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Palladium Nanoparticles Supported on Surface-Modified Metal Oxides for Catalytic Oxidation of Lean Methane

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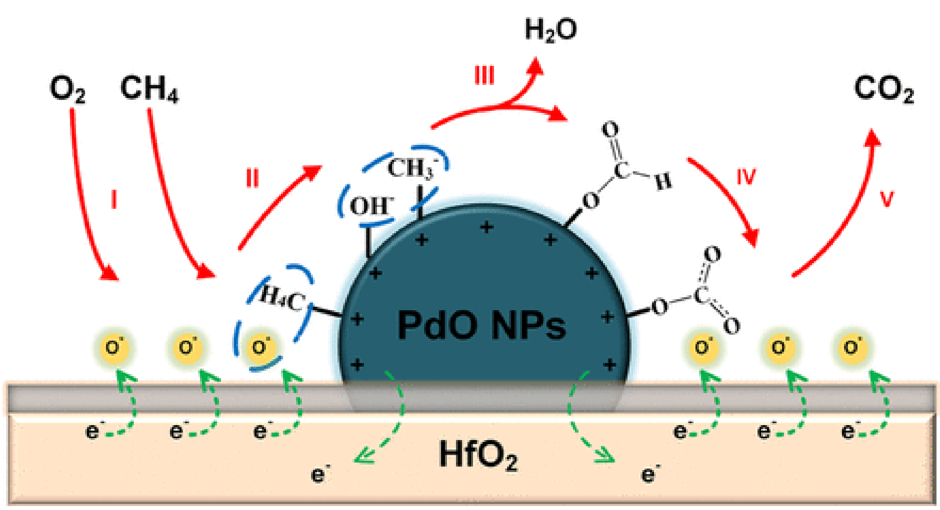
SUBJECTS:

- Catalysts,
- Hydrocarbons,
- Materials,
- Palladium,
- Silicon

Abstract



Palladium nanoparticles (NPs) were successfully deposited on surface-modified metal oxides (mod-MO_x, M = Hf, Ti, Zr, Ce, and Al) and applied as catalyst materials for lean methane combustion. It was found that the surface modification of support materials improved the light-off performance of 1.0Pd/mod-HfO_2 (palladium catalyst supported on surface-modified HfO_2 with a content of 1.0 wt %), 1.0Pd/mod-ZrO_2, and 1.0Pd/mod-CeO_2, but lowered the purification efficiency of 1.0Pd/mod-TiO_2 and 1.0Pd/mod-Al_2O_3 when compared with their 1.0Pd/MO_x counterparts. Over the best-performing 1.0Pd/mod-HfO_2 material, 90% of methane was removed at 317 °C and a space velocity of 60 000 mL g^{-1} h^{-1}, which was 120 °C lower than that required for the untreated 1.0Pd/HfO_2 sample. Detailed characterization of representative HfO_2-related materials showed that the introduced silicon modifier materials, which existed as an amorphous phase covering the HfO_2 surface, could improve the dispersion of palladium nanoparticles due to their steric confinement and strengthen the generation of surface-adsorbed oxygen species via electron transfer. We believe that this surface modification strategy, which could promote the catalytic performance of palladium nanoparticles supported on other cost-effective host materials as well, provides a feasible method for the design of methane combustion catalysts with excellent low-temperature performance.

KEYWORDS:

- palladium
- surface modification
- silicon modifier
- hafnium dioxide
- leanShow More

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.0c02614.

- Preparation, characterization, and performance evaluation of catalyst materials; light-off curves of palladium catalysts supported on various metal oxides (Figure S1) and fumed-silica (Figure S2A); XRD patterns of fumed-silica and its supported palladium catalyst (Figure S2B); representative microscopic images of HfO_2-supported samples (Figure S3); H_2-TPR (Figure S4A) and O_2-TPD (Figure S4B) profiles of selected samples; on-stream methane combustion over 1.0Pd/mod-HfO_2 without (Figure S5A) and with (Figure S5B) 5 vol % water vapor; specific performance data of samples supported on various metal oxides (Table S1); performance of reported Pd catalysts in published literature (Table S2); and the assignment of intermediates during methane combustion in this work (Table S3) (PDF)

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Supporting information for

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METHODS

Preparation of palladium catalysts supported on surface-modified metal oxides

3 g of support powder and 1.65 mL triethoxy(octyl)silane (TEOOS, 97%) were first dispersed in 60 mL toluene by sonication for 20 min. Under vigorous stirring, the resultant mixture was refluxed at 110 °C

for 3 h, then collected by centrifugation (6000 rpm for 3 min) and washed abundantly with toluene. Finally, the hydrophobic supports were obtained by drying under -0.09 MPa vacuum and stored as support materials for palladium catalysts.

Supported palladium catalysts were prepared by wetness impregnation method. For catalysts with a nominal Pd content of 1.0 wt%, 5.3 mL of palladium acetate solution (2 mg/mL, dissolved in toluene) was first stirred with 500 mg of hydrophobic support powder for 10 min, then the mixture was sonicated for another 30 min and dried at 70 °C under vacuum for 8 h before the final calcination (500 °C for 3 h).

Characterization of catalysts

Ion-coupled plasma atomic emission spectroscopy was performed to ensure the actual loading of Pd by a Optima 7300DV (PerkinElmer Co., USA). Before CO chemisorption (chemstar TPx chemisorption instrument, Quantachrome Co., USA), the samples were reduced in 10% H_2/Ar at 300 °C for 1 h, and the volume of pulse loop was calibrated to be 516μL. Nitrogen-physisorption was operated at ~77K on a Micromeritics Tristar III 3020 instrument to obtain the BET surface areas of discussed samples. Samples X-ray diffraction (XRD) patterns were obtained with a Rigaku TTR-III diffractor using Cu Kα radiation (40 kV, 200 mA). The diffraction spectra were recorded in

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