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Distributed Chain Growth Probabilities for the Fischer–Tropsch Synthesis

INTRODUCTION

In a recent paper, Huff and Satterfield (*1*) present selectivity data for the Fischer–Tropsch reaction, supporting the theory that two distinct sites exist on potassium-promoted iron Fischer–Tropsch catalysts. These two sites were characterized in their work by different chain growth probabilities that gave rise to a break in the Flory plot at approximately carbon number 10. Several other studies were cited by the authors that gave similar product distributions (*2–4*). They postulated that the presence of potassium could be correlated with the existence of the second site. In a study prior to Huff and Satterfield, Konig and Gaube (*2*) also report data supporting the theory that two chain growth probabilities exist when an iron catalyst is promoted with potassium. They postulate that the two iron sites are sites with potassium and sites without potassium. In earlier work, Madon and Taylor (*5*) also recognized this break in the Flory distribution for a potassium-promoted iron catalyst although they made no attempt to correlate it with the presence of potassium.

Spectroscopic analysis of the surface of a reduced-potassium-promoted iron catalyst by Ertl *et al.* (*6*) has shown that potassium is not homogeneously distributed over the catalyst surface. In their work, Auger mapping showed the surface to be significantly enriched in potassium with large clusters of potassium several micrometers across. Since potassium and iron do not form a solid solution (*7*), their observations are probably accurate.

Using Ertl's observations, it is difficult to argue that only two types of sites exist. Rather it is more reasonable that a distribution of sites exists each with a unique probability of chain growth, and a corresponding value of the local potassium concentration.

TWO-SITE MODEL

In Huff and Satterfield's model the molecular weight distribution of the products is described with a modification of the Flory distribution by including a second site. Their model is shown here as

$$m_n = x(1 - \alpha_1)\alpha_1^{n-1} + (1 - x)(1 - \alpha_2)\alpha_2^{n-1}, \quad (1)$$

where m_n = total moles of carbon number n relative to the total moles of organic product, α_1 and α_2 = chain growth probabilities for the two sites, and x = the mole fraction of organic product synthesized on site 1. α in Eq. (1) is defined as the rate of propagation/(rate of propagation + rate of termination). Note that three parameters are required in their modeling equation.

Distributed-Site Model

To describe the selectivity of a catalyst containing a distribution of sites, a random variable X is used. X is a dimensionless variable that is proportional to the concentration of potassium relative to iron at a given point on the catalyst surface. Postulating that potassium is normally distributed on the catalyst surface, the fraction of sites with a potassium concentration X, is given by

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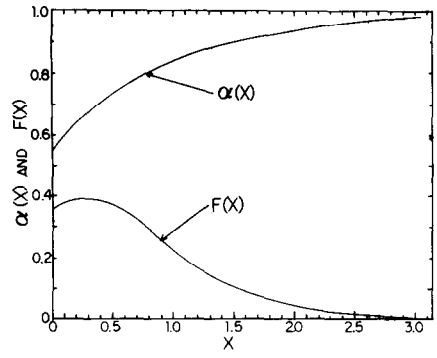

FIG. 1. Distribution function, $F(X)$ (Eq. (2)) and the distribution of chain growth probabilities, (X) (Eq. (4)) for the parameters: $X_{sm} = 0.262$, $b = 0.016$, $\alpha_0 = 0.55$.

$$F(X) = \frac{1}{\sqrt{2\pi}} \exp((X - X_{sm})^2), \qquad (2)$$

where X_{sm} is the potassium concentration of maximum probability. Equation (2) represents a normal distribution and is chosen since the dispersion of potassium on the surface is most likely a random process.

It is well established that potassium increases the molecular weight of the Fischer–Tropsch products, thus at low values of X, α will be correspondingly low, and as X increases α will asymptotically approach 1. Postulating an exponential dependence of α on X, we can describe α as a function of X by

$$\alpha(X) = 1 - (1 - \alpha_0)\exp(-bX), \qquad (3)$$

where α_0 is the chain growth probability at $X = 0$ (pure iron). In Eq. (3) the parameter b represents the strength of interaction between neighboring potassium and iron atoms. As b approaches zero, α approaches α_0 since at this limit the iron acts independently of the potassium. Other asymptotic functions could be used in replace of Eq. (3). For the present work an exponential dependence is assumed.

Using the Flory distribution model for a single site:

$$m_n = (1 - \alpha)\alpha^{n-1} \qquad (4)$$

and expanding it to account for the distributed-site theory, the molecular weight distribution can be calculated by

$$m_n = \frac{\int_0^\infty F(X)(1 - \alpha(X))\alpha(X)^{n-1}\,dX}{\sum_{n=1}^{\infty}\int_0^\infty F(X)(1 - \alpha(X))\alpha(X)^{n-1}\,dX}, \qquad (5)$$

where $F(X)$ and $\alpha(X)$ are taken from Eqs. (2) and (3), respectively. Equation (5) cannot be integrated analytically, however a numerical integration can be performed.

RESULTS

Plots of $F(X)$ and $\alpha(X)$ versus X for the parameters $b = 0.016$, $\alpha_0 = 0.55$ (a reasonable value for pure iron), and $X_{sm} = 0.262$, are shown in Fig. 1. $F(X)$ is a truncated Gaussian curve with a maximum at $X = X_{sm} = 0.262$ and $\alpha(X)$ is based on Eq. (4) which forces $\alpha(0) = 0.55$. Figure 2 is a Flory plot comparing the distributed-site model (Eq. (5) integrated numerically) with the two-site model (Eq. (1)). For Eq. (5) the same parameters are used as in Fig. 1. For Eq. (1) the parameters have been chosen as $\alpha_1 = 0.62$, $\alpha_2 = 0.90$, and $x = 0.77$. Figure 2 demonstrates that the two models are nearly indistinguishable.

Selectivity data taken from Huff (*8*) is plotted in Fig. 3 together with a curve cal-

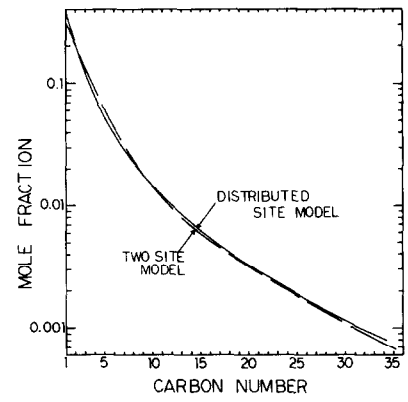

FIG. 2. Comparison of the distributed-site model (solid line) with the two-site model (dashed line). Parameters for the distributed-site model: $X_{sm} = 0.262$, $b = 0.016$, $\alpha_0 = 0.55$. Parameters for the two-site model: $\alpha_1 = 0.62$, $\alpha_2 = 0.90$, and $x = 0.77$.

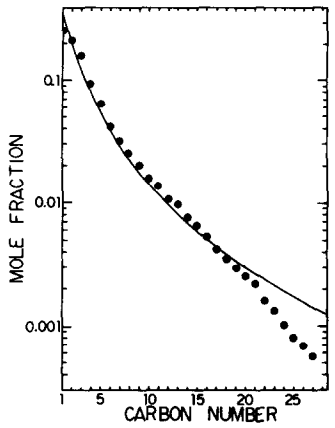

FIG. 3. Comparison of molecular weight distribution data from (*8*) with the distributed-site model. Parameters for the distributed-site model: $X_{sm} = 0.262$, $b = 0.016$, $\alpha_0 = 0.55$.

culated by the distributed-site model ($b = 0.016$, $\alpha_0 = 0.55$, and $X_{sm} = 0.262$). These parameters were found to give the best fit to the data for carbon numbers 1 to 20. The y axis in Fig. 3 is the mole fraction of all hydrocarbons (including oxygenates) at a given carbon number, relative to all the hydrocarbons produced. The distribution deviates from the model at carbon numbers greater than 20. As explained by Huff and Satterfield (*1*) this is a result of the higher-molecular-weight hydrocarbons being accumulated in the reactor.

At large carbon numbers, the distributed-site model (Eq. (5)) approximates a semilog straight line over a moderate range of carbon numbers. Comparison of the Fischer–Tropsch heavy wax data from Stenger *et al.* (*9*) for carbon numbers 30 to 49 with the distributed-site model ($b = 0.016$, $\alpha_0 = 0.55$, and $X_{sm} = 0.262$) shows good agreement in Fig. 4. In Fig. 4 the y axis is a normalized mole fraction for the C30 to C49 hydrocarbons.

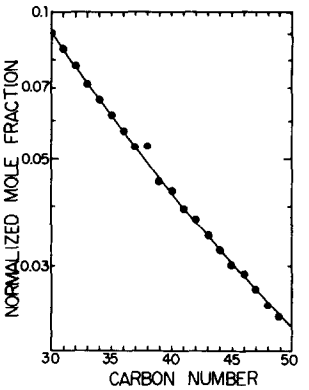

FIG. 4. Comparison of high-carbon-number molecular weight distribution data from (*9*) with the distributed-site model. Parameters for the distributed-site model: $X_{sm} = 0.262$, $b = 0.016$, $\alpha_0 = 0.55$.

SUMMARY

The two-site model and the distributed-site model have been shown to be equivalent in their ability to fit the molecular weight product distribution from an iron catalyst that is promoted with potassium. Both models require fitting the product distribution with three parameters. The two-site model has the advantage of being solvable analytically. However, the distributed-site model offers a model of the product distribution that is based on a realistic description of the catalyst surface.

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