The intrinsic effect of cofeeding water on the formation of active/deactivating species in the methanol-to-hydrocarbons reaction on a ZSM-5 zeolite

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This document presents additional experimental data to support our results as well as information on the models used.

Additional Experimental Data

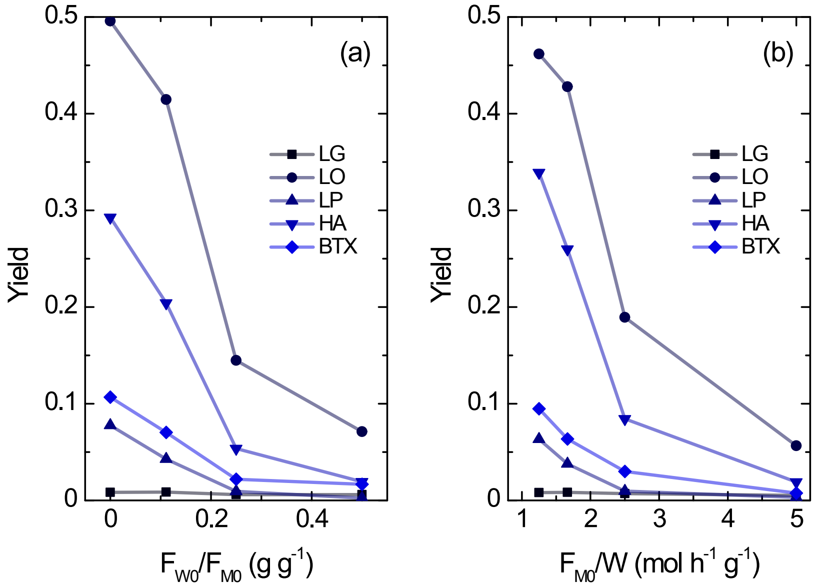

Figure S1. Effect of changing the (a) water-to-methanol (F_{W0}/F_{M0}) ratio and (b) space velocity (F_{M0}/W) on the product yields for the MTH reaction. Conditions for (a): T = 400 ºC, P_{M0} = 0.28, W/F_{M0} = 1 g h mol^{-1}, F_W/F_{M0} = 0-0.5. Conditions for (b): T = 400 ºC, P_{M0} = 1.57 bar, W/F_{M0} = 0.2-1.2 g h mol^{-1}, F_W/F_{M0} = 0.

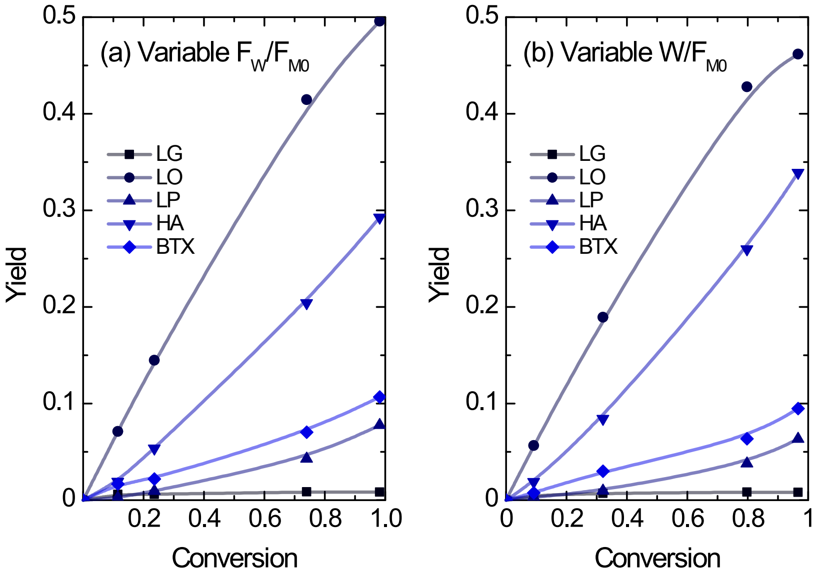

Figure S2. Effect of changing the (a) water-to-methanol (F_W/F_{M0}) ratio and (b) space time (W/F_{M0}) on the product yields against conversion for the MTH reaction. Conditions for (a): T = 400 ºC, P_{M0} = 0.28, W/F_{M0} = 1 g h mol^{-1}, F_W/F_{M0} = 0-0.5. Conditions for (b): T = 400 ºC, P_{M0} = 1.57 bar, W/F_{M0} = 0.2-1.2 g h mol^{-1}, F_W/F_{M0} = 0.

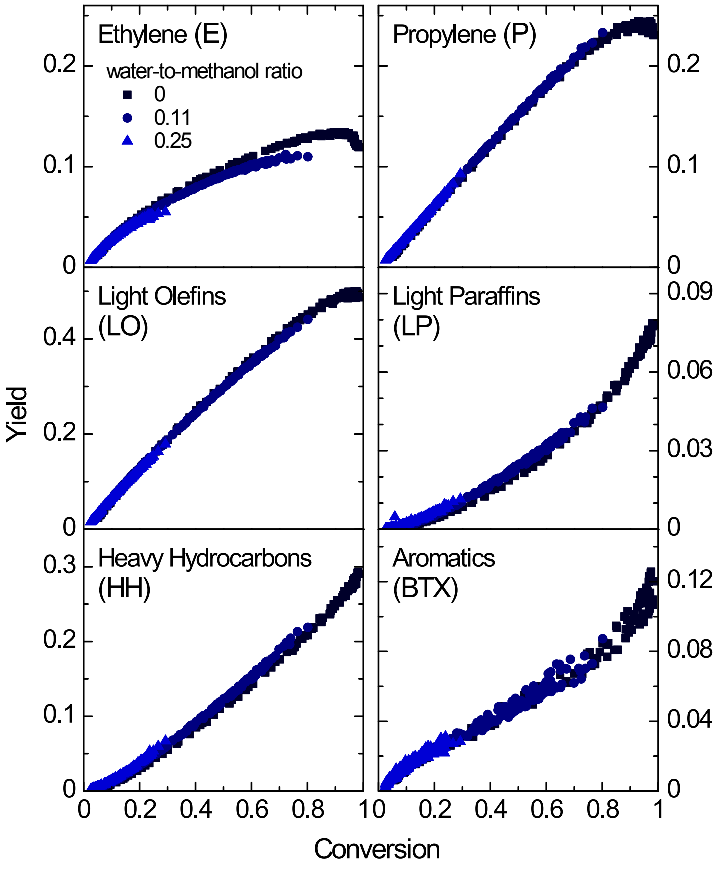

Figure S3. Product distribution for the experiments with different water-to-methanol ratios in the feed. Conditions: T = 400 ºC, P_{M0} = 0.28, W/F_{M0} = 1 g h mol^{-1}, F_W/F_{M0} = 0-0.5.

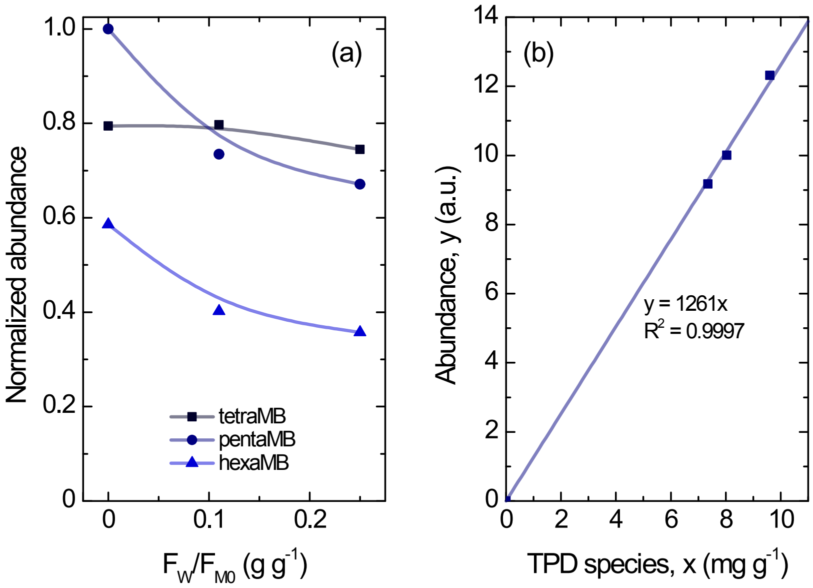

Figure S4. (a) Abundance of soluble retained species for different water-to-methanol ratios and (b) correlation between the amounts of species obtained during TPD measurements and the sum of chromatographic intensities of the identified retained species.

The chromatographic intensities of the identified retained species can be compared between one sample and the other because we performed an identical rigorous extraction procedure for all the samples. For the extraction procedure, we used the same amount of each sample of spent catalyst and the same amounts of HF and dichloromethane, so that we obtained an extract with concentration of retained species proportional to the amount of retained species in each sample of spent catalyst.

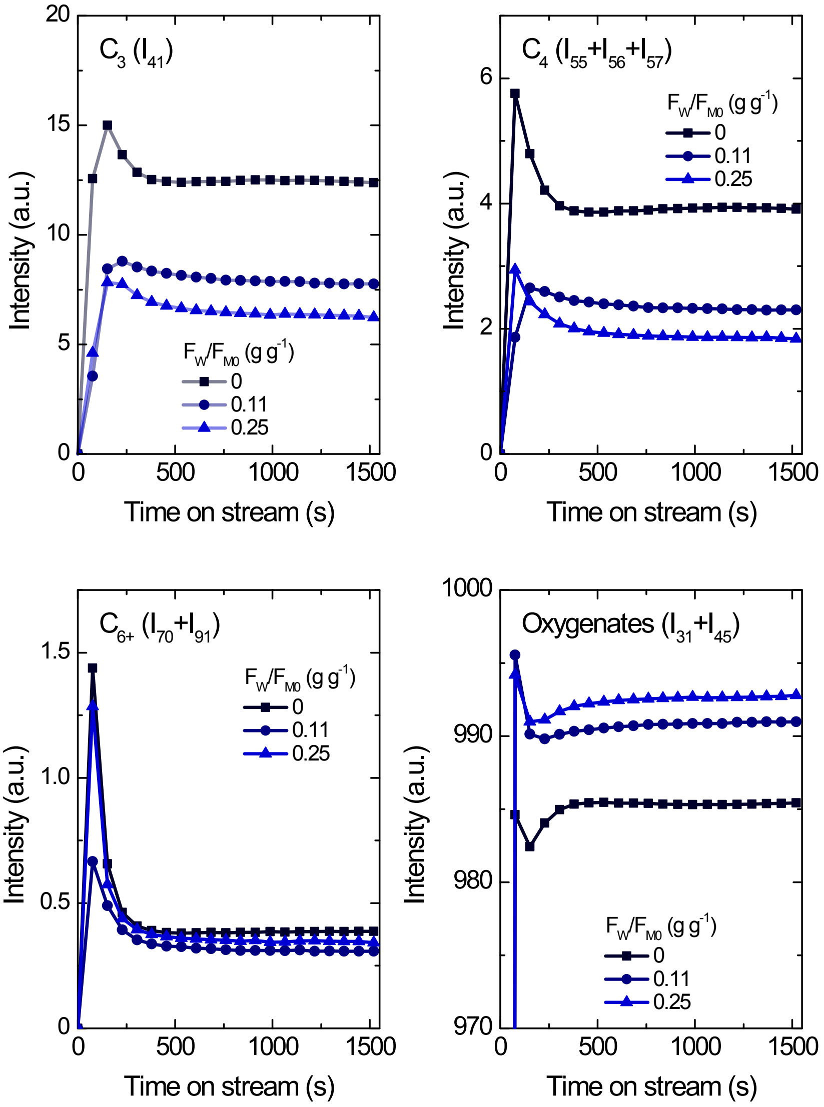

Figure S5. Evolution with time on stream of different MS signals during the MTH reaction in the UV-vis cell reactor with different water-to-methanol ratios in the feed.

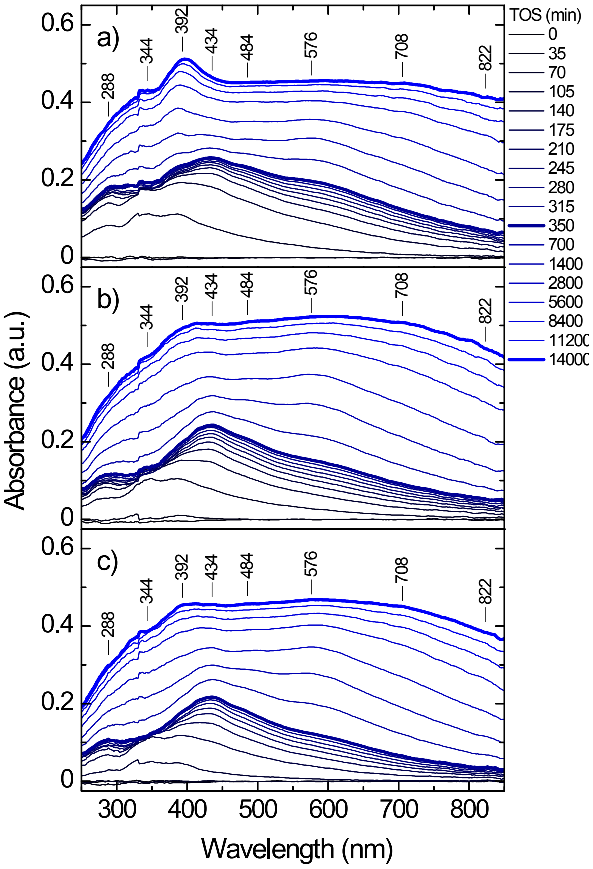

Figure S6. Evolution with time on stream of UV-vis spectra during the MTH reaction with water-to-methanol ratios of (a) 0, (b) 0.5 and (c) 1. Conditions: T = 400 ºC, P_{M0} = 0.014 bar, W/F_{M0} = 1 g h mol^{-1}.

Fitting models

We fitted the experimental dataset in the fixed-bed reactor by using simple models with the purpose of obtaining deactivation and water adsorption coefficients that describe our observations. For the fixed-bed reactor, we consider a plug-flow model and the mass balance for the conversion of oxygenates (*X*):

$$(-r) = \frac{dX}{d\left({}^{W}\!/F_{M0}\right)} \tag{S1}$$

Where *r* is the reaction rate of oxygenates and W/F_{M0} is the space time. For simplicity, we assumed a general autocatalytic reaction in which oxygenates (M) form hydrocarbons (H) and oxygenates and hydrocarbons form other hydrocarbons (autocatalytic reaction):

$$\mathrm{M} \overset{k_1'}{\rightarrow} \mathrm{H} \tag{S2}$$

$$\mathrm{M} + \mathrm{H} \overset{k_2'}{\rightarrow} \mathrm{H} + \mathrm{H} \tag{S3}$$

Where k'_1 is the kinetic coefficient of Equation S2 and k'_2 is the kinetic coefficient of Equation S3. Considering that 1) the co-fed water is an unreactive species that competes with reactants and products for the adsorption on acid sites, which attenuates the reaction rate [1], and 2) the concentration balance as $C_{M0} = C_M + C_H$ and $C_M = C_{M0}(1 - X)$, the reaction rate at "zero" time on stream for oxygenates is considered as an elemental rate with respect to the reactants and with a dividing term to quantify the water adsorption:

$$(-r) = \frac{k_1^{'}C_M + k_2^{'}C_MC_H}{1 + K_W^{'}C_W} = \frac{(1 - X)(k_1 + k_2X)}{1 + K_WR_W} \tag{S4}$$

Where C_M is the concentration of oxygenates, C_H is the concentration of hydrocarbons, C_W is the concentration of cofed water, K'_W is the adsorption constant of cofed water, k_1 and k_2 are the apparent kinetic coefficients of Equations S2 and S3, K_W is the apparent adsorption constant of cofed water and R_W is the water-to-methanol ratio in the feed. By substituting Equation S4 in Equation S1 and integrating with the limits of integration ($W/F_{M0} = 0$, $X = 0$) and ($W/F_{M0} = W/F_{M0}$, $X = X$), we obtained the following expression for the conversion:

$$X = \frac{k_1\left(e^{\frac{(k_1 + k_2)\left(W/F_{M0}\right)}{1 + K_WR_W}} - 1\right)}{k_2 + k_1e^{\frac{(k_1 + k_2)\left(W/F_{M0}\right)}{1 + K_WR_W}}} \tag{S5}$$

For the deactivation, we introduced a multiplying activity term (*a*) in Equation S4 derived from the typical expression of the deactivation kinetic assuming a zeroth-order dependency on the concentration of oxygenates and hydrocarbons and on activity and introducing a term (k_W) that accounts for the effect of water on attenuating catalyst deactivation [2,3]:

$$-\frac{da}{dt} = \frac{k_d}{1 + k_WR_W{}^n} \tag{S6}$$

Where t is the time on stream, k_d is the deactivation coefficient and k_W is the attenuation of the catalyst activity by the adsorption of cofed water. By solving Equation S6 with the limits of integration ($a = 1$, $t = 0$) and ($a = a$, $t = t$), substituting in Equation S4 and subsequently in Equation S1, and integrating with the limits of integration ($W/F_{M0} = 0$, $X = 0$) and ($W/F_{M0} = W/F_{M0}$, $X = X$), we obtained this fitting equation:

$$X = \frac{k_1\left(e^{\frac{(k_1+k_2)\left(W/F_{M0}\right)}{1+K_W R_W}\left(1-\frac{k_d t}{1+k_W R_W{}^n}\right)}-1\right)}{k_2+k_1 e^{\frac{(k_1+k_2)\left(W/F_{M0}\right)}{1+K_W R_W}\left(1-\frac{k_d t}{1+k_W R_W{}^n}\right)}} \tag{S7}$$

Alternatively, we consider a model in which a term for formed water is added, and therefore the reaction rate of oxygenates (*r*) is:

$$(-r) = \frac{(1-X)\left(k_1+k_2X\right)}{1+K_W R_W+K_{FW}Y_W} \tag{S8}$$

Where K_{FW} is the coefficient accounting for the formed water and assumed to affect the reaction rate due to its adsorption on acid sites, and Y_W is the formed water yield depending on the conversion of oxygenates (*X*). Figure S7 shows the relationship between Y_W and *X*, from which we obtained that $Y_W = 0.5235X + 0.4717$. Thus, Equation S8 becomes:

$$(-r) = \frac{(1-X)\left(k_1+k_2X\right)}{1+K_W R_W+K_{FW}(0.5235X+0.4717)} \tag{S9}$$

Equation S9 considers the effect of formed water on the attenuation of the reaction rate as solely function of *X*. The combination of Equations S1 and S9 leads to a difficult analytical solution. Therefore, we developed a numerical routine calculation using the software MatLab R2019b and solved separately the following equations using the experimental data:

$$\frac{dX}{d\left(W/F_{M0}\right)} = \frac{(1-X)\left(k_1+k_2X\right)}{1+K_W R_W} \tag{S10}$$

$$\frac{dX}{d\left(W/F_{M0}\right)} = \frac{(1-X)\left(k_1+k_2X\right)}{1+K_W R_W+K_{FW}(0.5235X+0.4717)} \tag{S11}$$

Being Equation S10 model A (only considers cofed water on the attenuation factor) and Equation S11 model B (considers both the cofed and formed water on the attenuation factor). Figure S8 shows the parity plots of *X* using both models and Table S1 lists the calculated fitting parameters. As seen, both models satisfactorily fit the experimental data with normalized errors of 0.02711 and 0.02531 for model A and B, respectively. The marginal difference between the normalized errors led us to choose model A, requiring the calculation of less fitting parameters. Thus, we assume that the effect of formed water is intrinsic in the calculated kinetic coefficients for model A.

Table S1. Fitting parameters for model A and B.

Parameter	**Model A (Equation S10)**	**Model B (Equation S11)**
k_1 (h^{-1})	0.05874	0.04276

k_2 (h^{-1})	10.85	13.60
K_W (mol^{-1})	3.449	4.114
K_{FW} (mol^{-1})	-	0.1699
Normalized error	0.02711	0.02531

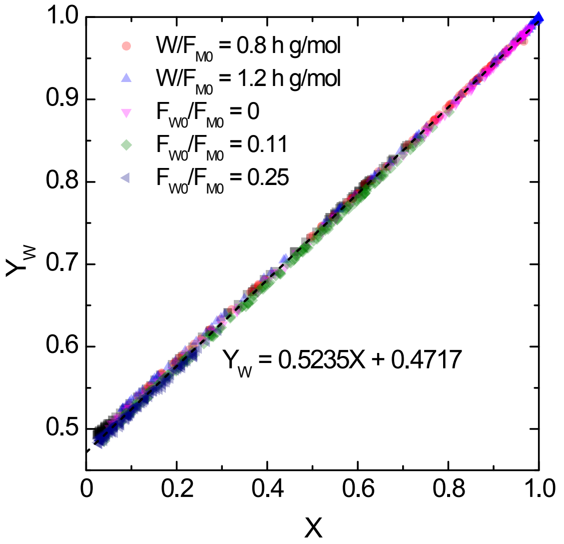

Figure S7. Relationship between the formed water yield (Y_W) and the conversion of oxygenates (X) for various experiments.

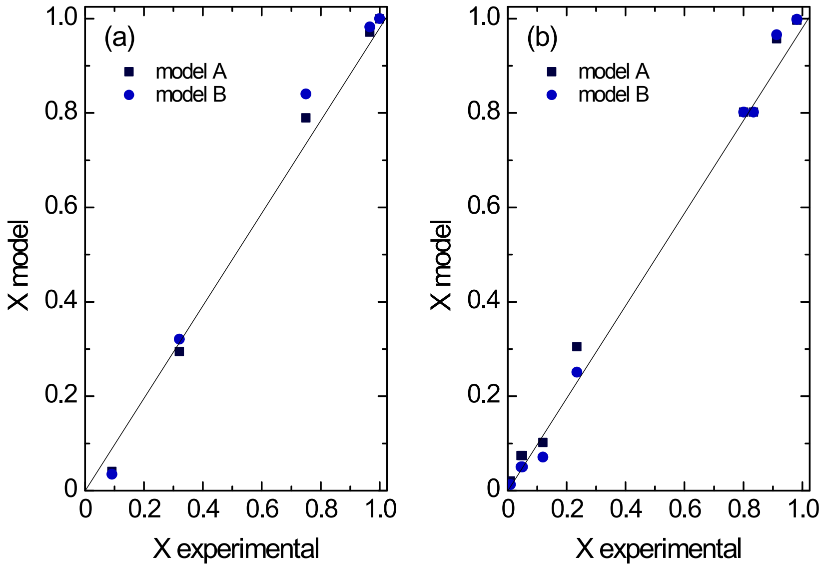

Figure S8. Parity plots for the fitting of models for the experimental data of the scenarios of (a) changing space time and (b) water-to-methanol ratios in the feed.

References

1 A. G. Gayubo, A. T. Aguayo, M. Castilla, A. L. Morán and J. Bilbao, *Chem. Eng. Commun.*, 2004, **191**, 944–967.

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