Defective Ce-Mn solid solution loaded Pd single atom for enhanced methane combustion reaction

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Materials

All materials are analytically pure grade and don't require further purification. Potassium permanganate (KMnO₄, Beijing Sihuan Lianyou Industry and Trade Centre), Cerium Nitrate Hexahydrate (Ce(NO₃)₃·6H₂O, Aladdin), Palladium nitrate (Pd(NO₃)₂, 15 g/100 g, Shanghai Tuosi Co., Ltd), ammonia water (NH₃·H₂O, Xilong Scientific Co., Ltd), Manganese nitrate tetrahydrate (Mn(NO₃)₂·4H₂O, Aladdin), Cerium oxide (CeO₂, Macklin), Manganese Sulfate Tetrahydrate (MnSO₄·4H₂O, Beijing Chemical Works), Ammonium sulfate ((NH₄)₂SO₄, Beijing Chemical Works) and Ammonium persulphate ((NH₄)₂SO₆, Beijing Chemical Industry Group Co., Ltd).

Catalysts synthesis

Synthesis of Pd/CeMn-AR: The molar composition of the CeMn solid solution is Ce:Mn=2:1. Firstly, 2.6048 g Ce(NO₃)₃·6H₂O was dissolved in 30 mL water to obtain Ce(NO₃)₃ solution (denoted as A), while 0.474 g KMnO₄ was dissolved in 50 mL water to obtain KMnO₄ solution (denoted as B). Solution A and Pd(NO₃)₂ solution are slowly added to solution B. The palladium content of the samples was 1 %. After stirring at 80 °C for 9 h, it was centrifuged several times with deionized water and ethanol. The product was dried at 60 °C and obtained the Pd/CeMn-AR catalyst.

Synthesis of Pd/CeMn-CP: 2.6048 g Ce(NO₃)₃·6H₂O, 0.752 g Mn(NO₃)₂·4H₂O and Pd(NO₃)₂ solution were dissolved in 80 mL water and stirred to get the mixed solution. The palladium content of the samples was 1 %. Ammonia was slowly added to the mixed solution until PH=10, stirred for 2 h, and then aged overnight. After centrifugation, the sample was washed several times with deionized water and ethanol, and then dried at 60 °C. Then the product was calcined at 500 °C for 4h by Muffle furnace to obtain Pd/CeMn-CP.

Synthesis of Pd/CeO₂ and Pd_{NP}/CeO₂: The Pd/CeO₂ was prepared by the wet impregnation method. 1 g CeO₂ was fully dispersed into 50 mL deionized water, a certain amount of Pd(NO₃)₂ solution was added, and stirred and dried at 80 °C. The palladium content of the samples was 1 %. The resulting product named Pd/CeO₂ is calcined at 500 °C for 4 h in the air. Pd_{NP}/CeO₂ is calcined at 400 °C for 2 h in the 5% H₂/Ar.

Synthesis of Pd/MnO_x: The MnO_x was prepared according to a previously reported method¹. 0.54 g MnSO₄·H₂O, 0.73 g (NH₄)₂S₂O₈, 1.691 g (NH₄)₂SO₄, Pd(NO₃)₂ solution and 80 mL H₂O were mixed together and transferred to Teflon-lined, stainless autoclave. The palladium content of the samples was 1 %. Then, the mixed solution was heated at 140 °C for 12 h in the oven. After the product was cooled to room temperature, the product was collected and washed several times with deionised water. Dried at 60 °C overnight to obtain MnO_x. The obtained MnO_x was loaded with 1% Pd by wet impregnation and calcined in air at 500 °C for 4 h to obtain Pd/MnO_x.

Synthesis of CeMn-AR-Pd: 2.6048 g Ce(NO₃)₃·6H₂O was dissolved in 30 mL water to obtain Ce(NO₃)₃ solution (denoted as A), while 0.474 g KMnO₄ was dissolved in 50 mL water to obtain KMnO₄ solution (denoted as B). Solution A are slowly added to solution B. After stirring at 80 °C for 9 h, the resulting product was centrifuged several times with deionized water and ethanol. The product was dried at 60 °C. 1 wt% Pd was loaded onto the dried product by wet impregnation and calcined at 500 °C for 4 h in air to obtain the CeMn-AR-Pd.

Catalyst characterization

Transmission electron microscopy (TEM) images were acquired by the FEI Tecnai G2 F20 high resolution transmission electron microscope operating at 200 kV. The X-ray diffraction spectra of catalysts were obtained by Bruker D8 Focus Powder with Cu K α radiation (λ = 0.15418 nm) at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were made by the ESCALAB-MKII 250 Photoelectron Spectrometer (VG Co.), and X-ray photoelectron spectroscopy was obtained. The specific surface areas of the catalysts were measured using an Autosorb-iQ system with the Brunauer-Emmett-Teller (BET) method. The Raman measurements were performed on a Horiba JobinYvon spectrometer at 532 nm on a Microscope System T64000.DRIFT spectra of CO adsorption were measured on a Thermo Scientific Nicolet iS50 spectrometer equipped with a mercury cadmium telluride (MCT) detector. Before CO adsorption, the catalyst was treated by N₂ atmosphere (30 mL/min) at 200 °C for 30 min. The temperature was then cooled to 50 °C and the background spectra were recorded. The samples

were then treated in a 10% CO/He atmosphere (30 mL/min) for 15 min, and then the CO adsorbed samples were treated in an N₂ atmosphere (30 mL/min) for 15 min and the spectra recorded. To investigate the reaction mechanism of the methane catalytic combustion, in situ DRIFTS of the samples was applied on a Nicolet iS 50 spectrometer apparatus. Firstly, the catalysts were treated with N₂ at 550 °C for 30 min and subsequently the background spectra were recorded. Then the reaction gas (0.5% CH₄, 20% O₂, Ar balanced) was introduced and the spectrum was recorded.

Methane temperature-programmed reductions (CH₄-TPD) were measured using a ChemStar TPx Chemisorption Analyzer (USA). Firstly, the catalyst was treated in Ar atmosphere (30 mL/min) at 300 °C for 60 min and then cooled to 50 °C. Subsequently, the catalyst was treated in 10% CH₄/He (30 mL/min) for 30 min. Next, the physically adsorbed CH₄ on the catalyst surface was removed in an Ar atmosphere (30 mL/min). Then, the sample was warmed up from 25 °C to 800 °C and the spectra were recorded. O₂ temperature-programmed desorption (O₂-TPD) were tested using the same instrumentation and methodology, which dealt with an atmosphere of 5% O₂/Ar.

Catalytic activity tests

The Methane oxidation reaction activity was tested in a fixed bed flow reactor system at atmospheric pressure. 50 mg of catalyst and 50 mg of quartz sand were mixed well and placed in a quartz tube. The reaction gas (0.5% CH_4 + 20% O_2 + 79.5% Ar) was introduced and heated from 250 °C to 550 °C. The products were monitored using a chromatograph with a thermal conductivity detector (TCD).

The CH₄ conversion determination

 CH_4 conversion = ([CH_4]_{in}-[CH_4]_{out})/[CH_4]_{in} × 100%

The [CH₄]_{out} and [CH₄]_{in} represent the molar amount of CH₄ after and before the reaction.



Fig. S1 (a) HAADF-STEM image of Pd/CeMn-AR. **(b)** The region enlarged HAADF-STEM image of Pd/CeMn-AR and **(c)** the corresponding intensity profile along the X–Y axis.



Fig. S2 The Pd/CeMn-CP of (a) TEM image and (b) EDX elemental mappings.



Fig. S3 The Pd/CeO_2 of (a) TEM image and (b) EDX elemental mappings.



Fig. S4 The Pd/MnO_x of (a) TEM image and (b) EDX elemental mappings.



Fig. S5 Mn 3d XPS spectra of Pd/CeMn-AR, Pd/CeMn-CP, and Pd/MnO_x catalysts.



Fig. S6 Ce 3d XPS spectra of Pd/CeMn-AR, Pd/CeMn-CP, and Pd/CeO₂ catalysts.



Fig. S7 O 1s XPS spectra of Pd/CeMn-AR, Pd/CeMn-CP, and Pd/CeO $_2$ catalysts.



Fig. S8 The Raman spectra of Pd/CeMn-AR, Pd/CeMn-CP, Pd/CeO₂, and Pd/MnO_x catalysts.



Fig. S9 EPR spectra of Pd/CeMn-AR, Pd/CeMn-CP, and Pd/CeO₂.



Fig. S10 N₂ adsorption-desorption isotherms of (a) Pd/CeMn-AR and (b) Pd/CeMn-CP.



Fig. S11 (a) TEM image and (b) XRD pattern of CeMn-AR-Pd.



Fig. S12 (a) The catalytic activity of the CeMn-AR-Pd and (b) the stability of the CeMn-AR-Pd.



Fig. S13 The activity of Pd/CeMn-AR in different (a) Ce:Mn molar ratio and (b) Pd content.



Fig. S14 The catalytic activity of Pd/CeMn-AR in different space velocity.



Fig. S15 (a) TEM image and (b) XRD pattern of Pd_{NP}/CeO_2 .



Fig. S16 (a) The catalytic activity of the Pd_{NP}/CeO_2 and (b) the stability of the Pd_{NP}/CeO_2 .



Fig. S17. (a) The TEM image of used Pd/CeMn-AR, (b) EDX elemental mappings of used Pd/CeMn-AR.



Fig. S18 The XRD pattern of used Pd/CeMn-AR.



Fig. S19 The XPS spectra of (a) Pd 3d, (b) Ce 3d, (c) Mn 3d, (d) O 1s over used Pd/CeMn-AR.



Fig. S20 O₂-TPD profiles of the Pd/CeMn-AR and CeMn-AR-Pd.

	Pd ²⁺ (%)	Ce ³⁺ (%)	O _{def} (%)	Mn ²⁺ (%)	Mn ³⁺ (%)	Mn ⁴⁺ (%)
Pd/CeMn-AR	56.28	19.94	59.4	16.46	54.78	28.76
Pd/CeMn-CP	56.37	15.20	42.4	57.75	32.49	9.76
Pd/CeO ₂	72.3	14.97	29.3			
Pd/MnO _x	48.72			13.73	66.59	19.68

Table S1 The proportion of different valence states of Pd, Ce, Mn and O species for all catalysts measured by XPS.

AR-used measured by APS.								
	Pd ²⁺ (%)	Ce ³⁺ (%)	O _{def} (%)	Mn ²⁺ (%)	Mn ³⁺ (%)	Mn ⁴⁺ (%)		
Pd/CeMn-AR-used	75.83	18.31	43.2	25.34	52.36	22.3		

Table S2 The proportion of different valence states of Pd, Ce, Mn and O species for Pd/CeMn-AR-used measured by XPS.

Catalyst	T ₅₀ (°C)	T ₉₀ (°C)	E _a (KJ/mol)	Feed gas	WHSV (mL g _{cat} ⁻¹ h ⁻ ¹)	Pd loadings (%)	Ref.
Pd/CeMn-AR	440	543	64.75	0.5%CH ₄ , 20%O ₂ , Ar	30000	1	This work
0.75Pd/CeO ₂ - ER0.8	475	600		0.5%CH ₄ , 4%O ₂ , N ₂	56600	0.75	Ref.2
Pd ₁ /CeO ₂	395	480	72.1	0.8%CH ₄ , 4%O ₂ , Ar	15000	0.5	Ref.3
1Pd/CeO ₂ - 800*	450	545	68.5	0.5%CH ₄ ,2.5%O ₂ , He	60000	1	Ref.4

 Table S3 Comparison of catalysts reported in the literature for methane oxidation.

References

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