Sandwich-like PdO/CeO_2 nanosheet@HZSM-5 membrane hybrid composite for methane combustion: self-redispersion, sintering-resistance and oxygen, water-tolerance

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Abstract: *PdO/CeO_2 nanosheets encapsulated by a monolayer of continuous and dense HZSM-5 zeolite membrane were prepared through a facile in situ hydrothermal growth process as a high-efficient and thermal stable catalyst for methane combustion. Uncoated PdO/CeO_2 suffered severe sintering at high temperature or high-oxygen concentration, in despite of a high catalytic activity due to the high dispersion of PdO_x on the monodispersed CeO_2 nanosheets, however, the encapsulation of HZSM-5 significantly improved the sintering-resistance via the anchoring and isolation effects of HZSM-5 coating for PdO_x nanoparticles, resulting in the outstanding thermal stability of PdO/CeO_2. Moreover, the synthesized hybrid materials exhibited good oxygen and water-tolerance for methane combustion. Additionally, a re-activation behavior was observed due to the self-redispersion of PdO_x on CeO_2 nanosheets in the reaction atmosphere and at high temperature.*

Experimental Section

Synthesis of monodispersed CeO_2 nanosheets

In a typical synthesis procedure, 1.39 g cerium (III) nitrate hexahydrate ($Ce(NO_3)_3•6H_2O$) and 0.75 g ammonium bicarbonate (NH_4HCO_3) were dissolved in 200 ml deionized water at 25 °C under magnetic stirring, respectively. After completely dissolved, the NH_4HCO_3 solution was poured rapidly into the $Ce(NO_3)_3$ solution, and then stirring for 0.5 h and statically aging 24 h at 25 °C. The final product was collected by filtration, washed with deionized water, and then dried at 50

°C and calcined at 450 °C for 4 h in air.

Preparation of PdO supported CeO_2 nanosheets (PdO/CeO_2)

1.0 g of CeO_2 nanosheet was suspended in 100 ml of ethanol-water (1:1) with stirring. Exactly 43 mg of $PdCl_2$ was suspended in 100 ml of ethanol with stirring until $PdCl_2$ was completely dissolved (for more 4 h). The metal-ethanol solution was added to CeO_2 nanosheet suspension with stirring at room temperature for 24 h. The residue was filtered and washed several times with hot water and the last with ethanol, dried in an oven at 50 °C for 24 h, the obtained sample was remarked as Pd/CeO_2. The Pd/CeO_2 was calcined at 450 °C for 4 h in air and denoted as PdO/CeO_2.

Preparation of CeO_2@ZSM-5 and PdO/CeO_2@ZSM-5

0.31 g of sodium chloride (NaCl), 2.5g of polyethylene glycol 600 (PEG 600) and 5.625g of tetrapropylammonium hydroxide (TPAOH, 25%) were added sequentially into 25 g of deionized water under stirring, followed by the addition of 0.1 g of aluminium isopropoxide (AIP). After ultrasonic treatment for 15 min and stirring for 10 min, 3.27 g of tetraethyl orthosilicate (TEOS) was added to the solution quickly under stirring, and then 0.75 g of CeO_2 nanosheet or PdO/CeO_2 was suspended. After stirred for 24 h at room temperature, the resulting solution was transferred into an autoclave (50 ml) for further crystallization at 80 °C for 24 h and then 170 °C for 48 h under dynamic condition (60 rpm). Finally, the as-synthesized products were collected by filtration, dried, and calcined at 450 °C in air to remove the template, and were denoted as CeO_2@ZSM-5 and PdO/CeO_2@ZSM-5, respectively. To produce HZSM-5, the calcined products were ion exchanged three times in a large excess of aqueous 1 M solutions of NH_4NO_3 (1 M, L/S = 30 mL/g) at 80 °C and calcined at 450 °C for 4 h. Synthesis procedures of HZSM-5 were the same as CeO_2@ZSM-5 except the addition of CeO_2 and calcined at 550 °C.

Catalytic tests

Methane combustion experiments were performed in a U-shaped quartz microreactor with an internal diameter of 3 mm at atmospheric pressure. The catalyst (100 mg) was sieved below 60-80 mush of grain size and loaded into the bottom of reactor between two layers of granular quartz, used both for preventing displacement of the catalyst powder and pre-heating the reactant mixture. The reactant mixture composition was controlled by varying the flow rates of CH_4 (0.5 vol. %), O_2 (10.0 vol. %) and Ar while the total flow rate was kept constant at 50 ml min^{-1}, and the conditions corresponded to Gas Hourly Space Velocity (GHSV) of 30,000 ml g^{-1} h^{-1}. To record light-off curves, the catalyst was heated from 100 °C to 850 °C at 5 °C min^{-1}, and the

conversion of methane was measured by an on-line gas chromatograph equipped with a flame ionization detector (FID). Sequentially, hold for 150 minutes at 850 °C and then cooled-down to 100 °C under the reaction atmosphere, the second light-off curve was recorded.

Synthesis of CeO_2 nanosheets by different methods

(1) CeO_2-NS

In a typical synthesis procedure, 1.39 g cerium (III) nitrate hexahydrate ($Ce(NO_3)_3•6H_2O$) and 0.75 g ammonium bicarbonate (NH_4HCO_3) were dissolved in 200 ml deionized water at 0 °C under magnetic stirring, respectively. After completely dissolved, the NH_4HCO_3 solution was poured rapidly into the $Ce(NO_3)_3$ solution, and then stirring for 0.5 h and statically aging 15 h at 0 °C. The final product was collected by filtration, washed with deionized water to remove any possible ionic remnants, and then dried at 110 °C and calcined at 450 °C for 4 h in air to prepare the petal-like CeO_2 nanosheets, marked as CeO_2-NS.

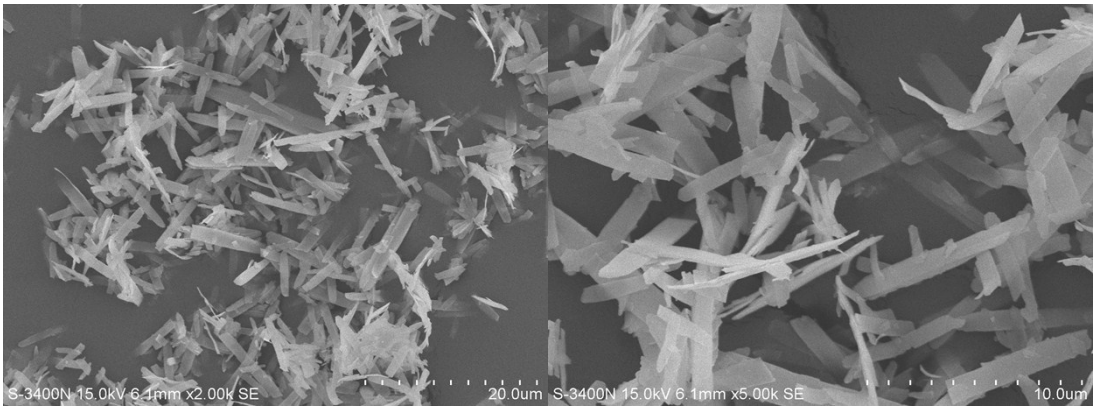
(2) CeO_2-HT

In a typical synthesis procedure, 1.39g $Ce(NO_3)_3•6H_2O$ was dissolved in 60 ml deionized water to form a transparent solution, then 3g hexamethylenetetramine (HMT) and 4ml acetic acid were added. The solution was stirred vigorously for 30 min and then poured in to a Teflon-lined stainless steel autoclave.After being sealed, the vessel was placed into a thermostat oven at 170 °C for 15 h.After cooling down to room temperature naturally, the white powder was collected by centrifugation, washed with deionized water and anhydrous alcohol for three times to remove other ions and then dried at 60 °C in air for 12h. The CeO_2 nanosheets were obtained via annealing the precursor at 450 °C for 4 h, and marked as CeO_2-HT.

(3) CeO_2-ST

Cerium nitrate hexahydrate ($Ce(NO_3)_3•6H_2O$) and ehylene glycol (C_2H_6OH, EG) as reagents. Initially, 6.10g $Ce(NO_3)_3•6H_2O$ was dissolved in 50ml EG and stirred vigorously toform a stable transparent solution.The mixed solution was transferred into a 75 ml Teflon autoclave containing a vertically immersed cleaned glass substrates. The stainless steel Teflon autoclave was kept in an oven at 180 °C for 28 h. Finally, the autoclave was cooled down to room temperature. The obtained nanosheets were washed several times with double distilled water, and dried in at 80 °C. Furthermore, CeO_2 nanosheets were obtained by annealing at 450 °C for 4 h, and marked as CeO_2-ST.

CeO_2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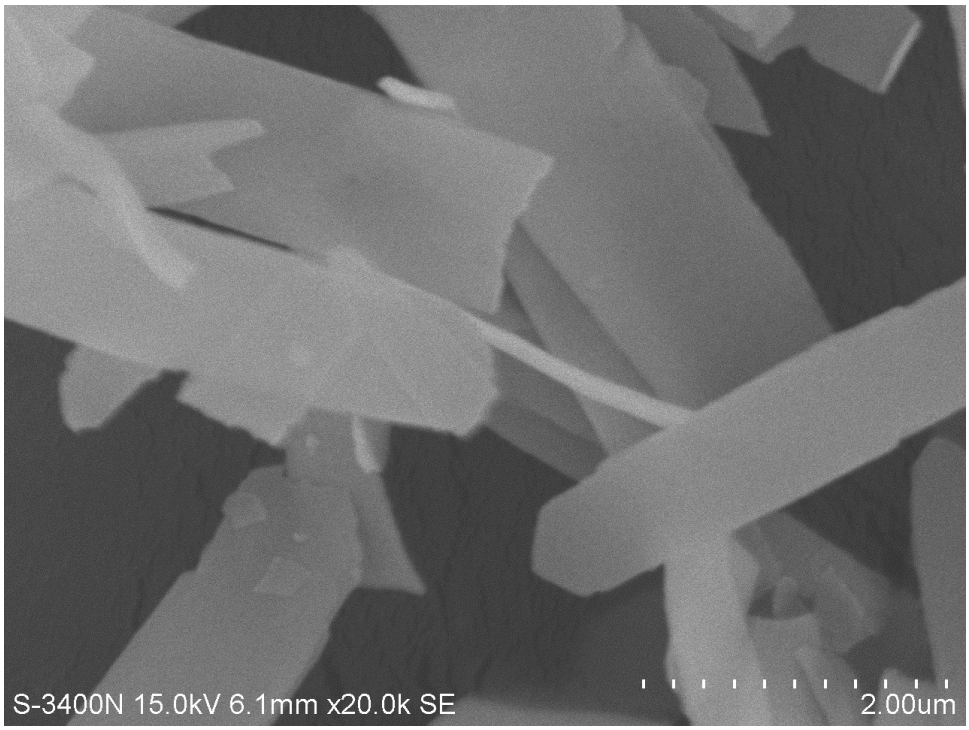
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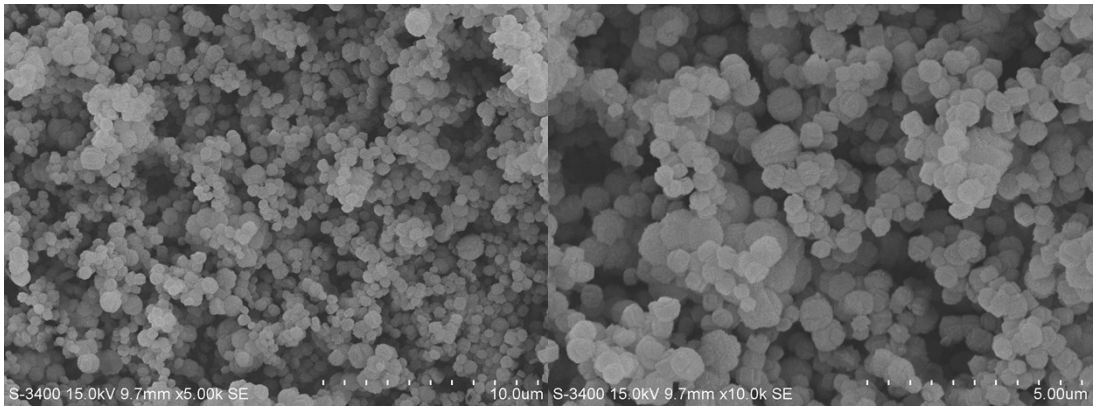
HZSM-5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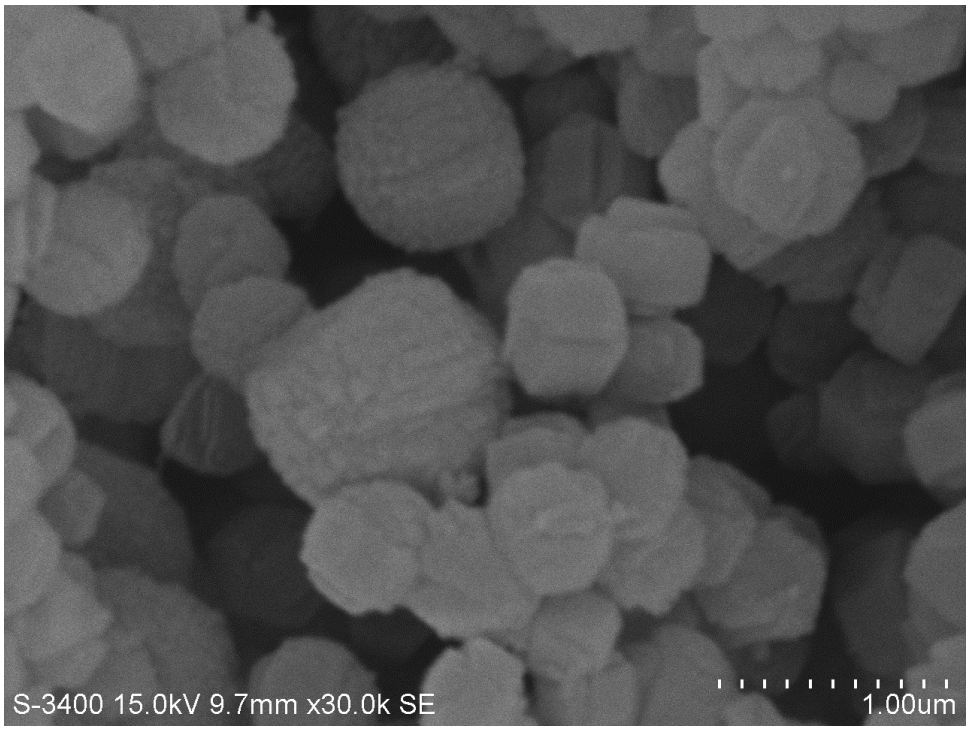
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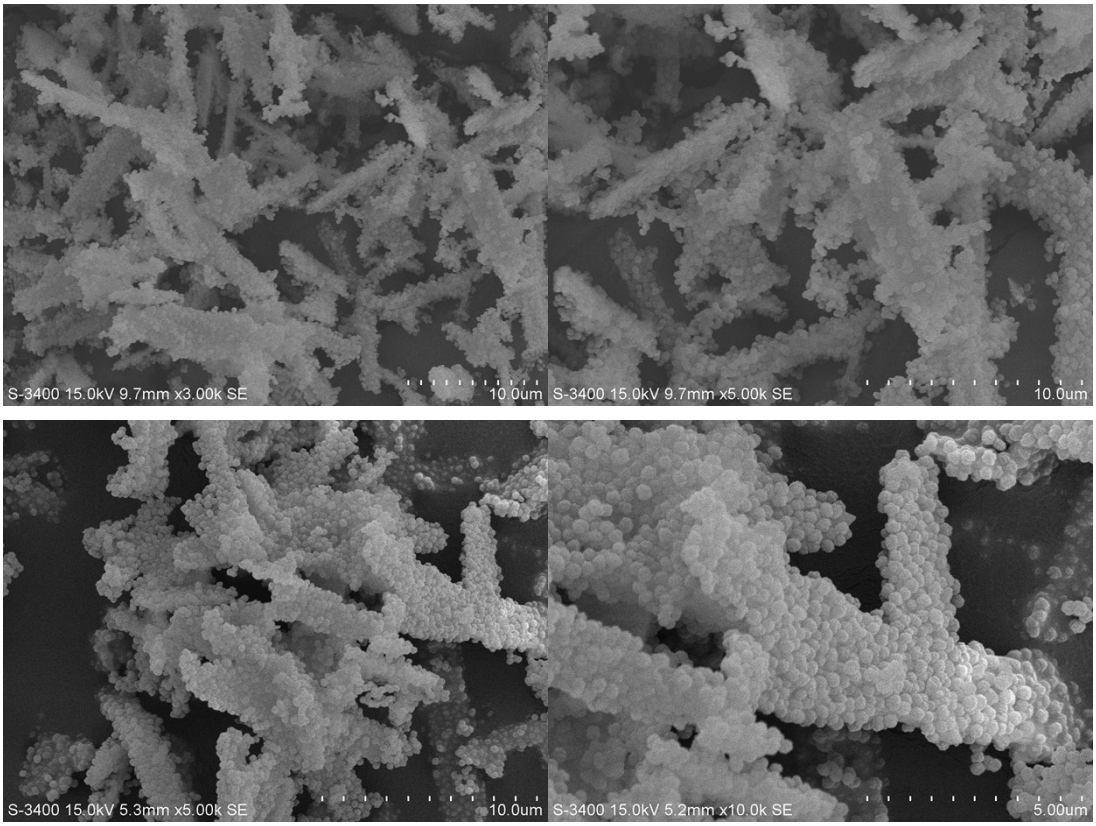
CeO_2@ZSM-5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PdO supported CeO_2 nanosheet@ZSM-5 (PdO/CeO_2@ZSM-5)

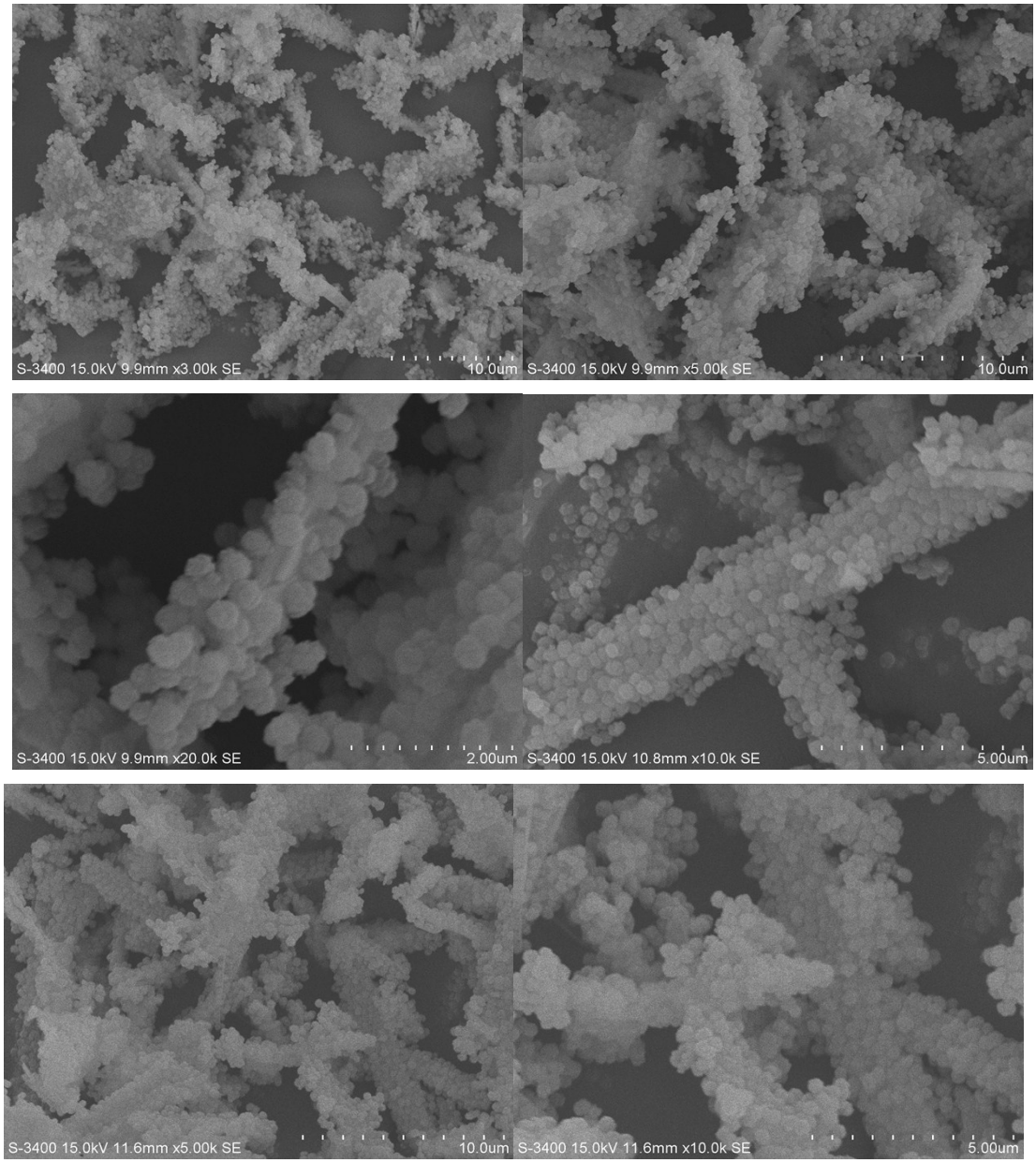


Figure S1 SEM images of the synthesized CeO_2 (a), HZSM-5 (b), CeO_2@HZSM-5 (c) and PdO/CeO_2@HZSM-5 (d) samples

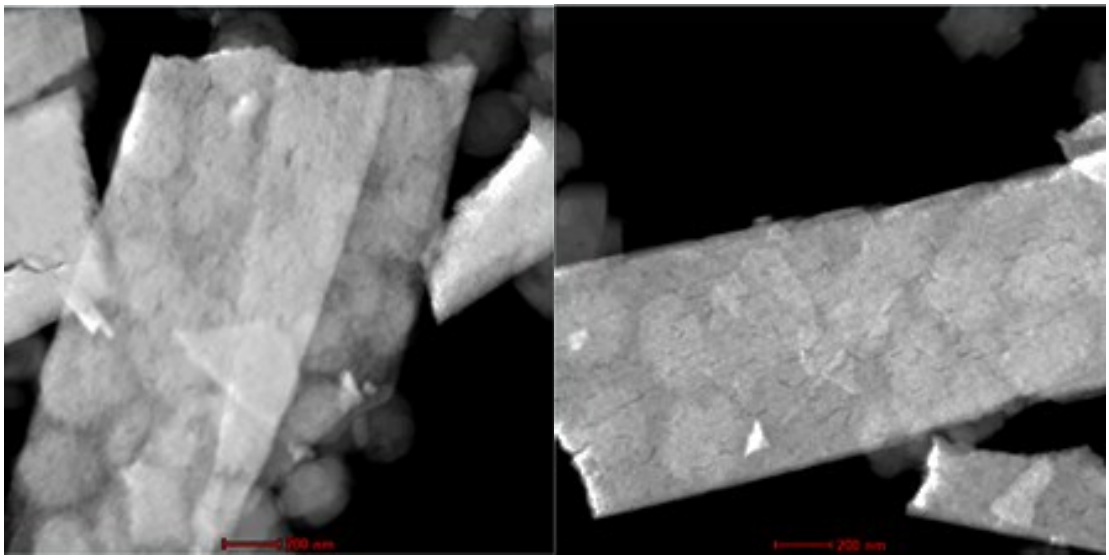


Figure S2 HAADF-STEM images of PdO/CeO_2@HZSM-5

Table S1 Physicochemical properties of synthesized materials

Samples	S_{BET} m^2/g	pore size nm	Pore Volume ml/g	XRF			Pd dispersion (%)	
				SiO_2/Al_2O_3	PdO wt%	CeO_2 wt%	Fresh	Spent
CeO_2-NB	78	3.2	0.06	-	-	-	-	-
HZSM-5	335	2.7	0.23	108	-	-	-	-
CeO_2@HZSM-5	171	4.2	0.18	151	-	45	-	-
PdO/CeO_2	50	3.8	0.05	-	2.3	-	78	88
PdO/HZSM-5	339	3.3	0.28	-	-	-	-	-
PdO/CeO_2@HZSM-5	172	3.7	0.16	145	0.93	42	30	41

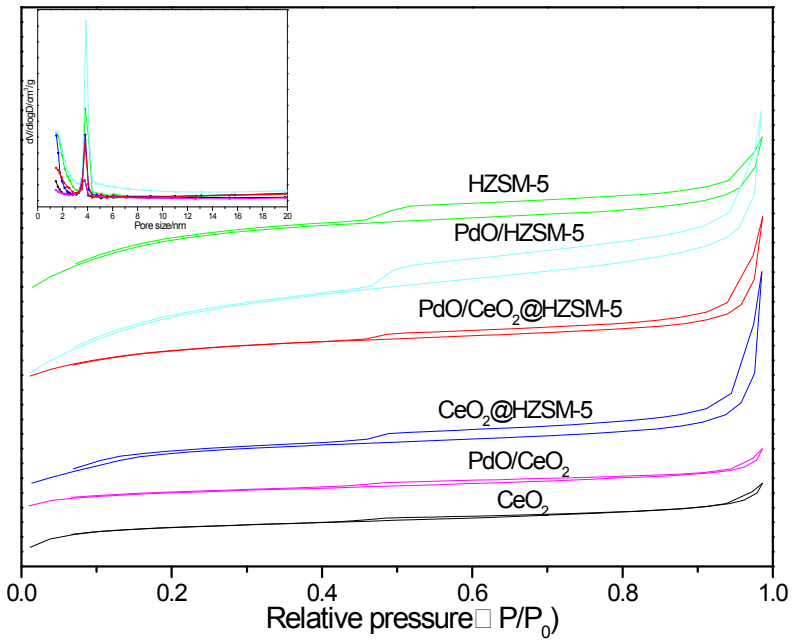
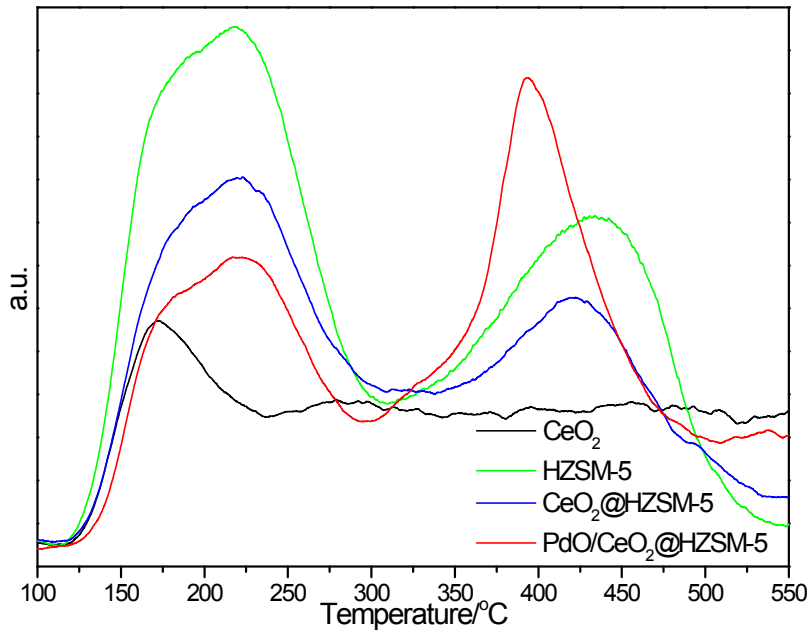


Figure S3 The N_2 adsorption-desorption isotherms and pore size distribution curves of synthesized composite catalysts.



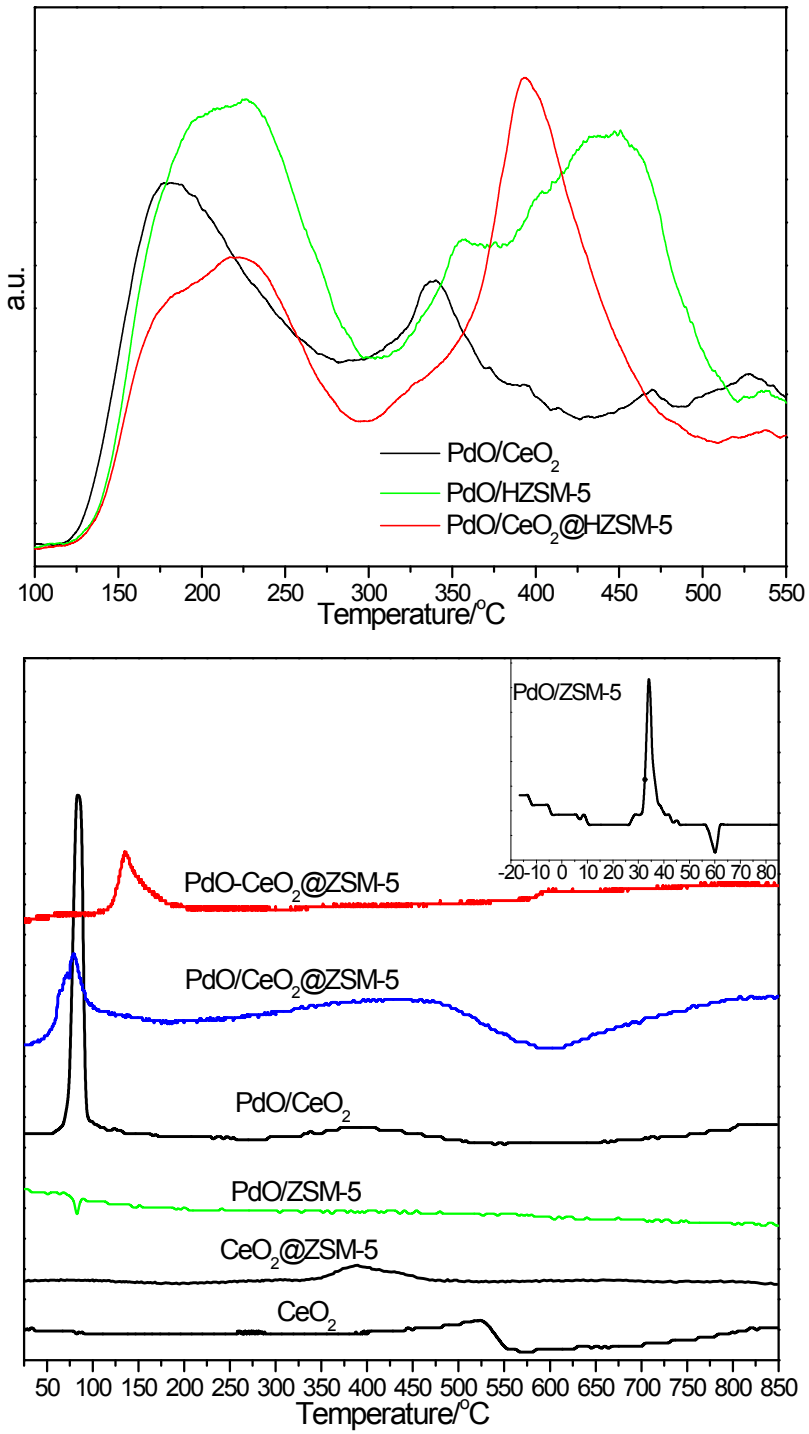


Figure S4 NH_3-TPD and H_2-TPR profiles of synthesized composite catalysts.

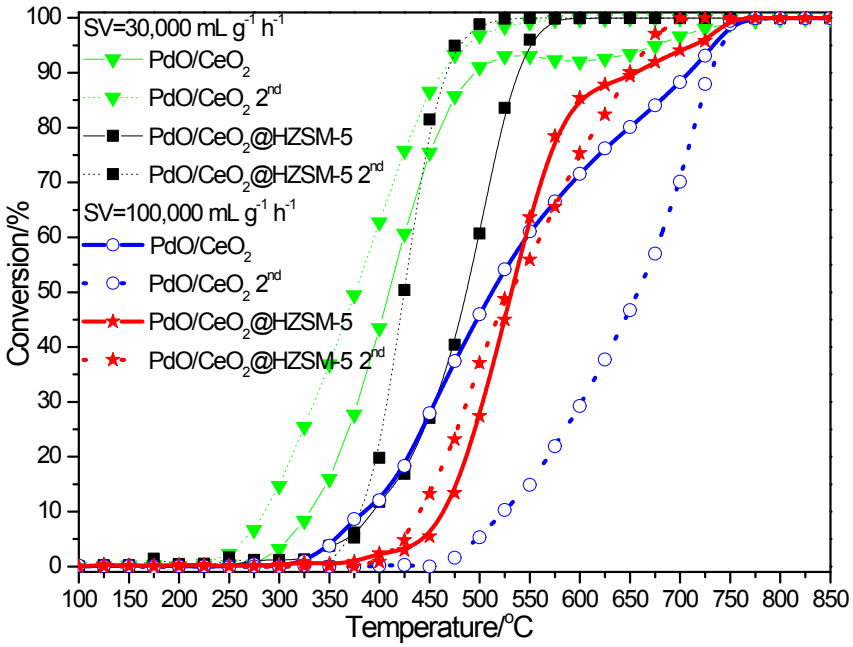


Figure S5 Light-off curves of CH_4 conversion vs the temperature over PdO/CeO_2 and PdO/CeO_2@HZSM-5. Conditions: 0.5 vol.% CH_4 + 10 vol.% O_2/Ar, GHSV of 30,000 and 100,000 mL g^{-1} h^{-1}.

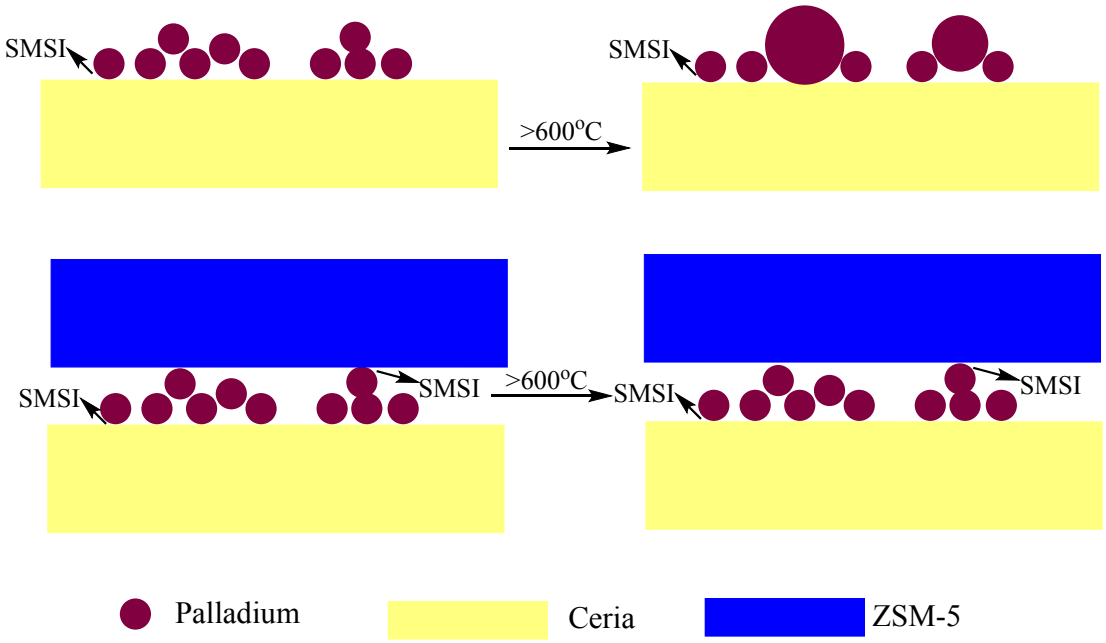
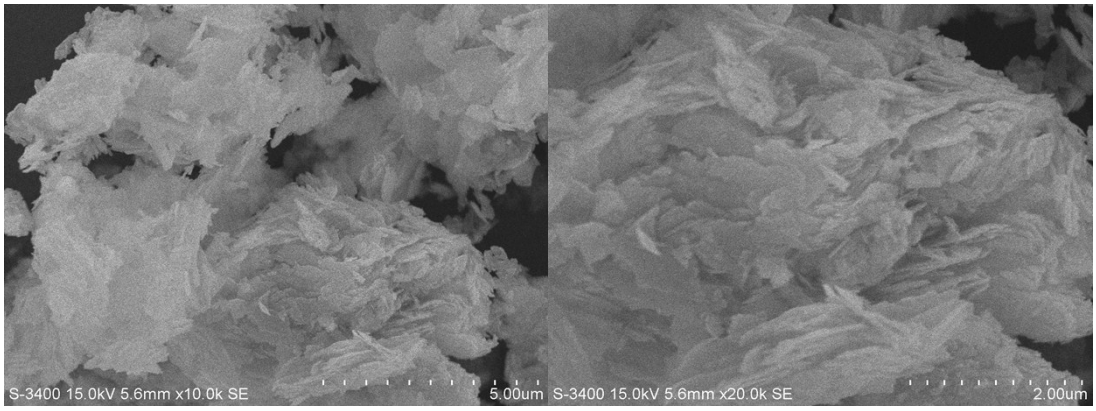
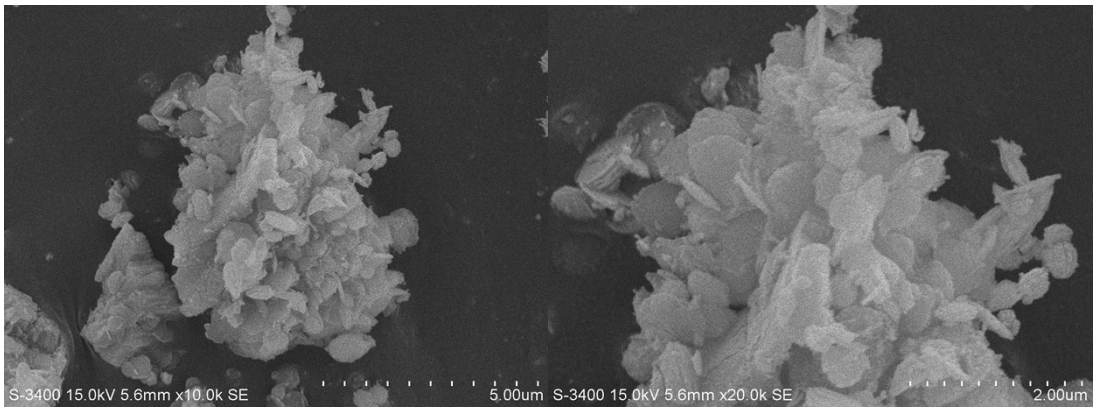


Figure S6 Schematic diagram showing a dip in the methane conversion (transient deactivation) is observed at 600−750°C.

PdO/CeO_2-HT



PdO/CeO_2-ST



PdO/CeO_2-NS

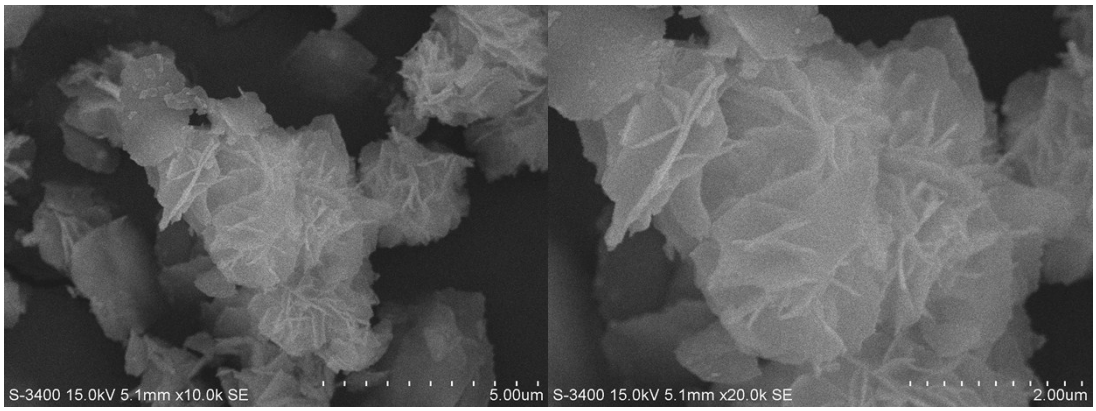


Figure S7 SEM images of the synthesized CeO_2 samples by different method.

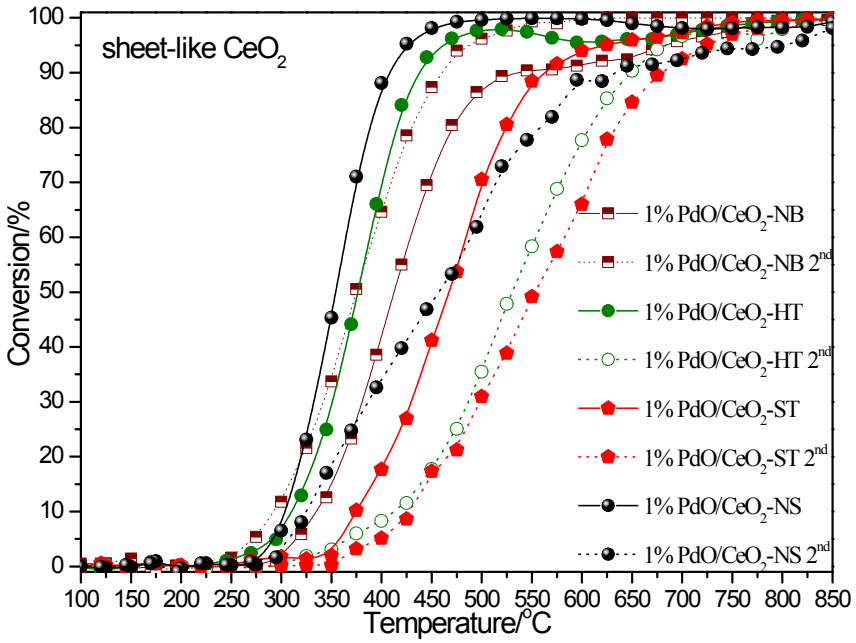


Figure S8 Light-off curves of CH_4 conversion vs the temperature. The dot lines correspond to the second cycle. Conditions: CH_4 (0.5 vol. %), O_2 (10 vol. %) in Ar, GHSV = 30,000 mL g^{-1} h^{-1}.

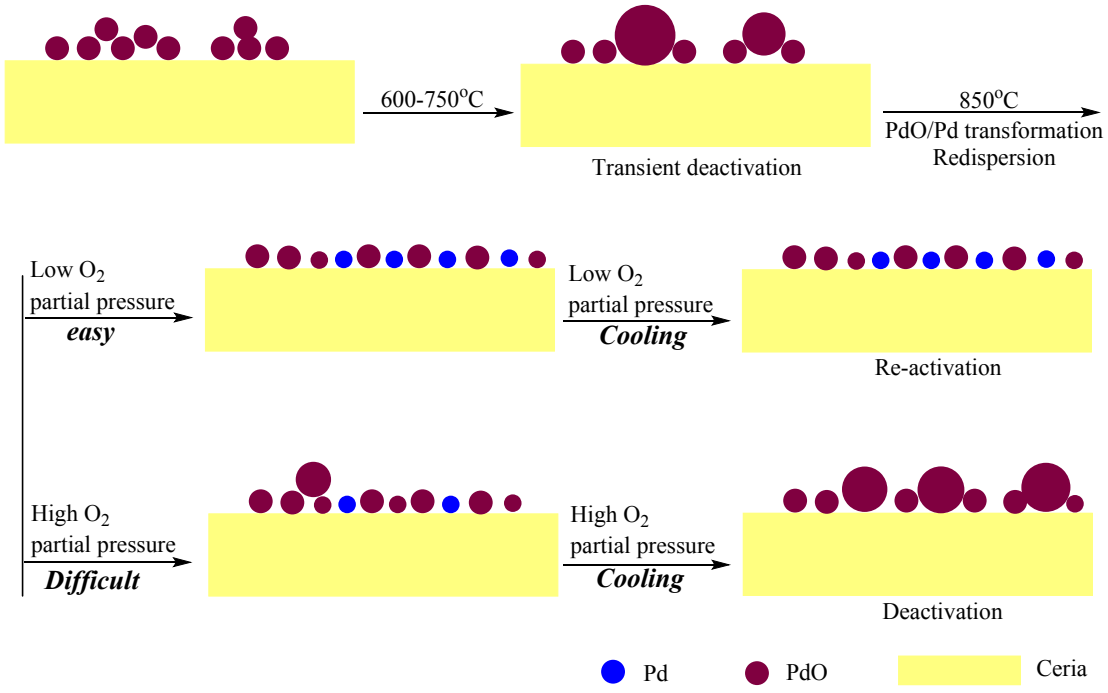
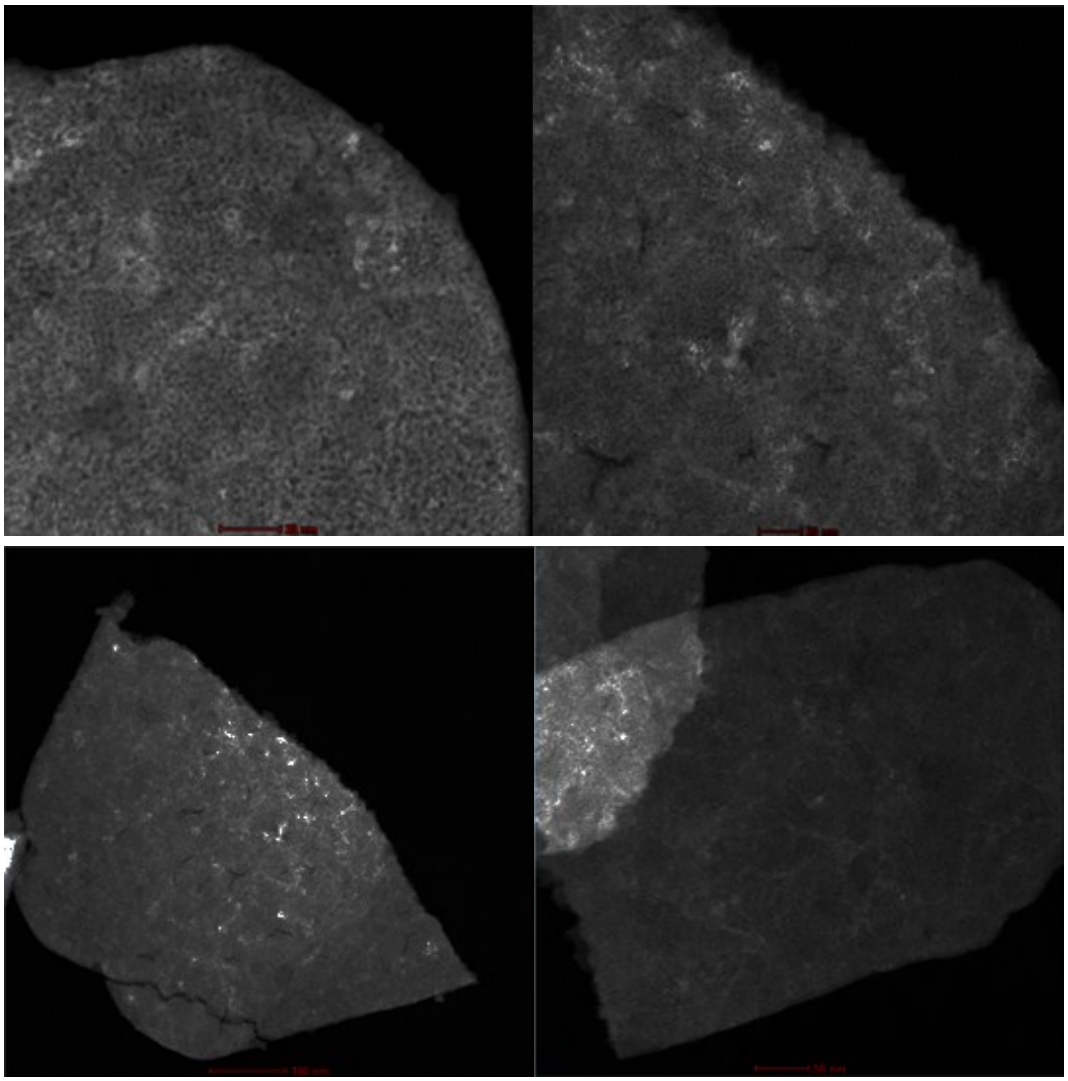
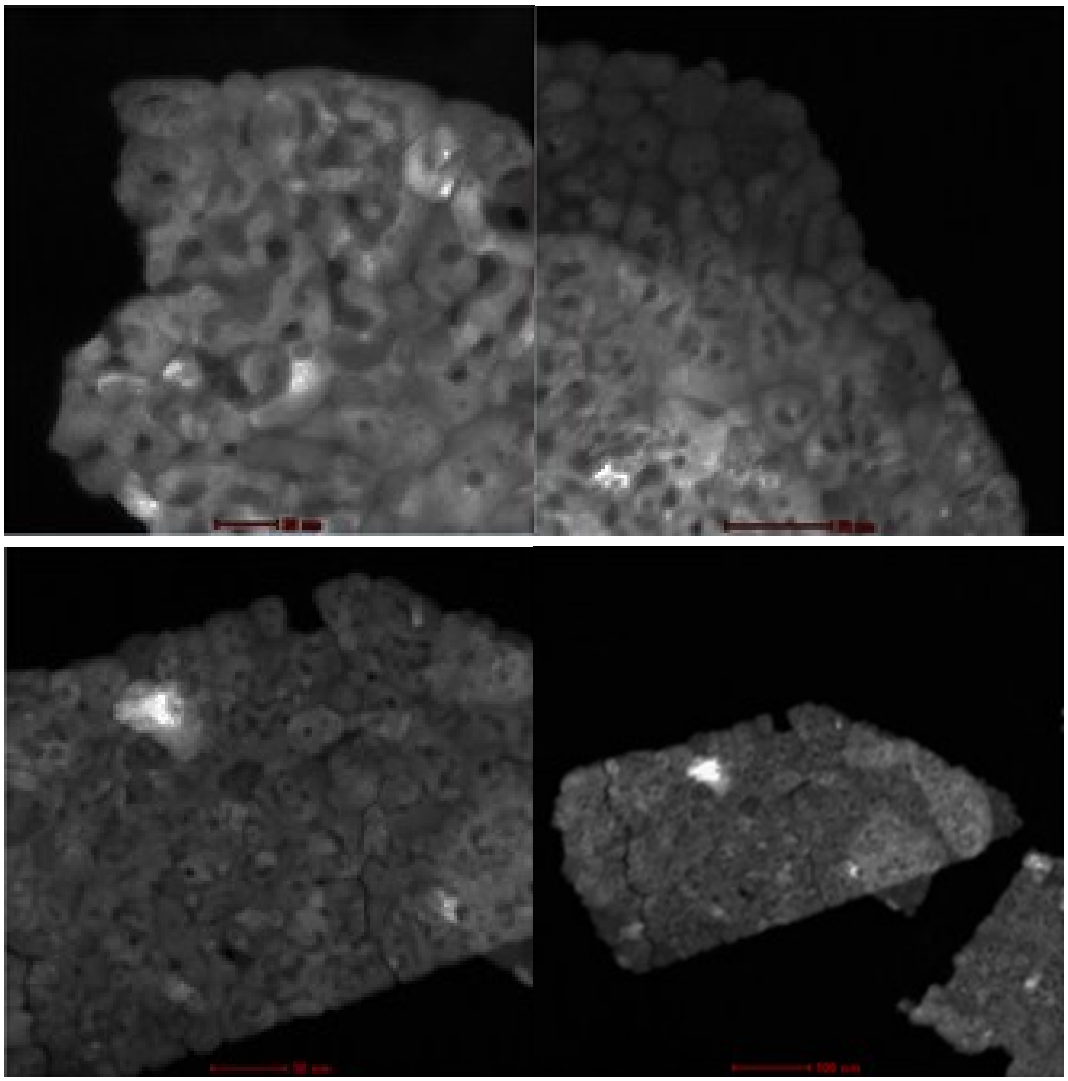


Figure S9 Schematic diagram showing the re-activation of PdO/CeO_2 catalysts at high temperature under methane atmosphere and appropriate oxygen content.

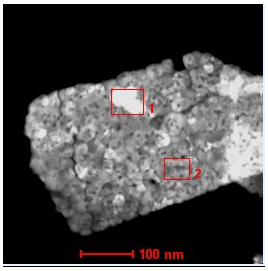
PdO/CeO_2-450 (fresh PdO/CeO_2)

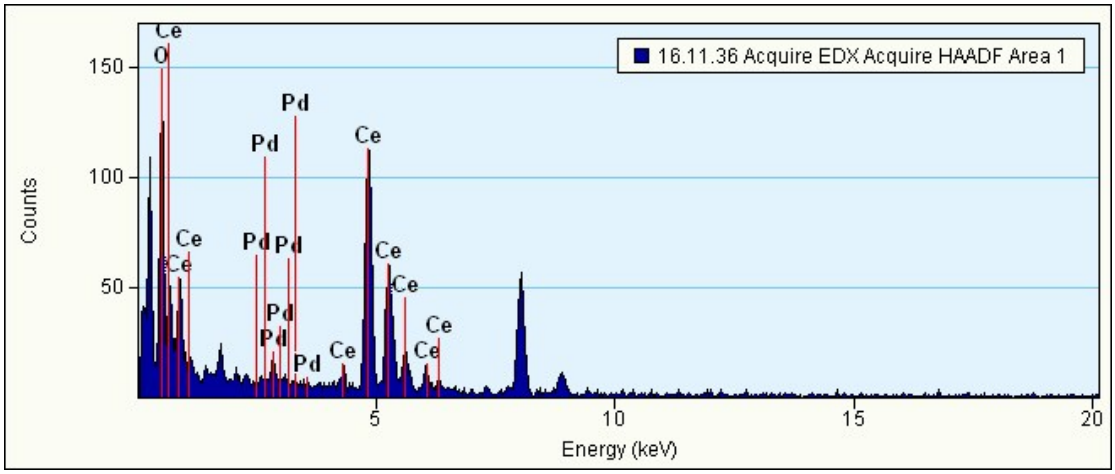


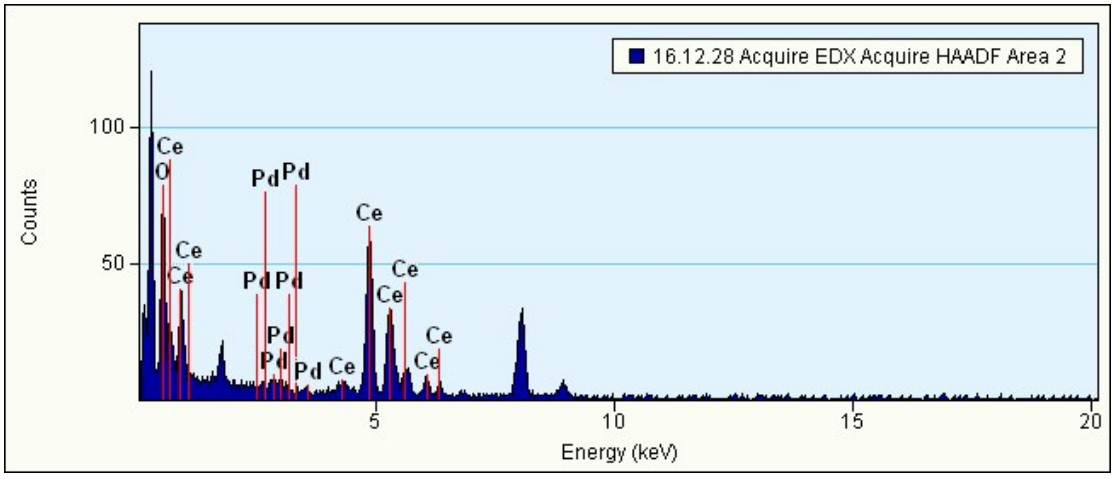
PdO/CeO_2-850 (aged PdO/CeO_2)



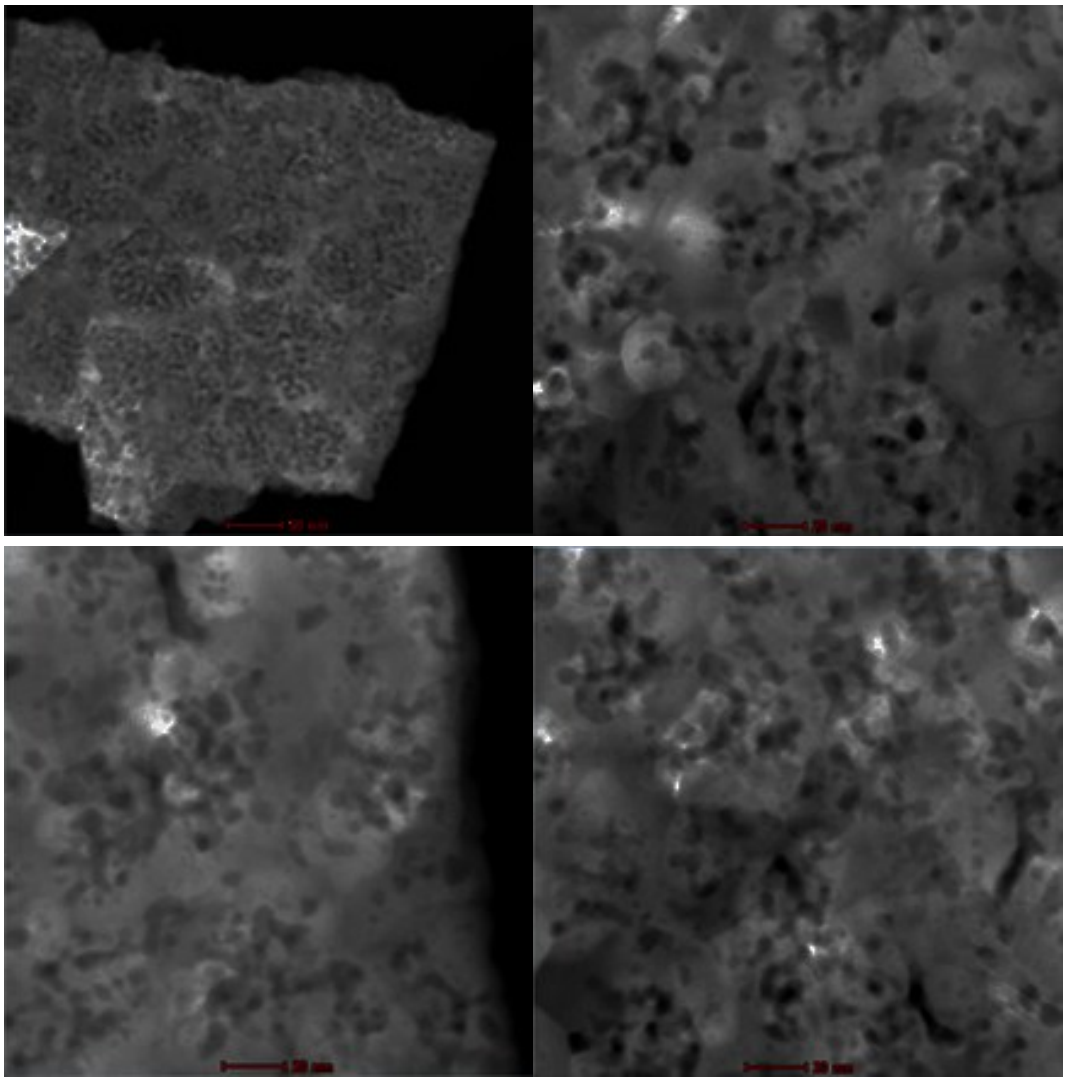
EDS of PdO/CeO_2-850



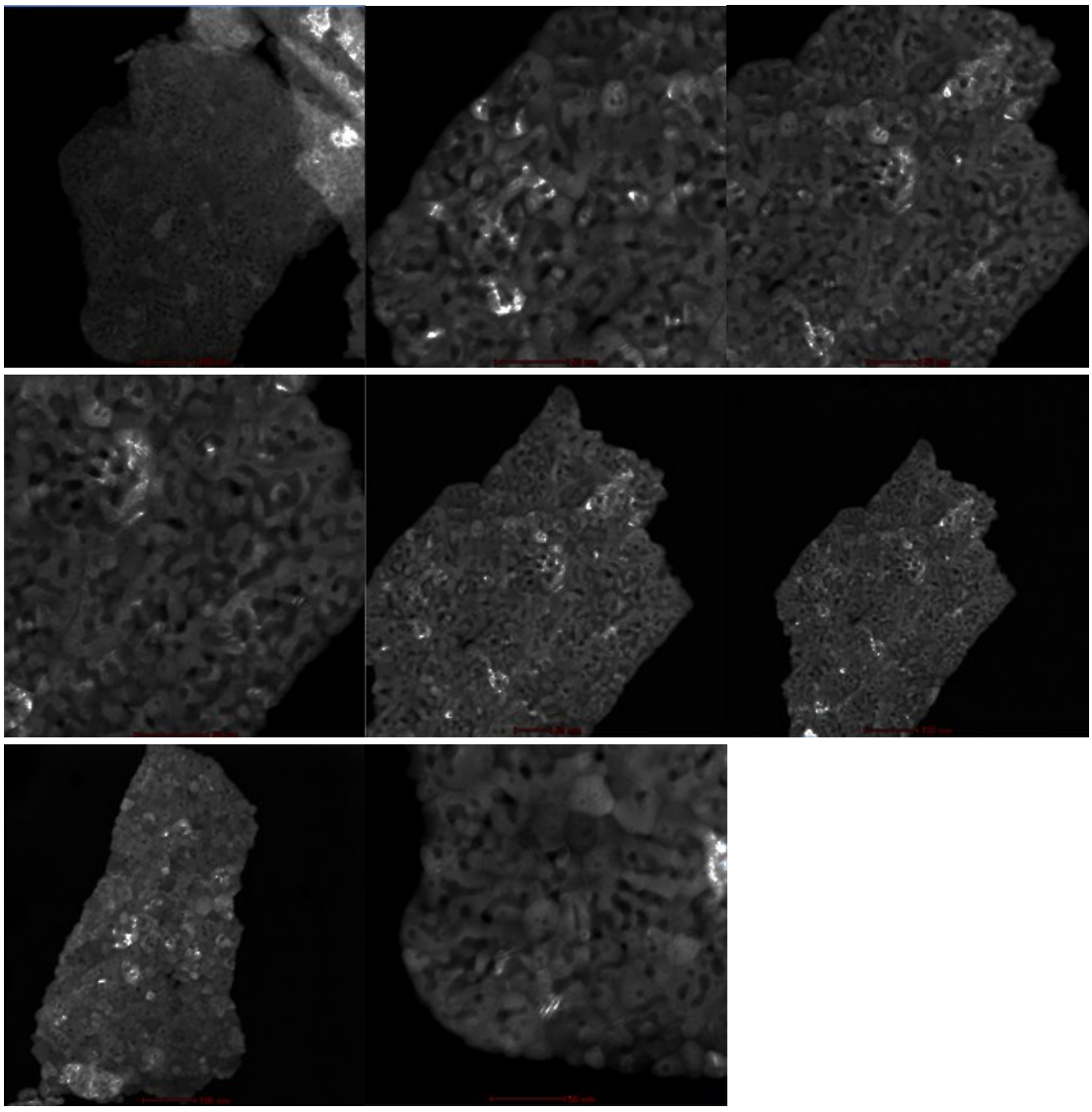




Spent PdO/CeO_2



Spent PdO/CeO_2-aged



Aged PdO/CeO_2@HZSM-5

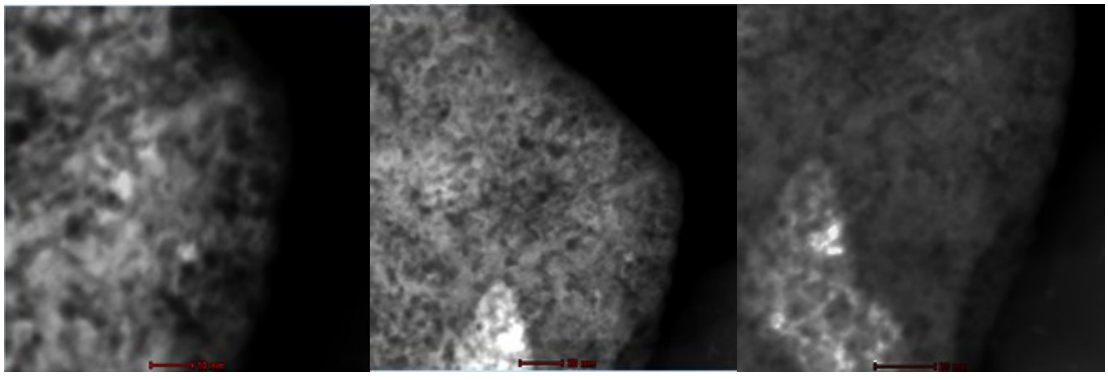


Figure S10 HAADF-STEM images of the fresh, aged and spent catalysts.

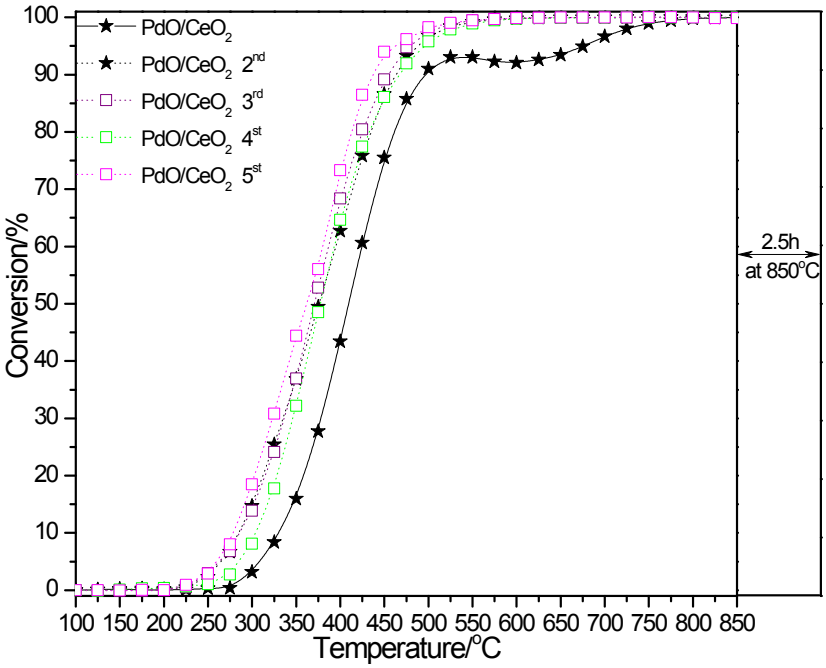


Figure S11 The stability of PdO/CeO_2.