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RESEARCH PAPER

Development of a Novel Conversion Equation as a Function of Catalytic Reaction Conditions in Tubular Reactors

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Abstract: A comprehensive conversion equation was developed to simulate the catalytic reaction conditions (include temperature, pressure, residence time, and reaction composition) in tubular reactors: $X_{\mathrm{M}} = 1 - \exp[-\exp(\mathrm{A}+\mathrm{B}/T_{\mathrm{r}} + \mathrm{C}T_{\mathrm{r}}) p_{\mathrm{r}}^{n_{p0}+n_{p1}p_{\mathrm{r}}} \tau_{\mathrm{r}}^{n_{\tau 0}+n_{\tau 1}\tau_{\mathrm{r}}} \prod_{i=1}^{m} y_i^{n_{y0}+n_{y1}y_i}]$. This conversion equation is based on the characteristics of the power-exponential function $g(u) = u^{\mathrm{a}+\mathrm{b}u}$ as well as the "variable reaction order" and "virtual reactant" concepts. Its validity was verified by fitting experiment data from three different catalytic systems such as the dehydrogenation of diethyl benzene, the hydrogenation of ethylbenzene, and the hydrodesulfurization of thiophene. The results show that the influences of reaction temperature, pressure, residence time, and reactant composition on the conversion of the reactant can be determined within a wide range of values. By comparison with the experimental data, the calculated conversions were all found to have a total average relative deviation of less than 2%. This suggests that the conversion equation is not limited to a specific catalyst system but could be suitable for various catalyst systems in tubular reactors.

Key words: conversion equation; reaction kinetics; hydrogenation; dehydrogenation; hydrodesulfurization; Arrhenius law

Much effort has been directed toward producing macroscopic kinetic models for various catalyst systems in industry [1–10]. For example, Hoang et al. [11] studied the influence of reaction conditions on the yield of hydrogen for the steam reforming of methane using a commercial γ-alumina supported sulfide nickel catalyst and they developed a two-dimensional model of the catalytic fixed-bed reformer. The predicted results from the reformer model agreed reasonably with the experimental data. This indicated that the kinetic data and the reforming model are reliable and can be used in the simulation and comprehensive analysis of an industrial reformer loaded with the same catalyst. A one-dimensional model for the oxidative coupling of methane (OCM) over a La_2O_3/CaO catalyst in a fixed-bed reactor has been developed by Tye et al. [12]. They tested their model under different operation modes and found that the OCM process that operates at a low CH_4/O_2 ratio and at an optimum temperature does not give a C_2 (ethylene and ethane) product yield higher than 25%. Therefore, other catalysts and reactor configurations should be investigated to obtain C_2 products at higher yields. Alves et al. [13] proposed a mechanistic kinetic expression for the liquid-phase hydrogenation of 1-butyne over a commercial palladium-based catalyst. It was an eggshell type reaction under the chosen experimental conditions and this is close to the operating conditions in an industrial hydrorefining reactor. Based on the kinetic expression, the predicted data had a precision of 2.1%. The kinetic parameters at 317 K and the activation energy were estimated with relative precision levels of ± 2.1% and ± 3.8%, respectively. Although the macroscopic kinetic models mentioned above could successfully simulate practical operations they are only suitable for a specific catalyst system or a specific catalyst. Therefore, Zheng et al. [14] developed a general ki-

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netic model for catalytic reaction conditions in tubular reactors and obtained satisfactory fitting results. However, they just considered the effect of temperature and residence time on conversion.

A novel conversion equation for use in most catalyst systems in tubular reactors is proposed in this article and the relationship between the conversion and temperature, pressure, residence time, and reactant composition is established.

1 Kinetic model development

For reactions that are isothermal, isochoric, plug-flow, and first-order irreversible, the conversion equation for a reactant M can be described as:

$$X_{\mathrm{M}} = 1 - \exp\left(-k\tau\right) \tag{1}$$

where k is the rate constant and τ is the residence time. For most catalytic reaction systems, k is related to the Arrhenius formula:

$$k = k_0 \exp\left(-E_{\mathrm{r}} / T_{\mathrm{r}}\right) \tag{2}$$

where E_{r} is the relative activation energy and T_{r} is the relative temperature.

When the catalyst system does not meet the above four requirements completely, the conversion equation can be written as:

$$X_{\mathrm{M}} = 1 - \exp\left[-k \times f\left(y_i, p_{\mathrm{r}}, \tau_{\mathrm{r}}\right)\right] \tag{3}$$

where y_i denotes the mole fraction of the different reactants, p_{r} represents the relative pressure, and τ_{r} is the relative residence time. The relativization of these variables makes the calculation more convenient.

Because of the complexity of heterogeneous catalyst systems, it is necessary to transform the Arrhenius formula to:

$$k = \exp^{\mathrm{A}+\mathrm{B}/T_{\mathrm{r}}+\mathrm{C}T_{\mathrm{r}}} \tag{4}$$

When C = 0 and B < 0, Eq. (4) reduces to the Arrhenius formula.

The following discussion is concerned with the specific expression for the function $f(y_i, p_{\mathrm{r}}, \tau_{\mathrm{r}})$. For simplification, we assume that each variable in the function $f(y_i, p_{\mathrm{r}}, \tau_{\mathrm{r}})$ can be separated and we thus obtain:

$$f\left(y_i, p_{\mathrm{r}}, \tau_{\mathrm{r}}\right) = f_1\left(y_i\right) f_2\left(p_{\mathrm{r}}\right) f_3\left(\tau_{\mathrm{r}}\right) \tag{5}$$

In terms of the reaction order, when m kinds of substances exist in the reaction system the function $f_1(y_i)$ can be expressed as:

$$f_1\left(y_i\right) = \prod_{i=1}^{m} y_i^{n_i} \tag{6}$$

However, in the practical application of Eq. (6) two problems exist: one is that $y_i^{n_i}$ can be multiplied by k only when the concentration of reactant i is constant at different positions in the catalyst bed. The other is that the reaction order n_i will not remain constant in some complex catalytic reaction systems and, therefore, n_i should be adjusted. If n_i changes linearly with y_i, we obtain:

$$n_i = n_{i0} + n_{i1} y_i \tag{7}$$

Therefore, Eq. (6) can be rewritten as:

$$f_1\left(y_i\right) = \prod_{i=1}^{m} y_i^{\left(n_{i0}+n_{i1}y_i\right)} \tag{8}$$

The two other functions, $f_2(p_{\mathrm{r}})$ and $f_3(\tau_{\mathrm{r}})$, can be expressed in a similar manner by regarding variables p_{r} and τ_{r} as virtual reactants:

$$f_2\left(p_{\mathrm{r}}\right) = p_{\mathrm{r}}^{n_{p0}+n_{p1}p_{\mathrm{r}}} \tag{9}$$

$$f_3\left(\tau_{\mathrm{r}}\right) = \tau_{\mathrm{r}}^{n_{\tau 0}+n_{\tau 1}\tau_{\mathrm{r}}} \tag{10}$$

Hence, the conversion equation with respect to reaction conditions can be rewritten as:

$$X_{\mathrm{M}} = 1 - \exp[-\exp^{(\mathrm{A}+\mathrm{B}/T_{\mathrm{r}}+\mathrm{C}T_{\mathrm{r}})} p_{\mathrm{r}}^{n_{p0}+n_{p1}p_{\mathrm{r}}} \tau_{\mathrm{r}}^{n_{\tau 0}+n_{\tau 1}\tau_{\mathrm{r}}} \prod_{i=1}^{m} y_i^{n_{y0}+n_{y1}y_i}] \tag{11}$$

The derivation process for this new conversion equation is general, consequently, it can be applied to various catalytic reaction systems.

2 Application examples

2.1 Catalytic dehydrogenation of diethylbenzene (DEB)

The catalyst used in this experiment was the commercial iron-based XH catalyst and it was supplied by the chemical factory at Xiamen University. The dehydrogenation reaction of DEB was carried out at atmospheric pressure (p_{r} is constant) in a tubular reactor containing 10 ml of the catalyst and the other experimental conditions were: temperature from 898–938 K, residence time from 2.34×10^{-2}–11.72×10^{-2} min, reactant composition H_2O/DEB volume ratio from 1–5. The experimental results are shown in Table 1, where X_{exp} and X_{cal} denote the experimental conversion and the calculated conversion, respectively, and RD is the absolute relative deviation.

Table 1 Effect of reaction conditions on conversion during the catalytic dehydrogenation of DEB

T_{r}	λ_{r}	τ_{r}	X_{exp}/%	X_{cal}/%	RD/%
0.9574	0.8	0.25	75.3	73.2	2.86
0.9680	0.8	0.25	78.2	80.1	2.47
0.9787	0.8	0.25	83.2	86.2	3.62
0.9893	0.8	0.25	89.6	91.1	1.62
1.0000	0.8	0.25	96.1	94.7	1.48
0.9680	0.2	0.25	44.3	43.6	1.57
0.9680	0.4	0.25	51.2	53.1	3.72
0.9680	0.6	0.25	65.2	65.5	0.48
0.9680	0.8	0.25	82.0	80.1	2.27
0.9680	1.0	0.25	91.9	92.8	0.98
0.9680	0.8	0.20	75.9	75.7	0.26
0.9680	0.8	0.25	82.0	80.1	2.27
0.9680	0.8	0.33	86.4	85.1	1.55
0.9680	0.8	0.50	90.3	90.8	0.54
0.9680	0.8	1.00	95.6	95.7	0.03