Electronic Supplementary Information

Zeolite-supported rhodium sub-nano cluster catalyst for low-temperature selective oxidation of methane to syngas

Yuhui Hou,[a] Sho Ogasawara,[a,b] Atsushi Fukuoka,[a] Hirokazu Kobayashi[a]*

[a]Institute for Catalysis, Hokkaido University, Sapporo, Hokkaido 001-0021, Japan.

[b]Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido 001-0021, Japan.

E-mail: kobayashi.hi@cat.hokudai.ac.jp

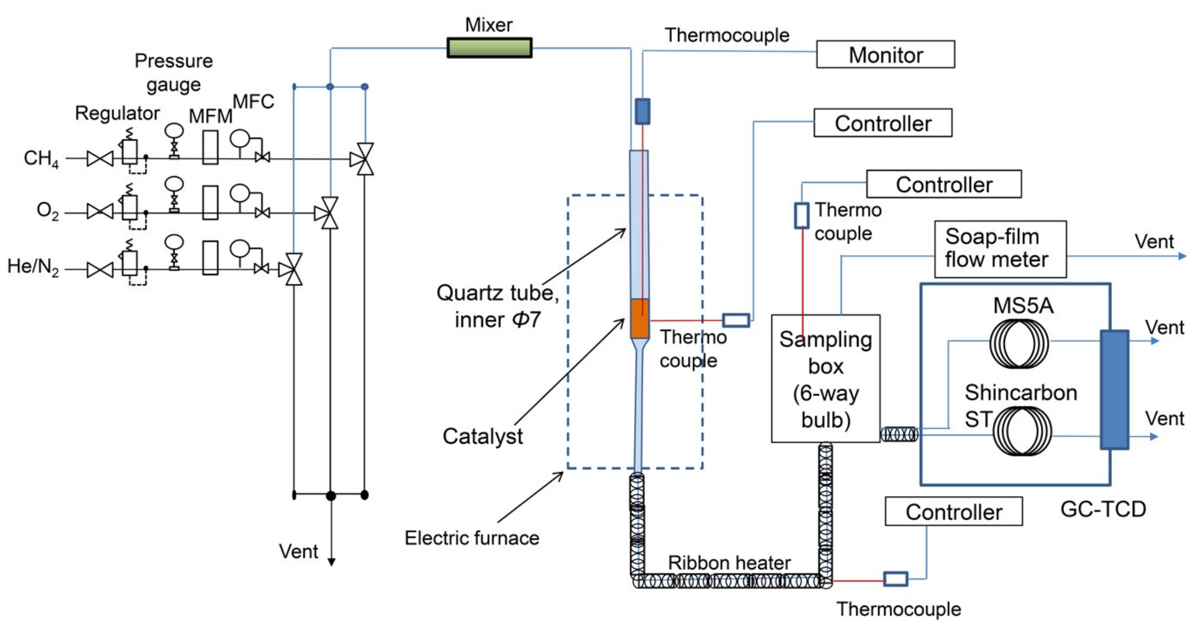

Fig. S1 Reaction setup.

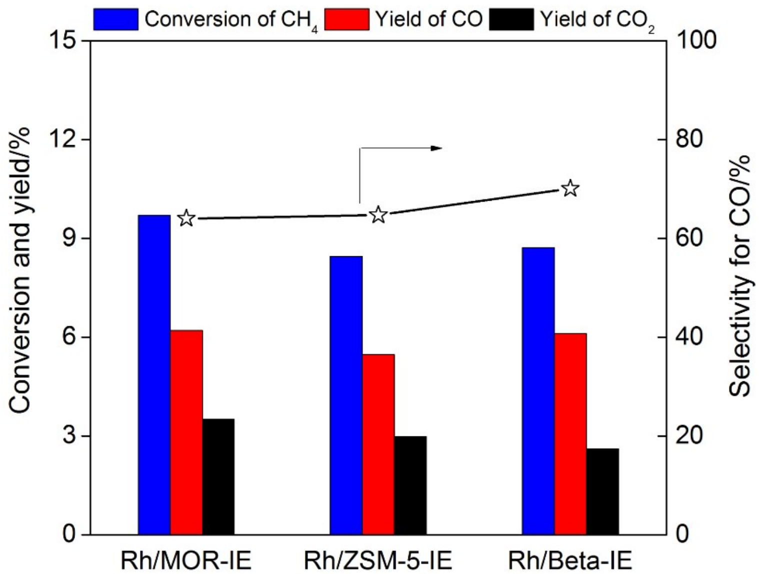

Fig. S2 Catalytic performance over Rh/zeolite catalysts prepared by ion exchange method.

Conditions: 450 °C, $CH_4/O_2/He = 50/4/46$, SV = 6000 mL $g^{-1}h^{-1}$.

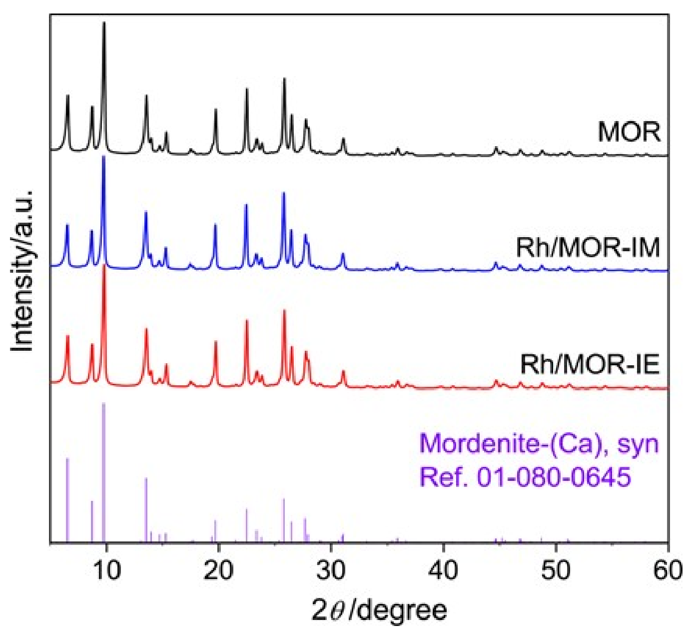

Fig. S3 XRD patterns of the samples

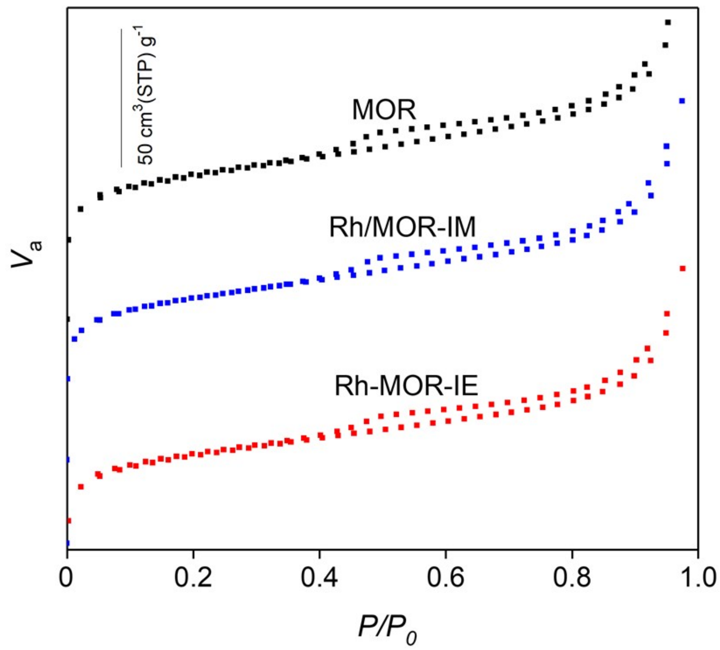

Fig. S4 N_2 adsorption-desorption isotherms at −196 °C for different samples.

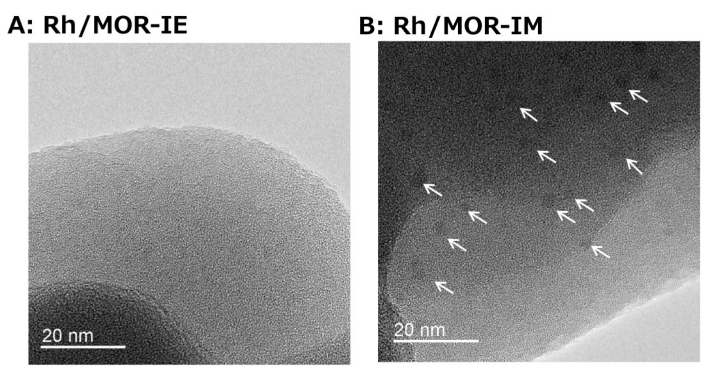

Fig. S5 TEM images of Rh/MOR-IE (A) and Rh/MOR-IM (B).

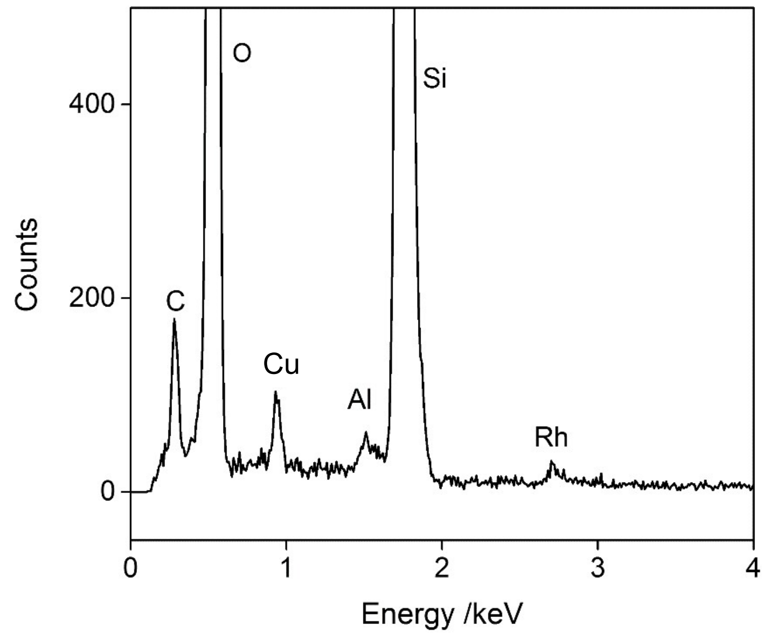

Fig. S6 EDX spectrum of Rh/MOR-IE at bright dots (008). *Cu and C come from the holey carbon supported copper grid.

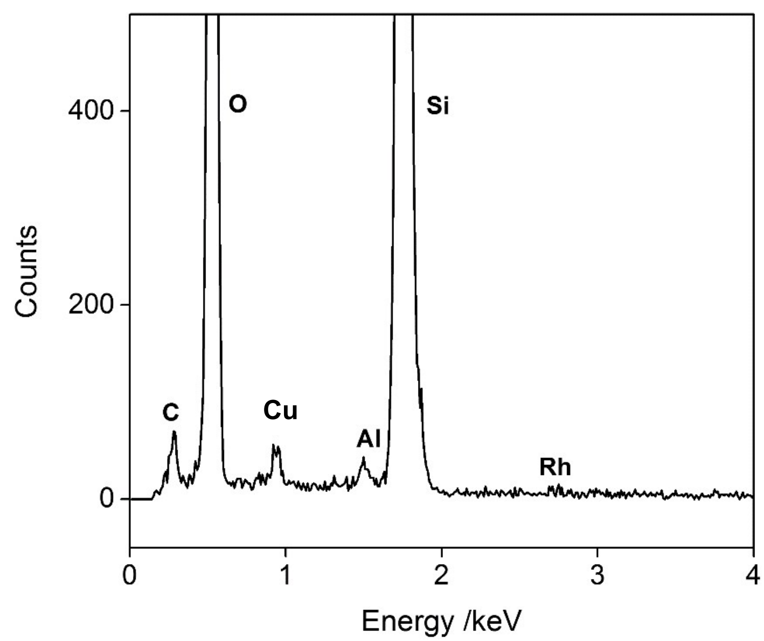

Fig. S7 EDX spectrum of Rh/MOR-IE at dark part. *Cu and C come from the holey carbon supported copper grid.

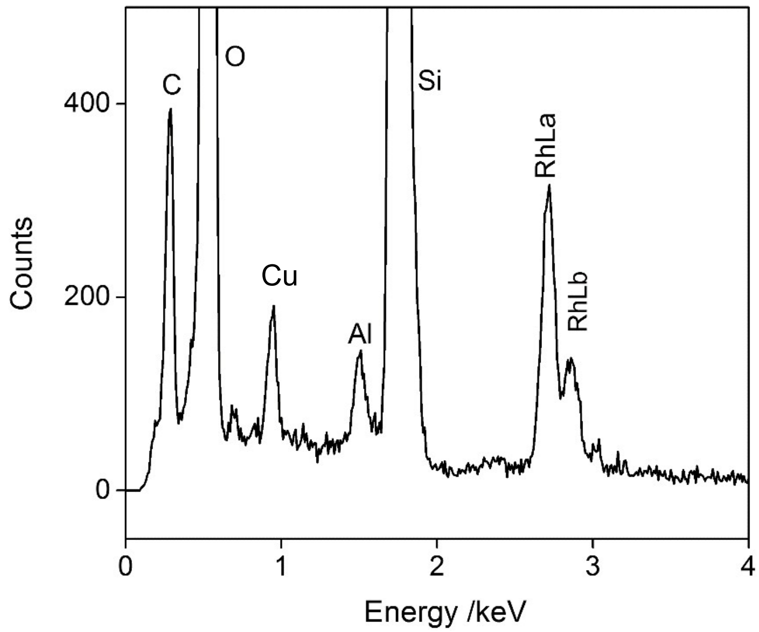

Fig. S8 EDX spectrum of Rh/MOR-IM at bright dots (003). *Cu and C come from the holey carbon supported copper grid.

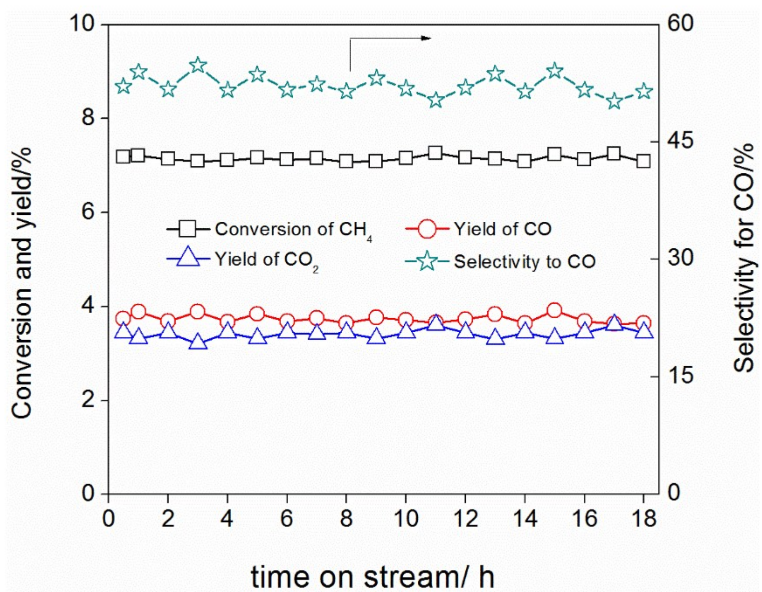

Fig. S9 Durability test of Rh/MOR-IE under non-equilibrium condition.

Conditions: 450 °C, $CH_4/O_2/He$ = 50/4/46, SV = 60,000 mL g^{-1} h^{-1}.

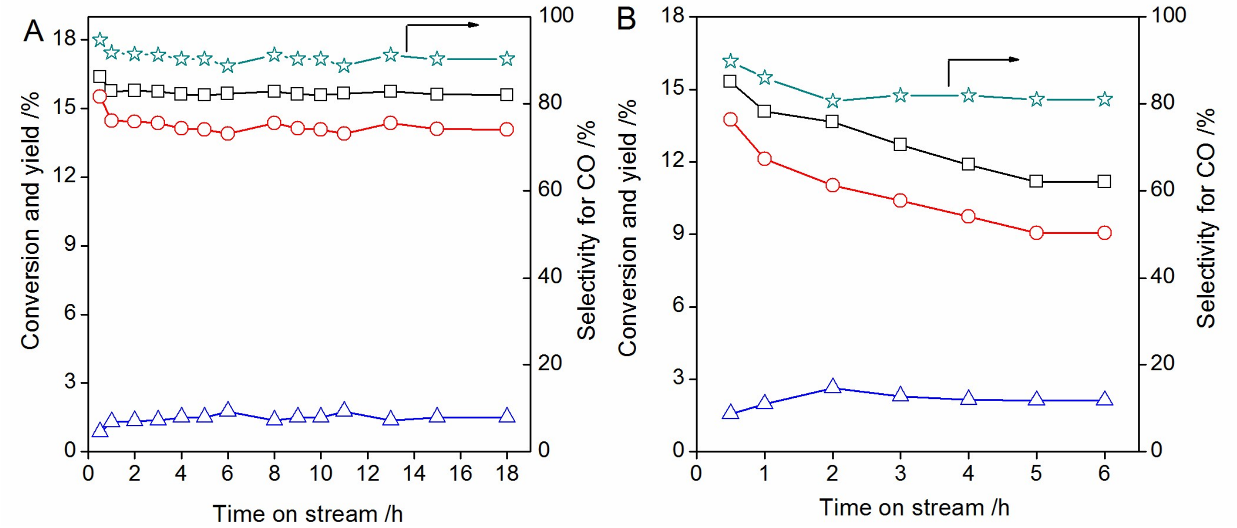

Fig. S10 Time course of POM by Rh/MOR-IE (A) and Rh/MOR-IM (B) at 600 °C, $CH_4/O_2/He = 50/4/46$, and SV = 6000 mL g^{-1} h^{-1}. Green star: CO selectivity; black square: conversion; red circle: CO yield; blue triangle: CO_2 yield.

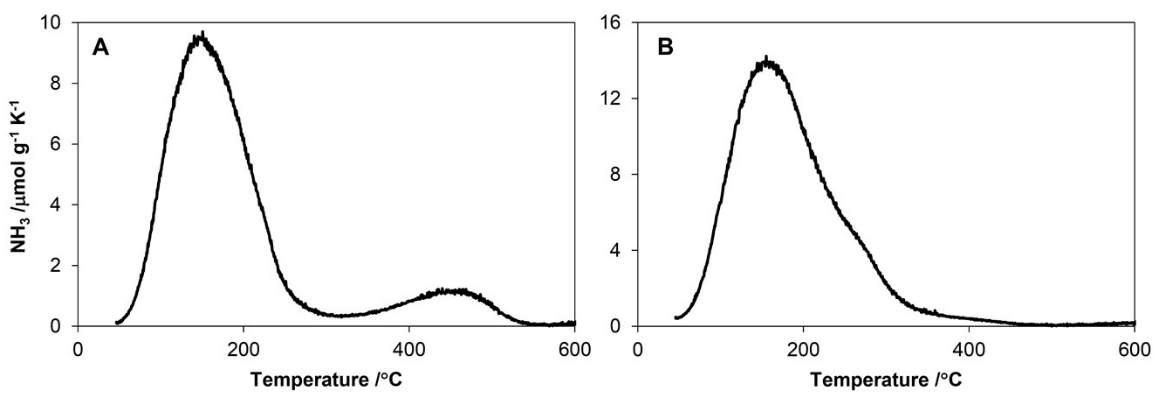

Fig. S11 NH_3-TPD for Rh/MOR-IE (A) and Rh/NaMOR-IE (B).

Table S1 Comparison of adsorbed amount of CO on Rh catalysts

Catalysts	CO/Rh ratio
Rh/MOR-IE	1.2
Rh/MOR-IM	0.61
Rh/ZSM-IE	1.2
Rh/Beta-IE	1.2
Rh/SiO_2-IM	0.51
Rh/Al_2O_3-IM	0.46

Table S2 Thermodynamic data for outlet gas in the POM.

	$\Delta H_f°(298)$[a] /kJ mol^{-1}	$S°(298)$[b] /J K^{-1} mol^{-1}	C_p /J K^{-1} mol^{-1} = $a + 10^{-3}bT + 10^{-6}cT^2 + 10^{-9}dT^3 + 10^6eT^{-2}$				
			a	b /K^{-1}	c /K^{-2}	d /K^{-3}	e /K^2
CH_4	-74.4	186.3	-0.703029	108.477	-42.5216	5.86279	0.678565
CO	-110.5	197.7	25.5676	6.09613	4.05466	-2.67130	0.131021
CO_2	-393.5	213.8	24.9974	55.1870	-33.6914	7.94839	-0.136638
H_2	0	130.7	33.0662	-11.3634	11.4328	-2.77287	-0.158558
H_2O	-241.8	188.8	30.0920	6.83251	6.79344	-2.53448	0.082139

[a] $\Delta H°(T) = \Delta H°(298) + \int_{298}^{T} C_p dT$ (S1). [b] $S°(T) = S°(298) + \int_{298}^{T} \frac{C_p dT}{T}$ (S2).

Table S3 Equilibrium data for POM under different conditions

$CH_4/O_2/He(N_2)$	Temp. /°C	Conv. CH_4 /%	Sel. CO/%	H_2/CO
50/4/46	450	10.2	68.1	2.5
50/4/46	600	16.5	97.4	2.1
36/18/46	450	40.2	65.2	2.0
3.33/1.67/95	600	85.0	96.0	2.0

Table S4 Equilibrium data for reforming and reverse WGS under different conditions

Conditions	Temp. /°C	Conv. /%	Sel. CO/%
Reforming[a]	450	58[c]	91.7
Reforming[a]	600	93[c]	99.7
Reverse WGS[b]	450	53[d]	8.0
Reverse WGS[b]	600	78[d]	87

[a]$CH_4 + H_2O \Leftrightarrow CO + 3H_2$, $CH_4/He/H_2O$ = 47/49/4. [b]$CO_2 + H_2 \Leftrightarrow CO + H_2O$, $CO_2/H_2/He$ = 2/12/86.
[c]Conversion of CH_4 based on the amount of H_2O. [d]Conversion of $CO_2 = (1 - n_{CO2\text{-}out}/n_{CO2\text{-}in}) \times 100\%$.

Table S5 Catalytic performance of different samples in the POM at CH_4/O_2 of 12.5.

Catalysts	Temp. /°C	SV /mL g^{-1} h^{-1}	Conv. (CH_4) /%	Yield (CO) /%	Sel. (CO) /%	H_2/CO
Rh/MOR-IE	450	6000	9.7	6.2	64	2.4
Rh/MOR-IM	450	6000	6.4	3.3	51	2.3
Rh/SiO_2-IM	450	6000	7.9	2.6	33	n.d.
Rh/Al_2O_3-IM	450	6000	8.2	2.7	34	n.d.
MOR	450	6000	0.01	<0.002	<20	n.d.

Reaction conditions: 450 °C, total flow rate: 20 mL min^{-1}, $CH_4/O_2/N_2$ (or He) = 50/4/46, 0.1 MPa. n.d.: not determined.

Table S6 Performance of POM catalysts at 873 K

Catalyst	SV /mL g^{-1} h^{-1}	CH_4/O_2/ inert gas	Conv. (CH_4) /%	Sel. (CO) /%	TOF for CO /h^{-1}	TON	Ref.
0.25 wt% Rh/MOR-IE	1.2×10^6	3.33/1.67/95	84	91	52,000	2.6×10^6 at 50 h	This work
0.5 wt% $Rh/Ce_{0.16}Zr_{0.84}O_2$	1.2×10^6	3.33/1.67/95	77	70	18,000	No data	[S1]
1 wt% $Rh/Ce_{0.5}Zr_{0.5}O_2$	2.5×10^5	28.6/14.3/57.1	50	52	7,800	78,000 at 10 h	[S2]
0.5 wt% Rh/ZrO_2	1.1×10^6	4.0/2.24/93.76	42	38	5,800	No data	[S3]
0.19 wt% Rh/*t*-ZrO_2	9.0×10^5	2.0/1.0/97	55	78	17,000	No data	[S4]
3.1 wt% Rh/CeO_2	6.0×10^4	5.0/2.5/92.5	84	78	270	No data	[S5]
0.5 wt% Rh/α-Al_2O_3	1.1×10^6	4.0/2.24/93.76	73	67	18,000	No data	[S3]
1 wt% Rh/α-Al_2O_3	2.5×10^5	28.6/14.3/57.1	62	68	13,000	1.3×10^5 at 10 h	[S2]

When the literature reported multiple catalysts and conditions with detailed results, we chose similar one to that of our case (0.25 wt% Rh, SV = 1.2×10^6 mL h^{-1} g^{-1}, $CH_4/O_2/He$ = 3.33/1.67/95).

Table S7 Catalytic performance of regenerated Rh/MOR-IE

Catalyst	Conv. CH_4/%	Yield CO/%	Sel. CO/%
Fresh	16.4	15.5	94.7
Regenerated[a]	16.5	15.7	95.1

Conditions: 600 °C, total flow rate: 20 mL min^{-1}, SV = 6000 mL h^{-1} g^{-1}, 0.1 MPa, $CH_4/O_2/N_2$ (or He) = 50/4/46.

[a]Calcined at 450 °C for 1 h with O_2 after using Rh/MOR-IE for the POM at 650 °C.

Table S8 Catalytic performance over Rh/MOR-IE with different pretreatment

Pretreatment	Conv. CH_4/%	Yield CO/%	Sel. CO/%
No treatment	9.7	6.2	64.0
H_2 reduction at 450 °C for 1 h	10.1	6.5	64.4

Conditions: 450 °C, total flow rate: 20 mL min^{-1}, SV = 6000 mL h^{-1} g^{-1}, 0.1 MPa, $CH_4/O_2/N_2$ (or He) = 50/4/46.

Table S9 Average coordination number (CN) of surface Rh

Rh metal species	CN
Rh_8 cluster	3.8
Rh_{13} cluster	5.0
Corner site on bulk Rh	5.5
Edge site on bulk Rh	7.0
Terrace site on bulk Rh	9.0

Supplementary references

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