**Supporting Information for:**

# Fabrication of $Pd_3$@Beta for catalytic combustion of VOC by efficient $Pd_3$ cluster and seed-directed hydrothermal syntheses

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**Synthesis procedure of $[Pd_3Cl(PPh_2)_2(PPh_3)_3]^+$ Cluster**: Firstly, the $PdCl_2$ solution was prepared by dissolving 8 mmol $PdCl_2$ in 16 mmol HCl solution, and the resulted solution was then diluted to 10 mL. Then 10 mL THF was dropped into the above solution with vigorous stirring for 10 min. Triphenylphosphine was added to the mixture and then stirred at room temperature for 10 min, the mixture became york-yellow. Then ethanol solution of $NaBH_4$ was added into the mixture. After a continuous stirring for 1.5 h, the derived catalyst was centrifugated at 10000 ppm to remove undissolved triphenylphosphine. The supernatant was then transferred to 10 mL eggplant type flask and evaporated to dryness under vacuum on a rotary evaporator. The remaining solid was re-dissolved in $CH_2Cl_2$, successively washed with water and ethanol, and then evaporated to dryness. The obtained product was the $Pd_3Cl$ cluster. [1] In addition, UV−vis absorption spectra presents the characteristic bands centered at 485, 418, and 340 nm of the $Pd_3Cl$ cluster (Fig. S1).

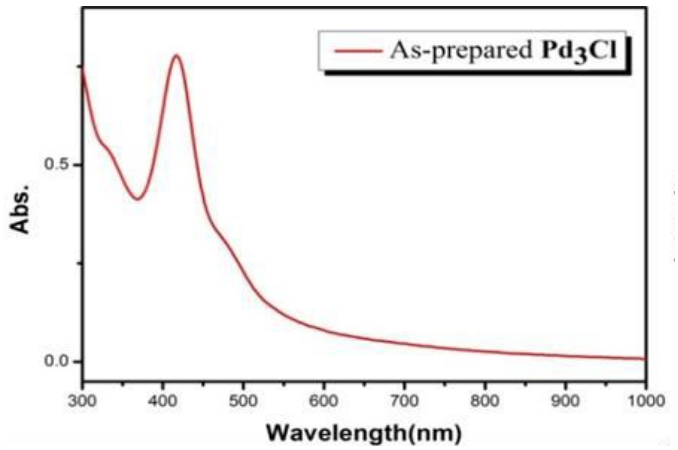


**Fig. S1.** UV-vis spectrum of $Pd_3Cl$.

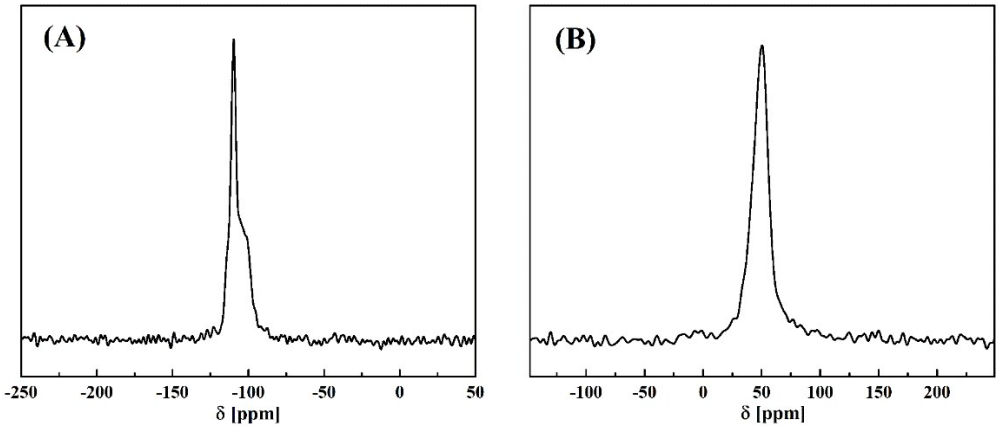


**Fig. S2.** Solid-state (A) $^{29}$Si MAS and (B) $^{27}$Al MAS NMR spectra of $Pd_3$@Beta.

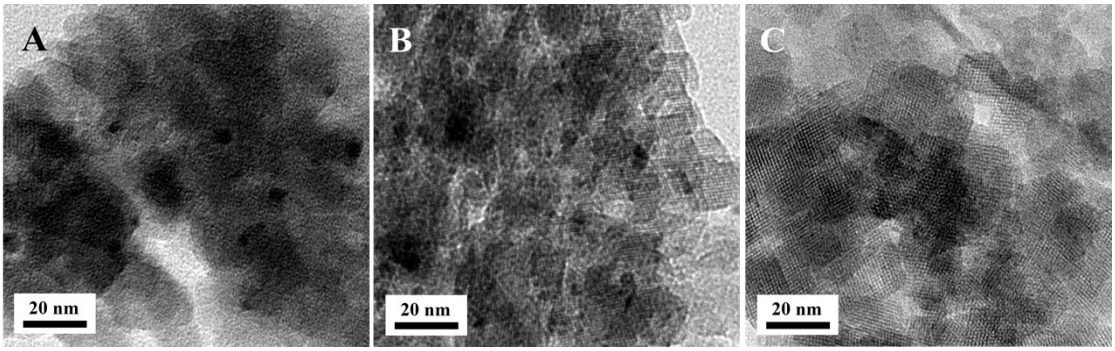


**Fig. S3**. TEM images of samples after toluene oxidation at 230 °C for 100 h: (A) Pd/Beta, (B) $Pd_3$/Beta and (C) $Pd_3$@Beta.

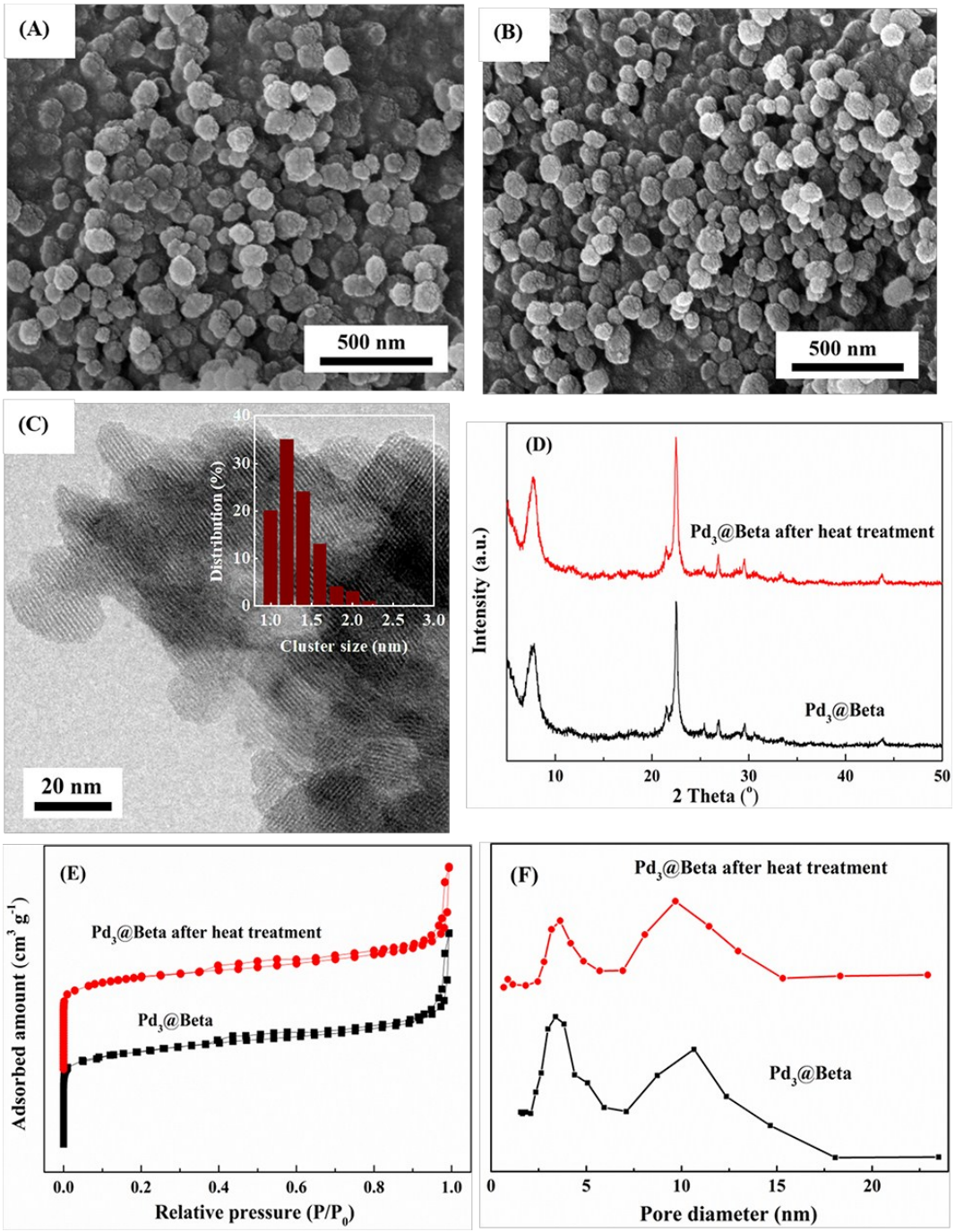


**Fig. S4.** SEM images of $Pd_3$@Beta (A). SEM images and HR-TEM images with corresponding particle size distribution of $Pd_3$@Beta after calcination at 600 °C for 1 h (B, C). XRD patterns, $N_2$ adsorption/desorption isotherms and pore-size distributions for $Pd_3$@Beta and $Pd_3$@Beta after calcination at 600 °C for 1 h (D-F).

**Table S1**. The values of $T_{50}$ and $T_{98}$ and Pd dispersion in the Pd loading rang of 0.1-0.9 wt% over $Pd_3$@Beta sample.

| Pd loading (wt%) | $T_{50}$ (°C) | $T_{98}$ (°C) | $D_{Pd}$ (%) |
|---|---|---|---|
| 0.1 | 198 | 220 | 61.9 |
| 0.3 | 181 | 202 | 59.8 |
| 0.5 | 169 | 187 | 57.3 |
| 0.7 | 161 | 180 | 50.9 |
| 0.9 | 159 | 175 | 45.1 |

**Table S2**. Rate constants (*k*) for toluene combustion in the temperature range of 135-175 °C.

| Catalyst | 135 °C | 140 °C | 145 °C | 150 °C | 155 °C | 160 °C | 165 °C | 170 °C | 175 °C |
|---|---|---|---|---|---|---|---|---|---|
| $Pd_3$@Beta | 0.056 | 0.074 | 0.092 | 0.12 | -- | -- | -- | -- | -- |
| $Pd_3$/Beta | -- | -- | -- | 0.030 | 0.041 | 0.054 | 0.075 | -- | -- |
| Pd/Beta | -- | -- | -- | -- | -- | 0.0089 | 0.014 | 0.022 | 0.034 |

**Table S3**. Pre-exponential factor, activation energy and correlation coefficients ($R^2$) for toluene combustion on these prepared catalysts.

| Catalyst | Metal loading (wt%) | A ($s^{-1}$) | Ea(kJ/mol) | $R^2$ | Ref |
|---|---|---|---|---|---|
| $Pd_3$@Beta | 0.5 | $3.10\times10^7$ | 70 | 0.998 | This work |
| $Pd_3$/Beta | 0.5 | $5.30\times10^8$ | 94 | 0.993 | This work |
| Pd/Beta | 0.5 | $1.12\times10^{11}$ | 145 | 0.996 | This work |
| 3DOM-structured $LaMnO_3$ | | | 57-62 | | 2 |
| Pt/$CeO_2$-$ZrO_2$-$Bi_2O_3$/$\gamma$-$Al_2O_3$ | 7.0 | | 62 | | 3 |
| Pd/SBA-15 | 0.5 | | 65-145 | | 4 |
| Pt-O/Beta | 1.0 | $2.02\times10^6$ | 66 | 0.995 | 5 |
| AuPd/3DOM $Co_3O_4$ | 1.99 | | 33 | | 6 |
| Pd/3DOM $Co_3O_4$ | 0.99 | | 90 | | 6 |
| Pt-Pd/$Al_2O_3$ | 0.5 | | 43 | | 7 |
| Pt@$Cr_2O_3$ | 0.82 | | 84.1 | | 8 |
| Pd/meso-$Cr_2O_3$ | 1.0 | | 45 | | 9 |
| Pt/$CeO_2$-1.3 | 0.25 | | 82.9 | | 10 |
| Pt/$CeO_2$- nanorod | 0.2 | | 77.1 | | 11 |
| Pt/HPMOR | 1.0 | | 104-156 | | 12 |
| Pt@PZN-2 | 0.5 | | 141 | | 13 |

**Table S4**. Turnover frequencies (TOFs, $mmol_{toluene}/(mol_{Pd}^{0}\cdot s)$) for toluene combustion in the temperature range of 135-175 °C.

| Catalyst | 135 °C | 140 °C | 145 °C | 150 °C | 155 °C | 160 °C | 165 °C | 170 °C | 175 °C |
|---|---|---|---|---|---|---|---|---|---|
| $Pd_3$@Beta | 2.48 | 7.79 | 6.72 | 9.21 | -- | -- | -- | -- | -- |
| $Pd_3$/Beta | -- | -- | -- | 1.68 | 3.12 | 5.25 | 8.10 | -- | -- |
| Pd/Beta | -- | -- | -- | -- | -- | 1.39 | 2.68 | 4.83 | 8.45 |

## Reference


1 F. Fu, J. Xiang, H. Cheng, L. Cheng, H. Chong, S. Wang, P. Li, S. Wei, M. Zhu and Y. Li, *ACS Catal.*, 2017, **7**, 1860-1867.

2 Y. Liu, H. Dai, Y. Du, J. Deng, L. Zhang, Z. Zhao and C. T. Au, *J. Catal.*, 2012, **287**, 149-160.

3 T. Masui, H. Imadzu, N. Matsuyama and N. Imanaka, *J. Hazard. Mater.*, 2010, **176**, 1106-1109.

4 C. He, X. Zhang, S. Gao, J. Chen and Z. Hao, *J. Ind. Eng. Chem.*, 2012, **18**, 1598-1605.

5 C. Chen, J. Zhu, F. Chen, X. Meng, X. Zheng, X. Gao and F.-S. Xiao, *Appl. Catal., B*, 2013, **140-141**, 199-205.

6 S. Xie, J. Deng, S. Zang, H. Yang, G. Guo, H. Arandiyan and H. Dai, *J. Catal.*, 2015, **322**, 38-48.

7 X. Liu, Q. Zhang, P. Ning, T. Tang, J. Hu and W. Su, *Catal. Commun.*, 2018, **115**, 26-30.

8 X. Chen, X. Chen, S. Cai, J. Chen, W. Xu, H. Jia and J. Chen, *Chem. Eng. J.*, 2018, **334**, 768-779.

9 Z. Wu, J. Deng, S. Xie, H. Yang, X. Zhao, K. Zhang, H. Lin, H. Dai and G. Guo, *Micropor. Mesopor. Mat*, 2016, **224**, 311-322.

10 R. Peng, S. Li, X. Sun, Q. Ren, L. Chen, M. Fu, J. Wu and D. Ye, *Appl. Catal., B*, 2018, **220**, 462-470.

11 R. Peng, X. Sun, S. Li, L. Chen, M. Fu, J. Wu and D. Ye, *Chem. Eng. J.*, 2016, **306**, 1234-1246.

12 J. Zhang, C. Rao, H. Peng, C. Peng, L. Zhang, X. Xu, W. Liu, Z. Wang, N. Zhang and X. Wang, *Chem. Eng. J.*, 2018, **334**, 10-18.

13 G. Liu, Y. Tian, B. Zhang, L. Wang and X. Zhang, *J. Hazard. Mater.*, 2019, **367**, 568-576.