Supporting Information for:

Efficient Catalytic Greenhouse Gas-Free Hydrogen and Aldehyde Formation from Aqueous Alcohol Solutions

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S1. Materials and Methods. Where specified, air-sensitive manipulations were carried out using standard glovebox and Schlenk line techniques. Argon (UHP) was purchased from Airgas. Anhydrous EtOH was obtained from Sigma -Aldrich and dried over 3 Å molecular sieves before use. Anhydrous-grade methanol (sure-seal) and toluene were obtained from Sigman-Aldrich and used as received. D_2O, CD_3CD_2OD, and CD_3OD were purchased from Cambridge Isotopes and used as received. Formalin (37 wt% in H_2O), $^{13}CH_3CH_2OH$, $^{13}CH_3OH$, 2,4-dinitrophenylhydrazine (2,4-DNPH), formaldehyde-2,4-DNPH adduct, and acetaldehyde-2,4-DNPH adduct were purchased from Sigma-Aldrich and used as received. **Mo@C** was prepared and fully characterized previously by this group from (dme)Mo(=O)$_2$Cl$_2$ (dme = 1,2-dimethoxyethane) and activated carbon.[1]

S2. Physical and Analytical Measurements. NMR spectra were recorded on a Varian Inova-500 (FT, 500 MHz, ^{1}H, 100 MHz, ^{13}C), a Varian Inova-400 (FT, 400 MHz, ^{1}H, 100 MHz, ^{13}C) or a Mercury-400 (FT, 400MHz, ^{1}H; 100 MHz, ^{13}C) spectrometer. Chemical shifts (δ) for ^{1}H are referenced to internal solvent. The gas phase mass spectrometer used was a Stanford Research Systems Universal Gas Analyzer 100 (UGA-100).

S3. Procedures

General procedure for MS analysis of gas-phase catalytic reaction products. A 50 mL Schlenk flask was charged with 0.030g of **Mo@C** (2.1 wt%), 0.8 mL of toluene, and 0.4 mL of either EtOH or MeOH. A reflux condenser was attached with a port to the gas-phase MS. The solution was degassed, placed under Ar(g) and sealed. The port to the MS was opened, and while stirring at 500 rpm, the flask was lowered into a 90, 60, or 40 °C sand bath.

MS analysis of gaseous products of reactions in neat alcohol or alcohol/H_2O solutions: The same set up was used with 0.030 g **Mo@C** and 1.0 mL of either neat alcohol or 9:1 H_2O:ROH.

MS analysis of gaseous products of reactions with D_2O: The same set-up was used with 0.030 g **Mo@C** and 1.0 mL of D_2O.

MS analysis of gaseous products of reactions with no solvent: The same set-up was used with 0.030 g of **Mo@C**.

J-Young NMR tube experiments: To a J-young NMR tube, 0.015 g of **Mo@C**, 0.2mL of EtOD-d_6 or MeOD-d_4 and 0.4 mL toluene-d_8 were added, and the tube was freeze-thaw degassed and placed under Ar. The tube was then heated in a 90 °C oil bath for 16 h. Note: This reaction only reaches ~ 1-5% conversion due to the system being closed.

General set-up for semi-batch reactions: A 250 mL 3-neck round bottom flask was charged with a magnetic stir bar and a special reflux condenser was attached that contained an adjustable gas inlet sparger inside. Gas flowed down the inside of the tube to the sparger at the end of the tube, near the reaction zone. The gas outlet was at the top of the reflux condenser which led to a T-joint connected to the MS and an outlet vent.

Procedures for H_2 quantification using MS: Ar(g) and 5% H_2/N_2 tanks were connected to mass flow controllers then to the gas inlet of the reactor. The H_2 pressure response was monitored by varying the total H_2 content in the gas stream while maintaining the same total flow rate. A calibration curve relating mol% H_2 to pressure response of H_2 was obtained at a set gas flow rate. The most linear response rate was obtained for a flow of 1.0 mL/s.

Determination of TOF's: In a typical experiment, the Ar(g) flow was set to 1 mL/s. The appropriate amount of **Mo@C** was charged in the flask with a magnetic stir bar and sealed with a septum. The flask was next heated in a 90 °C oil bath, and the alcohol (either neat or in H_2O) was added via syringe in a single portion. The pressure response was then recorded, and the H_2 conversion determined by taking the H_2 produced (in units of total pressure, Torr) and converting to mol% H_2 using the calibration curve (Figure S28). Knowing the total gas flow (1 mL/s), the total moles in a time period could be determined. For repeated additions over 5 days to determine the catalyst stability, 2.0 mL of H_2O was added to the flask and 0.6 mL MeOH was injected at predetermined time points (See Table S30).

Procedure for H_2 yield determination: To a 25 mL round-bottom flask attached to a reflux condenser with a tube leading to an inverted 50 mL volumetric flask filled with water in a beaker (total water volume $\leq$ 125 mL), was added 0.0075 g **Mo@C**, ROH (50 µl EtOH or 32 µl MeOH), the appropriate quantity of H_2O, and a magnetic stir bar. The reaction flask was next lowered into a 90 °C bath stirring at 500 rpm and the evolved H_2 collected in the graduated cylinder.

Procedure for Determining Aldehyde Adsorption on Activated Carbon. **Formaldehyde:** A solution of 1 wt% formaldehyde was prepared by dissolving 0.020 g of solid paraformaldehyde (Sigma-Aldrich) in 1.98 g of D_2O (Cambridge Isotopes). To this was added 0.1 mL t-butanol (Sigma-Aldrich, dried over 4A molecular sieves) as an internal ^{1}H NMR standard. A similar procedure was followed with acetaldehyde (Sigma-Aldrich). To 1.0 mL of 1.0 wt% aldehyde solution was added 10 mg of activated carbon. The mixture was stirred for 30 min before filtration. Disappearance of aldehyde in the supernatant was quantified by inverse-gated decoupling ^{13}C NMR using the *tert*-butanol signal at δ 29.5 ppm as internal standard.

Acetaldehyde: A solution of 1.0 wt% acetaldehyde was prepared by dissolving 0.020 g of solid acetaldehyde (Sigma-Aldrich) in 1.98 g of D_2O (Cambridge Isotopes). To this was added 0.1 mL tert-butanol (Sigma-Aldrich, dried over 4A molecular sieves) as an internal standard. To 1.0 mL of 1 wt% aldehyde solution was added 10 mg of activated carbon. The mixture was stirred for 30 minutes before being filtered. Disappearance of aldehyde was monitored by inverse-gated decoupling ^{13}C NMR using the *tert*-butanol signal at 29.5 ppm as internal standard.

Procedure for collecting evolved formaldehyde gas in toluene-d$_8$: A 25 mL round-bottom flask attached to a reflux condenser fitted with a rubber septum and cannula was charged with MeOH (3.0 mL), D_2O (1.0 mL), **Mo/C** (0.015g), and a magnetic stir bar. The cannula was inserted into a J-young NMR tube with 0.5 mL toluene-d$_8$ fitted with a rubber septum and vent needle, with the tip of the cannula submerged in the toluene-d$_8$. The NMR tube was cooled in a -78 ºC cold bath and the round-bottom flask was lowered into a 75 ºC heating batch with stirring at 500 rpm. Next, the gas was collected, and the NMR tube was then sealed with a Teflon screw cap and allowed to warm to room temperature, at which time an ^{1}H NMR spectrum was taken.

Procedure for quantifying aldehydes using 2,4-dinitrophenylhydrazine:[2] A 50 mL Schlenk flask was charged with 0.005 g of **Mo@C** (2.1 wt%), 1.0 mL H_2O, and 0.2 mL of either EtOH, MeOH, or 2.0 mL of formalin (37 % in H_2O). A reflux condenser was attached and the solution was degassed and placed under Ar(g) and sealed. A cannula was inserted at the top of the reflux condense through a septum leading to a solution of Brady's Reagent. While stirring at 500 rpm, the flask was lowered into a 90, °C oil bath until gas evolution ceased. The solution of Brady's reagent was next extracted with ethyl acetate (5 x 25 ml), the organic layer washed with H_2O (2 x 25 mL), dried over $MgSO_4$, and the solvent removed in vacuo to yield the yellow hydrozone solid. The solids were purified by chromatography (ethyl acetate/hexanes on silica) and compared to authentic standards purchased from Sigma-Aldrich. Formalin was used as a control to verify the procedure. Note: Allowing the solutions of aldehyde and Brady's reagent to stand at room temperature for significant periods of time (3-7 days) also resulted in precipitation of the corresponding hydrazone.

Preparation of Brady's Reagent for aldehydes/ketones (see undergraduate laboratory procedure: http://faculty.mdc.edu/qzhang/chm2211L/eperiment20aldehydesketones.htm): (Caution! 2,4-dintrophenylhydrazine is a shock explosive). ~ 20 g of 2,4-dinitrophenylhydrazine slurried in H_2O was added to a 500 mL Erlenmeyer flask containing 50 mL H_2O using a plastic scoopula. H_2SO_4 (35 mL) was added slowly concurrently with 50 mL EtOH. The solution was allowed to stir for 3 h and filtered to remove undissolved reagent. The solution was used directly for aldehyde quantification tests.

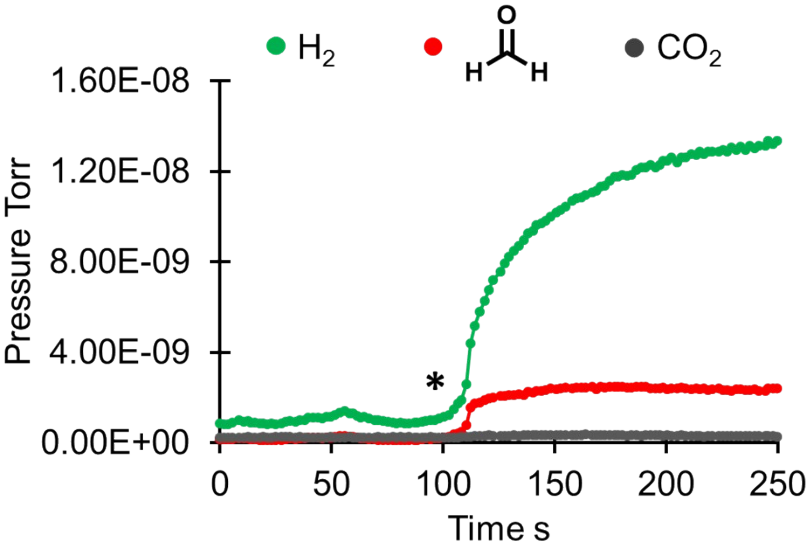


Figure S1. Gas phase MS pressure versus time scan of the reaction of **Mo@C** (0.030g) with MeOH at 90 °C (500 rpm, 0.4 mL EtOH and 0.8 mL toluene). No CO_2 is evolved. * = heating start.

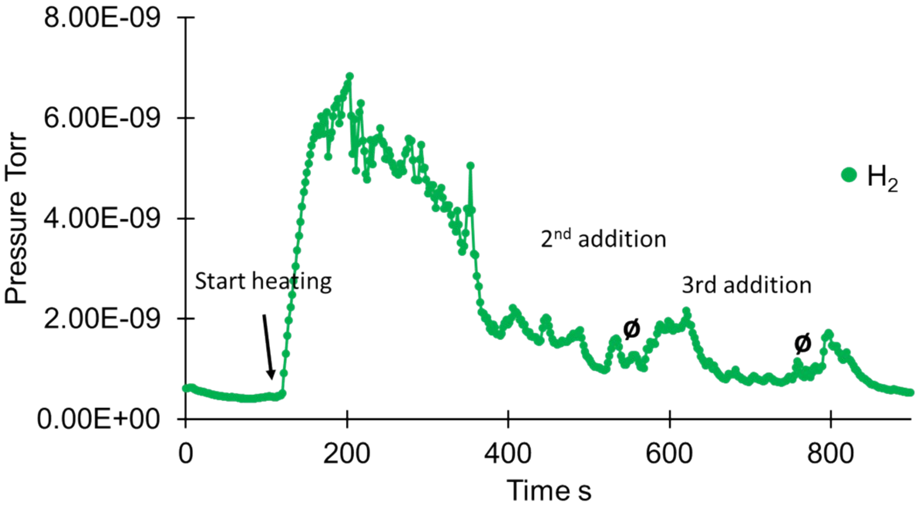


Figure S2. Gas phase MS scan (pressure vs time) trace of successive MeOH additions (1.0 mL at 590 s and 790 s, each marked by ø) to **Mo@C** (0.030g) at 90 °C in toluene showing that the catalyst deactivates over time in the absence of MeOH. Note: formaldehyde not shown.

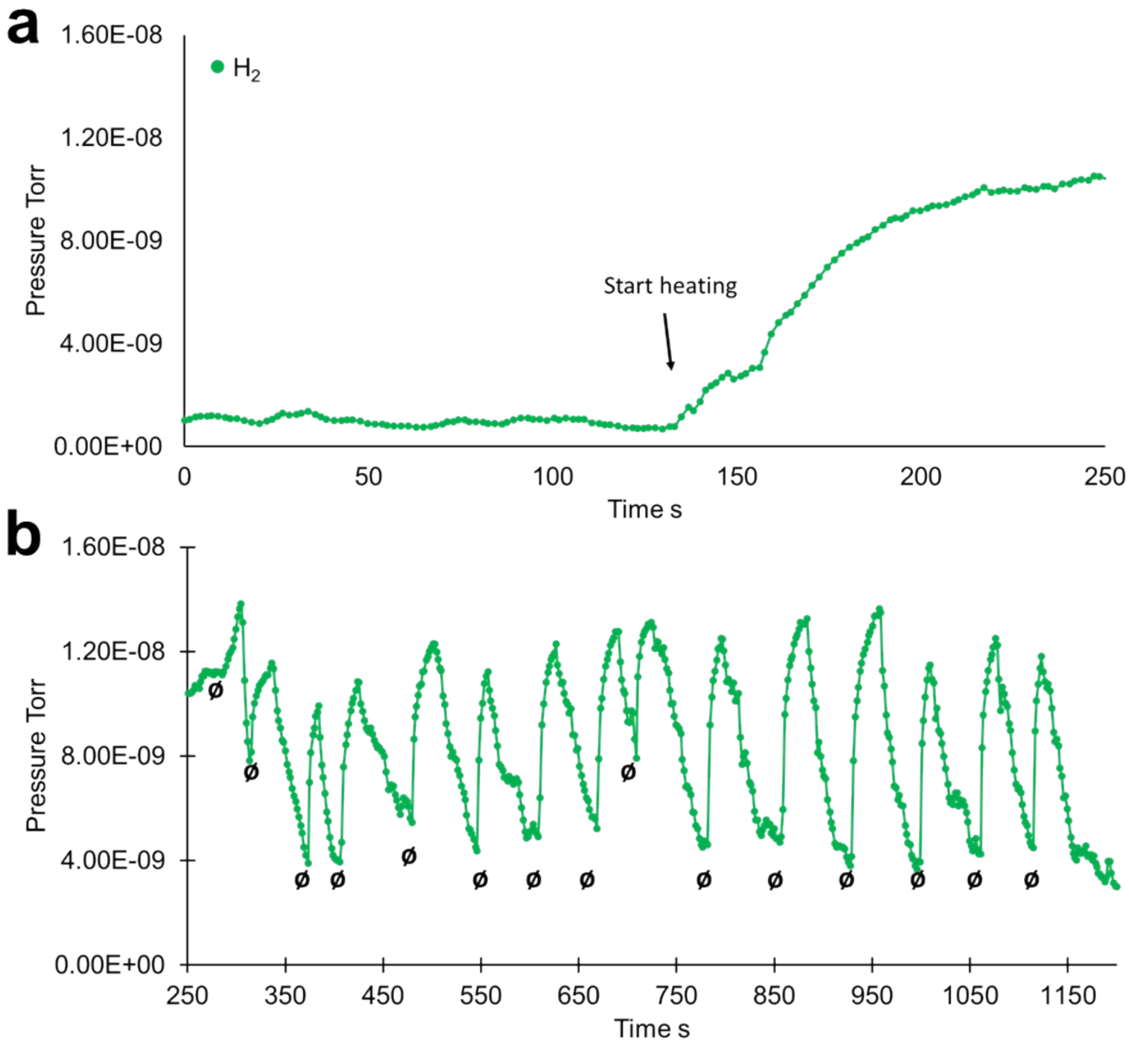


Figure S3. Gas phase MS (pressure vs time) traces of successive MeOH additions (1.0 mL, denoted by ø in graph b.) to **Mo@C** (0.030g) added before all MeOH is consumed (90 °C and 500 rpm). (**a)** Shows the point (time ~ 250 s) when another 1.0 mL portion of MeOH is added. (**b)** Shows the successive 1.0 mL MeOH additions, ø). Note: formaldehyde not shown.

Figure S3 shows that this catalytic system does not deactivate as long as MeOH remains in the reaction vessel. By adding another 1.0 mL of MeOH at the 250 s mark, catalytic activity is maintained over multiple MeOH addition cycles. It is postulated that the MeOH helps solubilize the formaldehyde oligomers and prevents catalyst coating. This is in marked contrast to Figure S2, where all MeOH in the system is consumed, and the catalyst gradually deactivates. If the system is left heating for several h, the catalyst completely deactivates and no longer produces H_2 on addition of fresh MeOH.

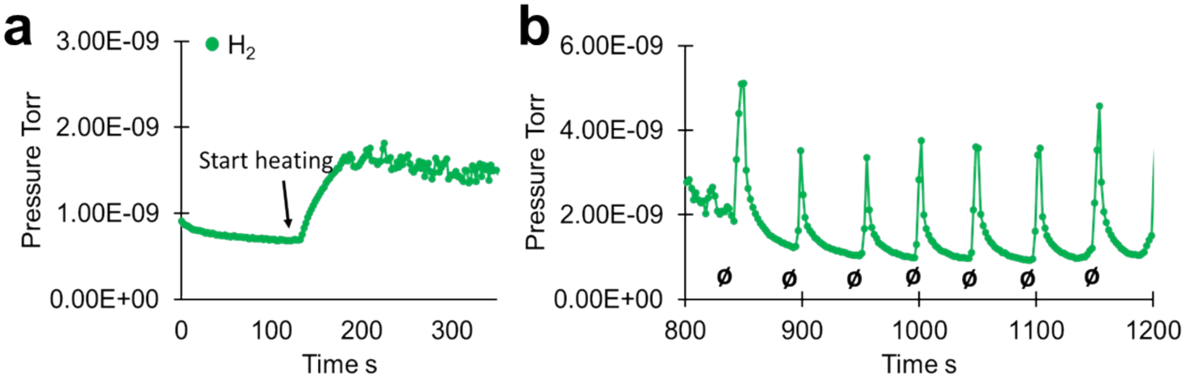


Figure S4. (**a**) Gas phase MS (pressure vs time) traces monitoring MeOH (0.1 mL) and H_2O (0.9 mL) addition to 0.030g **Mo@C** (90 °C and 500 rpm**). (b**) Multiple additions of 1.0 mL MeOH (denoted by ø) to the same reaction mixture at 90 °C showing that the presence of H_2O maintains catalytic activity. Note: formaldehyde not shown.

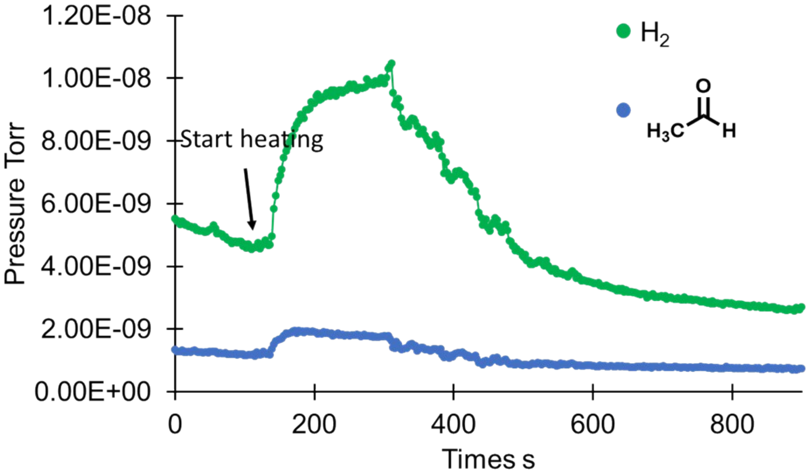


Figure S5. Gas phase MS (pressure versus time) scan of **Mo@C** (0.030g) with EtOH at 90 °C (500 rpm, 0.4 mL EtOH and 0.8 mL toluene).

Figure S5 shows the production of H_2 from EtOH. Acetaldehyde and CO_2 have the same mass of m/z = 44, so it cannot be determined explicitly that CO_2 is not produced, however, based on the lack of CO_2 observed in the reaction with MeOH, it is concluded that CO_2 is unlikely to form in the reaction with EtOH. After a period of 4 h (not shown), another aliquot of EtOH (0.4 mL) was added to this reaction mixture and no H_2 was produced, indicating the catalyst had deactivated.

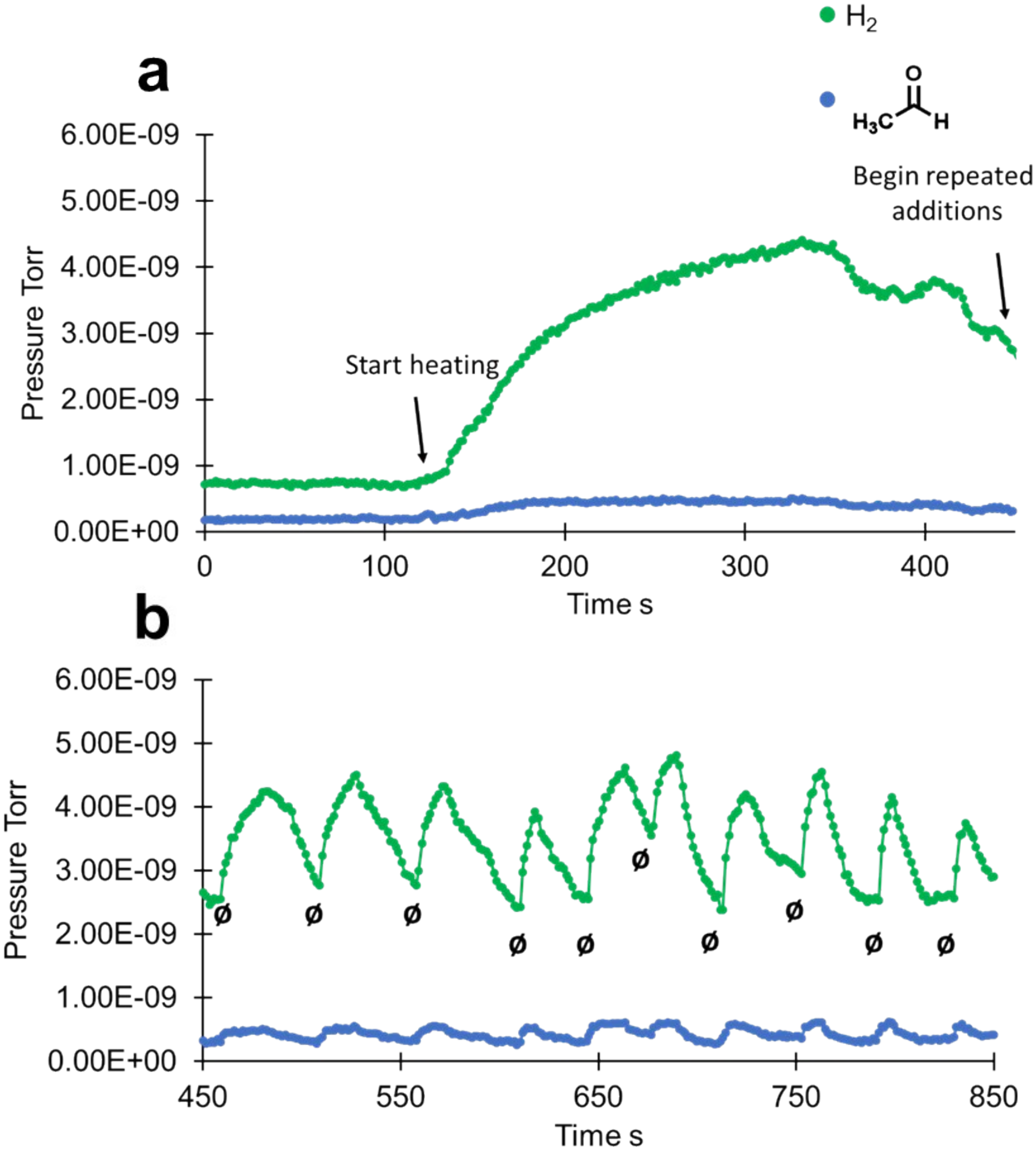


Figure S6. Gas phase MS (pressure vs time) trace of successive EtOH additions (1.0 mL, denoted by ø in graph to **Mo@C** (0.030g) added before all EtOH is consumed (90 °C and 500 rpm). a. Showing the point (time ~ 450 s) where another 1.0 mL of EtOH is added. b. Shows the successive 1.0 mL EtOH additions, ø).

Figure S6 shows that the system does not deactivate when there is still EtOH remaining in the reaction vessel. By adding another 1.0 mL of EtOH at the 450 s mark, activity is maintained for multiple cycles. It is proposed that the EtOH remaining helps to solubilize the acetaldehyde oligomers and prevents catalyst coating.

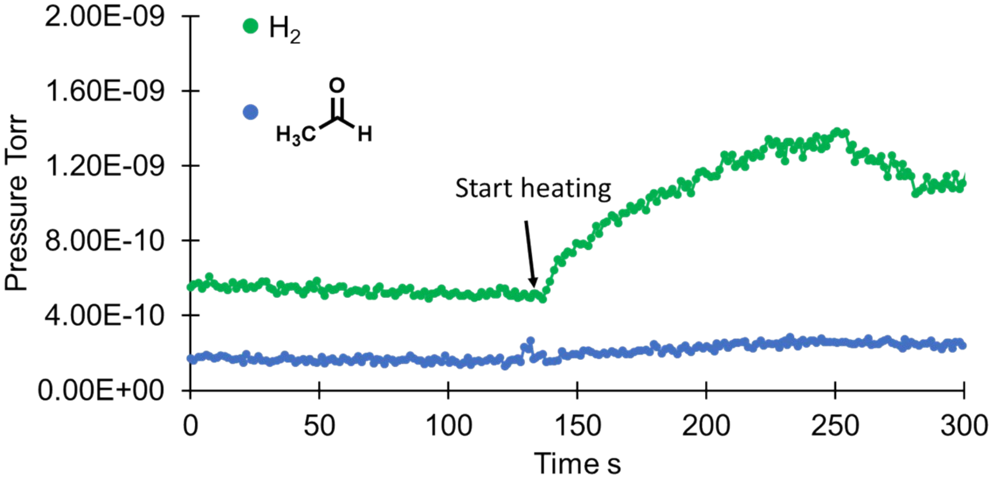


Figure S7. Gas phase MS (pressure vs time) trace monitoring of EtOH (0.10 mL) and H_2O (0.90 mL) addition to 0.030g **Mo@C** (90 °C and 500 rpm).

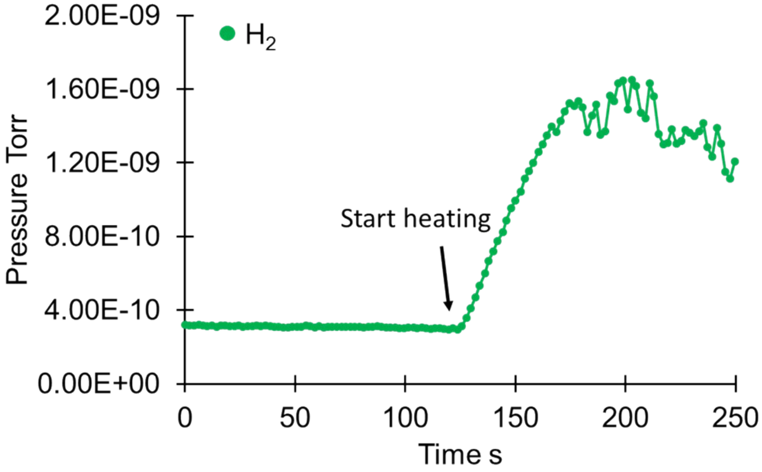


Figure S8. Regenerated **Mo@C** catalyst, prepared by sonicating the inactive catalyst in water, with 1.0 mL EtOH at 90 °C. Note: acetaldehyde not shown.

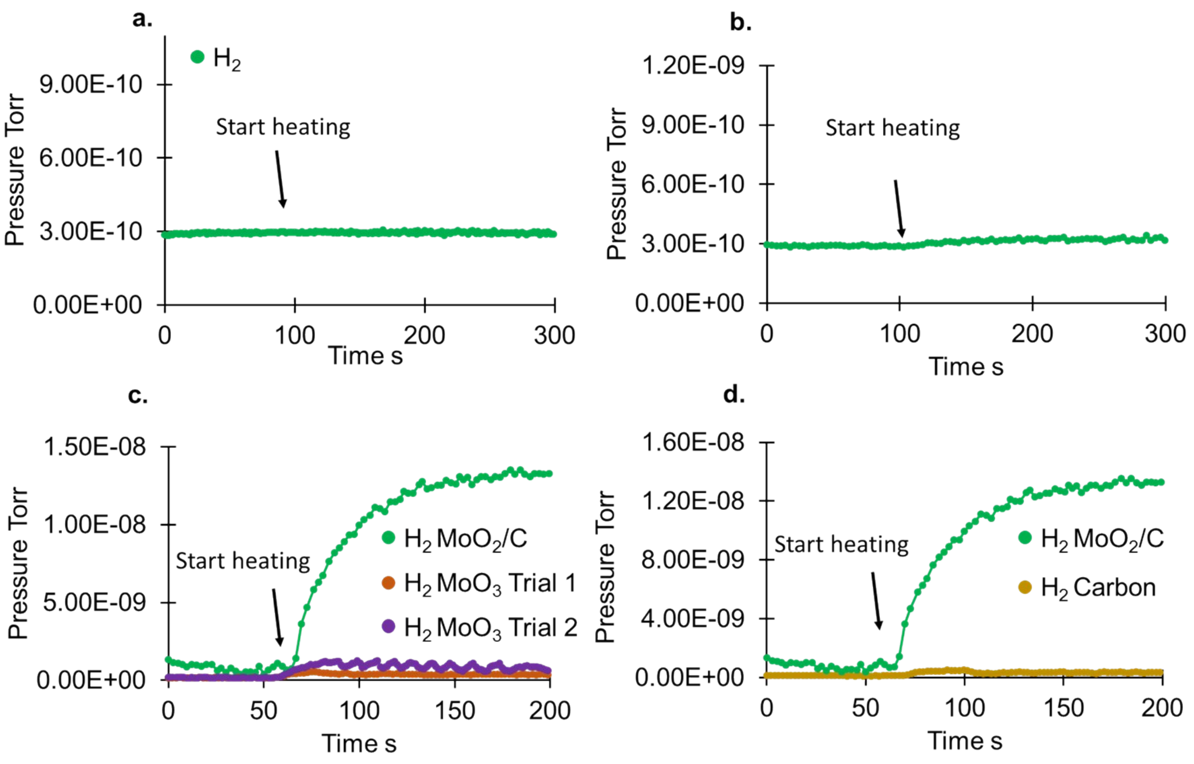


Figure S9. Control experiments at 90 °C and stirring at 500 rpm**.** **(a) Mo@C** (0.030g) with no alcohol**.** **(b**) H_2O (1.0 mL) and **Mo@C** (0.030 g). **(c)** Experiments with MoO_3 (0.0013 g, 9 μmol) and 1.0 mL EtOH**.** **(d**) Experiments with the activated carbon support (0.030 g) and 1.0 mL EtOH. Note: acetaldehyde not shown.

Figure S9 shows the control experiments. Figure S9a shows that no H_2 is produced when heating the catalyst without alcohol. Figure S9b shows that no H_2 is produced from H_2O. Figure S9c shows the reaction of commercially available MoO_3 (9 mmol) with EtOH. For comparison, a plot of H_2 production using **Mo@C** (6.3 μmol Mo) is shown as well. Figure S9d shows the reaction of activated carbon with EtOH, and includes a comparison plot when using **Mo@C**.

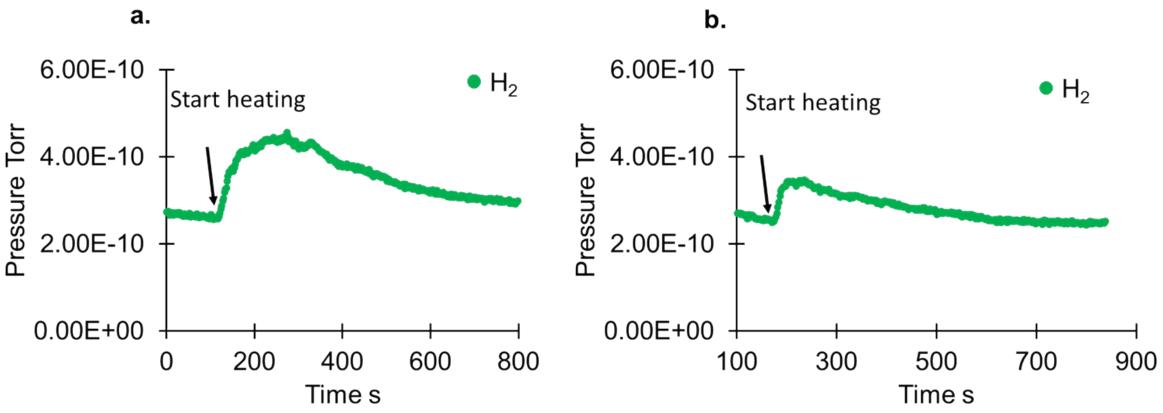


Figure S10. Gas phase MS (Pressure vs Time) graphs of H_2 production from EtOH (1 mL) using **Mo@C** (0.030 g) at a. 60 °C and b. 40 °C**.** Note: acetaldehyde not shown.

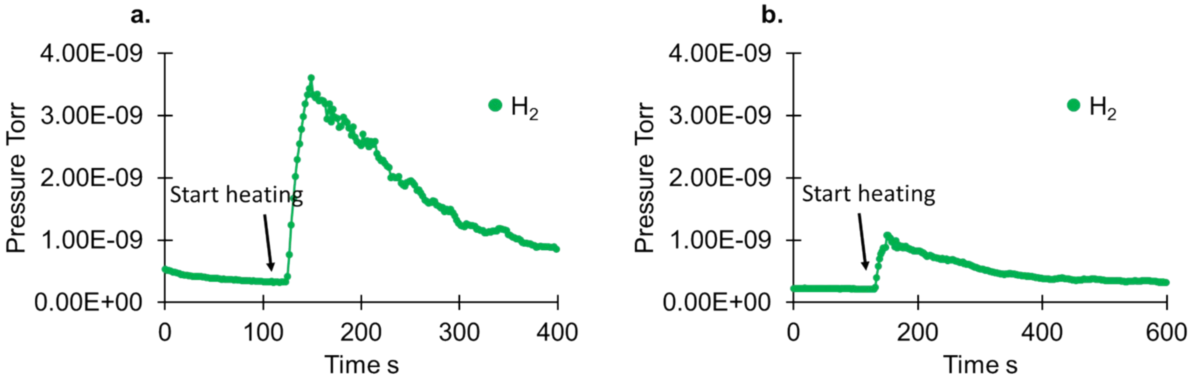


Figure S11. Gas phase MS (Pressure vs Time) graphs of H_2 production from MeOH (1 mL) using **Mo@C** (0.030 g) at a. 60 °C and b. 40 °C. Note: formaldehyde not shown.

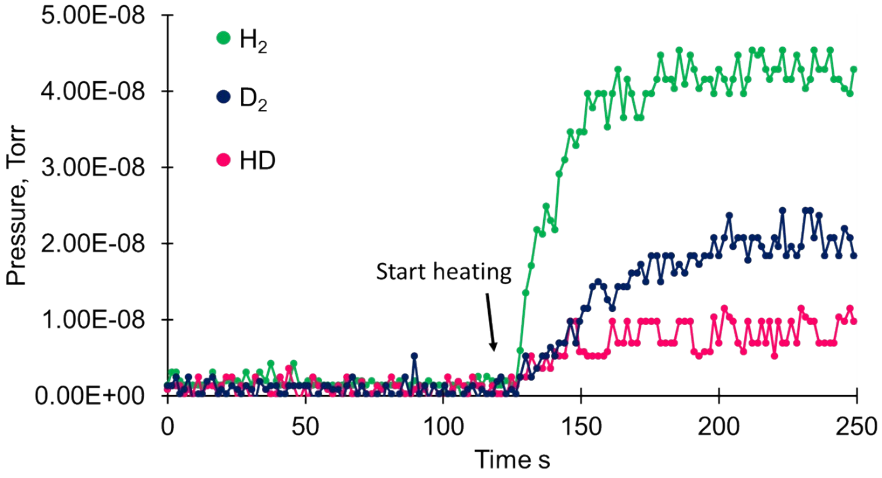


Figure S12. Gas phase MS (pressure vs time) trace of **Mo@C** (0.030g) with MeOD-d_4 at 90 °C (500 rpm, 0.40 mL MeOD-d_4 and 0.80 mL toluene). Note: formaldehyde not shown.

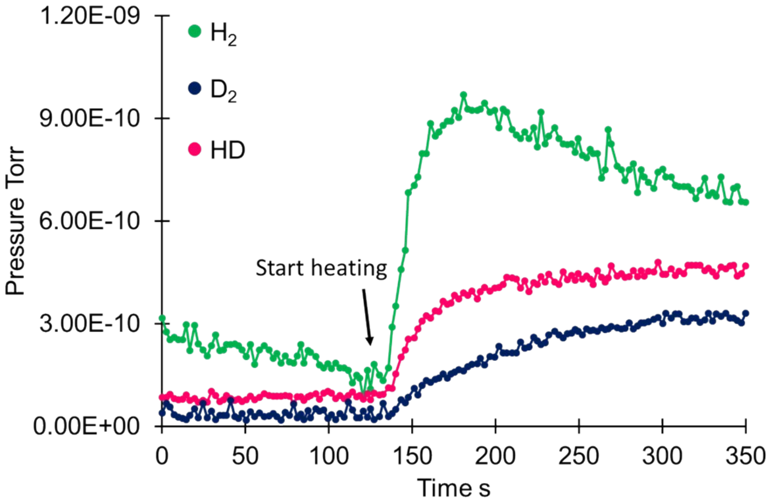


Figure S13. Gas phase MS (pressure vs time) trace of **Mo@C** (0.030g) with EtOD-d_6 at 90 °C (500 rpm, 0.40 mL EtOD-d_6 and 0.80 mL toluene). Note: acetaldehyde not shown.

Figures S12 and S13 show the reactions with MeOD-d_4 and EtOD-d_6, respectively. The presence of some H_2 and HD is detected in both samples, indicating that there is a source of protons in the system. To determine if the source is the activated carbon support, MeOD-d_4 was taken up with **Mo@C** in dry toluene-d_8 in a sealed J-young NMR tube and heated to 90 °C. Figure S17 shows the presence of H_2 as well as H_2O, which likely desorbed from the support. The gas phase MS (pressure vs time) of the deuterated alcohols MeOD-d_4 and EtOD-d_6 directly from Cambridge Isotopes were taken to determine if the reagents themselves were also sources of protons and their spectra are shown in Figure S14. As seen in Figure S14, the deuterated reagents also contain significant quantities of protons which could also be a source of HD and H_2. Alternatively, the mass spec rapidly scrambles H and D with protic sources in the instrument, which has been observed previously.[3, 4]

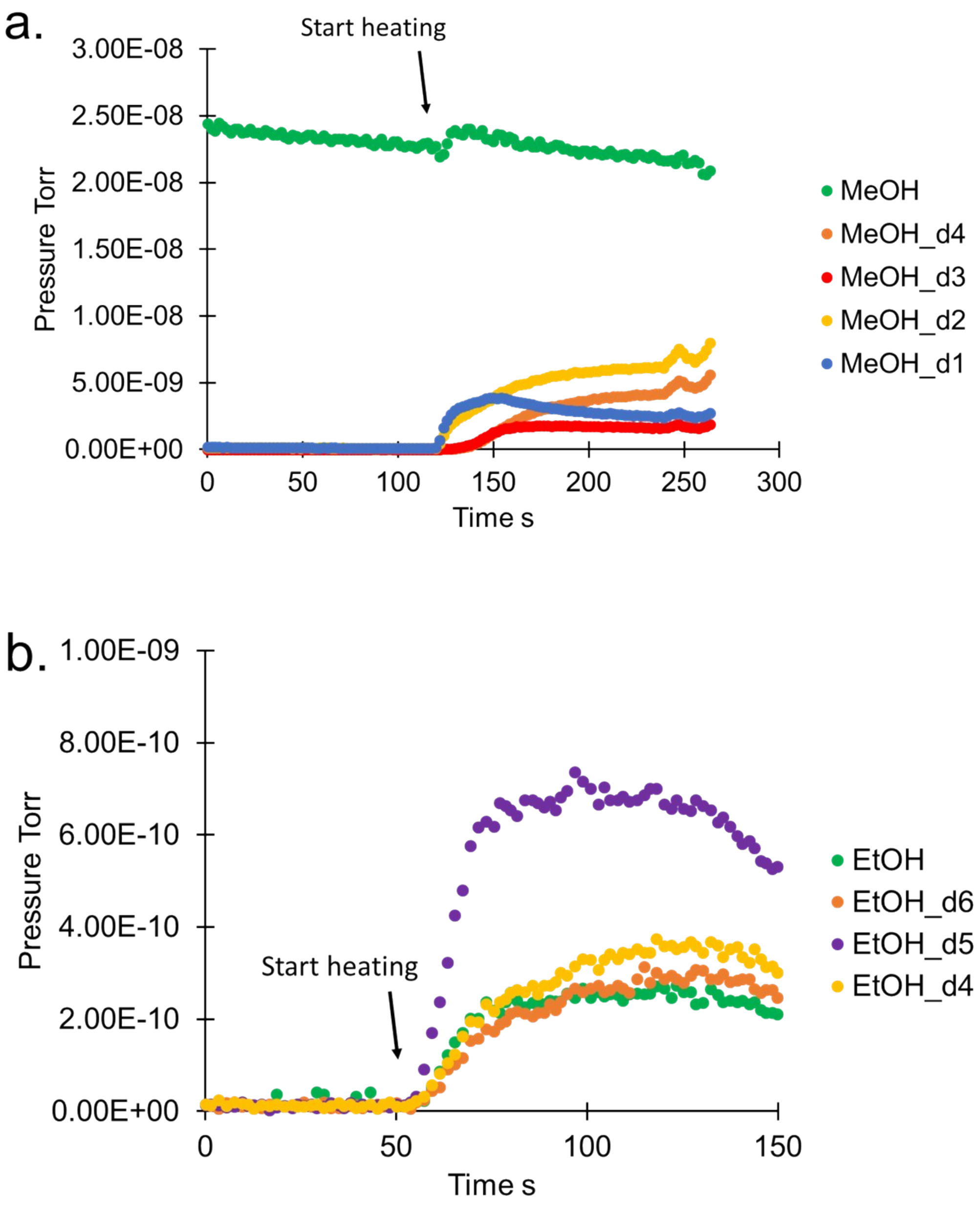


Figure S14. Gas phase MS (pressure vs time) trace. a. Freshly opened ampule of 1 mL MeOD-d_4 at 90 °C. b. 1mL of EtOD-d_6 (from a 10 mL bottle) at 90 °C.

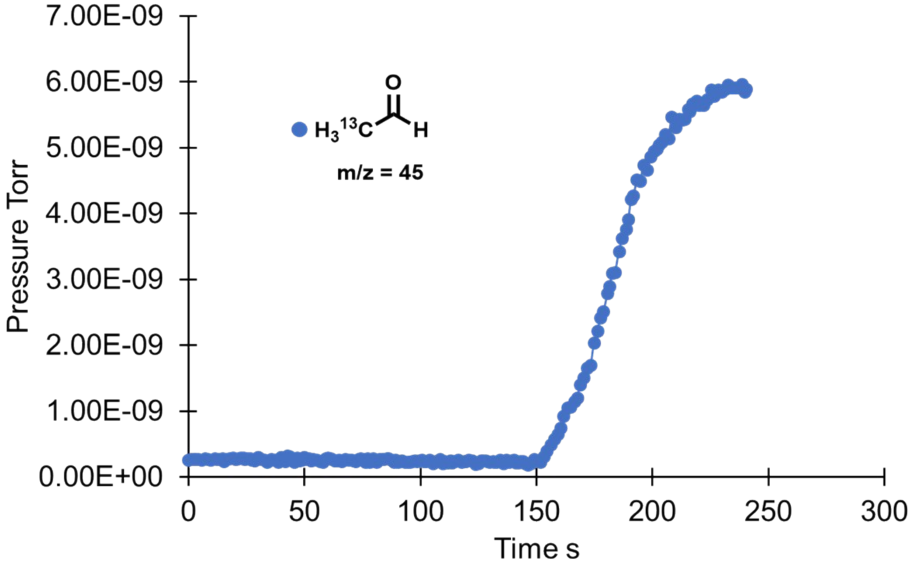


Figure S15. Gas Phase MS (pressure vs time) trace of **Mo@C** (0.030g) with $^{13}CH_3CH_2OH$ at 90 °C (500 rpm, start heating at 150 seconds). Note: H_2 not shown.

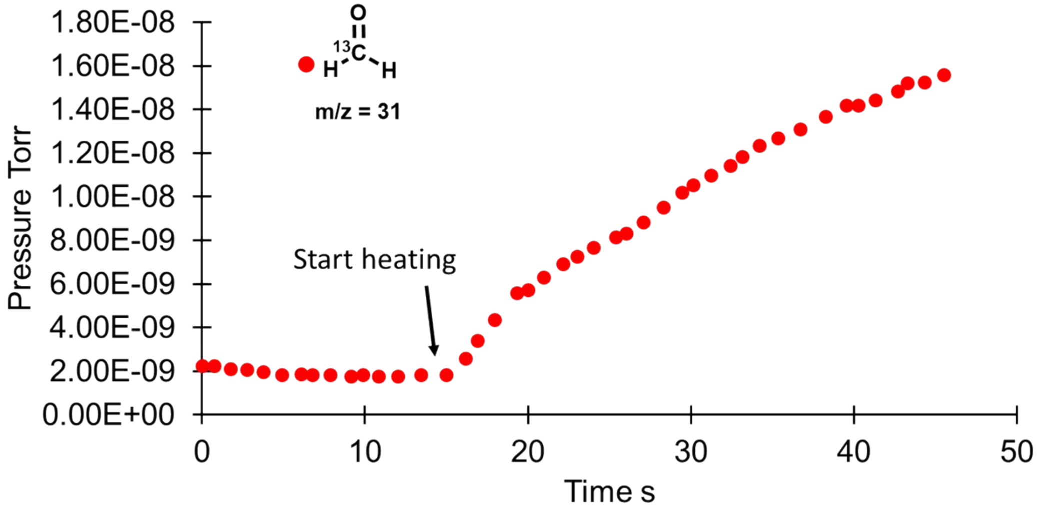


Figure S16. Gas Phase MS (pressure vs time) trace of **Mo@C** (0.030g) with $^{13}CH_3OH$ at 90 °C (500 rpm). Note: H_2 not shown.

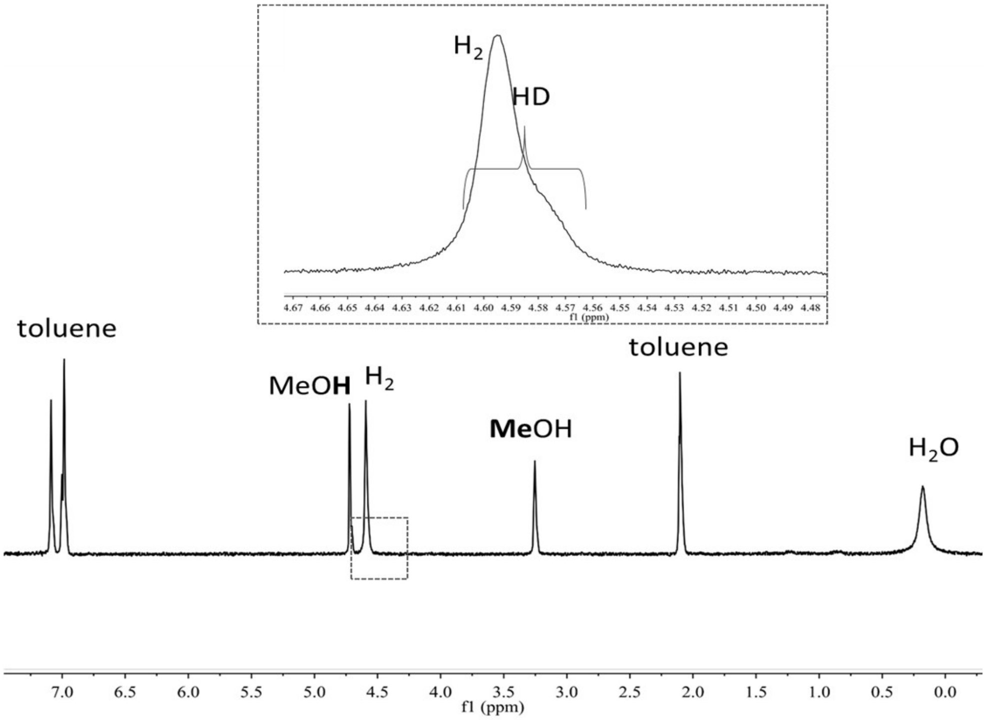


Figure S17. ^{1}H NMR spectrum (sealed J-young tube) of the reaction of MeOD-d_4 (0.2 mL) with **Mo@C** (0.015g) in toluene-d_8 at 90 °C for 16 h showing that the source of protons is the carbon support.

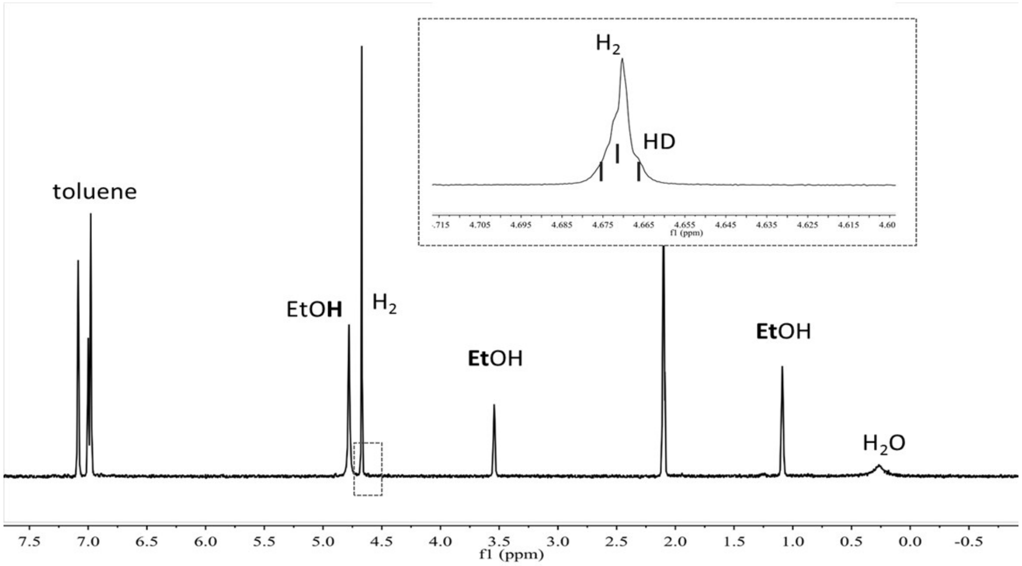


Figure S18. ^{1}H NMR (sealed J-young tube) of the reaction of EtOD-d_6 (0.2 mL) with **Mo@C** (0.015g) in toluene-d_8 at 90 °C for 16 h showing that the source of protons is the carbon support.

In Figures S17 and S18, the inset shows an expanded view of the H_2 signal. The signal for HD is tentatively assigned. Protic solvents that can hydrogen bond with the H or D species being measured, can result in a downfield or upfield displacement of the chemical shift, or remain in the same position as the original H signal.[S5-8] For gases that engage in hydrogen bonding (such as H_2, HD, or D_2), the chemical shift and HD J coupling constant is highly dependent on the pressure over the solution.[S9] Therefore, the assignment to HD can only be tentatively assigned, but is entirely reasonable, based on these considerations.

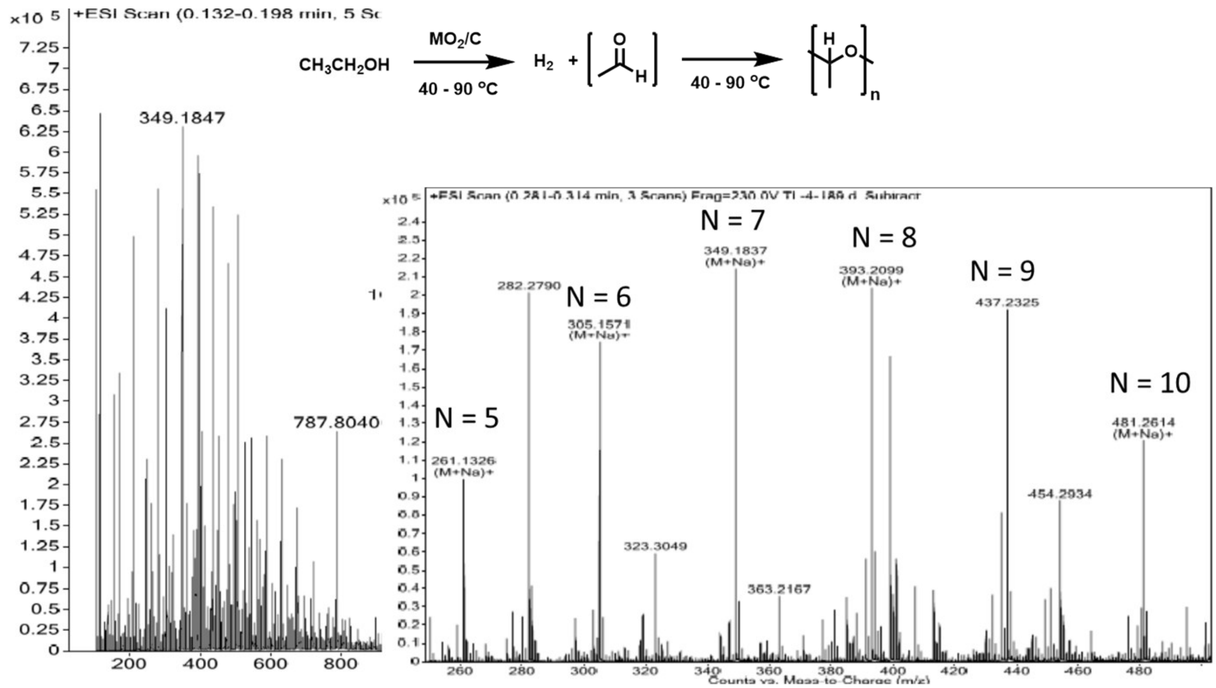
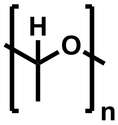
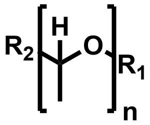


Figure S19. ESI-MS spectrum of the acetaldehyde oligomer from the mother liquor of the dehydrogenation reaction of EtOH over **Mo@C** at 90 °C.

Table S20. Mass spectrometric determination of oligomer degree of polymerization



n = 1   44 m/z



R_1, R_2 = end groups

Observed M+Na (m/z)	**End groups: R_1 = H, R_2 = OH (m/z)**	**New M+ (-Na, -H, and –OH) (m/z)**	**Value of n**
261	1, 17	261 – 23 – 1 - 17 = 220	220 / 44 = 5
305	1, 17	305 – 23 – 1 – 17 = 264	264 / 44 = 6
349	1, 17	349 – 23 – 1 – 17 = 308	308 / 44 = 7
393	1, 17	393 – 23 – 1 – 17 = 352	352 / 44 = 8
437	1, 17	437 – 23 – 1 – 17 = 396	396 / 44 = 9
481	1, 17	481 – 23 – 1 – 17 = 440	440 / 44 = 10

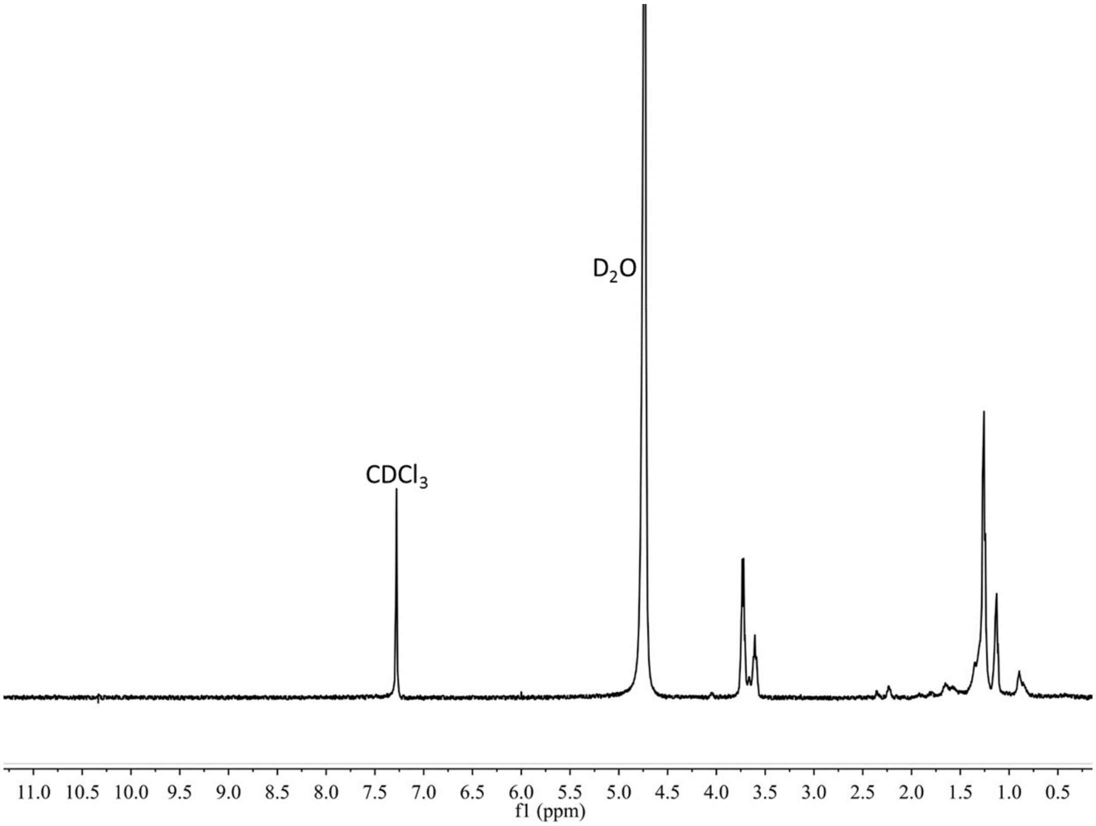


Figure S21. ^{1}H NMR of residual acetaldehyde oligomers (NMR solvent $CDCl_3$:D_2O)

To isolate the aldehyde oligomers, the reaction of EtOH over **Mo@C** was scaled up to 3.0 mL of EtOH. After removing the volatiles under vacuum at 25°C, ^{1}H NMR of the residues (~2 mg) in the flask (see above Figure S21 ^{1}H NMR) are assignable to short-chain ($n \leqslant 10$) oligomeric material.[S9] Based on the lack of material recovered (only 2 mg), it is evident that the small chain oligomers had mostly reverted to acetaldehyde (b.p. = 20 °C) which was removed in vacuo, minimizing the yield of material. Literature reports indicate elastomeric high MW polyaldehydes are unstable at room temperature, and gradually revert to gaseous monomers.[S10] Only highly crystalline high MW isotactic polyaldehydes are stable to depolymerization at 25°C, largely due to the favorable enthalpy of crystallization.[S10] Therefore, it is reasonable to assume that the present short-chain oligomers revert in a similar fashion to atactic polyaldehydes, and/or then to gaseous monomer.

The literature indicates that end group capping (ester, ether, siloxy, urethane groups) does not significantly stabilize atactic polyacetaldehydes since they undergo cleavage at any chain position in the presence of protic sources.[S2] In this work, quantification of the product short-chain oligomers is also hampered by the propensity to coat/adsorb onto the catalyst surface (See Table S22).

Table S22. Measured aldehyde adsorptive capacity of the carbon support at 25 ºC (10 mg C).

Substrate	**Amount Absorbed**	**Carbon Absorption Capacity**
Formaldehyde (1wt%/D_2O)	87 µmol (28%)	7850 µmol/g
Acetaldehyde (1wt%/D_2O)	28 µmol (12%)	2600 µmol/g

Weighing **Mo@C** catalyst after aldehyde adsorption (and drying under vacuum to remove residual solvent) yielded no detectable mass gain, indicating that the adsorbed aldehydes are removed in vacuo. This was confirmed by taking a spent, no-longer active **Mo@C** sample (after running in neat EtOH), drying it under vacuum, and re-subjecting it to catalytic reaction conditions. The **Mo@C** catalyst regained complete catalytic activity, indicating the adsorbed aldehyde oligomers/monomers had desorbed under vacuum.

Efforts were also made to characterize formaldehyde gas evolved in the dehydrogenation process beyond the aforementioned gas-phase MS.[S10] To this end, a catalytic run (90 ºC) with 3.0 mL of MeOH, 1.0 mL of D_2O, and 0.015 g **Mo@C** was set up with attachment to a reflux condenser fitted with a septa and cannula to a J-young NMR tube containing 0.5 mL toluene-d_8 and a vent needle so that all volatiles were bubbled through toluene-d_8 before escaping to atmosphere. The NMR tube with toluene-d_8 was cooled in a -78 ºC cold bath. Midway through the reaction (during rapid bubbling) the J-young NMR tube was isolated, sealed with a Teflon cap and allowed to warm to room temperature before recording an ^1H NMR spectrum (Figure S24).

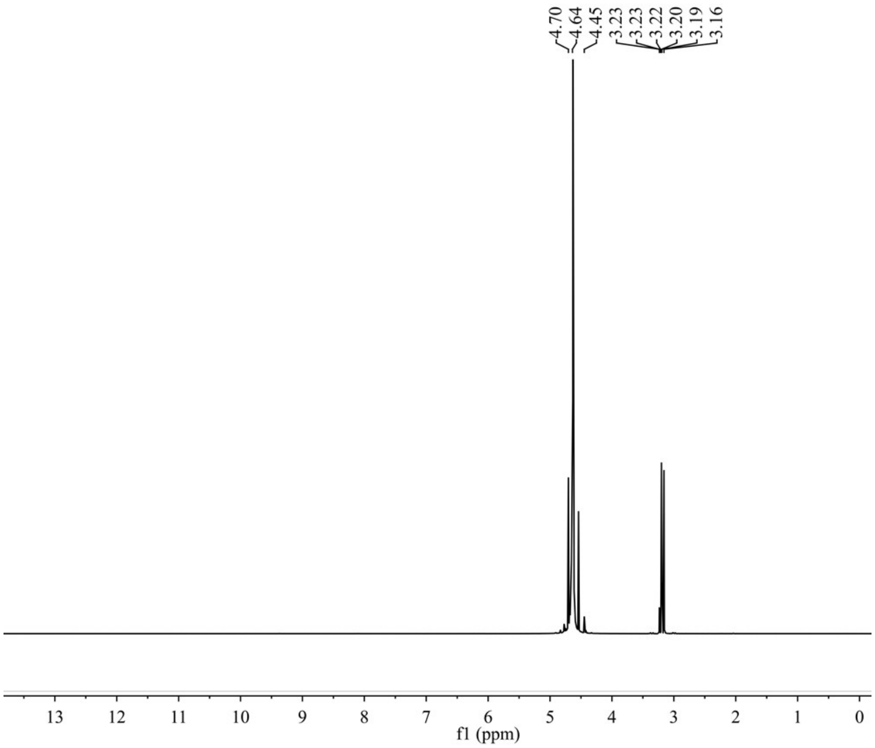
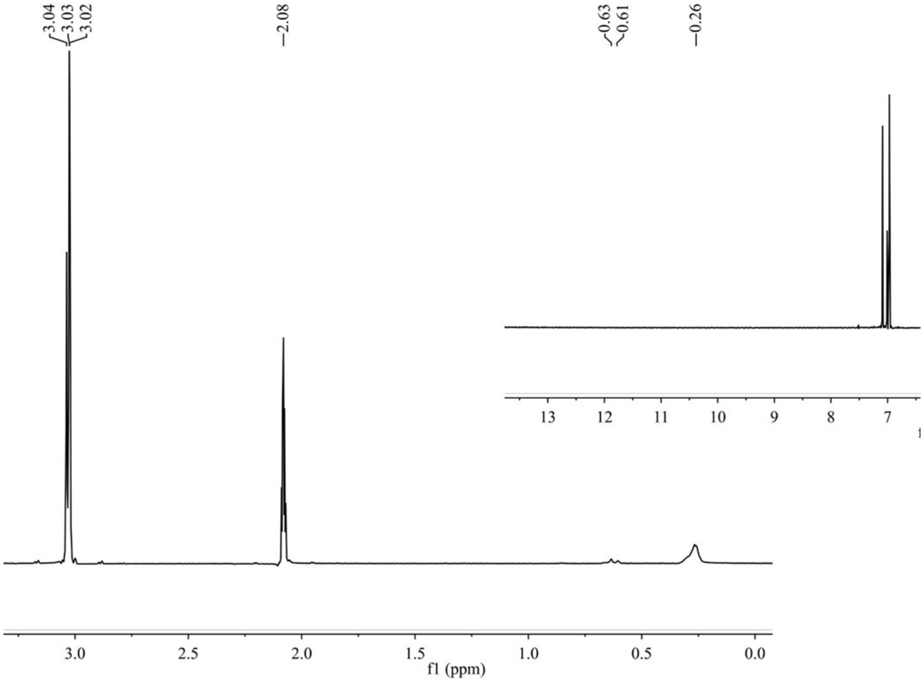


Figure S23. ^{1}H NMR spectrum of commercially available formalin (30 % v/v in H_2O) in D_2O showing multiple oligomeric species present. (for literature on formalin NMR in D_2O solutions see reference S10)



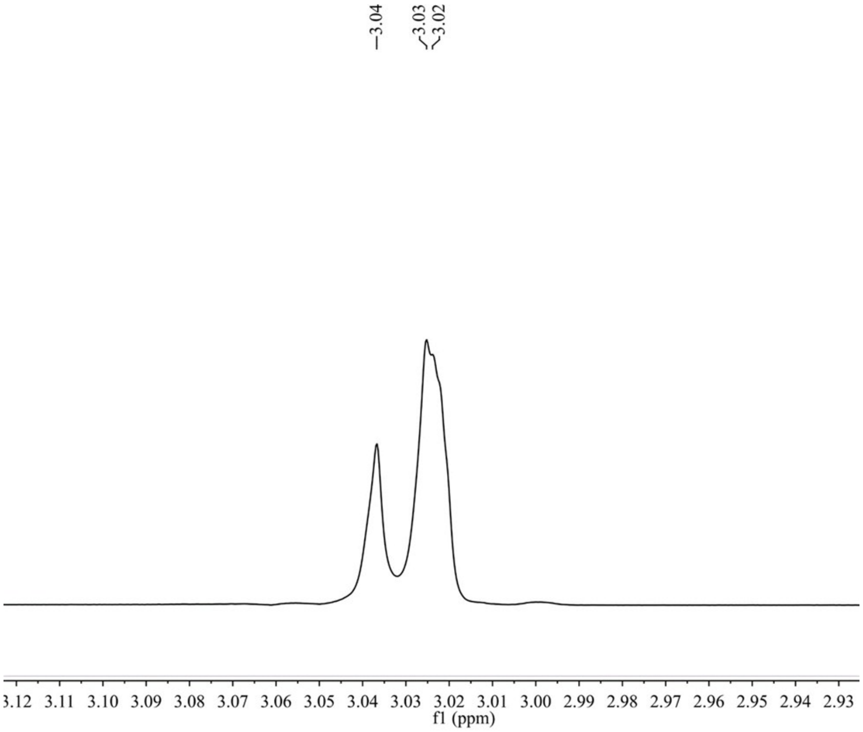
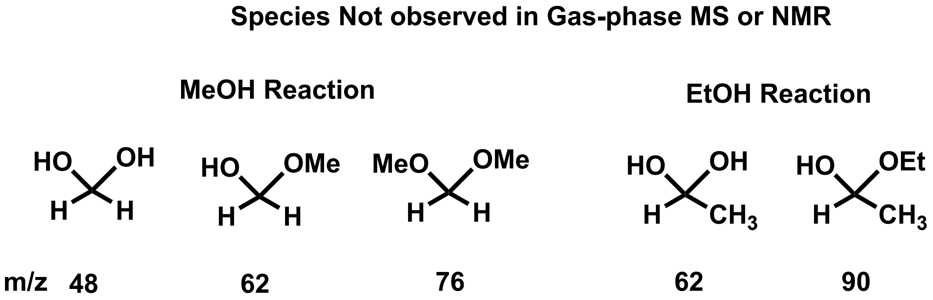
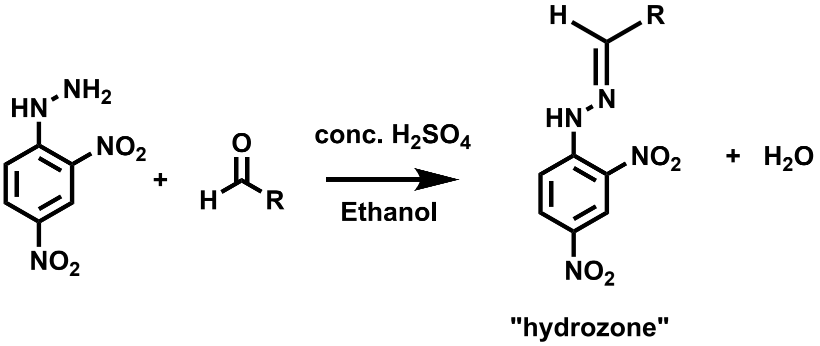


Figure S24. ^{1}H NMR spectrum of formaldehyde oligomers condensed from the gas phase in toluene-d_8.

No methylene glycols or hemi formals (monomers or small chain lengths) were observed by NMR (Fig. S40) or by gas phase MS analysis (instrument maximum is 100 m/z) of the vapor (See below):



Aldehyde Yields using Brady's Reagent:



Formalin control test: 2,4-nitrophenylhydroxone-formaldehyde yield: 30%

Reaction with MeOH: 2,4-nitrophenylhydroxone-formaldehyde yield: 25%

Reaction with EtOH: 2,4-nitrophenylhydroxone-acetaldehdye yield: 20%

Based on the control test with formalin, only 30% of the formaldehyde is captured with this procedure, most likely a result of trying to capture gaseous formaldehyde with a liquid reagent (yields have ranged between 60 to 85 %).[11] This indicates gaseous aldehyde escapes to the atmosphere before reacting with the reagent in solution and/or is lost during extraction and workup. The low yield may also be due to aldehyde adsorbing to the carbon. Note that the gaseous aldehyde yields using MeOH and EtOH are similar to that of the formalin control.

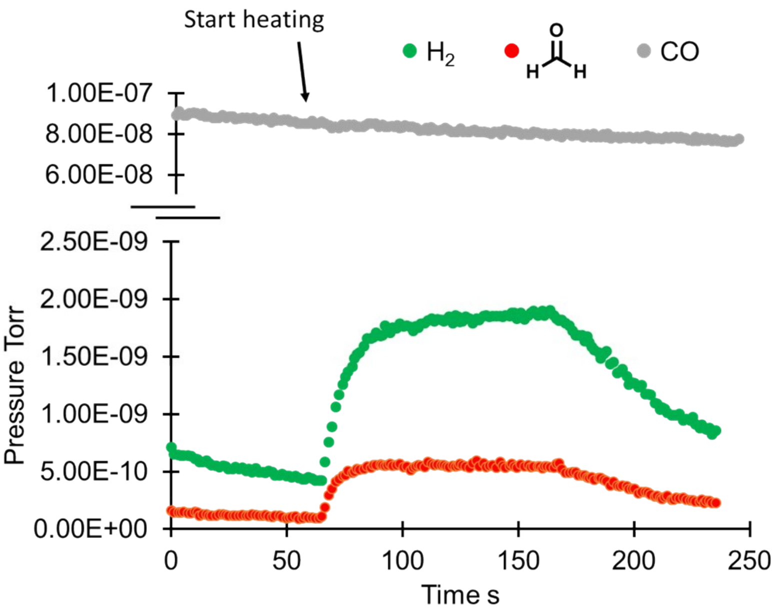


Figure S25. Gas phase MS (pressure vs time) trace of **Mo@C** (0.030g) with MeOH at 90 °C (500 rpm, 1.0 mL MeOH) showing no CO production.

Based on the lack of CO (Figure S25) and CO_2 (Figure S1) produced in the reaction and the yields of 1 eq. of H_2 near 100%, it is proposed that the oligomeric and monomeric aldehydes are formed nearly quantitatively. For both MeOH and EtOH, the product oligomeric and monomeric aldehydes either adsorb onto the catalyst surface and/or are released into the gas phase (as monomers) as evidenced by gas-phase MS, chemical titration, and NMR spectroscopy.

Example Calculation of H_2 Yield (Table S4 Trial 1, 32 μL of MeOH, 0.791 mmol):

(T) Temperature of H_2O: 25 °C = 298.15 K
Vapor pressure H_2O (@ 25 °C): 3173.1 Pa
Atmospheric pressure in Chicago (O'Hare)[S12]: 102298.3 Pa
(P) Pressure difference: 99125.2 Pa = 0.978 atm
Volume of H_2O: 100 mL

(V) Total Volume of H_2 collected: 17 mL

n(moles) = P.V/RT (ideal gas law, R = 0.08206 $L.atm.mol^{-1}.K^{-1}$)

$$n = \frac{(0.978\ \text{atm})(0.017\text{L})}{(0.08206\ \text{L.atm.mol}^{-1}.\text{K}^{-1})(298.15\text{K})}$$

Moles of H_2 collected (n) = 0.00068 moles

The number of moles of H_2 in water was calculated using Henry’s constant (H_2 solubility in water) assuming the displaced water was under 1 atm of H_2 inside the burette.

Moles of H_2 dissolved in 100 mL H_2O at 25 °C: 0.00008 moles

$$\text{Yield} = \frac{0.00068\ +\ 0.00008}{0.000791}\ \text{x}\ 100\%$$

Yield = 96 %.

Table S26. H_2 Yields at 90 °C, stirring at 500 rpm, 32 µL MeOH or 50 µL EtOH with H_2O and **Mo@C** (0.0075 g).

System	**H_2 Yields (%)**	**Average H_2 Yield (%)**
Neat MeOH	Trial 1: 96 % Trial 2: 86 %	91 ± 5 %
6:4 MeOH:H_2O	Trial 1: 91 % Trial 2: 90.5 %	91 ± 1 %
1:9 MeOH:H_2O	Trial 1: 88 % Trial 2: 85 %	87 ± 2 %
Neat EtOH	Trial 1: 100 % Trial 2: 102 %	100 ± 2%
6:4 EtOH:H_2O	Trial 1: 95 % Trial 2: 87 %	91 ± 4 %
1:9 EtOH:H_2O	Trial 1: 90 %	89 ± 2 %

	Trial 2: 87 %	

Table S27. H_2 calibration of gas phase MS under semi-batch conditions. (Total flow = 1 mL/s gas)

5% H_2/N_2 : Ar	mol % H_2	Pressure (H_2) Torr
0:100	0	2×10^{-10}
25:75	0.0125	2.88×10^{-8}
37.5:62.5	0.0187	4.1×10^{-8}
50:50	0.025	6.2×10^{-8}
75:25	0.0363	8.3×10^{-8}
100:0	0.05	1.3×10^{-7}

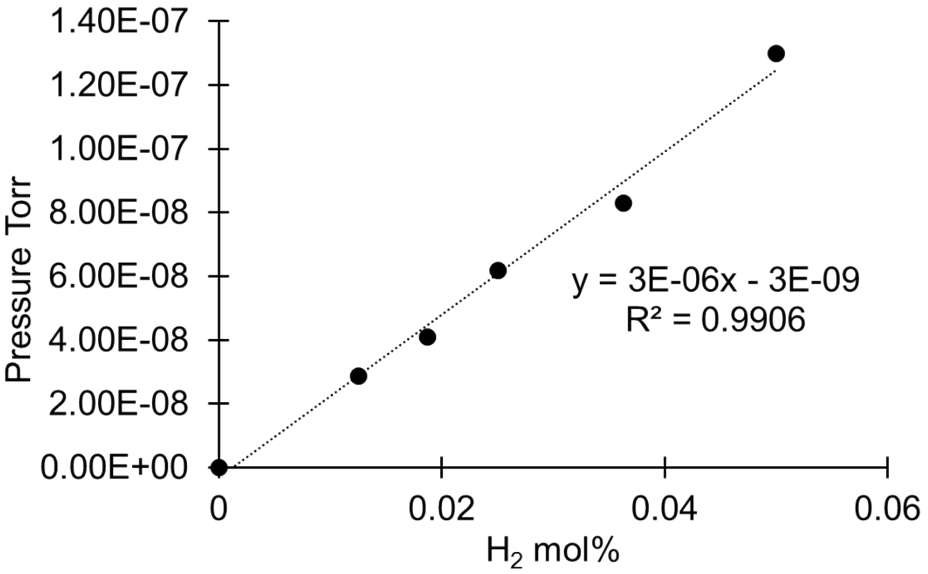


Figure S28. H_2 calibration curve for 1mL/s gas flow.

Example TOF determination:

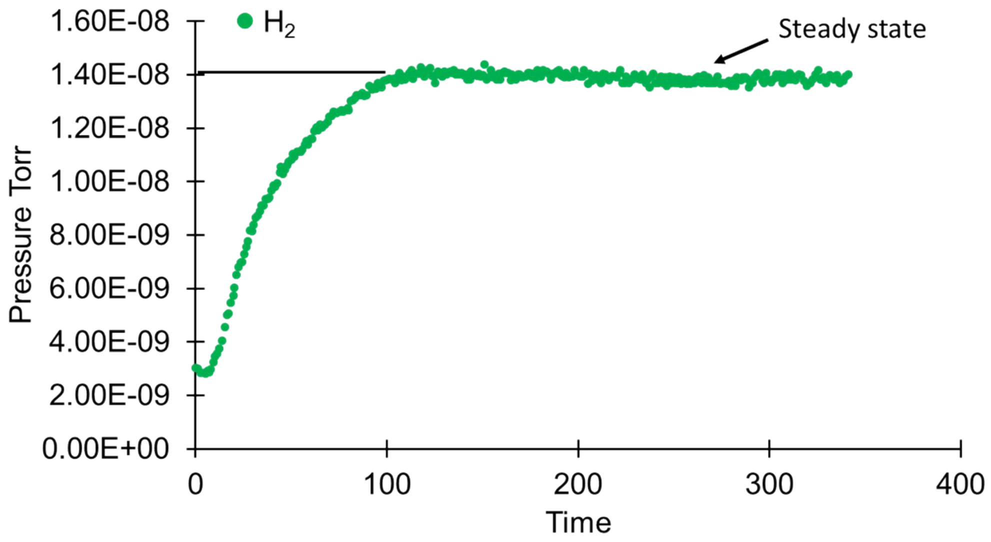


Figure S29. Example Graph to determine steady state TOF's (line = steady state pressure of H_2)

For data in Figure S29:

Calibration curve: Pressure (Torr, H_2) = 2.556×10^{-6}(mol% H_2) – 3×10^{-9}

Total gas flow: 3.976×10^{-5} mol/s

Total mol H_2 possible (1 mL MeOH): 0.02466 mol

mol Mo (30 mg of 2.1 wt% catalyst): 6.29×10^{-6} mol.

Take the pressure (Torr) at steady state and convert to mol% H_2 using the calibration curve.

Mol% H_2 at steady state = 0.889 mol%

Moles/s of H_2 at steady state (calculated using total gas flow): 3.578×10^{-7} mol/s

TOF = [rate/mol catalyst] = [(3.578×10^{-7} mol/s)*(3600 s/h)]/6.29×10^{-6} mol

TOF = 205 h^{-1}.

Table S30. TOF's under continuous heating (2 mL H_2O) with 0.030 g of **Mo@C** at 90 °C. (Total flow = 1 mL/s Ar gas).

mL MeOH	**TOF (h^{-1})**	**Day**
0.6	577	1
0.6	674	2
0.6	668	3
0.6	650	4
0.6	688	5

Table S31. TOF's while varying **Mo@C** (2.1 wt % Mo) at 90 °C (Madon-Boudart Test/Koros-Nowak Criterion).[13]

ROH	**Catalyst (mg)**	**TOF (h^{-1})**
1 mL MeOH	75	140 ± 6
1 mL MeOH	60	202 ± 8
1 mL MeOH	45	268 ± 24
1 mL MeOH	15	968 ± 56
1 mL MeOH	7.5	11,378 ± 180
1 mL MeOH	3.8	24,040 ± 214
2 mL EtOH	60	78 ± 2
2 mL EtOH	45	114 ± 4
2 mL EtOH	15	338 ± 3
2 mL EtOH	7.5	632 ± 28

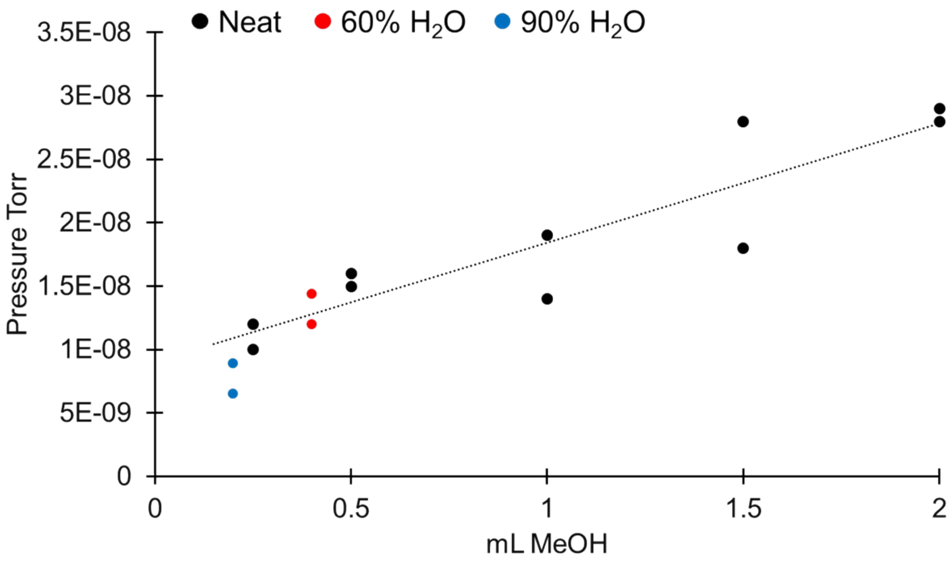


Figure S32. H_2 pressure at steady state with varying MeOH

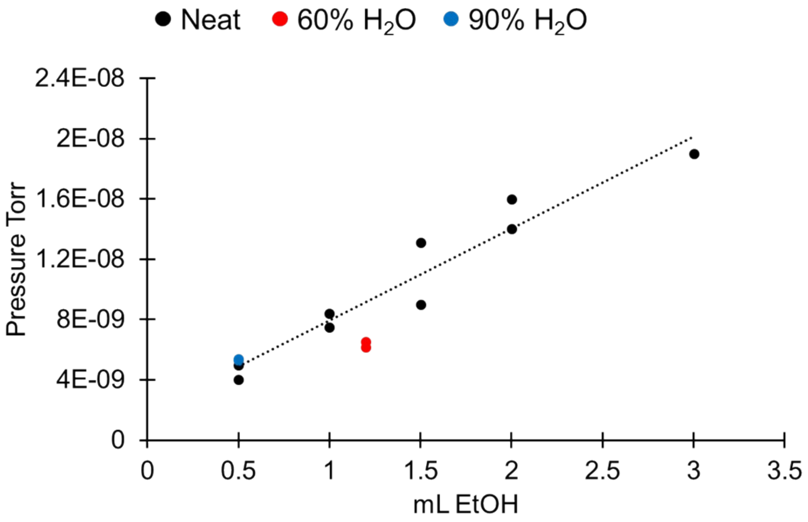


Figure S33. H_2 pressure at steady state with varying EtOH

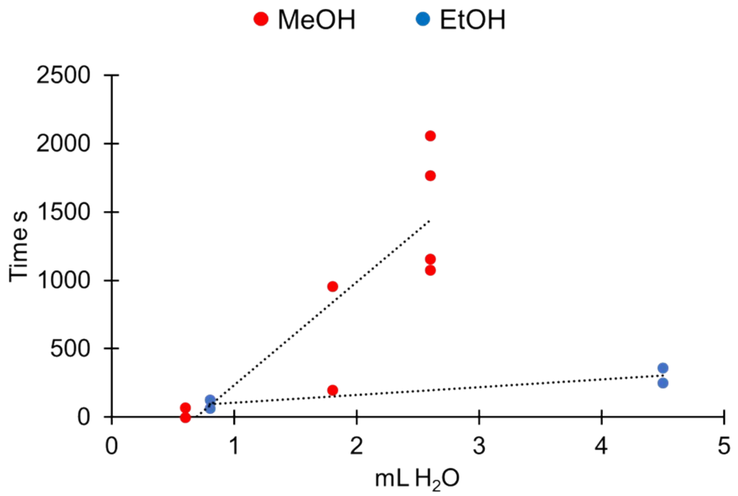


Figure S34. Delay Time for H_2 production from MeOH and EtOH observed with increasing H_2O

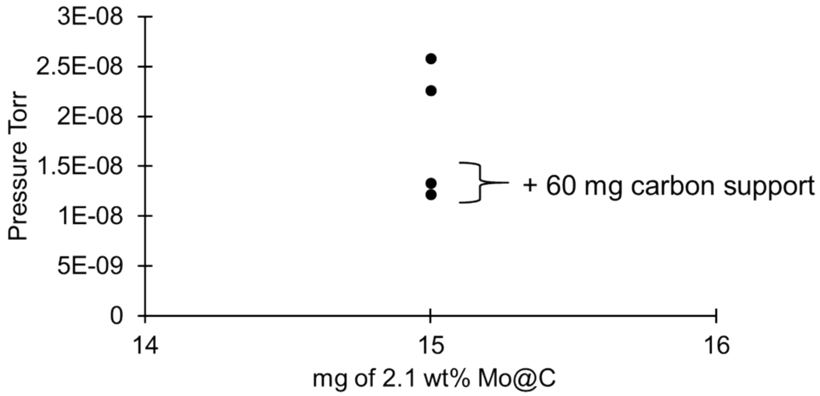


Figure S35. Pressure of H_2 after dilution of Mo@C with extra carbon support to determine if the system is transport limited (Madon-Boudart Test/Koros-Nowak Criterion).[13]

Due to the extremely high reaction rates and only slightly negative free energy of the overall reaction, we expect that the calculated rates in Table 1 reflect transport limitations, probably at both the liquid-solid interface and involvingby hydrogen gas transfer from the liquid phase to the gas phase (see ref. 11). This is based on several experimental observations: 1) the hydrogen production is steady after the initiation of the reaction, as opposed to exhibiting any decay that would be expected from typical first -order kinetics. 2) In neat alcohol, the time required for and the hydrogen evolution to reach steady- state and the final partial pressure of hydrogen were both dependent on the quantity of alcohol concentration. In this case, larger amounts of soluble medium allow for larger amounts of hydrogen to leave the reactor, (resulting in higher hydrogen partial pressures) and require longer times to saturate, (resulting in longer delay times).

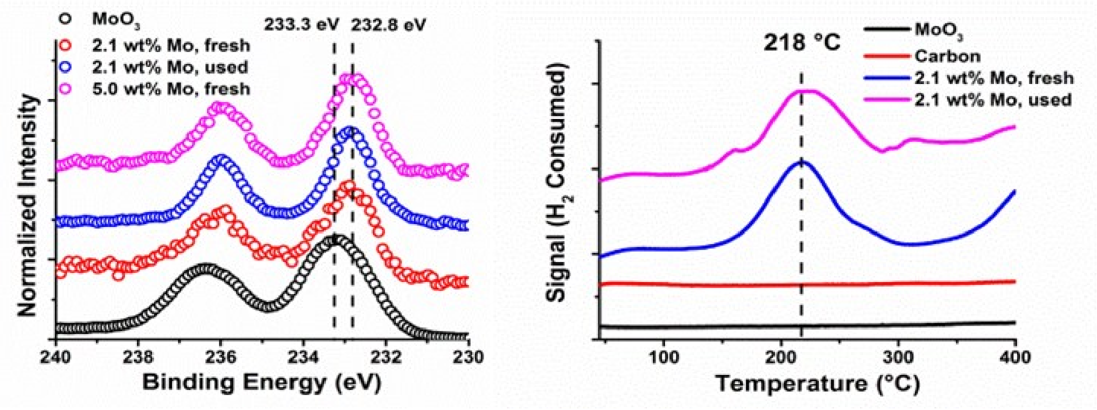


Figure S36. XPS and H_2-TPR of **Mo@C**.[1] Left: **Mo@C** Mo(3d) XPS spectrum. Black traces are from reference MoO_3. Right: H_2-TPR traces of reference MoO_3 (black), activated C (green), pristine 2.1wt% **Mo@C** (blue), and used 2.1wt% **Mo@C** (red). See reference S1 for more details.

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