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# **Electronic Supplementary Information**

# High-performance PdNi alloy in-situ structured on monolithic metal-foam for coalbed methane deoxygenation via catalytic combustion

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#### 1. Materials and Methods

#### 1.1. Catalyst preparation

The fresh Ni-foam@Pd-PdO-NiO catalyst (0.9 wt% Pd) was prepared by galvanic exchange reaction between Ni-foam and aqueous solution of palladium salts (such as Pd(NO<sub>3</sub>)<sub>2</sub>), followed by washing with deionized water, drying and calcining at 450 °C in air for 2 h. The galvanic reaction could proceed spontaneously at room temperature once Ni foam support impregnated with palladium salt solution due to the large electrode potential difference between Pd<sup>2+</sup>/Pd (0.95 V) and Ni<sup>2+</sup>/Ni (-0.26 V) pairs, and this preparation method is named as galvanic deposition (GD). Prior to the GD operation, Ni-foam support was cleaned by immersing it in a dilute aqueous solution of nitric acid (1 wt% HNO<sub>3</sub>) at room temperature for removing the NiO film originally existing on the fresh monolithic Ni-foam support.

#### 1.2. Catalyst characterization

The exact composition of the catalysts was determined by using a Thermo Scientific iCAP 6300 inductively coupled plasma atomic emission spectrometry (ICP-AES) on a USA Thermo IRIS Intrepid II XSP ICP spectrometer. The scanning electron microscopy (SEM) and back-scattering electron (BE) images were obtained on Hitachi S-4800 microscopy equipped with an energy dispersive X-Ray fluoresence spectrometer (EDX, Oxford; UK). The catalysts were also characterized by transmission electron microscopy (TEM, FEI-Tecnai G2F30). Specific surface area was determined using standard Brunauer-Emmett-Teller (BET) theory based on N2 adsorption isotherm at -196 °C obtained on a Quantachrome Autosorb-3B instrument. X-ray diffraction (XRD) patterns were obtained with a Rigaku Ultra IV diffractometer using Cu Ka radiation at 35 kV and 25 mA in the 20 scanning range of 5-90 ° and scanning rate of 60 ° min<sup>-1</sup>. The X-ray photoelectron spectroscopy (XPS) was recorded on an Escalab 250xi spectrometer, using a standard Al Ka X-ray source (300 W) and analyzer pass energy of 20 eV. All binding energies were referenced to the adventitious C1s line at 284.8 eV. H<sub>2</sub>-temperature-programmed reduction (H<sub>2</sub>-TPR) and CO pulse experiments were performed on a Quantachrome ChemBET-3000 chemisorption apparatus with a thermal conductivity detector (TCD) and an online mass spectrometer (Proline Dycor, AMETEK Process Instrument, USA).

# 1.3. Reactivity tests

The catalytic deoxygenation of coalbed methane (CBM) on these catalysts was performed on a

fixed-bed quartz tube reactor (600 mm length by 8 mm inner diameter) under atmospheric pressure. A gaseous mixture of CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> (40/3/57, vol%) was employed as feedstock and gas hourly space velocity (GHSV) was set to 12000 mL g<sup>-1</sup> h<sup>-1</sup>, if not specified. Circular chips (8.1 mm diameter) of the monolithic Ni-foam@Pd-PdO-NiO catalysts (0.25 g) were punched down from their large sheet sample and packed layer-up-layer into the tube reactor. Three calibrated mass flow controllers were used to control the methane, oxygen and nitrogen gas. The product effluent was analyzed online by an HP 6850 gas chromatography chromatograph equipped with TCD connected to Porapak Q and MS 5A parallel capillary columns (DIKMA). The gas pipeline and sampling 6-way valve between the reactor outlet and the GC injector were heated to ensure the effluent completely evaporated. The catalyst activity was defined by  $T_{10}$ ,  $T_{50}$  and  $T_{90}$ , representing the reaction temperatures for the oxygen conversion of 10%, 50% and 90%, respectively.

CBM deoxygenation may include four reactions as following:

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	main reaction (Eq. 1)
$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$	inefficient combustion (Eq. 2)
$CH_4 + H_2O \rightarrow CO + 3H_2$	steam reforming (Eq. 3)
$CO + H_2O \leftrightarrow CO_2 + H_2$	water gas shift reaction (Eq. 4)

Note that the steam reforming reaction becomes obvious only at reaction temperature above 550  $^{\circ}$ C.<sup>S1</sup> No CO is detectable over the entire temperature region for CBM deoxygenation, indicating no occurrence of the incomplete combustion, steam reforming and water gas shift reactions. Therefore, we assume that only the main reaction of CH<sub>4</sub> complete combustion is involved in CBM deoxygenation.

The O<sub>2</sub> conversion was calculated based on the O balance using standard normalization method. According to **Eq. 1**, every CO<sub>2</sub> generated will consume two O<sub>2</sub>.

$$O_2 \text{ conversion} = \frac{2A_{CO_2} \cdot f_{CO_2}}{2A_{CO_2} \cdot f_{CO_2} + A_{O_2} \cdot f_{O_2}} \cdot 100\%$$

Where *A* is TCD chromatographic peak area of  $O_2$  or  $CO_2$ , and *f* is the molar correction factor of  $O_2$  or  $CO_2$ .

For the calculation of  $CO_2$  selectivity, we used carbon balance rather than O balance, because the consumption of  $CH_4$  and  $O_2$  to generate  $CO_2$  and  $H_2O$  is simultaneous and stoichiometric. No CO is detectable in CBM deoxygenation and thus the  $CO_2$  selectivity is 100%.

#### 1.4. TOF calculation

In order to assess the intrinsic activity, so called turnover frequencies (TOFs) which is defined as the ratio of product molecules per active site of catalyst and time are calculated. The number of product molecules per time (mol s<sup>-1</sup>) is expressed by the flow of O<sub>2</sub> (F, L s<sup>-1</sup>) times  $\alpha$  (the yield of CO<sub>2</sub>), divided by the molar volume of gas (V<sub>m</sub>, L mol<sup>-1</sup>), assuming ideal behavior at 25 °C. The number (N, mol g<sup>-1</sup>) of active sites (*i.e.* surface Pd) is determined by CO pulse experiment. Accordingly, the TOF can be expressed by:

$$\text{TOF} = \frac{\text{Product Molecules}}{\text{Active Sites} \cdot \text{Time}} = \frac{F \cdot \alpha}{V_{\text{m}} \cdot \text{N}}$$

The O<sub>2</sub> conversion remains below 20% by tuning the GHSV during the TOF calculation. TOF of Ni-foam@Pd-PdO-NiO is calculated in the following. The flow of reactant O<sub>2</sub> gas F is set to 1.5 ml min<sup>-1</sup>. The surface Pd of Ni-foam@Pd-PdO-NiO catalysts is  $4.0 \times 10^{-6}$  mol g<sup>-1</sup>. At 280 °C, about 3.1% of O<sub>2</sub> is converted and the selectivity of CO<sub>2</sub> is 100%, thus the yield of CO<sub>2</sub> (*i.e.*,  $\alpha$ ) accounts to 1.6%. It is supposed that every surface Pd atom is an active site, the TOF of Ni-foam@Pd-PdO-NiO then can be calculated as:

$$TOF = \frac{\frac{1.5}{1000 \cdot 60} (L s^{-1}) \cdot 0.016}{24.8 (L mol^{-1}) \cdot 4.0 \cdot 10^{-6} (mol g^{-1}) \cdot 0.25 (g)} = 0.016 s^{-1} = 57 h^{-1}$$

TOF of Ni-foam@PdNi(alloy) is calculated in the following. The flow of reactant O<sub>2</sub> gas F is set to 9 ml min<sup>-1</sup>. The surface Pd of Ni-foam@PdNi(alloy) catalysts is  $2.2 \times 10^{-5}$  mol g<sup>-1</sup>. At 280 °C, about 14.8% of O<sub>2</sub> is converted and the selectivity of CO<sub>2</sub> is 100%, thus the yield of CO<sub>2</sub> (*i.e.*,  $\alpha$ ) accounts to 7.4%. It is supposed that every surface Pd atom is an active site, the TOF of Ni-foam@PdNi(alloy) then can be calculated as:

$$TOF = \frac{\frac{9}{1000 \cdot 60} (L s^{-1}) \cdot 0.074}{24.8 (L mol^{-1}) \cdot 2.2 \cdot 10^{-5} (mol g^{-1}) \cdot 0.25 (g)} = 0.081 s^{-1} = 292 h^{-1}$$

## 2. Computational Details for DFT Calculations

Spin-polarized DFT calculations were performed using the PBE functional by using the Vienna ab initio Simulation Package (VASP).<sup>S2</sup> The project-augmented wave (PAW)<sup>S3</sup> method was used to describe the electron-core interaction. Energy cutoff of 400 eV and Monkhorst-Pack grid of  $5 \times 5 \times 1$ 

were used for all calculations. The structure optimizations were converged until the Hellman-Feynman forces on each ion were less than 0.02 eV/Å. The calculated lattice parameter of bulk Pd was 3.95 Å, which is in good agreement with the values reported previously<sup>S4</sup>.

The Pd(111) surface was modeled by a 4-layer slab repeated in a 4×4 surface unit cell with the bottom one layer being fixed to the bulk parameters, while other layers were allowed to fully relax. To avoid interactions between slabs, all slabs were separated by a vacuum gap greater than 10 Å. To study the chemical effect of Ni at Ni-foam@PdNi(alloy) catalyst, various one monolayer (ML) Ni decorated Pd(111) were constructed (see Fig. S4).

The adsorption energies (E<sub>ads</sub>) of adsorbates at the substrates are calculated as follows:

 $E_{ads} = E_{ad} + E_{sub} - E_{ad/sub}$ 

Where  $E_{ad}$ ,  $E_{sub}$  and  $E_{ad/sub}$  are the DFT total energies of the gas-phase adsorbate (Note:  $E_{ad}$  is equal to  $0.5E_{O2}$  for calculating the adsorption energies of O;  $E_{O2}$  is the DFT total energy of O<sub>2</sub> molecule), the substrate and adsorption complex, respectively.

Transition states were searched with use of a constrained optimization scheme<sup>S5</sup>.

Catalyst	Pd loading <sup>a</sup>	$S_{ m BET}$	T <sub>10</sub>	T <sub>50</sub>	$T_{90}{}^b$	Surf. Pd <sup>c</sup>	$\mathrm{TOF}^d$
	(wt%)	$(m^2 g^{-1})$	(°C)	(°C)	(°C)	$(\text{mol } g^{-1})$	(h <sup>-1</sup> )
Fresh	0.9	7.9	305	330	340	4.0×10 <sup>-6</sup>	57
Activated	0.9	27.4	258	295	308	2.2×10 <sup>-5</sup>	292

**Table S1.** CBM deoxygenation catalyzed by the Ni-foam@Pd-PdO-NiO catalyst before and after in-situ activation.

<sup>*a*</sup> Measured by ICP-AES. <sup>*b*</sup> T<sub>10</sub>, T<sub>50</sub> and T<sub>90</sub> represent the reaction temperatures for the oxygen conversion of 10%, 50% and 90%, respectively (0.25 g Cat., CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> = 40/3/57 (vol%), GHSV = 12000 mL g<sub>cat.</sub><sup>-1</sup> h<sup>-1</sup>). <sup>*c*</sup> Determined by CO pulse absorption. <sup>*d*</sup> Turnover Frequency at 280 °C (TOF, mol<sub>CO2</sub> mol<sub>surf.Pd</sub><sup>-1</sup> h<sup>-1</sup>) based on CO<sub>2</sub> yield and surface Pd.

T (°C)	2θ of Pd peak (°)	$Pd_xNi_{1-x}^{d}$
350 <sup>a</sup>	40.08	Pd <sub>100</sub> Ni <sub>0</sub>
450 <sup>a</sup>	40.39	Pd <sub>94</sub> Ni <sub>6</sub>
480 <sup><i>a</i></sup>	40.43	Pd <sub>93</sub> Ni <sub>7</sub>
$400^{b}$	40.63	Pd <sub>88</sub> Ni <sub>12</sub>
300 <sup>b</sup>	40.36	Pd <sub>95</sub> Ni <sub>5</sub>
$220^{b}$	40.34	Pd <sub>95</sub> Ni <sub>5</sub>
400 <sup>c</sup>	40.62	Pd <sub>88</sub> Ni <sub>12</sub>

Table S2. The changes of composition of PdNi alloy against reaction temperatures.

<sup>*a*</sup> With reaction temperature increasing from 350 to 480 °C. <sup>*b*</sup> With reaction temperature decreasing from 480 to 220 °C. <sup>*c*</sup> With reaction temperature increasing again from 220 to 400 °C. <sup>*d*</sup> Determined by Vegard's law based on XRD patterns.

Catalyst	B.E. of Pd3d <sub>5/2</sub> (eV)		$Pd^0/Pd^{2+d}$	B.E. of Ni2p <sub>3/2</sub>
	$Pd^0$	$Pd^{2+}$	(atom)	(eV)
Fresh <sup>a</sup>	335.1	337.2	5.0	853.7
Activated <sup>b</sup>	335.9	337.3	6.4	853.7
Used <sup>c</sup>	335.8	337.2	5.7	853.7

Table S3. XPS results of monolithic Pd-based catalysts.

<sup>*a*</sup> Ni-foam@Pd-PdO-NiO catalyst used at 350 °C. <sup>*b*</sup> Ni-foam@PdNi(alloy) after in-situ activation at 480 °C for 1 h. <sup>*c*</sup> Ni-foam@PdNi(alloy) after 510 h stability testing. <sup>*d*</sup> Pd<sup>0</sup>: metallic Pd; Pd<sup>2+</sup>: Palladium oxide.

	Pd(	[111)	PdNi(111)		
Elementary step –	$E_a(eV)$	$\Delta E(eV)$	$E_a(eV)$	$\Delta E(eV)$	
$CH_4(g) \rightarrow CH_3^* + H^*$	0.85	0.18	1.14	0.64	
$O_2(g) \to O_2^*$	/	-0.81	/	-0.44	
$O_2^* -> 2O^*$	0.67	-1.71	0.67	-1.26	
O* + H* -> OH*	1.07	-0.03	0.85	-0.51	
$OH^* + H^* -> H_2O^*$	0.78	-0.37	0.68	-0.64	
$H_2O^* -> H_2O(g)$	/	0.25	/	0.22	
$O_2^* + H^* -> OOH^*$	0.88	0.16	0.69	-0.29	
OOH* -> O* + OH*	0.12	-1.90	0.19	-1.49	
OOH* + H* -> HOOH*	1.20	0.12	0.80	-0.18	
HOOH* -> 20H*	0.06	-2.04	0.14	-1.82	
CH* + O* -> HCO*	1.40	-0.52	1.00	-1.29	
HCO* -> CO* + H*	0.14	-1.52	0.26	-1.19	
$CO^* + O^* -> CO_2^*$	1.67	-0.05	1.23	-0.90	
$CO_2^* \to CO_2(g)$	/	0.01	/	0.02	

**Table S4.** DFT calculated activation barriers ( $E_a$ ) and reaction energies ( $\Delta E$ ) for elementary steps involved in reaction network of CBM deoxygenation at Pd(111) and PdNi(111).

 Table S5. Calculated Bader charges [e] (relative to neutral species) of surface Pd and adsorbed species.

Catalyst	Surf. Pd	0*	H*	OH*	$H_2O^*$	$O_2^*$	OOH*	HOOH*
Pd(111)	-0.03	-0.78	-0.13	-0.48	+0.05	-0.64	-0.46	-0.03
PdNi(111)	-0.16	-0.80	-0.15	-0.53	+0.04	-0.65	-0.48	-0.03



Fig. S1 XRD patterns of fresh Ni-foam@Pd-PdO-NiO catalyst.



**Fig. S2** (a) SEM-EDX line scanning image (Note: EDX data show that the at.% of  $O_{(M)}$  element is 40.6%, much higher than 28.09% of the Ni<sub>(L)</sub> element, and the extra O element should be detected from the formed PdO. These results reveal the presence of Pd, PdO, and NiO on the surface of fresh catalyst.). (b) BE image of the freshly-prepared catalyst, showing the self-assembled burr-like-composites of Pd-PdO-NiO.



Fig. S3 Bare Ni-foam without Pd for CBM deoxygenation. Reaction conditions: 0.25 g Cat.,  $CH_4/O_2/N_2 = 40/3/57 \text{ (vol\%)}, \text{GHSV} = 12000 \text{ mL } g_{\text{cat.}}^{-1} \text{ h}^{-1}.$ 



**Fig. S4** Heating and cooling light-off curves of O<sub>2</sub> conversion against temperature for the activated Ni-foam@PdNi(alloy). Note that O<sub>2</sub> conversion for heating and cooling curves at the same reaction temperature is very close, indicating the high heat conductivity of our monolithic catalyst. Reaction conditions: 0.25 g Cat., CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> = 40/3/57 (vol%), GHSV = 12000 mL g<sub>cat.</sub><sup>-1</sup> h<sup>-1</sup>.



**Fig. S5** TEM images of Ni-foam@Pd-PdO-NiO catalyst after in-situ activation at 480 °C for 1 h, showing that the lattice space (0.215 nm) of the PdNi alloy is between the 0.224 nm of face centered cubic Pd and the 0.203 nm of Ni(111) plane.



**Fig. S6** XPS spectra in Pd3d (a) and Ni2p (b) regions on the fresh surface of Ni-foam@Pd-PdO-NiO and activated surface of Ni-foam@PdNi(alloy). Note: a small amount of PdO species is detected on the surfaces of both catalysts while a large amount of NiO is on the surface of fresh one, consistent with TEM image (Fig. 1c). The fresh catalyst exhibits a Pd@PdO-NiO structure, thus we draw a Pd-core and oxides-shell to represent this structure. After in-situ activation at 480 °C for 1 h, Ni moves toward Pd nanoparticles to form PdNi alloy with a Pd-rich shell, driven by the preferential segregation of Pd because of its lower surface free energy at high reaction temperatures. Meanwhile there are a small amount of PdO and trace NiO species on the surface of Pd-rich shell as shown in the scheme.



**Fig. S7** Calculated structures of one monolayer (ML) Ni decorated Pd(111). Top- and sub-surface Ni patterns are represented by green and pink dash lines, respectively. Energies (E) relative to the Pd/Ni/Pd(111) model are also given. Thermodynamic analyses indicate that the (111) surface of the PdNi alloy prefers to form a sandwich-like structure with the Ni atoms being exclusively in the second topmost layer, which is consistent with some previous DFT studies on PdNi alloys.<sup>S6</sup>



Fig. S8 Calculated methane activation barriers for different cases at Pd(111) and PdNi(111) surfaces.



**Fig. S9** H diffusion process (fcc $\rightarrow$ bridge $\rightarrow$ hcp $\rightarrow$ bridge $\rightarrow$ fcc) at Pd(111) and PdNi(111). TSs are the transition states of corresponding diffusion steps. The energies are relative to  $0.5H_2(g)$  and a clean slab.



**Fig. S10** Potential energy for H adsorption at various surface sites of (a) Pd(111) and (b) PdNi(111). The energies are relative to  $0.5H_2(g)$  and a clean slab.



**Fig. S11** (a) O<sub>2</sub> conversion for CBM deoxygenation *vs.* time on stream for the activated Ni-foam@PdNi(alloy) catalyst. Reaction conditions: 0.25 g Cat.,  $CH_4/O_2/N_2 = 40/3/57$  (vol%),  $GHSV = 12000 \text{ mL g}_{cat.}^{-1} \text{ h}^{-1}$ . SEM images of Ni-foam@PdNi(alloy) before (b) and after (c) 510 h on stream.



**Fig. S12** XRD patterns for our fresh catalyst and activated catalysts before and after 510 h testing. Clearly, the XRD peak of PdNi alloy at  $2\theta$  of  $40.6^{\circ}$  for the activated catalyst almost remained unchanged with respect to diffraction angle and peak shape (*e.g.*, width and intensity) after 510 h on stream. This observation indicated the excellent stability of the formed PdNi alloy, being confirmed further by the unchanged Pd3d<sub>5/2</sub> XPS BE of 335.8 eV for such used catalyst compared to that (335.9 eV) of the activated one (Table S3).

### **Notes and References**

- S1 J. H. Lee and D. L. Trimm, *Fuel Process. Technol.*, 1995, **42**, 339-359.
- S2 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, 6, 15-50; G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, 49, 14251-14269.
- S3 P. E. Blöchl, Phys. Rev. B: Condens. Matter Mater. Phys., 1994, 50, 17953-17979.
- S4 A. A. B. Padama and H. Kasai, J. Chem. Phys., 2014, 140, 244707; S. Lin, A. K. Datye and H. Guo, Phys. Chem. Chem. Phys., 2013, 15, 7768-7776.
- S5 A. Alavi, P. J. Hu, T. Deutsch, P. L. Silvestrelli and J. Hutter, *Phys. Rev. Lett.*, 1998, 80, 3650-3653.
- S6 R. J. Hou, W. T. Yu, M. D. Porosoff, J. G. G. Chen and T. F. Wang, *J. Catal.*, 2014, 316, 1-10; F. C. H. Lim, J. Zhang, H. M. Jin, M. B. Sullivan and P. Wu, *Appl. Catal.*, *A*, 2013, 451, 79-85.