Supporting Information

Enhancing the methane steam reforming catalytic performance of Ni monolithic catalysts via Ni-Re surface alloying

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1. Evaluation of the effect of mass and heat transfer on the reaction

The effects of mass and heat transfer on the reaction were evaluated as follows. First, the mass-transfer coefficient k^0_{mt} and the heat-transfer coefficient h_p of methane were estimated by calculating the following dimensionless numbers: Sherwood number S_h ($S_h = k^0_{mt}d_h/D_{Am}$), the Reynolds number R_e ($R_e = d_h u \rho/\mu$), Schmidt number S_c ($S_c = \mu/\rho D_{Am}$), the Graetz number G_Z ($G_Z = R_e S_c d_h/L$), and Prandtl number Pr ($Pr = c_p\mu/\lambda_f$) [1, 2]. The definition of the involved parameters was listed in Table S1. The Sherwood number S_h was estimated by using the following correlation for honeycomb monoliths proposed by Hawthorn [3]. A correlation for S_h in square channels with laminar flow was also proposed by Tronconi et al., and a similar S_h value was obtained using both methods [4, 5].

$$S_h = 2.976(1 + 0.095/G_z)^{0.45} \quad (1)$$

Then, the difference between the bulk fluid concentration of CH_4 (C_{Ab}, mol m^{-3}) and the surface concentration of CH_4 (C_{As}, mol m^{-3}) on the surface of monolithic channel was estimated by the Eq. 2, and the difference between the temperature of the bulk fluid (T_b) and the channel surface temperature (T_s) was estimated by the Eq. 3 [2].

$$k_{mt}a_m(C_{Ab} - C_{As}) = r_{SR} \quad (2)$$

$$h_p a_m(T_s - T_b) = (-r_{SR})(-\Delta H_{SR}) \quad (3)$$

where the k_{mt} is the effective mass-transfer coefficient of CH_4 (defined as $k_{mt} = k^0_{mt}/y_{fA}$, y_{fA} reflects the influence of MSR on the diffusion in the boundary film on the surface of channels), a_m is the geometric surface area per volume of monolith (m^2 m^{-3}), h_p is the heat transfer coefficient, ΔH_{SR} is the reaction heat of MSR. The calculated values (for the temperature related parameters, the values at 773 and 973 K are shown.) were shown in Table S1.

The Mears criteria was also used to assess the mass and heat transport limitation [6, 7]. Only the interphase transport was considered since the coating layer is very thin (< 1 μm) which was confirmed by TEM observation of the cross-section of monolith (Not shown in this paper), and the intraparticle and interparticle transports were negligible.

For the heat transport, assuming that the temperature dependence of methane reaction rate for steam reforming follows the Arrhenius relationship.

$$r_{SR} = Ae^{-E/RT} \quad (4)$$

where A is a pre-exponential factor, R is the gas constant, E is the activation energy for methane steam reforming, T is the reaction temperature. Then the reaction rate at a temperature T close to T_0, the temperature of the bulk fluid, can be expressed as follows by a Taylor expansion of above equation neglecting the terms higher than the first.

$$r_{SR} = r_{SR,0}\left(1 + \frac{T - T_0}{T_0}\frac{E}{RT_0}\right) \tag{5}$$

where $R_{SR,0}$ corresponds to the reaction rate at temperature T_o. In the case of a honeycomb catalyst, an energy balance in a cylindrical channel with a length of l can be expressed as follows.

$$\Delta H_{SR} r_{SR} \pi(d_h/2)^2 l = h_p(T - T_0) 2\pi(d_h/2) l \tag{6}$$

where d_h is the hydraulic diameter of the channel. In order for the reaction rate r_{SR} at a temperature T not to deviate from the reaction rate $r_{SR,0}$ at temperature T_0 by more than 5%, the following inequality was obtained.

$$\frac{\Delta H_{SR} r_{SR} d_h}{h T_0} < 0.2 \frac{RT_0}{E} \tag{7}$$

For the mass transport, the criterion for the spherical catalytic particle was expressed as follows in order for the reaction rate $r_{SR,s}$ at particle surface not deviate by more than 5% from the rate $r_{SR,b}$ at bulk fluid [7].

$$\frac{r_{SR} d_h n}{C_{Ab} k_{mt}} < 0.15 \tag{8}$$

where C_{Ab} is the concentration of bulk fluid, n is the reaction order. Thus, in order to apply this criterion to the monolithic catalyst, the following expression can be obtained by the similar treatment as for treating the heat transport.

$$\frac{r_{SR} d_h n}{C_{Ab} k_{mt}} < 0.2 \tag{9}$$

Table S1 Definition and values (for the temperature related parameters, the values at 773 and 973 K are shown.) of the involved parameters in this study.

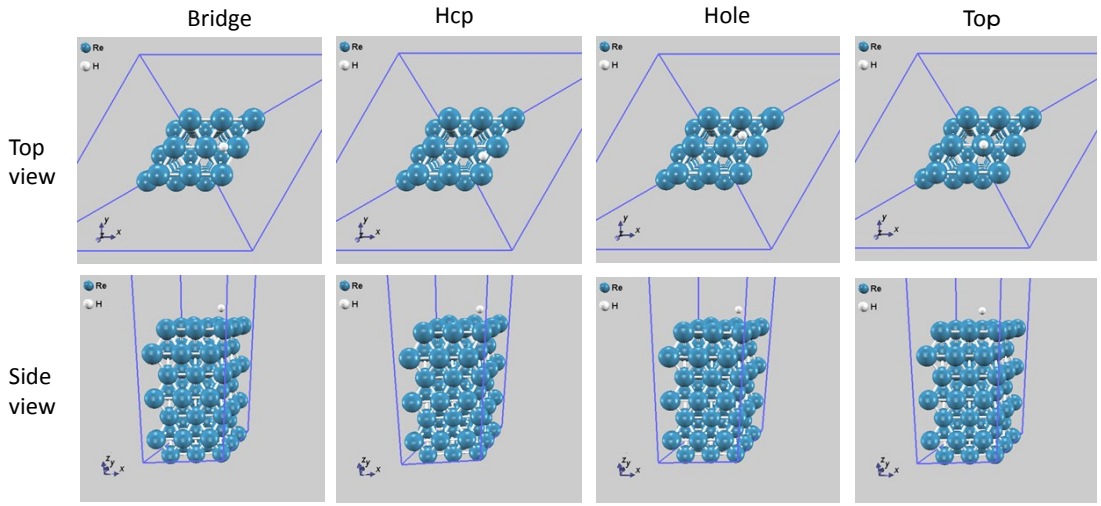
Parameters	Definition	Unit	Value (at 773 K)	Value (at 973 K)
a_m	Geometric surface area per volume of monolith	$m^2\ m^{-3}$	8700	8700
c_p	Heat capacity	$J\ kg^{-1}\ K^{-1}$	61.83 (CH_4)	70.66 (CH_4)
D_{Am}	Bulk diffusivity of species A	$m^2\ s^{-1}$	1.56×10^{-4} (CH_4 in CH_4-H_2O fluid)	2.24×10^{-4} (CH_4 in CH_4-H_2O fluid)
d_h	Hydraulic diameter	m	5.98×10^{-4}	5.98×10^{-4}
G_z	Graetz number ($G_Z = R_e S_c d_h/L$)		0.0063	0.0052
h_p	Heat transfer coefficient	$W\ m^{-2}\ s^{-1}\ K^{-1}$	621.3	840.1
L	Monolithic length	m	0.01	0.01
k^0_{mt}	Mass-transfer coefficient (caused by molecule diffusion only)	$m\ s^{-1}$	0.78 (CH_4)	1.11 (CH_4)
k_{mt}	Effective mass-transfer coefficient (caused by both molecule diffusion and reaction diffusion) ($k_{mt} = k^0_{mt}/\gamma_{fA}$)	$m\ s^{-1}$	0.57 (CH_4)	0.81 (CH_4)
P_r	Prandtl number ($Pr = c_p\mu/\lambda_f$)		0.8545	0.8600
R_e	Reynolds number ($R_e = d_h u\rho/\mu$)		0.17	0.13
S_c	Schmidt number ($S_c = \mu/\rho D_{Am}$)		0.64	0.65
S_h	Sherwood number ($S_h = k^0_{mt} d_h/D_{Am}$)		2.976	2.976
u	Superficial velocity	$m\ s^{-1}$	0.0275	0.0329
V	Monolith volume	m^3	5.03×10^{-7}	5.03×10^{-7}
γ_{fA}	Factor of reaction influence on film diffusion (For MSR, $\gamma_{fA} = \frac{(1+2y_{Ab})-(1+2y_{As})}{\ln[(1+2y_{Ab})/(1+2y_{As})]}$)		1.37 (MSR)	1.37 (MSR)
y_{Ab}	Mole fraction of CH_4 in the bulk fluid			
y_{As}	Mole fraction of CH_4 on the surface of monolithic channel			
λ_f	Thermal conductivity of the fluid	$W\ m^{-1}\ K^{-1}$	0.1193	0.1193
μ	Fluid viscosity	$kg\ m^{-1}\ s^{-1}$	2.64×10^{-5} (CH_4-H_2O)	3.15×10^{-5} (CH_4-H_2O)
ρ	Gas density	$kg\ m^{-3}$	0.2651 (CH_4-H_2O)	0.2156 (CH_4-H_2O)
ΔH_{SR}	Heat of methane steam reforming	$kJ\ mol^{-1}$	-189.9	-186.8

2. Schematic representation of the slab for calculation of adsorption energy of hydrogen

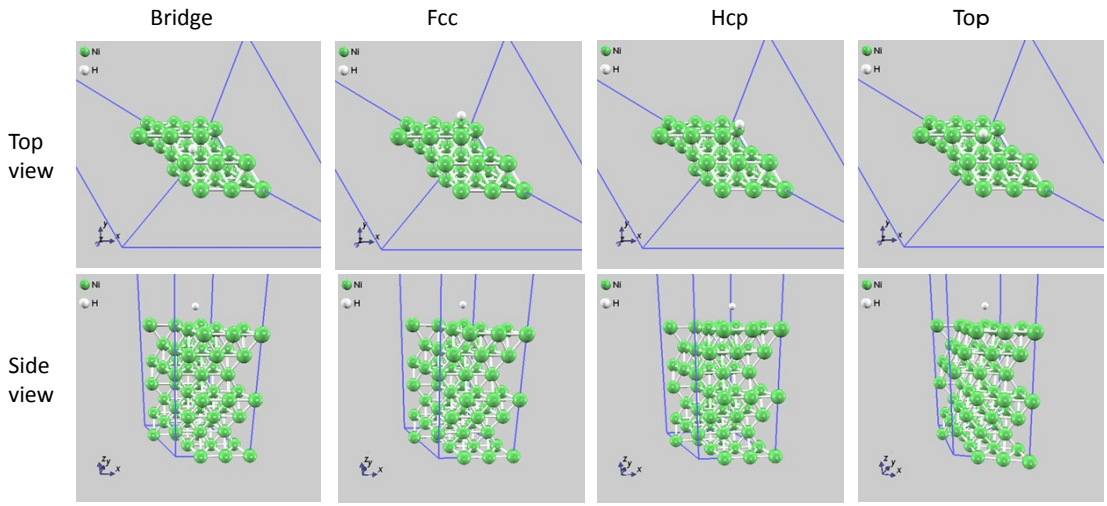
The calculation results of adsorption energy of one hydrogen atom on various possible sites of the Ni (111), Ni (011), Ni (001), and Re (001) surfaces were summarized in Table 4 in the manuscript. These various possible sites of the Ni (111) and Re (001) surfaces were schematically represented in Figure S1. Whereas the various possible sites of the Ni (011) and Ni (001) surfaces can be referred in reference [8].

Figure S1 Schematic representation of the slab consisting of 63 atoms in seven atomic layers (each layer = 3 × 3 atoms) for the DFT calculations. (a) Re (001); (b) Ni (111). The hydrogen atom adsorbed on bridge, fcc, hcp, hole, and top sites of Ni(111) and Re(001) surfaces are shown.

(a)



(b)



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