Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.


**SUPPORTING INFORMATION**

# Spectroscopic insights leading to a better understanding of site-isolation in heterogeneous nanocatalysts

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**Table SI-1.** Investigations into the production of cyclohexanone from cyclohexanol.

| **Catalyst Active Species** | **Support** | **Process** | **Substrate** | **Oxidant** | **Temp. / ºC** | **Time / hr** | **Cyol Conv. / %** | **Cyone Yield / %** | **Ref.** |
|---|---|---|---|---|---|---|---|---|---|
| Cu NPs | Zn / Si Oxide | Flow | Cyol | * | 300 | 2 | 91 | 77 | 1 |
| CuO / MgO | - | Flow | Cyol | * | 330 | 1 | 83 | 77 | 2 |
| CaO | Ti Oxide | Flow | Cyol | * | 350 | 1 | 90 | 68 | 3 |
| $CuO / Al_2O_3$ | - | Flow | Cyol | * | 330 | 1 | 48 | 45 | 2 |
| Cu / Ni NPs | Ce Oxide | Flow | Cyol | * | 350 | 1 | 42 | 38 | 4 |
| $CaO / V_2O_5$ | Ti Oxide | Flow | Cyol | * | 427 | 1 | 75 | 38 | 3 |
| Cu NPs | Ce Oxide | Flow | Cyol | * | 350 | 1 | 32 | 28 | 4 |
| Ni NPs | Ce Oxide | Flow | Cyol | * | 350 | 1 | 26 | 24 | 4 |
| Au NPs | Ti Oxide | Batch | Cyol | $H_2O_2$ | 90 | 1 | 87 | 87 | 5 |
| $V_2O_3$ | K / Mn Oxide | Batch | Cyol | $H_2O_2$ | 90 | 8 | 26 | 26 | 6 |
| $V_2O_3$ | K / Mn Oxide | Batch | Cyol | TBHP | 90 | 8 | 49 | 49 | 6 |
| Cu | Aluminosilicate | Batch | Cyol | TBHP | 50 | 8 | 42 | 42 | 7 |
| Cr | Si Oxide | Batch | Cyol | TBHP | 70 | 5 | 38 | 38 | 8 |
| Ru Complex | Metal Oxide | Batch | Cyol | Air | 25 | 5 | 71 | 71 | 2 |
| $RuO_2$ | Aluminosilicate | Batch | Cyol | Air | 80 | 4 | 43 | 43 | 9 |
| Pt NPs | Aluminosilicate | Batch | Cyol | Air | 25 | 20 | 21 | 18 | 10 |
| Au / Ag NPs | Solution | Batch | Cyol | $O_2$ | 150 | 0.25 | 76 | 76 | 11 |
| Au / Cu NPs | Cu Oxide | Flow | Cyol | $O_2$ | 250 | 1 | 76 | 75 | 12 |
| Ru | Tungstosilicate | Batch | Cyol | $O_2$ | 100 | 48 | 83 | 67 | 13 |
| Pd NPs | Ce Oxide | Batch | Cyol | $O_2$ | 120 | 12 | 58 | 57 | 14 |

*Cyol = Cyclohexanol, Cyone = Cyclohexanone, TBHP = tert-Butyl Hydroperoxide. * = Dehydrogenation.*

**Figure SI-1.** Digital image taken to display the colours of the Pt/CuClP materials depending on the Pt loading. From left to the right: 7, 5, 3 and 1 wt. % Pt/CuClP samples and the un-doped framework.

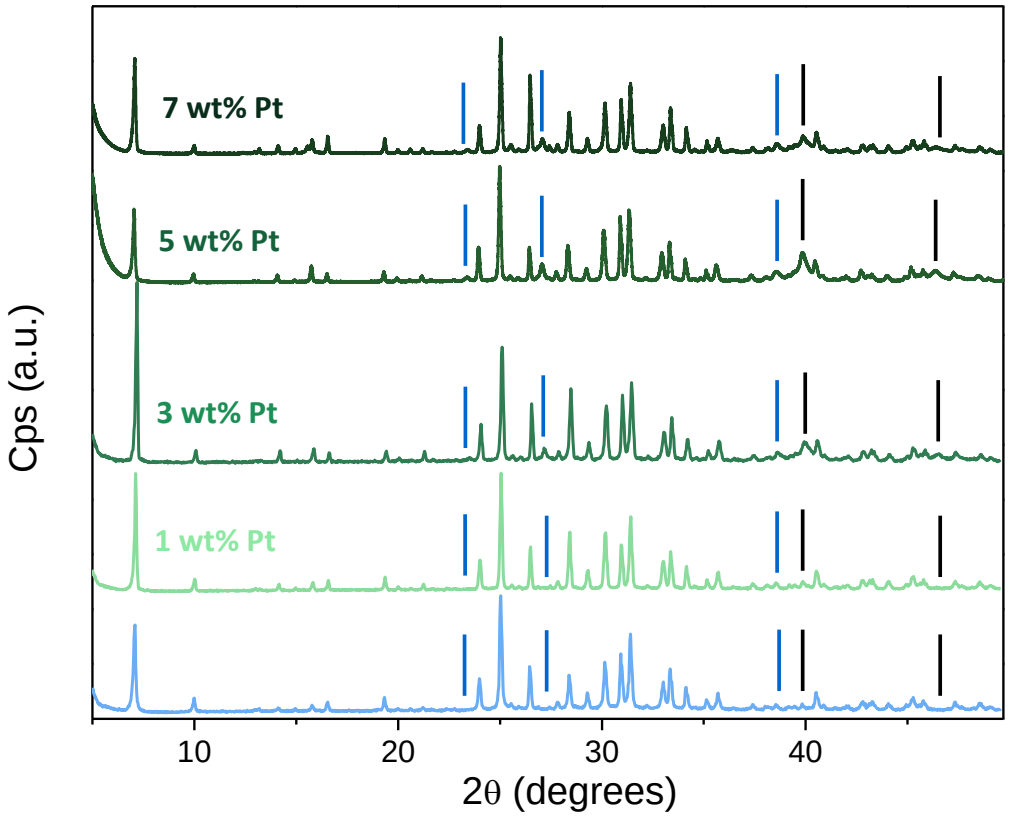



**Figure SI-2.** PXRD patterns of all percentage loading of Pt in Pt/CuClP used materials (green curves) and blank framework (light blue curves). The peaks assigned to RbCl (blue bars) and metallic Pt (black bars) phases are indicated.

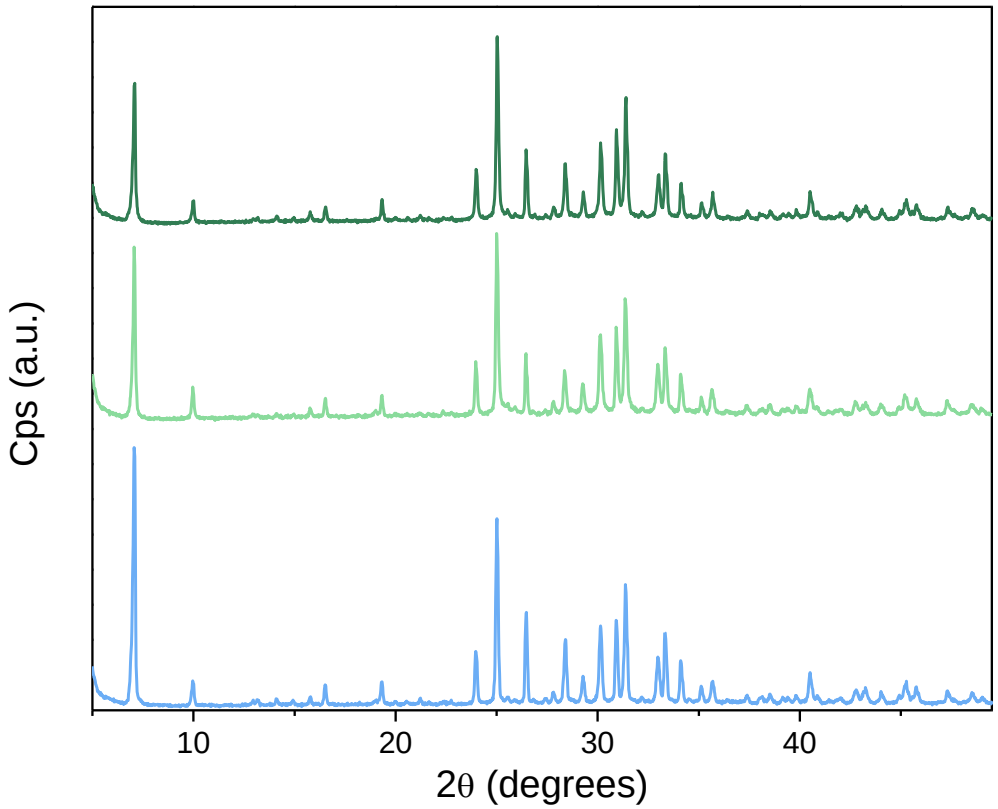



**Figure SI-3.** PXRD patterns of the as-synthesized (pale blue curve), reduced (pale green curve) and used (dark green curve) blank framework material.

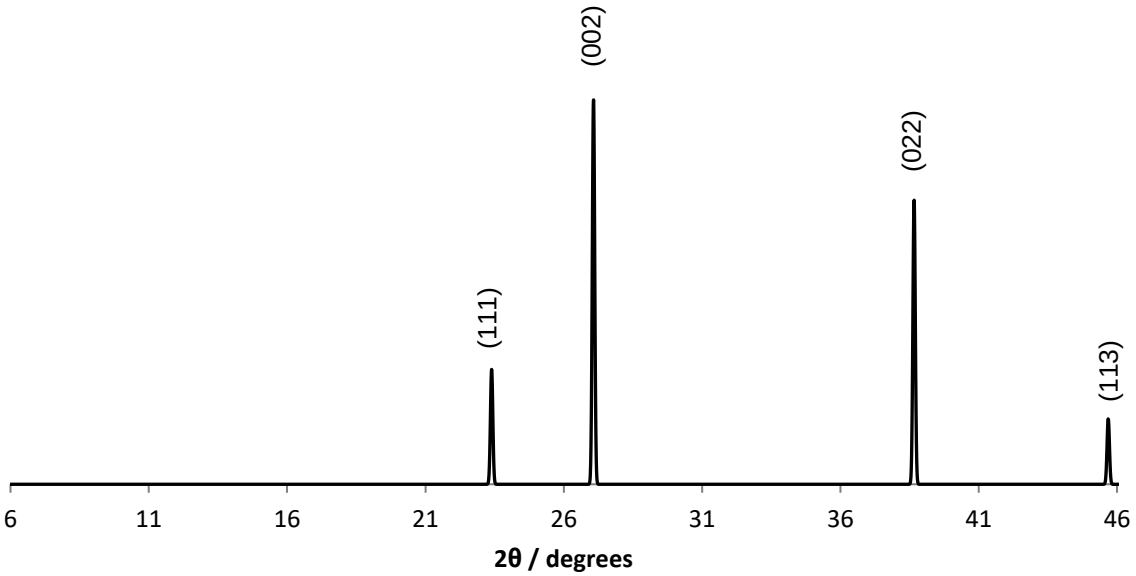



**Figure SI-4.** Simulated PXRD pattern of the RbCl, rubidium chloride phase.[15]

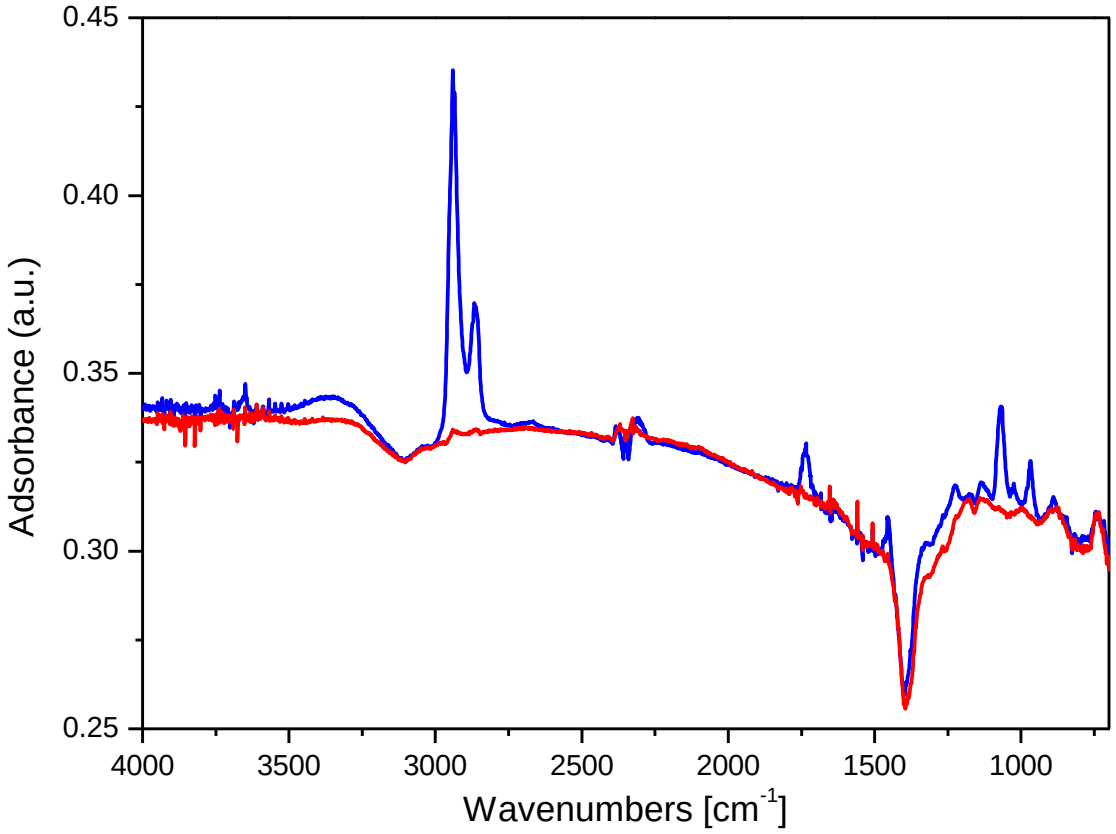



**Figure SI-5.** Comparison between the FTIR spectra collected on the 7 wt. % catalyst after 50 min at 200° C in cyclohexanol (blue curve) and after outgassing at 200 °C at a residual pressure below $1 \cdot 10^{-3}$ mbar (red curve).

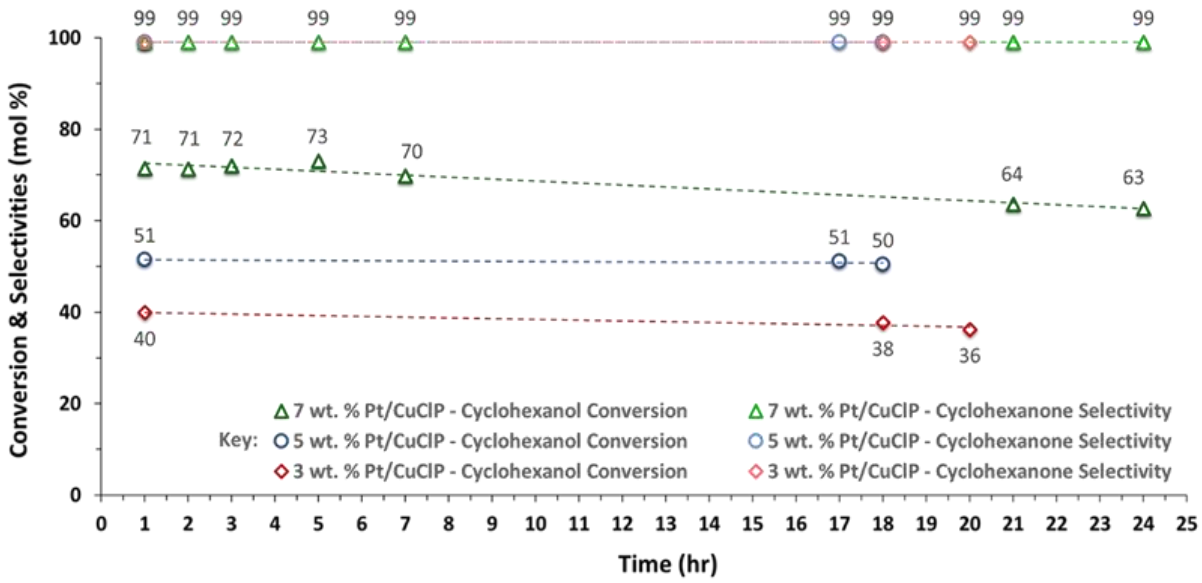



**Figure SI-6.** Time on stream data showing cyclohexanol conversion (bold colour) and cyclohexanone selectivity (pale colour) for the 3 (red), 5 (blue) and 7 (green) wt. % Pt/CuClP catalysts. Note: both the 1 wt. % Pt/CuClP sample and the un-doped framework showed no catalytic activity.

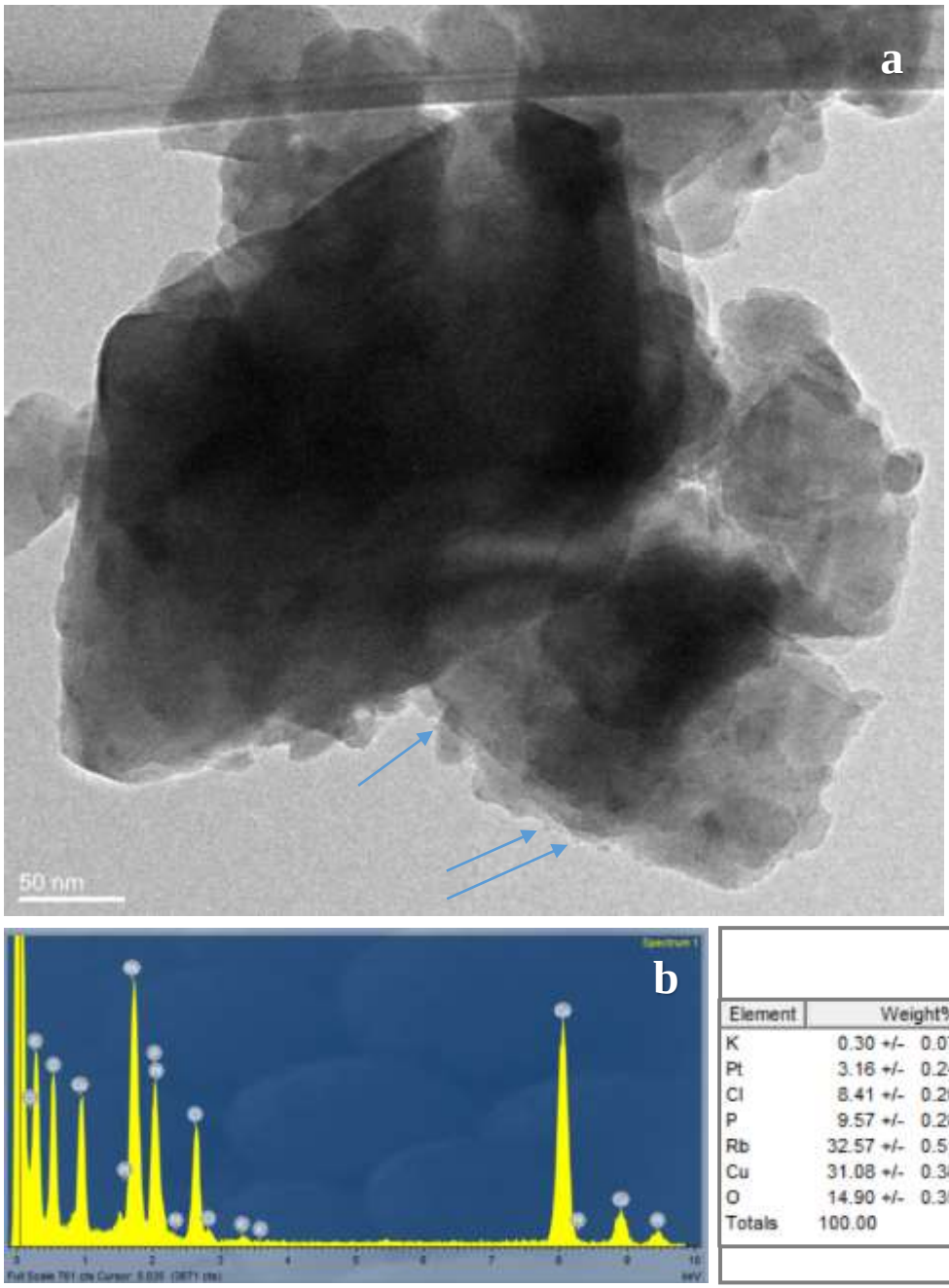
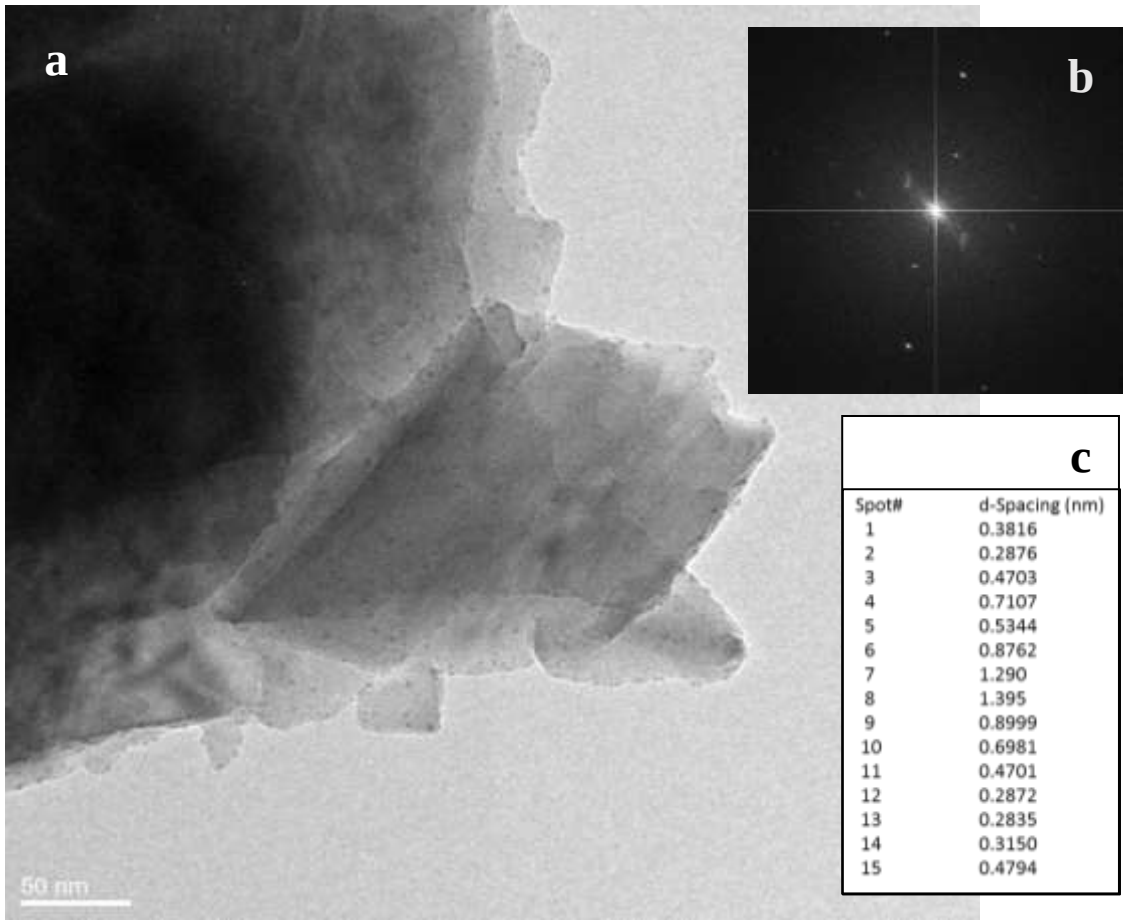
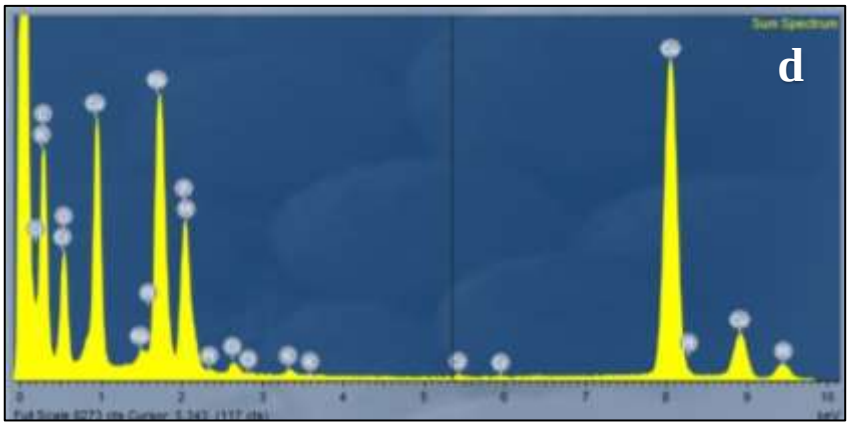



**Figure SI-7.** Section a: TEM image of the fresh 3 wt. % Pt/CuClP catalyst, instrumental magnification 50000×. The blue arrows indicate isolated Pt nanoparticles. Section b: EDS spectrum. Section C: Elemental analysis of the image in section a.




c

| Spot# | d-Spacing (nm) |
|---|---|
| 1 | 0.3816 |
| 2 | 0.2876 |
| 3 | 0.4703 |
| 4 | 0.7107 |
| 5 | 0.5344 |
| 6 | 0.8762 |
| 7 | 1.290 |
| 8 | 1.395 |
| 9 | 0.8999 |
| 10 | 0.6981 |
| 11 | 0.4701 |
| 12 | 0.2872 |
| 13 | 0.2835 |
| 14 | 0.3150 |
| 15 | 0.4794 |




e

| Element | Weight% | | Atomic% |
|---|---|---|---|
| Cr | 0.15 +/- | 0.03 | 0.09 |
| K | 0.32 +/- | 0.03 | 0.25 |
| Pt | 3.15 +/- | 0.10 | 0.49 |
| Cl | 0.58 +/- | 0.04 | 0.49 |
| P | 6.28 +/- | 0.10 | 6.13 |
| Rb | 26.95 +/- | 0.22 | 9.54 |
| O | 7.09 +/- | 0.14 | 13.41 |
| Cu | 34.35 +/- | 0.21 | 16.36 |
| C | 21.13 +/- | 0.33 | 53.24 |
| Totals | 100.00 | | 100.00 |

**Figure SI-8.** Section a: TEM image of the activated 3 wt. % Pt/CuClP catalyst, instrumental magnification 50000×. Section b: FFT of the image in section a proving the crystallinity of the CuClP framework. Section c: EDS spectrum of the sample shown in section a. Section d: Elemental analysis of the image in section a. Note - the small peaks related to the presence of Chromium (highlighted in section e) are due to the microscope column. A 20wt. % C, due to the lacey carbon film of the grid, was also detected.

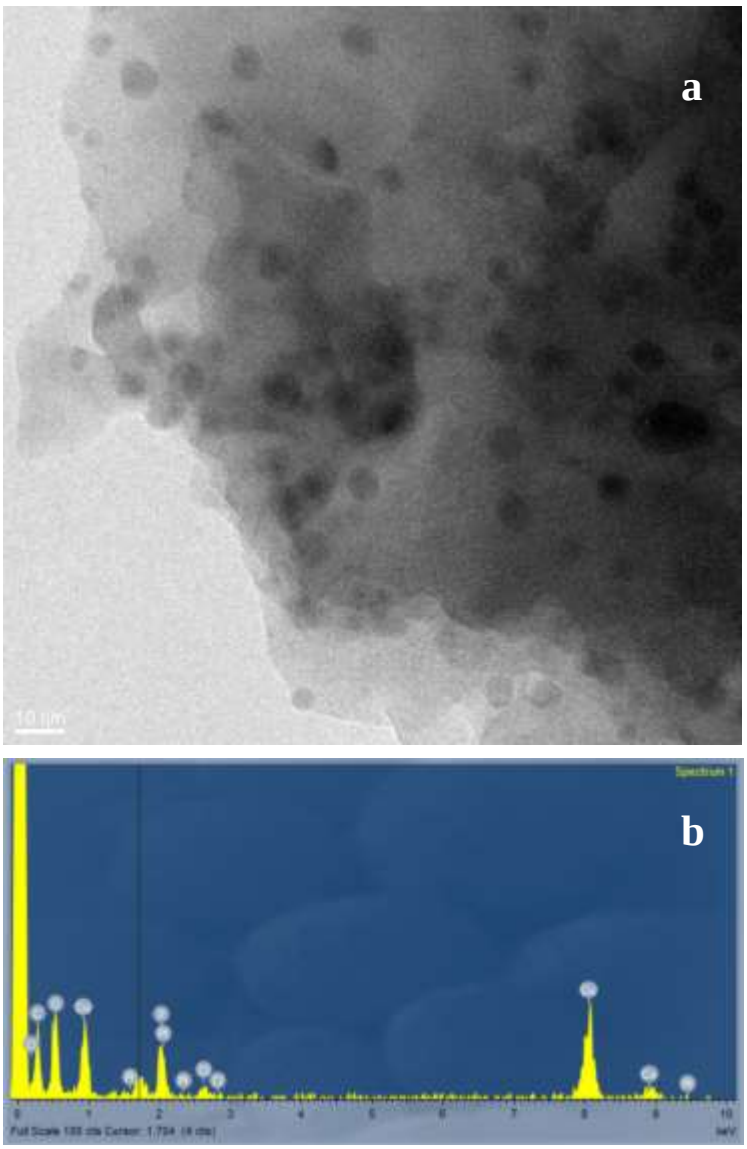



**Figure SI-9.** Section a: TEM image of the used 3 wt. % Pt/CuClP catalyst, instrumental magnification 150000×. Section b: EDS spectrum of the sample shown in section a.

| h | K | l | $D_{hkl}$ (Å) | 2-Theta |
|---|---|---|---|---|
| 1 | 1 | 0 | 12.75 | 6.99 |
| 2 | 2 | 0 | 6.35 | 14.00 |
| 1 | 3 | 0 | 5.77 | 15.66 |
| 0 | 2 | 2 | 5.49 | 16.46 |
| 0 | 4 | 2 | 3.77 | 23.87 |
| 3 | 3 | 2 | 3.61 | 24.90 |
| 3 | 4 | 1 | 3.42 | 25.76 |

**Table SI-2.** List of the d-spacings obtained from HR-TEM images collected on the activated 3 wt. % Pt/CuClP catalyst.

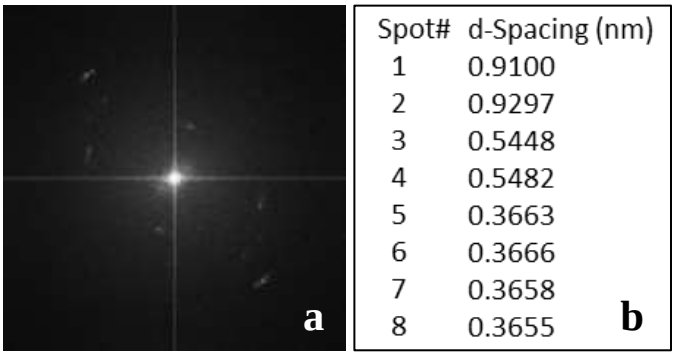



**Figure SI-10.** Section a: Fourier transform (FT) of the TEM image reported in Figure SI-9. Section b: List of *d* spacings measured on the FT shown in section a.

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