the possibility of contamination due to desorption of any species, such as water, from the support surface. The sample was then cooled under constant evacuation to the selected temperature for adsorption measurements. After the adsorption measurements, the apparent dead volume of the catalyst cell was determined using helium by keeping the cell at the same conditions under which the adsorption measurements had been made. When other adsorption experiments were conducted under different conditions on the same catalyst, the sample was heat-treated again at 673 K for 1 h under flowing H<sub>2</sub>, evacuated, cooled to the desired temperature, and the adsorption and dead volume measurements were again made. A dry ice-acetone bath was used for the adsorption experiments at 195 K.

For bulk iron catalysts, the surface area was also determined by N<sub>2</sub> or Ar BET measurements. The experimental procedure was similar to that for CO and H<sub>2</sub> adsorption experiments except that the adsorption measurements were carried out at 80 K with a liquid N<sub>2</sub> bath and the range of  $P/P_0$  was between 0.05 and 0.35, where  $P$  is the adsorbate gas pressure in the catalyst cell after equilibration and  $P_0$  is the vapor pressure of the adsorbate gas at the measurement temperature.

**D. Kinetic Studies.** The catalytic behavior of the samples in benzene hydrogenation was determined using the plug-flow microreactor system shown in Figure 1. The small, down-flow, glass tubular reactor consisted of a main reactor column, a preheating column, and an outlet tube. At the top of the preheating column a tee was attached. One of its branches was connected to a liquid feed pump and the other to a gas mixture (H<sub>2</sub> and He) line. A high-temperature sealant (Pyro-Coat 565, Aremco Products Inc.) was put around the Swagelok joints of the reactor to prevent air leaks. The liquid benzene feed was vaporized in the preheating column and mixed with the incoming gas. The liquid feed pump used was a Slow Speed Model



**Figure 1.** Microreactor system: (1) H<sub>2</sub> cylinder; (2) He cylinder; (3) molecular sieve traps; (4) oxytraps; (5) metering valves; (6) mass flow meters; (7) pressure regulator; (8) He-swept benzene reservoir; (9) peristaltic pump; (10) pressure gauge; (11) reactor in fluidized sand bath; (12) preheater column; (13) temperature controller and indicator; (14) sampling valve; (15) gas chromatograph.

miniature peristaltic pump (Rainin Instruments) with 0.63 mm i.d. Viton manifold tubing, giving a full operating flow range from 0.002 to 1.0 cm<sup>3</sup> min<sup>-1</sup>. The reactor was immersed in a fluidized sandbath (SBS-4, Techno Inc.) which provided temperatures up to 773 K. A temperature controller (West 400, Gulton Industries, Inc.) and a power controller (WZP-1225, Gulton Industries, Inc.) were used for temperature control, and reactor temperatures could be maintained constant within  $\pm 0.2$  K between room temperature and 523 K. A temperature indicator (412 A, Doric Scientific) and an iron-constantan thermocouple were used to monitor reactor temperatures with an accuracy of  $\pm 0.2$  K. The reactor system was operated at a total pressure of 1 atm (101 kPa). Pressures in the system were measured by using a diaphragm-type pressure transducer (AP-10-42, Validyne Eng. Corp.) with an accuracy of 1 torr. Individual gas flows were monitored using metering valves (Micromite 1656G24, Hoke Inc.) and calibrated mass flowmeters (Model NALL-50, Teledyne Hastings-Raydist), which were accurate to 0.1 cm<sup>3</sup> min<sup>-1</sup>. Although the pump flow rate was calibrated, the feed rate of liquid benzene was always measured by using a buret and a stopwatch, and the flow rate of benzene vapor through the reactor was calculated by assuming it to be an ideal gas. The analysis of the exit gas was conducted by using a gas chromatograph (Model 700-00, Hewlett-Packard) with isothermal operation at 338 K. Six-foot columns with GP 10% 1,2,3-tris(2-cyanoethoxy)propane on 100/120 Chromosorb P AW (Supelco, Inc.) were used with helium as the carrier gas. Peak areas were determined by an electronic integrator (Model 3390A, Hewlett-Packard).

Before use, the H<sub>2</sub> (Aircro, 99.999%) was passed through a 5A molecular sieve trap and an Oxytrap (Alltech Assoc.) and the He was passed through a Drierite molecular sieve Gas Purifier (Alltech) and an Oxytrap (Alltech). HPLC benzene (J. T. Baker, 99.9%) was degassed by several freeze-thaw cycles under flowing helium and then stored in a helium-swept glovebox in order to prevent air from dissolving into the benzene. The maximum solubility of O<sub>2</sub> in benzene is 1.8  $\mu\text{mol}/\text{cm}^3$  benzene when benzene is stored under air at room temperature (Seidell and Linke, 1958). A higher purity Ultrex benzene (J. T. Baker, 99.99%) was also used to allow comparison with the HPLC benzene, but no differences were observed within experimental error; therefore, the HPLC benzene was used for most of the kinetic studies.

The sequence in the kinetic study of a catalyst sample was: (1) activity variation with varying temperatures at standard fixed H<sub>2</sub> and benzene partial pressures, (2) ac-

tivity variation with varying H<sub>2</sub> and benzene partial pressures at different temperatures, and (3) activity change with time on-stream in a continuous run at chosen experimental conditions. The catalyst charges in the reactor were about 0.3 g for supported catalysts and 2–5 g pure iron for unsupported catalysts. The flow rates of H<sub>2</sub> were 20 to 50 cm<sup>3</sup> (STP) min<sup>-1</sup>, the flow rates of benzene were 0.005 to 0.02 cm<sup>3</sup> (liquid) min<sup>-1</sup> or 1 to 6 cm<sup>3</sup> vapor (STP) min<sup>-1</sup> (STP = 273 K and 1 atm), and helium was used to vary the partial pressures of H<sub>2</sub> and benzene. The partial pressure ranges studied were 300 to 690 torr for H<sub>2</sub> and 10 to 100 torr for benzene. High space velocities of 1000 to 3000 h<sup>-1</sup> were utilized to keep benzene conversions near 5% or less, thereby eliminating detectable heat and mass transfer effects (Yoon, 1982). The standard pretreatment described in the previous section was used for all samples in the reactor, except that after the 16 h reduction the catalyst was cooled under H<sub>2</sub> to the desired temperature which was usually between 393 and 513 K. To achieve stable operation in the reactor for measuring initial activity, the reactant gases were normally passed over the catalyst for 20 min prior to sampling the exit stream for analysis. After sampling, the benzene flow was stopped and only H<sub>2</sub> was flowed for 20 min to help regenerate and maintain a clean metal surface for the next reaction period. This bracketing technique was usually very effective in eliminating short-term complications due to catalyst deactivation and the variations observed in activity during one day of measurement were very small, except for a few catalysts which are discussed later. Cyclohexane was the only product detected in this study.

## Results

**A. Adsorption and XRD.** The irreversibly adsorbed CO was determined by the difference between the two isotherms at 200 torr and 195 K, and the uptakes are listed in Tables II and III. Iron dispersion (fraction exposed), *D*, defined as the ratio of surface iron atoms (Fe<sub>s</sub>) to total iron atoms (Fe<sub>t</sub>), was calculated assuming an adsorption stoichiometry of CO/Fe<sub>s</sub> = 0.5 (Boudart et al., 1975; Jung et al., 1982a). From these dispersions, average crystallite sizes were calculated from the equation  $d(\text{nm}) = 0.75/D$ , in which a value of 0.094 nm<sup>2</sup> Fe<sub>s</sub><sup>-1</sup> was used (Jung et al., 1982a) and these values are listed along with those obtained from the XRD data using the Scherrer equation. Hydrogen chemisorption at 300 K is not a satisfactory method to determine iron surface area (Vannice et al., 1981; Jung et al., 1982a) and, as found previously, H<sub>2</sub> uptakes on various catalysts, when measured, were always much lower than the CO uptakes, as shown in Table II. After reduction, the initial BET surface areas for the iron powder and the reduced iron oxide were 0.15 and 0.98 m<sup>2</sup> g<sup>-1</sup>, respectively.

**B. Kinetic.** Three of the catalysts, 10% Fe/Al<sub>2</sub>O<sub>3</sub>, 5.0% Fe/C-1, and the iron powder, exhibited significant deactivation despite the 20-min bracketing periods in pure H<sub>2</sub> after each activity measurement. The behavior of the 10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst is shown in Figure 2 where both the HPLC and Ultrex benzene samples were used. Excellent reproducibility in initial rates was obtained and the rate of deactivation was essentially identical with either level of benzene purity, with the Ultrex having a sulfur content below 1 ppb. This catalyst could be completely regenerated by the standard pretreatment after a set of runs (during which only the bracketing technique was used), as indicated in Figure 2. The other two catalysts could not be completely regenerated.

The other iron catalysts maintained quite stable activities during a given set of runs with the B-doped carbon

Table II. Initial Adsorption and Average Iron Crystallite Sizes Before Kinetic Studies

cat.	sample no.	irreversible uptake, $\mu\text{mol}\cdot\text{g of cat.}^{-1}$		dispersion	diameter, nm	
		CO	H <sub>2</sub>		CO chem.	XRD
4.8% Fe/MC		26		0.037	12	---
4.8% Fe/GMC		27.5		0.063	12	27
4.8% Fe/BC-1		21.5		0.050	15	---
5.3% Fe/BC-11	(1)	27	0.5	0.058	13	
	(2)					
5.2% Fe/BC-12		22		0.044	16	27
4.5% Fe/V3G <sup>a</sup>		5.6		0.014	54	33
5.8% Fe/SiO <sub>2</sub>		10.5		0.020	37	28
10% Fe/Al <sub>2</sub> O <sub>3</sub>	(1)	97		0.107	7.0	26
10% Fe/Al <sub>2</sub> O <sub>3</sub>	(2)	115	1	0.127	5.9	26
5.0% Fe/C-1		160	15	0.34	2.2	NV <sup>b</sup>
3.4% Fe/K-GC <sup>a</sup>		105		0.34	2.2	25
Fe powder		1.0		0.00011	6700	7100 <sup>c</sup>
reduced Fe <sub>2</sub> O <sub>3</sub>		6.8		0.00076	990	780 <sup>c</sup>

<sup>a</sup> Previously used for CO hydrogenation (Jung et al., 1982). <sup>b</sup> NV = nonvisible. <sup>c</sup> From BET measurements.

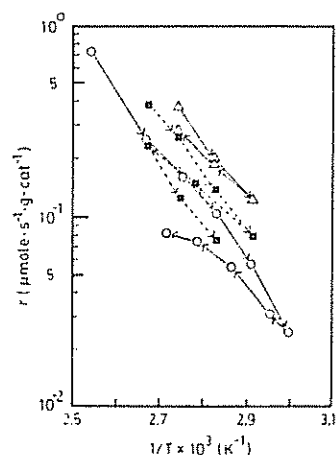


Figure 2. Deactivation measured using HPLC and Ultrax benzene over 10% Fe/Al<sub>2</sub>O<sub>3</sub>;  $P_{\text{H}_2} = 680$  torr,  $P_{\text{B}} = 57$  torr: (O) set I (HPLC); ( $\Delta$ ) set I (Ultrax); ( $\square$ ) set II (Ultrax). The sequence of runs within each set is shown by the arrows. The catalyst was regenerated after each set of runs.

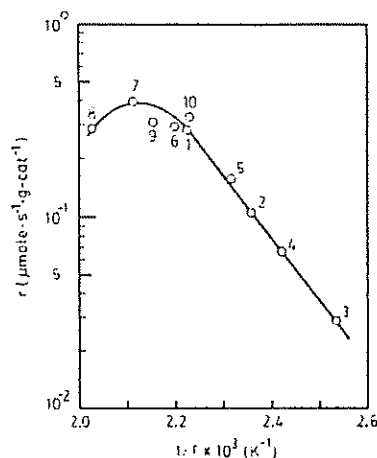


Figure 3. Activity vs. temperature over 5.3% Fe/BC-11; set I,  $P_{\text{H}_2} = 690$  torr,  $P_{\text{B}} = 40$  torr. The numbers indicate the sequence of runs.

catalysts, especially the 5.3% Fe/BC-11 sample, exhibiting excellent activity maintenance, as shown in Figures 3-5. These figures show data from many sets of runs involving changes in temperature, H<sub>2</sub> pressure, and benzene pressure, and excellent reproducibility was obtained in each set, with each set being conducted in one day. However, over the course of the many sets of runs needed to determine the partial pressure dependencies at various temperatures, the

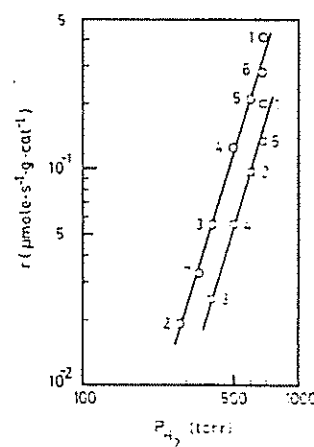


Figure 4. Rate dependence on H<sub>2</sub> pressure at 448 and 463 K over 5.3% Fe/BC-11, sample 1;  $P_{\text{B}} = 50$  torr: (O) 448 K (set II); ( $\square$ ) 463 K (set VIII). The numbers indicate the sequence of runs.

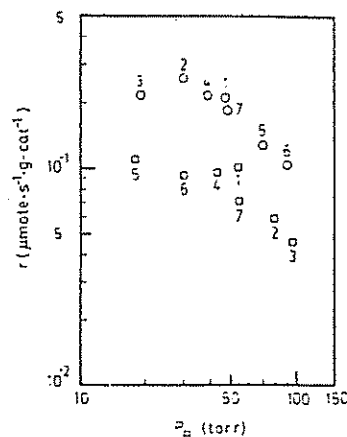


Figure 5. Rate dependence on benzene pressure at 448 and 463 K over 5.3% Fe/BC-11, sample 1;  $P_{\text{H}_2} = 600$  torr: (O) 448 K (set III); ( $\square$ ) 463 K (set IX). The numbers indicate the sequence of runs.

activity slowly declined, as shown in Table IV, where the activity at 488 K in the first set of runs is compared to that in the final set. Initial turnover frequencies (TOF = molecules C<sub>6</sub>H<sub>6</sub>·s<sup>-1</sup>·Fe<sub>s</sub><sup>-1</sup>) were calculated using CO uptakes on the fresh catalysts (Table II) while final turnover frequency values were based on CO adsorption on the used catalyst (Table III). On this basis of specific activity, the decreases are much less severe, indicating that loss of iron surface area is a major contributor to the deactivation process. The activities could be reproduced quite satis-

Table III. Final CO Uptakes and Average Iron Crystallite Sizes After Kinetic Studies

cat.	sample no.	irreversible CO, $\mu\text{mol}\cdot\text{g}^{-1}$	dispersion	diameter, nm	
				CO chem.	XRD
4.8% Fe/MC		8.5	0.020	38	27
4.8% Fe/GMC		11.5	0.027	28	22
4.8% Fe/BC-1		20.5	0.047	16	26
5.3% Fe/BC-11	(1)	15	0.029	26	22
5.3% Fe/BC-11	(2)	8.5	0.018	42	22
5.3% Fe/BC-11	(3) <sup>a</sup>	7.0	0.015	51	27
5.2% Fe/BC-12		4.5	0.0096	78	25
4.5% Fe/V3G		3.6	0.0089	84	30
5.8% Fe/SiO <sub>2</sub>		7.5	0.014	52	26
10% Fe/Al <sub>2</sub> O <sub>3</sub>	(1)	170	0.188	4.0	24
10% Fe/Al <sub>2</sub> O <sub>3</sub>	(2)	121	0.134	5.6	24
Fe powder		0.29	$3 \times 10^{-5}$	$2.3 \times 10^4$	6500 <sup>b</sup>
reduced Fe <sub>2</sub> O <sub>3</sub>		3.0	0.00033	2200	990 <sup>b</sup>

<sup>a</sup> Measurements were made on used sample 2 after being treated under flowing air at 673 K for 1 h and then reduced at 673 K for 16 h. <sup>b</sup> From BET measurements.

Table IV. Benzene Hydrogenation Activity over Iron Catalysts ( $P_{\text{H}_2} = 680$  torr;  $P_{\text{B}} = 50$  torr)

cat.	sample no.	$\bar{d}$ , nm	activity, $\mu\text{mol C}_6\text{H}_6\cdot\text{s}^{-1}\cdot\text{g}^{-1}$			TOF (molecules $\text{C}_6\text{H}_6\cdot\text{Fe}_s^{-1}\cdot\text{s}^{-1}) \times 10^5$			$E_{\text{app}}$ , kcal mol <sup>-1</sup> 390 < T < 450 K
			initial		final	initial		final	
			393 K	448 K	448 K	393 K	448 K	448 K	
3.4% Fe/K-GC		2.2	nil	nil	nil	---	---	---	---
5.0% Fe/C-1		2.2	0.30	---	---	0.93	---	---	---
10% Fe/Al <sub>2</sub> O <sub>3</sub>	2	5.9	0.77	1.35	1.36 <sup>b</sup>	3.2	5.6	---	11 ± 2
10% Fe/Al <sub>2</sub> O <sub>3</sub>	1	7.0	0.74	---	---	3.8	---	5.6	11 ± 2
4.8% Fe/GMC		12	0.012	0.44	0.13	0.22	8.0	5.8	23 ± 1
4.8% Fe/MC		12	---	0.20	0.060	---	3.8	3.5	27 ± 2
5.3% Fe/BC-11	1	13	0.023	0.31 <sup>a</sup>	0.043	0.43	5.6 <sup>a</sup>	4.0	15 ± 1
5.3% Fe/BC-11	2	13	0.022	0.65	0.053	0.41	12.0	3.1	23 ± 2
5.3% Fe/BC-11	3	---	---	---	0.031	---	---	2.2	---
4.8% Fe/BC-1		15	---	0.35	0.11	---	8.2	2.8	---
5.2% Fe/BC-12		17	---	0.88	0.040	---	20.0	4.7	23 ± 1
5.8% Fe/SiO <sub>2</sub>		37	---	0.23	0.018	---	11.0	1.2	22 ± 3
4.5% Fe/V3G		54	---	0.068	0.011	---	6.1	3.3	17 ± 2
Al <sub>2</sub> O <sub>3</sub> -promoted Fe <sup>c</sup>		61	0.019	5.74	---	0.12 <sup>d</sup>	36 <sup>d</sup>	---	~20
reduced Fe <sub>2</sub> O <sub>3</sub>	1	990	---	0.014	0.0080	---	1.0	1.2	26 ± 3
reduced Fe <sub>2</sub> O <sub>3</sub>	2	990	---	0.022	---	---	1.6	---	26 ± 3
iron powder		6700	0.0013	0.030	nil	0.65	15.0	---	20 ± 6

<sup>a</sup> Average of two runs. <sup>b</sup> Obtained in run immediately after the heat-treatment at 673 K. <sup>c</sup> From Badilla-Ohlbaum et al. (1977). <sup>d</sup> Extrapolated from rate equation in Badilla-Ohlbaum et al. (1977).

factorily as indicated by a comparison of the results from two different samples of 10% Fe/Al<sub>2</sub>O<sub>3</sub>, 5.3% Fe/BC-11, and reduced Fe<sub>2</sub>O<sub>3</sub>. The activity of the reduced iron oxide powder actually showed a small increase as time on-stream increased, which is attributable to an increase in Fe surface area as the BET areas changed from 0.98 to 1.07 m<sup>2</sup> g<sup>-1</sup>.

Every iron catalyst studied showed an activity maximum similar to that in Figure 3, and all occurred near 473 K with the exception of the reduced Fe<sub>2</sub>O<sub>3</sub> sample which had a maximum near 493 K. Other clear examples of this behavior are shown by the 4.8% Fe/MC and the 5.8% Fe/SiO<sub>2</sub> catalysts whose activity as a function of temperature is indicated in Figure 6. For this reason, apparent activation energies could be determined only in the low-temperature region below 450 K and these values are also listed in Table IV. The partial pressure dependencies at five temperatures between 413 and 493 K, the activity maximum, and the reaction mechanism proposed to explain this behavior are described in detail in another paper (Yoon and Vannice, 1983). Suffice it to say here that hydrogen partial pressure dependencies were near third order or somewhat higher for all catalysts except the 10% Fe/Al<sub>2</sub>O<sub>3</sub> sample, which showed a temperature-dependent order varying from 1/2 to 3/2. Negative benzene pressure dependencies between 0 and inverse first order, again temperature-dependent, were found for all catalysts (Yoon,

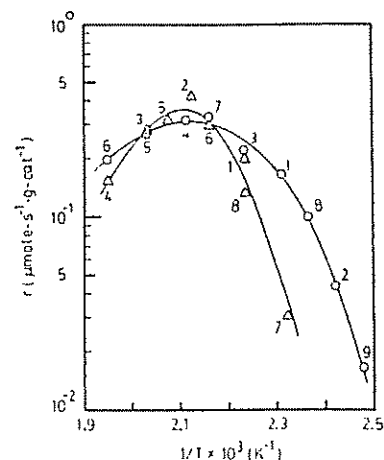


Figure 6. Activity vs. temperature over 5.8% Fe/SiO<sub>2</sub> (O) and 4.8% Fe/MC ( $\Delta$ );  $P_{\text{H}_2} = 680$  torr,  $P_{\text{B}} = 50$  torr. The numbers indicate the sequence of runs.

1982; Yoon and Vannice, 1983). A proposed rate equation of the form

$$r = kP_{\text{H}_2}^3 P_{\text{B}} / (1 + K_{\text{B}} P_{\text{B}})^2$$

where  $k$  and  $K_{\text{B}}$  are constants and  $P_{\text{H}_2}$  and  $P_{\text{B}}$  are the hydrogen and benzene pressures, respectively, was found

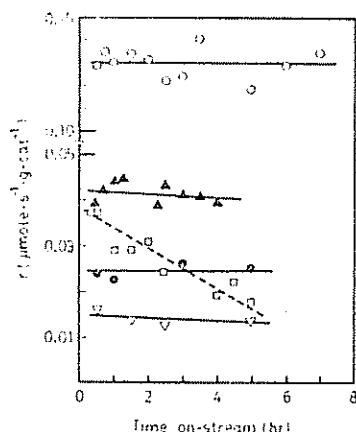


Figure 7. Activity maintenance of supported iron catalysts:  $T = 448$  K,  $P_{H_2} = 680$  torr,  $P_B = 50$  torr: (O) 4.8% Fe/GMC; ( $\nabla$ ) 5.3% Fe/BC-11; ( $\Delta$ ) 5.2% Fe/BC-12; ( $\diamond$ ) 4.5% Fe/V3G; ( $\square$ ) 5.8% Fe/SiO<sub>2</sub>.

Table V. Activity Maintenance and TOF Values Occurring at Activity Maximum

cat.	sample no.	% act. <sup>a</sup> after 5 h	$N_{max} \times 10^3$ <sup>b</sup> molecule s <sup>-1</sup> Fe <sub>s</sub> <sup>-1</sup>
10% Fe/Al <sub>2</sub> O <sub>3</sub>	2	>90	5.7
4.8% Fe/MC	1	30	7.8
4.8% Fe/GMC	1	0	15
5.3% Fe/BC-11	1	--	6.8
5.3% Fe/BC-11	2	--	26
5.3% Fe/BC-11	3	5	--
4.8% Fe/BC-1	1	50	8.9
5.2% Fe/BC-12	1	5	26
4.5% Fe/V3G	1	0	~8
5.8% Fe/SiO <sub>2</sub>	1	40	16
reduced Fe <sub>2</sub> O <sub>3</sub>	1	15	5.2

<sup>a</sup> The initial activity was estimated by extrapolation to zero time on-stream; reaction conditions:  $T = 448$  K;  $P_{H_2} = 680$  torr;  $P_B = 50$  torr. <sup>b</sup> The initial specific activity at  $T_{max} = 493$  K for reduced Fe<sub>2</sub>O<sub>3</sub>,  $T_{max} = 473$  K for the others; reaction conditions:  $P_{H_2} = 680$  torr;  $P_B = 50$  torr.

to describe the data very well and also to predict the rate maximum (Yoon, 1982; Yoon and Vannice, 1983).

After completion of the kinetic studies, activity maintenance was studied during continuous on-stream operation under a standard set of reaction conditions ( $T = 448$  K;  $P_{H_2} = 680$  torr;  $P_B = 50$  torr). The behavior typical of the catalysts exhibiting no, little, or moderate activity loss is shown in Figure 7, and the degree of activity loss after 5 h on-stream for all samples studied is reported in Table V. Also in Table V are listed the maximum TOF values observed for each catalyst.

## Discussion

The hydrogenation of benzene has been studied on iron films (Anderson and Kemball, 1957; Beeck and Ritchie, 1950; James and Moyes, 1978), iron powder (Deberbentsev et al., 1972; Emmett and Skau, 1943; Long et al., 1934), bulk promoted iron (Badilla-Ohlbaum et al., 1977; Phillips and Emmett, 1961), and silica-supported iron (Schuit and Reijen, 1958). However, a thorough kinetic analysis was reported only in the study of Badilla-Ohlbaum et al. (1977), although James and Moyes (1978) reported partial pressure dependencies at 273 K. No kinetic studies have been conducted on supported iron or on unsupported, nonpromoted bulk iron. Even with inexpensive metals such as iron, dispersing the metal on a support can be beneficial because higher metal surface areas per gram of catalyst

can be achieved along with greater stabilization toward sintering under reaction conditions. In addition, the type of support can affect catalytic activity in certain reactions. For example, Sagert and Pouteau (1972, 1973) have found that the specific activity of Graphon-supported platinum in the D<sub>2</sub>-H<sub>2</sub>O exchange reaction increased with the degree of graphitization of the carbon, and Aika et al. (1972) have reported that carbon-supported Ru and Fe catalysts showed enhanced activity for ammonia synthesis when potassium was deposited on the carbon surface. In the benzene hydrogenation reaction, Taylor and Staffin (1967) reported that carbon-supported cobalt had a similar specific activity but a lower activation energy compared to silica- and alumina-supported cobalt. Finally, highly dispersed iron can be prepared on certain carbon supports, and the catalytic behavior of very small iron crystallites for CO hydrogenation is significantly different from that of large iron crystallites (Vannice et al., 1981; Jung et al., 1982a,b). As a consequence of these studies it was of considerable interest not only to determine the specific activities and kinetic behavior of iron dispersed on various supports including boron- and potassium-doped carbons, but also to learn whether the support or iron crystallite size has any significant effect on the catalytic properties of iron for benzene hydrogenation.

A number of studies have indicated that CO chemisorption at 195 K is an accurate method of measuring reduced iron surface area (Emmett and Brunauer, 1937; Boudart et al., 1975; Jung et al., 1982a) and the results of this investigation support this conclusion. With the unsupported iron, quite satisfactory agreement was obtained between surface areas calculated by BET measurements and those calculated from CO chemisorption. As indicated in Table II, only the 5.0% Fe/C-1 catalyst was well-dispersed although the 10% Fe/Al<sub>2</sub>O<sub>3</sub> did appear to have iron crystallites well below 10 nm. The chemisorption measurement on the K-doped sample (3.4% Fe/K-GC) was complicated by the presence of the potassium, and the larger particle size indicated by XRD may be a more accurate indication because of the high-temperature treatment utilized during preparation (Moreno-Castilla et al., 1980). Agreement between particle sizes obtained from chemisorption and XRD measurements was only moderate, although values typically agreed within a factor of 2, particularly for the C-supported catalysts. The higher CO uptakes on the used 10% Fe/Al<sub>2</sub>O<sub>3</sub> samples are probably a consequence of more complete reduction because of the repeated regeneration steps at 673 K. The average iron crystallite size determined by CO chemisorption is almost certainly more accurate than that from XRD because of the insensitivity of the latter to crystallites below 4 nm. Regardless, the assumption of a CO<sub>(ad)</sub>/Fe<sub>s</sub> ratio of one-half provides reasonable agreement and allows the calculation of turnover frequencies.

These turnover frequencies (TOF) indicate consistent behavior among these iron catalysts even with the complication of rapid deactivation in some systems, as mentioned previously. With the exception of 10% Fe/Al<sub>2</sub>O<sub>3</sub>, TOF values at 393 K were between 0.2 and  $0.9 \times 10^{-3} \text{ s}^{-1}$  while a somewhat wider range of initial activities occurred at 448 K; however, for most supported catalysts a TOF near  $8 \times 10^{-3} \text{ s}^{-1}$  existed. After long periods on-stream, the final activities were similar, with a value of  $(3.5 \pm 2) \times 10^{-3} \text{ s}^{-1}$  at 448 K describing all catalysts. There are few previous values to which these turnover frequencies can be compared. Estimating a value for Fe<sub>s</sub> from the BET measurement on the promoted catalyst studied by Badilla-Ohlbaum et al. (1977) and extrapolating their rate equation

to the pressures in Table IV provides the values listed. The agreement is not unreasonable considering the approximations. Using the apparent activation energies and the TOF values at 393 K and  $P_{H_2}$  of 680 torr, specific activities at 273 K can be estimated. These values of  $9.8 \times 10^{-10} \text{ s}^{-1}$  for 5.3% Fe/BC-11 (sample 2),  $7.8 \times 10^{-6} \text{ s}^{-1}$  for 10% Fe/Al<sub>2</sub>O<sub>3</sub> (sample 1), and  $8.4 \times 10^{-9} \text{ s}^{-1}$  for iron powder are all lower than the value of  $2.2 \times 10^{-5} \text{ s}^{-1}$  reported by James and Moyes (1978) on iron films. This last value was obtained by dividing the reported rate by 6 as it represented the rate in terms of H atoms reacted. The hydrogen partial pressure (20 torr) used therein was much lower, and, in addition, the Fe surface area was measured by D<sub>2</sub> chemisorption. When compared to other group 8 metals at identical conditions, iron is clearly the least active and has a TOF that is from one to three orders of magnitude lower than those on other metals (Yoon, 1982; Yoon and Vannice, 1983).

The cause for the rapid deactivation of three catalysts—5.0% Fe/C-1, 10% Fe/Al<sub>2</sub>O<sub>3</sub>, and iron powder—is not precisely known, but this behavior was quite reproducible because at least two different samples of each catalyst gave essentially identical results. However, significant differences existed among the three catalysts as the 10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst could be completely regenerated by the standard pretreatment whereas the other two could not. This result plus the absence of deactivation with some catalysts and the similar deactivation pattern with two different benzene purities, as shown in Figure 2, strongly argue against the possibility of poisoning by trace amounts of sulfur (or other impurities). Also, sintering cannot adequately describe loss of activity because iron surface areas of these catalysts did not change significantly as shown in Tables II and III. The pretreatment (and regeneration) procedure used in this study is known to reduce the iron (Jung et al., 1982a); therefore, deactivation by oxygen entering via an air leak or in the benzene is not a satisfactory explanation because complete regeneration should have been achieved after rereduction of the iron. In addition, tests were run to check for air leaks and the benzene had been degassed and kept under flowing helium.

These considerations lead us to conclude at this time that deposition of carbonaceous material on the iron surface and/or the formation of iron carbide phases represent the most likely explanation of the deactivation process. The small iron crystallites in the 5.0% Fe/C-1 catalyst are known to have suppressed H<sub>2</sub> adsorption, lower CO hydrogenation activity, and to readily form iron carbides (Jung et al., 1982a) and this could account for their rapid activity loss. Such explanations have been proposed for the deactivation observed during benzene hydrogenation over Ni and Pt catalysts (Huang and Richardson, 1978; Marangozis et al., 1979; Akyurtlu and Stewart, 1978). Graphitic carbons can be obtained by passing benzene and hydrogen over iron at higher temperatures of 673–1423 K (Kawasumi et al., 1981), and three different forms of carbon have been identified by Bonzel and Krebs (1980) on an Fe (110) surface during CO hydrogenation. The graphitic form of carbon was very unreactive toward hydrogenation. Therefore, the possibility exists that residual benzene or carbonaceous material on the iron in some cases might even be converted into unreactive graphitic carbon during the regeneration step, thereby nullifying its effectiveness. To determine if the very slow activity decline observed for 5.3% Fe/BC-11 might be reversed by an activation in air to remove carbon species, sample 2 of this catalyst was heated in situ in flowing air at 673 K for 1 h and then given the standard pretreatment. The specific

activity of this sample (sample 3) was not regenerated and was somewhat lower than that for sample 2, while CO chemisorption also decreased (Table III). This result is consistent, however, with the supposition of a very stable unreactive graphitic carbon species.

The activity maximum that was always observed as the temperature increased, as shown in Figures 3 and 6, and the partial pressure dependencies represented in Figures 4 and 5 are consistent with a reaction model that assumes that the rate-determining step is the addition of the last H atom to an adsorbed C<sub>6</sub>H<sub>11</sub> species. Such a model predicts the rate equation given previously. This has been discussed in detail in another paper (Yoon and Vannice, 1983). However, the appearance in this study of an activity maximum which was clearly reversible has been observed over other metals (van Meerten and Coenen, 1975, 1977; Kubicka, 1968) and is not a consequence of thermodynamic limitations on conversion as equilibrium conversions of benzene under the conditions employed here are 97.5% or higher.

No significant trend in TOF values was observed among the various catalysts; however, the B-doped carbons did provide the highest values and the K-containing catalyst had no detectable activity. This behavior is more apparent when the maximum activities obtained with each catalyst are compared, and Table V shows that the two carbon supports doped with 1% boron produced catalysts which were 2–5 times more active than the other catalysts. The iron dispersed on these two B-doped carbons also showed very good activity maintenance; however, Table V indicates that this may well be a feature of the graphitic state of the carbon because the two graphitized carbon supports (GMC and V3G) also produced catalysts with essentially constant activity during 7 h on-stream as shown in Figure 7. The difference in behavior for the SiO<sub>2</sub>-supported iron is clearly evident. Although the 4.8% Fe/BC-1 and 4.8% Fe/MC catalysts exhibited noticeable activity loss during the first hour or two on-stream, their activity was constant for the remainder of the 6-h run while stable activities on-stream were never achieved for the 10% Fe/Al<sub>2</sub>O<sub>3</sub> and reduced Fe<sub>2</sub>O<sub>3</sub> powder catalysts (Yoon, 1982). The 5.0% Fe/C-1 which had the smallest crystallites deactivated very rapidly and unsupported iron also showed continuous large activity declines. Because of the influence of deactivation and the use of different supports, 2 to 3-fold variations in final activity at 448 K were not considered significant. However, similar variations in activity loss for a given catalyst were assumed significant as all final activities were internally consistent because of the comparison to initial activity for that particular catalyst.

## Summary

This study has measured specific activities for benzene hydrogenation over a variety of supported iron catalysts through a range of well-defined reaction conditions by use of a differential reactor. Iron surface areas based on CO chemisorption at 195 K were to estimate particle sizes and to calculate turnover frequencies on supported iron for the first time. In addition, any influence of crystallite size or of the support could be clarified. The turnover frequency on iron is the lowest of the group 8 metals; however, the activity per gram of iron can be greatly increased by dispersion on a support material. All iron catalysts showed an activity maximum near 473 K, a pressure dependence on H<sub>2</sub> near 3, and on benzene between 0 and -1.

After substantial time in the reactor, the active iron catalysts had very similar turnover frequencies at 448 K, indicating little effect of the support on specific activity; however, the highest achievable activities occurring at the

activity maximum were obtained with the boron-doped carbon catalysts, which were 2-5 times more active than the other iron catalysts. Carbon-supported iron possessed superior activity maintenance, with two graphitized carbon supports (GMC and V3G) showing stable activity and the two 1% B-doped graphitized carbons showing almost no decline in activity. In contrast, large continuous decreases occurred for unsupported iron and iron supported on silica and alumina. Evidence at this time favors formation of surface carbon and/or iron carbide as the explanation for this deactivation process and the possibility exists that carbon supports may retard or eliminate this problem.

No significant effect of crystallite size on TOF values was observed over a range of 2-6700 nm; however, deactivation occurred extremely rapidly on the smaller iron particles. This is attributed to the decreased H<sub>2</sub> adsorption and reduced hydrogenation activity observed over small iron crystallites and the strong possibility of rapid iron carbide formation (Jung et al., 1982a). Addition of potassium to an Fe/C system had only negative effects. However, of the iron catalysts studied, the carbon-supported systems, especially B-doped carbon, appear to be superior catalytic systems.

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Registry No. Fe, 7439-89-6; Al<sub>2</sub>O<sub>3</sub>, 1344-28-1; Cab-O-Sil, 7631-86-9; benzene, 71-43-2; boron, 7440-42-8; carbon, 7440-44-0.

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