

## Supporting information

# Ultradispersed Mo/TiO<sub>2</sub> catalysts for CO<sub>2</sub> hydrogenation to methanol

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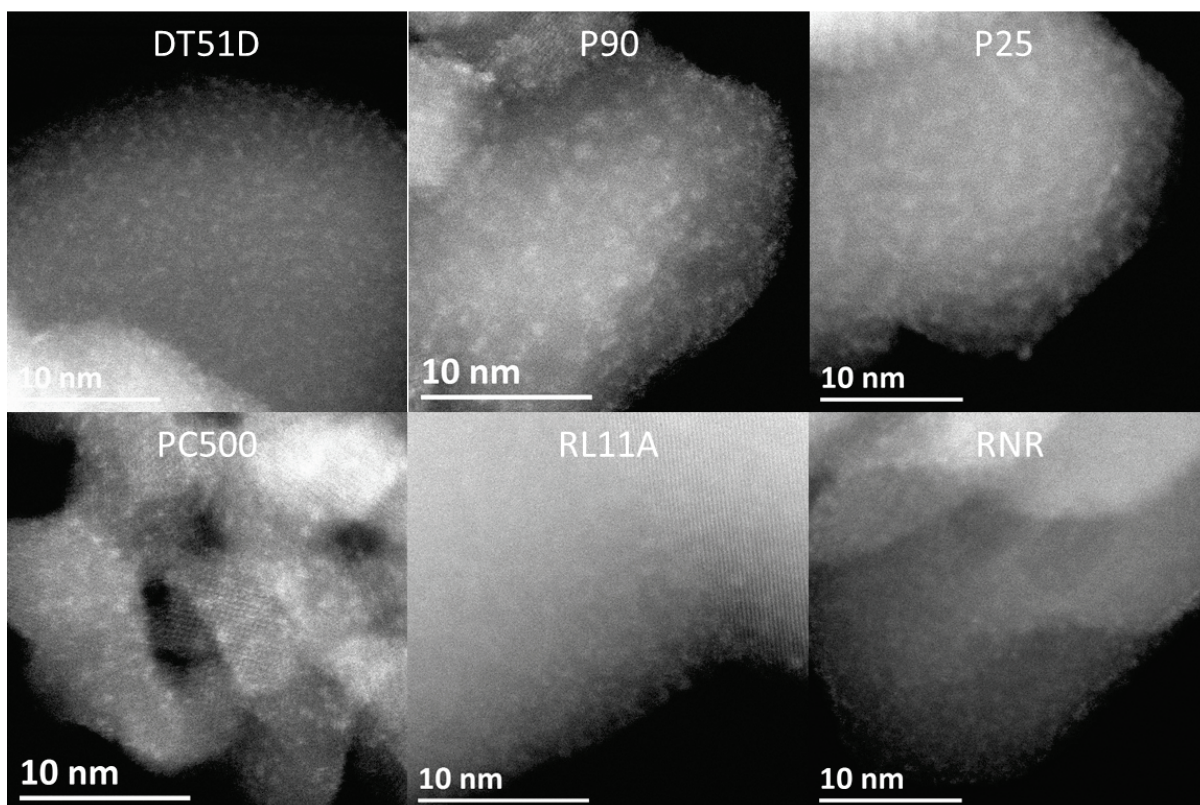


Figure S1 – Representative aberration-corrected STEM-HAADF micrographs of 3 wt% Mo/TiO<sub>2</sub> catalysts.

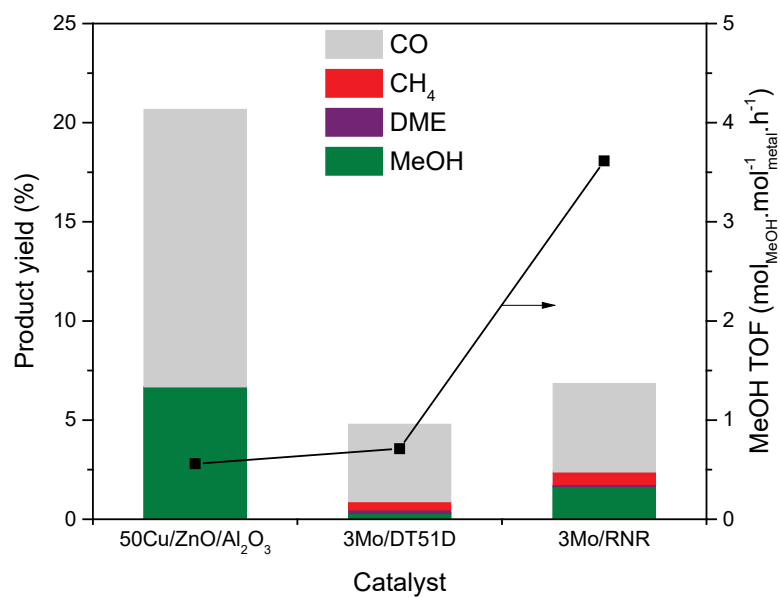


Figure S2 – CO/MeOH/CH<sub>4</sub>/DME yields and methanol TOF per mol of Mo or Cu for the two best 3Mo/TiO<sub>2</sub>-R450 catalysts and the 50 wt% Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> reference at 275 °C under 30 bar of H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> (3/1/1), GHSV = 7500 mL.g<sup>-1</sup>.h<sup>-1</sup>.

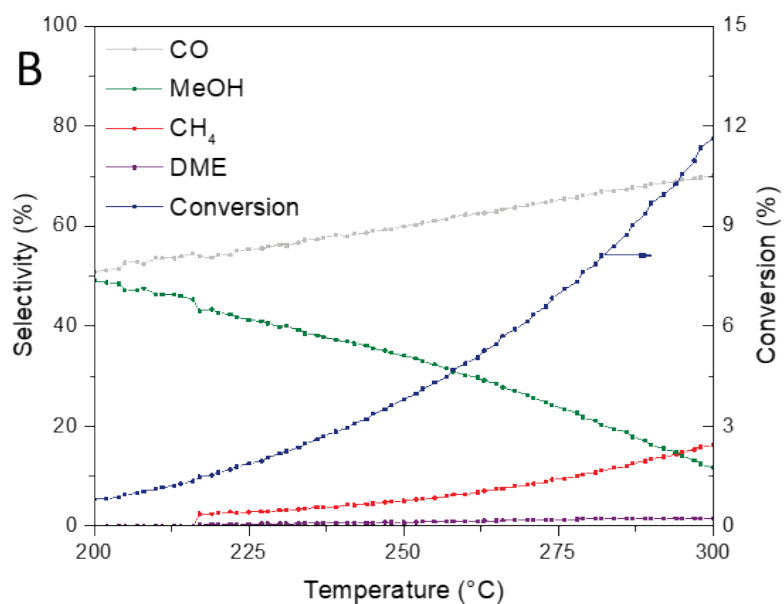
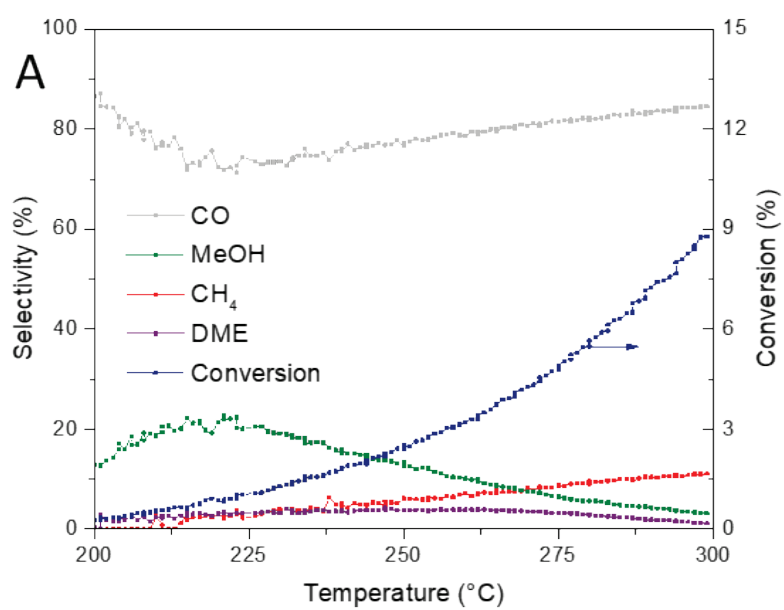


Figure S3 – CO<sub>2</sub> conversion and CO/MeOH/CH<sub>4</sub>/DME selectivities for A: 3Mo/DT51D-R450 and B: 3Mo/RNR-R450 between 200 °C and 300 °C under 30 bar of H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> (3/1/1), GHSV = 7500 mL.g<sup>-1</sup>.h<sup>-1</sup>.

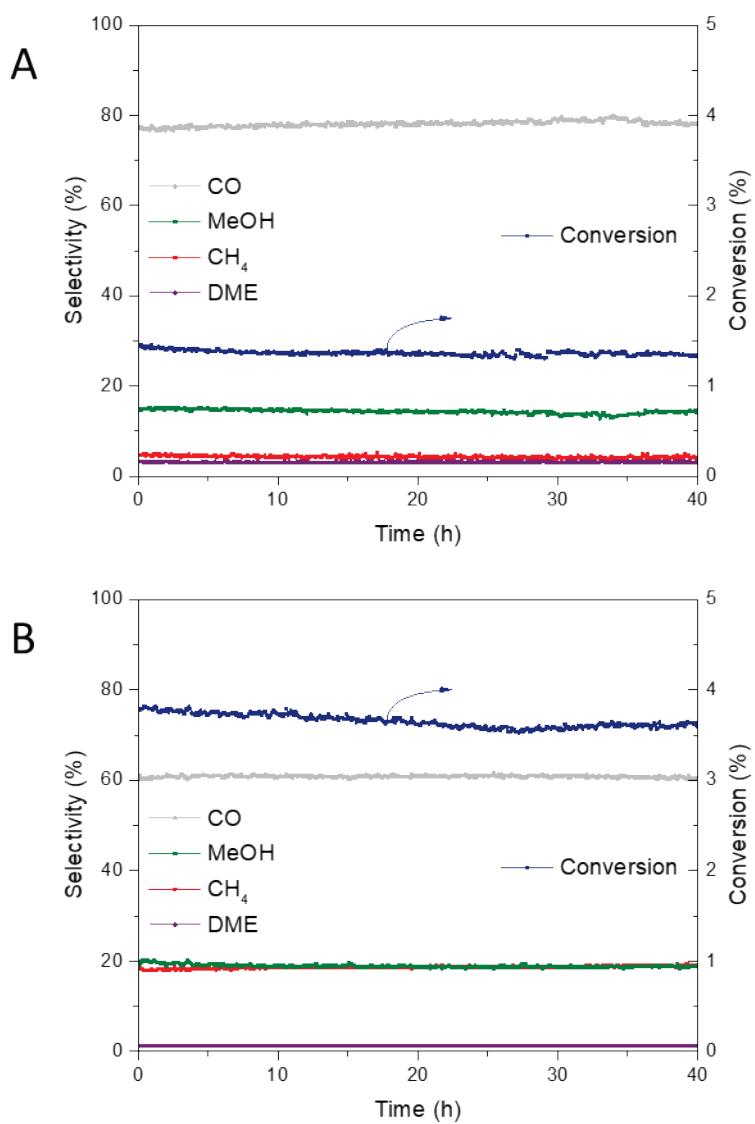


Figure S4 – CO<sub>2</sub> conversion and CO/MeOH/CH<sub>4</sub>/DME selectivities for A: 3Mo/DT51D-R450 and B: 3Mo/RNR-R450 at 250 °C under 30 bar of H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> (3/1/1), GHSV = 7500 mL.g<sup>-1</sup>.h<sup>-1</sup>.

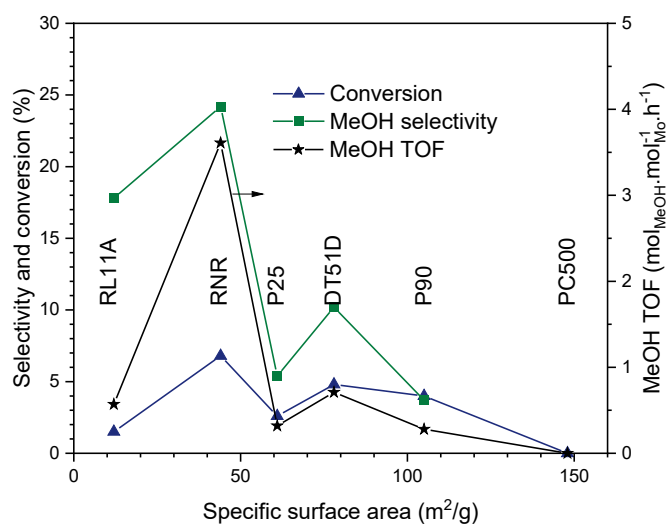


Figure S5 – CO<sub>2</sub> conversion, methanol selectivity, and methanol TOF vs catalysts specific surface area at 275 °C under 30 bar of H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> (3/1/1), GHSV = 7500 mL·g<sup>-1</sup>·h<sup>-1</sup>.

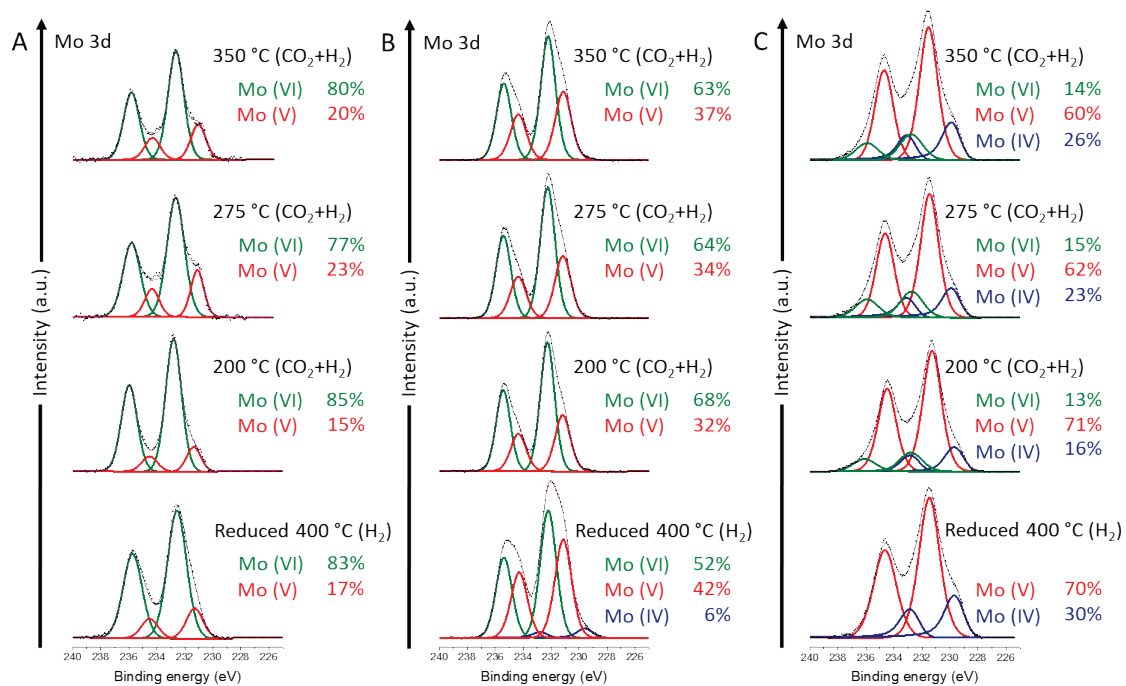


Figure S6 – NAP-XPS analysis of 3 wt% Mo on A: DT51D ; B: P25 ; C: RNR.

Table S1 – Integration parameters of Mo 3d NAP-XPS experiment on 3 wt% Mo on DT51D, P25 and RNR during *in situ* reduction treatment at 400 °C (R400), and exposure to CO<sub>2</sub>/H<sub>2</sub> reactant mixture (3/1) at 200 °C (M200), 275 °C (M275), and 350 °C (M350).

		DT51D			P25			RNR		
		Energy (eV)	FWHM (eV)	% of components	Energy (eV)	FWHM (eV)	% of components	Energy (eV)	FWHM (eV)	% of components
R400	Mo <sup>VI</sup>	232.6	1.6	83	232.2	1.4	52	X	X	X
	Mo <sup>V</sup>	231.3	1.4	17	231.2	1.4	42	231.4	1.7	70
	Mo <sup>IV</sup>	X	X	X	229.5	1.4	6	229.6	1.5	30
M200	Mo <sup>VI</sup>	232.8	1.4	85	232.3	1.3	68	232.8	1.9	13
	Mo <sup>V</sup>	231.4	1.2	15	231.2	1.3	32	231.3	1.6	71
	Mo <sup>IV</sup>	X	X	X	X	X	X	229.6	1.5	16
M275	Mo <sup>VI</sup>	232.6	1.5	77	232.3	1.3	66	232.7	1.9	15
	Mo <sup>V</sup>	231.2	1.1	23	231.2	1.3	34	231.4	1.5	62
	Mo <sup>IV</sup>	X	X	X	X	X	X	229.8	1.4	23
M350	Mo <sup>VI</sup>	232.6	1.4	80	232.2	1.3	63	232.7	1.9	14
	Mo <sup>V</sup>	231.2	1.2	20	231.1	1.3	37	231.5	1.6	60
	Mo <sup>IV</sup>	X	X	X	X	X	X	229.8	1.9	14

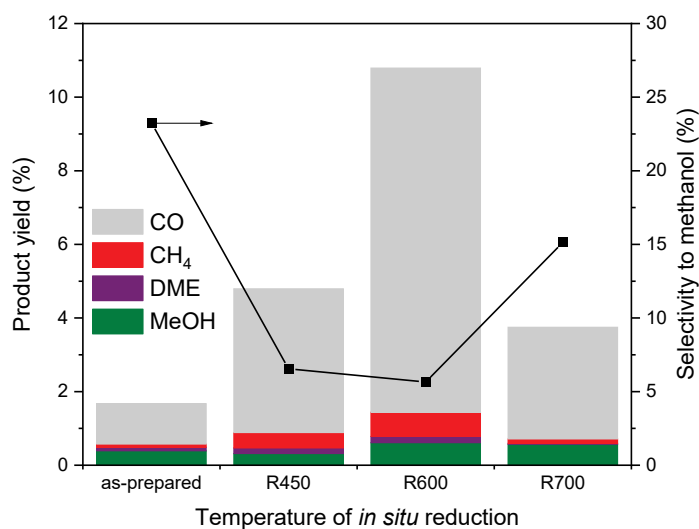


Figure S7 – Effect of *in situ* reduction temperature on CO/MeOH/CH<sub>4</sub>/DME yields and methanol selectivity for 3Mo/DT51D at 275 °C under 30 bar of H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> (3/1/1), GHSV = 7500 mL.g<sup>-1</sup>.h<sup>-1</sup>.

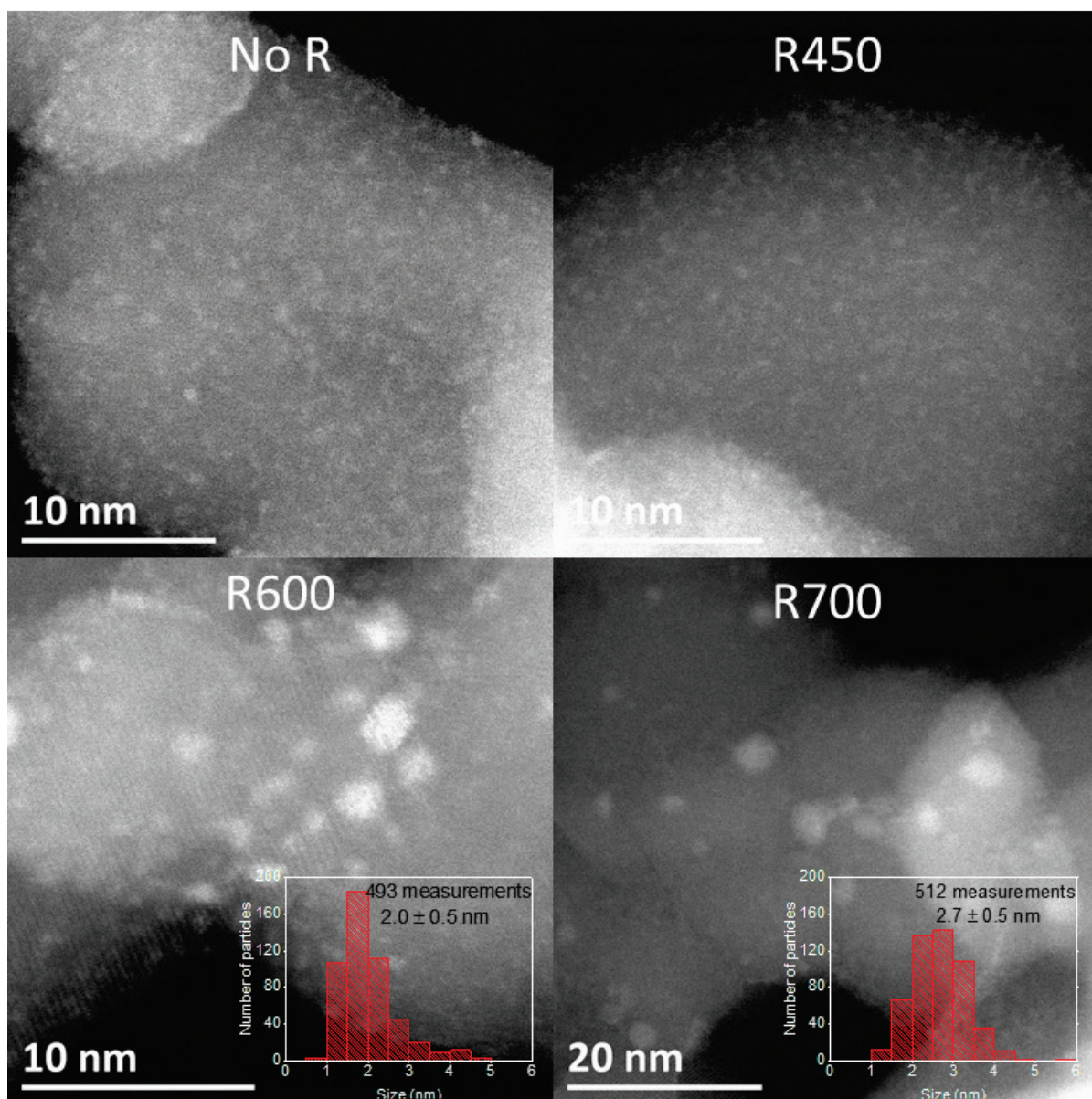


Figure S8 – Representative aberration-corrected STEM-HAADF micrographs of the 3Mo/DT51D catalyst, as-prepared or in situ reduced at different temperatures (450, 600 and 700 °C).

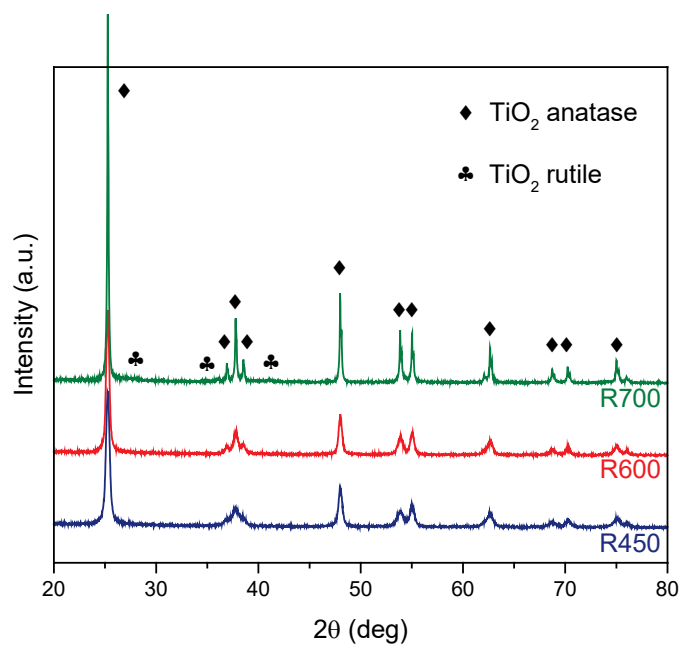


Figure S9 – XRD pattern of 3Mo/DT51D in situ reduced at different temperature. Calculated anatase crystallite sizes are 17, 19 and 46 nm for R450, R600 and R700, respectively.

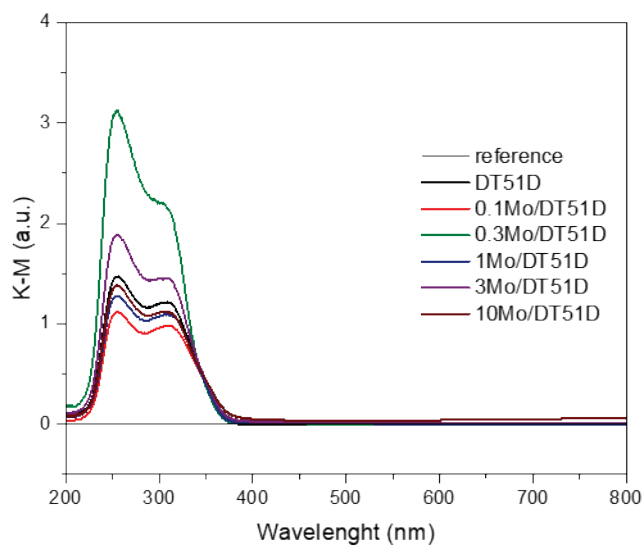


Figure S10 – Diffuse reflectance UV-vis spectra of 0-10 wt% Mo/DT51D samples.



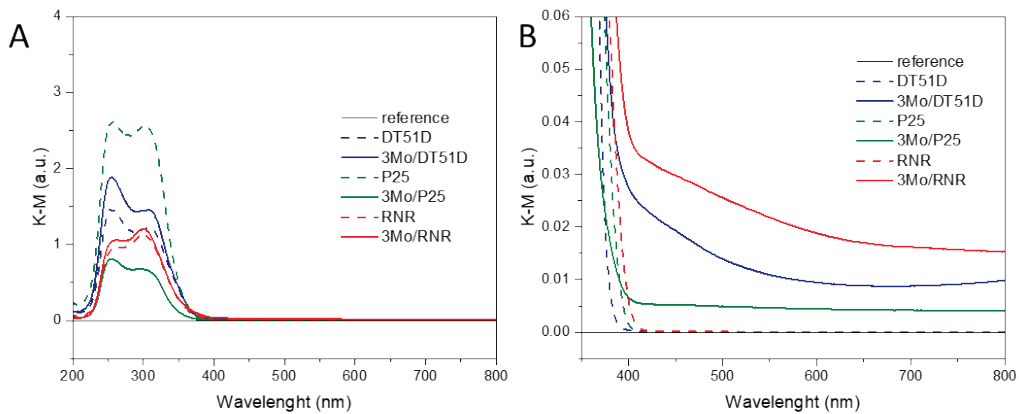


Figure S11 – A: Diffuse reflectance UV-vis spectra of 3Mo/TiO<sub>2</sub> and TiO<sub>2</sub> samples. B: UV-vis Diffuse reflectance spectra zoomed in the 350-800 nm range.

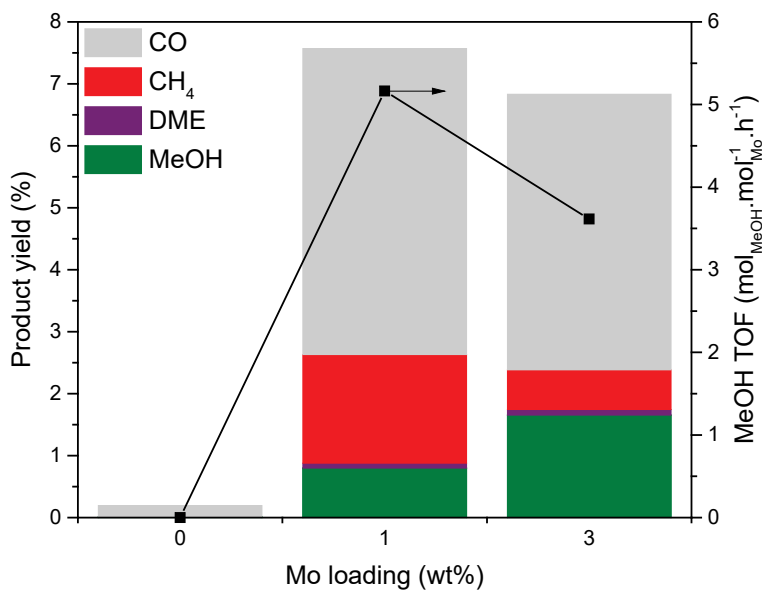


Figure S12 – Effect of Mo loading on CO/MeOH/CH<sub>4</sub>/DME yields and methanol TOF for 0-3 wt% Mo/RNR-R450 at 275 °C under 30 bar of H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> (3/1/1), GHSV = 7500 mL.g<sup>-1</sup>.h<sup>-1</sup>.