



- Particle Size and PdO-Support Interactions in
  PdO/CeO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub> Catalysts and Effect on Methane
- 3 Combustion
- 4 Domenica R. Fertal<sup>1</sup>, Maxim P. Bukhovko<sup>2</sup>, Yong Ding<sup>3</sup>, Mehmet Z. Billor<sup>4</sup>, Anil C. Banerjee<sup>1\*</sup>
- 5 1 Department of Chemistry, Columbus State University, Columbus, GA 31907, USA.
- 6 2 Department of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332,
  7 USA.
- 8 3 School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA.
- 9 4 Department of Geosciences, Auburn University, Auburn, AL 36849, USA.
- 10 \*Correspondence: banerjee\_anil@columbusstate.edu; Tel.: +1-706-569-3030
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#### SUPPLEMENTARY MATERIALS

#### **B** <u>Catalysis Synthesis</u>

- 14 The catalysts and the supports were synthesized using the following apparatus.
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- 17 **Figure S1**. Catalyst synthesis apparatus
- 18 (a). Synthesis of dual support of 20CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>: A pre-calculated mass of cerium nitrate hexahydrate
- 19 [Aldrich, USA] (equivalent of 20 wt% CeO<sub>2</sub> in the dual support) was dissolved in DI water and
- 20 taken in the sterile syringe. A slurry of solid  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Aldrich, USA) was made with DI in the vortex
- 21 tube. The cerium nitrate solution was added in 20 microliter increments to the vortex tube and

- 22 solution was vortexed for 3h. The slurry was dried in an air oven at 105 °C for 12 h, followed by
- 23 calcination in a calcining furnace at 500 °C for 5h. The solid was powdered in a mortar and pestle
- $24 \qquad \text{and stored in a sealed tube. The final composition of the dual support was 20 wt\% CeO_2 \text{ and } 80$
- $25 \qquad wt\% \; Al_2O_3 \; [abbreviated \; as \; 20 CeO_2/Al_2O_3].$
- $26 \qquad (b). \ 4Pd-20CeO_2/Al_2O_3 \ Catalyst: \ This \ catalyst \ was \ prepared \ by \ impregnating \ an \ aqueous \ solution \ of$
- $27 \qquad \text{palladium nitrate hydrate to an aqueous slurry of a solid dual support made of 20 wt\% CeO_2 and 80$
- $28 \qquad \text{wt\% Al}_2\text{O}_3. \text{ The solid dual support } [20\text{CeO}_2/\text{Al}_2\text{O}_3] \text{ was first turned into a slurry by adding distilled } \\$
- water in the vortex tube. An aqueous precursor solution of palladium nitrate hydrate was added in
  20 microliter increments to the aqueous solution of the dual support as it was being vortexed. The
- 30 20 microliter increments to the aqueous solution of the dual support as it was being vortexed. The 31 slurry was dried in an air oven at 105 °C for 12 h, followed by calcination in a calcining furnace at
- 32 500 °C for 5 h. The solid was powdered in a mortar and pestle and stored in a sealed tube.
- 33 (c). Synthesis of 5Pd/Al<sub>2</sub>O<sub>3</sub>: The dry, solid support of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was placed in a vortex tube and
- 34 turned into a slurry liquid-like substance with distilled water. Then the aqueous precursor solution
- 35 of palladium nitrate hydrate was impregnated in 20 microliter increments. The mixture was
- 36 vortexed as the precursor was added for a total time of 3 h. The slurry catalyst was dried at 105 °C
- 37 overnight (12 h). Once dried, the solid support was ground in a mortar and pestle and then calcined
- 38 at 500 °C for 5 h. The final composition was 5.0 wt% Pd (as PdO).
- 39 (d).  $20CeO_2-4Pd/Al_2O_3$  Catalyst: This catalyst was prepared by impregnating an aqueous solution of
- $40 \qquad \text{cerium nitrate hexahydrate to an aqueous slurry of 5Pd/Al_2O_3. The solid [5Pd/Al_2O_3] was powdered}$
- 41 again, placed in a clean vortex tube, and turned into a slurry with the addition of distilled water.
- 42 An aqueous solution of cerium nitrate hexahydrate [equivalent to 20 wt% CeO<sub>2</sub>] was then added in
- 43 20 microliter increments from the syringe to the slurry in the vortex tube as the mixture was
- 44 vortexed for 3 h. The slurry was dried in an air oven at 105 °C for 12 h, followed by calcination in a
- 45 calcining furnace at 500 °C for 5 h. The solid was powdered in a mortar and pestle and stored in a
- 46 sealed tube.

#### 47 Activity Measurements

- 48 Activity measurements were conducted in a temperature-controlled horizontal tubular fixed-bed
- 49 quartz reactor (internal diameter 12 mm) as shown in Figure S2. The catalyst bed was heated to a
- 50 desired temperature using a temperature-controlled furnace (Carbolite MTF1000, Verder Scientific,
- 51 Newtown, PA, USA). The catalytic reactor unit is shown in Figure S2. A mass of 0.2 g of a catalyst
- 52 was packed in the reactor tube using quartz wool to hold the catalyst sample in place and quartz
- 53 beads to allow the gas mixture to flow. The reacting gas mixture consisted of 4% O<sub>2</sub>, 2% CH<sub>4</sub> and
- 54 balance nitrogen (NexAir, Memphis, TN, USA). The catalyst bed was heated to a desired
- 55 temperature as nitrogen gas was being passed through the mass flow controller (Aalborg,
- 56 Orangeburg, NY, USA). Each run ran the gas mixture through the quartz flow reactor tube for a
- 57 length of 20 minutes at a fixed temperature and a flow rate of 150 cc/min. The catalyst bed was
- 58 heated to a desired temperature as nitrogen gas was being passed using a temperature-controlled
- 59 tube furnace. The temperature ranged from 200 °C to 450 °C. Between each activity run, pure
- 60 nitrogen gas was sent through the reactor tube in order to "sweep" the system of any leftover gas
- 61 mixture. The reacted gas mixture was passed through a moisture trap to remove any moisture that
- 62 may have occurred from the reaction. A volume of 1.0 cc of the outlet gas sample was collected in a
- 63 gas tight syringe and injected to the column (6 ft. ShinCarbon; Restek Corporation, Bellefonte, PA,

- 64 USA). The gas mixture was analyzed in a gas chromatograph (GC Model 310, SRI Instruments,
- 65 Torrance, CA, USA) using the *PeakSimple* software. For all activity experiments, particle of sizes of
- 66 63–75 mm, a gas flow rate of 150 cc/min (calculated at 25 °C and 1 atm.), and a Gas Hourly Space
- 67 Velocity (GHSV) of 45,000 cc.g.cat<sup>-1</sup>.h<sup>-1</sup> (calculated at 25 °C and 1 atm.) were chosen. Activity runs
- 68 were repeated and only runs with deviations below 2–3% were accepted. The inlet and outlet gas
- 69 feed composition was measured in volume % at 25 °C and 1 atm.



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71 Figure S2. Catalytic reactor unit

#### 72 Chemisorption and Physisorption Methods

73 Pulse CO chemisorption and temperature programmed reduction with hydrogen (TPR) were

74 performed in Micromeritics AutoChem II 2920 (Micromeritics Corporation, Norcross, GA, USA).

75 Nitrogen physisorption was performed in a Micromeritics Tristar II (Micromeritics Corporation,

76 Norcross, GA, USA). For TPR with hydrogen, approximately 50 mg of each catalyst was heated in

20 mL/min of He (UHP, Airgas, PA, USA) to 200 °C at 5 °C/min, held 2 h, and then cooled to 50 °C

78 in a 20 mL/min flow of 10% H<sub>2</sub>/He. The catalyst was then reduced by increasing the temperature to

79 800 °C at a ramp rate of 5 °C/min under a flow of 10% H<sub>2</sub>/He (20 mL/min). The effluent gas flow

- 80 was fed through a cold trap of liquid nitrogen and acetone and then into a thermal conductivity
- 81 detector (TCD) to determine hydrogen uptake.

82 Pd dispersion and metal particle size were measured with pulse chemisorption using CO as the 83 probe gas. Approximately 50 mg of each catalyst was heated in 20 mL/min of He (Airgas, PA, USA) 84 at 200 °C for 2 h to remove any water or other absorbed species. Next, the catalyst was cooled to 50 85 °C and temperature programmed reduction of the catalyst was performed using a flow of 10% 86 H<sub>2</sub>/He (20 mL/min). Temperature was increased to 450 °C at 5 °C/min and held for 1 h. The sample 87 was then cooled to 40 °C for the pulse CO testing. 20 doses of 10% CO/He (Airgas, PA, USA) were 88 passed over the sample and adsorption peaks were analyzed using a thermal conductivity detector 89 (TCD). Next, 20 mL/min of He flowed over the sample for 60 min to remove physisorbed species. A 90 second round of 10% CO/He pulses was conducted to observe if further CO could be adsorbed. 91 Dispersion and particle size (crystallite size) of the catalysts were calculated using the following: the 92 CO uptake from pulse measurements, the wt% of Pd in the catalyst from ICP analyses. A 1:1 ratio

93 between the CO-adsorbed and Pd-active site was also assumed for the calculations.

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- 94 Nitrogen physisorption was performed in a Micromeritics Tristar II (Micromeritics Corporation,
- 95 Norcross, GA, USA). Approximately 100 mg of each catalyst was heated at 110 °C under vacuum
- 96 for 12 h to degas the catalyst. The nitrogen physisorption isotherms were collected at 77 K. The
- 97 catalyst surface area was estimated using the Brunauer–Emmett–Teller (BET) method within the
- 98 relative pressure range (P/P<sub>0</sub>) of 0.05–0.3 from each isotherm.



101 **Figure S3.** XPS in Ce3d regions for the two catalysts.



103 **Figure S4.** XPS of two catalysts pre and post reaction in the Pd3d and Ce3d regions.



## 106 Figure S5. STEM image and EDS mapping of 4Pd-20CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. (a) STEM image; (b) three

- 107 elementary distribution of Pd, Ce and Al overlapped together showing PdO on alumina and also
- 108 isolated PdO particles; Pd, Ce, Al are color coded as red, green and blue respectively.



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- 110 Figure S6. HAADF-STEM and SEM images of 4Pd-20CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst (Post reaction). (Top left)
- 111 HAADF-STEM; (top right) three elementary distribution of Pd, Ce and Al overlapped together;
- 112 (bottom left) show HAADF-STEM images from the same area in (a); (bottom right) indicates PdO
- 113 and CeO<sub>2</sub> overlap as shown in the overlapped EDS mapping; Pd, Ce, Al are color coded as red, green
- 114 and blue respectively.



## 115

116 Figure S7. PdO shapes and interfaces in 4Pd-20CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. (a,c,d) show PdO nanoparticles

117 are spherical/round in shape, crystalline with lattice images ; the PdO nanoparticles are on the surface

118 of alumina support (black background); (b) the ceria particles at high magnification do not show clear

119 shape, appears to be partly amorphous and crystalline with no or a very few PdO particles embedded.



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Figure S8. PdO shapes and interfaces in 4Pd-20CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst (Post reaction). (a) HAADF-STEM
 image; (b) elementary distribution of Pd, Ce, and Al are overlapped together; (c) STEM image of CeO<sub>2</sub>

123 from (a) at high magnification showing lattice images and with no PdO on ceria; (d, e, f) are the STEM

124 and SEM images from the white rectangular area in (a) showing crystalline PdO nanoparticles on the

125 surface of alumina. The blurred contrast in STEM image (a) is due to the CeO<sub>2</sub> nanoparticles not being

- 126 at the same focus plane of PdO nanoparticles; Pd, Ce, Al are color coded as red, green and blue
- 127 respectively.



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**Figure S9.** HAADF-STEM and SEM images of 20CeO<sub>2</sub>-4Pd/Al<sub>2</sub>O<sub>3</sub> catalyst before reaction. (a) and (c) are

- HAADF-STEM images, while (b) and (d) are their corresponding SEM images from the same area; (c) is a
  magnified image of PdO from the white rectangle area in (a); (e) and (f) are the HAADF-STEM and SEM images
- 132 from the red rectangle area in (a).



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- 134 **Figure S10.** PdO shapes and interface in 20CeO<sub>2</sub>-4Pd/Al<sub>2</sub>O<sub>3</sub> catalyst (Post reaction). (a) STEM images
- of PdO-ceria particles; (b) SEM image from the same area; (c) and (d) clearly show amorphous-like

136 PdO particles embedded on ceria and the PdO-ceria interfaces are diffused.

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150 **Figure S11.** Particle size of PdO in 4Pd-20CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst







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154 **Figure S13**. PdO particle sizes in 20CeO<sub>2</sub>-4Pd/Al<sub>2</sub>O<sub>3</sub> catalyst.



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