Supplemental Information: Evidence of Methane Adsorption Over Mo₂C Involving Single C-H Bond Dissociation Instead of Facile Carbon Exchange

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Figure S1: General flow pattern for the 5-port valve and isotope sample loop. a) "Load" position, where isotopically labeled gas is loaded into the sample loop. b) "Inject" position, used to deliver the pulse of isotopically labeled methane to the reactor



Figure S2: a) XRD spectra of Alfa Aesar Commercial Mo₂C and b) reference spectra for Mo₂C.



Figure S3: Raw mass spectrometry signals (a-d) and normalized responses (e-h) for ¹³CH₄ pulses while flowing 5.5 SCCM 95% CH₄/5% Ar over Mo₂C at room temperature (a & e), 200°C (b & f), 600°C (c & g), and 800°C (d & h). In Figures S3e-S3h, masses 12, 13, 14, 15, and 16 have been inverted in addition to normalized, in order to overlay the pulse response functions. Pretreatment was 50 SCCM flowing H₂ at 600C for 3 hours. The masses correspond to the following species or fragments: 12: ¹²C; 13: ¹²CH, ¹³C; 14:¹²CH₂, ¹³CH; 15: ¹²CH₃, ¹³CH₂; 16: ¹²CH₄, ¹³CH₃; 17: ¹³CH₄; 40: Ar (inert tracer).



Figure S4: Mass Spectrometry signals (a-d) and normalized responses (e-h) for CD₄ pulses while flowing 5.5 SCCM 95% CH₄/5% Ar over Mo₂C in the bypass (a & e), at 200°C (b & f), at 600°C (c & g), and at 800°C (d & h). In Figures S4a-S4d, masses 17 and 19 have been multiplied by 20. In Figures S4a-S4d, mass 18 has been corrected by subtracting 0.78*(mass 20), then multiplied by 20, but has been left uncorrected for Figures S4e-S4h. In Figures S4e-S4g, masses 12, 13, 14, 15, 16, and 17 have been inverted in addition to normalized in order to overlay the pulse response functions. In Figure S4h, only masses 12, 13, 14, 15, and 16 have been inverted. The masses correspond to the following species or fragments:12: C; 13: CH; 14: CH₂, CD; 15: CH₃, CDH; 16: CH₄, CD₂, CDH₂; 17: CH₃D, CD₂H; 18: CD₃, CD₂H₂; 19: CD₃H; 20: CD₄; 40: Ar (inert tracer).



Figure S5: Raw mass spectrometry curves for 13 CH₄ pulses delivered while flowing 18 SCCM He, and 2 SCCM 95% CH₄/5% Ar after 3 hours of H₂ pretreatment at 600C. Plots for masses 2 (H₂), 15 (12 CH₄), 17 (13 CH₄), and 40 (Ar) are shown in Figures 4a and 4b. Figures for masses 40 (Ar), 28 (12 CO), 29 (13 CO), and 18 (H₂O) are shown in Figures 4c and 4d, and represent a 10x magnification from Figures 4a and 4b. Figures 4a and 4c represent a pulse performed at room temperature, and Figures 4b and 4d represent a pulse performed while ramping from 200 °C to 800 °C at 25 °C/min, as indicated by the cyan temperature curve overlaid on the mass spectrometer curves.



Figure S6: Raw mass spectrometry curves for ¹³CH₄ pulses delivered while flowing 18 SCCM He, and 2 SCCM 95% CH₄/5% Ar after 1 hour of H₂ pretreatment at 600 °C. Plots for H₂, ¹²CH₄, ¹³CH₄, and Ar are shown in Figures S6a and S6b. Figures for Ar, ¹²CO, ¹³CO, and H₂O are shown in Figures S6c and S6d, and represent a 10x magnification from Figures S6a and S6b. Figures S6a and S6c represent a pulse performed at room temperature, and Figures S6b and S6d represent a pulse performed while ramping from 200 °C to 800 °C at 25 °C/min, as indicated by the cyan temperature curve overlaid on the mass spectrometer curves.



Figure S7: H_2O production during 3 hour H_2 pretreatment of Mo_2C . Line indicated the end of 1 hour of pretreatment, demonstrating the additional oxygenated species that would still be in the catalyst without the 2^{nd} and 3^{rd} hour of pretreatment.



Figure S8: Mass Spectrometry signals of a) 16 (CH₄), b) 2 (H₂), c) 28 (CO), and d) 18 (H₂O) during ramp from 200 °C to 600 °C at 10 °C/min while flowing 5.5 SCCM 95% CH₄/5% Ar. One can notice a small decrease in the CH₄ signal of the 1 hour pretreatment curve compared with the 3 hour pretreatment curve. However, a noticeable increase in H₂, CO, or H₂O production cannot be easily seen.

Ramp to 600C with different H₂ Pretreatments



Ramp to 800C with different H₂ Pretreatments

Figure S9: Mass Spectrometry signals of a) 16 (CH₄), b) 2 (H₂), c) 28 (CO), and d) 18 (H₂O) during ramp from 600 °C to 800 °C at 10 °C/min while flowing 5.5 SCCM 95% CH₄/5% Ar. There appears to be the presence of oxygenated species reduced by the flowing methane, and possibly a slightly larger amount in the 1 hour pretreatment sample, as seen in Figure S9b of the H₂ plots and Figure S9c of the CO plots.



Figure S10: Raw mass spectrometry signals (a-d) and normalized responses (e-h) for ¹³CH₄ pulses while flowing 5.5 SCCM 95% CH₄/5% Ar over Mo₂C at room temperature (a & e), 200°C (b & f), 600°C (c & g), and 800°C (d & h). In Figures S10e-S10h, masses 12, 13, 14, 15, and 16 have been inverted in addition to normalized, in order to overlay the pulse response functions. Pretreatment was 50 SCCM flowing H₂ at 600 °C for 1 hour. The masses correspond to the following species or fragments: 12: ¹²C; 13: ¹²CH, ¹³C; 14:¹²CH₂, ¹³CH; 15: ¹²CH₃, ¹³CH₂; 16: ¹²CH₄, ¹³CH₃; 17: ¹³CH₄; 40: Ar (inert tracer).



Figure S11: Raw mass spectrometry curves for CD₄ pulses delivered while flowing 18 SCCM He, and 2 SCCM 95% CH₄/5% Ar after 3 hours of H₂ pretreatment at 600 °C. Plots for 2 (H₂), 3(HD), 4 (D₂), 15 (CH₄), 20 (CD₄) and 40 (Ar) are shown in Figures S11a and S11b. Figures for 17 (CH₃D and H₂O fragment), 19 (CD₃H and HDO), 40 (Ar), and 44 (CO₂) are shown in Figures S11c and S11d, and represent a 10x magnification from Figures S11a and S11b. Figures S11a and S11c represent a pulse performed at room temperature, and Figures S11b and S11d represent a pulse performed while ramping from 200 °C to 800 °C at 25 °C/min, as indicated by the cyan temperature curve overlaid on the mass spectrometer curves.