Supporting Information

Mordenite-stabilised Rhenium catalyst for partial oxidation of methane to syngas

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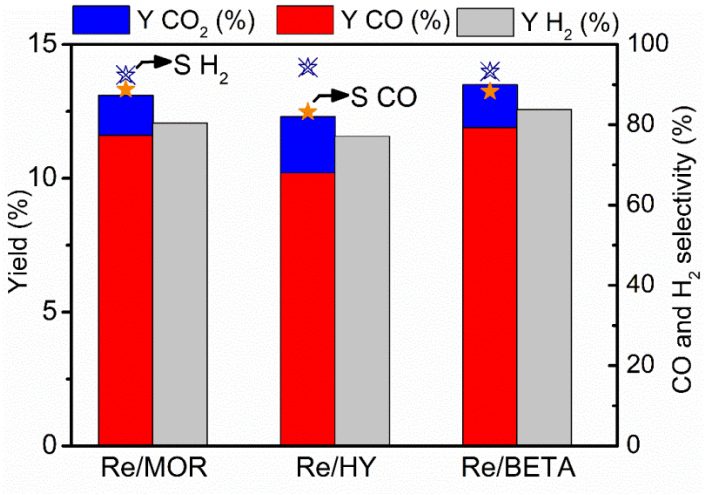

Fig. S1 Effect of Re loading on different type of zeolites on the POM reaction. Conditions: 600 °C, CH_4: O_2: N_2 = 50:4:46, space velocity (SV): 60, 000 mL g^{-1} h^{-1}. Results at 1 h of time on stream.

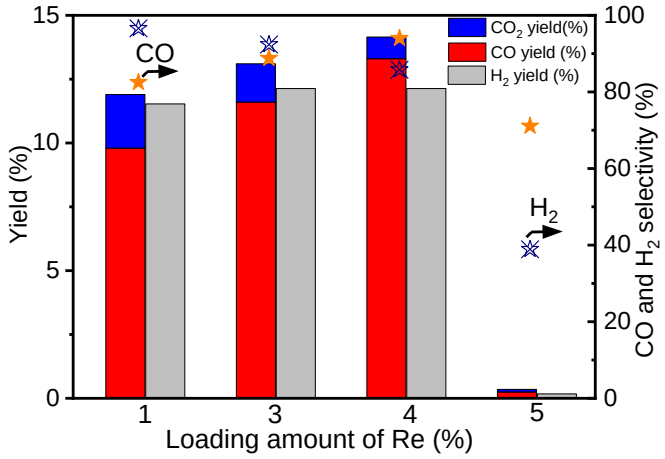

Fig. S2 Effect of loading amount of Re on the oxidation of methane. Conditions: 600 °C, CH_4: O_2: N_2 = 50:4:46, space velocity (SV): 60, 000 mL g^{-1} h^{-1}. Results at 1 h of time on stream.

Catalytic activity was maximized at 3 to 4 wt% of Re loading, but the activity suddenly dropped at 5 wt%. Therefore, we decided to use 3 wt% of Re to obtain active catalysts stably.

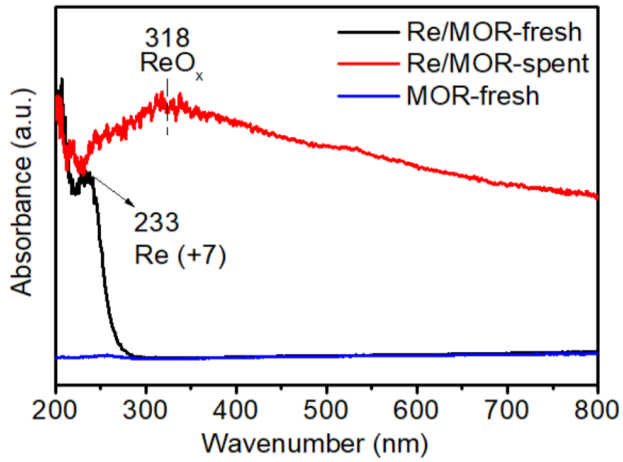

Fig. S3 UV-vis DRS of fresh and spent Re/MOR catalyst

UV-vis diffuse reflectance spectroscopy (DRS) of the supported ReO_x catalysts were obtained with a Jasco V-650 spectrophotometer. The UV-vis spectra were collected in the 200-800 nm. The absorbance of the MgO white standard was used for the background absorbance correction. The peak at 233 nm is ascribed to an LMCT band for Re^{7+} species (I. E. Wachs *et al.*, *J. Phys. Chem. C*, **2008**, 112, 20418.)

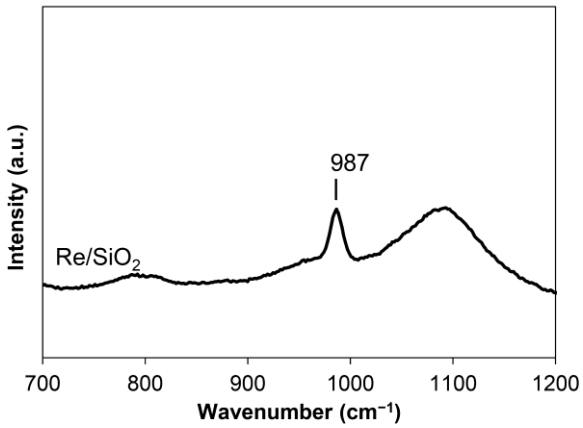

Fig. S4 Raman spectrum of pristine Re/SiO_2.

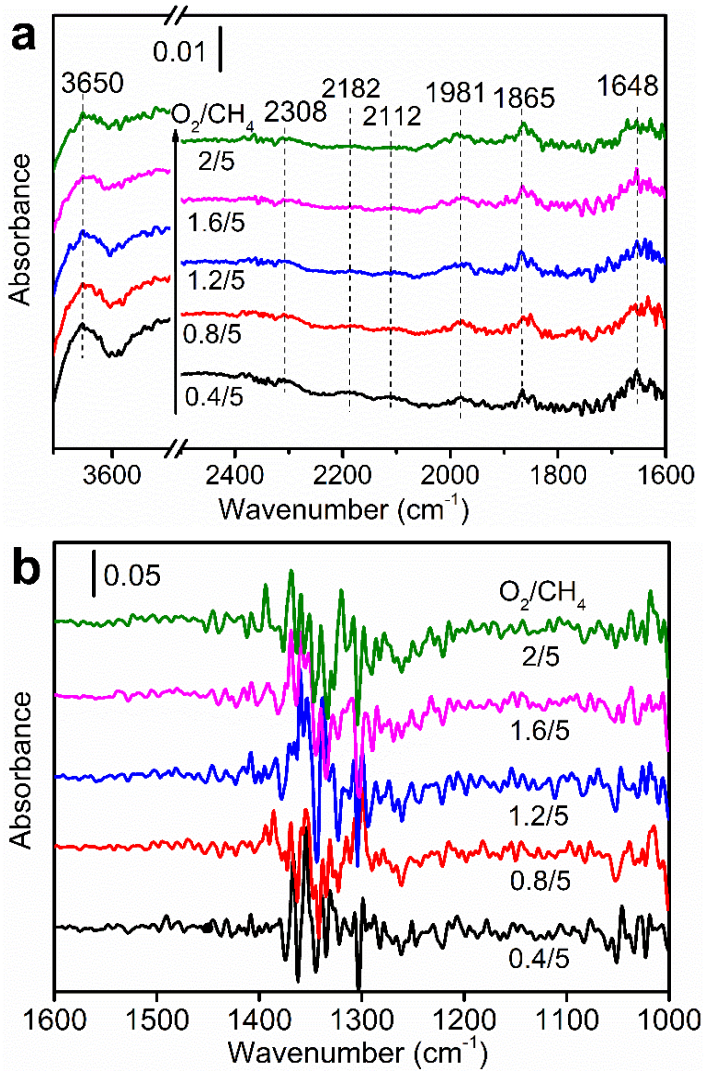

Fig. S5 In-situ DRIFT spectra of Re/MOR at different O_2/CH_4 ratios. Background: the catalyst with pure CH_4. (a) Wavenumber at 3700–1600 cm^{-1}, (b) wavenumber at 1600–1200 cm^{-1}.

Table S1 Atomic coordinate of the species (ii) in the format of Gaussian input.

-1 1

Si	-1	2.11545500	2.57324800	2.46357000
Si	-1	-3.55643400	-1.72920200	2.48507100
O	-1	-3.28154600	-3.29653600	2.69575100
O	-1	3.55159200	1.88715000	2.66984700
O	-1	-3.50315000	-0.97871600	3.91828400
O	-1	1.38507500	2.72958200	3.89970700
Si	-1	-2.70395000	-2.87410400	-1.72679000
Si	-1	2.96790700	1.42859000	-1.74858900
Al	0	-1.94851000	-0.57644700	0.09204400
O	-1	-4.47367300	1.65335900	-2.39203900
O	-1	-1.43579200	5.04467500	0.14981900
O	-1	-4.99069400	2.34784200	0.16315300
O	-1	-0.91851400	4.35030100	-2.40546400
O	0	-1.71463100	-1.90360800	-0.95285400
O	0	1.21377800	1.55057700	1.60320300
O	0	-2.36794400	-1.10137000	1.65141400
O	0	1.65126200	1.00738900	-0.92301700
O	-1	4.30566900	0.87448700	-1.05616800
O	-1	-2.52751300	-4.30919400	-1.03021700
O	0	-3.06260400	0.58408900	-0.48264300
O	0	-0.26948900	2.76525100	-0.27942600
O	-1	-2.06018400	-2.91647100	-3.21149900
O	-1	2.82805600	0.79178400	-3.23006000
O	-1	-4.95726800	-1.48785500	1.77526900
O	-1	2.97833000	3.01596200	-1.81703500
O	-1	-4.23576200	-2.45664200	-1.78968600
O	-1	2.25685100	3.98486200	1.74790400
O	-1	-2.83816400	3.19578100	-1.05595600
O	0	-0.35282500	0.06633800	0.26714500
H	-1	3.05069400	-0.12117000	-3.43145000
H	-1	3.71907000	3.52603400	-2.15412900
H	-1	4.49323900	0.97108300	-0.11554500
H	-1	1.50970300	4.57412200	1.59159100
H	-1	4.19525500	2.23525100	3.29312200
H	-1	-2.81464800	-3.80238100	2.02110400
H	-1	-4.77089400	-2.22096900	-1.02315200
H	-1	-4.15673500	0.89704900	-2.89576700
H	-1	-0.00585200	4.57881600	-2.60901400
H	-1	-3.09445900	-5.05962100	-1.22312600
H	-1	-5.54885000	1.66574200	0.54945900
H	-1	-2.16135200	5.67530600	0.12449600
H	-1	-2.47899200	-3.34202500	-3.96348300
H	-1	-5.78608400	-1.74823700	2.18621800
H	-1	-3.09333200	-1.40379000	4.67584900
H	-1	0.81724800	2.04055000	4.25689700
Si	0	0.51133800	1.39897000	0.14829500
Si	0	-1.35529000	3.80402200	-0.91780900
Si	0	-3.83020000	1.90095900	-0.91190100
Re	0	2.85745500	-2.14654800	0.00104600
O	0	3.28912900	-3.76929200	0.28810800
O	0	3.88691400	-1.14238400	0.91858800
O	0	3.06835700	-1.79871300	-1.65709600
O	0	1.14484000	-1.92649100	0.52764000
H	0	0.50311100	-1.11283700	0.41467500

Position of some of the Si and O atoms were fixed to keep the MOR structure, and that of terminal H atoms were fixed after the structural optimisation without Re species to avoid their rotation giving artificial energy changes.

Table S2 Effect of contact time on the conversion of methane and product distribution over Re/MOR catalyst to POM reaction (H_2 pre-reduction for 1 h, T = 600 °C, CH_4: O_2: N_2 = 50:4:46).

Contact time (10^{-5} g h mL^{-1})	SV (mL g^{-1} h^{-1})	Conv. (%)		Product yield (%)			Selectivity (%)
		CH_4	O_2	CO	CO_2	H_2	CO
0.17	600,000	0.47	<5	0.37	0.10	0.06	80
0.33	300,000	0.71	18	0.55	0.17	0.13	77
0.5	200,000	1.8	37	1.6	0.24	0.15	86
0.83	120,000	11	100	9.5	1.9	11	84
1.7	60,000	13	100	12	1.5	12	89
3.3	30,000	13	100	12	1.5	12	89
8.3	12,000	15	100	14	0.5	14	96