Molybdenum Carbide Catalyst for the Reduction of CO_2 to CO: Surface Science Aspects by NAPPES and Catalysis Studies.

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Electronic Supplementary Information (ESI)

Conversion and Selectivity calculation:

CO_2 Conversion:

$$X_{CO2}\,\% = \frac{\text{Moles CO2 in} - \text{Moles CO2 out}}{\text{Moles CO2 in}} \boldsymbol{X\ 100}$$

H_2 Conversion

$$X_{H2}\,\% = \frac{\text{Moles H2 in} - \text{Moles H2out}}{\text{Moles H2 in}} \boldsymbol{X\ 100}$$

CO Selectivity:

$$S_{CO}\,\% = \frac{\text{Moles CO out}}{\text{Moles CO out+Moles CH4 out}} \boldsymbol{X\ 100}$$

CH_4 Selectivity:

$$S_{CH4}\,\% = \frac{\text{Moles CH4 out}}{\text{Moles CO out+Moles CH4 out}} \boldsymbol{X\ 100}$$

Table S1: Physiochemical properties of as synthesized β-Mo_2C.

BET Surface Area (m^2/g)	Total Pore Volume (cc/g)	Average pore diameter (nm)
11.6	0.0124	4.2

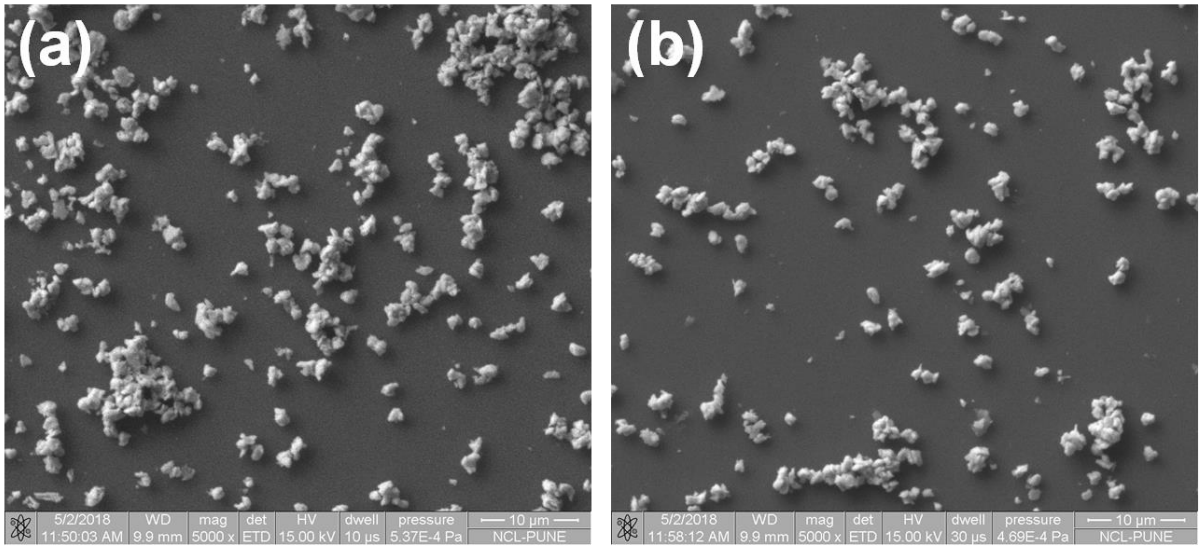

Figure S1. Scanning Electron Microscopy (SEM) images of synthesized Mo_2C powder catalyst a) Before b) After reaction CO_2 hydrogenation reaction.

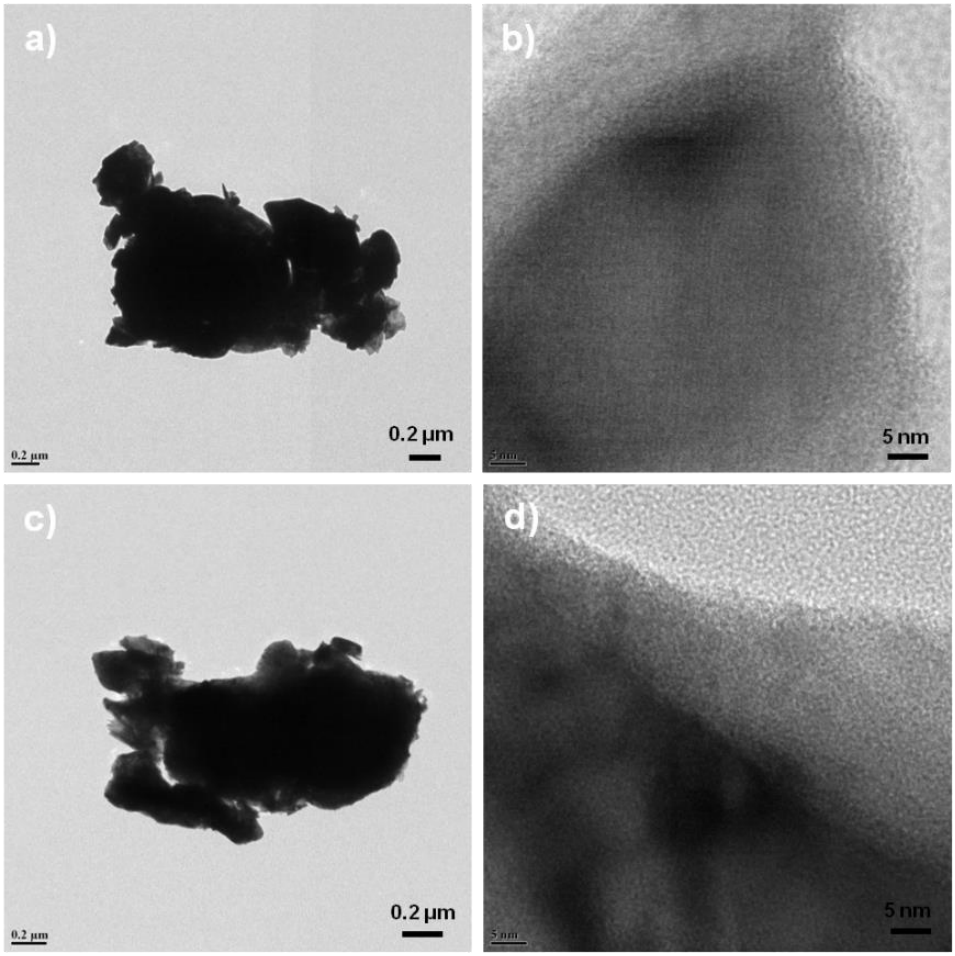

Figure S2. Transmission Electron Microscopy (TEM) and HRTEM images of (a-b) as-synthesized Mo_2C powder catalyst, and,(c-d) after CO_2 hydrogenation reaction. Surface texture and particle size remains the same for fresh and spent catalysts.

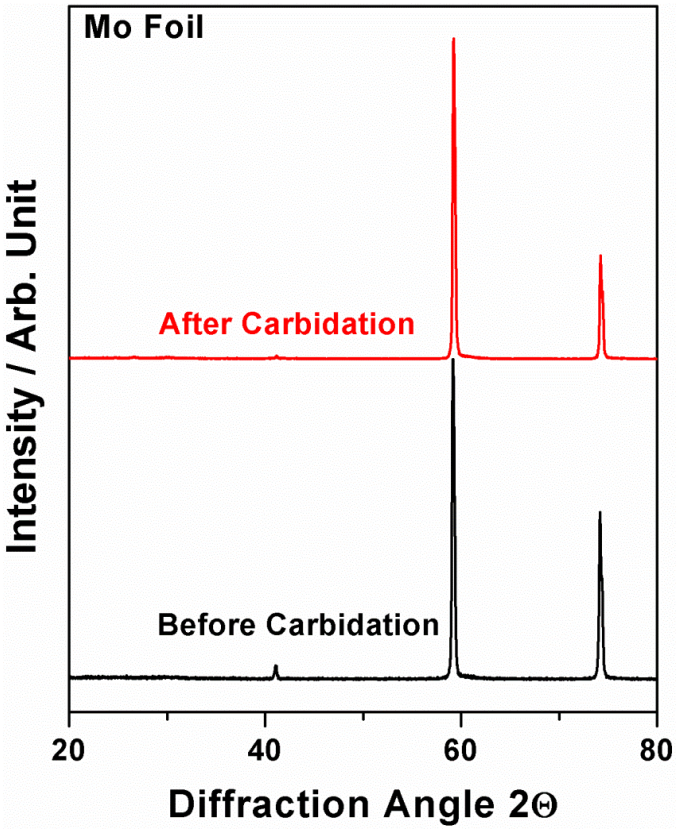

Figure S3. XRD spectra of Mo foil before and after carburization process.

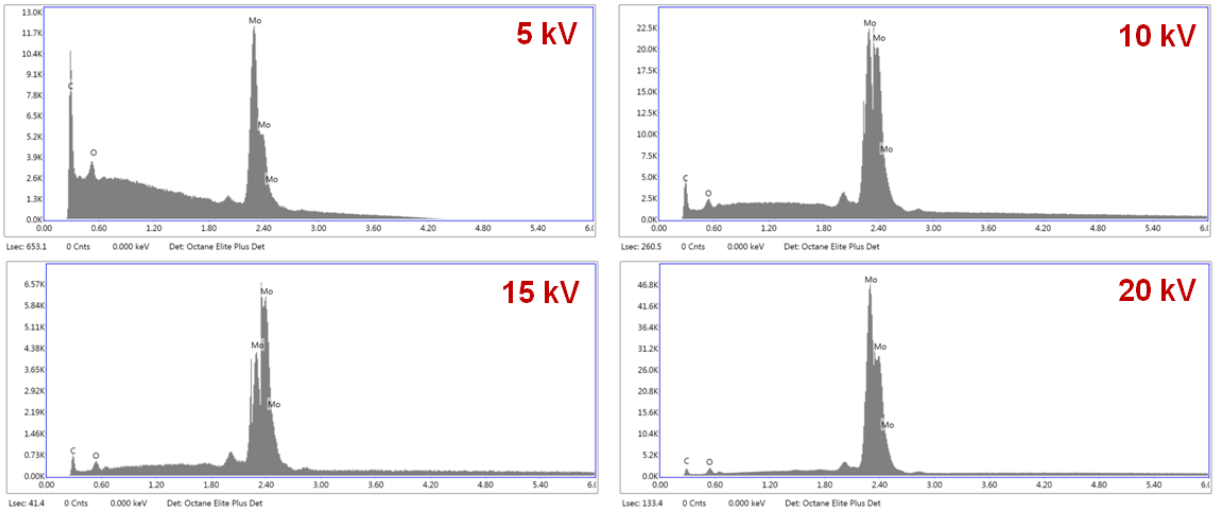

Figure S4. SEM-EDX analysis of as prepared Mo_2C foil with different electron energy source.

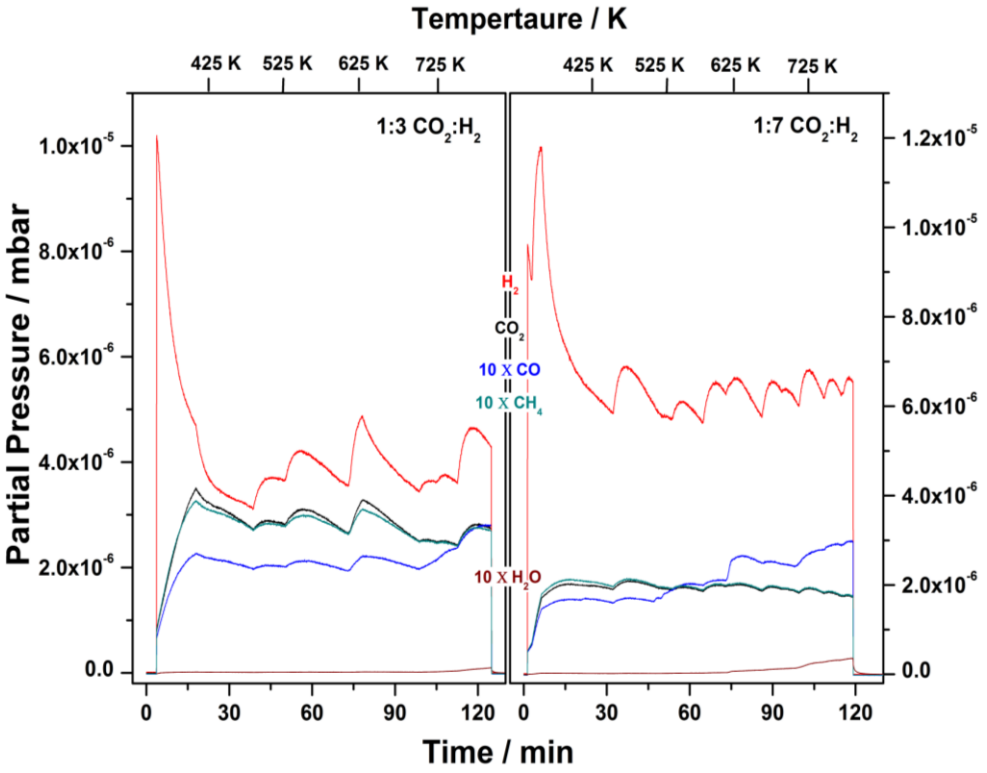

Figure S5. Mass spectrometry analysis of CO_2 hydrogenation on Mo_2C foil with different ratios of CO_2:H_2 (1:3) and CO_2:H_2 (1:7) at various temperatures. It is to be noted that CO_2, CO and CH_4 shows very similar intensity pattern, mainly due to secondary fragments (CO for CO_2) or same mass species bur originating from different sources (16 O from CO_2 and CO, and CH_4). Hence it is difficult to ascertain the reaction details from this data alone. However, more CO generation is observed with 1:7 compositions at high temperatures. Fluctuations in the intensity pattern are due to opening of leak valve to maintain the same pressure during reaction measurements.

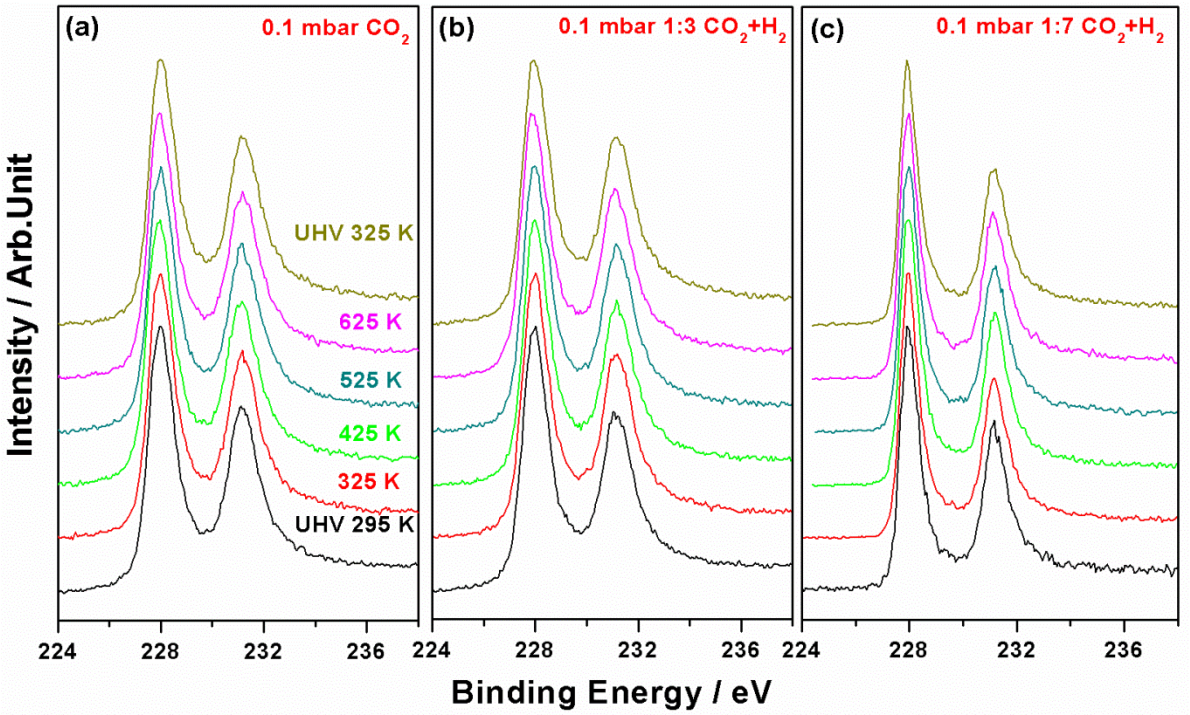

Figure S6. Mo 3d spectra of CO_2 hydrogenation on Mo_2C foil with different ratios a) Alone CO_2 b) CO_2:H_2 1:3 and c) CO_2:H_2 1:7 at various temperatures.

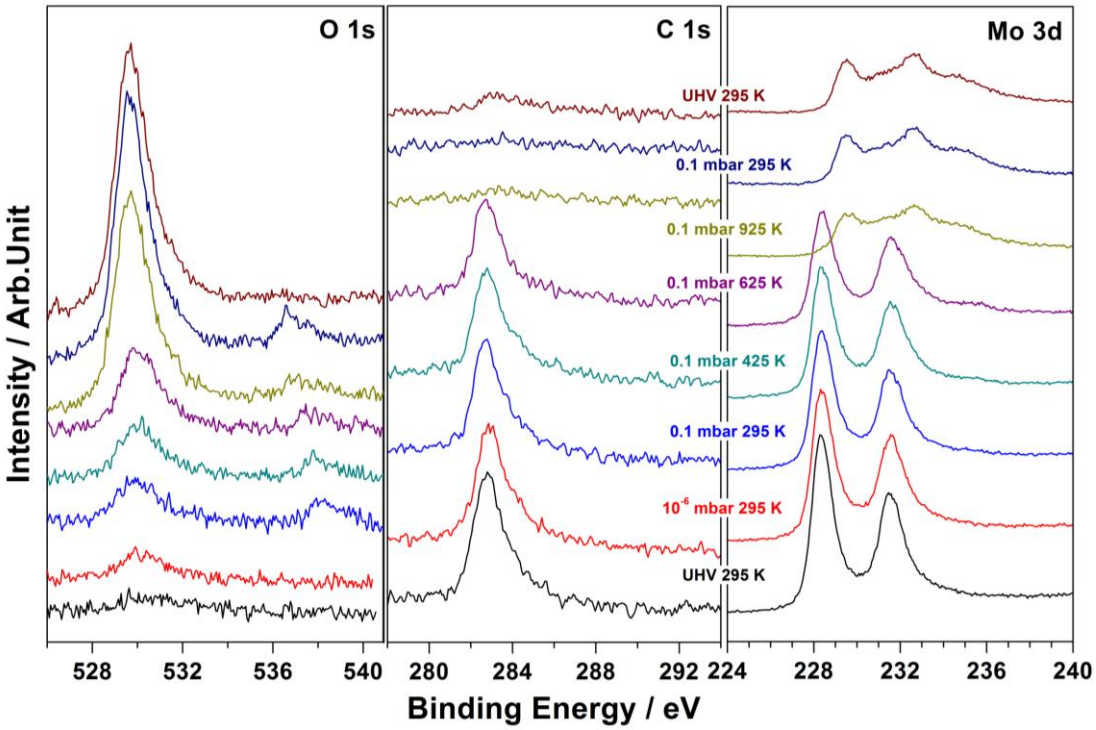

Figure S7. NAPXPS spectra of Mo_2C foil oxidation at 0.1 mbar O_2 with various temperatures.