# Control of the Probability of Chain Growth in the Catalytic Hydrogenation of Carbon Monoxide on an Iron Catalyst

## Rafael L. Espinoza*† and Ruud Snel

Chemical Engineering Research Group, Council for Scientific and Industrial Research, P.O. Box 395, Pretoria 0001, Republic of South Africa

The probability of chain growth in the hydrogenation of carbon monoxide with iron catalysts can be decreased in a controlled manner by modifying the basic catalyst with small amounts of benzene; the method provides the first chemical means of control that does not involve catalyst promotion.

The product spectrum obtained from the catalytic hydrogenation of carbon monoxide almost invariably follows a mathematical relationship known as the Anderson–Schulz–Flory product distribution law,[1] which can be expressed as $\theta_n = \theta_i \times P^{n-i}$, where $\theta_n$ and $\theta_i$ are the number of moles of a hydrocarbon with carbon number $n$ or $i$ respectively, and $P$ is the probability of chain growth.

The hydrocarbon synthesis is notorious for its lack of selectivity,[2] and for a given value of $P$ the product spectrum is fixed. Extensive studies[3] have shown that a measure of control over $P$ can be achieved, either by modifying the basic catalyst or by varying the reaction temperature and, to a lesser extent, the pressure and/or composition of the synthesis gas.

Research into ways of modifying the basic catalyst has been restricted to catalyst promotion. Alkali elements,[4] in particular K, were found to increase the value of $P$, whereas promotion with compounds involving electronegative elements, in particular halogens[5] or S,[6] resulted in a decrease. In this communication we report on the first chemical method for modifying the basic catalyst that can be used in situ, even after the catalyst has been exposed to synthesis conditions.

The catalyst used in this study was prepared by thermal degradation of iron complexes,[7] and reduced in flowing hydrogen at 573 K. No other pretreatment was applied. Catalytic reaction experiments were carried out in a fixed-bed microreactor system with on-line gas chromatographic analysis of the product. The reactants were prepared in a gas-mixing–feeding station before being fed to the reactor system. The complete experimental facility has been described in detail elsewhere.[8] The benzene used in this study was obtained from Merck and was of Guaranteed Reagent grade. The concentration of sulphur-containing compounds was very low, less than 0.005% when expressed as S.

The reaction conditions were 300 kPa and 543 K. Synthesis gas with an $H_2$:CO ratio of 0.5 was passed at a gas hourly space velocity of 1000 and the exit gas was analysed. After 51.5 hours on stream, the feed was replaced with pure helium, until no hydrocarbons could be detected in the exit steam. A benzene–helium (1 mol % benzene) stream was then introduced onto the catalyst at a rate of 130 cm³ min⁻¹ (normal temperature and pressure). When benzene had passed over the catalyst for a preselected period, the flow was replaced with pure helium. Feeding of synthesis gas was resumed once no traces of benzene could be detected and the products were again analysed. This process was repeated five times. Table 1 shows the amounts of benzene fed through the catalyst, and the time at which this was done.

Immediately after the first benzene dosage, a sudden decrease was observed in the hydrocarbon synthesis activity of the catalyst, $r_{HC}$, expressed as the rate of CO conversion into hydrocarbons (Figure 1). Subsequent dosages of benzene did not have any step-wise effect on the activity behaviour of the catalyst.

In contrast to the activity behaviour, $P$ decreased with each successive benzene dosage (Figure 1). Although the mechan-
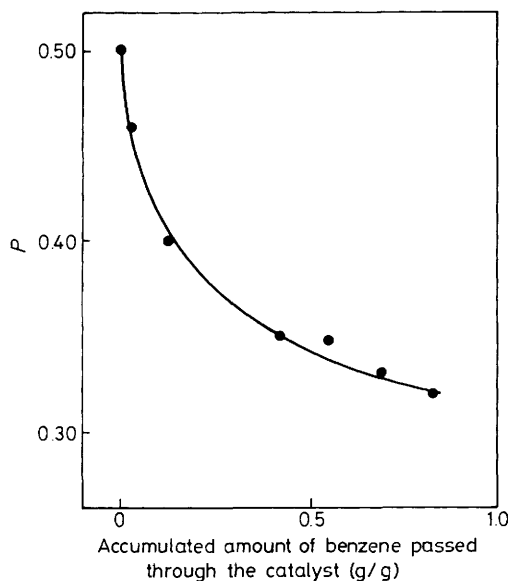
**Table 1.** Dosing of the catalyst with benzene.

| Dosing number | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Cumulative time on stream/h | 51.5 | 69.5 | 71.8 | 91.8 | 94.2 | 113.2 |
| Amount of benzene fed/g | 0.03 | 0.1 | 0.29 | 0.135 | 0.135 | 0.135 |
| Accumulated amount fed/g | 0.03 | 0.13 | 0.42 | 0.555 | 0.69 | 0.825 |
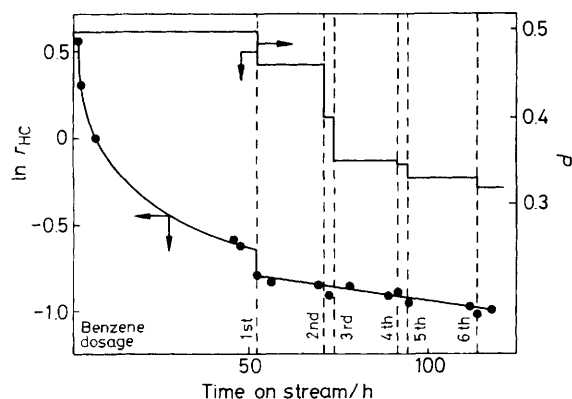
**Figure 1.** Influence of consecutive benzene dosages on $P$ and $r_{HC}$ [in $\mu$mol CO converted into hydrocarbons $s^{-1}$ $(g\ Fe)^{-1}$].



**Figure 2.** Variation in the value of $P$ with consecutive benzene dosages.

ism of chain growth was affected, the Anderson–Schulz–Flory product distribution law was adhered to at all times.

Poisoning by sulphur-containing compounds in the feed is known[9] to decrease the value of $P$, but the catalyst undergoes rapid deactivation under such conditions. In the present case the catalyst was exposed only to hydrocarbons. Moreover,

such poisoning would result in a relationship between $r_{HC}$ and $P$. This was not the case since a step-wise decrease in the activity was observed only after the first dosage, whereas such a decrease in $P$ is normal for each dosage. (It is emphasized that $P$ does not change during the time that deactivation occurs.)

The first dosage of benzene resulted in an irreversible effect on both $r_{HC}$ and $P$, probably due to irreversible benzene adsorption on active sites. Subsequent dosages had a different irreversible effect. Synthesis activity was not affected but the growth mechanism was. The effect on the latter was related to the accumulated dosage of benzene, being strong at first, but becoming less pronounced with consecutive benzene dosages (Figure 2).

We suggest that this second effect, being activity-independent, does not imply site poisoning but rather a modification of the active sites. It could be speculated that benzene decreased the average time that a growing hydrocarbon species remains on the catalyst surface, but further studies are needed for a deeper understanding of how benzene affects the growth mechanism.

In conclusion we note that judicious treatment of an iron catalyst with benzene constitutes a novel technique for achieving a controlled and irreversible decrease in $P$. A special feature of the technique is that it can be applied *in situ* and even after the catalyst has participated in hydrocarbon synthesis.

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