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# Simple Criteria to Differentiate a Two-Site Model from a Distributed-Site Model for Fischer–Tropsch Synthesis

Although it is generally accepted that the carbon number distribution of the Fischer-Tropsch reaction products can be expressed by the Anderson–Schulz–Flory (A–S–F) equation (*1–3*), numerous exceptions that can be classified into four categories as illustrated in Fig. 1 have also been reported. Besides the well-known deviation at lower carbon number (Type A), A–S–F plots can give a convex curve (Type B), a concave curve (Type C), or a bell-shaped curve (Type D). Only a few catalysts are known which have given the product distribution of Type D (*4, 5*), and three interpretations (Poisson distribution (*6*), limited chain growth governed by catalyst particle size (*7*), and sharp decrease in propagation probabilities ($\alpha_n$ values) with carbon number (*8*)) have been proposed. Type B plots may come from (a) technical problems in analyzing the product (*9–11*), (b) data taken before the reaction reaches steady state (*9, 12*), or (c) concentration gradients in the fixed-bed reactor with the product being reincorporated by the chain propagation (*13*). Zeolite-supported catalysts may inherently give Type B plots (*14, 15*); to our knowledge, however, such product distributions have not been determined under steady-state conditions with a prolonged time on stream. Type C plots may be caused by (a) temperature gradients in the fixed-bed reactor (*9*), (b) an increase in propagation probabilities ($\alpha_n$ values) with carbon number, (c) data taken from collected products over a period of the reaction where propagation probability ($\alpha$ value) gradually changes, or (d) two or more active sites having different $\alpha$ values. The $\alpha_n$ value is defined by $1/(1 + \beta_n)$; $\beta_n$ was originally introduced by Herington (*16*) and is defined by $m_n/\Sigma_{n+1}^{\infty} m_i$, where $m_i$ is the mole fraction of a product of carbon number $i$. Some catalyst systems have been reported to show a slight increase in $\alpha_n$ with an increase in carbon number $n$ (*14, 17*) (hereafter, this analysis will be called Herington's model), and ordinary A–S–F plots for these results will show a concave curve as Type C.

Because the heterogeneity in the surface of practical catalysts, a catalyst can have various sites with different $\alpha$ values. Two extreme cases will be discussed, i.e., a catalyst with two different active sites (two-site model) and a catalyst with an infinite number of sites with different $\alpha$ values (distributed-site model). The latter model was recently introduced by Stenger (*18*). He assumed that the fraction of active sites obeys a Gaussian-type distribution as a function of alkali concentration around the active site, which in turn affects the $\alpha$ value of the active site by an arbitrarily fixed equation. Alternatively, we assumed that the fraction of active sites is described by a Gaussian distribution as a function of the activation-energy difference between that for chain propagation and that for the termination reaction. This modified model described well the carbon number distribution of the results formerly explained by Herington's model (*14, 17*). However, as Stenger has pointed out (*18*), the two-site and distributed-site models are essentially equivalent in terms of the ability to fit to the empirical results; we cannot differentiate these two models by examining the fit. The purpose of this note is to propose simple criteria by which to differentiate these two models.

In the two site-model, the carbon number

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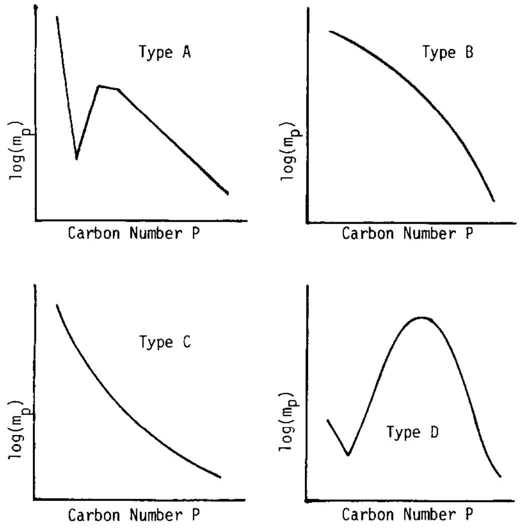

FIG. 1. Four types of deviation from ordinary Anderson–Schulz–Flory kinetics.

distribution of the product can be expressed by the following equation:

$$m_p = m_{n1}\alpha_1^{p-n} + m_{n2}\alpha_2^{p-n},$$

where $m_p$ is mole yield of the product having carbon number $p$, $n$ is the carbon number, higher than that which is concerned, and $m_{n1}$ and $m_{n2}$ are mole yields of the products of carbon number $n$ formed by active sites having propagation probabilities of $\alpha_1$ and $\alpha_2$, respectively. If $\alpha_1$ is smaller than $\alpha_2$, $m_{n1}\alpha_1^{p-n}$ will become negligible compared with $m_{n2}\alpha_2^{p-n}$ at large enough carbon numbers ($p$). Therefore, in the two-site model, the ordinary A–S–F plot should be linear in the higher carbon number region, and $\alpha_2$ and $m_{n2}$ values can be determined directly. This is the first criterion. Then using these determined $\alpha_2$ and $m_{n2}$ values, $m_p - m_{n2}\alpha_2^{p-n}$ values are calculated and their logarithms are plotted against the carbon number. If this plot gives a straight line (the second criterion), one can conclude that the catalyst has two types of active sites, and from the slope and intercept of the plot, $\alpha_1$ and $m_{n1}$ values can be determined. Note that the obtained $\alpha_1$ value is always smaller than the value determined from the slope of the original A–S–F plot in the lower carbon number region. The latter value is *of no meaning* unless one assumes that the reaction mechanisms for the formation of lower products and higher products are completely different. If these two criteria are not satisfied, one should consider the model to be one other than the two-site model, for example, the distributed-site model or Herington's model.

An example is taken from our recent work on the direct alcohol synthesis over a Ru–Mo–Na/$Al_2O_3$ catalyst (*19*). When this catalyst was prepared by simultaneous impregnation of precursor salts (one-step impregnation), the catalyst gave alcohols with the carbon number distribution shown in Fig. 2. The plot fell in a straight line in the higher carbon number region, and the plot for $m_p - m_{12}\alpha_2^{p-1}$ vs the carbon number gave a straight line. Therefore, we concluded that this catalyst had two different active sites for the formation of alcohols. On the other hand, we have recently reported that thermal treatment following simultaneous impregnation of $RuCl_3 \cdot 3H_2O$ and $NaNO_3$ on alumina resulted in double decomposition of these two salts, yielding stoichiometric amounts of $RuO_2$ and NaCl (*20*). Because the present catalyst was prepared by loading of excess amounts of $RuCl_3$ for double decomposition, some $RuCl_3$ remained after thermal treatment, which was reduced directly to $Ru^0$ at the reduction stage. Therefore, we assumed that these two Ru sites, produced by the different sequences correspond to the two sites predicted from Fig. 2 to have different $\alpha$ values. To check this assumption, a catalyst was prepared by a two-step impregnation method: $RuCl_3 \cdot 3H_2O$ was impregnated first and reduced; then Mo and Na salts were impregnated, thermally treated, and reduced again. In this case, $RuCl_3$ was reduced directly without formation of $RuO_2$ during the thermal treatment. As expected, this catalyst gave a straight line A–S–F plot (Fig. 3) and the $\alpha$ value of this catalyst was close to the $\alpha_2$ value for the catalyst prepared by the one-step impregnation method. Therefore, we

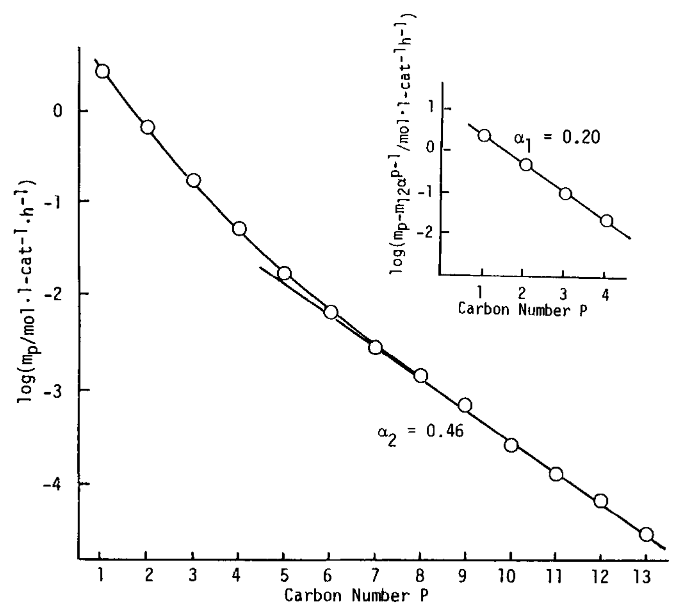

FIG. 2. Carbon number distribution of alcoholic products formed on 3% Ru–5% Mo–1.25% $Na_2O$ (nominal concentration)/$Al_2O_3$ catalyst prepared by a one-step impregnation method. An illustration for the calculation based on the two-site model: All the carbon number region was taken into calculation ($n = 1$). From the slope of the plot at the higher carbon number, $\alpha_2$ and $m_{I2}$ were determined and then $m_p - m_{I2}\alpha_2^{p-1}$ values were calculated, the logarithms of which were plotted against the carbon number (upper right). From the latter plot, $\alpha_1$ and $m_{I1}$ were determined. The curve in the original Anderson–Schulz–Flory plot is a theoretical line calculated from the thus-determined parameters and has a formula of $\log(m_p) = \log(2.333 \times 0.197^{p-1} + 0.319 \times 0.460^{p-1})$.

concluded that the Ru sites formed by direct reduction of $RuCl_3$ have a larger $\alpha$ value but are relatively less active, while the Ru sites formed by the reduction of $RuO_2$ generated by the decomposition of $RuCl_3$ by the action of $NaNO_3$ have a smaller $\alpha$ value but are highly active.

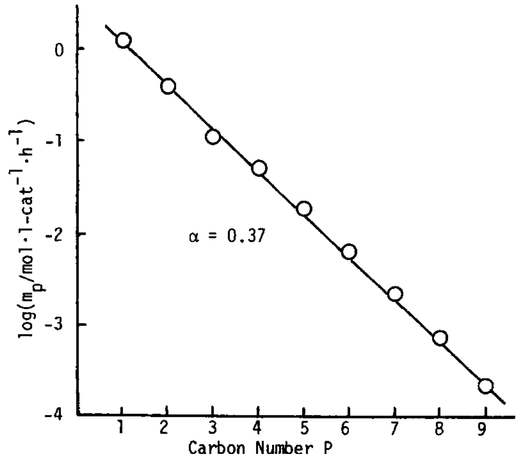

FIG. 3. Carbon number distribution of alcoholic products formed on 3% Ru–5% Mo–1.25% $Na_2O$ (nominal concentration)/$Al_2O_3$ catalyst prepared by a two-step impregnation method.

As a concluding remark, the criteria presented in this note are simple and can differentiate the two-site model from the distributed-site model for the Fischer–Tropsch reaction without the aid of a computer.

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