

Supplementary Material

# Intrinsic Kinetics Study of Biogas Methanation Coupling with Water Gas Shift over Re-Promoted Ni Bifunctional Catalysts

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## S1. Weisz-Prater Criterion for Internal Diffusion

The key to calculate  $N_{W-P}$  is to obtain the value of  $D_{eff}$  first, which can be predicted from Fuller-Schettler-Giddings method for binary gas phase diffusion [1]:

$$D_{eff} = D_{AB}\varepsilon/\tau$$

$$D_{AB} = 10^{-3}T^{1.75} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}} / P \left[ \left( \sum V_A \right)^{\frac{1}{3}} + \left( \sum V_B \right)^{\frac{1}{3}} \right]^2$$

where  $D_{AB}$  is the binary gas phase diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ),  $\varepsilon$  is the catalyst porosity,  $\tau$  is the tortuosity factor,  $T$  is the reaction temperature (K),  $M_A$  and  $M_B$  is the molecular weight for gas  $A$  and  $B$ ,  $P$  is the pressure (bar),  $\sum V_A$  and  $\sum V_B$  is the sum of diffusion volume for component  $A$  and  $B$ .

During internal diffusion elimination test in Section 2.1,  $T=350 \text{ }^\circ\text{C}=623 \text{ K}$ ,  $P=0.2 \text{ MPa}=2 \text{ bar}$ . The catalyst porosity  $\varepsilon$  is calculated from the BJH data from literature [2], which is 0.11. The tortuosity factor  $\tau$  is normally in the range of 2-7, here we use the mean value 4.5. The methanation coupling with water gas shift could be split into two reactions.

(1) For methanation,  $A=\text{CO}$ ,  $B=\text{H}_2$ , so  $M_A=28$ ,  $M_B=2$ .  $\sum V_A$  and  $\sum V_B$  could be obtained directly from literature [1], which is 18.9 and 7.07, respectively. As a result,

$$D_{AB}=10^{-3}(623)^{1.75}(1/28+1/2)^{0.5}/2/(18.9^{1/3}+7.07^{1/3})^2=1.35$$

$$D_{eff}=1.35 \times 0.11 / 4.5 = 0.033$$

(2) For water gas shift,  $A=\text{CO}$ ,  $B=\text{H}_2\text{O}$ , so  $M_A=28$ ,  $M_B=18$ .  $\sum V_A$  and  $\sum V_B$  could also be obtained directly from literature [1], which is 18.9 and 12.7, respectively. As a result,

$$D_{AB}=10^{-3}(623)^{1.75}(1/28+1/18)^{0.5}/2/(18.9^{1/3}+12.7^{1/3})^2=0.47$$

$$D_{eff}=0.47 \times 0.11 / 4.5 = 0.011$$

According to the analysis of external diffusion in Section S2, when  $\text{GHSV}=2000 \text{ h}^{-1}$  the external diffusion could be neglected, so  $C_s=C_b$ . The final values of  $N_{W-P}$  under different catalyst particle sizes are listed in the following Table S1.

**Table S1.** The parameters of Weisz-Prater criterion at various catalyst particle sizes.

Particle size $R$		CO reaction rate $r$ ( $10^{-5} \text{ mol s}^{-1} \text{ cm}^{-3}$ )	CO concentration at the particle surface $C_s$ ( $10^{-5} \text{ mol cm}^{-3}$ )	$N_{W-P}$	
in meshes	in cm			methanation	water gas shift
8-10	0.085-0.10	1.047	1.736	0.132-0.183	0.396-0.548
10-12	0.07-0.085	1.078	1.736	0.092-0.136	0.277-0.408
12-14	0.059-0.07	1.081	1.736	0.066-0.092	0.197-0.277
14-16	0.05-0.059	1.076	1.736	0.047-0.065	0.141-0.196
16-18	0.042-0.05	1.080	1.736	0.033-0.047	0.100-0.141

## S2. Mears Criterion for External Diffusion

The key to calculate  $N_M$  is to obtain the value of  $k_c$  first, which derives from Sherwood number [3]:

$$\text{Sh} = k_c L / D_{AB}$$

and Sherwood number could be further correlated into the following equation:

$$\text{Sh} = 2 + 0.552 \text{Re}^{\frac{1}{2}} \text{Sc}^{\frac{1}{3}}$$

$$\text{Re} = uL/\nu$$

$$\text{Sc} = \nu/D_{AB}$$

where Sh is the Sherwood number,  $L$  is the characteristic length (cm),  $D_{AB}$  is the binary gas phase diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ), Re is the Reynolds number, Sc is the Schmidt number,  $u$  is the fluid velocity ( $\text{cm s}^{-1}$ ) and  $\nu$  is the kinetic viscosity ( $\text{cm}^2 \text{s}^{-1}$ ).

During the external diffusion elimination test in Section 2.1, the gas space hourly velocity is 1000-3000  $\text{h}^{-1}$ , the catalyst volume is 30 mL and the inner diameter of the reactor tube is 50 mm. As a result, the fluid velocity  $u$  is 0.424-1.273  $\text{cm s}^{-1}$ . When under the reaction of 350 °C and 0.2 MPa, the gas kinetic viscosity  $\nu$  will be expanded compared to normal temperature and pressure. Thus, Sherwood number could assumed to be 2.

(1) For methanation,  $L=5$ ,  $D_{AB}=1.35$ . As a result,

$$k_c=2 \times 1.35/5=0.54$$

(2) For water gas shift,  $L=5$ ,  $D_{AB}=0.47$ . As a result,

$$k_c=2 \times 0.47/5=0.188$$

On the basis of previous researches, the CO reaction order  $n$  for methanation and water gas shift usually falls on the scope of 0.5-2.0 [4, 5] and 0.80-1.96 [6-9], respectively. For the convenience of calculation, the CO reaction order  $n$  for methanation and water gas shift could be valued by average which is 1.25 and 1.38, respectively. The final values of  $N_M$  under different gas hourly space velocities (GHSV) are listed in the following Table S2.

**Table S2.** The parameters of Mears criterion at various gas hourly space velocities.

GHSV ( $\text{h}^{-1}$ )	Particle size $R$		CO reaction rate $r$ ( $10^{-5} \text{ mol s}^{-1} \text{ cm}^{-3}$ )	CO bulk concentration $C_b$ ( $10^{-5} \text{ mol cm}^{-3}$ )	$N_M$	
	in meshes	in cm			methanation	water gas shift
1000	12-14	0.059-0.07	1.658	1.736	0.130-0.155	0.414-0.491
1500	12-14	0.059-0.07	1.274	1.736	0.100-0.119	0.318-0.377
2000	12-14	0.059-0.07	0.955	1.736	0.083-0.098	0.238-0.282
2500	12-14	0.059-0.07	0.609	1.736	0.064-0.076	0.152-0.180
3000	12-14	0.059-0.07	0.550	1.736	0.043-0.051	0.137-0.162

### S3. Intrinsic Kinetics Experimental Design

Table S3. Orthogonal array.

Case number	Temperature (°C)	Pressure (MPa)	H <sub>2</sub> /CO
1	300	0.10	0.6
2	300	0.15	0.7
3	300	0.20	0.8
4	300	0.25	0.9
5	300	0.30	1.0
6	325	0.10	0.7
7	325	0.15	0.8
8	325	0.20	0.9
9	325	0.25	1.0
10	325	0.30	0.6
11	350	0.10	0.8
12	350	0.15	0.9
13	350	0.20	1.0
14	350	0.25	0.6
15	350	0.30	0.7
16	375	0.10	0.9
17	375	0.15	1.0
18	375	0.20	0.6
19	375	0.25	0.7
20	375	0.30	0.8
21	400	0.10	1.0
22	400	0.15	0.6
23	400	0.20	0.7
24	400	0.25	0.8
25	400	0.30	0.9

### S4. Equilibrium Constant Calculation

$$K_{eq,SMR} = 1.198 \times 10^{23} \exp(-26830/T) \text{ [Pa}^2\text{]}$$

$$K_{eq,WGS} = 1.767 \times 10^{-2} \exp(4400/T)$$

Table S4. Equilibrium constant of methanation and water gas shift under different reaction temperatures.

Reaction temperature <i>T</i> (°C)	Reaction temperature <i>T</i> (K)	<i>K</i> <sub>eq,methanation</sub> (kPa <sup>2</sup> )	<i>K</i> <sub>eq,WGS</sub>
300	573.15	560.39E-06	38.1294
325	598.15	3964.52E-06	27.6639
350	623.15	23972.59E-06	20.5943
375	648.15	126168.27E-06	15.6844
400	673.15	586966.91E-06	12.1891

### S5. Model Parameters Solution

$$r_{\text{CH}_4} = k_1^0 \exp(-E_1/RT) P_{\text{CO}}^{a_1} P_{\text{H}_2}^{b_1} P_{\text{CH}_4}^{c_1} P_{\text{H}_2\text{O}}^{d_1}$$

$$r_{\text{CO}_2} = k_2^0 \exp(-E_2/RT) P_{\text{CO}}^{a_2} P_{\text{H}_2\text{O}}^{b_2} P_{\text{H}_2}^{c_2} P_{\text{CO}_2}^{d_2} (1 - \beta)$$

The model formulas could be deformed into the following ones by taking the logarithm of both sides:

$$\ln r_{\text{CH}_4} = a_1 \ln P_{\text{CO}} + b_1 \ln P_{\text{H}_2} + c_1 \ln P_{\text{CH}_4} + d_1 \ln P_{\text{H}_2\text{O}} + \ln k_1^0 + E_1(-/RT)$$

$$\ln\left(\frac{r_{\text{CO}_2}}{1 - \beta}\right) = a_2 \ln P_{\text{CO}} + b_2 \ln P_{\text{H}_2\text{O}} + c_2 \ln P_{\text{H}_2} + d_2 \ln P_{\text{CO}_2} + \ln k_2^0 + E_2(-/RT)$$

Since there are 25 sets of kinetics data, each formula will have 25 equations which could be expressed by the following matrix (the superscript 1-25 on the right stands for the case number and is not relevant to any exponent):

$$\begin{bmatrix} \ln P_{\text{CO}}^1 & \ln P_{\text{H}_2}^1 & \ln P_{\text{CH}_4}^1 & \ln P_{\text{H}_2\text{O}}^1 & 1 & \frac{-1^1}{RT} \\ \ln P_{\text{CO}}^2 & \ln P_{\text{H}_2}^2 & \ln P_{\text{CH}_4}^2 & \ln P_{\text{H}_2\text{O}}^2 & 1 & \frac{-1^2}{RT} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \ln P_{\text{CO}}^{25} & \ln P_{\text{H}_2}^{25} & \ln P_{\text{CH}_4}^{25} & \ln P_{\text{H}_2\text{O}}^{25} & 1 & \frac{-1^{25}}{RT} \end{bmatrix} \times \begin{bmatrix} a_1 \\ b_1 \\ c_1 \\ d_1 \\ \ln k_1^0 \\ E_1 \end{bmatrix} = \begin{bmatrix} \ln r_{\text{CH}_4}^1 \\ \ln r_{\text{CH}_4}^2 \\ \vdots \\ \ln r_{\text{CH}_4}^{25} \end{bmatrix}$$

$$\begin{bmatrix} \ln P_{\text{CO}}^1 & \ln P_{\text{H}_2\text{O}}^1 & \ln P_{\text{H}_2}^1 & \ln P_{\text{CO}_2}^1 & 1 & \frac{-1^1}{RT} \\ \ln P_{\text{CO}}^2 & \ln P_{\text{H}_2\text{O}}^2 & \ln P_{\text{H}_2}^2 & \ln P_{\text{CO}_2}^2 & 1 & \frac{-1^2}{RT} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \ln P_{\text{CO}}^{25} & \ln P_{\text{H}_2\text{O}}^{25} & \ln P_{\text{H}_2}^{25} & \ln P_{\text{CO}_2}^{25} & 1 & \frac{-1^{25}}{RT} \end{bmatrix} \times \begin{bmatrix} a_2 \\ b_2 \\ c_2 \\ d_2 \\ \ln k_2^0 \\ E_2 \end{bmatrix} = \begin{bmatrix} \ln\left(\frac{r_{\text{CO}_2}}{1 - \beta}\right)^1 \\ \ln\left(\frac{r_{\text{CO}_2}}{1 - \beta}\right)^2 \\ \vdots \\ \ln\left(\frac{r_{\text{CO}_2}}{1 - \beta}\right)^{25} \end{bmatrix}$$

For each matrix, the number of linear equations (25) surpasses the number of unknown parameters (6) so it belongs to overdetermined set of equations. The matrix equation above could be denoted as  $A \times X = B$  and the corresponding MATLAB code is shown in Figure S1.

```
>> X=pinv(A)*B
X =
    0.5803
    0.2468
   -0.0000
    0.5803
  -14.2791
    23.2546

>> X=pinv(A)*B
X =
    1.9645
    1.9645
    4.2979
   -9.4584
  -12.8796
    33.4752
```

Figure S1. MATLAB solving results of empirical model.

### S6. Catalyst Photos

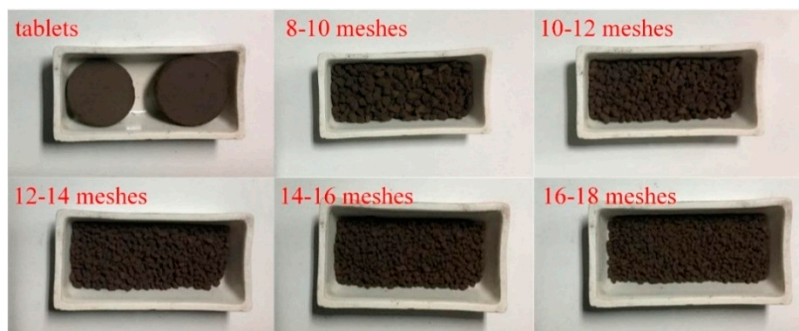


Figure S2. Pictures of prepared catalysts with different particle sizes.

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