

Yttrium stabilization and Pt addition to Pd/ZrO₂ catalyst for the oxidation of methane in the presence of ethylene and water

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Details of catalyst characterization

Crystalline structures were analyzed by X-ray powder diffractometer (Bruker D2 Advance) employing Cu K α radiation ($\lambda = 0.15418$ nm) at 30 kV and 40 mA.

Specific surface areas and pore volumes were determined by N₂ physisorption at -196 °C using Micromeritics ASAP-2020. The catalysts (0.5 g) were first degassed for 6 h at 100 °C. Specific surface area was calculated in the relative pressure (P/P_0) range of 0.01–0.2 assuming a cross-sectional area of 0.162 nm² for N₂. The loading of active metal component was measured by X-ray fluorescence spectroscopy.

Carbon monoxide (CO) chemisorption was performed in a pulse mode with the Micromeritics ASAP-2020 apparatus. Prior to the measurements, 0.05 g of the sample was thermally treated in a 5 % O₂/He stream at 120 °C for 30 min to remove physically adsorbed water and other impurities. The sample was cooled down to room temperature, and heated to 300 °C with a heating rate of 10 °C/min in 5% H₂/Ar at a flow rate of 50 mL/min for 30 min. After the reduction, the sample was purged with He gas at the same temperature for 20 min. After cooling to ambient temperature, 10% CO/He gas was introduced for CO chemisorption. The CO loop gas was used for each pulse (a sample loop of 0.543 mL) and the pulse injections were repeated until saturation. The metal dispersion in each catalyst was calculated from the amount of CO adsorbed, assuming the stoichiometry factor (SF) for Pd/CO to be 1.0, as follows:

$$\text{Dispersion (\%)} = \frac{100 \times V_s \times S_F \times M_W}{S_W \times F_n \times 22,414}$$

where V_S is the cumulative volume of adsorbed CO (cm^3 at STP), MW is the molecular weight of Pd metal (g/mol), SW is the weight of the sample, and F_n is the Pd fraction in relation to the total weight of the catalyst sample.

Temperature-programmed desorption (O_2 -TPD) analysis was carried out using Micromeritics AutoChem II 2920 apparatus. Desorbed species were analyzed by quadrupole mass spectrometry (Balzers QMS 200 Omnistar). The catalyst (0.2 g) was fixed in a quartz reactor by packing quartz wool at both ends. Prior to the measurement, the sample was oxidized in 5% O_2 in He flow ($50 \text{ cm}^3/\text{min}$) at $800 \text{ }^\circ\text{C}$ for 1 h. After cooling the sample to room temperature under 5% O_2 in He flow, the feed gas was switched to pure He stream ($50 \text{ cm}^3/\text{min}$) for O_2 -TPD. The sample was ramped from room temperature to $850 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C}/\text{min}$.

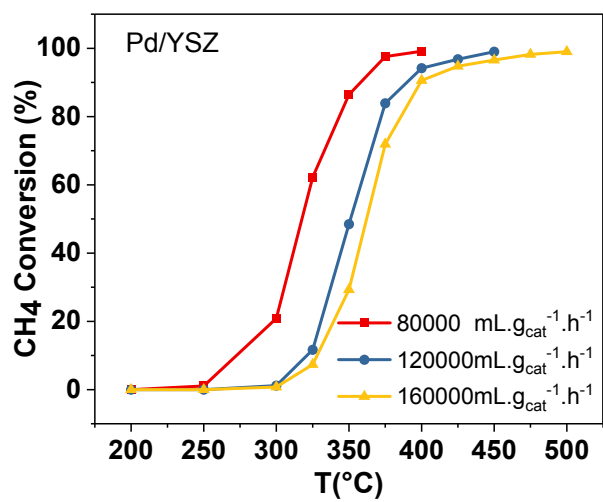


Figure S1. Dependency of Methane conversion on GHSV over Pd/YSZ catalyst.

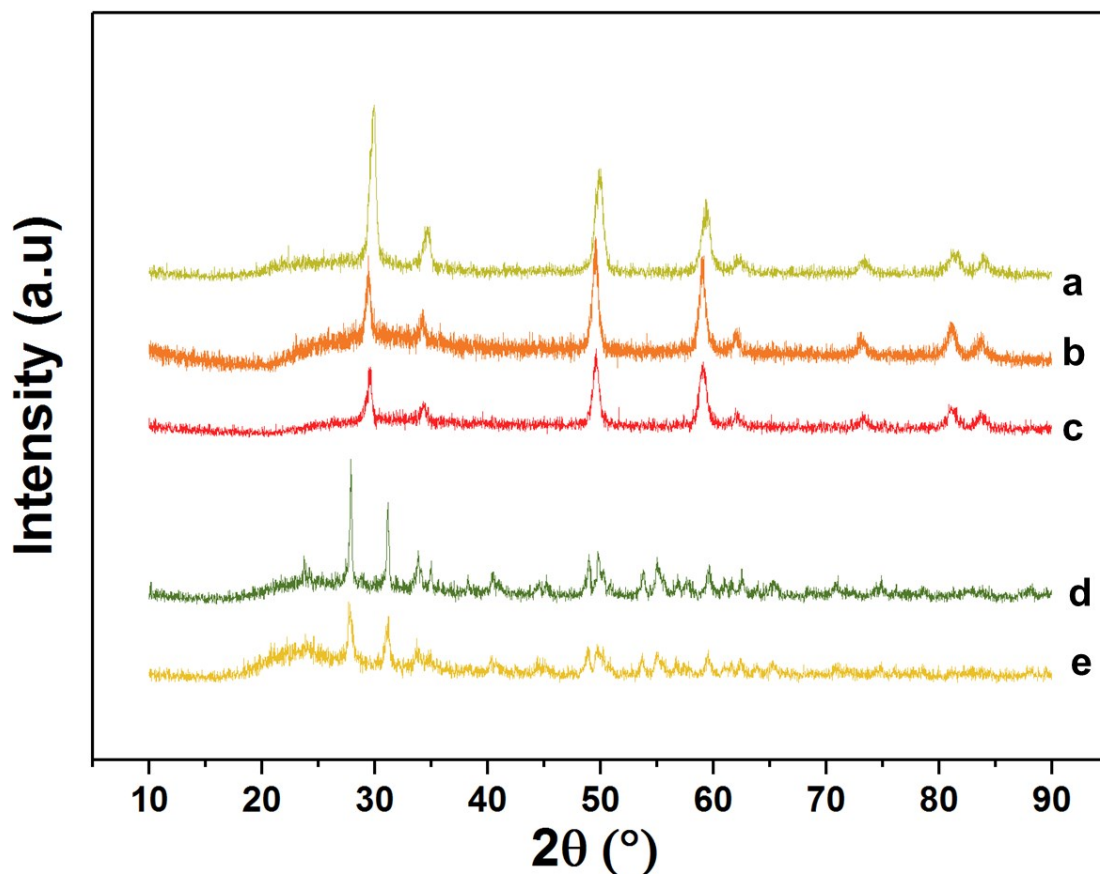


Figure S2. XRD patterns of spent catalyst after cyclic study in dry and wet conditions over the temperature range of 350-600 °C. (a) Pd/YSZ (b) Pt/YSZ (c) PdPt/YSZ (d) Pd/ZrO₂ (e) PdPt/ ZrO₂.

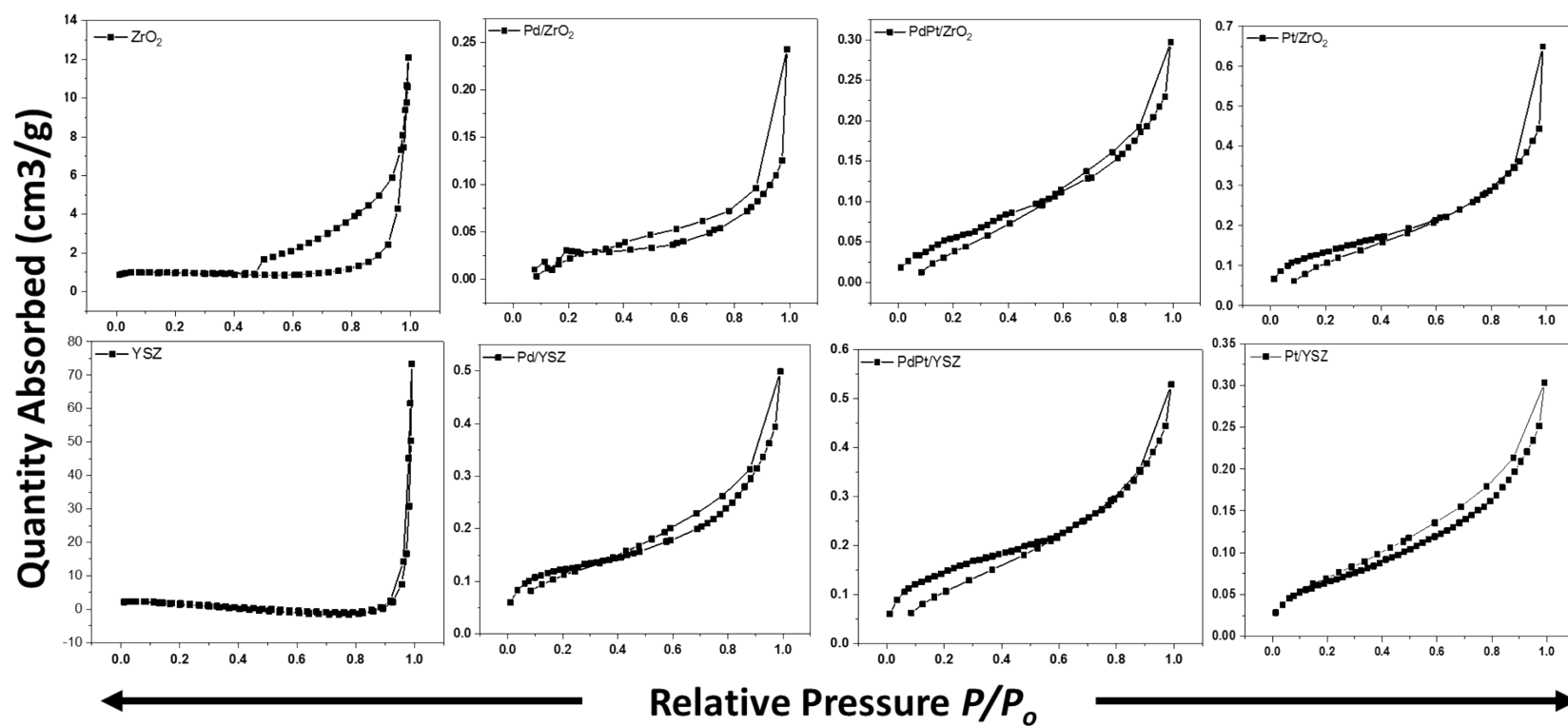


Figure S3. N₂ Adsorption-desorption isotherms of supports (ZrO₂ and YSZ) and Pd, Pt, PdPt catalysts.

Table S1. BET surface area of prepared pristine catalysts

Catalyst	S_{BET} (m² g⁻¹)	Pore diameter (nm)^a	Average pore volume (cm³g⁻¹)	BET Surface by Krypton gas
ZrO ₂	3.4	41.3	1.8	5.43
YSZ	9.0	12.1	0.7	9.198
Pd/ZrO ₂	2.8	24.4	0.09	2.745
Pd/YSZ	8.9	10.9	0.10	-
PtPd/ZrO ₂	2.8	10.5	0.01	-
PtPd/YSZ	4.4	8.2	0.09	-
Pt/ZrO ₂	4.2	8.0	0.02	-
Pt/YSZ	10.6	8.1	0.01	-