# Supplemental Information

## Selective oxidation of benzyl alcohol using *in situ* generated $H_2O_2$ over hierarchical Au-Pd titanium silicalite catalysts.

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**Table S1** Low temperature benzyl alcohol oxidation in autoclave reactor over various catalysts and the product distribution.

| Catalyst | Conversion (%) | Selectivity (%) | | | | | Benzaldehyde production (mol/h/$Kg_{cat}$)[1] |
|---|---|---|---|---|---|---|---|
| | | benzene | toluene | benzaldehyde | benzoic acid | benzyl benzoate | |
| TS-1 (XG-REF) | 1.0 | 0 | 0 | 100 | 0 | 0 | 5 |
| TS-1 (LG-12%) | 1.0 | 0 | 0 | 100 | 0 | 0 | 5 |
| AX | 0.1 | 0 | 0 | 100 | 0 | 0 | 1 |
| A12 | 0 | - | - | - | - | - | 0 |
| APX | 0.2 | 0 | 0 | 100 | 0 | 0 | 1 |
| AP12 | 0.2 | 0 | 0 | 100 | 0 | 0 | 1 |
| PX | 0.1 | 0 | 0 | 100 | 0 | 0 | 1 |
| P12 | 0.1 | 0 | 0 | 100 | 0 | 0 | 1 |

Conditions; 0-2°C, methanol (5.6 g), water (2.9 g), 2.3 mmol benzyl alcohol (0.25 g), 30 minutes, catalyst (10 mg), 25%$O_2$/$CO_2$ (10.4 bar, 150 psi). [1] ±0.5 mol/h/$Kg_{cat}$.

**Table S2** $H_2O_2$ productivity at 2°C of various catalysts.

| **Catalyst** | **Productivity ($mol_{H_2O_2}/h/Kg_{cat}$)[1]** | **$H_2O_2$ (wt.%)** |
|---|---|---|
| TS-1 (XG-REF) | 0 | 0 |
| TS-1 (LG-12%) | 0 | 0 |
| AX | 0 | 0 |
| A12 | 0 | 0 |
| APX | 34 | 0.07 |
| AP12 | 25 | 0.05 |
| PX | 6 | 0.01 |
| P12 | 15 | 0.03 |

Conditions; 0-2°C, methanol (5.6 g), water (2.9 g), 30 minutes, catalyst (10 mg), 5 % $H_2/CO_2$ (28.96 bar, 420 psi), 25%$O_2/CO_2$ (10.4 bar, 150 psi). [1] ±0.5 mol/h/$Kg_{cat}$.

**Table S3** $H_2O_2$ productivity at 30°C of various catalysts.

| **Catalyst** | **Productivity ($mol_{H_2O_2}/h/Kg_{cat}$)[1]** | **$H_2O_2$ (wt.%)** |
|---|---|---|
| TS-1 (XG-REF) | 0 | 0 |
| TS-1 (LG-12%) | 0 | 0 |
| AX | 0 | 0 |
| A12 | 0 | 0 |
| APX | 124 | 0.25 |
| AP5 | 96 | 0.19 |
| AP8 | 84 | 0.17 |
| AP12 | 95 | 0.19 |
| DAPX | 12 | 0.02 |
| DAP12 | 40 | 0.08 |
| PX | 16 | 0.03 |
| P12 | 77 | 0.15 |

Conditions; 30°C, methanol (5.6 g), water (2.9 g), 30 minutes, catalyst (10 mg), 5 % $H_2/CO_2$ (28.96 bar, 420 psi), 25%$O_2/CO_2$ (10.4 bar, 150 psi). [1] ±0.5 mol/h/$Kg_{cat}$.

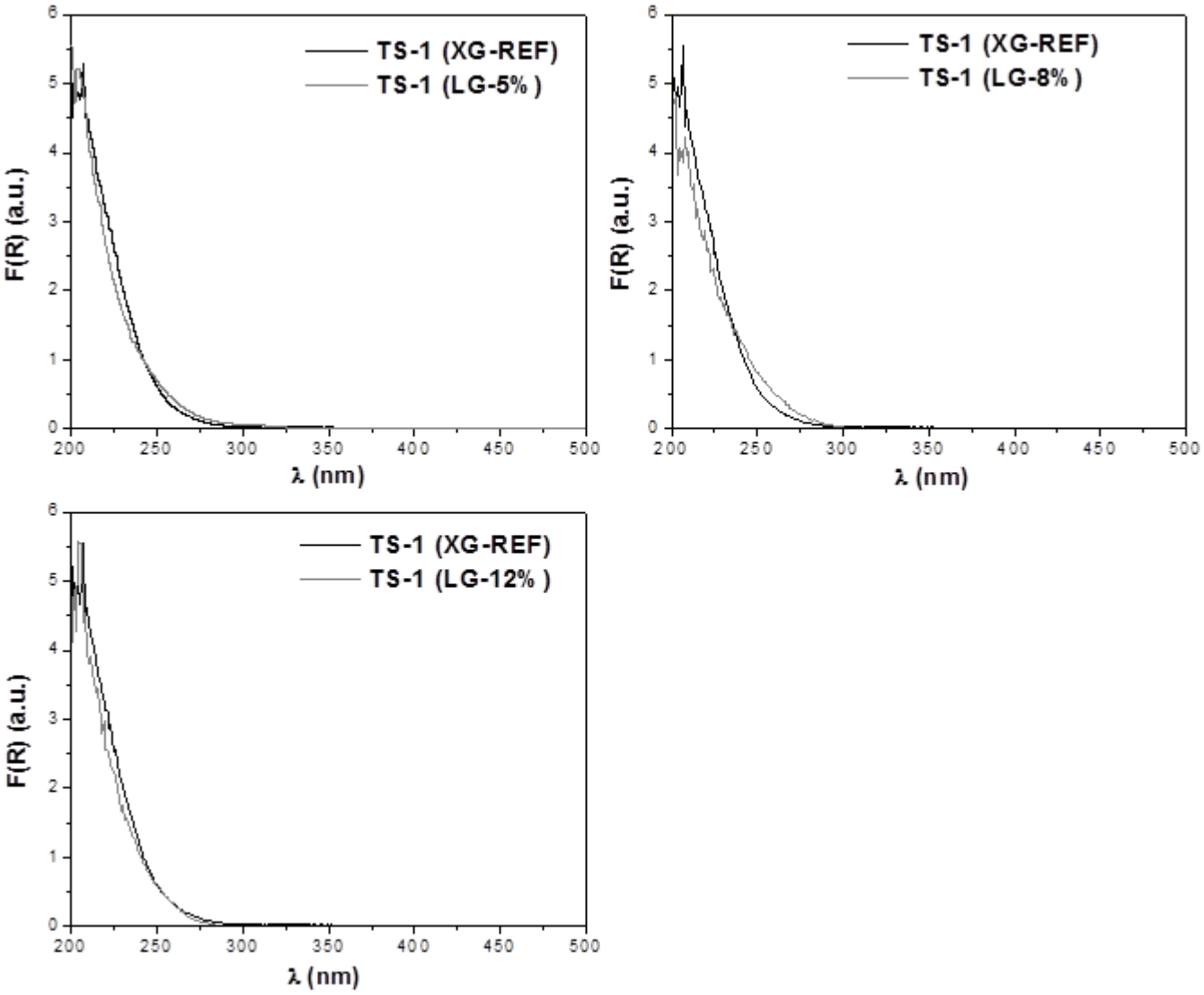


**Fig. S1** Comparison DR UV/Vis spectroscopy of hierarchical TS-1 samples and TS-1 reference zeolite (calcined).