Methane Partial Oxidation using FeO_x@La_{0.8}Sr_{0.2}FeO_{3-δ}

Core-Shell Catalyst - Transient Pulse Studies

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Methane oxidation pattern during long term pulse injections and comparison



of selectivities in pulse and continuous injection modes

Figure S1. Methane oxidation pattern over FeO_x@LSF catalyst during 300 methane pulse (50

Vol. % methane) injections at 900 °C.

Table S1. Comparison of product selectivity over FeO_x@LSF catalyst at 900 °C in pulse and

Region	Pulse injections			5% methane continuous			10% methane continuous		
	H ₂	СО	CO_2	H ₂	СО	CO_2	H ₂	СО	CO_2
1	0.24	0.12	0.40	0.18	0.15	0.55	0.37	0.36	1.27
	(22%)	(23%)	(77%)	(12.9%)	(21%)	(79%)	(22.7%)	(22%)	(78%)
2	4.65	1.72	0.53	2.66	1.95	0.78	4.59	3.56	1.71
	(103%)	(76%)	(24%)	(48.7%)	(72%)	(28%)	(43.5)	(68%)	(32%)
3	3.05	1.32	0.00	3.13	1.85	0.04	4.53	2.50	0.20
	(116%)	(100%)	(0%)	(82.8%)	(98%)	(2%)	(83.8%)	(93%)	(7%)

continuous methane injection modes.

Temperature Programed Reduction (TPR) of the core-shell catalyst

A TPR experiment was done on the core-shell catalyst to figure out the temperatures at which catalyst starts activating methane and donating lattice oxygen. The experiment was performed in 10 Vol.% methane (balance Ar) with the ramping rate of 5 °C/min. The outlet gases were analyzed using an inline mass spectrometer. Figure S2 demonstrates the resulting product distribution as a function of temperature. The data below 600 °C does not show in the graph as no signal is observed below this temperature. As can be seen, the core-shell catalyst started activating and converting methane at around 780 °C and by about 880 °C all the accessible lattice oxygen is removed. Further increase of temperature to 950 °C causes methane decomposition and coke formation indicated by increase in hydrogen production.



Figure S2. Product distribution during a TPR experiment on the core-shell catalyst (10% CH₄, balance Ar, 5 °C/min)

Detailed information about injection of a sharp ¹⁸O₂ pulse during a broadened

pulse of methane in the first region

The total amount of ¹⁸O injected is about 5.83% of the total lattice oxygen capacity of the sample and ~10 times higher than the available surface oxygen. Only ~13.2% of the CO₂ produced after $^{18}O_2$ injection contained ^{18}O atoms (C $^{18}O_2$ and C $^{16}O^{18}O$), which corresponds to about 7% of the total oxygen atoms converted to CO₂. Similar experiments were performed at 3 times larger space velocity, and the contribution of ¹⁸O to CO₂ formation is observed to be around 11% (Figure 9b). This suggests that, in the oxidized state, the rate of oxygen dissipation through the lattice is lower than the methane oxidation rate; however, concluding a much slower diffusion rate would also require either a higher than 7-11% contribution of ¹⁸O or a subsequent oxygen exchange between C¹⁸O₂ and ¹⁶O-rich catalyst. The latter must be true, as our experimental results show no significant sign of $C^{18}O_2$ and relatively small amounts of $C^{16}O^{18}O$. The likelihood of such high oxygen exchange rate is tested by injection of C¹⁶O₂ pulses over an ¹⁸Orich catalyst (Figure S2). It is confirmed that within the first 5 pulses of C¹⁶O₂ (5% C¹⁶O₂, balance argon) more than 90% of the oxygen atoms are exchanged. The higher concentration of ¹⁸O in products at higher space velocity also endorses this explanation. These observations further confirm that oxygen availability on the surface, and, consequently, the rate of oxygen diffusion to the surface, controls the selectivity of the catalyst.





Figure S3. Response to injection of C¹⁶O₂ pulses (5%, balance Ar) to ¹⁸O-rich catalyst at 900°C

Five pulses of $C^{16}O_2$ (5%, balance Ar, 1mL) were injected on an ¹⁸O-rich catalyst at 900 °C. Results showed more than 90% oxygen ionic exchange between the ¹⁶O atoms of the reactant with lattice ¹⁸O atoms.



TPD-DRIFTS experiment on the fully reduced redox catalyst

Figure S4. DRIFTS spectra for methanol TPD on completely reduced FeO_x@LSF redox catalyst

The figure above shows DRIFTS spectra of a methanol TPD experiment on fully reduced $FeO_x@LSF$. The catalyst is reduced in a u-tube quartz reactor in 10% hydrogen (balance Ar) at 900 °C for 18 hours and then transferred to the DRIFTS cell in which it is exposed to a similar reducing environment overnight. The cell is then purged with argon and cooled to room temperature. CO is injected to the cell for two hours and the cell is purged again prior to collecting spectra. Cell temperature is increased from room temperature to 500 °C with 100 °C steps and spectra are collected at each temperature after a five minute relaxation period. While reduced catalyst confirmed formation of some surface species at lower than 200 °C, running similar experiments on the oxidized sample did not show any signs of chemisorption.

Injection of a sharp ¹⁸O₂ pulse during a broadened pulse of methane in the



second region

Figure S5. Response to a broadened pulse of methane combined with a sharp pulse of ¹⁸O₂ at 900°C in the second region at (a) 50 and (b) 150 mL/min total flow rate.

Injection of a sharp pulse of oxygen isotope while reducing the sample in methane increased the methane conversion by giving rise to the production of both CO and CO₂ (Figure S4). It should be noted that CO₂ production increased noticeably more compared to CO production. At 50 and 150 mL/min total inlet gas flow rates, instantaneous CO₂ production rate increased by 103% and 244% respectively, whereas CO production merely increased by 35% and 33%. This is concrete evidence that availability of the surface oxygen controls the conversion and selectivity of products. It also implies that methane conversion could follow a combustion reforming mechanism during this region. Similar to the first and the third regions, very small amounts of isotopic products are observed at lower space velocities and reducing the residence time increased their concentrations. Relaxation of the sample in this region had a similar effect on the selectivity of the products as discussed for analogous studies in region I and

III (Figure S5). In all cases, resting the sample leads to decrease in CO selectivity, confirming that oxygen diffusion is a rate controlling step.



Figure S6. Effect of relaxation time on CO selectivity in the second region (pulse 1-5 have a relation time of 15 seconds whereas pulses 5-6 have a longer relaxation time of 150 seconds).

Analysis of methane conversion after longer relaxation time in the three regions also showed that in the first region methane conversion increased after longer relaxation time whereas in the third region it decreased. This could be an indication of different methane activation mechanism. As surface oxygen is responsible for hydrogen abstraction and methane activation in the first region, increased amount of surface oxygen after the relaxation time enhances the methane conversion. However, in the third region, methane activation occurs on metallic sites and a more oxygen deprived surface increases the amount of activated methane on the surface.