Supporting Information

Understanding selectivity in CO\textsubscript{2} hydrogenation to methanol for MoP nanoparticle catalysts using in situ techniques

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| Conditions     | Path | N  | R (Å)  | σ² (Å²)  | ΔE (eV) | R-factor |
|----------------|------|----|--------|----------|---------|----------|
| MoP std        | Mo-P | 6ª | 2.449(7)| 0.0022(9)| 5.8(7)  | 0.02     |
|                | Mo-Mo| 8ª | 3.212(6)| 0.0042(7)|         |          |
| RT, Heᵇ       | Mo-O | 0.5(3)| 1.95(5)| 0.002²  | 4(1)    | 0.009    |
|                | Mo-P | 5(1)| 2.43(2) | 0.013(2) |         |          |
| 450°C, H₂      | Mo-P | 5.3 | 2.440(8)| 0.006(1) | 5(1)    | 0.013    |
|                | Mo-Mo| 3(1)| 3.209(9)| 0.007(2) |         |          |
| 700°C, H₂      | Mo-P | 5.4 | 2.440(8)| 0.008(1) | 5(1)    | 0.016    |
|                | Mo-Mo| 4(1)| 3.22(1) | 0.008(2) |         |          |
Figure S2: XANES difference between crystalline MoP and as-prepared colloidal nanoparticles.

Figure S3: First derivative of the XANES region of the Mo K-edge for different standards and as prepared Mo NPs at room temperature.
Figure S4: comparison of the FT of EXAFS signal at Mo K-edge for silica supported and unsupported Mo NPs

Table S2: Surface area (reported by manufacturer), Mo and P loadings determined via ICP and Mo/P ratios for amorphous MoP nanoparticles on various metal oxide supports.

| Catalyst       | Surface area for support (m²/g) | Mo loading (wt%) | P loading (wt%) | Mo/P molar ratio |
|----------------|---------------------------------|------------------|-----------------|------------------|
| MoP/Al₂O₃      | 185                             | 3.13%            | 0.79%           | 1.28             |
| MoP/ZrO₂       | 103                             | 0.05%            | 0.01%           | 1.99             |
| MoP/SiO₂       | 15-45                           | 1.61%            | 0.51%           | 1.01             |
| MoP/TiO₂       | 35-65                           | 0.75%            | 0.28%           | 0.86             |
| MoP/CeO₂       | 30                              | 1.83%            | 0.60%           | 0.98             |
| MoP/ZnO        | 10.8                            | 0.33%            | 0.29%           | 0.87             |
Figure S5: Conversion and methanol selectivity of MoP nanoparticle catalysts on various supports during CO₂ hydrogenation. Test conditions: CO₂ hydrogenation, 40 bar, 250°C, H₂/CO₂=3, Conversion=0.3-1.8%. Data shown were collected after 7 hours on stream.

Table S3: Conversion and activity towards alcohols. Data shown collected after 7 hours on stream.

| Catalyst      | Conversion | g C₁OH/h gcat |
|---------------|------------|---------------|
| MoP/Al₂O₃     | 1.4%       | 9.0x10⁻²      |
| MoP/ZrO₂      | 1.4%       | 3.4x10⁻²      |
| MoP/SiO₂      | 0.8%       | 0.4x10⁻²      |
| MoP/TiO₂      | 0.8%       | 0.2x10⁻²      |
| MoP/CeO₂      | 1.8%       | 1.1x10⁻²      |
| MoP/ZnO       | 0.3%       | 0.4x10⁻²      |
Figure S6: X-ray Photoelectron Spectroscopy (XPS) of air exposed unsupported and zirconia supported MoP nanoparticles

Figure S7: Activity of ZrO$_2$ support during CO$_2$ hydrogenation. Test conditions: CO$_2$ hydrogenation, 40 bar, 250$^\circ$C, H$_2$/CO$_2$=3
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