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Global Kinetics of Direct Dimethyl Ether Synthesis Process from Syngas in Slurry Reactor over a Novel Cu-Zn-Al-Zr Slurry Catalyst

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***Abstract*—**The direct synthesis process of dimethyl ether (DME) from syngas in slurry reactors is considered to be promising because of its advantages in caloric transfer. In this paper, the influences of operating conditions (temperature, pressure and weight hourly space velocity) on the conversion of CO, selectivity of DME and methanol were studied in a stirred autoclave over Cu-Zn-Al-Zr slurry catalyst, which is far more suitable to liquid phase dimethyl ether synthesis process than bifunctional catalyst commercially. A Langmuir-Hinshelwood mechanism type global kinetics model for liquid phase DME direct synthesis based on methanol synthesis models and a methanol dehydration model has been investigated by fitting our experimental data. The model parameters were estimated with MATLAB program based on general Genetic Algorithms and Levenberg-Marquardt method, which is suitably fitting experimental data and its reliability was verified by statistical test and residual error analysis.

***Keywords*—**alcohol/ether fuel, Cu-Zn-Al-Zr slurry catalyst, global kinetics, slurry reactor

I. Introduction

DIMETHYL ether (DME) has been widely used as an excellent aerosol propellant and refrigerant for its environmentally benign properties. In recent years, with development of new chemical energy technologies in coal industry, it is becoming a hot research topic as an alternative clean fuel for diesel engines for its high cetane number (55-60) and as a substitute for liquefied petroleum gas [1]. As the result, synthesis gas to dimethyl ether (STD) process has received growing attention in those areas with poor oil resources but rich coal or natural gas resources for its dramatic economic value and theoretical significance, in addition to Alcohol /Ether products are important feedstock and intermediate for the preparation of olefins in MTO/MTP process.

DME is commercially produced by either of the following two synthesis processes: (1) a two-step process, which is consist of methanol synthesis from syngas based on a metallic catalyst and subsequent methanol dehydration on an acid catalyst in fixed-bed reactors; (2) a single-step method, which is developed by Topsøe for DME direct synthesis process from syngas in a single fixed-bed reactor/three-phase slurry reactor using a bifunctional catalyst[2]-[3] which is commonly the mechanical mixture of methanol synthesis catalyst (CuO-ZnO-Al_2O_3) and methanol dehydration catalyst (γ-Al_2O_3 /ZSM-5).

The main reactions in DME single-step synthesis process should be considered as follows:

methanol synthesis from CO hydrogenation:

$$CO + 2H_2 \rightleftharpoons CH_3OH \quad (1)$$

methanol synthesis from CO_2 hydrogenation:

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \quad (2)$$

methanol dehydration to DME:

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \quad (3)$$

water gas shift reaction (WGS):

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (4)$$

direct synthesis of DME from CO hydrogenation:

$$2CO + 4H_2 \rightleftharpoons CH_3OCH_3 + H_2O \quad (5)$$

and direct synthesis of DME from CO_2 hydrogenation:

$$2CO_2 + 6H_2 \rightleftharpoons CH_3OCH_3 + H_2O \quad (6)$$

In comparison with methanol synthesis from syngas, the synergic effect [4] of bifunctional catalyst in results in the alleviation of the thermodynamical equilibrium limitation of methanol synthesis and a higher once-through conversion of syngas. DME synthesis from syngas is a highly exothermic process from thermodynamical point of view, which will cause temperature runaway in the traditional tubular fixed-bed reactor and the catalyst irreversible deactivated, so DME direct synthesis in three-phase slurry reactor is attracting growing attention for prevention of the phenomena of hot spots with inert medium oil that has high specific thermal capacity. But the deactivation problem of bifunctional catalysts must be considered for the existence of water [5] adhering to the surface of catalysts.

The research of DME direct synthesis process is mainly focused on discrimination of bifunctional catalysts, development of different kinetic models and relevant reactor design of mathematical simulation either in a fixed-bed reactor or fluidized bed reactor [6]-[7]. Besides kinetic models of exponential form, the most common kinetic models for DME direct synthesis[8]-[10] is the combination of methanol synthesis model proposed by Graaf[11] based a strictly sequential reaction mechanism via surface carbonate and methanol dehydration model proposed by Bercic and Levec[12] based on reaction of dissociatively adsorbed methanol, which was simplified by supposed that water gas shift reaction in liquid-phase DME synthesis is in equilibrium in several literatures. Nie *et al* [13] has been presented an intrinsic kinetics

and reactor simulation model for DME direct synthesis from syngas over a bifunctional catalyst of CuO-ZnO-Al_2O_3 and γ-Al_2O_3 in a fixed-bed reactor. A few literatures [14] have been published for the kinetics and mathematical model in BCSR for liquid-phase DME synthesis from syngas.

In this paper, the influences of different operation conditions, such as temperature, pressure and space velocity has been studied in detail in continuous stirred tank reactor (CSTR) over a novel Cu-Zn-Al-Zr slurry catalyst [15], which is prepared by a novel complete liquid-phase technology and has small and uniform granularity, high dispersion degree, lower viscosity and higher activity stability. A global kinetics model for liquid phase DME direct synthesis has been proposed subsequently based on the Langmuir-Hinshelwood mechanism by fitting our experimental data. All the results may provide a reference for scaling-up and plant design.

II. Experimental Section

A. Catalyst

In comparison with bifunctional catalyst extensively used in the DME synthesis process, Cu-Zn-Al-Zr slurry catalyst was prepared by a complete liquid-phase technology from a solution to the slurry, and has high dispersive, activity stability, well rheological property, stable surface structure, and coexistent acid sites of strong and weak of dehydration. The description in detail about preparation method, physical properties and characterization test such as X-ray diffraction, N_2 adsorption, H_2 temperature-programmed reduction, X-ray photoelectron and NH3 temperature- programmed desorption can be found in [15].

Before each experimental analysis, The Cu-Zn-Al-Zr slurry catalyst was dispersed in liquid paraffin under mechanical stirring, then put into the slurry reactor and activated in situ by reduction using 20% hydrogen in nitrogen in steady-state flow at atmospheric pressure according to the following given temperature-programmed reduction procedure: heated from room temperature to 290℃ with heating temperature program of 5℃/min, and was kept for 10h at this temperature, then decreased to the required experimental temperature. When the catalyst bed temperature is arrived, premixed syngas at typical feed composition (H_2, N_2, CO, CO_2) was fed into the reactor. The presence of N_2 served as the internal standard for conversion and selectivity calculation purposes.

B. Experimental Equipment

A schematic diagram of the lab scale equipment is shown in Figure 1.

Before experimental testing, the whole pipeline system was carried out leak hunting and cleaned by nitrogen, and then the catalyst was reactivated in situ by reducing gas. After these pre-treatments, the fully-mixing syngas was introduced into 0.5L stirred autoclave to take place catalytic reactions via

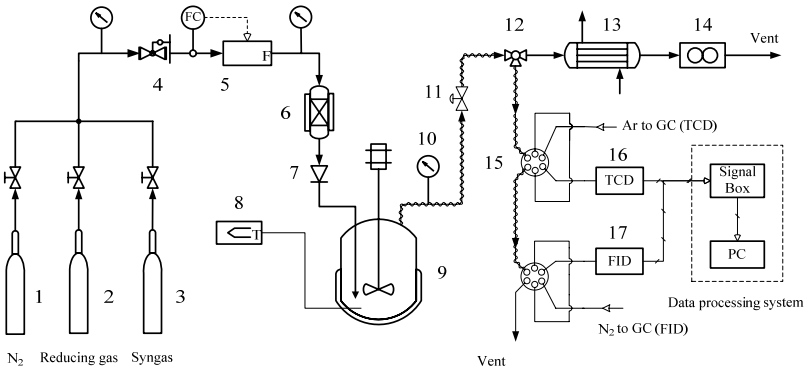

Fig. 1 Schematic diagram of global kinetics experiments in slurry reactor
1, 2, 3 Gas cylinder, 4 Pressure regulator valve, 5 Mass flowmeter, 6 Purifier, 7 Check valve, 8 Temperature controller; 9 Stirred autoclave, 10 Pressure gauge, 11 Back pressure valve, 12 Change valve, 13 Cold hydrazine, 14 Soap film flowmeter; 15 Six-way sampling valve, 16 Gas Chromatograph (TCD), 17 Gas Chromatograph (FID)

pressure regulating valve, mass flowmeter and purifier which removed oxygen, water and other trace poisons that can lead to for minimizing methanation reaction, which was equipped with an auto-inhale agitator for perfecting gas-liquid fully back-mixing. Two thermocouples were inserted into the slurry bed and heated chamber separately to regulate the reaction temperature. The reactor pressure was maintained with a back pressure regulator on the downstream line, which simultaneously reduced the outlet stream pressure to atmosphere pressure. To avoid possible condensation of liquid products, the downstream line from the stirred tank reactor was trace heated by heat preservation ribbon and constantly kept at temperature over 120℃.

Both of the internal and external diffusion resistances of catalyst grains with the size of 40-80 μm were confirmed to be eliminated using an impeller speed of 1000 rpm in CSTR. The experiments were carried out under the conditions of temperature from 220 to 260℃, pressure from 3.0 to 7.0 MPa and the space velocity from 0.6-1.2 L/(gcat·h). And the weight

of catalyst loaded in CSTR was 10.0065g suspended in 300mL liquid paraffin. The syngas was mixed by H_2, N_2, CO, CO_2 at proper ratio, and the composition of syngas in our experiments was y_{H2} = 0.65-0.75, y_{N2} = 0.07-0.10, y_{CO} = 0.14-0.20, y_{CO2} = 0.04-0.08.

C. Products Analysis

A small fraction of the reactor effluent was piped to two gas chromatographs (GC) in series for on-line analysis. One gas chromatograph was equipped with a thermal conductivity detector (TCD) and a Porapak Q packed column for separating H_2, N_2, CO, CO_2 and CH_4 (Pure argon as the carrier gas). The other gas chromatograph with a flame ionization detector (FID) was equipped with AT.FFAP capillary column for separating methanol, DME and other organic products (High pure nitrogen as the carrier gas). Composition of inlet and outlet gas were obtained by gas chromatogram analyzing, and methane and light olefins can be neglected in the calculation of material balance due to the content of byproducts in outlet gas less than 1%.

For the purposes of quantitative determination of the effect of the operation conditions (pressure, temperature and space velocity) on slurry catalyst, the conversion of CO and selectivity of DME/methanol were used. Given that the content of hydrocarbons as byproducts can be negligible, on the basis of feed and product flow rates and carbon balance, the CO conversion was defined by

$$x_{CO} = \frac{N_{in} y_{CO,in} - N_{out} y_{CO,out}}{N_{in} y_{CO,in}} \quad (7)$$

And selectivity of DME/methanol is defined as follows

$$S_{DME} = \frac{2N_{out} y_{DME,out}}{N_{in} y_{CO,in} - N_{out} y_{CO,out}} \quad (8)$$

$$S_M = \frac{N_{out} y_{M,out}}{N_{in} y_{CO,in} - N_{out} y_{CO,out}} \quad (9)$$

III. Results and Discussion

A. Effect of Reaction Temperature

The effects of reaction temperature on conversion of CO and selectivity of products with the experimental results correspond to pressure of 5 MPa and WHSV of 0.6 L/(gcat·h) were shown in Fig.2- Fig.3, respectively. It is found that the conversion of CO and selectivity of DME increase gradually with increasing temperature in the range of 220-260℃, and selectivity of methanol decreases with increasing temperature. From thermodynamical point of view, DME direct synthesis from syngas is a highly exothermic process, as the temperature increases the equilibrium conversion of CO declines gradually, but the reaction process is almost kinetically controlled in the operation region far away from equilibrium states. When the reaction temperature is further increasing, the thermodynamic influence will be greater than kinetic influence, DME direct synthesis process will be controlled by thermodynamic equilibrium.

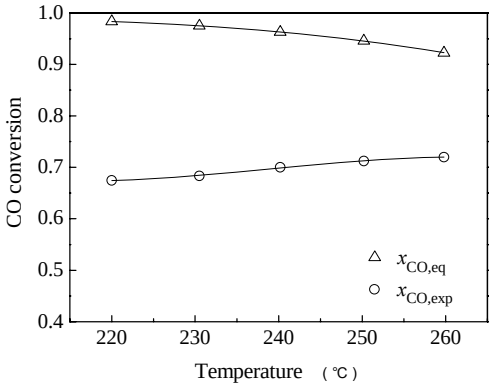

Fig. 2 Effect of reaction temperature on conversion of CO

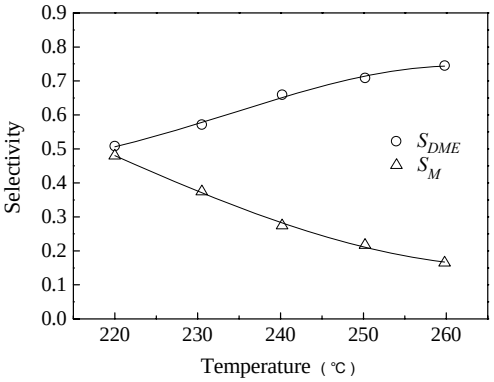

Fig.3 Effect of reaction temperature on selectivity of products

B. Effect of Reactor Pressure

The influences of reaction pressure on conversion of CO and selectivity of products with the experimental results corresponding to a temperature of 240℃ and WHSV of 0.6 L/(gcat·h) were presented in Fig.4-Fig.5, respectively. It is confirmed that when the pressure increases in the range from 3.0-7.0MPa, conversion of CO and selectivity of DME increase gradually, yet selectivity of methanol has different changes with increasing pressure. As is shown in (1) - (3), methanol synthesis reaction is stoichiometric-number-reducing reaction, yet methanol dehydration and water gas shift reaction are equivalent-mole-number reaction. So that pressure enhancement is only favorable theoretically to the conversion of CO and methanol yield. On the other hand, DME direct synthesis process can be regard as the cascade reaction which consists of methanol synthesis and methanol dehydration. Hence, methanol as intermediate product has adequate time for further transforming to dimethyl ether in this case, so selectivity of DME is increased obviously with increasing pressure, selectivity of methanol is just the opposite.

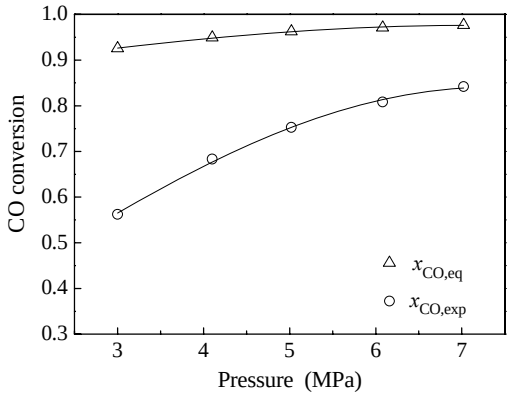

Fig. 4 Effect of reactor pressure on conversion of CO

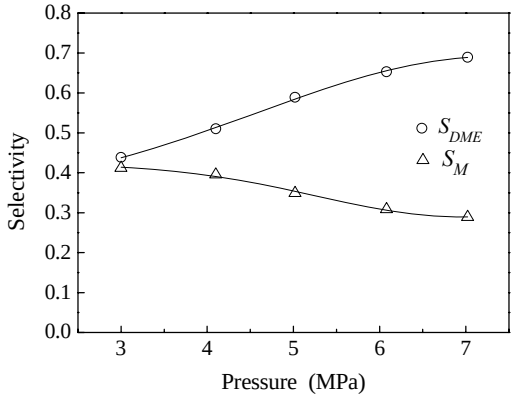

Fig. 5 Effect of reactor pressure on selectivity of products

C. Effect of WHSV

The influence of WHSV on conversion of CO and selectivity of products with the experimental results corresponding to a pressure of 5 MPa and temperature of 240 ℃ was shown in Fig.6- Fig.7, respectively. As can be seen, both conversion of CO and selectivity of DME decrease gradually with the increasing WHSV in the range from 0.4-1.2 L/(gcat·h), selectivity of methanol is just steadily increased. It is the logical consequence that means residence time of syngas in stirred tank reactor decreases with the increasing WHSV. From viewpoint of chemical equilibrium, the catalyst reaction will reach the state of chemical equilibrium gradually with continuous increase of catalytic reaction time, and has higher once-through conversion of CO. Therefore, the increasing WHSV results in the decline of catalytic reaction time between syngas and slurry catalyst and lower once-through conversion of CO. Meanwhile, because reaction rate of methanol synthesis is much faster than that of methanol dehydration, it is inadequate time for methanol dehydration to DME for increasing WHSV, and which result in the accumulation of methanol as products and lower selectivity of DME.

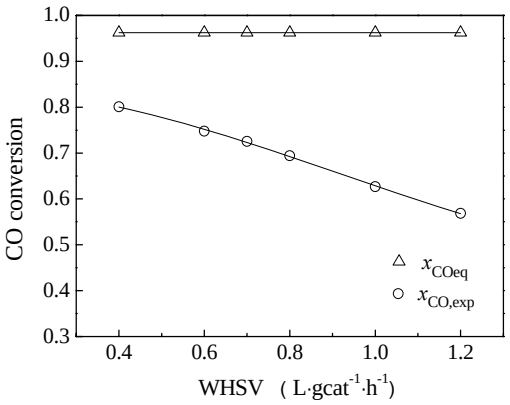

Fig. 6 Effect of WHSV on conversion of CO

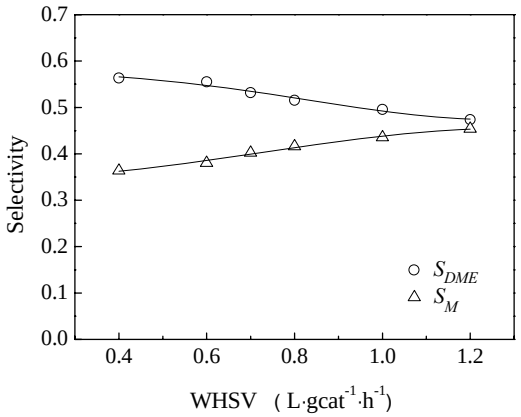

Fig. 7 Effect of WHSV on selectivity of products

IV. Global Kinetic Simulation

A. Global Kinetic Model Simulation

From phase law point of view, there are six gas species: H_2, N_2, CO, CO_2, CH_3OH, and DME, and three elements: C, H, and O in direct synthesis process of dimethyl ether from syngas, so the number of either independent reactions or independent components is three. Therefore, the reaction system can be expressed by methanol synthesis from CO and CO_2, methanol dehydration to DME, viz. (1)-(3). Choosing CO, CO_2, and DME as key components, the global kinetics equations based on the Langmiur-Hinshelwood mechanism were expressed by:

$$r_{CO}=\frac{-\mathrm{d}N_{CO}}{\mathrm{d}W}=\frac{k_1 f_{CO} f_{H_2}{}^2(1-\beta_1)}{(1+K_{CO}f_{CO}+K_{CO_2}f_{CO_2}+K_{H_2}f_{H_2})^3} \quad (10)$$

$$r_{CO_2}=\frac{-\mathrm{d}N_{CO_2}}{\mathrm{d}W}=\frac{k_2 f_{CO_2} f_{H_2}{}^3(1-\beta_2)}{(1+K_{CO}f_{CO}+K_{CO_2}f_{CO_2}+K_{H_2}f_{H_2})^4} \quad (11)$$

$$r_{DME}=\frac{\mathrm{d}N_{DME}}{\mathrm{d}W}=\frac{k_3 f_M(1-\beta_3)}{(1+\sqrt{K_M f_M})^2} \quad (12)$$

where $\beta_1 = \frac{f_M}{K_{f_1} f_{CO} f_{H_2}^2}$, $\beta_2 = \frac{f_M f_{H_2O}}{K_{f_2} f_{CO_2} f_{H_2}^3}$, $\beta_3 = \frac{f_{DME} f_{H_2O}}{K_{f_3} f_M^2}$, β_i refers to equilibrium degree of *i*th independent reaction, respectively, and f_j stands for the fugacity of component *j*, which is calculated by SHBWR equation of state[16]. K_{fi} is the equilibrium constant in form of each component fugacity for *i*th independent reactions, and the thermodynamic calculation expressions were given by the following relations [17].

Reaction rate constant as model parameters, namely k_i, can be defined by Arrhenius relations:

$$K_{f_1} = \exp[13.1652 + \frac{9203.26}{T} - 5.92839 \ln T - 0.352404 \times 10^{-2} T + 0.102264 \times 10^{-4} T^2 - 0.769446 \times 10^{-8} T^3 + 0.238583 \times 10^{-11} T^4] \times (0.10135)^{-2} \quad (13)$$

$$K_{f_2} = \exp[1.6654 + \frac{4553.34}{T} - 2.72613 \ln T - 1.106294 \times 10^{-2} T + 0.172060 \times 10^{-4} T^2 - 1.106294 \times 10^{-8} T^3 + 0.319698 \times 10^{-11} T^4] \times (0.101325)^{-2} \quad (14)$$

$$K_{f_3} = \exp[-9.3932 + \frac{3204.71}{T} + 0.83593 \ln T + 2.35267 \times 10^{-3} T - 1.8736 \times 10^{-6} T^2 + 5.1606 \times 10^{-10} T^3] \quad (15)$$

$$k_i = k_{0i} \exp(-E_i / RT) \quad (i=1, 2, 3) \quad (16)$$

and the adsorption equilibrium constant, namely K_j, can be defined by Van't Hoff relations:

$$K_j = K_{0j} \exp(-E_j / RT) \quad (j=\mathrm{CO}, \mathrm{CO_2}, \mathrm{H_2}, \mathrm{M}) \quad (17)$$

where k_{0i} or K_{0j} is the pre-exponential factor, E_i is the apparent activation energy for the *i*th independent reaction , and E_j is the apparent adsorption heat for the adsorption equilibrium constant of component *j*.

The rate of reaction of for each key component can be calculated by (10), (11), and (12) from the assumed initial values of model parameters and the outlet concentration of each gas component, namely $r_{j,cal}$ (*j*=CO, CO_2, DME). Meanwhile, for continuous stirred tank reactor as fully back-mixing ideal reactor, it also can be obtained directly from the components of the inlet and outlet, the flow rates of the inlet and outlet and weight of catalyst, namely $r_{j,\mathrm{exp}}$ (*j*=CO, CO_2, DME). The function expressions were given by

$$r_{CO,\mathrm{exp}} = \frac{N_{in} y_{in,CO} - N_{out} y_{out,CO}}{W} \quad (18)$$

$$r_{CO_2,\mathrm{exp}} = \frac{N_{in} y_{in,CO_2} - N_{out} y_{out,CO_2}}{W} \quad (19)$$

$$r_{DME,\mathrm{exp}} = \frac{N_{out} y_{out,DME}}{W} \quad (20)$$

The estimation of the global kinetics parameters has been carried out by nonlinear regression using program written in Matlab based on general Genetic Algorithms and the Levenberg-Marquardt method. Parameter optimization was based on the minimization of the following objective function being the weighted sum of square residuals for reaction rates of three key components.

$$F = \sum_j \sum_{i=1}^{M} w_j (r_{j,i,\mathrm{exp}} - r_{j,i,cal})^2 \quad (21)$$

where *M* is the total number of experiments and w_j stands for the distribution weighting factor of component *j*. In mathematical statistics the latter can be substituted for by the variance σ^2 that is a unknown value but approximately the relative errors for all experimental points, the distribution weighting factor w_j can be defined by $w_j = 1/r_{j,\mathrm{exp}}^n$.

B. Parameter Estimation and Statistical Test

According to a total of 25 experimental data, the parameters

TABLE I
REGRESSION PARAMETERS FOR THE GLOBAL KINETICS MODEL

Parameters	Pre-exponential factors ($mol \cdot g^{-1} \cdot h^{-1}$)	Apparent activation energy ($J \cdot mol^{-1}$)
k_1	7.704×10^3	26348.74
k_2	8.558×10^2	20587.82
k_3	1.8455×10^2	25845.97
K_{CO}	5.76×10^{-6}	-33499.95
K_{CO2}	9.66×10^{-6}	-20830.80
K_{H2}	4.307×10^{-2}	-20692.27
K_M	2.888	-20171.23

values of the global kinetic model in CSTR, with a 95% confidence internal, are calculated by the previous methodology mentioned and listed in Table I.

Model discrimination and statistical analysis have been carried out by hypothesis testing based on the value of the *F* (Fisher) sampling distribution and the correlation coefficient of determination ρ^2.

Correlation coefficient ρ^2 of the experimental and calculated value is defined by

$$\rho^2 = 1 - \sum_{j=1}^{M} (r_{j,\mathrm{exp}} - r_{j,cal})^2 / \sum_{i=1}^{M} r_{j,\mathrm{exp}}^2 \quad (22)$$

The value of the statistic *F* is the ratio of the sum of mean square to the sum of mean square of residual of the experimental and calculated values, which is defined by

$$F = \frac{[\sum_{j=1}^{M} r_{j,\mathrm{exp}}^2 - \sum_{j=1}^{M} (r_{j,\mathrm{exp}} - r_{j,cal})^2] / Mp}{\sum_{j=1}^{M} (r_{j,\mathrm{exp}} - r_{j,cal})^2 / (M - Mp)} \quad (23)$$

where M_p is number of parameters in each model equation.

The results of the statistical significance test of the global kinetics model of (10), (11), and (12) are shown in Table II. If $\rho^2 > 0.9$ and $F > 10F_{0.05}$, we can say that the model is reliable. Consequently, the results of the statistical significance test to the parameters of the model obtained were notably reliable

because $\rho^2 > 0.99$ and $F>10F_{0.05}$. $F_{0.05}$ is a value of the F Table corresponding to 95% confidence interval.

In comparison with experimental values, the calculated values of reaction rate of each key component are shown in Fig.

TABLE II
STATISTICS RESULTS OF THE GLOBAL KINETICS MODEL

Model	*Mp*	*M-Mp*	ρ^2	*F*	$10F_{0.05}$
(10)	8	17	0.990	210.249	25.5
(11)	8	17	0.992	293.726	25.5
(12)	4	21	0.994	685.207	28.4

8-Fig.10. As is shows that it is uniform distribution for relative errors of reaction rate of each key component, maximum interval values of which are ±18.06%, ±17.08%, ±14.49%, respectively.

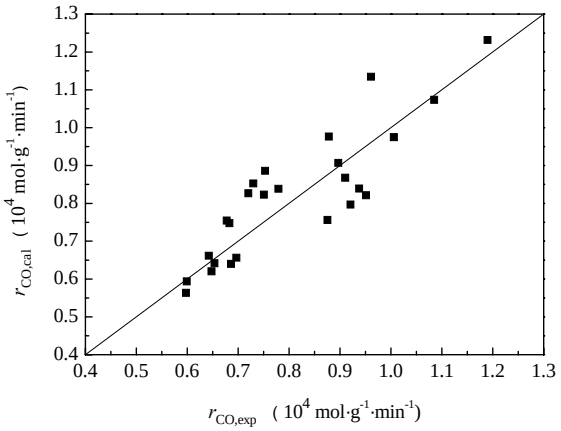

Fig. 8 Comparison of calculated and experimental values for CO reaction rate

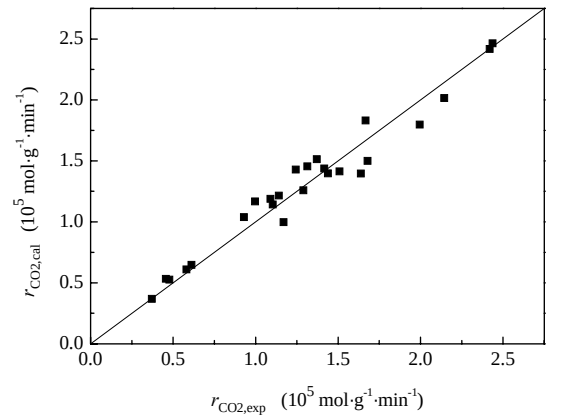

Fig. 9 Comparison of calculated and experimental values for CO_2 reaction rate

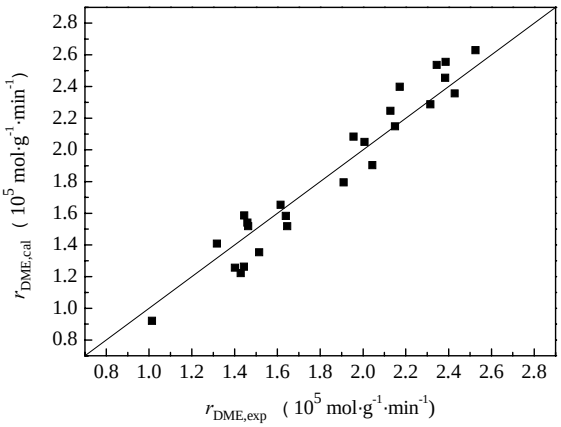

Fig. 10 Comparison of calculated and experimental values for DME reaction rate

V. CONCLUSION

The influences of pressure, temperature and WHSV on the once-through conversion of CO, selectivity of DME were studied in detail in the CSTR over Cu-Zn-Al-Zr slurry catalyst in wide range of experimental operation conditions: 3-7MPa, 220-260 ℃, WHSV 0.6-1.2L/(gcat·h). It is shown that Cu-Zn-Al-Zr slurry catalyst was more suitable to liquid phase DME direct synthesis process than bifunctional catalyst commercially used with CO conversion up to 0.75 and selectivity of DME up to 0.65.

A global kinetics model for liquid phase DME direct synthesis has been proposed by choosing methanol synthesis from CO hydrogenation and CO_2 hydrogenation and methanol dehydration as independent reactions, The model parameters were estimated with Matlab program based on general Genetic Algorithms and Levenberg-Marquardt method, which is suitably fitting experimental data, and its reliability was verified by the statistical test and the residual error analysis. The calculated apparent activation energy of three independent reactions is 26.3 kJ/mol, 20.6 kJ/mol and 25.8 kJ/mol, respectively. The optimal operation conditions were proposed.

NOMENCLATURE

E_i: apparent activation energy for *i*th independent reaction
E_j: apparent adsorption heat for adsorption equilibrium constant of component *j*
f_j: fugacity of component *j*, Pa
F: objective function of optimization for minimizing
k_j: Reaction rate constant of component *j*, kg·m^{-1}·s^{-1}
K_j: adsorption equilibrium constant of component *j*, kg·m^{-1}·s^{-1}
K_{fi}: equilibrium constant in form of each component fugacity for independent reaction *i*
M: number of experimental data
Mp: number of parameters in each model equation
r_j: reaction rate of component *j*, kg·m^{-1}·s^{-1}
R: gas constant，kJ·kmol^{-1}·K^{-1}
S: selectivity of products
T: reaction temperature, K
w_j: distribution weighting factor in (21)
W: weight of catalyst, kg

y_j: mole fraction of component *j* in gas phase

Subscripts

cal: calculated value
eq: equilibrium value
exp: experimental value
in: at the inlet of reactor bed
out: at the outlet of reactor bed

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