Supporting Information

Understanding selectivity in CO_2 hydrogenation to methanol for MoP nanoparticle catalysts using *in situ* techniques

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Table of Contents:

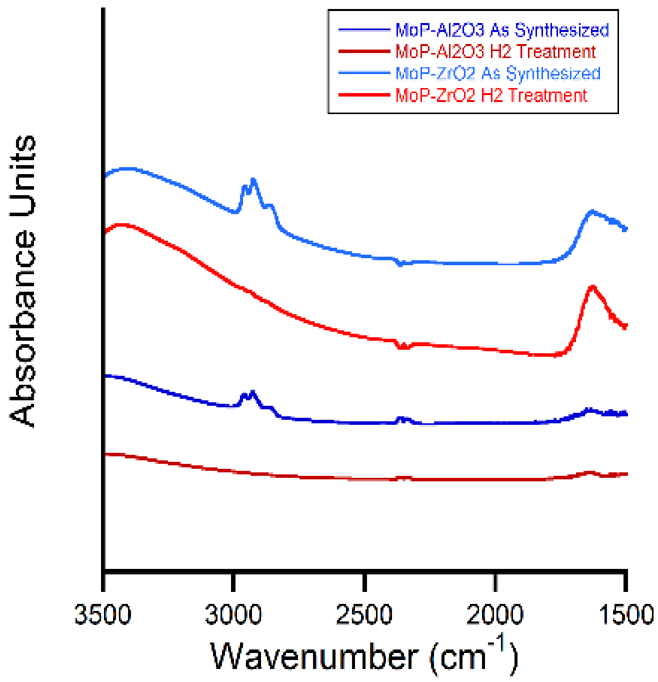

Figure S1: C-H stretching region of the ex-situ IR spectra for supported MoP catalysts with the highest and lowest loading of MoP, showing the removal of ligands after hydrogen reduction treatment (450°C, 1hour)

Table S1: Curve-fit results for the EXAFS data for Mo K-edge: S02 was set to 0.72 for all samples as determined by the fit of MoP standards (0.72±0.07). The data ranges used in the fit are 3.0 ≤ k ≤ 12.5 Å−1 and 1.0 Å ≤ R ≤ 3.3 Å (b1.0 Å ≤ R ≤ 2.3 Å). a Set to the crystallographic values. c set value. Uncertainties in the last digit are shown in parentheses.

Conditions	Path	N	R (**Å)**	**σ^2 (Å^2)**	**ΔE (eV)**	R-factor
MoP std	Mo-P	6[a]	2.449(7)	0.0022(9)	5.8(7)	0.02
	Mo-Mo	8[a]	3.212(6)	0.0042(7)		
RT, He[b]	Mo-O	0.5(3)	1.95(5)	0.002[c]	4(1)	0.009
	Mo-P	5(1)	2.43(2)	0.013(2)		
450°C, H_2	Mo-P	5.3 (6)	2.440 (8)	0.006(1)	5(1)	0.013
	Mo-Mo	3(1)	3.209(9)	0.007(2)		
700°C, H_2	Mo-P	5.4(5)	2.440(8)	0.008(1)	5(1)	0.016
	Mo-Mo	4(1)	3.22(1)	0.008(2)		

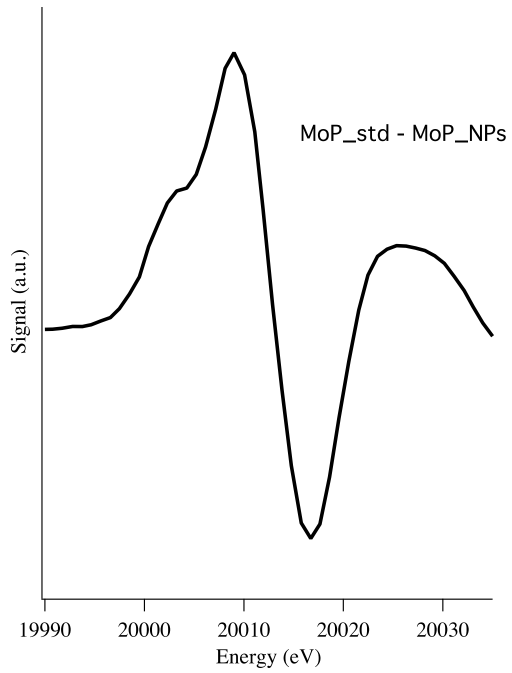

Figure S2: XANES difference between crystalline MoP and as-prepared colloidal nanoparticles.

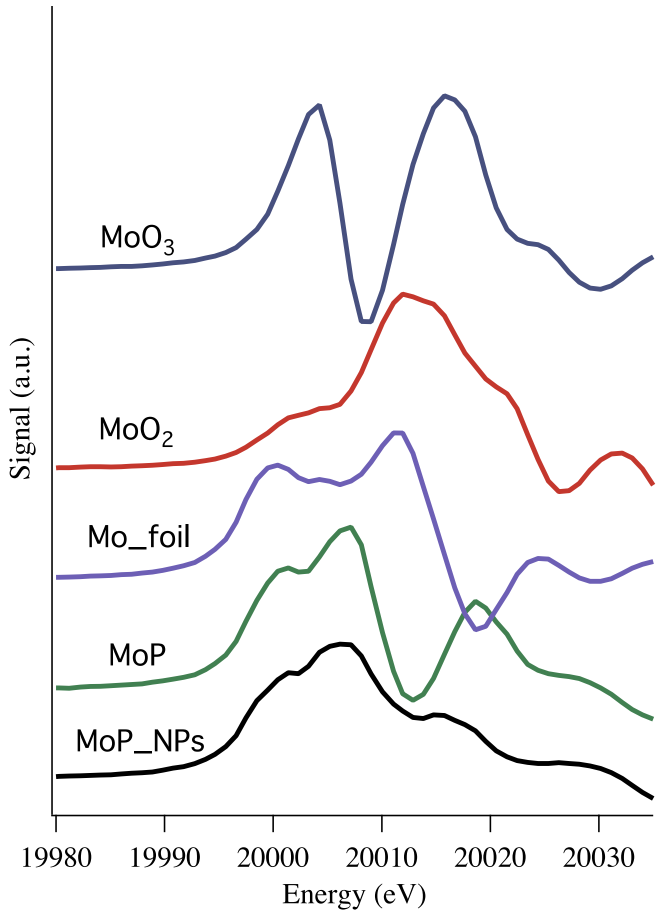

Figure S3: First derivative of the XANES region of the Mo K-edge for different standards and as prepared Mo NPs at room temperature.

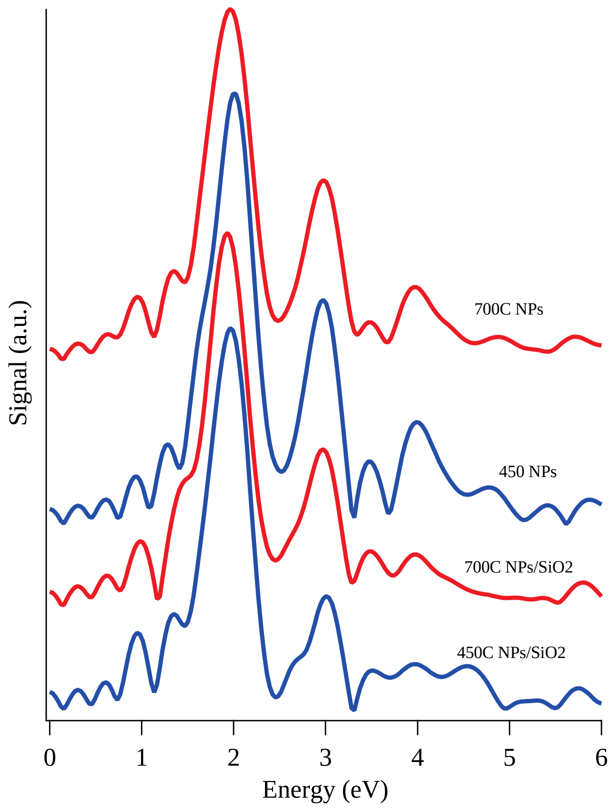

Figure S4: comparison of the FT of EXAFS signal at Mo K-edge for silica supported and unsupported Mo NPs

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 (m^2/g)**	**Mo loading (wt%)**	**P loading (wt%)**	**Mo/P molar ratio**
MoP/Al_2O_3	185	3.13%	0.79%	1.28
MoP/ZrO_2	103	0.05%	0.01%	1.99
MoP/SiO_2	15-45	1.61%	0.51%	1.01
MoP/TiO_2	35-65	0.75%	0.28%	0.86
MoP/CeO_2	30	1.83%	0.60%	0.98
MoP/ZnO	10.8	0.33%	0.29%	0.87

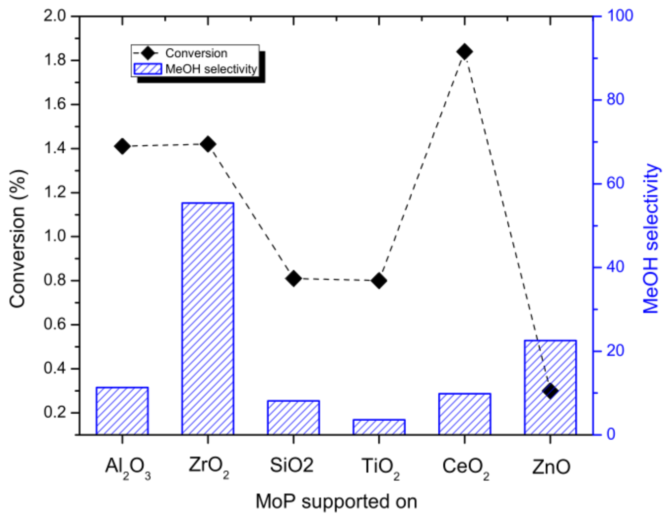

Figure S5: Conversion and methanol selectivity of MoP nanoparticle catalysts on various supports during CO_2 hydrogenation. Test conditions: CO_2 hydrogenation, 40 bar, 250°C, H_2/CO_2=3, Conversion=0.3-1.8%. Data shown were collected after 7 hours on stream.

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

Catalyst	Conversion	g $C_{1+}OH$/h gcat
MoP/Al_2O_3	1.4%	$9.0x10^{-2}$
MoP/ZrO_2	1.4%	$3.4x10^{-2}$
MoP/SiO_2	0.8%	$0.4x10^{-2}$
MoP/TiO_2	0.8%	$0.2x10^{-2}$
MoP/CeO_2	1.8%	$1.1x10^{-2}$
MoP/ZnO	0.3%	$0.4x10^{-2}$

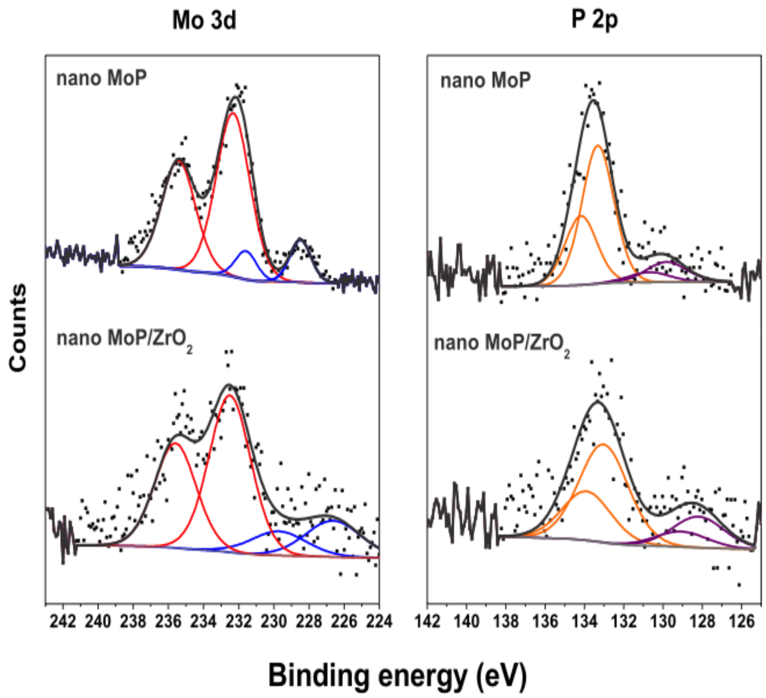

Figure S6: X-ray Photoelectron Spectroscopy (XPS) of air exposed unsupported and zirconia supported MoP nanoparticles

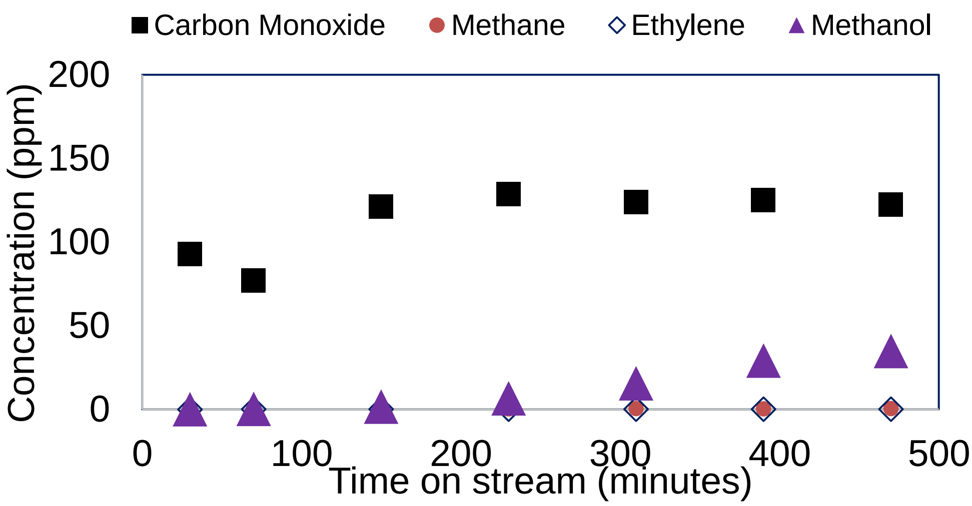

Figure S7: Activity of ZrO_2 support during CO_2 hydrogenation. Test conditions: CO_2 hydrogenation, 40 bar, 250°C, H_2/CO_2=3

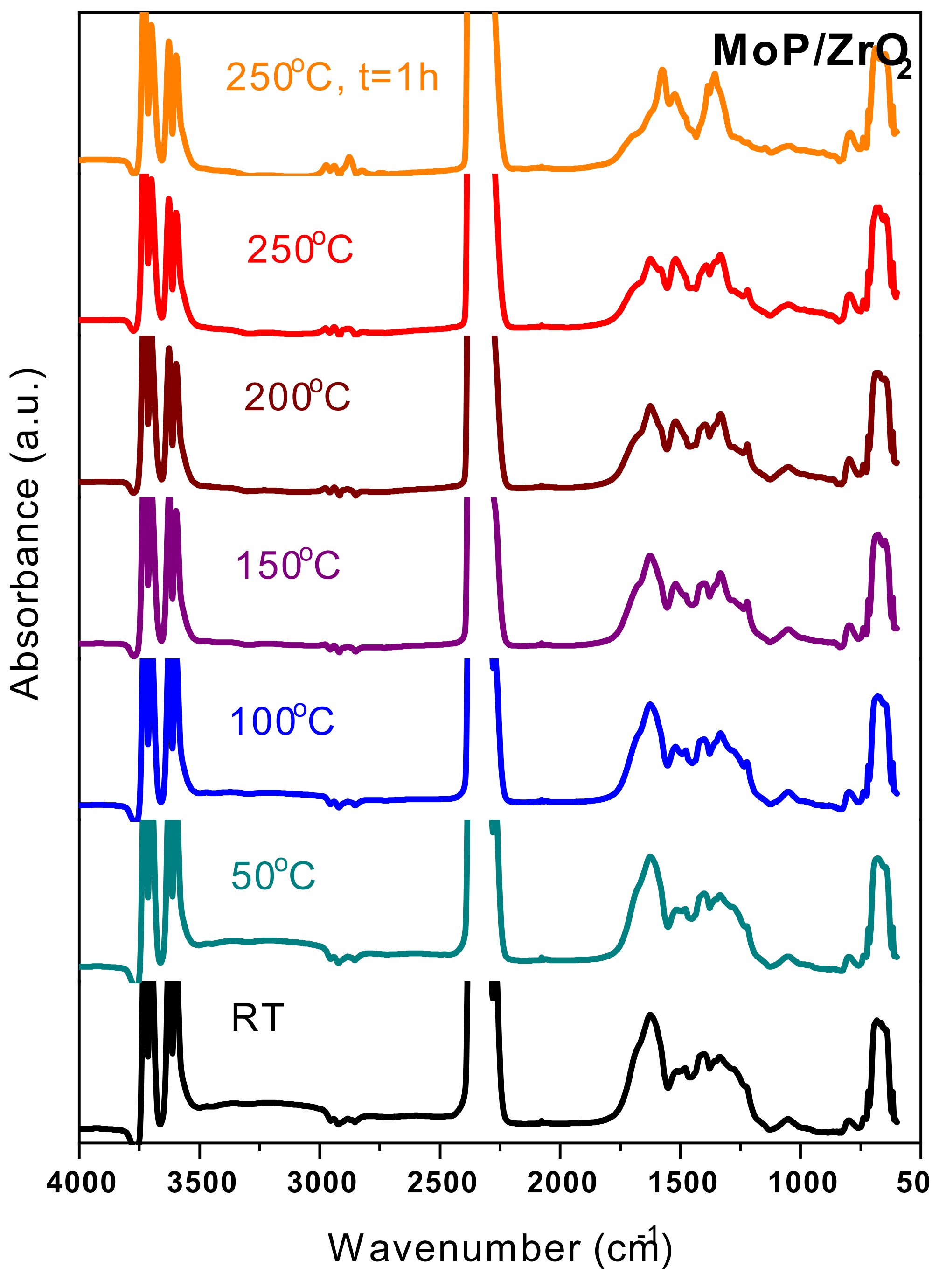

Figure S8: TPSR-DRIFTS full spectrum for MoP/ZrO_2. Spectra were normalized to initial room temperature background taken under vacuum which is why the TOP ligands (see Figure S1) can be seen as negative peaks in the C-H stretching region (ligands were removed with the reduction treatment prior to TPSR) until higher temperatures when the formates begin to form and associated C-H stretching bands become dominant.

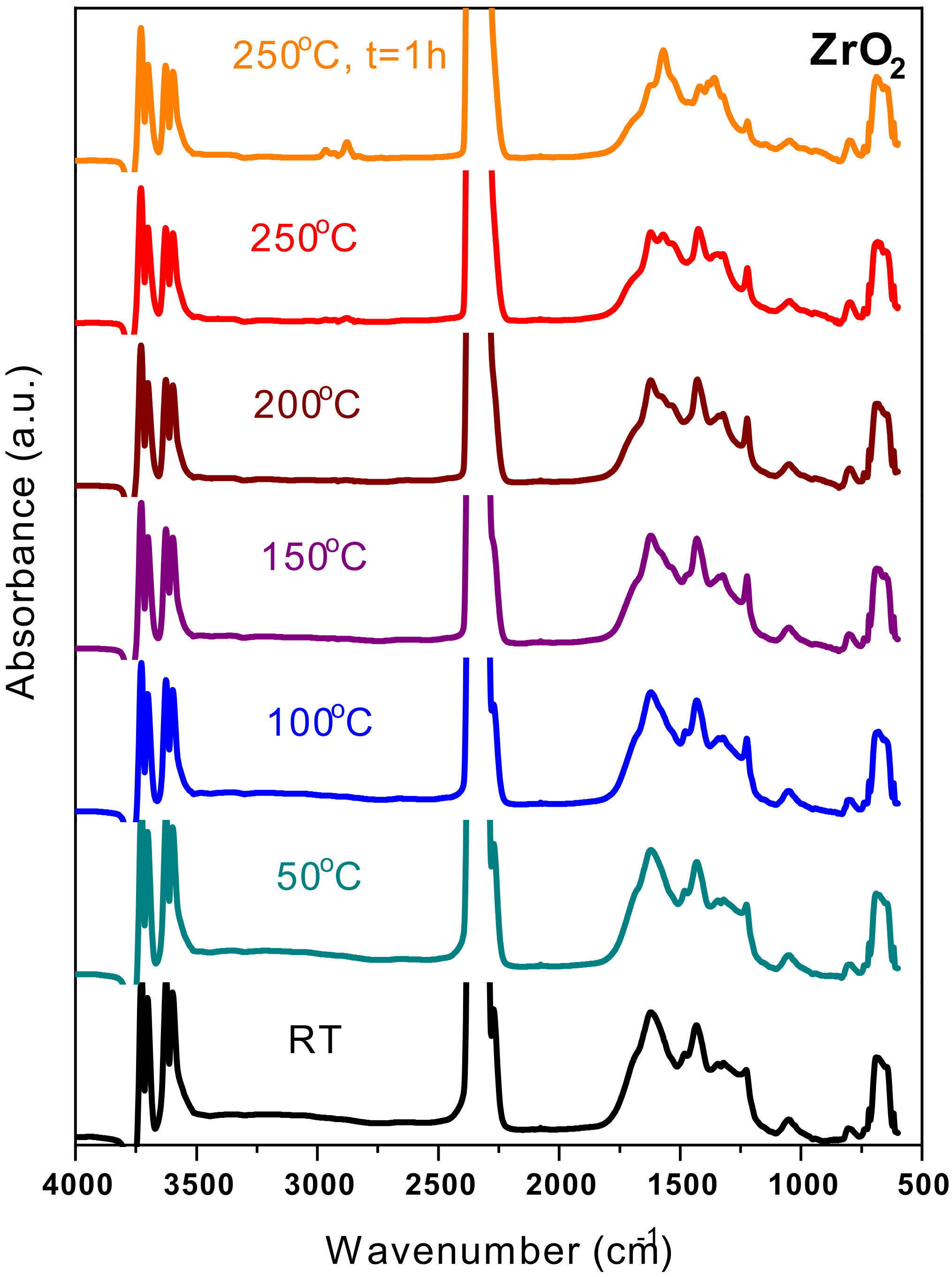

Figure S9: TPSR-DRIFTS full spectrum for ZrO_2

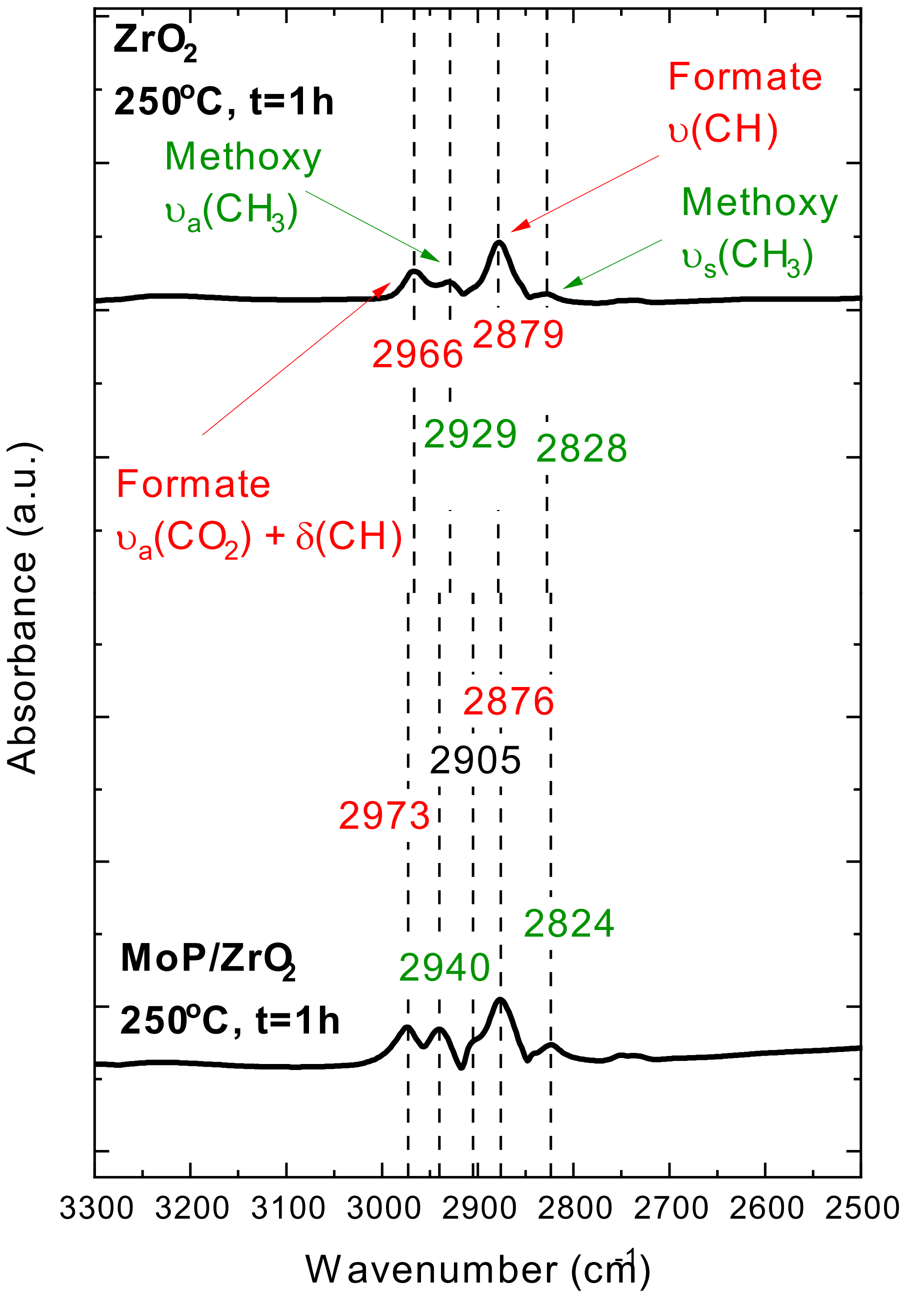

Figure S10: TPSR-DRIFTS C-H region