## Supplementary Material

## Oxidative dehydrogenation of cyclohexene on atomically precise subnanometer Cu<sub>4-n</sub>Pd<sub>n</sub> (0≤n≤4) tetramer clusters: The effect of cluster composition and support on performance.

Juraj Jašík<sup>1€</sup>, Stanislav Valtera<sup>1€</sup>, Mykhailo Vaidulych<sup>1</sup>, Muntaseer Bunian<sup>2</sup>, Yu Lei<sup>2</sup>, Avik Halder<sup>3</sup>, Hana Tarábková<sup>4</sup>, Martin Jindra<sup>4,5</sup>, Ladislav Kavan<sup>4</sup>, Otakar Frank<sup>4</sup>, Stephan Bartling<sup>6</sup>, Štefan Vajda<sup>1\*</sup>

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 $\epsilon$  equally contributing (first) authors

\*Corresponding author's email (SV): stefan.vajda@jh-inst.cas.cz



**Figure S1.** Mass spectra of the molecular beam of pure  $Cu_n^+$  clusters produced by cluster source 1 and optimized to obtain the highest flux of  $Cu_4^+$  clusters for deposition recorded: (a) at higher resolution with the insert showing the resolved distribution of isotopes of  $Cu_4^+$  (black line) compared with the distribution of isotopes calculated by isotope calculator using natural abundance of copper isotopes (red line, https://www.sisweb.com/mstools/isotope.htm). (b) at lowered resolution for deposition to increase the flux of deposited clusters. With Ar atom(s) tagged  $Cu_n^+$  clusters which also form in the magnetron source are assigned as well.



**Figure S2**. Mass spectra of  $Cu_mPd_n^+$  clusters produced by cluster source 2 and recorded: (a) at higher resolution with the insert showing resolved distribution of isotopes (black line) compared with the distribution of isotopes calculated by isotope calculator (red line) using natural abundance of copper and palladium isotopes. (b) at lowered resolution for deposition to increase the flux of deposited clusters.



**Figure S3**. Mass spectra of pure  $Pd^+$  clusters produced by cluster source 2 and optimized for the deposition of  $Pd_4$ , recorded: (a) at higher resolution with the insert showing resolved distribution of isotopes (black line) compared with the distribution of isotopes calculated by isotope calculator (red line) using natural abundance of copper isotopes. (b) at lowered resolution for deposition to increase flux of deposited clusters. The unlabeled peaks in the mass spectrum corresponds to  $Ar_m^+$  ions; the peaks corresponding to Ar atom(s) tagged  $Pd_n^+$  clusters are labeled in the plot as well.



**Figure S4.** Top: temperature ramp sequence consisting of two temperature ramps  $1^{st}$  – "short" (all temperature steps with dwell time of 20 min) and  $2^{nd}$  "long" (with dwell time 120 min at 400 °C) is shown in upper part of figure. For 0.5 hour, a constant flow of helium (5 sccm) was maintained through the reaction cell at 800 Torr at 25 °C. After 0.5 hour of flushing with pure helium, the gas was switched to the reactant mixture (maintaining the 800 Torr pressure and 17.5 sccm flowrate) and sampling of gas to the mass spectrometer started. The flow reactant mixture was kept for 6 hours to stabilize the background in the mass spectrometer before the start of the temperature ramp. The reactant mixture consisted of 0.29 % cyclohexene and 0.29 % oxygen in helium (i.e., a 1:1 cyclohexene to oxygen molar ratio), obtained by mixing 12.50 sccm of 4000 ppm cyclohexene in helium with 5.00 sccm of 1.0 % oxygen diluted in helium. Bottom: Typical evolution of the mass-spec signal of reactants and identified products during the double temperature ramp showed on the example of zirconia supported Pd<sub>4</sub> clusters (water, oxygen, carbon dioxide, cyclohexene, cyclohexadiene and benzene, with their corresponding mass to charge ratio m/z showed in the plot).



**Figure S5.** Electron impact ionization mass spectra of the effluent gas from the reactor acquired during TPR of Pd<sub>4</sub>/UNCD sample (a) at 25 °C before start of the temperature ramp, (b) at 400 °C during the  $2^{nd}$  temperature ramp. Mass spectra of (c) cyclohexene, (d) benzene and (e) cyclohexadiene (mean of 1,3- and 1,4- cyclohexadiene measurements) calibration gases. Mass peaks considered in the model for fitting the concentrations of cyclohexene reactant and benzene and cyclohexadiene products (m/z 67, 77, 78, 79 and 80) are marked by blue lines.



**Figure S6.** (a) Temperature ramp. Comparison of processed mass spectra of  $Pd_4/ZrO_2$  and blank reference. Normalized concentration of (b) cyclohexene, (c) benzene, (d) cyclohexadiene, (e)  $CO_2$  and (f) sum of the concentrations obtained from fitting of mass spectra acquired during the first (short) ramp in TPR proves that no product is missing. The two peaks at the first two temperature increments are caused by temperature desorption of cyclohexene, while the two peaks with negative values at the end of the ramp are caused by adsorption or the reactant. Values are normalized for the concentration of cyclohexene at 25 °C.



Figure S7. AFM images of UNCD layer on Si substrate measured in tapping mode. Comparison of images of UNCD layer before reaction a) topography (1 x 1  $\mu$ m<sup>2</sup>) with mean roughness R<sub>a</sub> = 7.5 nm, b) topography (0.5 x 0.5  $\mu$ m<sup>2</sup>) and c) phase image (0.5 x 0.5  $\mu$ m<sup>2</sup>) with Cu<sub>2</sub>Pd<sub>2</sub> on UNCD after reaction d) topography (1 x 1  $\mu$ m<sup>2</sup>) with mean roughness R<sub>a</sub> = 6.8 nm, e) topography (0.5 x 0.5  $\mu$ m<sup>2</sup>) and f) phase image (0.5 x 0.5  $\mu$ m<sup>2</sup>). The phase imaging highlights the details of their microstructures, including nanograin boundaries, which are not well resolved by topographic imaging.



**Figure S8.** (a) AFM height image of the native oxide of the base silicon carrier with mean roughness  $R_a = 0.09 \text{ nm.}$  (b- c) AFM height images of the ZrO<sub>2</sub> layer on SiO<sub>2</sub>/Si substrate (0.5 x 0.5  $\mu$ m<sup>2</sup>), blank ZrO<sub>2</sub> support before (b) and after (c) reaction with mean roughness  $R_a = 0.08$  and 0.24 nm respectively; (d-e) AFM height images of the Cu<sub>2</sub>Pd<sub>2</sub>/ZrO<sub>2</sub> sample after reaction in (d) and (e) outside of the cluster spot, with mean roughness  $R_a = 0.36$  and 0.37 nm, respectively.



**Figure S9.** AFM height images  $(0.5 \times 0.5 \ \mu\text{m}^2)$  of ALD TiO<sub>2</sub> support before (a) and after (b) R<sub>a</sub> = 0.12 and 0.29 nm respectively; (c-d) AFM height images of the Cu<sub>2</sub>Pd<sub>2</sub>/TiO<sub>2</sub> sample after the reaction in (c) and (d) outside of the cluster spot, with mean roughness R<sub>a</sub>=0.17 and 0.14 nm, respectively.



**Figure S10** (a) Temperature ramp. Comparison of  $CO_2$  production with blank and  $Pd_4$  clusters on (b) UNCD and (c)  $ZrO_2$ . The picture shows, that the palladium clusters produce no  $CO_2$  on the UNCD while on the  $ZrO_2$ , a combustion is observed, which demonstrates the support effect. Values are normalized for concentration of cyclohexene at 25 °C.



**Figure S11**. Per total atom carbon-based rate of  $Pd_x$  on UNCD of (a) benzene – short, (b) benzene – long, (c) cyclohexadiene – short, (d) cyclohexadiene – long, (e)  $CO_2$  – short, (f)  $CO_2$  – long; Carbon-based selectivity for benzene, cyclohexadiene and  $CO_2$  at 400 °C during (g) short ramp and (h) long ramp.



**Figure S12**. Per total atom carbon-based rate of  $Pd_x$  on  $ZrO_2$  of (a) benzene – short, (b) benzene – long, (c) cyclohexadiene – short, (d) cyclohexadiene – long, (e)  $CO_2$  – short, (f)  $CO_2$  – long; Carbon-based selectivity for benzene, cyclohexadiene and  $CO_2$  at 400 °C during (g) short ramp and (h) long ramp.



**Figure S13.** XPS spectra of the Pd 3d region for Pd<sub>1</sub> on ZrO<sub>2</sub> before (top) and after (bottom) reaction are shown. The Pd 3d region strongly overlaps with Zr 3p, which complicates the deconvolution of the spectra as well as the quantitative assignment of Pd oxidation states. Between the Zr 3p peaks the Pd  $3d_{5/2}$  and Pd  $3d_{3/2}$  peaks can be found. For fresh sample Pd  $3d_{5/2}$  reveals a binding energy of 338.0 eV. After TPR, two Pd doublets can be found with Pd  $3d_{5/2}$  binding energies of 337.1 and 338.5 eV.



**Figure S14.** The evolution of the benzene formation rate over  $Cu_1Pd_3$  on  $TiO_2$  with time in the course of the two double ramps. (a): first ("short") temperature ramp of the applied double ramp, (b): second ("long") temperature ramp of the applied double ramp. (c-d): benzene formation during the applied first double ramp; (e-f): benzene formation during the second double ramp. (g): "short" and "long" temperature ramps, overlapped; (h): benzene rates from both double ramps, overlapped. Between the two double ramps, the sample was not exposed to air, it was kept it in the reactor under the stream of reactant mixture for 6 hours.

	Short - 1 <sup>st</sup> ramp			Long - 2 <sup>nd</sup> ramp		
cluster	UNCD	ZrO <sub>2</sub>	TiO <sub>2</sub>	UNCD	ZrO <sub>2</sub>	TiO <sub>2</sub>
Pd4	350	110	Х	400	80	Х
Cu <sub>1</sub> Pd <sub>3</sub>	15	4	17	60	7	170
Cu <sub>2</sub> Pd <sub>2</sub>	35	4	15	80	7	230
Cu <sub>3</sub> Pd <sub>1</sub>	4	2	5	9	4	9
Cu <sub>4</sub>	0	1	X	0	1	X

Table S1. Total benzene production rates (atom<sup>-1</sup> s<sup>-1</sup>) for tetramers

Table S2. Total benzene production rates (atom<sup>-1</sup> s<sup>-1</sup>) for Pd<sub>1</sub> and Pd<sub>2</sub>

cluster	support	short	long
Pd <sub>1</sub>	UNCD	175	175
Pd <sub>1</sub>	ZrO <sub>2</sub>	150	25
Pd <sub>2</sub>	$ZrO_2$	80	25