Supporting Information

Pt/ZrO_2 Prepared by Atomic Trapping: an Efficient Catalyst for the Conversion of Glycerol to Lactic Acid with Concomitant Transfer Hydrogenation of Cyclohexene

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This Supporting Information contains 9 pages including 8 Figures and 5 Tables.

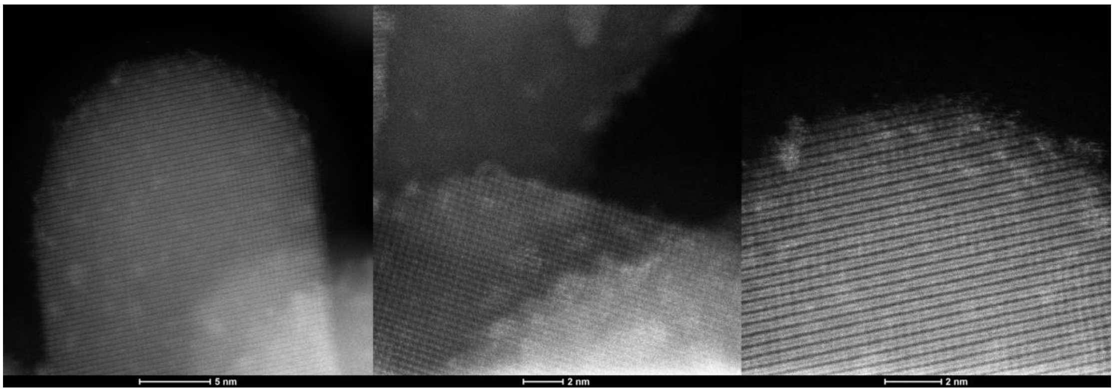

Figure S1. Supplementary HAADF-STEM images for 2Pt/ZrO_2-550.

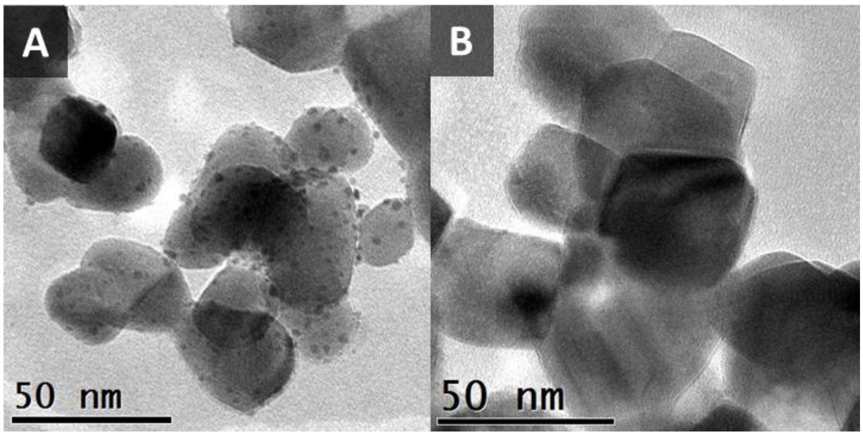

Figure S2. TEM images of 2Pt/ZrO_2 catalysts calcined and reduced with different procedures. (A) 2Pt/ZrO_2-400-R250, average particle size of Pt: 2.0 nm; (B) 2Pt/ZrO_2-800-R250.

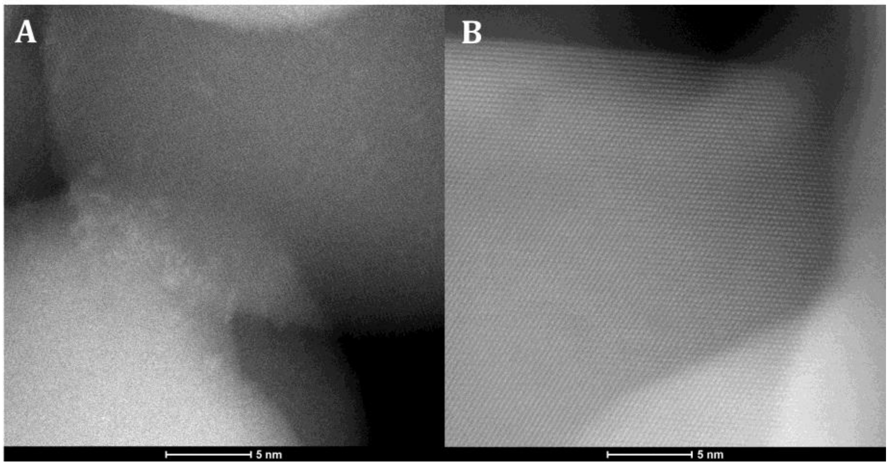

Figure S3. HAADF-STEM images of 0.5Pt/ZrO_2 catalysts calcined at different temperatures. (A) 0.5Pt/ZrO_2-550; (B) 0.5Pt/ZrO_2-800.

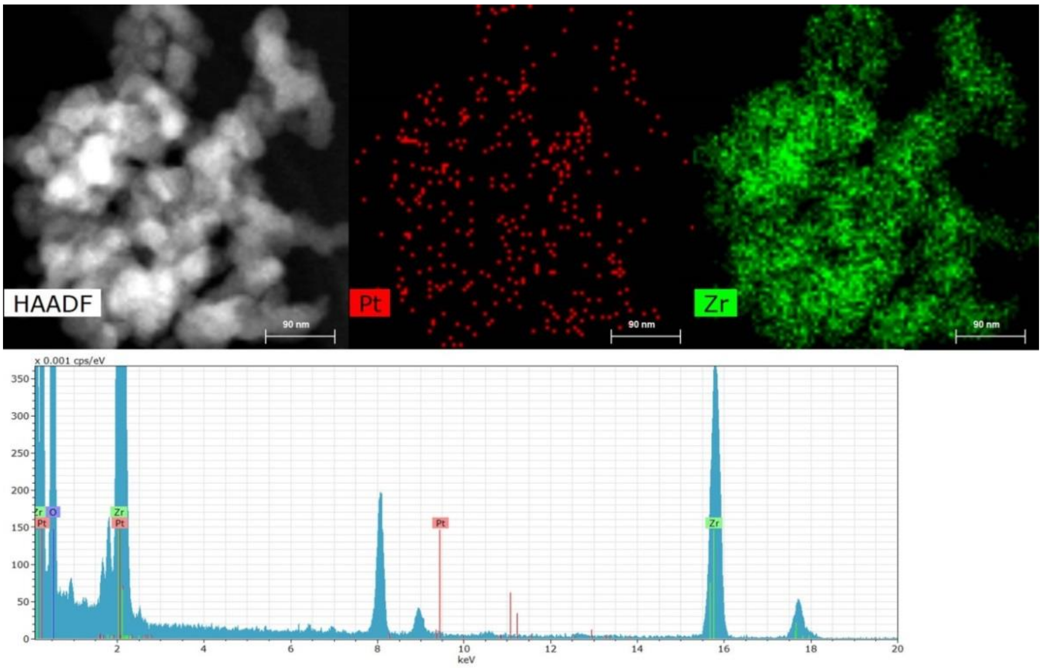

Figure S4. HAADF-STEM images coupled with EDX-mapping for 0.5Pt/ ZrO_2-800. Note: the red spots in the EDX-mapping of Pt might be caused by noise and not represent actual Pt species. This EDX-mapping of Pt is shown with the purpose of demonstrating the absence of large Pt nanoparticles in this sample.

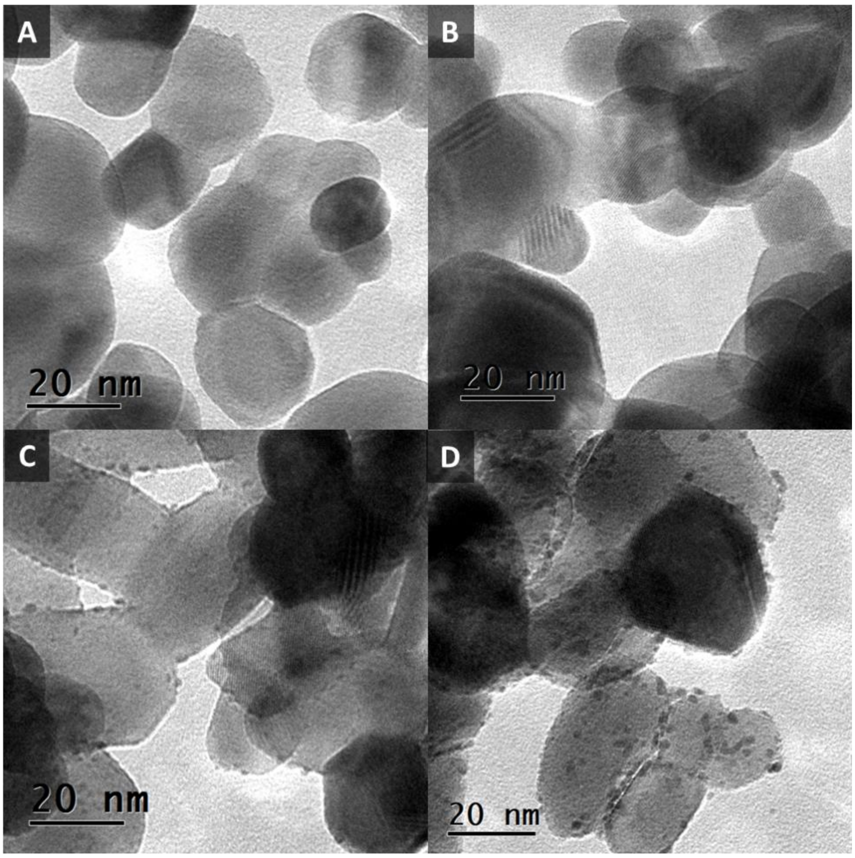

Figure S5. TEM images of Pt/ZrO_2 catalysts with different loading after calcination at 550 °C. (A) $0.5Pt/ZrO_2$-550; (B) $1Pt/ZrO_2$-550; (C) $5Pt/ZrO_2$-550, average particle size of Pt: 1.3 nm; (D) $9Pt/ZrO_2$-550, average particle size of Pt: 1.5 nm. Note: the resolution of these TEM images does not allow identification of nanoparticles < 0.5 nm.

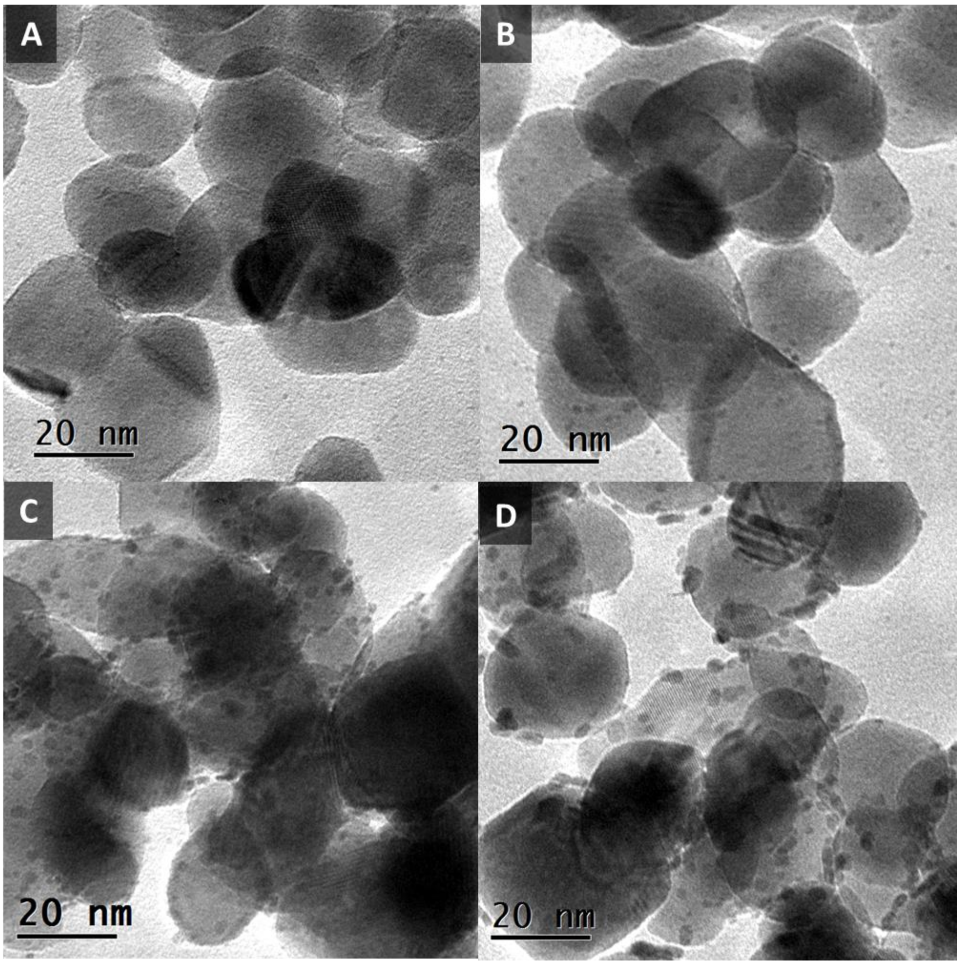

Figure S6. TEM images of Pt/ZrO_2 catalysts with different loading after calcination at 550 ºC and reduction at 250 ºC. (A) $0.5Pt/ZrO_2$-550, average particle size of Pt: 0.8 nm; (B) $1Pt/ZrO_2$-550, average particle size of Pt: 1.2 nm; (C) $5Pt/ZrO_2$-550, average particle size of Pt: 2.0 nm; (D) $9Pt/ZrO_2$-550, average particle size of Pt: 2.6 nm.

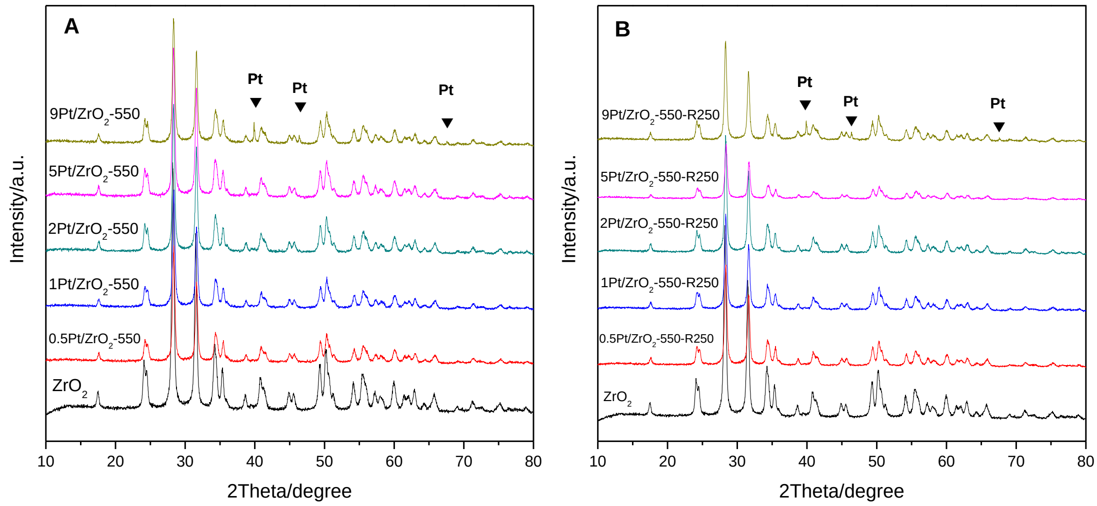

Figure S7. XRD patterns of calcined ZrO_2 and Pt/ZrO_2 catalysts with various Pt loadings (0.5-9%), before (A) and after reduction (B).

Table S1. Catalytic conversion of glycerol to lactic acid using Pt catalysts supported on different oxides. [a]

					Selectivity in the conversion of glycerol (%)				Yield in the conversion of cyclohexene (%)[b]	
Entry	Catalyst	$Conv._{GLY}$ (%)	Y_{LA} (%)	$S_{(transfer\text{-}H)}$ (%)	Lactic acid	Glyceric acid	Glycolic acid	Propane-diol	Cyclohexane	Benzene
1	$2Pt/TiO_2$-550-R250	9.4	8.6	28	91	1.0	0	2.0	1.3	0
2	$2Pt/ZrO_2$-550-R250	96	95	36	99	0.5	0.2	0.7	17	0
3	$2Pt/CeO_2$-800-R250	90	88	45	98	0.5	0	0.5	20	0

[a] Reaction conditions: aqueous glycerol solution: 10 mmol (0.5 M, 20 mL); cyclohexene: 20 mmol; nominal Pt/glycerol ratio = 1/1950; NaOH: 15 mmol; temperature: 160°C; reaction time: 4.5 h; N_2 pressure: 20 bar. [b] Under the employed reaction conditions ($mol_{glycerol}$: $mol_{cyclohexene}$ = 1 : 2) the maximum theoretical yield of cyclohexane is 50%.

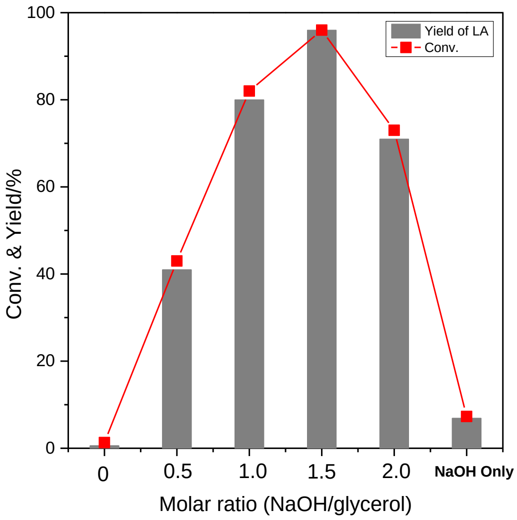

Figure S8. Effect of the amount of NaOH on the catalytic performance of 2Pt/ZrO_2-550-R250. Reaction conditions: aqueous glycerol solution: 10 mmol (0.5 M, 20 mL); cyclohexene: 20 mmol; nominal Pt/glycerol ratio = 1/1950; NaOH: 15 mmol; temperature: 160°C; reaction time: 4.5 h; N_2 pressure: 20 bar.

Table S2. Catalytic conversion of glycerol to lactic acid using a Pt/ZrO_2 catalyst at different reaction temperature.

						Selectivity in the conversion of glycerol (%)				Yield in the conversion of cyclohexene (%)[a]	
Entry	Catalyst	Temp. (°C)	$Conv._{GLY}$ (%)	Y_{LA} (%)	$S_{(transfer\text{-}H)}$ (%)	Lactic acid	Glyceric acid	Glycolic acid	Propane-diol	Cyclohexane	Benzene
1	$2Pt/ZrO_2$-550-R250	120	25	24	62	96	0.2	0.2	0.4	7.5	0.4
2	$2Pt/ZrO_2$-550-R250	140	40	39	69	95	0.4	0.2	0.9	14	0
3	$2Pt/ZrO_2$-550-R250	160	96	95	36	99	0.5	0.2	0.7	17	0
4	$2Pt/ZrO_2$-550-R250	180	> 99	97	47	97	0.7	0.6	1.8	23	0

Reaction conditions: aqueous glycerol solution: 10 mmol (0.5 M, 20 mL); cyclohexene: 20 mmol; nominal Pt/glycerol ratio = 1/1950; NaOH: 15 mmol; reaction time: 4.5 h; N_2 pressure: 20 bar. [a] Under the employed reaction conditions ($mol_{glycerol}$: $mol_{cyclohexene}$ = 1 : 2) the maximum theoretical yield of cyclohexane is 50%.

Table S3. Catalytic conversion of glycerol to lactic acid using a Pt/ZrO_2 catalyst, as a function of the presence of cyclohexene.

						Selectivity in the conversion of glycerol (%)				Yield in the conversion of cyclohexene (%)[a]	
Entry	Catalyst	Cyclohexene (mmol)	$Conv._{GLY}$ (%)	Y_{LA} (%)	$S_{(transfer\text{-}H)}$ (%)	Lactic acid	Glyceric acid	Glycolic acid	Propane-diol	Cyclohexane	Benzene
1	$2Pt/ZrO_2$-550-R250	20	40	39	69	95	0.4	0.2	0.9	14	0
2	$2Pt/ZrO_2$-550-R250	none	39	38	n.a.	97	1.0	0.4	1.6	n.a.	n.a.

Reaction conditions: aqueous glycerol solution: 10 mmol (0.5 M, 20 mL); cyclohexene: 20 mmol; nominal Pt/glycerol ratio = 1/1950; NaOH: 15 mmol; temperature: 140°C; reaction time: 4.5 h; N_2 pressure: 20 bar. [a] Under the employed reaction conditions ($mol_{glycerol}$: $mol_{cyclohexene}$ = 1 : 2) the maximum theoretical yield of cyclohexane is 50%.

Table S4. Catalytic conversion of glycerol to lactic acid using 2Pt/ZrO_2 550-R250. [a]

Entry	Catalyst	$Conv._{GLY}$ (%)	Y_{LA} (%)	Selectivity in the conversion of glycerol (%)				Yield in the gas phase (%)[b]
				Lactic acid	Glyceric acid	Glycolic acid	Propane-diol	H_2
1	2Pt/ZrO_2-550-R250	96	94	98	0	0	0.5	98

[a] Reaction conditions: aqueous glycerol solution: 30 mmol (1.0 M, 30 mL); nominal Pt/glycerol ratio = 1/1950; NaOH: 40 mmol; temperature: 160°C; reaction time: 4.5 h; N_2 pressure: 3 bar. [b] Around 10 bar H_2 (77% in the H_2 and N_2 mixture) was detected after reaction, corresponding to a volume of 65 mL. The moles of H_2 were calculated assuming an ideal gas behavior (pV = nRT) at 298 K.

Table S5. Catalytic conversion of glycerol over 2Pt/ZrO_2-550-R250 in the presence of 1-decene or 1-decyne as hydrogen acceptor. [a]

Entry	Hydrogen Acceptors	$Conv._{GLY}$ (%)	Y_{LA} (%)	$S_{(transfer\text{-}H)}$ (%)	Selectivity in the conversion of glycerol (%)				Yield in the conversion of hydrogen acceptors (%)[b]	
					Lactic acid	Glyceric acid	Glycolic acid	Propane -diol	Decene	Decane
1	1-decene	97	96	92	99	0.7	0.1	0.1	-	45
2	1-decyne	1.3	1.2	n.a.	94	2.5	0	0.3	n.a.	n.a.

[a] Reaction conditions: aqueous glycerol solution: 10 mmol (0.5 M, 20 mL); hydrogen acceptors: 20 mmol; nominal Pt/glycerol ratio = 1/1950; NaOH: 15 mmol; temperature: 160°C; reaction time: 4.5 h; N_2 pressure: 20 bar. [b] Under the employed reaction conditions ($mol_{glycerol}$: mol_{decene} = 1 : 2) the maximum theoretical yield of decane is 50%. n.a. = not available.