Aqueous phase homogeneous formic acid disproportionation into methanol

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ELECTRONIC SUPPLEMENTARY INFORMATION

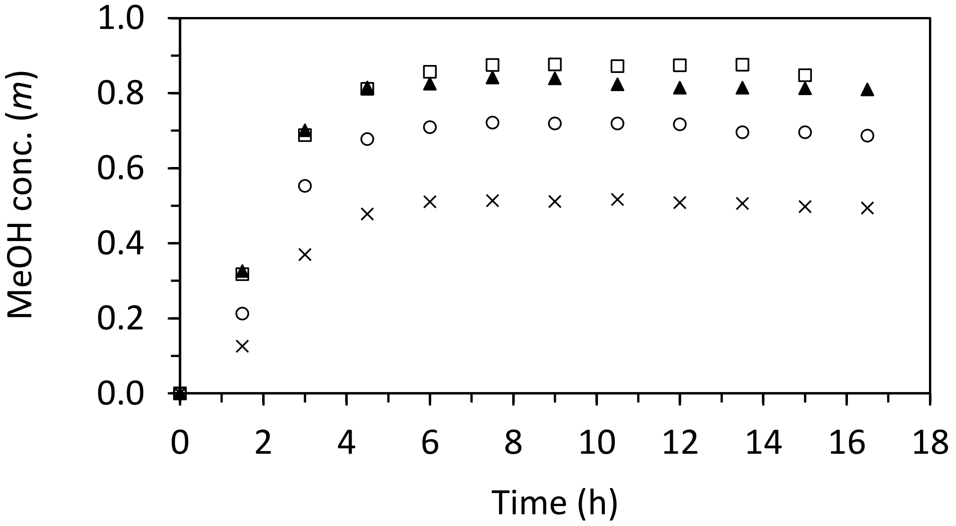

Figure S1. The effect of initial H_2 pressure on the methanol concentration obtained from formic acid. Initial pressure of 40 bar (squares), 20 bar (triangles), 10 bar (circles) and none (crosses), 10.0 mmol $H^{13}COOH$, 2.5 *m* H_2SO_4, n_{cat} = 15.9 µmol, m_{H2O}= 2.0 g, T = 80 °C.

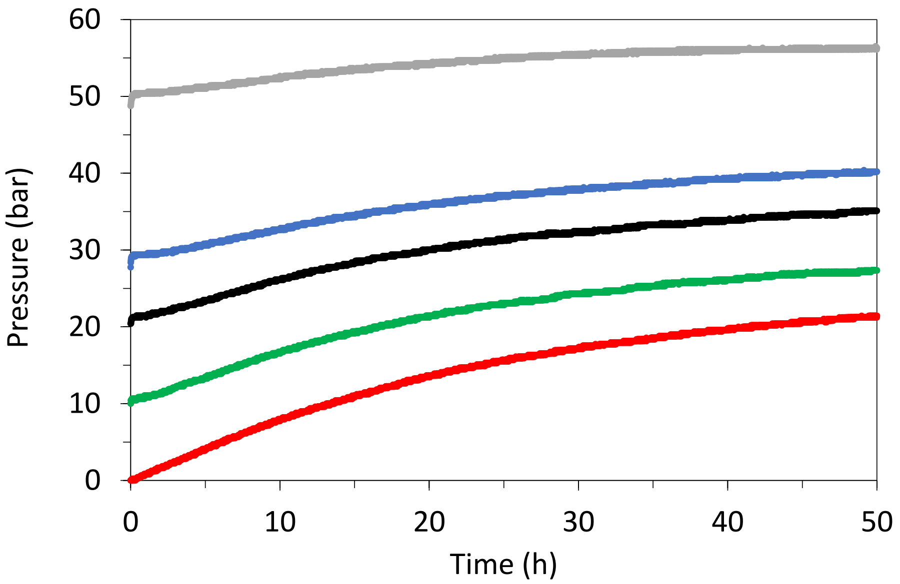

Figure S2. Pressure profile for FA disproportionation/dehydrogenation reaction in D_2O under various initial H_2 pressures. Reaction conditions: 10.0 mmol $H^{13}COOH$, 2.5 *m* H_2SO_4, n_{cat} = 15.9 µmol, m_{D2O} = 2.0 g, T = 50 °C.

In our experiments, formic acid conversions and methanol yields were calculated from quantitative ^{13}C NMR spectra using acetonitrile (which was always added at the end of the reaction) as an internal standard. The prerequisite for obtaining ^{13}C NMR spectra with full intensities and therefore correct relative peak areas (i.e. quantitative spectra), is that all signals of interest must have relaxed completely before a pulse is applied.[1] In particular, after a 90° pulse, the rate at which magnetization relaxes is a function of the longitudinal relaxation time (T_1) of the nucleus. In order to minimize the error to ≤1%, the time between pulses (d_1) should be at least five times higher than the T_1 of the slowest relaxing signal of interest in the spectrum (the magnetization recovery is 99.3% and 99.91% of its original size after $5T_1$ and $7T_1$, respectively). The ^{13}C T_1 value for formic acid was reported in our previous work[2] and corresponds to approximately 15 sec at pH<2. The respective ^{13}C T_1 value for methanol was calculated for the purposes of this work, as shown in Fig. S3, and corresponds to 16.6 sec. Therefore, quantitative ^{13}C NMR spectra were always taken with a d_1 value of 100 sec.

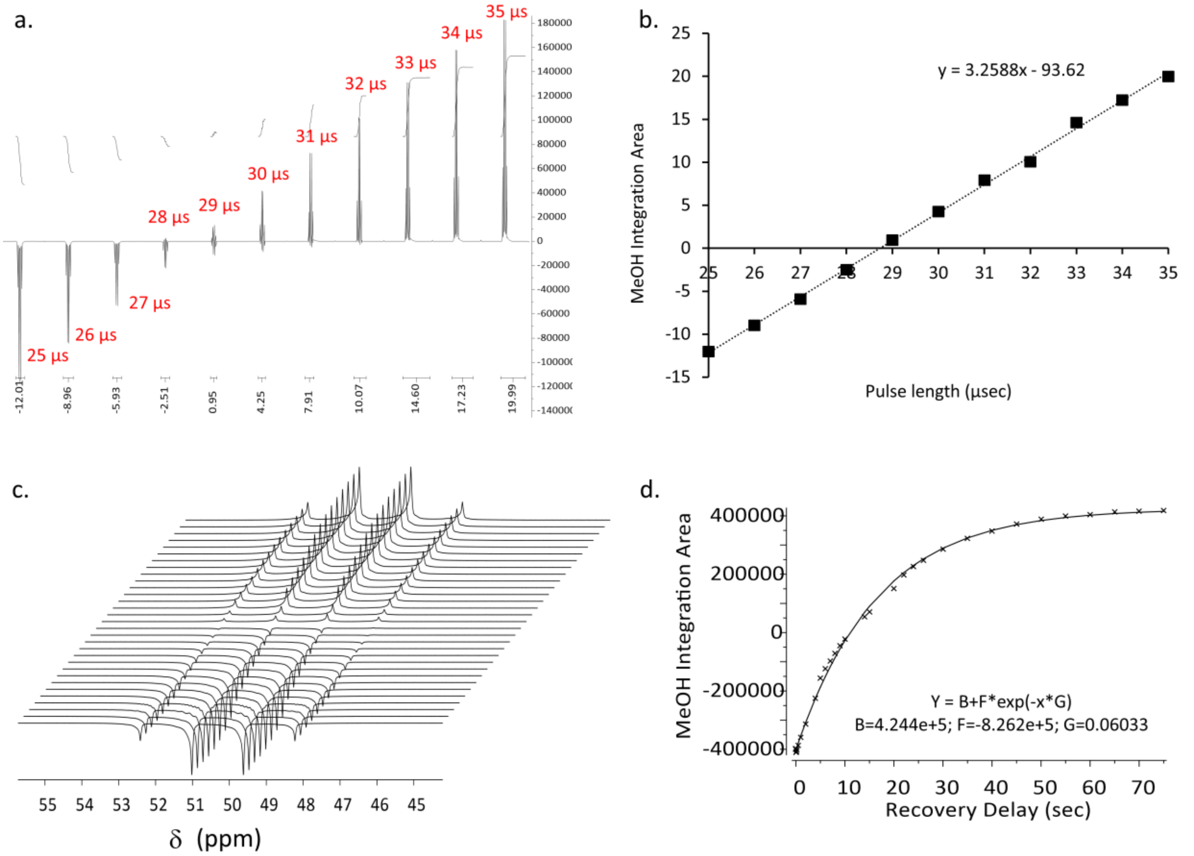

Figure S3. Determination of ^{13}C longitudinal relaxation time T_1 of methanol. a) Calibration of 90° pulse-^{13}C NMR spectra of methanol obtained for difference pulse lengths between 25-35 µsec, b) Plot of MeOH integration area derived from (a) versus the pulse length time, c) ^{13}C NMR spectra of methanol obtained from a standard inversion recovery experiment varying the recovery delay time (d_7) between 0.00001-75 sec, d) Plot of MeOH integration area derived from (c) versus the recovery delay time.

In order to calculate the ^{13}C longitudinal relaxation time T_1 of methanol, the 90° pulse had to be measured using a sufficiently long relaxation delay (d_1). From Fig. S6b, the 180° pulse (zero point) was determined to be 28.7 µsec (see equation on graph), corresponding to a 90° pulse of 14.35 µsec. This value was then employed for the inversion recovery experiment depicted in Fig. S3c. The plot of the resulting MeOH integration areas as a function of the recovery delay times (Fig. S3d) was fitted with a three parameter exponential curve, from which T_1 could be calculated as follows.

$$y = B + F * \exp(-x*G)$$

where B: $4.244*10^5$, F: $-8.262*10^5$ and G: 0.06033.

Since $T_1 = 1/G$, it can be calculated $T_1 = 16.6$ sec.

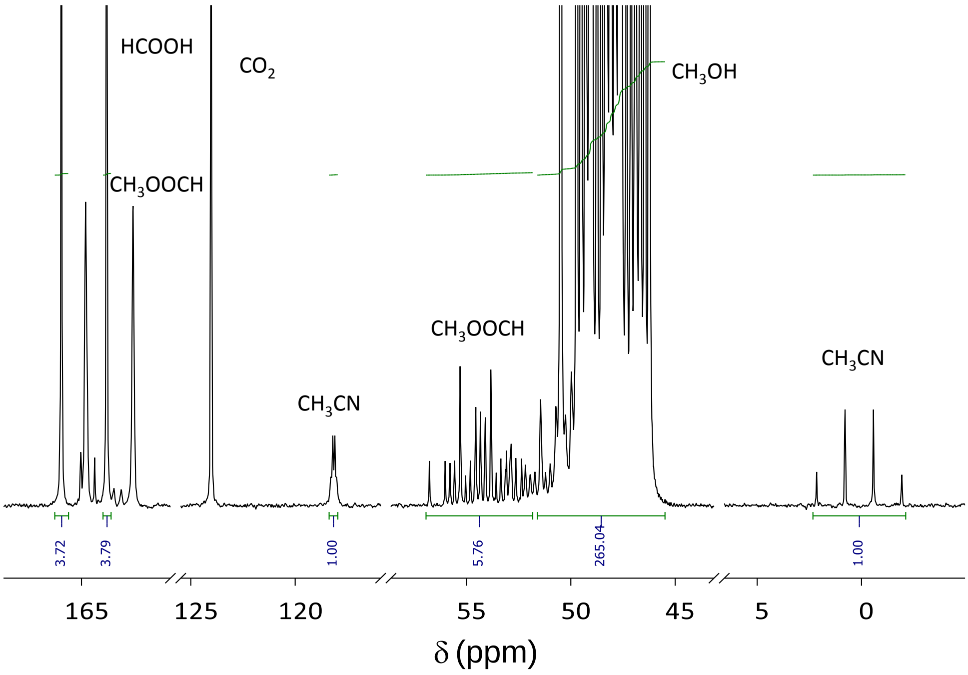

Figure S4. Quantitative ^{13}C NMR spectrum (d_1 = 100sec) taken at the end of five consecutive FA disproportionation/hydrogenation reactions in the presence of complex **(1)**. Reaction conditions: 10.0 mmol $H^{13}COOH$/cycle, 2.5 *m* H_2SO_4, n_{cat} = 15.9 µmol, m_{D2O} = 2.0 g, $P_{init.}(H_2)$ = 50 bar/cycle, T = 50 °C. Acetonitrile, CH_3CN (0.271 g), was added at the end of the reaction as an internal standard for quantitative integration.

Taking into account the abundancy of $^{13}C/^{12}C$ (1.109%/98.89%) the methanol quantity was calculated as follows:

$n_{MeOH} = m_{CH3CN}/Mr_{CH3CN} * 265.04 * 0.01109/0.9889/1000 \approx 19.6$ mmol,

$n_{FA} = m_{CH3CN}/Mr_{CH3CN} * (3.72+3.79) * 0.01109/0.9889/1000 \approx 0.55$ mmol,

$n_{MeOOCH} = m_{CH3CN}/Mr_{CH3CN} * 5.76 * 0.01109/0.9889/1000 \approx 0.42$ mmol,

$Conv._{FA}(\%) = 100 - (0.55/50 * 100) = 98.9\%$,

$Concentration_{MeOH} = n_{MeOH}/m_{D2O} = 9.8$ *m*

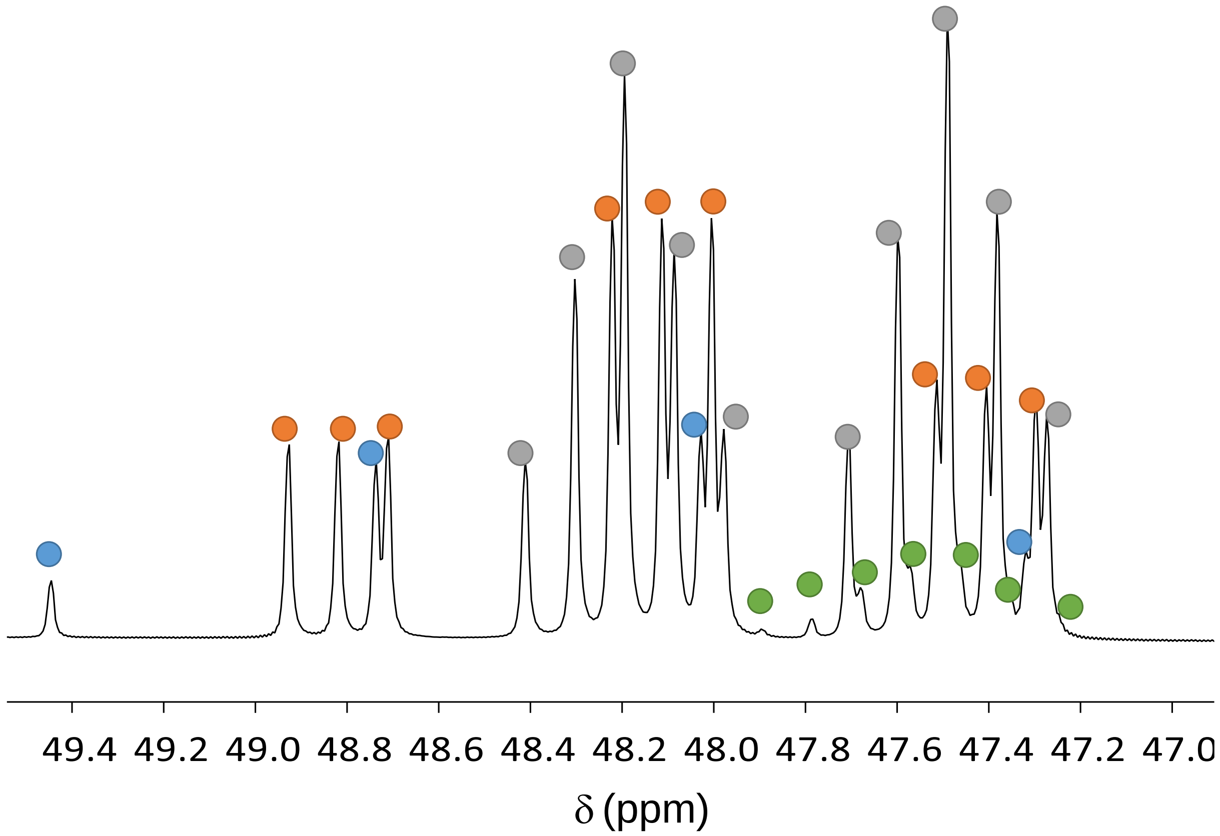

Figure S5. 200 MHz ^{13}C NMR spectrum of methanol area of Scheme 2a in main text. Reaction conditions: 10.0 mmol H^{13}COOH, n_{cat} = 15.9 µmol, m_{D2O} = 2.0 g, T = 50 °C, P(H$_2$)$_{init.}$ = 50 bar. Isotopologues of methanol: Doublet of quintets-CD$_2$H (●), triplet of triplets-CDH$_2$ (●), septet-CD$_3$ (●), quartet-CH$_3$ (●).

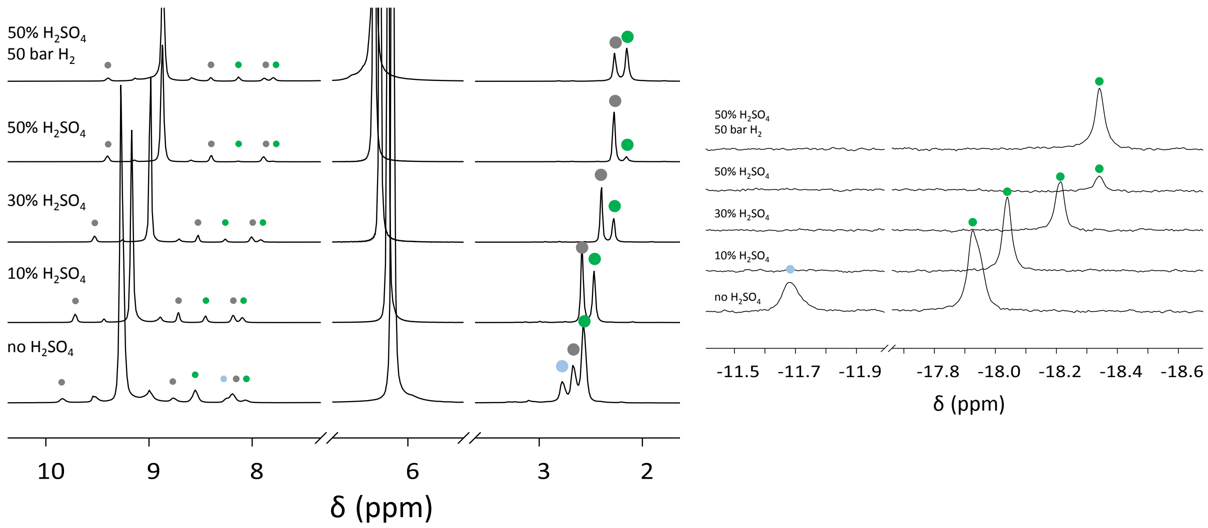

Figure S6. ^{1}H NMR spectra showing the conversion of catalyst **(1)** to hydrides **(1')** and **(1'')** under various reaction conditions. 5 mmol HCOOH, n_{cat} = 15.9 µmol, m_{D2O} = 2.0 g, T = 20 °C, H_2SO_4 concentration is given in mol% relative to HCOOH. Resonances characteristic of **(1)** grey circles, **(1')** blue circles and **(1'')** green circles.

[1] P. J. Hore, *Nuclear Magnetic Resonance*, Oxford University Press, Oxford ; New York, **1995**.

[2] S. Moret, P. J. Dyson, G. Laurenczy, *Dalton Trans.* **2013**, *42*, 4353–4356.