Supporting information

Synthesis of highly stable Pd@CeO_2 catalyst for methane combustion with the synergistic effect of urea and citric acid

Guohui Cai, Wei Luo, Yihong Xiao, Yong Zheng, Fulan Zhong, Yingying Zhan*, Lilong Jiang

National Engineering Research Center of Chemical Fertilizer Catalyst, College of Chemical Engineering, Fuzhou University, Gongye Road No.523, Fuzhou 350002, Fujian, P. R. China

*Corresponding author:

PhD. Yingying Zhan

Tel: +86 0591 83731234-8601, Fax: +86 0591 83709796, E-mail: zhanyingying@fzu.edu.cn

1. Synthesis of I-Pd/CeO_2-*T* catalyst by impregnation method

1.1. Synthesis of catalyst carriers

In a typical synthesis, 0.21 g of cerium nitrate, 0.03 g of urea and 0.051 g of citric acid were successively dissolved in a water/ethanol mixture with a volume ratio of 7:1 at room temperature. The resultant mixture was vigorously stirred for 20 min, then 0.3 mL of hydrogen peroxide solution was added. Afterward, the final solution was sealed into an autoclave with a Teflon-lined, heated to 120 ℃ and maintained for 24 h. The as-prepared product was centrifuged, washed with deionized water and ethanol repeatedly until pH ≈ 7, and subsequently dried at 60 ℃ for 7 h. The product was further calcined at 400 ℃ with a ramping rate of 1 ℃·min^{-1} and held for 2 h. After naturally cooling to room temperature, the catalyst carriers CeO_2 was obtained.

1.2. Synthesis of catalysts

Taking the as-synthesized CeO_2 as a carrier, and $Pd(NO_3)_2$ solution as a precursor, the supported Pd/CeO_2 catalysts with a constant Pd loading of 1 wt% (theoretic value) were prepared by the incipient wetness impregnation method at room temperature. The product was calcined at 400 ℃ for 4 h (1 ℃·min^{-1} ramping rate), then calcined at 600 ℃ or 1000 ℃ for 2 h at the same speed. The prepared catalysts were referred to I-Pd/CeO_2-*T*, where *T* represented the calcination temperature (*T* = 600, 1000 ℃).

2. Synthesis of C-Pd/CeO_2-*T* catalyst by coprecipitation method

In a typical synthesis, 2.0 g of cerium nitrate and a specific amount of $Pd(NO_3)_2$ solution with a theoretic Pd loading of 1 wt% were mixed and stirred for 20 min at room temperature. The obtained solution and NaOH solution were added into the distilled water, adjusting the final pH to 11. The as-prepared product was centrifuged, washed with deionized water and ethanol,

and then dried at 60 ℃ for 7 h. The product was calcined at 400 ℃ for 4 h (1 ℃ min^{-1} ramping rate), then calcined at 600 ℃ or 1000 ℃ for 2 h with the same heating rate. The prepared samples were denoted as C-Pd/CeO_2-*T*, where *T* represented the calcination temperature (*T* = 600, 1000 ℃).

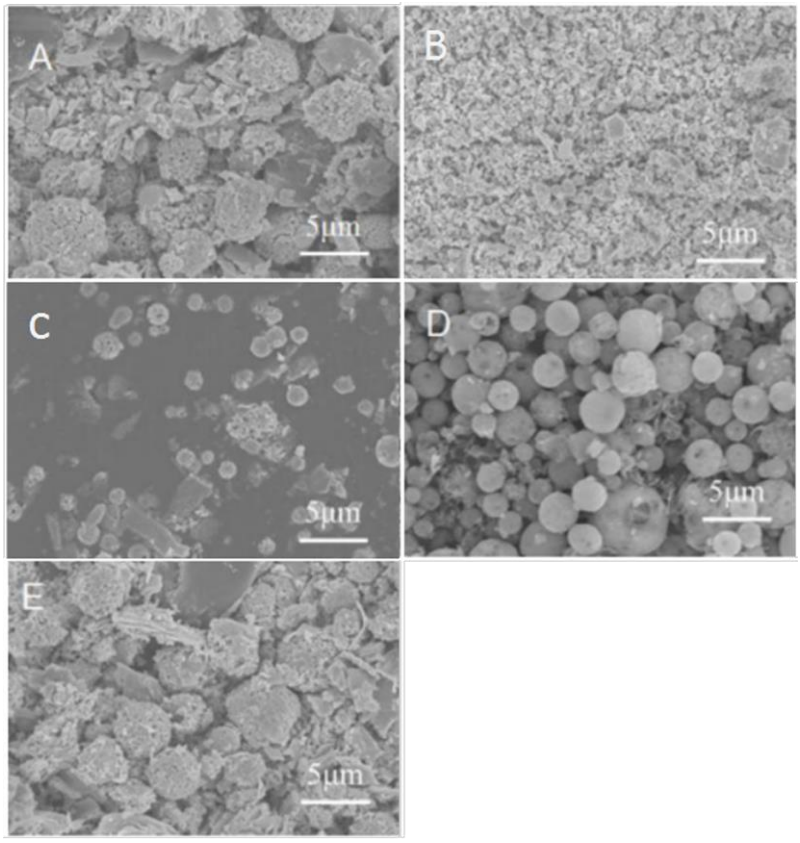

Figure S1. SEM images of H-Pd@CeO_2-600(t) catalysts (A–E: t = 6, 12, 18, 24, 30).

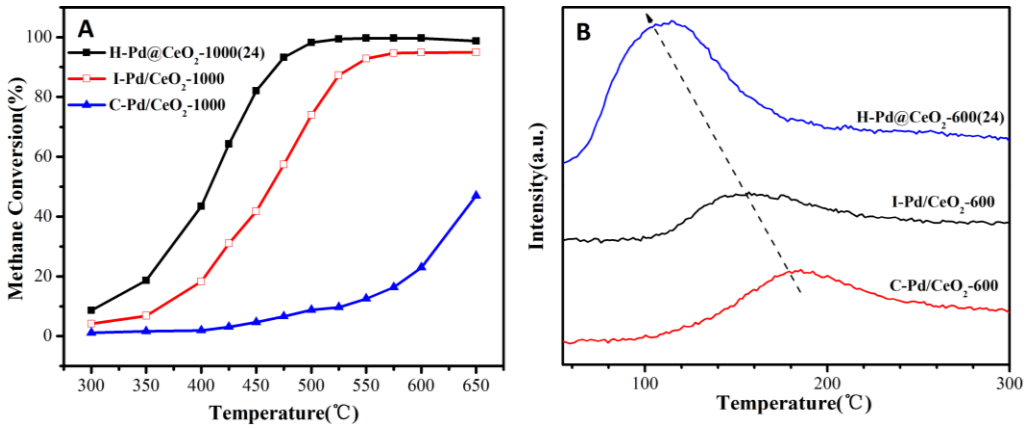

Figure S2. (A) Methane conversion and (B) CO_2-TPD curves of H-Pd@CeO_2-600(24), I-Pd/CeO_2-600 and C-Pd/CeO_2-600.

Table S1 CO pulse adsorption results of the catalysts

Catalyst	Pd Dispersion(%)	Pd particle size (nm)
H-Pd/CeO_2-600(6)	5.34	21.0
H-Pd/CeO_2-600(12)	42.4	2.6
H-Pd/CeO_2-600(18)	40.3	2.8
H-Pd@CeO_2-600(24)	43.4	2.6
H-Pd/CeO_2-600(30)	42.5	2.6
I-Pd/CeO_2-600	16.1	7.0
C-Pd/CeO_2-600	6.1	18.6

Table S2 The relevant parameters of the catalysts obtained from XPS results

Catalyst	Pd/Ce atomic ratio	Ce^{3+} in Ce(%)	Ce^{4+}/Ce^{3+} atomic ratio
H-Pd/CeO_2-600(6)	0.0189	5.74	16.4
H-Pd/CeO_2-600(12)	0.0212	4.48	21.3
H-Pd/CeO_2-600(18)	0.0145	5.51	17.1
H-Pd@CeO_2-600(24)	0.0138	12.6	6.9
H-Pd/CeO_2-600(30)	0.0214	12.5	7.0