反映工艺条件对管式反应器催化反应影响的转化率方程

李巧灵[1]，张元华[1]，陈世萍[1]，方维平[1,2]，杨意泉[1,2]

[1]厦门大学化学化工学院化工系, 福建厦门 361005

[2]厦门大学化学化工学院化学系醇醚酯清洁生产国家工程实验室, 福建厦门 361005

摘要: 根据幂指函数 $g(u) = u^{a+bu}$ 的特点, 借用"虚拟反应组分"和"变动级数"的概念, 提出了管式反应器系统中反应转化率与工艺条件的关系式 $X_M = 1 - \exp[-\exp(A+B/T_r + CT_r)p_r^{n_{p0}+n_{p1}p_r}\tau_r^{n_{\tau0}+n_{\tau1}\tau_r}\prod_{i=1}^{m}y_i^{n_{y0}+n_{y1}y_i}]$. 为了验证该转化率方程的普适性, 考察了二乙苯催化脱氢、乙苯加氢和噻吩加氢脱硫等, 并利用 Matlab 软件分别对这三个催化体系的实验数据进行拟合. 结果表明, 此方程在较宽的范围内均能很好地反映温度、反应压力、空速和物料比对转化率的影响. 预测结果与实验数据之间的总平均相对偏差均小于 2%, 说明该方程并不是针对某一特定的催化反应或催化剂, 可用于大多数的管式反应器催化反应系统中.

关键词: 转化率方程; 反应动力学; 加氢; 脱氢; 加氢脱硫; 阿伦尼乌斯法则

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

LI Qiaoling[1], ZHANG Yuanhua[1], CHEN Shiping[1], FANG Weiping[1,2,*], YANG Yiquan[1,2,#]

[1]*Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering,*
Xiamen University, Xiamen 361005, Fujian, China

[2]*Department of Chemistry, College of Chemistry and Chemical Engineering and National Engineering Laboratory for Green Chemical Production of Alcohols, Ethers and Esters, Xiamen University, Xiamen 361005, Fujian, China*

Abstract: A comprehensive conversion equation was developed to simulate the catalytic reaction conditions (include temperature, pressure, residence time, and reaction composition) in tubular reactors: $X_M = 1 - \exp[-\exp(A+B/T_r + CT_r)p_r^{n_{p0}+n_{p1}p_r}\tau_r^{n_{\tau0}+n_{\tau1}\tau_r}\prod_{i=1}^{m}y_i^{n_{y0}+n_{y1}y_i}]$.

This conversion equation is based on the characteristics of the power-exponential function $g(u) = u^{a+bu}$ 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 kinetic 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:

$$X_M = 1 - \exp(-k\tau) \tag{1}$$

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

$$k = k_0 \exp(-E_r / T_r) \tag{2}$$

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:

$$X_M = 1 - \exp[-k \times f(y_i, p_r, \tau_r)] \tag{3}$$

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:

$$k = \exp^{A + B/T_r + CT_r} \tag{4}$$

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 $f(y_i, p_r, \tau_r)$. For simplification, we assume that each variable in the function $f(y_i, p_r, \tau_r)$ can be separated and we thus obtain:

$$f(y_i, p_r, \tau_r) = f_1(y_i)f_2(p_r)f_3(\tau_r) \tag{5}$$

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:

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

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:

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

The two other functions, $f_2(p_r)$ and $f_3(\tau_r)$, can be expressed in a similar manner by regarding variables p_r and τ_r as virtual reactants:

$$f_2(p_r) = p_r^{n_{p0} + n_{p1}p_r} \tag{9}$$

$$f_3(\tau_r) = \tau_r^{n_{\tau0} + n_{\tau1}\tau_r} \tag{10}$$

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

$$X_M = 1 - \exp[-\exp^{(A + B/T_r + CT_r)} p_r^{n_{p0} + n_{p1}p_r} \tau_r^{n_{\tau0} + n_{\tau1}\tau_r} \prod_{i=1}^{m} y_i^{n_{y0} + n_{y1}y_i}] \tag{11}$$

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

Because an increase in temperature is beneficial to this endothermic reaction in terms of kinetics and thermodynamics, k is accorded with the Arrhenius formula and Eq. (11) can be simplified to:

$$X_{DEB} = 1 - \exp[-\exp^{(A+B/T_r)} \tau_r^{n_{\tau 0}+n_{\tau 1}\tau_r} \lambda_r^{n_{\lambda 0}+n_{\lambda 1}\lambda_r}] \quad (12)$$

Using Matlab software to fit the experimental data, we obtain:

$$X_{DEB} = 1 - \exp[-\exp^{(20.2649-18.0374/T_r)} \tau_r^{0.5613-0.3295\tau_r} \lambda_r^{0.5352+2.0601\lambda_r}] \quad (13)$$

The simulation program was run with different input data for one variable to validate the model. The other two variables were kept constant. Typical modeling results and a comparison with the experimental data at different temperatures, H_2O/DEB volume ratios and residence times are shown in Figs. 1–3. These figures show the good predictive
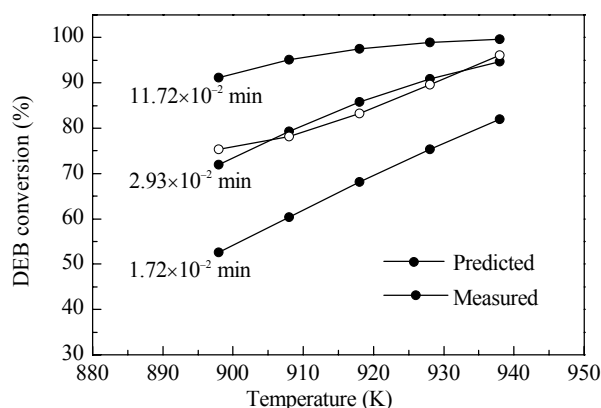

Fig. 1. Comparison of the predicted and measured conversion vs temperature at different residence time with a H_2O/DEB volume ratio of 4.
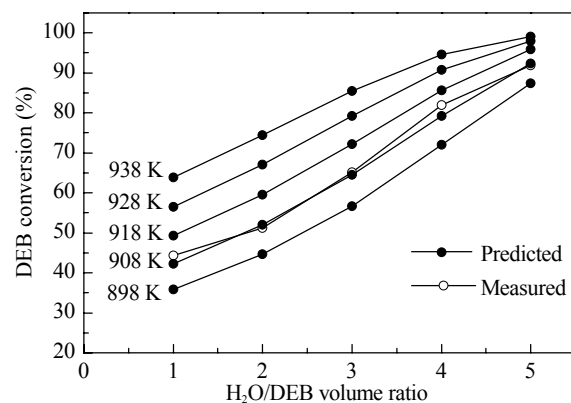

Fig. 2. Comparison of the predicted and measured conversion vs the H_2O/DEB volume ratio at different temperatures. The residence time was 2.93×10^{-2} min.

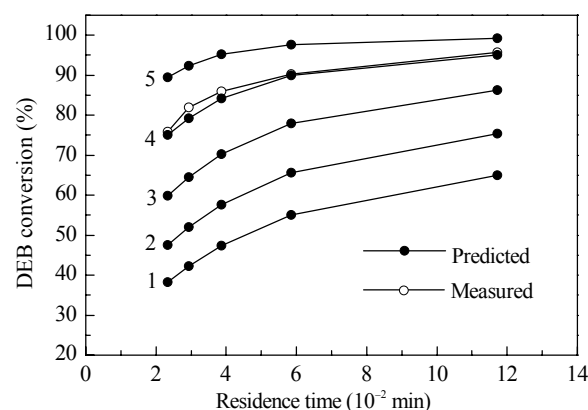**Fig. 3.** Comparison of the predicted and measured conversion vs residence time at different H_2O/DEB volume ratios. The temperature was 908 K.

ability of this equation with an average relative deviation (ARD) of 1.72%. It is also clear that temperature, residence time, and H_2O/DEB volume ratios have a positive effect in improving DEB conversion, and this is consistent with the results reported by Bai [15].

2.2 Catalytic hydrogenation of ethylbenzene (EB)

The kinetics of aromatic hydrogenation has been reported previously [16,17], however, our experiment was only concerned with the catalytic hydrogenation of EB. The catalyst used in our experiment was 0.13 g of unsupported MoWNi, and the experimental apparatus used has been reported previously [18]. The H_2 flow rate was maintained at a constant 100 ml/min, the temperature ranged from 373–573 K, and the pressure ranged from 0.1–4 MPa. The residence time varied from 9.2037×10^{-4} to 9.7197×10^{-4} min and the ethylcyclohexane/EB molar ratio was 0.2–1. The experimental results are listed in Table 2.

Table 2 Effect of reaction conditions on conversion in the catalytic hydrogenation of EB

T_r	p_r	λ_r	τ_r	X_{exp}/%	X_{cal}/%	RD/%
0.6509	0.25	0.6	0.6602	23.0	23.6	2.43
0.7382	0.25	0.6	0.6602	50.3	50.4	0.10
0.8255	0.25	0.6	0.6602	68.1	68.2	0.18
0.9127	0.25	0.6	0.6602	71.4	74.0	3.64
1.0000	0.25	0.6	0.6602	72.5	71.0	2.01
0.7382	0.025	0.6	0.6602	29.3	29.1	0.76
0.7382	0.25	0.6	0.6602	50.3	50.4	0.09
0.7382	0.50	0.6	0.6602	59.5	58.6	1.48
0.7382	0.75	0.6	0.6602	65.4	64.6	1.32
0.7382	1.00	0.6	0.6602	69.3	69.9	0.82
0.7382	0.25	0.2	0.6602	69.5	69.7	0.32
0.7382	0.25	0.4	0.6602	58.4	57.6	1.44
0.7382	0.25	0.6	0.6602	50.3	50.4	0.10
0.7382	0.25	0.8	0.6602	45.4	45.2	0.37
0.7382	0.25	1.0	0.6602	41.3	41.2	0.16
0.7382	0.25	0.6	1.0000	70.1	70.2	0.12
0.7382	0.25	0.6	0.8118	61.2	61.0	0.28
0.7382	0.25	0.6	0.6602	50.3	50.4	0.09
0.7382	0.25	0.6	0.5387	39.4	39.7	0.66
0.7382	0.25	0.6	0.4411	30.2	30.1	0.37

Using Matlab software to fit the experimental data, we obtained:

$$X_{EB} = 1 - \exp[-\exp^{(27.3639-12.1125/T_r-14.227T_r)}$$
$$p_r^{0.3334+0.2193p_r}\tau_r^{1.8318-0.7792\tau_r}\lambda_r^{-0.4851-0.0901\lambda_r}] \quad (14)$$

here, the ARD was 0.84% suggesting that a high fitting accuracy was obtained. Equation (14) shows that the conversion decreased significantly when the residence time was shorter and increased with temperature and pressure. Moreover, the ethylcyclohexane/EB molar ratio (λ) also influenced the conversion but not as remarkably as the other factors. Additionally, an increase of ethylcyclohexane in the inlet mixture led to a decrease in conversion suggesting that λ inhibits the forward reaction. Therefore, the λ fitting indexes in Eq. (14) are negative ($n_{\lambda0} < 0$, $n_{\lambda1} < 0$).

2.3 Catalytic hydrodesulfurization of thiophene (TP)

For environmental protection the requirement to produce high-quality gasoline and diesel oil by especially reducing the sulfur content in oil products is of interest. Consequently, research is required on the quantitative relationship between the conversion of sulfur-containing compounds and the operating conditions chosen. Wang et al. [19] studied the HDS of benzothiophene and dihydrobenzothiophene over sulfided Mo/Al_2O_3. The catalyst used in our experiment consisted of 500 mg of $MoNiP/Al_2O_3$ and the experimental apparatus has been reported elsewhere [20]. The reaction conditions were as follows: temperature from 513 to 573 K, hydrogen partial pressure from 0.5 to 2.2 MPa, residence time from 8.46×10^{-3} to 67.7×10^{-3} min and hydrogen/TP volume ratio from 225 to 700. The experimental results are shown in Table 3.

Table 3 Effect of reaction conditions on conversion in the catalytic hydrodesulfurization of TP

T_r	p_r	λ_r	τ_r	X_{exp}/%	X_{cal}/%	RD/%
0.8953	0.5	0.5	0.25	22.4	22.1	1.17
0.9300	0.5	0.5	0.25	53.1	54.6	2.74
0.9651	0.5	0.5	0.25	88.6	89.6	1.17
1.0000	0.5	0.5	0.25	99.6	99.7	0.03
0.9651	0.2272	0.5	0.25	87.3	86.6	0.84
0.9651	0.5	0.5	0.25	92.1	89.9	2.38
0.9651	0.6818	0.5	0.25	95.9	93.4	2.59
0.9651	1.0	0.5	0.25	98.1	98.4	0.29
0.9651	0.5	0.3214	0.25	74.1	74.0	0.18
0.9651	0.5	0.6429	0.25	90.0	95.6	6.17
0.9651	0.5	0.7857	0.25	99.5	98.1	1.38
0.9651	0.5	1.0	0.25	99.3	99.5	0.23
0.9651	0.5	0.5	1.00	99.6	99.6	0.00
0.9651	0.5	0.5	0.25	87.3	89.9	2.99
0.9651	0.5	0.5	0.17	80.2	78.3	2.42
0.9651	0.5	0.5	0.125	65.4	66.6	1.82

Using Matlab software to fit the experimental data, we obtain:

$$X_{TP} = 1 - \exp[-\exp^{(46.8584-34.4611/T_r-8.3094T_r)}$$
$$p_r^{0.1855+1.3244p_r}\tau_r^{0.921-1.1499\tau_r}\lambda_r^{1.2048+0.0355\lambda_r}] \quad (15)$$

here, the ARD was 1.65%. In this case, a higher conversion of TP was obtained at higher temperature, which improved by nearly 10% and even 35% as the temperature was increased by 20 K implying that the $MoNiP/Al_2O_3$ catalyst had superior performance. The short residence time resulted in a decrease in the conversion. A positive effect was noticed for an increase in the hydrogen partial pressure and increasing the H_2/TP volume ratio favored TP conversion. However, when the conversion was high the effect of the H_2/TP volume ratio was weak.

3 Conclusions

A novel conversion equation is proposed based on the "variable reaction order" and "virtual reactant" concepts. Three examples of catalytic reactions are given and the average relative derivation after fitting the experimental data was less than 2%. This indicates that the new equation can be used to describe the quantitative relationship between reactant conversion and reaction conditions with satisfactory precision for various catalytic reaction systems.

Nomenclature

A: model parameter
ARD: average relative deviation, %
B: model parameter
C: model parameter
E_r: relative activation energy
k: rate constant
n_{i0}, n_{i1}, n_{p0}, n_{p1}, $n_{\tau0}$, $n_{\tau1}$: model parameters
p: pressure, MPa
p_r: relative pressure ($p_r = p/p_{max}$)
RD: relative deviation, %
T: temperature, K
T_r: relative temperature ($T_r = T/T_{max}$)
X_M: conversion of reactant M, %
y_i: molar fraction of species i, %
τ: residence time, min
τ_r: relative residence time ($\tau_r = \tau/\tau_{max}$)
λ: material ratio
λ_r: relative material ratio ($\lambda_r = \lambda/\lambda_{max}$)

Subscript

cal: calculated value
exp: experimental value
r: relative value

References

1 米冠杰, 李建伟, 邱东, 陈标华. 催化学报 (Mi G J, Li J W, Qiu D, Chen B H. *Chin J Catal*), 2010, **31**: 547

2 宋树芹, 王毅, 沈培康. 催化学报 (Song Sh Q, Wang Y, Shen P K. *Chin J Catal*), 2007, **28**: 752

3 王敏, 李军, 桑雪梅, 谢家庆. 催化学报 (Wang M, Li J, Sang X M, Xie J Q. *Chin J Catal*), 2007, **28**: 383

4 Barkat M, Nibou D, Chegrouche S, Mellah A. *Chem Eng Process*, 2009, **48**: 38

5 Kvamsdal H M, Jakobsen J P, Hoff K A. *Chem Eng Process*, 2009, **48**: 135

6 Boehme T R, Onder C H, Guzzella L G. *Comput Chem Eng*, 2008, **32**: 2445

7 Jaree A, Boonsomlanjit B, Limtrakul J. *Comput Chem Eng*, 2008, **32**: 2897

8 Akpan E, Akande A, Aboudheir A, Ibrahim H, Idem R. *Chem Eng Sci*, 2007, **62**: 3112

9 Visconti C G, Tronconi E, Lietti L, Zennaro R, Forzatti P. *Chem Eng Sci*, 2007, **62**: 5338

10 Quiney A S, Schuurman Y. *Chem Eng Sci*, 2007, **62**: 5026

11 Hoang D L, Chan S H, Ding O L. *Chem Eng J*, 2005, **112**: 1

12 Tye C T, Mohamed A R, Bhatia S. *Chem Eng J*, 2002, **87**: 49

13 Alves J A, Bressa S P, Martine O M, Barreto G F. *Chem Eng J*, 2007, **125**: 131

14 郑泉兴, 刘纪端, 王琪, 杨意泉, 方维平, 张鸿斌. 化学反应工程与工艺 (Zheng Q X, Liu J D, Wang Q, Yang Y Q, Fang W P, Zhang H B. *Chem React Eng Technol*), 2005, **21**: 360

15 白雪. 上海化工 (Bai X. *Shanghai Chem Ind*), 1985, **3**: 29

16 Wang J, Huang L M, Li Q Zh. *Appl Catal A*, 1998, **175**: 191

17 Bertero N M, Apesteguia C R, Marchi A J. *Appl Catal A*, 2008, **349**: 100

18 盛景云. [博士学位论文]. 厦门: 厦门大学 (Sheng J Y. [PhD Dissertation]. Xiaman: Xiaman Univ), 2007

19 Wang H M, Prins R. *Appl Catal A*, 2008, **350**: 191

20 林凌. [硕士学位论文]. 厦门: 厦门大学 (Lin L. [MS Dissertation]. Xiaman: Xiaman Univ), 2007