

**Electronic Supplementary Information (ESI)**

**Three Dimensionally Ordered Macroporous Pd-LaMnO<sub>3</sub> Self-  
Regeneration Catalyst for Methane Combustion**

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### Synthesis of 3DOM LaMnO<sub>3</sub> and LaMnPdO<sub>3</sub> samples

3DOM LaMnO<sub>3</sub> were prepared using the surfactant-assisted PMMA colloidal crystal template method [1]. The regularly arrayed PMMA microspheres with an average diameter of ca. 300 nm were synthesized according to the procedures described elsewhere. Then the PMMA latex was centrifuged at 1000 r/min for 12 h to form colloidal crystal templates (CCT).

In a typical procedure, the stoichiometric amounts of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Mn(NO<sub>3</sub>)<sub>2</sub> (50 wt% aqueous solution) and Pd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O were dissolved in 0.33 mL of PEG with a molecular weight of 400 g/mol and 1 mL of methanol (MeOH) at room temperature (RT) under stirring for 4 h to obtain a transparent solution. 1.33 of L-lysine was dissolved in a HNO<sub>3</sub> aqueous solution, and the pH value of this solution was adjusted to ca. 6 for avoiding the formation of metal hydroxide precipitates in the following steps. Then, the L-lysine-containing solution was mixed with the metal nitrate-containing transparent solution under stirring for 1 h to obtain a uniform precursor solution, to which a certain amount of MeOH was added to achieve a total metal concentration of 2 mol/L. 2.0 g PMMA hard template was soaked in the above precursor solution for 4 h. After being filtered, the obtained wet PMMA template was dried in air at RT for 48 h, and then transferred to a ceramic boat which was placed in a tubular furnace. The thermal treatment process was divided into two steps: (i) firstly the solid was calcined in a N<sub>2</sub> flow of 50 mL/min at a ramp of 1 °C/min from RT to 300 °C and kept at this temperature for 3 h, and then cooled to 50 °C in the same atmosphere; and (ii) after being purged in an air flow of 50 mL/min, the solid was heated in the same atmosphere at a ramp of 1 °C /min from RT to 300 °C and held at 300 °C for 2 h, and then was calcined continuously at the same ramp from 300 to 750 °C and maintained at 750 °C for 4 h. After cooling down to the room temperature, the 3DOM LM was obtained. The 3DOM-structured sample obtained with hydrogen gas processing at 300-800 °C was denoted as 300-LMP, 400-LMP, 500-LMP, 600-LMP, 700-LMP, 800-LMP.

Pd (1.2 wt % and 0.48 wt %) supported on 3DOM LaMnO<sub>3</sub> were prepared by incipient impregnation with Pd(NO<sub>3</sub>)<sub>2</sub> solution [2]. The obtained precursors were calcinated at 500 °C for 2 h.

All of the chemicals (A.R. in purity) were purchased from Beijing Chemical Company and used without further purification.

### References

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### Catalyst characterizations

The catalysts were characterized using the techniques of X-ray diffraction (XRD), N<sub>2</sub> adsorption-desorption (BET), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM, selected-area electron diffraction (SAED), and X-ray photoelectron spectroscopy (XPS).

X-ray diffraction (XRD) patterns of the as-fabricated LaMnO<sub>3</sub> samples were recorded on a Bruker/AXS D8 Advance X-ray diffractometer operated at 40 kV and 35 mA with a Cu K $\alpha$  X-ray irradiation source ( $\lambda = 0.15406$  nm). Surface areas of the catalysts were determined via N<sub>2</sub> adsorption at -196 °C on a Micromeritics ASAP 2020 adsorption analyzer. Before measurement, each of the catalysts was degassed at 250 °C for 2 h. The surface areas and pore-size distributions were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method, respectively. The investigation by means of scanning electron microscope (SEM) was conducted on a S-4700 apparatus operated at 10 kV. Transmission electron microscopic (TEM) and high-resolution TEM images and the selected-area electron diffraction (SAED) patterns of the typical samples were obtained using a JEOL JEM-2010 instrument. The macropore diameters were roughly estimated according to the SEM and TEM images. The X-ray photoelectron spectroscopy (XPS) was used to determine the Pd 3d, and O 1s binding energies (BEs) of surface lanthanum, manganese, and oxygen species, respectively, with Al K $\alpha$  ( $h\nu = 1486.6$  eV) as the excitation source. The C 1s signal at BE = 284.6 eV was taken as a reference for BE calibration.

Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics). Before TPR measurement, ca. 0.02 g of catalyst was loaded to a fixed-bed U-shaped quartz microreactor (i.d.= 4 mm) and pretreated in an O<sub>2</sub> flow of 30 mL/min at 500 °C for 1 h. After being cooled at the same atmosphere to RT, the pretreated sample was exposed to a flow (50 mL/min) of 5% H<sub>2</sub>-95% Ar (v/v) mixture and heated from RT to 900 °C at a ramp of 10 °C/min. The alteration in H<sub>2</sub> concentration of the effluent was monitored on-line by the chemical adsorption analyzer.

### **Catalytic activity tests**

A continuous flow fixed-bed quartz microreactor (i.d.= 6 mm) was used to measure the catalytic activities of the samples at atmospheric pressure for the complete oxidation of methane. To minimize the effect of hot spots, 0.05 g of the catalyst sample was diluted with 0.2 g of quartz sands (40-60 mesh). The total flow rate of the reactant mixture (1% CH<sub>4</sub> + 17% O<sub>2</sub> +He (balance)) was 30 mL/min, giving a SV of 32,000 mL/(g h). Reactants and products were analyzed on-line by a gas chromatograph (GC-9790, FULI) equipped with a flame ionization detector (FID), using a 1/8 in TDX-01 column (3 m in length) for CH<sub>4</sub> separation for permanent gas separation. The balance of carbon throughout the investigation was estimated to be 99.5%.

**Table S1** Lattice parameters of the samples  
(R refers to Rhombohedral; O refers to Orthorhombic)

	LaMnO <sub>3.15</sub> <sup>1</sup>	LM	LMP	LaMnO <sub>3</sub> <sup>2</sup>	300-LMP	400-LMP	500-LMP	600-LMP
Crystalline	R	R	R	O	O	O	O	O
a(Å)	5.515	5.509	5.511	5.679	5.693	5.672	5.640	5.645
b(Å)	5.515	5.509	5.511	7.703	7.696	7.641	7.742	7.744
c(Å)	13.336	13.342	13.337	5.541	5.497	5.528	5.546	5.542
V(Å <sup>3</sup> )	351.26	351.11	350.86	242.41	240.89	240.64	241.97	242.72

Commercial Jade 6.0 software package (Materials Data, Inc.) was used to calculate the lattice parameters of the as-prepared samples.

For example, the XRD data of LMP was read by the software firstly, and the diffraction peaks could be assigned to rhombohedral LaMnO<sub>3.15</sub> (JCPDS PDF# 89-8775). Then, deducted background and  $K_{\alpha 2}$ , smoothed the curve, and fitted from 20° to 70°.

Using the cell refinement function, the cell parameters  $a = 5.511 \text{ \AA}$  and  $c = 13.337 \text{ \AA}$  could be obtained.

<sup>1</sup> Data from JCPDS PDF# 87-8775.

<sup>2</sup> Data from JCPDS PDF# 89-8074.

**Table S2**  $T_{10\%}$ ,  $T_{50\%}$ ,  $T_{90\%}$ , activation energy data and reaction rate ( $\times 10^{-2} \text{ mmol}_{\text{CH}_4} \text{ s}^{-1} \text{ g}_{\text{pd}}^{-1}$ ) of the samples

	800-LMP	700-LMP	600-LMP	500-LMP	400-LMP	300-LMP	LMP	LM
$T_{10\%}$	425	455	402	325	365	387	450	445
$T_{50\%}$	560	550	505	412	455	514	545	560
$T_{90\%}$	631	616	575	504	553	642	653	655
Ea (kJ/mol)	81.7	104.7	83.9	51.5	72.3	92.6	86.5	93.1
Reaction rate <sup>3</sup> ( $\times 10^{-2} \text{ mmol}_{\text{CH}_4} \text{ s}^{-1} \text{ g}_{\text{pd}}^{-1}$ )	1.4	0.45	1.58	10.9	4.67	3.38	0.84	-

<sup>3</sup> At 350 °C.

**Table S3** Reaction rate in  $\text{mmol}_{\text{CH}_4} \text{s}^{-1} \text{g}_{\text{pd}}^{-1}$  and in  $\text{mmol}_{\text{CH}_4} \text{s}^{-1} \text{m}_{\text{cat}}^{-2}$  of the catalysts reported in the literature and this work

Catalysts	Pd content (wt %)	Reaction temperature (°C)	Reaction rate ( $\times 10^{-2} \text{mmol}_{\text{CH}_4} \text{s}^{-1} \text{g}_{\text{pd}}^{-1}$ )	Reaction rate ( $\times 10^{-5} \text{mmol}_{\text{CH}_4} \text{s}^{-1} \text{m}_{\text{cat}}^{-2}$ )	Literature
LaMnO <sub>3</sub>	-	373	-	0.526	1
LaMnO <sub>3</sub>	-	350	-	0.402	2
La(Mn,Pd)O <sub>3</sub>	2	350	0.775	0.517	3
La(Mn,Pd)O <sub>3</sub>	1.9	350	2.40	3.8	4
La(Mn,Pd)O <sub>3</sub>	2.9	350	0.41	0.992	5
La(Mn,Pd)O <sub>3</sub>	2	350	6.15	9.18	6
La(Fe,Pd)O <sub>3</sub>	2.1	350	0.488	1.22	7
Ce <sub>x</sub> Zr <sub>1-x</sub> O <sub>2</sub>	-	350	-	0.676	8
CoCr <sub>2</sub> O <sub>4</sub>	-	350	-	0.417	9
500-LMP	0.5	350	10.9	2.52	this work

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### Calculation of activation energies

According to the Weisz-Prater criterion, when effectiveness factor  $\eta \geq 0.95$  and reaction order  $n=1$ , the dimensionless Weisz-Prater parameter ( $\phi_{W-P}$ ) value is less than 0.3, which can be considered a sufficient condition for the absence of significant pore diffusion limitations [1]. At methane conversion  $\leq 20\%$ , we carried out the Weisz-Prater analysis and calculated the  $\phi_{W-P}$  values, which were in the range of 0.00254-0.0432. Obviously, the  $\phi_{W-P}$  values obtained in our present work were much less than 0.3. Therefore, the internal diffusion effect could be neglected for the kinetic study of methane combustion. The detailed calculation process is as followed.

Weisz-Prater Criterion ( $\phi_{W-P}$ ):

The absence of internal mass diffusion transport resistance was checked by the Weisz-Prater Criterion ( $\phi_{W-P}$ ).

$$\phi_{W-P} = \frac{r_a \cdot R_p^2}{C_s \cdot D_{eff}}$$

Where  $r_a$  = reaction rate per volume of catalyst, mol/(m<sup>3</sup> s)

$R_p$  = catalyst particle radius, m

$D_{eff}$  = effective diffusivity, m<sup>2</sup>/s

$C_s$  = reactant concentration at the external surface of the catalyst, mol/m<sup>3</sup>

For methane combustion, a total gas flow rate of 30 mL/min and an average catalyst particle size of 270  $\mu\text{m}$  were employed for the kinetic study. The concentration of methane employed in the feed was 1 %. For the 500-LMP catalyst, the reaction rate was  $5.45 \times 10^{-1}$  mol/(m<sup>3</sup> s) at 623 K.

$$r_a = 5.45 \times 10^{-1} \text{ mol}/(\text{m}^3 \text{ s})$$

$$R_p = 1.35 \times 10^{-4} \text{ m}$$

$$C_s = 4.46 \times 10^{-1} \text{ mol}/\text{m}^3$$

$$D_{eff} = 3.82 \times 10^{-8} \text{ m}^2/\text{s}$$

$$\phi_{W-P} = \frac{r_a \cdot R_p^2}{C_s \cdot D_{eff}}$$

$$= [(5.45 \times 10^{-1}) \times (1.35 \times 10^{-4})^2] / [(4.46 \times 10^{-1}) \times (3.82 \times 10^{-8})]$$

$$= 4.32 \times 10^{-2} \ll 0.3$$

In addition, in order to investigate the effect of heat or mass transport on the reaction rate, Pd loaded 3DOM LaMnO<sub>3</sub> were also prepared by incipient impregnation method, and used for Koros-Nowak test [2]. The result shows that the discrepancies in TOF<sub>Pd</sub> value of 500-LMP and Pd/3DOM LaMnO<sub>3</sub> catalysts for methane combustion are small (Table S4). Therefore, no significant heat and mass transfer limitations exist in our study.

**Table S4.** Koros–Nowak test for heat and mass transfer limitations under the reaction conditions of methane concentration = 1 %, methane/O<sub>2</sub> molar ratio = 1/17, SV = 32,000 mL/(g·h), and temperature = 350 °C.

Catalysts	TOF <sub>Pd</sub> ( $\times 10^{-2}$ mol <sub>CH4</sub> /(mol <sub>Pd</sub> s <sup>-1</sup> ))
500-LMP (0.5 wt% Pd)	1.15
1.2 wt% Pd/3DOM LaMnO <sub>3</sub>	1.02
0.48 wt% Pd/3DOM LaMnO <sub>3</sub>	0.81

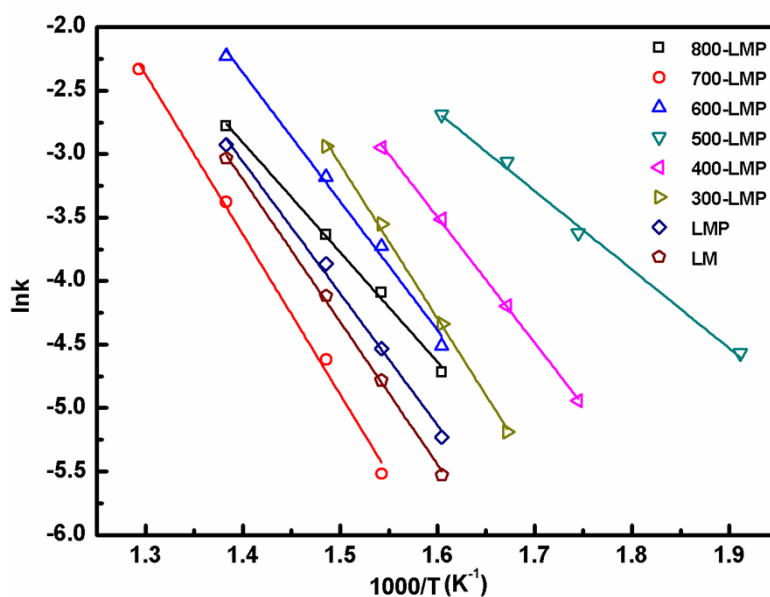


Fig. S1 Arrhenius plots for the oxidation of methane over the as-prepared catalysts

It is supposed that the oxidation of CH<sub>4</sub> in the presence of excess oxygen (CH<sub>4</sub>/O<sub>2</sub> molar ratio= 1/17) would fit first-order reaction mechanism,

$$r = -kc = (-A \exp(-Ea/RT))c;$$

where  $r$ ,  $k$ ,  $c$ ,  $A$ , and  $Ea$  are the reaction rate (mol/s), rate constant (s<sup>-1</sup>), concentration of methane, pre-exponential factor and apparent activation energy (kJ/mol), respectively.

The activation energy of 500-LMP (51.5 kJ/mol) is lower than Pd/Al<sub>2</sub>O<sub>3</sub> (65 kJ/mol) [3], Au/Al<sub>2</sub>O<sub>3</sub> catalyst (73 kJ/mol) [4] and LaMnO<sub>3</sub> (82.7 kJ/mol) [5].

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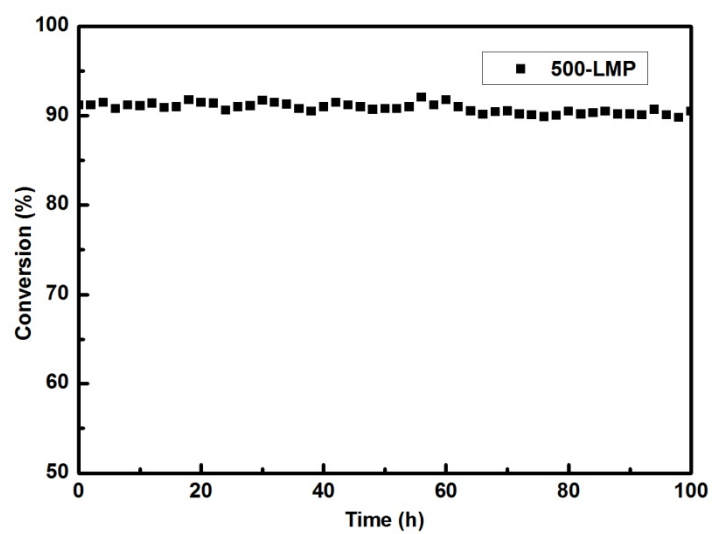


Fig. S2. Methane conversion of 500-LMP after 100 h on-stream reaction under the conditions of 1% CH<sub>4</sub> + 17% O<sub>2</sub> + 82% He (balance) and GHSV = 32,000 mL/(g·h).

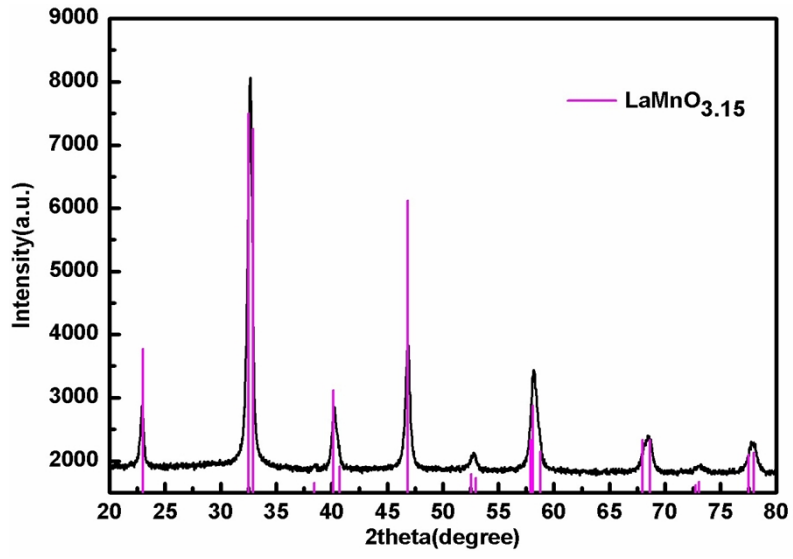


Fig. S3 XRD pattern of A500-LMP.

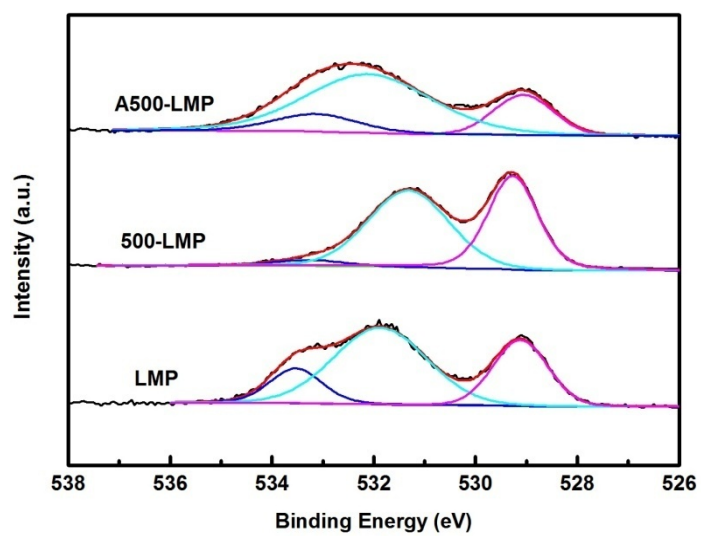


Fig. S4 O1s XPS spectra of LMP, 500-LMP and A500-LMP.