SUPPLEMENTARY 1

Weisz – Prater and Mears criteria: results of calculations

Internal diffusion

In order to determine if internal diffusion is limiting the reaction the Weisz – Prater criterion can be used. It uses measured values of the rate of reaction to determine if the reaction suffers from problem of internal diffusion as follows:

$$C_{WP} = \frac{Actual\ reaction\ rate}{A\ diffusion\ rate} = \frac{A\rho_c R^2}{D_e C_{CO,s-g}}.$$

Internal mass transfer effect can be neglected when the value of C_{WP} is less than 1 [S1].

The parameters used for the criterion calculations are represented in Table S1.

Table S1. Experimental parameters to calculate the CWP criterion at 483K, GHSV = 300 hr^{-1}, 2 MPa

A ($\mu mol_{CO}/(s \cdot g_{Co})$)	Observed reaction rate	5.4
ρ_c, (kg/m^3)	Solid catalyst density	1166
R, m	Radius of catalyst particle	0.00075
D_e, m^2/s	Effective diffusivity	1.71 x 10^{-6}
$C_{CO,s-g}$, (mol/l)	Concentration of CO in syngas	0.156

The effective diffusivity De in the criterion will in this case be substituted by Knudsen diffusion because the average pore diameter (Dp) is 4.8 nm and pore diffusion will therefore be dominated by Knudsen diffusion (DKn) and is calculated by formula:

$$D_{Kn} = \frac{V_{ave}\, Dp}{3},$$

where V_{ave} is the average velocity for the CO. V_{ave} is calculated by the formula:

$$V_{ave} = [8k_B T/\pi m]^{1/2},$$

where k_B is Boltzmann's constant, m is the mass of molecular species and π is atomic mass unit.

The parameter $C_{CO,s-g}$ is the gas concentration at the catalyst surface, which is calculated by the formula:

$$C_{CO,s-g} = \frac{N_{CO}}{V_{s-g}},$$

were N_{CO} is a quantity moles of CO and V_{s-g} is a volume of syngas.

The observed activity rates A for all of the reactions and corresponding Weisz – Prater Criterion are presented in the Table S2.

Table S2. The observed activity rates and corresponding Weisz – Prater criterion at 300 hr^{-1}.

Temperature		Activity	Weisz – Prater Criterion
(°C)	(K)	A ($\mu mol_{CO}/(s \cdot g_{Co})$)	C_{WP}
180	453	0.8	0.001895
190	463	1.3	0.003114
200	473	2.4	0.005810

210	483	5.4	0.013210
232	505	10.2	0.025515
235	508	15.6	0.039138
237	510	18.6	0.046756
239	512	22.5	0.056671
241	514	22.9	0.057791
243	516	25.2	0.063719

As it mentioned above, the internal mass transfer effects can be neglected when the value of C_{WP} is less than 1. The maximum value of C_{WP} is 0.063. This indicates that internal mass transfer effects can be neglected.

External Diffusion

Mears criterion [S1] is used to check whether the reaction is limited by external diffusion which is given below:

$$C_m = \frac{A\rho_b R^2}{k_c C_{CO,s-g}} < 0.15.$$

The parameters used for the criterion calculations are represented in Table S3.

Table S3. Parameters values for calculating Mears criterion at 483K, 2 MPa and GHSV 300 hr^{-1}

A (μmolCO/(s·gCo))	Observed reaction rate	5.4
pv, kg/m^3	Bulk density	638
R, m	Radius of catalyst particle	0.00075
n	Reaction order	0.5
ϕ	Porosity of catalyst bed	0.45
$C_{CO,s-g}$, mol/l	Concentration of CO in syngas	0.156
k_c, m/s	Mass transfer coefficient	0.098

Mass transfer coefficient k_c was found from Thones–Kramers correlation:

$$k_c = \frac{D_{CO,s-g}\, Sh\, (1-\phi)}{dp\, \phi},$$

were $D_{CO,s-g}$ — diffusivity of CO in syngas mixture. Diffusivity of CO in H_2 is 7.26×10^{-4} m^2/s at 822°C (1095K), based on literature [S2];

Sh — Sherwood number;

ϕ — porosity of catalyst bed;

dp – volume-average particle diameter, м.

The parameter $C_{CO,s-g}$ is the gas concentration at the catalyst surface, which is calculated by the formula:

$$C_{CO,s-g} = \frac{N_{CO}}{V_{s-g}},$$

were N_{CO} is a quantity moles of CO and Vs-g is a volume of syngas.

The observed activity rates A for all of the reactions and corresponding Mears criterion are presented in the Table S4.

Table S4. The observed activity rates and corresponding Mears criterion at GHSV 300 hr^{-1}

Temperature		Activity	Mears criterion
(°C)	(K)	A ($\mu mol_{CO}/(s \cdot g_{Co})$)	C_m
180	453	0.8	0.000013
190	463	1.3	0.000021
200	473	2.4	0.000038
210	483	5.4	0.000084
232	505	10.2	0.000154
235	508	15.6	0.000235
237	510	18.6	0.000279
239	512	22.5	0.000336
241	514	22.9	0.000341
243	516	25.2	0.000374

The values of C_m are in the order of $10^{-4} – 10^{-5}$. This indicates that both internal and external diffusion transfer effects can be neglected.

References

S1. Fogler, H. S. Elements of Chemical Reaction Engineering (International Series in the Physical and Chemical Engineering Sciences). 5th edition. Pearson: 2016, pp. 957. ISBN 0133887510.

S2. Kleiminger, L.; Li, T.; Li, K.; Kelsall, G.H. Syngas ($CO-H_2$) production using high temperature micro-tubular solid oxide electrolysers. Electrochimica Acta 2015, 179, 565–77. https://doi.org/10.1016/j.electacta.2015.07.062.