Supplementary Information (SI) for Catalysis Science & Technology.

Supplementary Materials

Highly efficient and stable methane dry reforming enabled by confinement-mass transfer balancing of Ni/DFNS catalysts

Chao Hu [a, *], Guorui Wang [a], Yifan Hu [a], Ying Jiang [a], Mingju Yang [a], Hongye Chen [a], Nai Rong [b], Xiaokang Wan [a]

a. School of Environment and Energy Engineering, Anhui Jianzhu University, Ziyun Rd. 292, Hefei 230601, China

b. Energy Saving Research Institute, Anhui Jianzhu University, Ziyun Rd. 292, Hefei 230601, China

To whom correspondence should be addressed
E-mail address: chaohu@mail.ustc.edu.cn.

Table S1. Summary of the peak position of Ni^0 and Ni^{2+}.

Catalysts	$Ni2p_{3/2}$ Binding Energy		The ratio of Ni^0/Ni^{2+}
	Ni^{2+} (eV)	Ni^0 (eV)	
Ni/DFNS-2-EG	855.6	852.6	30.1%
Ni/DFNS-4-EG	855.8	852.5	44.8%
Ni/DFNS-6-EG	856.1	852.9	50.1%
Ni/DFNS-8-EG	855.7	853.0	46.7%
Ni/DFNS-6-WI	856.0	852.6	24.1%

Table S2. Summary of the peak position of O 1s

Catalysts	O1s Binding Energy			The ratio of O_{surf} / ($O_{latt+}O_{surf+}O_{ads}$)
	O_{latt} (eV)	O_{surf} (eV)	O_{ads} (eV)	
Ni/DFNS-2-EG	531.8	532.8	534.0	71.8%
Ni/DFNS-4-EG	531.7	532.9	533.9	81.7%
Ni/DFNS-6-EG	531.8	533.1	534.1	83.1%
Ni/DFNS-8-EG	531.7	532.9	533.9	70.2%
Ni/DFNS-6-WI	531.6	533.0	534.0	68.3%

Table S3. The CH_4 conversion rates at different GHSV and temperature conditions

Catalysts	**CH_4 conversion (%)**	**Temperature (°C)**				
	GHSV（$mL \cdot g^{-1} \cdot h^{-1}$）	**450**	**470**	**490**	**510**	**530**
Ni/DFNS-6-EG	18000	7.35	9.70	13.13	17.21	21.96
	72000	2.45	3.27	4.56	6.42	8.50
	90000	1.98	2.79	3.63	4.67	6.06

Table S4. Catalytic reaction rate for CH_4 at different GHSV and temperature

conditions

Catalysts	**Rate*10^4 (mol • g^{-1} • s)** **GHSV（mL • g^{-1} • h^{-1}）**	**Temperature (°C)**				
		450	**470**	**490**	**510**	**530**
Ni/DFNS-6-EG	18000	1.642	2.165	2.930	3.840	4.902
	72000	2.183	2.917	4.069	5.730	7.589
	90000	2.207	3.018	4.048	5.506	6.963

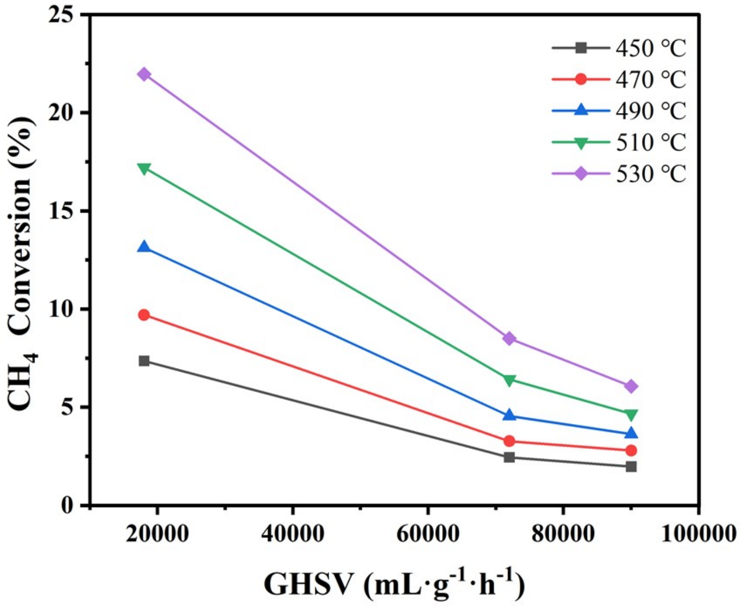

Fig. S1. Effect of external diffusions on the Ni/DFNS-6-EG catalysts.

Computational approach employed in the kinetic analysis:

The reaction rates for CH_4 were determined by employing the formula below:

$$r_i = \frac{X_i * F_{i,in}}{V_m * g_{cat} * wt_{(metal)}\%} \quad (i = CH_4)$$

Where r_i was the reaction rates for CH_4 ($mol_i \cdot g_{cat}^{-1} \cdot s^{-1}$), X_i was the conversion for CH_4 (%), $F_{i,\ in}$ show the inlet flow rate of each component at standard temperature and pressure ($mol_i \cdot s^{-1}$), g_{cat} was the mass of the catalyst used to test the rate value, V_m represents the standard molar volume, $wt_{(metal)}\%$ represents the actual metal content of the catalyst [1].

The Arrhenius equation was stated as follows:

$$\ln r_i = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right) \quad (i = CH_4)$$

Where A was the preexponential factor, Ea was the activation energy ($kJ \cdot mol^{-1}$), R was the gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$), and T was the thermodynamic temperature of reaction (K).

According to the Arrhenius equation ln(rate) = -Ea/RT + lnA. The logarithm of the reaction rate of the reacting gas, ln(rate)CH_4, was used as the Y-axis, and the reciprocal of the temperature (1/T) was used as the X-axis. The slope of the resulting graph was calculated and found to be Ea/R.

Experiments were carried out to ensure the negligible effects of external diffusion limitation on the recorded kinetic data. The effects of external limitation were ruled out by varying the GHSV [2, 3]. In Table S3 and Fig. S1, the CH_4 conversion rate of Ni/DFNS-6-EG significantly decreased at a GHSV of 72,000 $mL \cdot g^{-1} \cdot h^{-1}$, while it further declined and stabilized at 90,000 $mL \cdot g^{-1} \cdot h^{-1}$. Moreover, in Table S4, the CH_4 reaction rate at GHSV values of 72,000 $mL \cdot g^{-1} \cdot h^{-1}$and 90,000 $mL \cdot g^{-1} \cdot h^{-1}$ exhibited nearly identical values at the same temperature and maintained a stable trend. This indicated that external diffusion limitation was largely eliminated when GHSV exceeded 72000 $mL \cdot g^{-1} \cdot h^{-1}$. To obtain more accurate data and minimize the effect of external diffusion limitation, we conducted kinetic tests at high space velocity (90,000 $mL \cdot g^{-1} \cdot h^{-1}$). Meanwhile, the effect of catalyst particle size on internal diffusion limitation was negligible owing to its uniform and fine particle size [3, 4]. The DRM reaction was in the kinetic region under the aforementioned reaction conditions and the apparent activation energies approached the intrinsic values.

Supplementary references

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