# Effect of Promoters on Benzene Hydrogenation over Fused Iron Catalysts

The hydrogenation of benzene to cyclohexane is a structure-insensitive reaction (1) which, at atmospheric pressure, is thermodynamically favoured at temperatures below 550 K (2). The Group VIIIA metals are the most active catalysts for this reaction; studies prior to the 1960s showed zero (or very low) activity for iron (3–7). Badilla-Ohlbaum et al. (8) reported the first thorough kinetic study of the reaction over a 7.95 mass% $Al_2O_3$-promoted fused iron catalyst; a rate maximum was observed at 443 K and the authors suggested that the rate-determining step was the surface reaction of adsorbed benzene with adsorbed hydrogen.

Vannice and co-workers (9, 10) have reported the activities of and kinetic data over a series of supported iron catalysts. Rate maxima were observed near 473 K; activities (mol $s^{-1}$ $g_{cat}^{-1}$) were roughly one order of magnitude less than that reported by Badilla-Ohlbaum et al. (8) under similar conditions. While it is apparent that the catalytic activity of iron for this reaction is too low to be of industrial significance, it was of interest to know to what extent the difference in the rates is due to chemical promotion. To this end, the activities of four multiply promoted ammonia synthesis catalysts were compared with that of a precipitated iron in an effort to determine the effect of acidic and basic promoters on the reaction rate.

## EXPERIMENTAL

The catalysts studied were ICI 35-4 (obtained from Imperial Chemical Industries PLC, Billingham, UK), FNL 189 (one of the series prepared at the former Fixed Nitrogen Laboratory, U.S.D.A., Washington, DC), and Haldor Topsøe catalysts KMIR and KMIIR (obtained from Cominco Canada Ltd., Trail, BC). The former two were obtained in an unreduced state and the latter two were prereduced. The precipitated iron catalyst was prepared by NaOH precipitation from an $Fe(NO_3)_3$ solution (11). The samples were handground with a ceramic mortar and pestle and the 100–200 mesh fraction was used in all experiments. The characterization of these catalysts by X-ray diffraction and Mossbauer spectroscopy (MES and CEMS) and their respective compositions has been reported (12); the catalyst compositions are reproduced in Table 1.

$N_2$ (78 K), CO (78 K), and $CO_2$ (195 K) BET isotherms were measured for each catalyst following the method of Emmett and Brunauer (13). The total surface area was calculated from the $N_2$ isotherm. The difference (at $P > 40$ kPa) between the initial CO isotherm and a second 78 K isotherm obtained following 20 min pumping at 195 K was taken to represent chemisorption on the reduced iron surface; a ratio of 1:2 for adsorbed CO to surface iron atoms was assumed. The difference (at $P > 40$ kPa) between the initial $CO_2$ isotherm and a second obtained after 20 min pumping at 195 K was taken to represent chemisorption on the alkali oxide surface.

In each case, 100–400 mg of catalyst was reduced in situ in flowing $H_2$ (Canadian Liquid Air) at 673 K, the prereduced samples for 48 h and the unreduced samples for 120 h. The activities were determined in a Pyrex U-tube differential microreactor, and the catalysts were regenerated in flowing

TABLE 1

Catalyst Compositions

| Metal (wt%) | FNL 189 | ICI 35-4 | KMIR | KMIIR |
|---|---|---|---|---|
| Fe | 72.1 ± 1 | 66.9 ± 1 | 91.6 ± 1 | 91.8 ± 1 |
| Al | 0.7 ± 0.1 | 1.4 ± 0.1 | 2.8 ± 0.3 | 1.4 ± 0.1 |
| Si | 1.3 ± 0.1 | 0.6 ± 0.1 | 1.0 ± 0.1 | 1.0 ± 0.1 |
| K | 1.3 ± 0.1 | 1.7 ± 0.2 | 0.9 ± 0.1 | 1.2 ± 0.1 |
| Ca | 0.0 ± 0.1 | 1.9 ± 0.2 | 4.4 ± 0.3 | 2.9 ± 0.2 |

$H_2$ at 673 K for 2 h. Turnover numbers (TONs) were calculated from the measured activities and the number of surface iron atoms as determined by CO chemisorption. Hydrogen, regulated by a Brooks #8944 flow controller to 20 cm³ (STP)/min, bubbled through thiophene-free benzene (Caledon Laboratories); the benzene partial pressure was subsequently lowered to 6.02 kPa ($H_2$ partial pressure = 100 kPa) in a condenser held at 283 K. GLC separations were performed on a Varian 1800 aerograph equipped with an FID and a Hewlett Packard HP 3380A integrator; the column was 2.4 m 15% polyethylene glycol 600 on acid washed Atron W (70–80 mesh).

RESULTS AND DISCUSSION

Cyclohexane was the only product detected over the temperature range studied. The activities (after 15 min on stream) are presented in Fig. 1 as a function of inverse temperature. Table 2 compares the activities at 448 K (after 15 min on stream), the
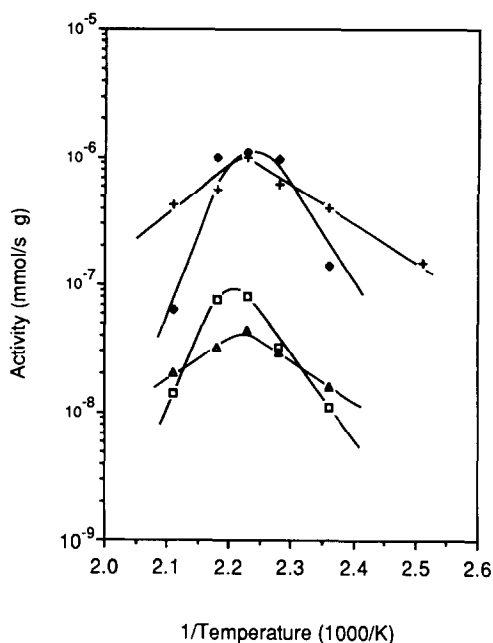


FIG. 1. Activity (after 15 min time on stream) vs inverse temperature for promoted iron catalysts at $P_H$ = 100 kPa, $P_B$ = 6 kPa. (+) precipitated iron, (●) ICI 35-4, (□) KMIR, (△) KMIIR.

corresponding TONs, and the deactivation half-times (the time required for catalytic activity to decrease by 50%, obtained from activity vs time-on-stream studies). Catalyst FNL 189 could not be activated even after a severe reduction of 24 h at 800 K; that the catalyst was reduced by this treatment was apparent from its Mossbauer spectrum (12) and from its chemisorption of CO.

TABLE 2

Catalyst Activities

| | $V_m$ (cm³ STP $g_{Fe}^{-1}$) | | | Activities (448 K) | | Deactivation half-time (min) |
|---|---|---|---|---|---|---|
| | $N_2$ | CO | $CO_2$ | (mmol s⁻¹ $g_{Fe}^{-1}$) | (molecule s⁻¹ $Fe_s^{-1}$) | |
| FNL 189 | 0.09 | 0.07 | 0.05 | Inactive | | |
| ICI 35-4 | 3.61 | 0.29 | 3.47 | $1.1 \times 10^{-6}$ | $4.3 \times 10^{-5}$ | 4 |
| KMIR | 2.42 | 0.28 | 1.85 | $8.1 \times 10^{-8}$ | $3.2 \times 10^{-6}$ | 25 |
| KMIIR | 1.71 | 0.07 | 1.08 | $4.4 \times 10^{-8}$ | $7.5 \times 10^{-6}$ | 10 |
| Fe$_{(ppt)}$ | 2.31 | 1.90 | 1.53 | $1.0 \times 10^{-6}$ | $5.9 \times 10^{-6}$ | [a] |

[a] Catalyst activity constant.

The results of this study, a low specific activity for iron and a rate maximum near 450 K, are in good agreement with previously reported studies (6–11). The TONs for the four active catalysts are 2–3 orders of magnitude lower than those reported by Vannice and co-workers (9, 10) for supported iron catalysts; the specific activities are in good agreement with the only previously reported value of $8 \times 10^{-9}$ mol s$^{-1}$ g$_{Fe}^{-1}$ for a doubly promoted iron catalyst (11). The activities are at least 3 orders of magnitude lower than that reported by Badilla-Ohlbaum et al. (8) for their $Al_2O_3$-promoted iron. As the TON estimated from the results of Badilla-Ohlbaum et al. agrees well with those reported by Vannice and co-workers (9, 10) it is reasonable to conclude that the $Al_2O_3$ acts as a structural promoter, increasing the Fe surface area and hence the activity per unit catalyst mass.

It is apparent that addition of basic promoters has a severe effect on both the activity and rate of deactivation of the catalysts. Because of its genesis, the precipitated iron catalyst is in reality a $Na_2O$-promoted catalyst. In support of this contention, it should be noted that it chemisorbed $CO_2$ and that its iron surface area is greater than that of reduced hematite ($Fe_2O_3$) (9). Basic oxides, as chemical promoters, can donate electron density to surface iron atoms. On adsorption, benzene donates $\pi$-electron density to the metal surface (14) which is dispersed to adjacent atoms or to the bulk (15). Addition of Na, K, or Ca could cause a weakening of the $\pi$-adsorptive bond resulting in a lower catalytic activity. This interpretation is supported by the results of Garfunkel et al. (16) in which a significant decrease in the desorption peak temperature of benzene from K sputtered Pt relative to clean Pt was observed; this would explain the lack of activity of the $K_2O$ promoted iron catalyst, FNL 189.

On the other hand, Phillips and Emmett (11) have demonstrated that benzene is more strongly adsorbed on doubly pro-

moted catalysts than on singly promoted or reduced iron catalysts. That multiply promoted catalysts have significantly lower TONs and that the rate maximum occurs at a lower temperature than for supported catalysts (9, 10) suggests that this strongly adsorbed benzene is not hydrogenated. The rapid deactivation of multiply promoted catalysts in this reaction has been shown to be due to the strong adsorption of hydrocarbon complexes which can lead to the formation of surface iron carbides (11). $\pi$-Adsorbed benzene is able to rotate to form a dissociatively adsorbed $\sigma$-bonded species, the $\sigma$-bond being weaker than a normal C-metal $\sigma$-bond (17, 18). Electron donation from the basic promoters could strengthen this bond, resulting in a strongly chemisorbed species leading to surface carbide formation.

Cracking products were not observed in this study but were observed in those of Badilla-Ohlbaum et al. (8) and Phillips and Emmett (11). The cracking would occur over the slightly acidic $Al_2O_3$ phase; in the multiply promoted catalyst, the acidity has been neutralized by the addition of the basic promoters. While iron is a poor catalyst for benzene hydrogenation, it is evident that basic chemical promoters decrease its activity.

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