Pd supported on Metal Mixed Oxide as an Efficient Catalyst for the Reductive Amination of Bio-derived Acetol to 2-Methylpiperazine

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SUPPORTING INFORMATION

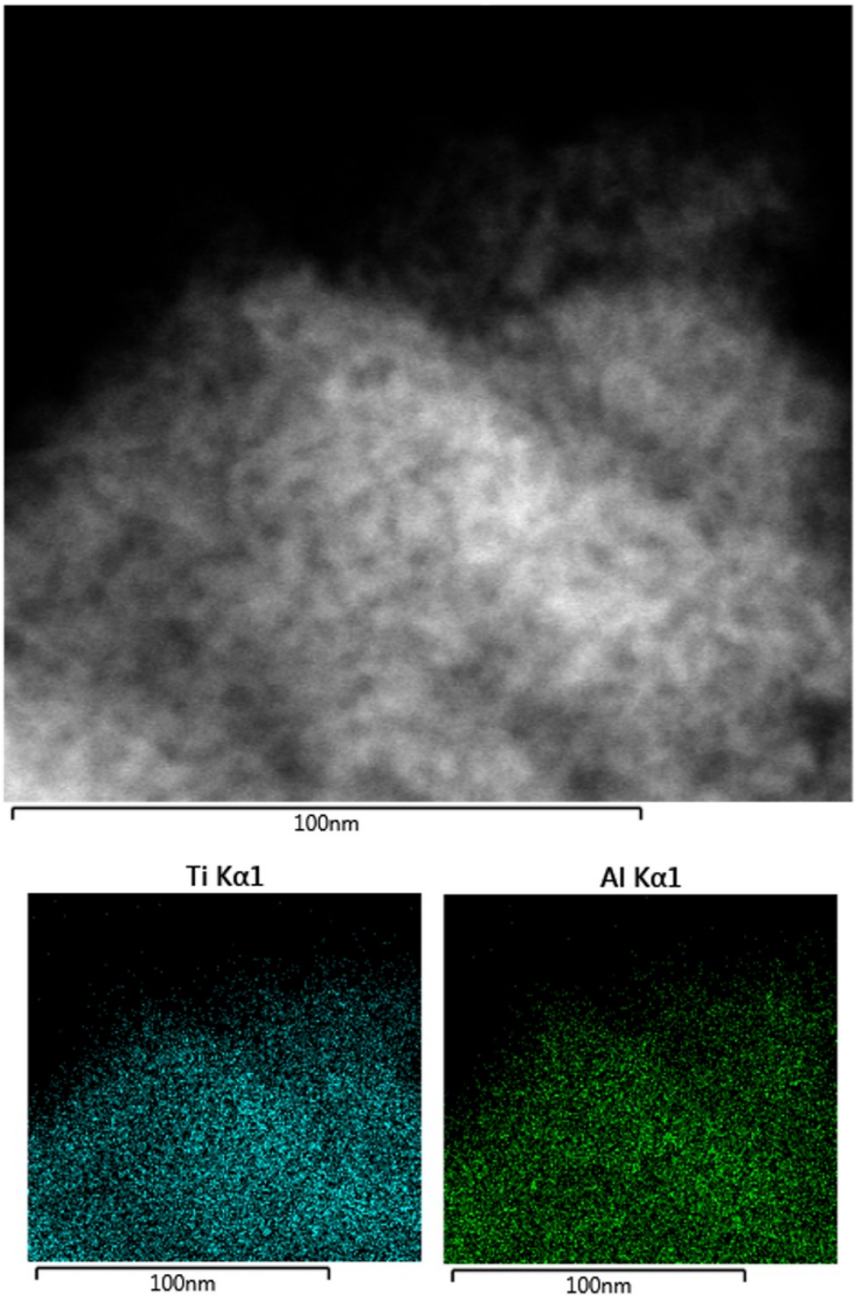


Figure S1. EDS mapping of Ti-Al-O_x support.

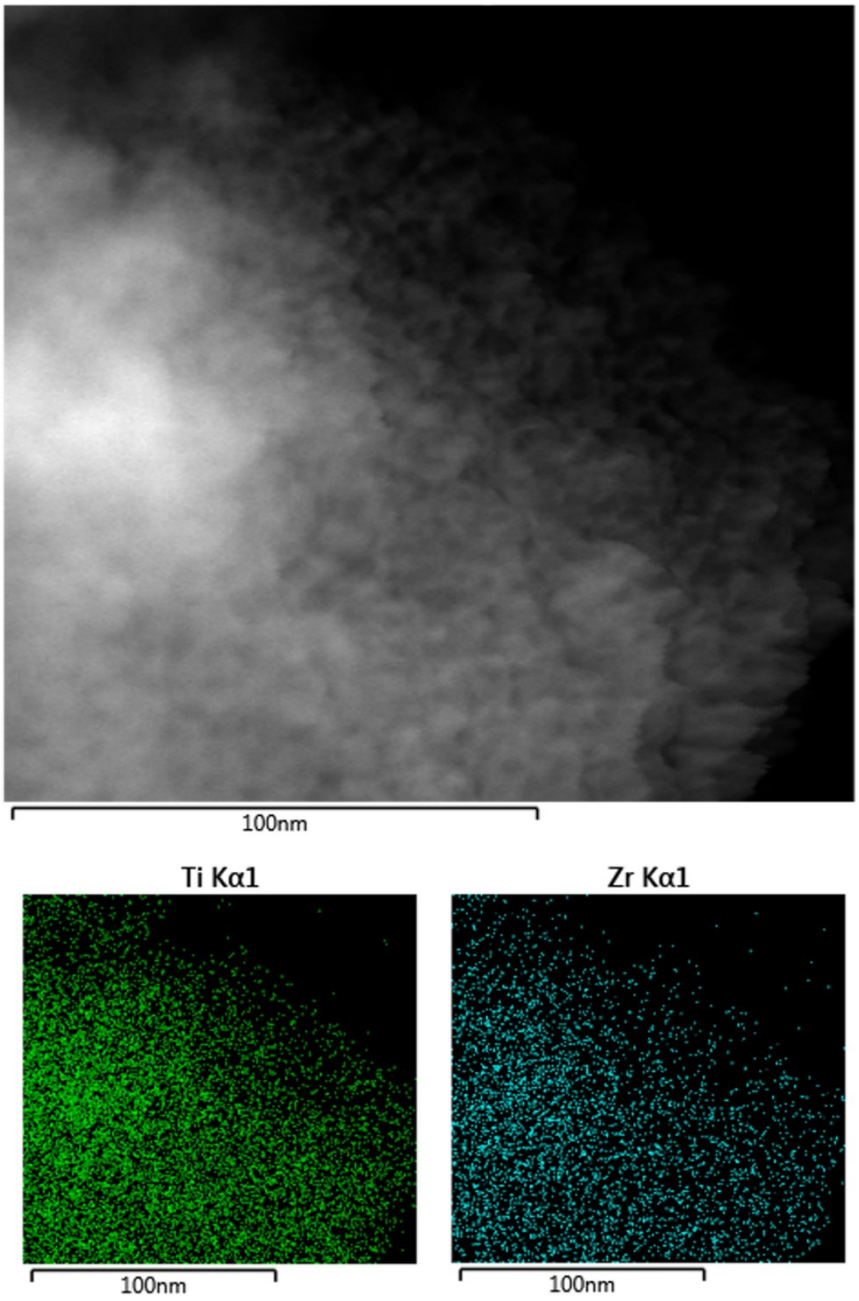


Figure S2. EDS mapping of Ti-Zr-O_x support.

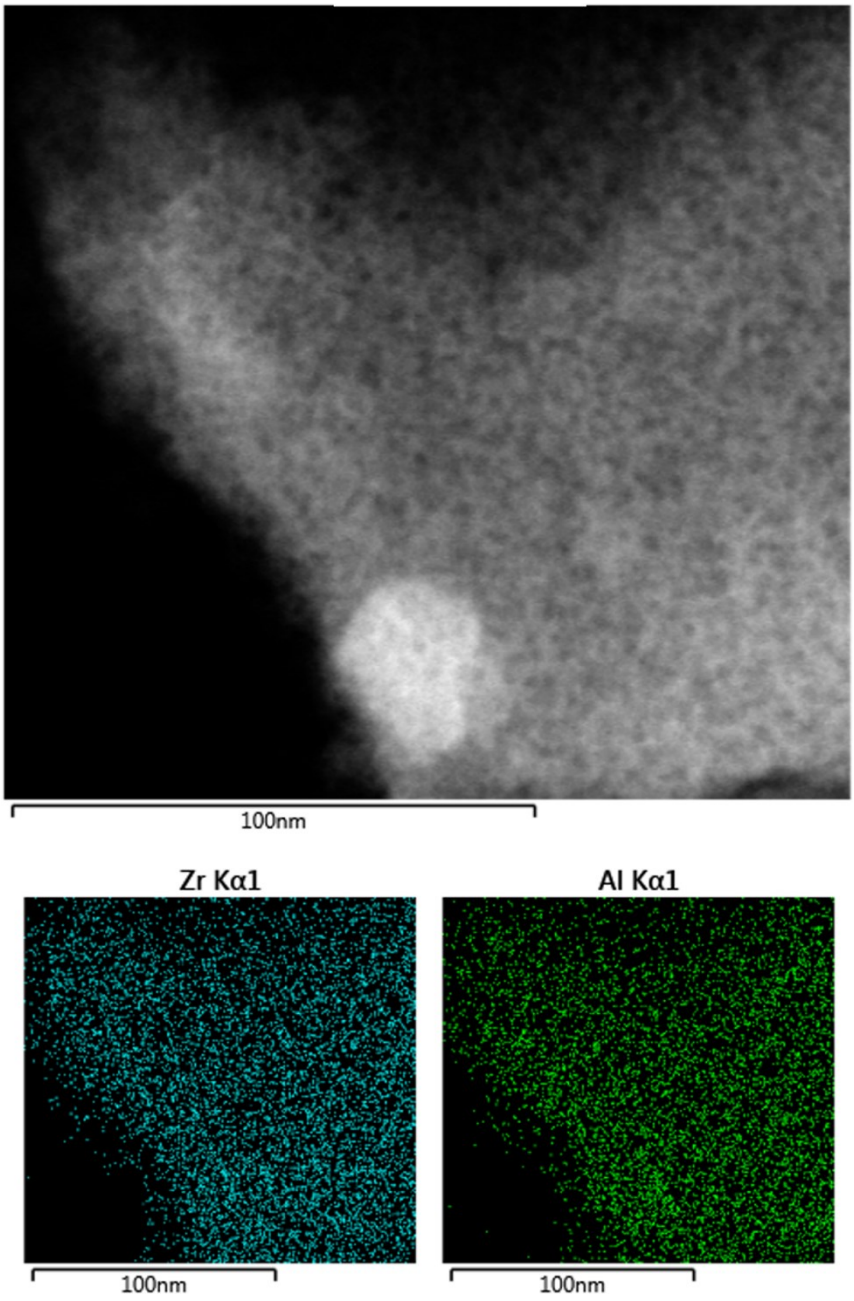


Figure S3. EDS mapping of Zr-Al-O_x support.

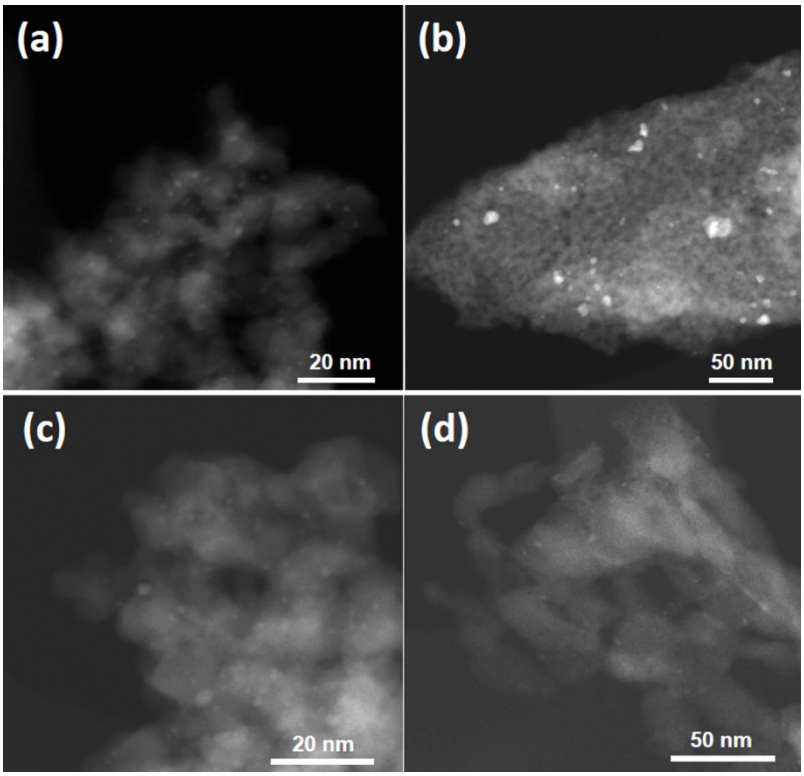


Figure S4. HR-STEM of a) Pd/TiO_2, b) Pd/Al_2O_3, c) Pd/ZrO_2 and d) Pd/MgO (after reduction).

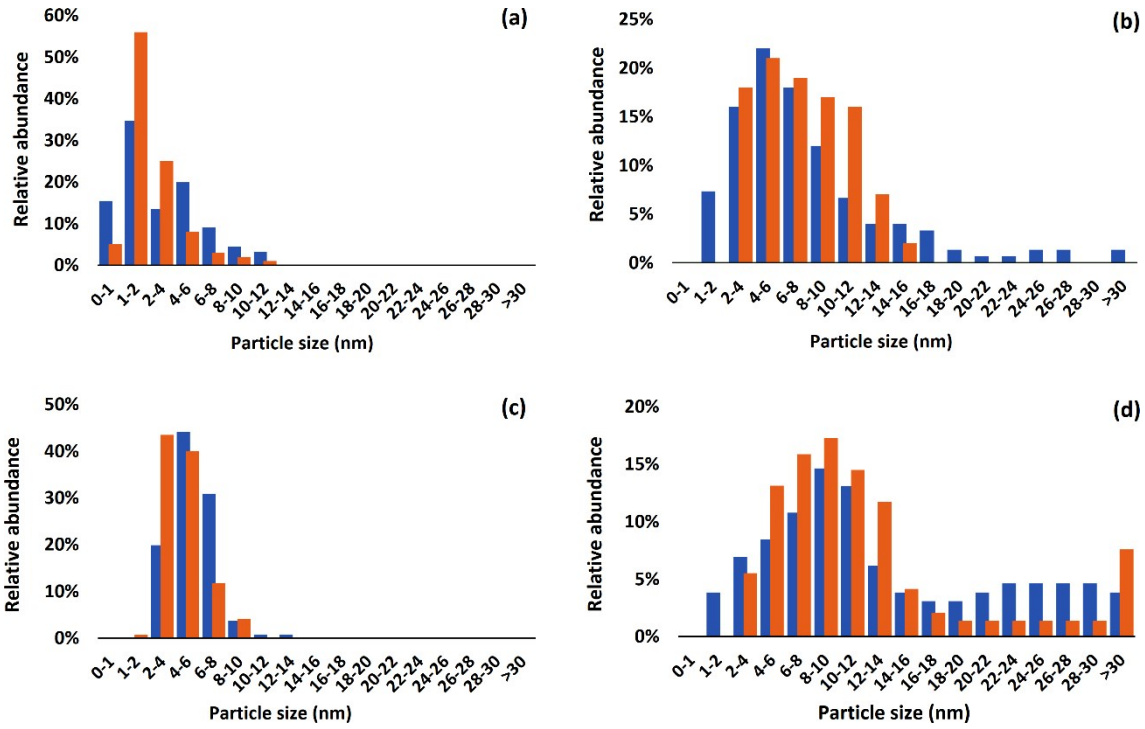


Figure S5. Metal particle size distribution of (a) Pd/TiO_2 (fresh:156 particles, regenerated: 100 particles), (b) Pd/Al_2O_3 catalyst (fresh: 150 particles, regenerated: 100 particles), (c) Pd/ZrO_2 catalyst (fresh: 136 particles, regenerated: 145), (d) Pd/MgO catalyst (fresh: 130, regenerated: 145). (▪): fresh, (▪): regenerated after 7 h reaction at 90 ^{0}C, 13 bar of H_2, with 25wt% catalyst loading and using MeOH as solvent.

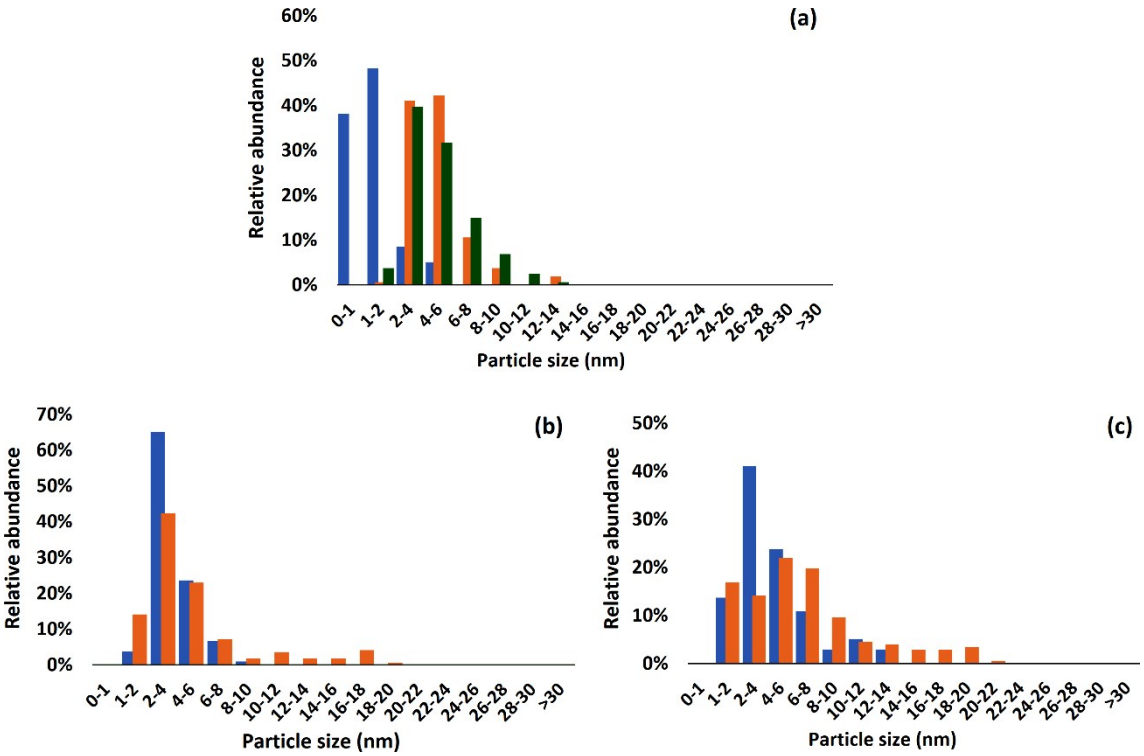


Figure S6. Metal particle size distribution of (a) Pd/TiO_2-Al_2O_3 (fresh:118 particles, regenerated: 161 particles), (b) Pd/TiO_2-ZrO_2 catalyst (fresh: 106 particles, regenerated: 170 particles), (c) Pd/ZrO_2-Al_2O_3 catalyst (fresh: 139 particles, regenerated: 178). (▪): fresh, (▪): regenerated after 7 h reaction at 90 ^{0}C and 13 bar of H_2, with 25wt% catalyst loading and using MeOH as solvent, (▪): regenerated after 7 h reaction at 90 ^{0}C and 13 bar of H_2, with 5wt% catalyst loading, and using MeOH as solvent.

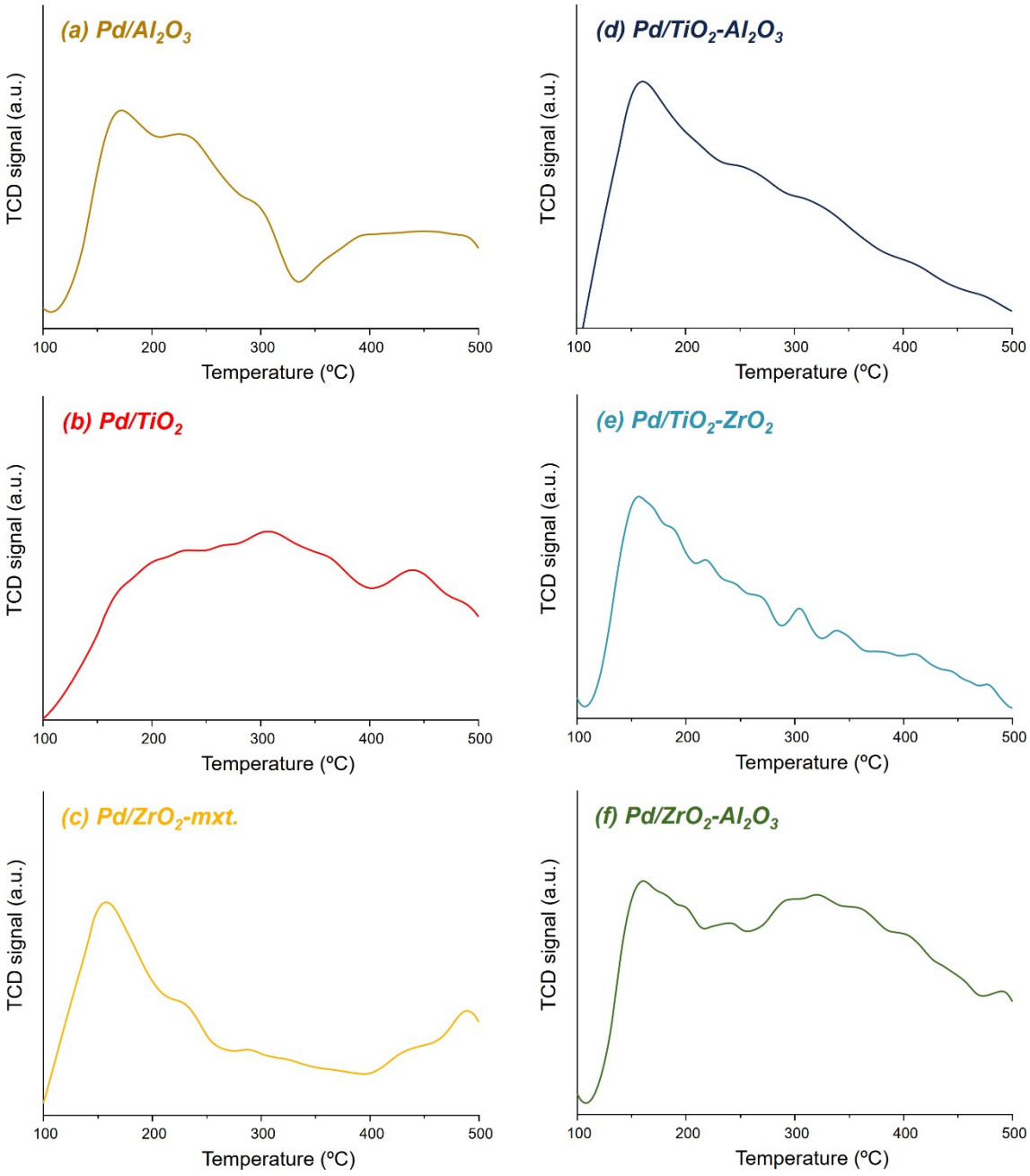


Figure S7. Smoothed NH_3-TPD profiles of Pd-based materials.

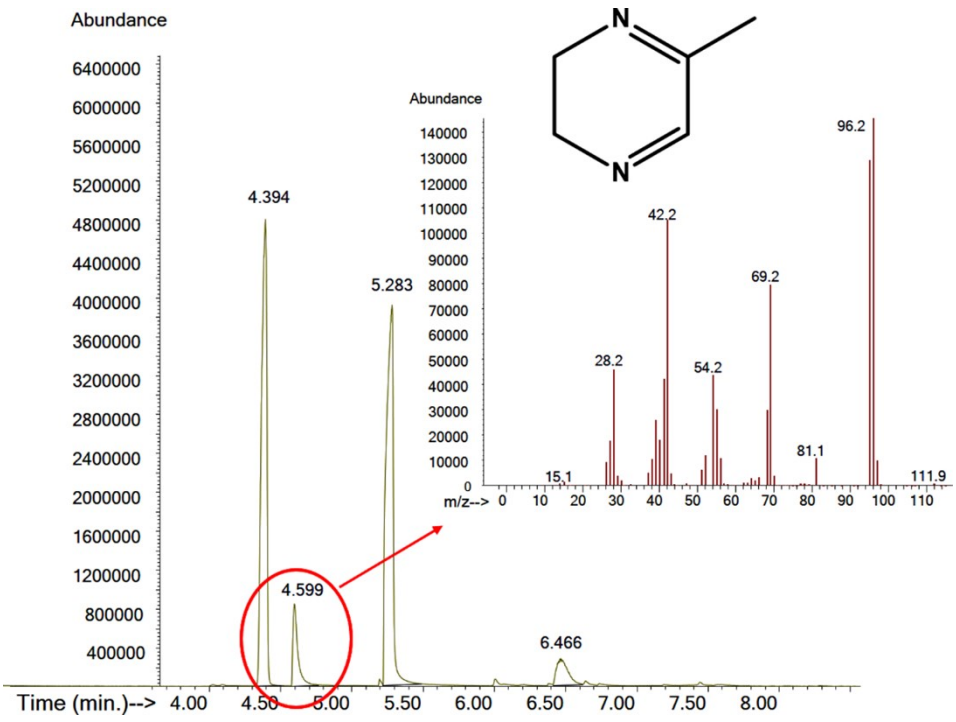


Figure S8. Factor average chromatogram and mass spectra for reaction intermediate (cyclic diimine) obtained after 7 h with the following reaction conditions: 0.325 g acetol, 0.227 g ethylenediamine, 1.250 g MeOH, 0.056 g of Pd/Al_2O_3 (commercial) at 90 ^{0}C and 13 bar of H_2, MS ((m/z), (relative intensity)): 96 (999), 95 (867), 42 (708), 69 (535), 28 (307), 54 (294), 41 (284), 55 (201), 68 (201), 39 (174); 96 M*

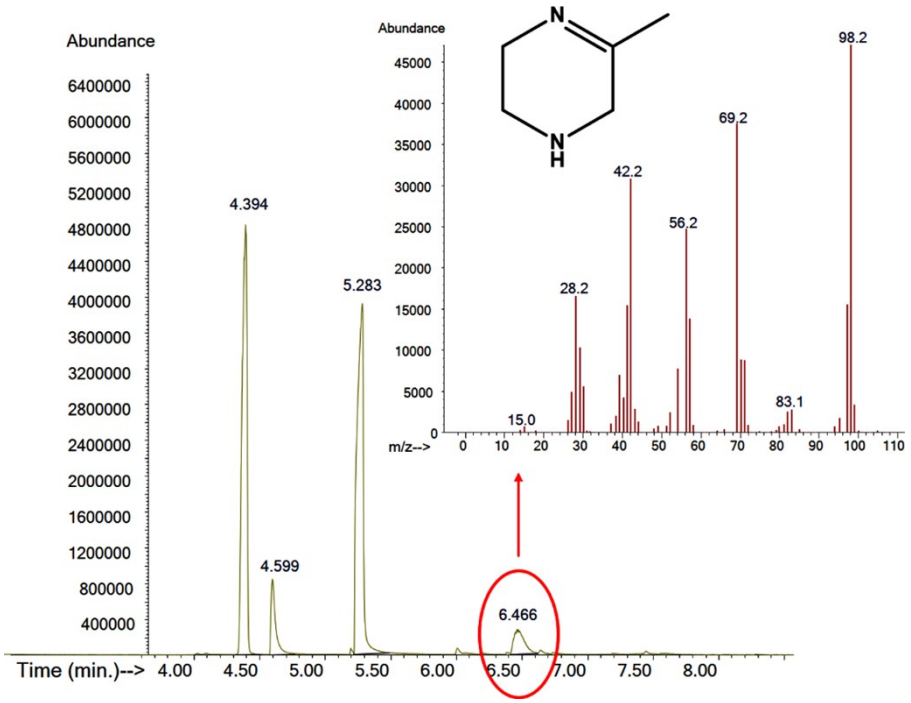


Figure S9. Factor average chromatogram and mass spectra for reaction intermediate (cyclic monoimine) obtained after 7 h with the following reaction conditions: 0.325 g acetol, 0.227 g ethylenediamine, 1.250 g MeOH, 0.056 g of Pd/Al_2O_3 (commercial) at 90 ^{0}C and 13 bar of H_2, MS ((m/z), (relative intensity)): 98 (999), 68 (782), 42 (642), 56 (515), 28 (344), 97 (323), 41 (321), 57 (287), 29 (214), 70 (183); 98 M*

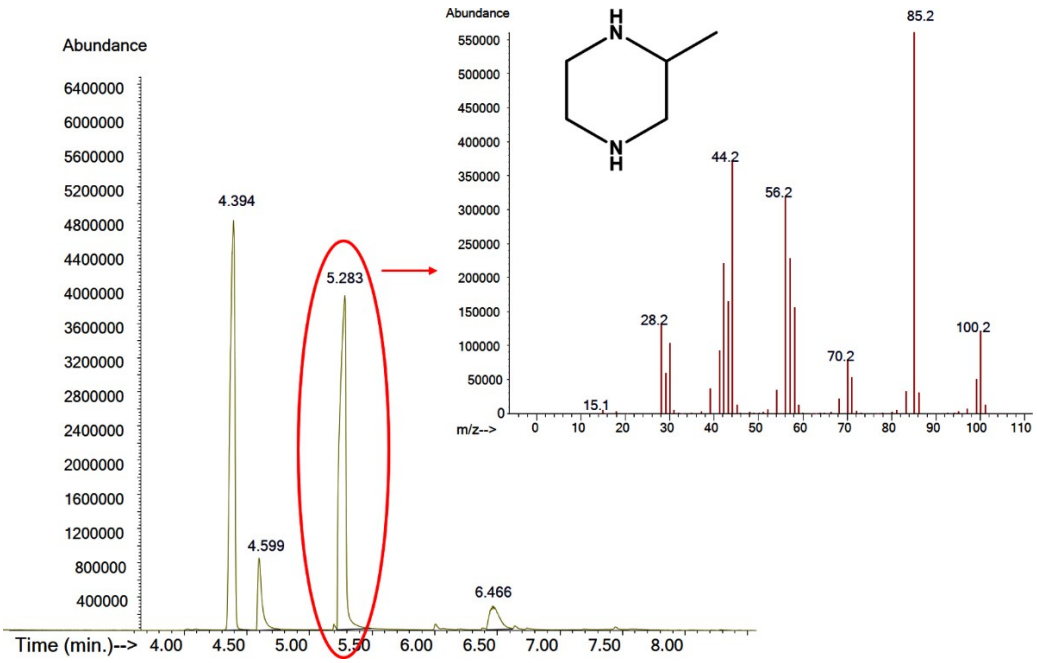


Figure S10. Factor average chromatogram and mass spectra for reaction product (2-methylpiperazine) obtained after 7 h with the following reaction conditions: 0.325 g acetol, 0.227 g ethylenediamine, 1.250 g MeOH, 0.056 g of Pd/Al_2O_3 (commercial) at 90 ^{0}C and 13 bar of H_2, MS ((m/z), (relative intensity)): 85 (999), 44 (654), 56 (561), 57 (402), 42 (390), 43 (291), 58 (274), 28 (229), 100 (211), 30 (181); 100 M*

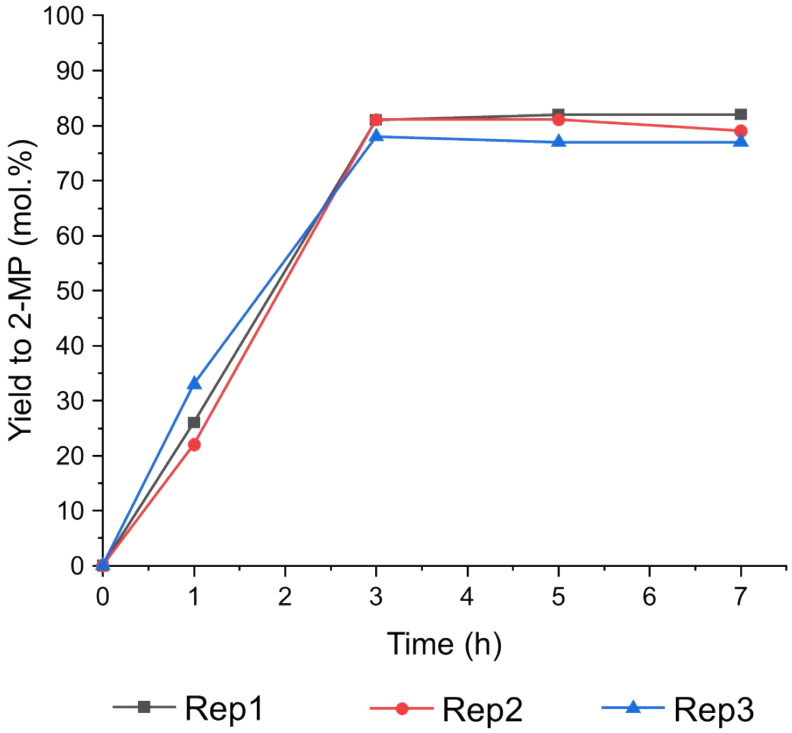


Figure S11. Reproducibility test with commercial Pd/Al_2O_3. Reaction conditions: 0.325 g acetol, 0.227 g ethylenediamine, 1.250 g MeOH, 0.056 g of Pd/Al_2O_3-commercial, at 13 bar of H_2, and 90 ^{0}C, during 7 h and with slow addition of acetol (100 µl/h).

Table S1. Sampling test.

Reaction time (h)	Yield to 2-MP (mol.%)		
	A	B	C
3	57	54	57 ± 2
7	77	78	78 ± 4

A: One reaction with 4 sample collections
B: Two independent reactions (just one sample collection)
C: Average results (4 different repetitions per every reaction time, including those in this table)
Reaction conditions: 0.325 g acetol, 0.227 g ethylenediamine, 1.250 g MeOH, 0.011 g of Pd/TiO_2-Al_2O_3 at 13 bar of H_2, and 90 ^{0}C, during 7 h and with slow addition of acetol (100 µl/h).

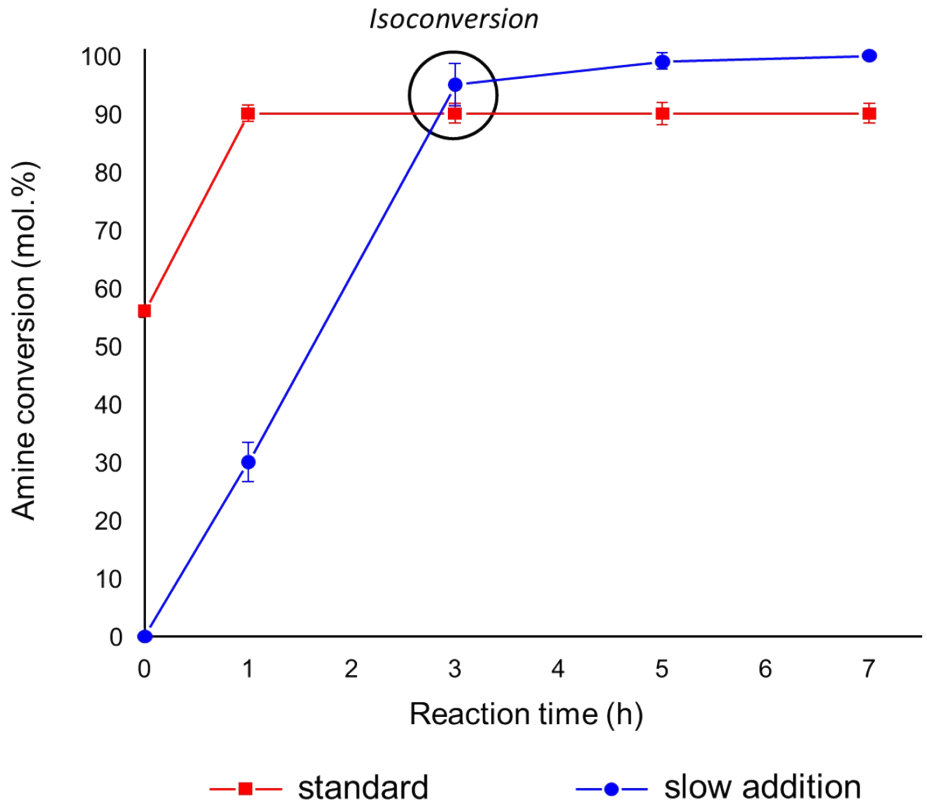


Figure S12. Ethylenediamine conversion for a standard reaction and an experiment with slow acetol addition. Reaction conditions: 0.325 g acetol, 0.227 g ethylenediamine, 1.250 g MeOH, 0.056 g of Pd/Al_2O_3 (commercial), at 90 ^{0}C and 13 bar of H_2, during 7 h.

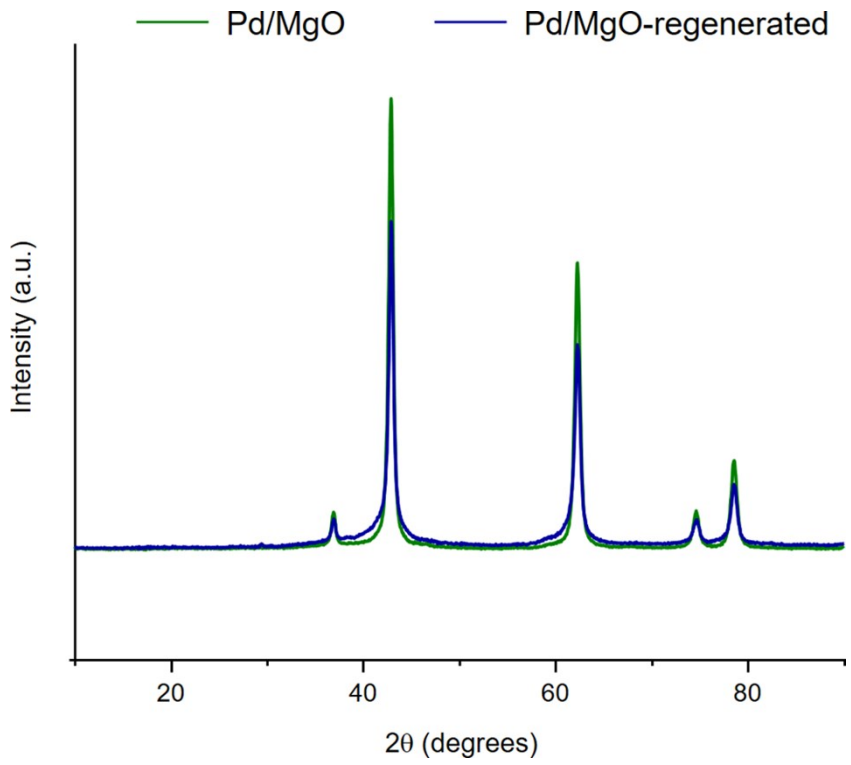


Figure S13. Comparison between the X-ray diffraction patterns of fresh Pd/MgO and Pd/MgO after the regeneration treatment.

Table S2. Results of elemental analysis (EA) of Pd supported on simple oxides after several reaction cycles.

Catalyst	**C/N (wt%)[a] [after 2nd use]**	**C/N (wt%)[b] [after 3rd use]**
Pd/ZrO_2	0.5/1.5	0.5/1.7
Pd/Al_2O_3	0.5/1.5	0.5/1.6

Reaction conditions: 0.325 g acetol, 0.227 g ethylenediamine, 0.056 g of catalyst at 90 ^{0}C and 13 bar of H_2, during 7 h and with slow addition of acetol (100 µl/h).

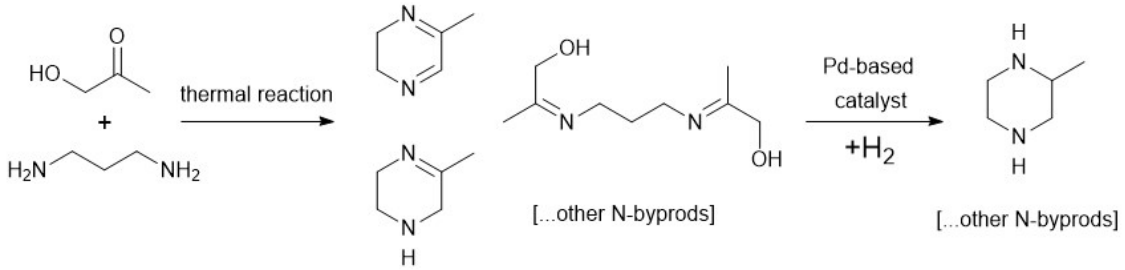
Catalyst	Pd/Al_2O_3	Pd/TiO_2-ZrO_2	Pd/TiO_2	Pd/ZrO_2-Al_2O_3	Pd/TiO_2-Al_2O_3	Pd/ZrO_2	Thermal reaction
Amine Conversion[a]	85	86	89	91	92	91	n/d
Amine Conversion[b]	90	n/d	n/d	n/d	93	95	94
Selectivity to N-byproducts[a]	24	24	24	19	17	40	n/d
Selectivity to Imines[a]	47	41	25	20	14	22	n/d
Yield to 2-MP[a]	23	26	44	49	57	30	n/d

Table S3. Catalytic data for Pd supported catalysts for tests with 5wt.% catalyst loading.

Reaction conditions: 0.325 g acetol, 0.227 g ethylenediamine, 1.250 g MeOH, 0.011 g of catalyst at 90 ^{0}C, during 3 h and with slow addition of acetol (100 µl/h). a: 13 bar of H_2, b: 13 bar of N_2.

NOTE:

One of the particularities of this reductive cyclo-amination is the fact that ethylenediamine instantly attacks acetol (nucleophilic addition) to yield either the corresponding imines or other nitrogenated by-products (mainly depending on the amount of acetol in the reaction media). A Scheme is presented below to illustrate this:



Scheme S1. Reaction pathway.

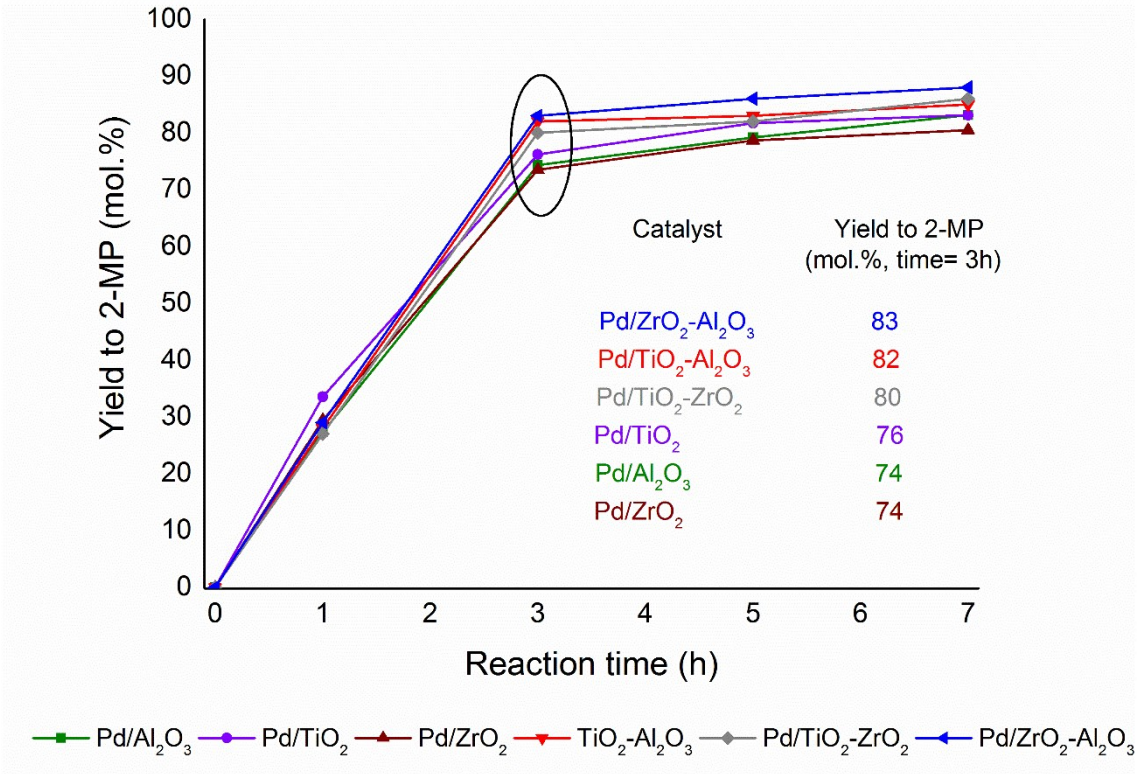


Figure S14. Kinetic comparison of Pd supported on simple and mixed metal oxides. Reaction conditions: 0.325 g acetol, 0.227 g ethylenediamine, 1.250 g MeOH, 0.056 g of catalyst, at 90 ^{0}C and 13 bar of H_2, during 7 h and with slow addition of acetol (100 µl/h).

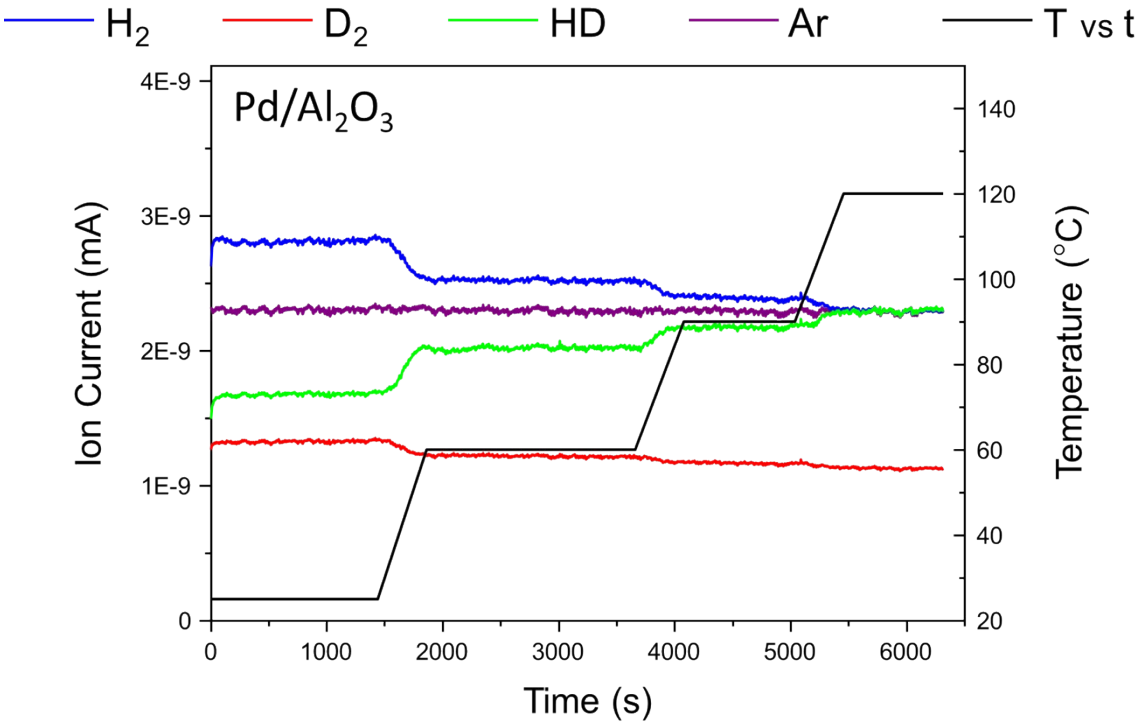


Figure S15. Evolution of HD (m/z=3), H_2 (m/z=2) and D_2 (m/z=4) in the isotopic exchange H/D over Pd/Al_2O_3 (Black line corresponds to the temperature profile during measurement).

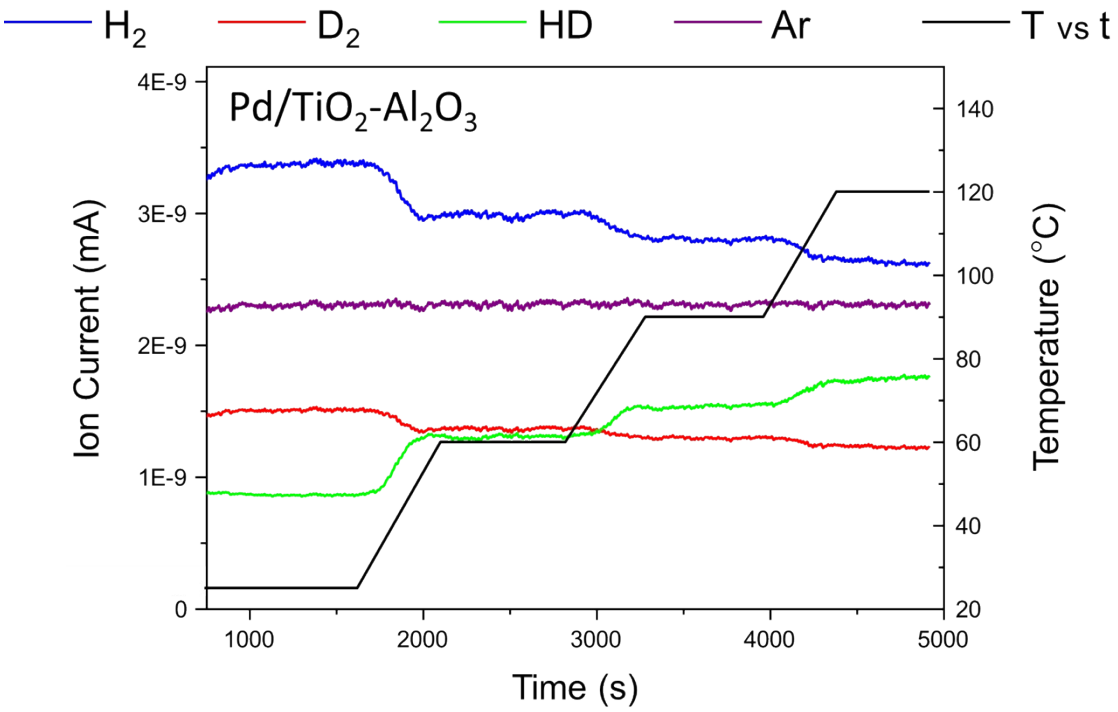


Figure S16. Evolution of HD (m/z=3), H_2 (m/z=2) and D_2 (m/z=4) in the isotopic exchange H/D over Pd/TiO_2-Al_2O_3 (Black line corresponds to the temperature profile during measurement).

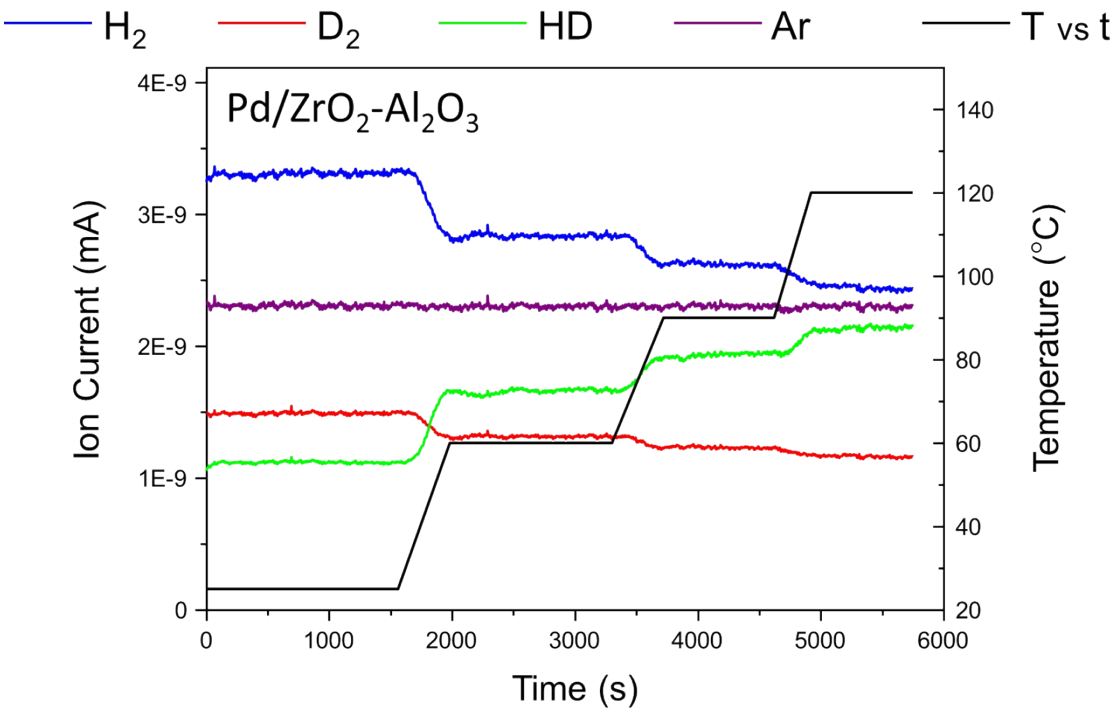


Figure S17. Evolution of HD (m/z=3), H_2 (m/z=2) and D_2 (m/z=4) in the isotopic exchange H/D over Pd/ZrO_2-Al_2O_3 (Black line corresponds to the temperature profile during measurement).

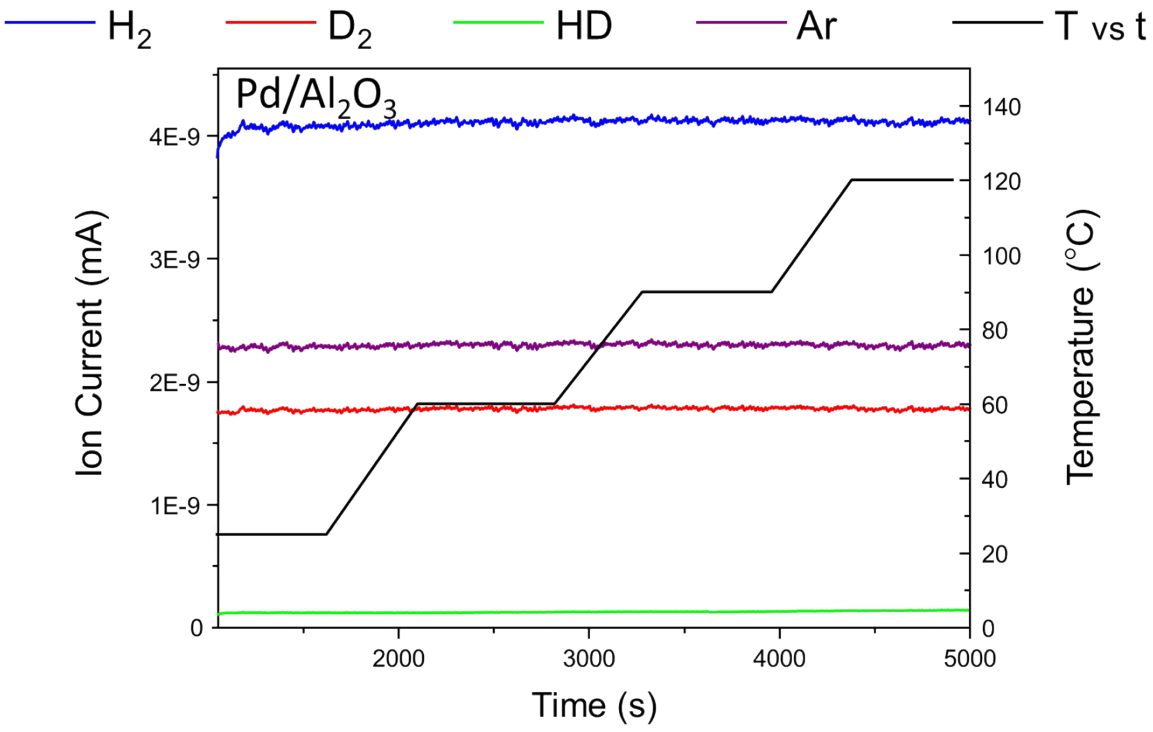


Figure S18. Evolution of HD (m/z=3), H_2 (m/z=2) and D_2 (m/z=4) in the isotopic exchange H/D over Pd/Al_2O_3 (Black line corresponds to the temperature profile during measurement).

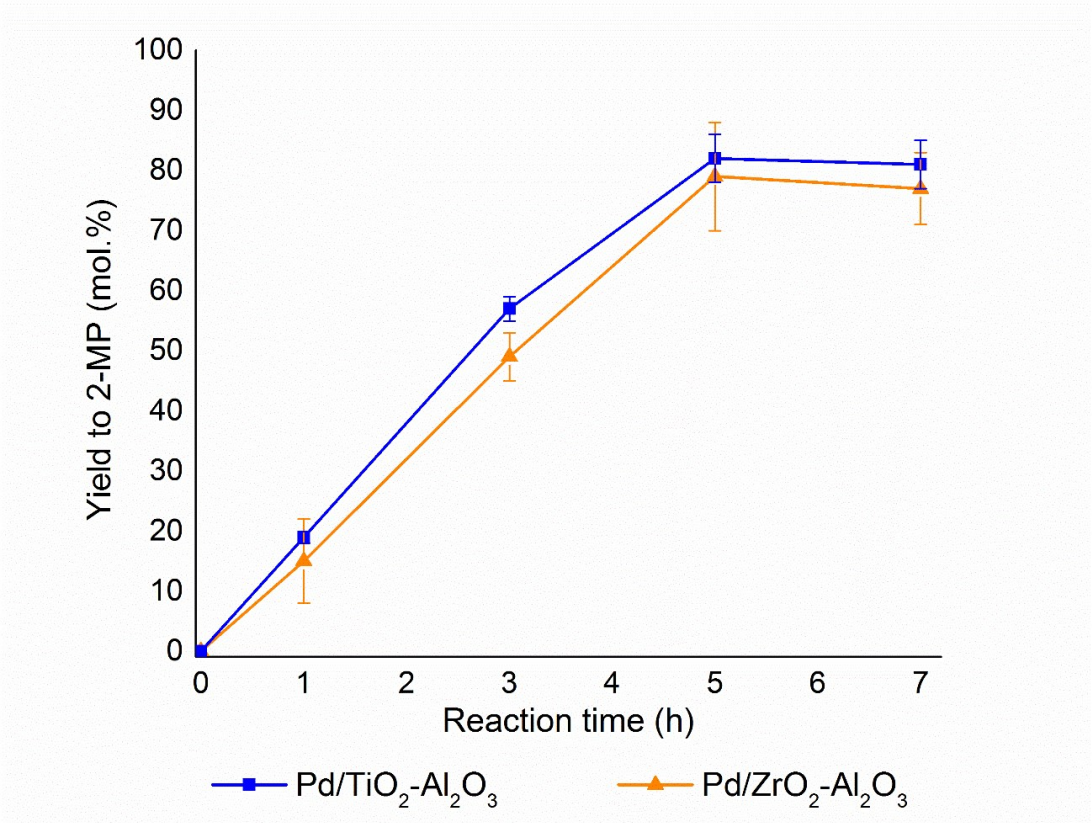


Figure S19. Kinetic comparison of Pd/TiO_2-Al_2O_3 with Pd/ZrO_2-Al_2O_3. Reaction conditions: 0.325 g acetol, 0.227 g ethylenediamine, 1.250 g MeOH, 0.011 g of catalyst, at 90 ^{0}C and 13 bar of H_2, during 7 h and with slow addition of acetol (100 µl/h). Note: Results correspond to the average values of three repetitions per point, with error bars calculated as the internal standard deviation.

Table S4. Results of elemental analysis (EA) of Pd/TiO_2-Al_2O_3 after reaction under optimum conditions and after regeneration.

Solvent	C/N (wt%)[a] [after 1st use]	C/N (wt%)[b] [after regeneration]
H_2O	3.1/1.3	0.4/0.0
MeOH	5.1/2.5	0.1/0.0

Reaction conditions: 0.325 g acetol, 0.227 g ethylenediamine, 0.011 g of Pd/TiO_2-Al_2O_3 at 90 ^{0}C and 13 bar of H_2, during 7 h and with slow addition of acetol (100 µl/h).