Supplementary material

Effect of Support on Complete Hydrocarbon Oxidation over Pd-Based Catalysts

Tatyana Tabakova [1,*], Bozhidar Grahovski [1], Yordanka Karakirova [1], Petya Petrova [1], Anna Maria Venezia [2], Leonarda Francesca Liotta [2] and Silviya Todorova [1,3,*]

[1] Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria; grahovski@ic.bas.bg (B.G.); daniepr@ic.bas.bg (Y.K.); petia@ic.bas.bg (P.P.)

[2] Istituto per lo Studio dei Materiali Nanostrutturati, CNR, Via Ugo La Malfa, 153, 90146 Palermo, Italy; annamaria.venezia@cnr.it (A.M.V.); leonardafrancesca.liotta@cnr.it (L.F.L.)

[3] National Centre of Excellence Mechatronics and Clean Technologies, Kliment Ohridski Blvd., 8, 1756 Sofia, Bulgaria

* Correspondence: tabakova@ic.bas.bg (T.T.); todorova@ic.bas.bg (S.T.)

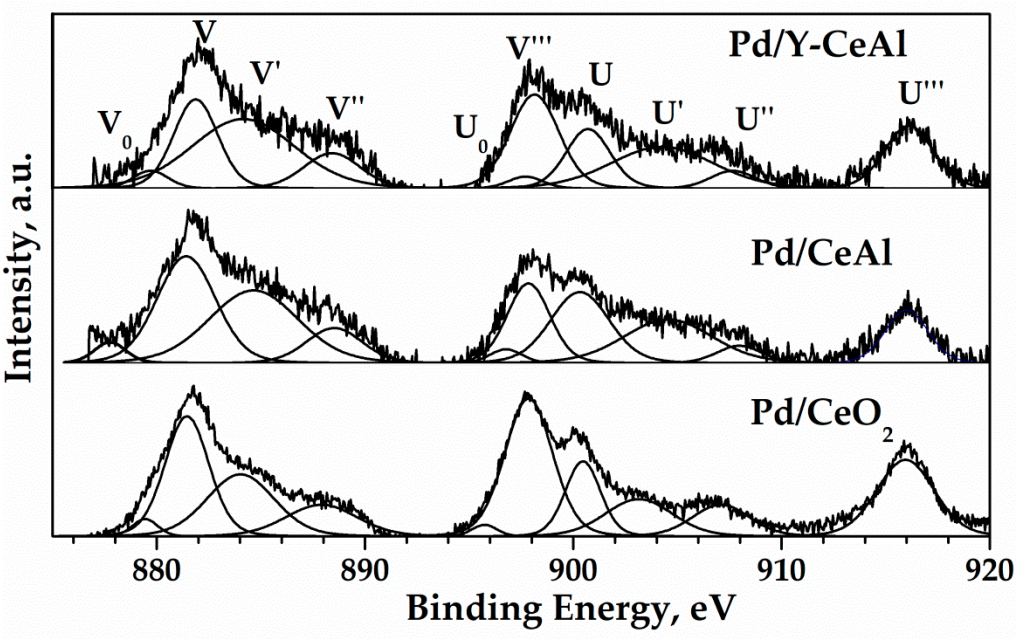

Figure S1. Ce 3d XP spectra of the studied catalysts

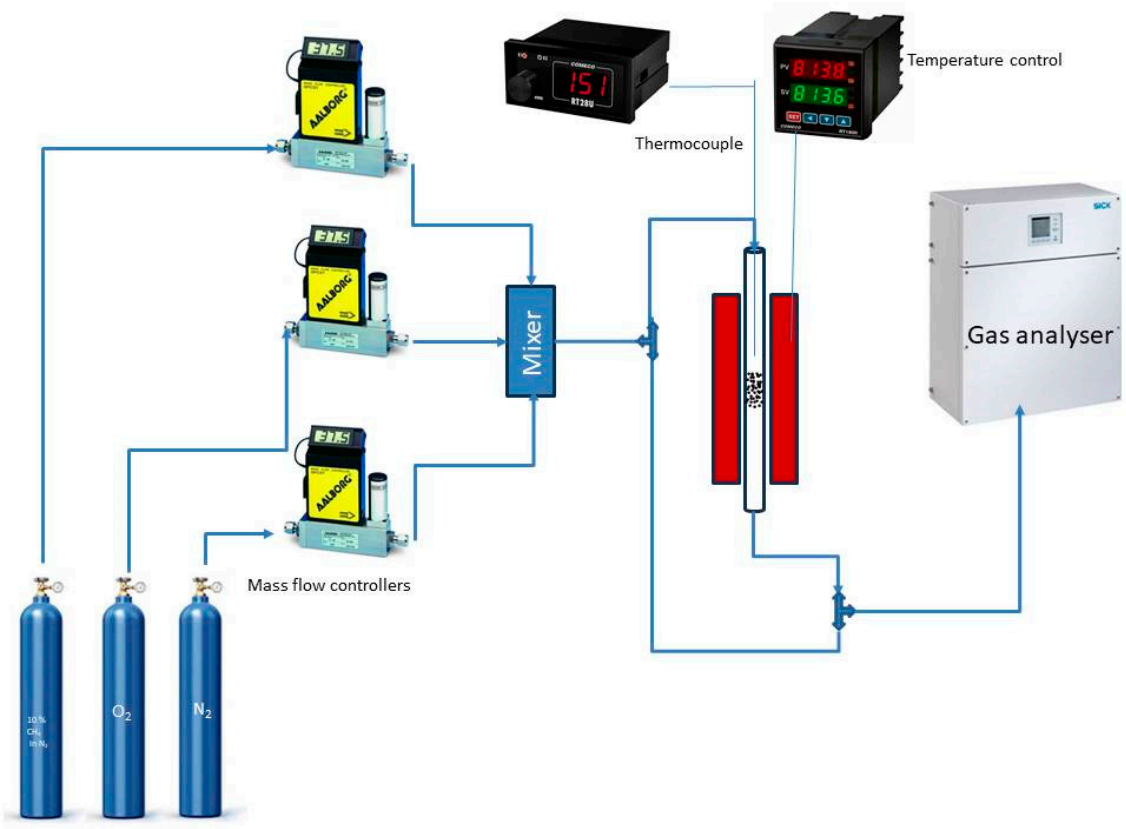

Figure S2. Scheme of the catalytic setup used for CH_4 oxidation measurements.

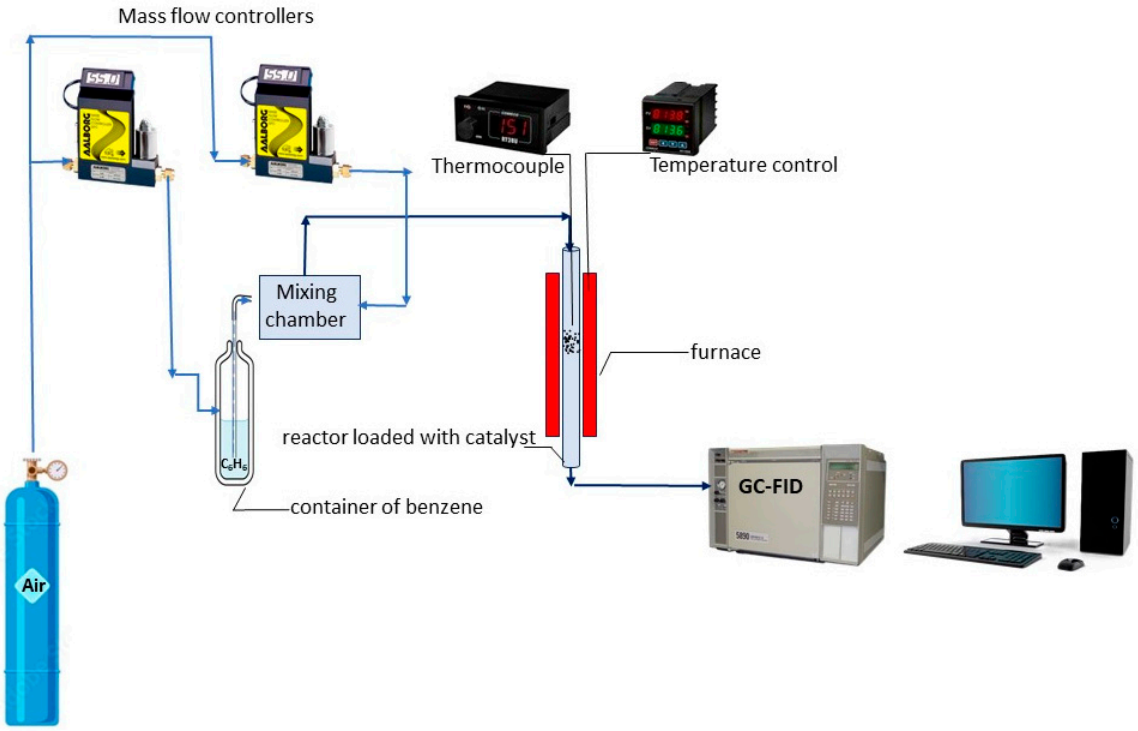

Figure S3. Scheme of the catalytic setup used for benzene oxidation measurements.

Table S1. Catalytic performance comparison between CH_4 oxidation over Pd-based catalysts developed in this work and reported reference literature.

Catalyst	Preparation Method	CH_4 Concentration	Space Velocity	Oxidation Efficiency [1] T_{90}/°C	Ref.
1 Pd/γ-Al_2O_3	Deposition-precipitation	1000 ppmv CH_4, 25 vol.% O_2, balanced Ar	20 000 h^{-1}	355	this work
1 Pd/30 CeO_2-Al_2O_3	CeO_2-Al_2O_3 by mechanochemical mixing	1000 ppmv CH_4, 25 vol.% O_2, balanced Ar	20 000 h^{-1}	300	this work
1 Pd/CeO_2	Deposition-precipitation	1000 ppmv CH_4, 25 vol.% O_2, balanced Ar	20 000 h^{-1}	300	this work
4 Pd-20 CeO_2/Al_2O_3	Sequential impregnation	1 vol.% CH_4, 4 vol.% O_2 balance N_2	45 000 $mL \cdot g^{-1} \cdot h^{-1}$	~ 275	1
20 CeO_2-4 Pd/Al_2O_3	Sequential impregnation	1 vol.% CH_4, 4 vol.% O_2 balance N_2	45 000 $mL \cdot g^{-1} \cdot h^{-1}$	~ 350	1
0.5 Pd/Co/Al_2O_3	Impregnation	500–1500 ppm CH_4, O_2 1–20 vol.%, H_2O 0–2 vol.%, balance to 100% Ar	60 000 h^{-1}	420	2
0.5 Pd/Co/LaCe/Al_2O_3	Impregnation	500–1500 ppm CH_4, O_2 1–20 vol.%, H_2O 0–2 vol.%, balance to 100% Ar	60 000 h^{-1}	430	2
0.18 Pd/2 CeO_2-Al_2O_3	Sol–gel method	0.5 vol.% CH_4, 1 vol.% O_2, 98.5 vol.% He	52 000 h^{-1}	~ 425	3
1 Pd/CeO_2	Solvothermal method	1 vol.% CH_4, 4 vol.% O_2, 95 vol.% N_2.	60 000 $mL \cdot g^{-1} \cdot h^{-1}$	535	4
1 Pd/20 CeO_2-Al_2O_3	Solvothermal method	1 vol.% CH_4, 4 vol.% O_2, 95 vol.% N_2	60 000 $mL \cdot g^{-1} \cdot h^{-1}$	410	4

Table S2. Comparison of benzene conversion over Pd-based catalysts developed in this work and reported reference literature.

Catalyst	Preparation Method	Benzene Concentration (ppm)	Space Velocity	Oxidation Efficiency [1] T_{90}/°C	Ref.
2.66 Pd/γ-Al_2O_3	Commercial catalyst (Hangzhou Kaiming Catalysts Co. Ltd, China)	1000	3150 $mL \cdot h^{-1}$	250	5
0.5 Pd/γ-Al_2O_3	Impregnation	2600	54,000 $mL \cdot g^{-1} \cdot h^{-1}$	250	6
0.5 Pd/γ- Al_2O_3–Ce	Impregnation	2600	54,000 $mL \cdot g^{-1} \cdot h^{-1}$	T_{100} /280	6
1 Pd-Na/Al_2O_3	Wet impregnation	1500	90,000 $mL \cdot g^{-1} \cdot h^{-1}$	193	7
1 Pd-5Mo/Al_2O_3	Incipient wetness impregnation	0.2 vol.% C_6H_6, 20 vol.% O_2, N_2	4800 h^{-1}	190	8
1 Pd/γ-Al_2O_3	Deposition-precipitation	1314	4000 h^{-1}	180	this work

0.5 Pd/kit-CeO_2	Biogenic synthesis	1000	20,000 $mL \cdot g^{-1} \cdot h^{-1}$	187	9
0.3 Pd-10Ce/Silica-pillared clays	Impregnation	1000	20,000 h^{-1}	T_{100}/280	10
0.2 Pd/6Ce-pearl shell powder	Impregnation, reduction with $N_2H_4.xH_2O$	1000	20,000 h^{-1}	~285	11
1 Pd/CeO_2	Deposition-precipitation	1314	4000 h^{-1}	150	12
1 Pd/Y-CeO_2	Y-CeO_2 by co-precipitation	1314	4000 h^{-1}	150	12
1 Pd/CeAl	CeO_2-Al_2O_3 by mechanochemical mixing	1314	4000 h^{-1}	150	this work
1 Pd/Y-CeAl	Y/CeO_2-Al_2O_3 by mechanochemical mixing	1314	4000 h^{-1}	100	this work
1 Pd/5 Fe-CeO_2	5 Fe-CeO_2 by mechanochemical mixing	1314	4000 h^{-1}	180	13
3 Au/5 Fe-CeO_2	5 Fe-CeO_2 by mechanochemical mixing	1314	4000 h^{-1}	200	13
0.5 Pt/4.5 Fe-zeolite X	Wet impregnation	1314	4000 h^{-1}	240	14

References:

1. Fertal, D.; Bukhovko, M.; Ding, Y.; Billor, M.; Banerjee, A. Particle size and PdO support interactions in PdO/CeO_2-γAl_2O_3 catalysts and effect on methane combustion, *Catalysts* **2020**, *10*, 976.
2. Todorova, S.; Naydenov, A.; Velinova, R.; Kolev, H.; Larin, A.V.; Stoyanova, D.; Shopska, M.; Tenchev, K.; Stefanov, P. Pd–MeOx/Al2O3 (Me = Co, La, Ce) catalysts for methane combustion. *React. Kin. Mech. Catal*. **2019**, *126* (2), 663–678.
3. Ramírez-López, R.; Elizalde-Martinez, I.; Balderas-Tapia, L. Complete catalytic oxidation of methane over Pd/CeO_2-Al_2O_3: The influence of different ceria loading. *Catal. Today* **2010**, *150*, 358–362.
4. Yang, X.; Du, C.; Guo, Y.; Guo, Y.; Wang, L.; Wang, Y.; Zhan, W. Al_2O_3 supported hybrid Pd–CeO_2 colloidal spheres and its enhanced catalytic performances for methane combustion. *J. Rare Earths* **2019**, *37*, 714–719.
5. Liu, J.; Wang, H.; Chen, Y.; Yang, M.; Wu, Y. Effects of pretreatment atmospheres on the catalytic performance of Pd/γ-Al_2O_3 catalyst in benzene degradation. *Catal. Commun*. **2014**, *46*, 11–16.
6. Padilla, J. M.; Del Angel, G.; Navarrete, J. Improved Pd/γ-Al_2O_3-Ce catalysts for benzene combustion. *Catal. Today* **2008**, *133–135*, 541–547.
7. Kang, S.; Wang, M.; Zhu, N.; Wang, C.; Deng, H.; He, H. Significant enhancement in water resistance of Pd/Al_2O_3 catalyst for benzene oxidation by Na addition. *Chin. Chem. Lett.* **2019**, *30*, 1450–1454.
8. He, Z.; He, Z.;Wang, D.; Bo, Q.; Fan, T.; Jiang, Y. Mo-modified Pd/Al_2O_3 catalysts for benzene catalytic combustion. *J. Environ. Sci.* **2014**, *26*, 1481–1487.
9. Guo, Y.; Gao, Y.; Li, X.; Zhuang, G.; Wang, K.; Zheng, Y.; Sun, D.; Huang, J.; Li, Q. Catalytic benzene oxidation by biogenic Pd nanoparticles over 3D-ordered mesoporous CeO_2. *Chem. Eng. J.* **2019**, *362*, 41–52.
10. Zhao, B.; Cheng, Z.; Zheng, J.; Wang, Z.; Zuo, S. Synthesis of $C_{21}H_{38}ClN$ assisted Si pillared clays and the effects of CeO_2 addition on its supported palladium catalyst for benzene oxidation. *Catal. Lett*. **2021**, *151*, 3287–3297.
11. Zuo, S.; Du, Y.; Liu, F.; Han, D.; Qi, C. Influence of ceria promoter on shell-powder-supported Pd catalyst for the complete oxidation of benzene. *Appl. Catal. A Gen*. **2013**, *451*, 65–70.
12. Ilieva, L.; Venezia, A.M.; Petrova, P.; Pantaleo, G.; Liotta, L.F.; Zanella, R.; Kaszkur, Z.; Tabakova T. Effect of Y modified ceria support in mono and bimetallic Pd-Au catalysts for complete benzene oxidation. *Catalysts* **2018**, *8* (7), art. no. 283.
13. Tabakova, T.; Ilieva, L.; Petrova, P.; Venezia, A.M.; Avdeev, G.; Zanella, R.; Karakirova, Y. Complete benzene oxidation over mono and bimetallic Au–Pd catalysts supported on Fe-modified ceria. *Chem. Eng. J.* **2015**, *260*, 133–141.
14. Kalvachev, Y.; Todorova, T.; Kolev, H.; Merker, D.; Popov, C. Benzene oxidation over Pt loaded on fly ash zeolite X. *Catalysts* **2023,** *13*, 1128.