

Iron as a Catalyst for the Hydrogenation of Benzene

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The activities are reported of reduced precipitated iron catalysts and promoted and unpromoted iron synthetic ammonia catalysts for benzene hydrogenation over the temperature range 380–473 K. Singly promoted iron (5.50% Al₂O₃) was the most active of the iron catalysts, being, at 450 K, some 22 times more active than unpromoted iron and some 4.5 times more active than iron prepared by NaOH precipitation of the hydroxide. The results with doubly promoted iron (2.29% Al₂O₃, 1.64% K₂O) were somewhat equivocal in that benzene was more strongly absorbed on this catalyst and cracking was more extensive at all temperatures. Both iron nitride, Fe₄N, and iron carbide, Fe₂C, prepared by nitriding and carbiding reduced unpromoted iron showed no benzene hydrogenation activity. A reduced copper catalyst had, effectively, zero activity under these reaction conditions (~7:1 H₂:C₆H₆). However, a reduced nickel catalyst was more than 4 times more active than singly promoted iron at 450 K and was able to maintain this higher activity for long contact periods. All of the iron catalysts showed a (frequently sharp) decrease in activity with time attributed to adsorption of hydrocarbon complexes which can under certain conditions lead to the formation of nuclei of an iron carbide. © 1986 Academic Press, Inc.

INTRODUCTION

These results on the activity of carefully reduced iron catalysts in benzene hydrogenation were reported at the XVIIIth International Congress on Pure and Applied Chemistry (1) and have been referred to in later published work but have not, heretofore, been submitted for publication. In view of the work of Badilla-Ohlbaum (2) and Vannice and co-workers (3, 4), among others, on the activity of a wide variety of iron catalysts in this reaction and the reaction kinetics, it seems useful to summarize, briefly, our early work in this area. When this research was begun in 1957, all the *bulk* metals active as catalysts for the low-temperature benzene–cyclohexane reaction belonged to the hexagonal or fcc system with atomic radii in the range 0.1399–0.1236 nm in agreement with Balandin's prediction (5). Evaporated unoriented iron *films* (6) had a

reported benzene hydrogenation activity at 296 K about 4% of that of oriented nickel films. In 1958, a *supported* iron catalyst (0.150 g Fe/g SiO₂, "Sorpsil" impregnated with Fe(NO₃)₃) was reported (7) to have a finite specific activity for benzene hydrogenation though 200 times less than the activity of a similar rhodium catalyst.

We studied, altogether, five iron catalysts: three fused iron synthetic ammonia catalysts from the series prepared by the former Fixed Nitrogen Laboratory of the U.S. Department of Agriculture and designated by their catalog numbers (unpromoted **928**; **198** containing 5.50% Al₂O₃; **438** containing 2.29% Al₂O₃ and 1.64% K₂O) and two pure iron catalysts, **Fe I** prepared by ammonia precipitation (8) and **Fe II** by NaOH precipitation of the hydroxide from Fe(NO₃)_{3(aq)}. A copper catalyst prepared by the method of Skau (9) and a nickel catalyst prepared by R. J. Kokes using the method of Best and Russell (10) were also tested. Since the iron atoms in Fe₄N form a fcc lattice with an interatom distance in the (111) plane which satisfies Balandin's re-

[†] Deceased April 22, 1985. This work was carried out under Professor Emmett's direction and this paper represents a final tribute to him.

quirement, catalyst **928** was nitrided and the activity of the Fe_4N so prepared was investigated. Fe_2C prepared by carbiding **928** was also tested for activity.

EXPERIMENTAL

The promoted and unpromoted iron and the nickel and copper catalysts were reduced in hydrogen at volume hourly space velocities of 1800 to 6000. The maximum reduction temperature was a function of catalyst composition: 753 K for **198** and **438**; 673–723 K for **928**; 593 K for **Fe I**; 653 K for **Fe II**; and 613 K for **Cu** and **Ni**. Catalyst sample sizes varied from 8.90 g (**928**) and 8.11 g (**198**) to 1.13 g (**Ni**). A total of nine samples of unpromoted **928** was studied.

Fe_4N was prepared by passing a 35 vol% NH_3 –65 vol% H_2 mixture over reduced **928** at 693 K, 1000 VHSV, for 4–5 h. No carbon monoxide chemisorption could be detected at 78 K on this catalyst.

Fe_2C was prepared by the method of Emmett and co-workers (11) by passing, typically, *n*-butane over reduced **928** at 573 K, 250 VHSV, for 9 h. Carbon monoxide physical adsorption and total adsorption at 78 K were identical and equal to, within the limits of experimental error, the physical adsorption of nitrogen at that temperature.

Reaction products were analyzed gas chromatographically on a 3.6-m dioctyl phthalate on Celite column thermostated at 360 K and connected to a four-filament Gow-Mac cell, Model TE3. A molecular sieve column, Perkin–Elmer Column J, in series with the dioctyl phthalate column resolved hydrogen and the hydrocarbons through C_3 .

Gaseous reactants and the helium carrier gas were pretreated by standard procedures. A single 3.0-liter lot of Matheson, Coleman and Bell Spectroquality benzene was used in all experiments; prior to use, it was passed through a small column filled with Davison Chemical Company Grade 12 silica gel.

Both flow and static vapor-phase experi-

ments were carried out in an all-glass reaction system. In the former, the hydrogen–benzene stream (generally, 7:1 H_2 : C_6H_6 , 500–900 VHSV) passed over the catalyst, then through a 273 K condenser. The refractive index of the condensate was determined at half-hourly intervals. At 20-min intervals, the reaction stream was diverted by manipulation of the stopcocks and the reactor was swept by carrier gas. The reaction mixture in the gas phase and reversibly held on the surface was carried into the chromatograph column. The values of activity determined chromatographically are only about one-fourth of those determined by refractive index measurement due, most likely, to removal by the carrier gas of weakly bound reactant from the catalyst surface. In static experiments, the reactant mixture was trapped in the reactor for arbitrary periods of time, after which the reactant–product “slug” was swept into the chromatograph column. Between the introduction of successive volumes of reaction mixture, the catalyst was either left in helium or was swept with hydrogen at reaction temperature.

RESULTS AND DISCUSSION

Surface areas and representative activities for the catalysts which showed benzene hydrogenation activity are listed in Table I.

Nitrided and Carbided Iron

No activity for benzene hydrogenation was shown by any of three different Fe_4N samples at 368, 399, 429, or 472 K. However, reduction of the nitride with hydrogen at temperatures as low as 473 K restored activity to the expected levels. Since nitriding increases the surface area by as much as 40%, it was hoped that careful reduction of the nitride would give a high-area iron catalyst which would show measurable activity below, say, 353 K. This was not the case. The completely carbided catalysts were also inactive for benzene hydrogenation and cracking at 403 to 473 K even with ex-

TABLE I

Catalyst (sample mass, g)	BET area (m ² g ⁻¹ metal)	Activity (μmol benzene converted · s ⁻¹ g ⁻¹ metal)	Temper- ature (K)	Apparent activation energy ^a (kJ mol ⁻¹)
Ni (1.13)	0.82	Flow ^b : 3.8 to 4.5	451	~32 to 33
		"Slug": 0.084	331	
		0.78	409	
Cu (1.76)		"Slug": 1.4 × 10 ⁻⁴	435	~42
		3.6 × 10 ⁻⁴	473	
			395	
Fe I (2.36)	2.35	"Slug": 0.10	430	~14.5
		0.15	430	
Fe II (1.23)		Flow ^b : 0.21	438	~26
		"Slug": 0.06	414	
		0.12	459	
198 (8.11)	18.4	Flow ^b : 0.74	431	~32
		"Slug": 0.023	368	
438 (7.94) (5.64)	7.03	Flow: 8 × 10 ⁻³ ^c	429	~53
		"Slug": 0.024	364	
		0.012 ^c	460	
928 (2.72) (3.78) (4.84) (5.13) (8.81)	0.83	Flow ^b : 0.043	451	~53
		"Slug": 0.008	435	
		0.025	460	
		"Slug": 0.016	403	
		0.043	458	
		"Slug": 0.0035	435	
		0.0105	469	
		"Slug": 8.5 × 10 ⁻⁴	376	
		8.5 × 10 ⁻³	429	
		0.011	453	

^a Values calculated from a series of "slug" activities.

^b Activity based on condensate refractive index.

^c C₁, C₂ cracking products observed in addition to C₆H₁₂.

tended contact times (up to 4 min). Reduction in hydrogen at 673 K restored activity to about 80% of precarbiding values. It should be noted that both Fe₄N and Fe₂C were active for the hydrogenation and disproportionation (to cyclohexane and benzene) of cyclohexene at 403–433 K.

Promoted Iron

The results with the doubly promoted **438** are somewhat equivocal since it was apparent that benzene was more strongly adsorbed on this catalyst than on the other iron catalysts. Cracking was more extensive at all temperatures and was detected at lower temperatures than over unpromoted iron. For example, analysis of a "slug" of reactant trapped for 30 s on **438** at 429 K suggested that ~7% of the benzene had

been hydrogenated to cyclohexane. A second sweeping by carrier gas of the catalyst some 25 min later desorbed substantial amounts of benzene, cyclohexane and cracking products (C₁ through C₅). A third sweeping with carrier gas after yet another 25 min produced still more benzene, cyclohexane, and C₁–C₂ hydrocarbons. In fact, the benzene in the first sample analyzed was only 65% of the total benzene recovered in four carrier gas sweepings of the catalyst and the cyclohexane in the first sample was only 50% of the total cyclohexane recovered. In comparison, trapping a 7:1 H₂:C₆H₁₂ "slug" on the catalyst at the same temperature for 30 s, followed by three sweepings with carrier gas showed neither cracking products nor significant cyclohexane retention on the catalyst. Similar results were obtained for benzene and cyclohexane on this catalyst at 382 and 463 K.

Singly promoted **198** was the most active of the iron catalysts studied. Complete conversion of benzene was observed over 1.5 h in a flow experiment at 413 K even though small amounts of C₁ through C₄ hydrocarbons were detected, indicating that, with this catalyst, cracking did not lead to significant catalyst deactivation. At 358 K and at 444 K although not at 473 K, some retention of benzene by **198** after a 2-min sweeping with carrier gas was observed. At no temperature, however, was it significant in comparison to the strong retention by **438**.

Unpromoted Iron

In reviewing the results with all of the active iron catalysts, it is noted that their high initial activity decreases fairly sharply with time. While the activity of a fresh catalyst sample was relatively constant (or decreased less rapidly with time than that of a regenerated catalyst), after one or two periods of use followed by reduction, the activity showed the more typical pattern of a sharp decrease to a much lower, relatively constant, level. With **928**, at 425 K, with a 42 ml min⁻¹ flow of 7:1 H₂:C₆H₆ (*t_c* ≈ 5 s),

conversion to cyclohexane decreased from 59% at 1 min, to 27% at 30 minutes, to 16% at 1 h and, at the end of 3 h, was more or less constant at 9–10%. Initial activity could be restored by a short reduction, 1 h at 673 K, but if a second similar flow experiment was performed, it was always observed that the activity decreased less rapidly and levelled off at a value higher than that expected for a “completely” reduced catalyst.

In static experiments with **928**, activity could be maintained at all temperatures studied, even at 380 and at 470 K, by passing 100–200 ml min⁻¹ of hydrogen over the catalyst for as little as 15 min at reaction temperature between “slugs.” Reproducible values of conversion obtained under such conditions for $t_c = 30$ s gave a value for an apparent energy of activation of ~ 53 kJ mol⁻¹. Increasing the H₂:C₆H₆ ratio in the reactant stream from about 7:1 to 188:1 did not, on the other hand, maintain catalyst activity for successive reactant “slugs” at any temperature.

In agreement with thermodynamic calculations, cyclohexane in hydrogen on **928** at 470 K, underwent neither dehydrogenation nor cracking whereas in helium on helium-covered **928** some dehydrogenation and cracking were observed at ~ 433 K. No reaction products were observed for benzene in helium on **928** between 400 and 470 K. Cyclohexane in helium on helium-covered **928** at 471 K underwent significant disproportionation into benzene and cyclohexane.

Times of contact and benzene concentrations were such that cracking obscured any maximum in hydrogenation activity at ~ 453 K as observed by Badilla-Ohlbaum (2).

The simplest explanation for the sharp fall and subsequent leveling-off in activity of the iron catalysts was that, at lower temperatures and shorter times of contact, the surface becomes covered with some sort of chemisorbed hydrocarbon complex while, at higher temperatures or longer contact

times, when cracking of the chemisorbed fragments occurs, nuclei of a surface carbide, probably Fe₂C form, gradually restricting the active surface area. Work by Emmett and co-workers (11) on the formation of Fe₂C and its characteristics had shown that carburizing occurs in patches, a certain amount of free iron surface remaining as the carbidic carbon content approaches that corresponding to Fe₂C. The total available surface area is not greatly altered as carburizing takes place nor is the adsorption of hydrogen at and above 100°C greatly affected until the iron is half converted to Fe₂C. The initially higher rates of carburizing of doubly promoted **435** (0.8% Al₂O₃, 0.25% K₂O) observed by Emmett *et al.* (11) anticipated the more extensive cracking of benzene on **438** reported here.

In an effort to determine the extent of carbon retention by the iron catalysts, the hydrocarbon products formed during regenerative reduction at 673 K were, in some 20 cases, trapped on silica gel at 78 K. The catalyst had been swept with helium several times as the temperature was raised to about 600 K to remove any adsorbed hydrocarbons. The hydrocarbons evolved on warming the silica gel trap were analyzed over Perkin–Elmer Column J. Only CH₄ was detected, in amounts corresponding to several monolayers of Fe₂C—in some cases to as many as 7 to 8 layers. The amount of CH₄ collected appeared to be a function of reaction temperature rather than of time of contact for both flow and static experiments: for example, at 456 K after 60 min reaction time 3.3 ml (STP) CH₄ were collected while after 15 min reaction time, 3.0 ml (STP) CH₄ were formed. Since the completely carburized iron catalyst was inactive for benzene hydrogenation, the low, constant activity shown by all the catalysts must be associated with the iron surface and thus, any carbide nuclei that form must be many atoms layers in depth.

That the relatively constant high activity of a new catalyst sample during its initial period of use may be due to a predomi-

nance of surface (111) planes (12) is supported by the observation that samples reduced under a high hydrogen flow were, initially more active than those reduced at a flow $\sim 100 \text{ ml min}^{-1}$. With use and regeneration, the planes of open structure will disappear with a preferential increase in close-packed (100) planes of lower activity (13). That elemental carbon as graphitic platelets or films or, probably, even as amorphous films or filaments does not form is shown by restoration of activity on reduction at 673 K.

Comparison With Ni and Cu Catalysts

The one copper catalyst sample of the three tested which showed any activity (Table 1) was reduced at a maximum temperature of only 488 K.

The nickel catalyst was active at 332 K (TON $\approx 4 \times 10^{16}$ molecules benzene $\cdot \text{m}^{-2} \text{ s}^{-1}$) whereas the lowest temperature at which any activity was observed for an iron catalyst was about 326 K (928, TON $\approx 3 \times 10^{14}$ molecules benzene $\cdot \text{m}^{-2} \text{ s}^{-1}$). While no significant reduction in activity of the nickel catalyst sample was observed in 13.25 min contact with reactant at 332 K or in 1.5 h contact at 448 K (55 ml min^{-1} flow of 6:1 H_2 : C_6H_6 mixture), the hydrocarbon products of the reduction at 523 K when analyzed on Column J were identified as CH_4 , C_2H_6 , and C_3H_8 in the same proportions observed by Bahr and Bahr on reduction of Ni_3C by hydrogen at 523 K and atmospheric pressure (14).

CONCLUSIONS

Reduced promoted and unpromoted iron catalysts have been shown to be active for benzene hydrogenation at temperatures between 373 and 473 K, their activity, however, decreasing rapidly with use and leveling off at a low, fairly constant value. This decrease in activity appears to be due to adsorption of hydrocarbon complexes

which can lead to the formation of nuclei of an iron carbide. Singly promoted iron, catalyst 198, while only about one-fourth as active as nickel, appears to be ~ 3.6 times more active than Fe II (NaOH precipitation) and ~ 22 times more active than unpromoted 928. Copper showed, effectively, zero activity for benzene hydrogenation under these conditions. Nickel, however, was shown to be at 408 K, ~ 50 times, and at 328 K, ~ 150 times more active than iron and was able to maintain this activity for long contact periods in spite of a similar adsorption of hydrocarbon complexes and probable carbide formation.

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