Supporting Information

Active Sites, Kinetics, and Inhibiting Species in the Catalytic Dehydration of Methanol

over MIL-100(Cr)

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S.1. Characterization results
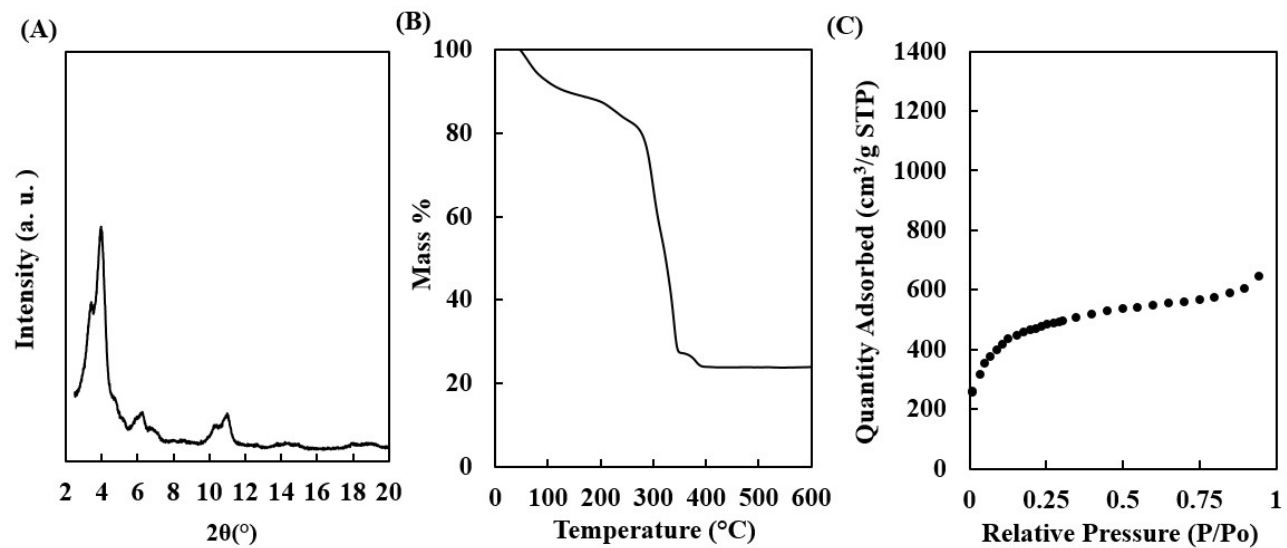
(A)

(B)

(C)

Figure S1. (A) X-ray diffraction pattern (B) TGA profile (C) N_2 physisorption isotherm for MIL-100(Cr)

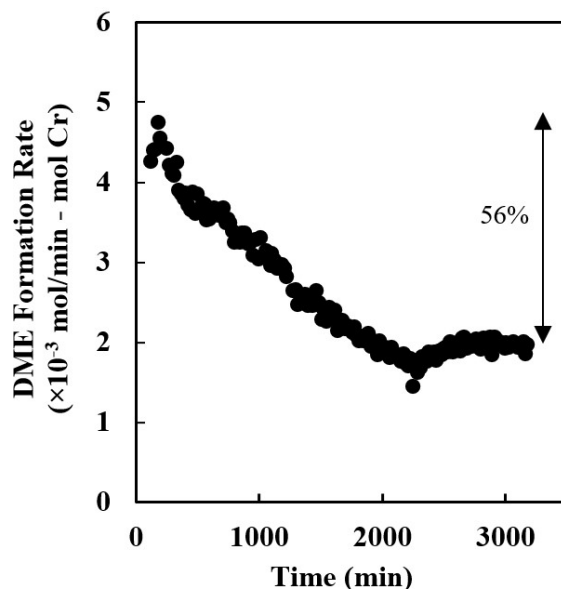**S.2. In-situ titration with 2,6 DTBP over MIL-100(Cr)**

Figure S2. DME formation rate as a function of time during in-situ titration with 2,6 DTBP. Reaction conditions: 493 K, 26 Pa 2,6 DTBP, 0.4 kPa methanol, 0.013 mol methanol (mol Cr)$^{-1}$ s^{-1}.

S.3. Assessment of transport limitations

Table S1. Summary of criteria used for assessing internal and external mass and heat transfer, as well as the formation of hot spots. All values are estimated at a temperature of 493 K and contact time of 5.28 s.

	Criterion	Upper limit	Highest value
Internal mass transfer	Weisz-Prater[1]	$\dfrac{-r_A^{'}\rho_c R^2}{D_{eff}C_{AS}} \ll 1$	0.0018
External mass transfer	Mears[2]	$\dfrac{-r_A^{'}\rho_b Rn}{K_c C_{As}} < 0.15$	1.54×10^{-9}
Internal heat transfer	Anderson[3]	$\dfrac{|\Delta H_R||r_A^{'}|\rho_c R^2 E_a}{k_{eff}T^2 R_g} < 0.75$	1.09×10^{-5}
External heat transfer	Mears[4,5]	$\dfrac{|\Delta H_R||r_A^{'}|\rho_b R E_a}{hT^2 R_g} < 0.15$	1.52×10^{-10}
Hot spot formation	Balakotaiah[6]	$\dfrac{\tau_h}{\tau_g} = \dfrac{E_a}{RT_f}\dfrac{\Delta T_{ad}}{T_f}k(T_f)\tau_h < 0.368$	2.84×10^{-6}
Radial temperature gradient	Mears[2]	$\dfrac{E_a}{RT_f}\dfrac{\Delta T_{ad}}{T_f}\dfrac{k(T_f)D_t^2}{k_{eff}/C_{pv}(T_f)} < 1$	0.0056

Nomenclature:

$r_A^{'}$: observed reaction rate $mol/(s*g)$

ρ_c : catalyst particle density, g/m^3

R : particle radius, m

D_{eff}: effective diffusion coefficient, m^2/s

C_{AS} : reactant concentration at the surface of the pellet mol/m^3

ρ_b : catalyst bulk density, g/m^3

n : reaction order

K_c : external mass transfer coefficient

K_c : external mass transfer coefficient

ΔH_R : heat of reaction J/mol

E_a : activation energy, J/mol

k_{eff} : effective catalyst thermal conductivity, $W/(m*K)$

T : catalyst surface temperature, K

R_g : ideal gas constant, $J/(mol*K)$

h : heat transfer coefficient, $kW/(m^2*K)$

$k(T_f)$: rate constant, s^{-1}

T_f : furnace temperature, K

ΔT_{ad} : adiabatic temperature rise, K
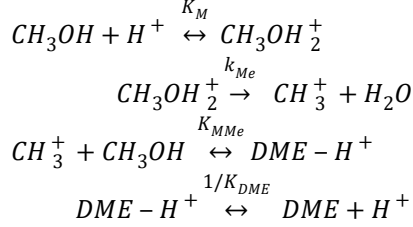
D_t : tube diameter, m

C_{pv} : volumetric specific heat capacity of the gas mixture, $J/(m^3*K)$

τ_g : characteristic heat generation times, s

τ_h : characteristic heat removal times, s

S.4. Derivation of plausible methanol dehydration rate expressions

S.4.1 Kinetically-relevant methoxy formation in the dissociative scheme

$$CH_3OH + H^+ \overset{K_M}{\leftrightarrow} CH_3OH_2^+$$

$$CH_3OH_2^+ \overset{k_{Me}}{\rightarrow} CH_3^+ + H_2O$$

$$CH_3^+ + CH_3OH \overset{K_{MMe}}{\leftrightarrow} DME - H^+$$

$$DME - H^+ \overset{1/K_{DME}}{\leftrightarrow} DME + H^+$$

Assuming the formation of surface methoxy groups through the dehydration of methanol monomers is the rate determining step, and all the other steps are quasi-equilibrated, the rate expression can be written as:

$$\frac{r_{DME}}{[L]} = \frac{k_{Me}[CH_3OH_2^+]}{[L]} \qquad (S1a)$$

where k_{Me} is the rate constant for the dehydration of methanol monomers. The total number of active sites (L) can be expressed as follows:

$$[L] = [H^+] + [CH_3OH_2^+] + [CH_3^+] + [DME - H^+] \qquad (S1b)$$

The concentration of surface intermediates can be expressed as:

$$[CH_3OH_2^+] = K_M[CH_3OH][H^+] \qquad (S1c)$$
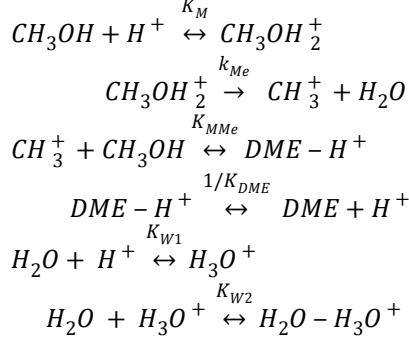
$$[DME - H^+] = K_{DME}[DME][H^+] \qquad (S1d)$$

$$[CH_3^+] = \frac{K_{DME}[DME][H^+]}{K_{MMe}[CH_3OH]} \qquad (S1e)$$

where K_M, K_{MMe} and $1/K_{DME}$ are equilibrium constants for the formation of methanol monomers, the formation of surface methoxies, and the desorption of DME.

Substituting Eq. S1b - e into Eq. S1a gives the resulting rate expression for DME formation:

$$\frac{r_{DME}}{[H^+]} = \frac{k_{Me}K_M[CH_3OH]}{1 + K_M[CH_3OH] + \dfrac{K_{DME}[DME]}{K_{MMe}[CH_3OH]} + K_{DME}[DME]} \qquad (S1f)$$

S.4.2 Kinetically-relevant methoxy formation in the dissociative scheme with water monomers and water dimers as inhibitory species

$$CH_3OH + H^+ \overset{K_M}{\leftrightarrow} CH_3OH_2^+$$

$$CH_3OH_2^+ \overset{k_{Me}}{\rightarrow} CH_3^+ + H_2O$$

$$CH_3^+ + CH_3OH \overset{K_{MMe}}{\leftrightarrow} DME - H^+$$

$$DME - H^+ \overset{1/K_{DME}}{\leftrightarrow} DME + H^+$$

$$H_2O + H^+ \overset{K_{W1}}{\leftrightarrow} H_3O^+$$

$$H_2O + H_3O^+ \overset{K_{W2}}{\leftrightarrow} H_2O - H_3O^+$$

Assuming the formation of surface methoxies through the dehydration of methanol monomers is the rate determining step, and all other steps are quasi-equilibrated, the rate expression can be written as:

$$\frac{r_{DME}}{[L]} = \frac{k_{Me}[CH_3OH_2^+]}{[L]} \qquad (S2a)$$

where k_{Me} is the rate constant for the dehydration of methanol monomers. The total number of active sites (L) can be expressed as following:

$$[L] = [H^+] + [CH_3OH_2^+] + [CH_3^+] + [DME - H^+] + [H_3O^+] + [H_2O - H_3O]^+ \qquad (S2b)$$

Concentrations of surface intermediates can be expressed as:

$$[CH_3OH_2^+] = K_M[CH_3OH][H^+] \qquad (S2c)$$

$$[DME - H^+] = K_{DME}[DME][H^+] \qquad (S2d)$$

$$[CH_3^+] = \frac{K_{DME}[DME][H^+]}{K_{MMe}[CH_3OH]} \qquad (S2e)$$
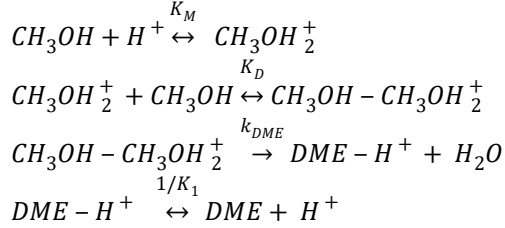
$$[H_3O^+] = K_{W1}[H_2O][H^+] \qquad (S2f)$$

$$[H_2O - H_3O^+] = K_{W1}K_{W2}[H_2O]^2[H^+] \qquad (S2g)$$

where K_M, K_{MMe}, $1/K_{DME}$, K_{W1}, and K_{W2} are the equilibrium constants for the formation of methanol monomers, the formation of surface methoxies, the desorption of DME, and the formation of water monomers and water dimers.

Substituting Eq. S2b - g into Eq. S2a gives the resulting rate expression for DME formation:

$$\frac{r_{DME}}{[H^+]} = \frac{k_{Me} K_M [CH_3OH]}{1 + K_M[CH_3OH] + \dfrac{K_{DME}[DME]}{K_{MMe}[CH_3OH]} + K_{DME}[DME] + K_{W1}[H_2O] + K_{W1}K_{W2}[H_2O]^2} \qquad (S2f)$$

S.4.3 Kinetically-relevant dehydration of methanol dimers in the associative scheme

$$CH_3OH + H^+ \overset{K_M}{\leftrightarrow} CH_3OH_2^+$$

$$CH_3OH_2^+ + CH_3OH \overset{K_D}{\leftrightarrow} CH_3OH - CH_3OH_2^+$$

$$CH_3OH - CH_3OH_2^+ \overset{k_{DME}}{\to} DME - H^+ + H_2O$$

$$DME - H^+ \overset{1/K_1}{\leftrightarrow} DME + H^+$$

Assume the decomposition of methanol dimers is rate determining, and all other steps are quasi-equilibrated, the rate expression can be written as:

$$\frac{r_{DME}}{[L]} = \frac{k_{DME}\left[CH_3OH - CH_3OH_2^+\right]}{[L]} \qquad (S3a)$$

where k_{DME} is the rate constant for decomposition of the methanol dimer. The total number of active sites (L) can be expressed as following:

$$[L] = [H^+] + \left[CH_3OH_2^+\right] + \left[CH_3OH - CH_3OH_2^+\right] + [DME - H^+] \qquad (S3b)$$

Concentrations of surface intermediates can be expressed as:

$$\left[CH_3OH_2^+\right] = K_M[CH_3OH][H^+] \qquad (S3c)$$

$$\left[CH_3OH - CH_3OH_2^+\right] = K_D K_M[CH_3OH]^2[H^+] \qquad (S3d)$$
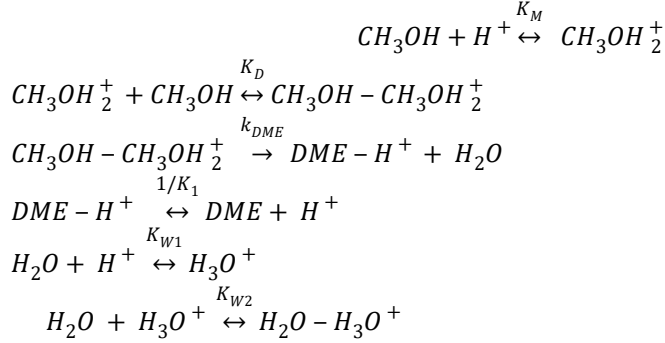
$$[DME - H^+] = K_1[DME][H^+] \qquad (S3e)$$

where K_M, K_D and $1/K_1$ are the equilibrium constants for the formation of methanol monomers, methanol dimers, and the desorption of DME.

The rate expression can be written as:

$$\frac{r_{DME}}{[H^+]} = \frac{k_{DME} K_M K_D [CH_3OH]^2}{1 + K_M[CH_3OH] + K_M K_D[CH_3OH]^2 + K_1[DME]} \qquad (S3f)$$

S.4.4 Kinetically-relevant dehydration of methanol dimers in the associative scheme with water monomers and water dimers as inhibitory species.

$$CH_3OH + H^+ \overset{K_M}{\leftrightarrow} CH_3OH_2^+$$

$$CH_3OH_2^+ + CH_3OH \overset{K_D}{\leftrightarrow} CH_3OH - CH_3OH_2^+$$

$$CH_3OH - CH_3OH_2^+ \overset{k_{DME}}{\rightarrow} DME - H^+ + H_2O$$

$$DME - H^+ \overset{1/K_1}{\leftrightarrow} DME + H^+$$

$$H_2O + H^+ \overset{K_{W1}}{\leftrightarrow} H_3O^+$$

$$H_2O + H_3O^+ \overset{K_{W2}}{\leftrightarrow} H_2O - H_3O^+$$

Assuming the decomposition of methanol dimers is rate determining, and all other steps are quasi-equilibrated, the rate expression can be written as:

$$\frac{r_{DME}}{[L]} = \frac{k_{DME}\left[CH_3OH - CH_3OH_2^+\right]}{[L]} \qquad (S4a)$$

where k_{DME} is the rate constant for decomposition of the methanol dimer. The total number of active sites (L) can be expressed as following:

$$[L] = [H^+] + \left[CH_3OH_2^+\right] + \left[CH_3OH - CH_3OH_2^+\right] + [DME - H^+] + [H_3O]^+ + [H_2O - H_3O]^+$$
$$(S4b)$$

Concentrations of surface intermediates can be expressed as:

$$\left[CH_3OH_2^+\right] = K_M[CH_3OH][H^+] \qquad\qquad (S4c)$$

$$\left[CH_3OH - CH_3OH_2^+\right] = K_D K_M[CH_3OH]^2[H^+] \qquad\qquad (S4d)$$

$$[DME - H^+] = K_1[DME][H^+] \qquad\qquad (S4e)$$

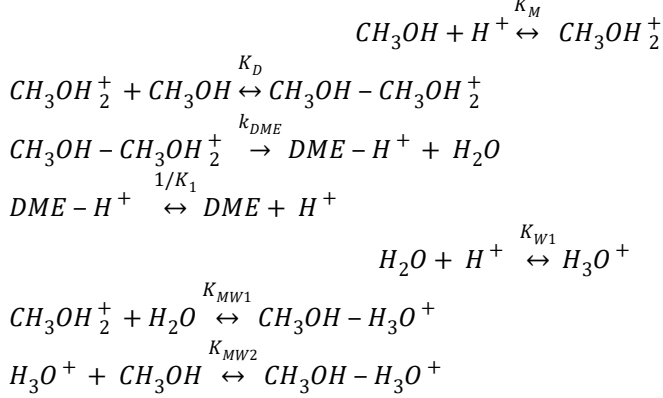$$\left[H_3O^+\right] = K_{W1}[H_2O][H^+] \qquad\qquad (S4f)$$

$$\left[H_2O - H_3O^+\right] = K_{W1}K_{W2}[H_2O]^2[H^+] \qquad\qquad (S4g)$$

where K_M, K_D, $1/K_1$, K_{W1}, and K_{W2} are the equilibrium constants for the formation of methanol monomers, methanol dimers, the desorption of DME, the formation of water monomers, and the formation of water dimers.

The rate expression can be written as:

$$\frac{r_{DME}}{[H^+]} = \frac{k_{DME}K_M K_D[CH_3OH]^2}{1 + K_M[CH_3OH] + K_M K_D[CH_3OH]^2 + K_1[DME] + K_{W1}[H_2O] + K_{W1}K_{W2}[H_2O]^2} \quad (S4f)$$

S.4.5 Kinetically-relevant dehydration of methanol dimers with methanol monomers, methanol dimers and methanol-water dimers as MASIs.

$$CH_3OH + H^+ \overset{K_M}{\leftrightarrow} CH_3OH_2^+$$

$$CH_3OH_2^+ + CH_3OH \overset{K_D}{\leftrightarrow} CH_3OH - CH_3OH_2^+$$

$$CH_3OH - CH_3OH_2^+ \overset{k_{DME}}{\rightarrow} DME - H^+ + H_2O$$

$$DME - H^+ \overset{1/K_1}{\leftrightarrow} DME + H^+$$

$$H_2O + H^+ \overset{K_{W1}}{\leftrightarrow} H_3O^+$$

$$CH_3OH_2^+ + H_2O \overset{K_{MW1}}{\leftrightarrow} CH_3OH - H_3O^+$$

$$H_3O^+ + CH_3OH \overset{K_{MW2}}{\leftrightarrow} CH_3OH - H_3O^+$$

Assuming the decomposition of methanol dimers is rate determining, including water monomers and water-methanol dimers as possible inhibitory species, and assuming all other steps are quasi-equilibrated, the rate expression can be written as:

$$\frac{r_{DME}}{[L]} = \frac{k_{DME}\left[CH_3OH - CH_3OH_2^+\right]}{[L]} \quad (S5a)$$

where k_{DME} is the rate constant for the decomposition of a methanol dimer to DME.

$$[L]$$
$$= [H^+] + \left[CH_3OH_2^+\right] + \left[CH_3OH - CH_3OH_2^+\right] + \left[DME - H^+\right] + \left[CH_3OH - H_3O^+\right] +$$
$$(S5b)$$

Concentrations of surface intermediates can be expressed as:

$$\left[CH_3OH_2^+\right] = K_M[CH_3OH][H^+] \quad (S5c)$$

$$\left[CH_3OH - CH_3OH_2^+\right] = K_D K_M[CH_3OH]^2[H^+] \quad (S5d)$$

$$\left[DME - H^+\right] = K_1[DME][H^+] \quad (S5e)$$

$$\left[H_3O^+\right] = K_{W1}[H_2O][H^+] \quad (S5f)$$

$$\left[CH_3OH - H_3O^+\right] = (K_{MW2}K_{W1} + K_{MW1}K_M)[CH_3OH][H_2O][H^+] \quad (S5g)$$

The rate expression can be written as:

$$\frac{r_{DME}}{[H^+]} = \frac{k_{DME}\,K_M\,K_D[CH_3OH]^2}{1 + K_M[CH_3OH] + K_M\,K_D[CH_3OH]^2 + K_{W1}[H_2O] + K^{'}[CH_3OH][H_2O] + K_1[DME])}$$

$$\text{where } K^{'} = (K_{MW2}K_{W1} + K_{MW1}K_M) \tag{S5h}$$

Assuming that methanol monomers, methanol dimers, and water-methanol dimers are abundant intermediates, Eq. S5h can be simplified to:

$$\frac{r_{DME}}{[H^+]} = \frac{k_{DME}K_D K_M[CH_3OH]^2}{K_M[CH_3OH] + K_D K_M[CH_3OH]^2 + K^{'}[CH_3OH][H_2O]} \tag{S5i}$$

S.5. Dependence of DME formation rate on DME and water partial pressure
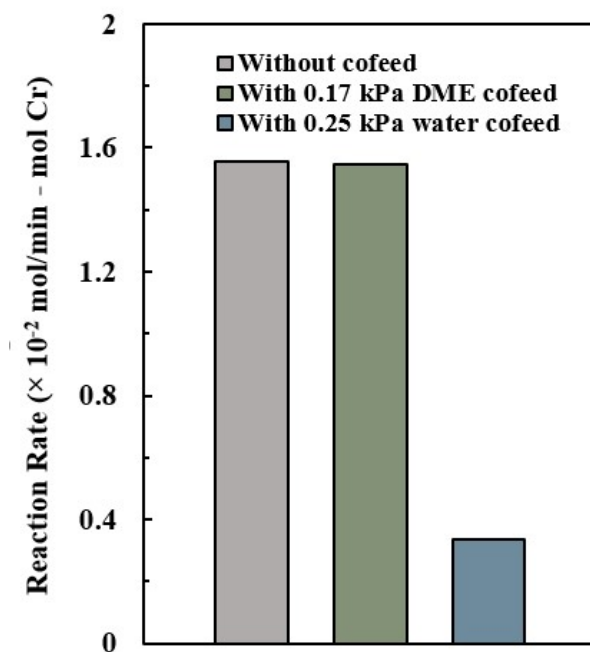
Figure S3. Reaction rates measured at 493 K with 1) 0.4 kPa methanol, 2) 0.4 kPa methanol and 0.17 kPa DME cofeed, and 3) 0.4 kPa methanol and 0.25 kPa water cofeed. 7.3 - 7.6 × 10^{-4} mol methanol (mol Cr)$^{-1}$ s^{-1}.

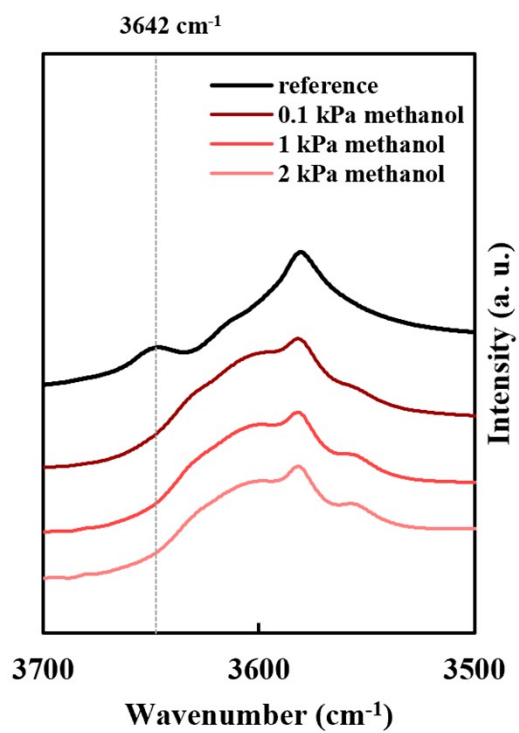**S.6. Evolution of Brønsted acid site intensity after flowing 0.1 – 2 kPa methanol**

Figure S4. In-situ infrared spectra in the presence of 0.1 - 2 kPa methanol at 493 K compared to the reference spectrum collected prior to the introduction of methanol.
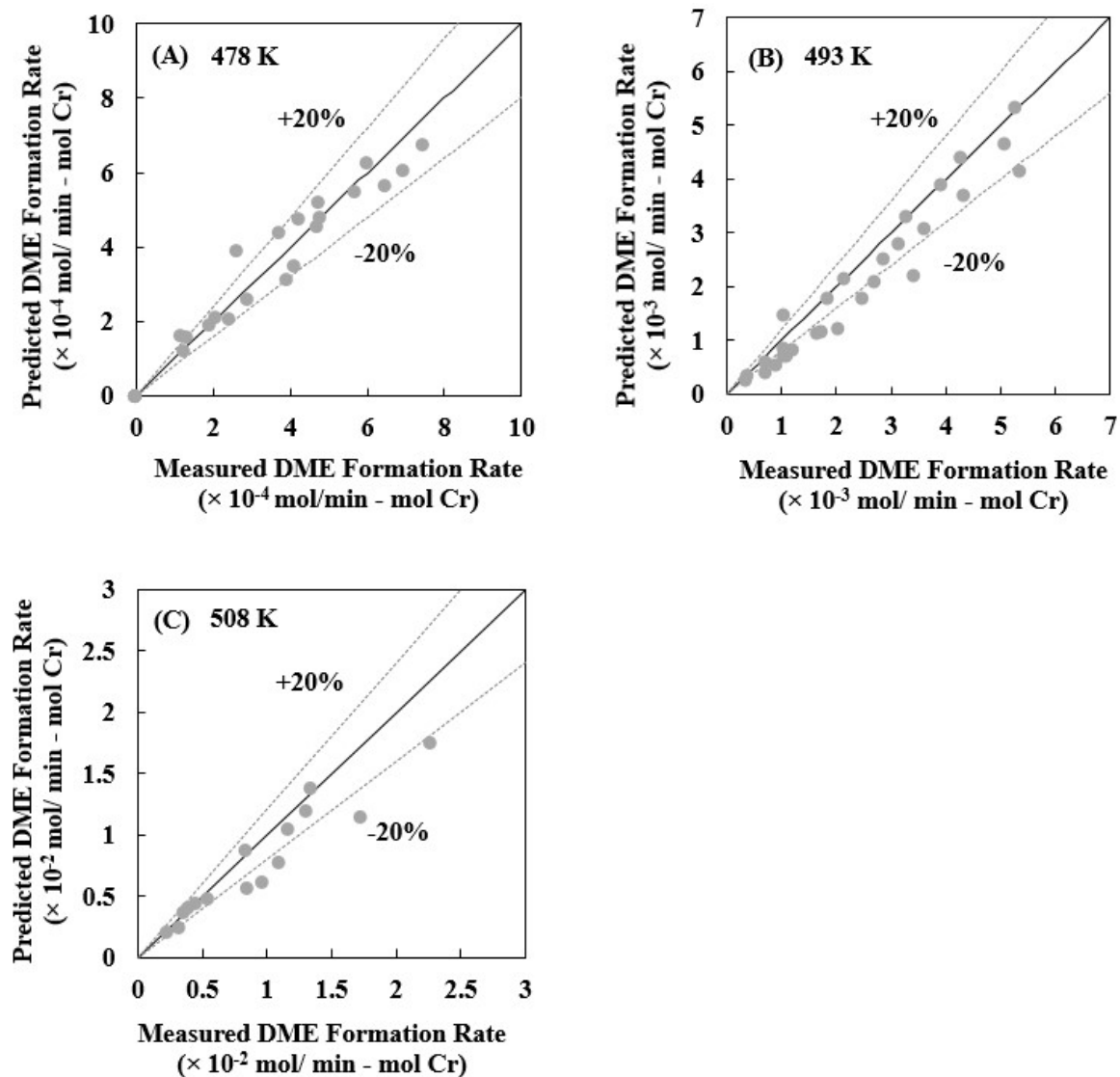
S.7. Parity Plots

Figure S5. Parity plots comparing kinetic model predictions against measured DME formation rates at (A) 478 K, (B) 493 K, and (C) 508 K. Dashed lines represent ± 20% deviation.

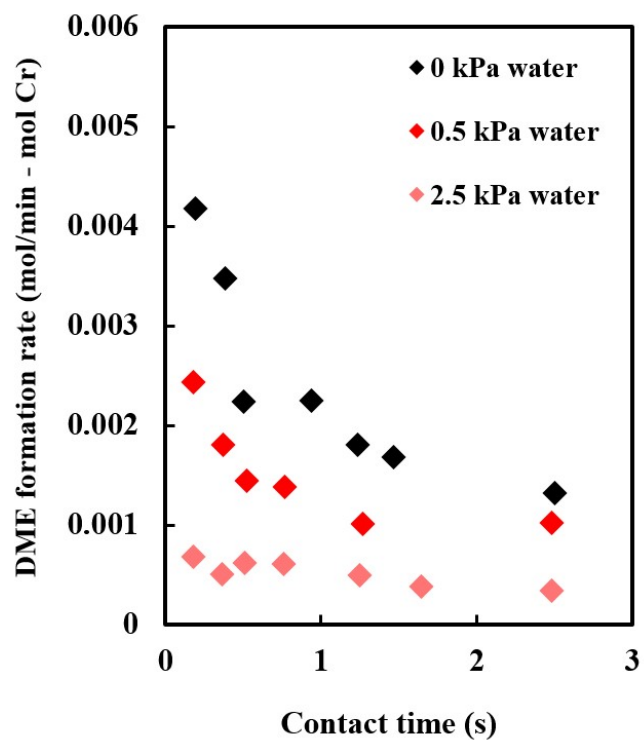## S.8. Dependence of DME formation rates on contact time

Figure S6. DME formation rates at 0.4 kPa methanol partial pressure and 0, 0.5, and 2.5 kPa water co-feed at 493 K. 5.7×10^{-3} - 1.4×10^{-1} mol methanol (mol Cr)$^{-1}$ s^{-1}.

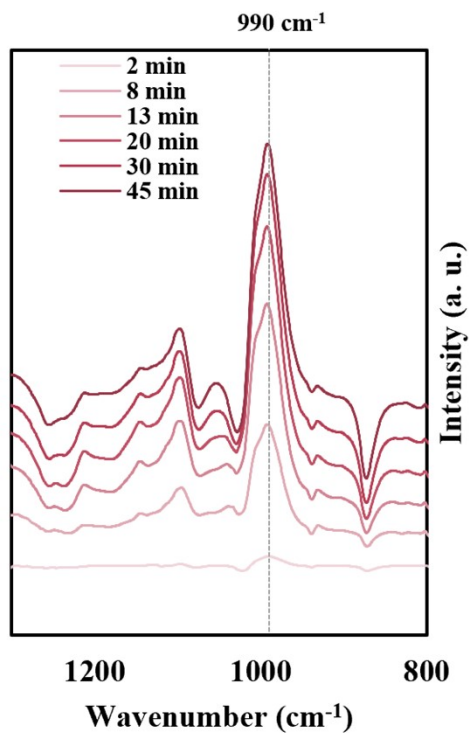**S.9. Evolution of methanol monomer coverage after dosing 1 μL methanol**

Figure S7. Accumulation of methanol monomers (C-O stretch of hydrogen-bonded methanol at 990 cm^{-1})[7] on the surface as a function of time.

References

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4 N. Wakao and T. Funazkri, *Chem. Eng. Sci.*, 1978, **33**, 1375–1384.
5 D. E. Mears, *Ind. Eng. Chem. Process Des. Dev.*, 2002, **10**, 541–547.
6 V. Balakotaiah, D. Kodra and D. Nguyen, *Chem. Eng. Sci.*, 1995, **50**, 1149–1171.
7 S. K. Matam, S. A. F. Nastase, A. J. Logsdail and C. R. A. Catlow, *Chem. Sci.* 2020, **11**, 6805-6814.