Supporting Information

Evidence of water dissociation and hydrogenation on molybdenum carbide nanocatalyst for hydroprocessing reactions

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Table S1 Hydrocarbon feedstock properties

Olefin content (wt%)*	1.2 ± 0.1
H/C ratio**	1.17 ± 0.01
Viscosity at 373 K (cP)**	103,280 ± 971
Specific gravity at 288.6 K**	1.111 ± 0.002
Hydrocarbon distribution by normal boiling point (NBP) range:** 489 K < NBP < 616 K, wt% 616 K < NBP < 818 K, wt% NBP > 818 K, wt%	 3% 17% 80%

** Based on ^{1}H-NMR analysis explained elsewhere* [1]

*** Measurement methodologies explained elsewhere* [2]

Table S2 Analysis for H_2-treated α-MoC_{1-x} XRD peaks

2θ (°)	**Plane**	**$d_{spacing}$ (nm)**	**Crystallite size (nm)**
37.4	111	0.241	1.53
43.6	200	0.207	1.56
63.1	220	0.147	1.70
76.9	311	0.124	1.50

Table S3 Calculation of water consumption based on CO_2 yield for the cases of CAT-100S and CAT-50H/50S

	CO_2 yield (mg.h^{-1})*	Water consumption (mg.h^{-1})**	Water consumption (cc.min^{-1})	Feed water (cc.min^{-1})
CAT-100S (Water only)	10.92	2.48×10^{-4}	1.5×10^{-4}	4.0×10^{-3}
CAT-50H/50S H_2:H_2O = 1:1	5.32	1.17×10^{-4}	7.0×10^{-5}	2.0×10^{-3}

** The yield of CO_2 for thermal counterpart experiments under water vapor-only (Therm-100S) and Therm-50H/50S (H_2O:H_2 = 1:1, molar ratio) was subtracted, 0.5715 and 0.1448 mg.h^{-1}, respectively, to only account for production of CO_2 solely due to the water activation reaction network*

*** A stoichiometric molar ratio of CO_2:H_2O of 1:2 was assumed*

Table S4 Hydrogen consumption estimation based on inlet and outlet hydrogen flowrates*

	H_2 flowrate in (μg.h^{-1})	H_2 flowrate out (μg.h^{-1})	H_2 consumption (%)
CAT-100H (Hydrogen only)	22.88	3.51	84.7

CAT-100S (Water only)	0	0.55	N/A
CAT-50H/50S H_2:H_2O = 1:1	11.44	2.23	80.5

** Hydrogen flowrate was calculated based on the compositions, determined by GC, and the flowrates of inlet/outlet gas streams.*

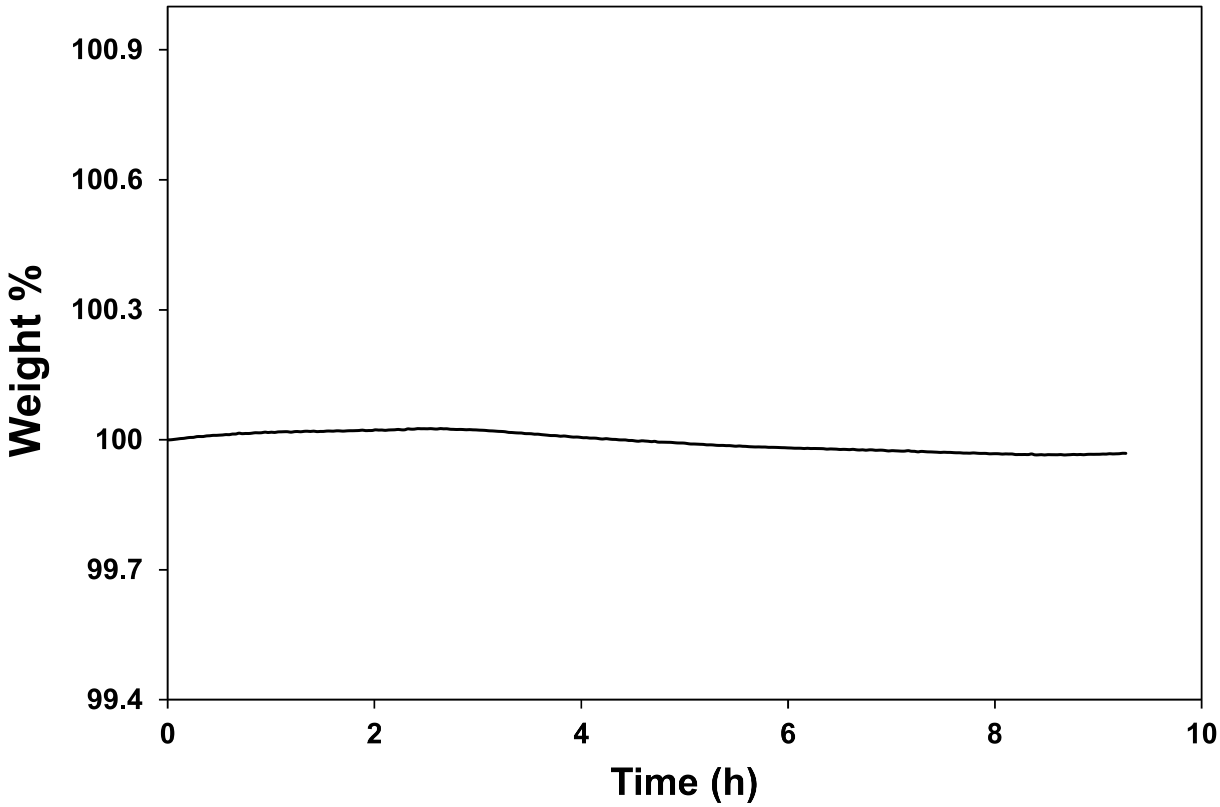

Fig S1 Control adsorption experiment of D_2 on in-situ activated molybdenum carbide catalyst: Mass change vs. time on stream using TG at 623 K and 0.1 MPag, and D_2:N_2 = 1:3 (20 sccm gas, 25 mg catalyst, no heavy hydrocarbons).

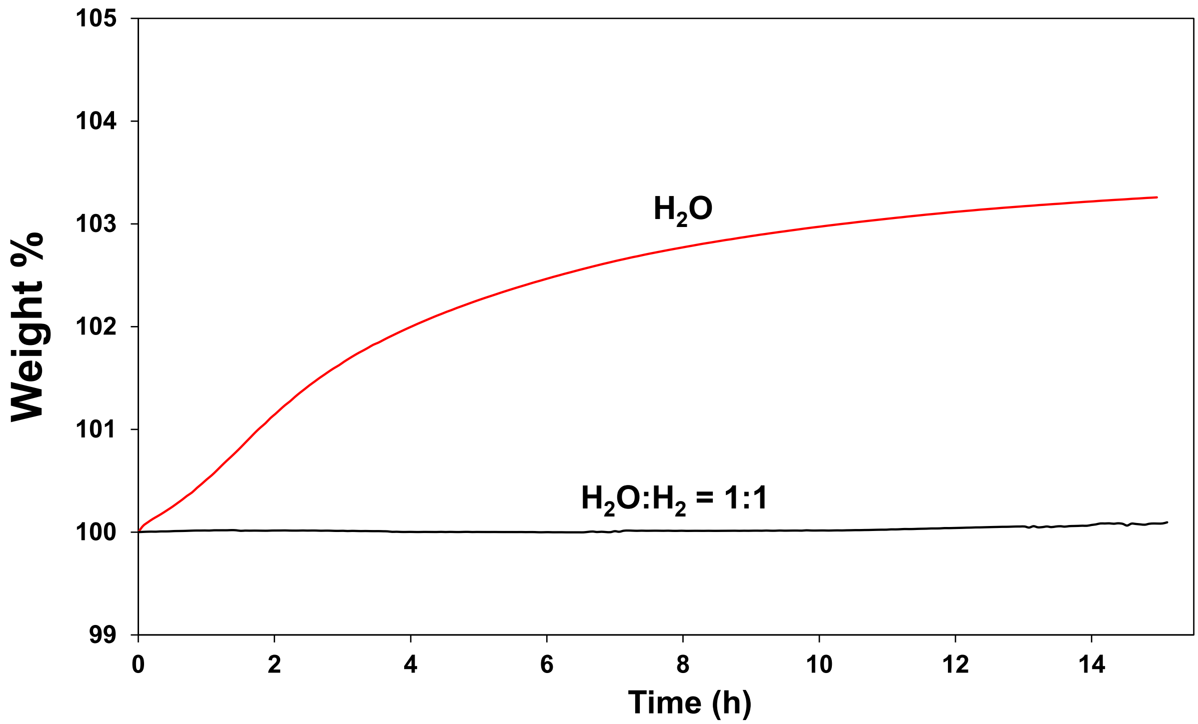

Fig S2 Long-term adsorption of water on in-situ activated molybdenum carbide catalyst, studied by TG at 623 K and 0.1 MPag, in the absence (Water-saturated N_2) and presence of hydrogen (H_2O:H_2 = 1:1) (20 sccm gas, 25 mg catalyst, no heavy hydrocarbons).

References:

1 L. Carbognani, K. O. Sebakhy, M. Trujillo and P. Pereira-Almao, *Energy & Fuels*, 2020, **34**, 9252–9261.

2 M. Ahmadi Khoshooei, S. M. Elahi, L. Carbognani, C. E. Scott and P. Pereira-Almao, *Fuel*, 2021, **288**, 119664.