Electronic Supplementary Information for

Methane Functionalization in Water with Micellar Catalysis

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Materials and Methods

General

The catalyst Tp$^{(CF3)2,Br}$Ag(thf) was prepared following previously described methods.[1] Gaseous alkanes were obtained from Air Liquide and used as received. Ethyl diazoacetate and the surfactants were also purchased from Sigma-Aldrich and used as received. Calibration curves were built using commercial or synthetically prepared products, as previously reported for gaseous alkanes.[1] The water employed in the experiments was Milli-Q quality. Experiments under pressure were run in a PARR Micro Bench Top Reactor with inside Teflon beaker. NMR experiments were run in an Agilent Technologies 400 MHz and 500 MHz spectrometer, and GC in a Bruker CP3900 model and Bruker 450 model.

Experimental Procedures

1) Determination of methane uptake by surfactant solutions in water.

20 mL of water were placed inside a 100 mL high pressure reactor. An exact amount of the surfactant (sodium dodecyl sulfate, SDS; Triton X-100; dodecyltrimethylammonium chloride. DTAC; TPGS-750-M; potassium perfluorooctanesufonate, PFOS) was dissolved and the reactor was closed and connected to a methane tank. The reactor was filled at 160 atm, the valve was closed, and the solution was stirred for 15 min. The decay of the pressure was annotated. The amount of dissolved methane was calculated assuming that such decay corresponds to the amount incorporated in the liquid phase. Both the ideal and real gas equations were employed to convert pressure decay into methane moles, the difference being not significant toward the purpose of this work, thus ideal gas equation was employed. The available gas volume inside the reactor is 47 mL and the volume of the solution is 20 mL.

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[1] R. Gava, A. Olmos, B. Noverges, T. Varea, E. Álvarez, T. R. Belderrain, A. Caballero, G. Asensio and P. J. Pérez, *ACS Catal.*, 2015, **5**, 3726–3730.

Table S1. *Methane uptake (mM) of surfactant water solutions at 160 atm of CH_4 and room temperature.*

mM surfactant	SDS	DTAC	Triton X-100	TPGS-750-M	PFOS
0	0	0	0	0	0
40	520	491	1309	1145	491
100	710	654	1636	1309	818
200	755	1145	1963	1472	818
300	865	1145	2127		720
500	755	982	1800		556

2) Surfactant screening catalytic experiments for methane functionalization reaction.

The experiments were carried out in a 100 mL high pressure reactor in which the catalyst (0.016 mmol) and diazocompound (0.5 mmol) were placed. Solutions of SDS, DTAC, Triton X-100, TPGS-750-M and PFOS were prepared using 20 mL of water at 345 mM concentrations. The reactor was charged with methane at 160 bar and stirred for 14 h, before depressurization of the vessel. The reaction mixture was transferred to a volumetric flask and diluted to an exact volume with methanol. All insertion products and ethyl glycolate are commercially available and they were quantified using calibration curves by GC analysis in a gas chromatograph Bruker CP3900 (column HP-Innowax 30 m x 0,250 mm x 0.25 μm. Tiny 250 °C, Tdet 250 °C, ϕN_2 1.0 mL/min. Program: 50 °C x 1 min 10 °C/min 250 °C x 5 min. Examples of chromatograms and calibration curves displayed for the analysis of the reaction crudes catalyzed by $Tp^{(CF3)2,Br}Ag(thf)$ are shown in Figures S1 and S2.

Table S2. *Screening of surfactants in methane catalytic functionalization*

Surfactant	Ethyl Propionate (%)	Ethyl Glycolate (%)
Triton X-100	0	0
DTAC*	0	0
TPGS-750-M	2	-
SDS	10	38
PFOS	14	34

*Multiple products observed, no EDA observed.

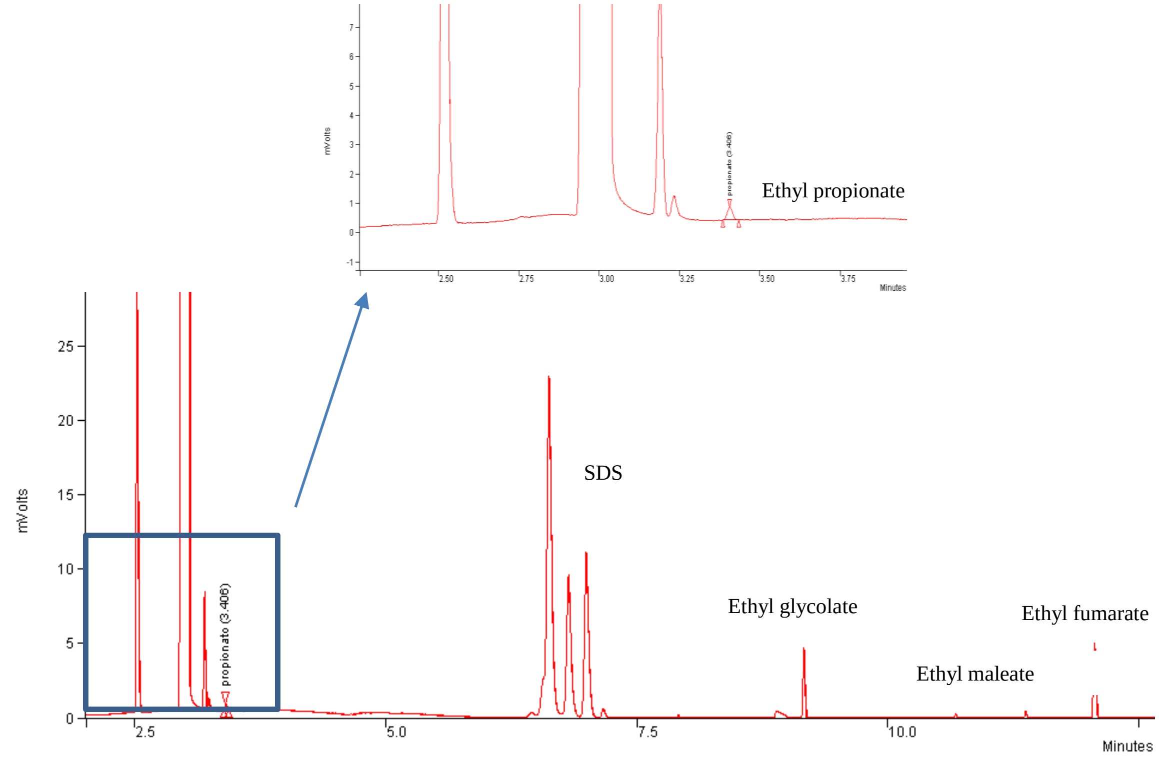

Figure S1. *GC trace of the experiment of methane functionalization with SDS*

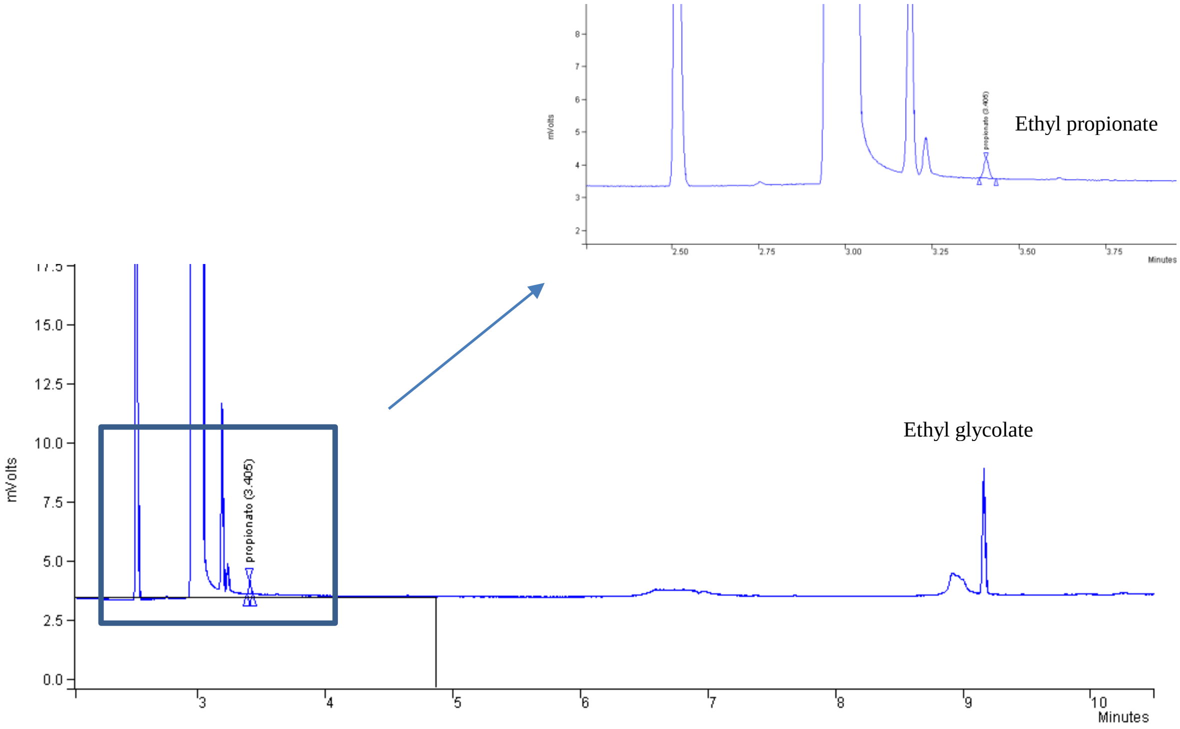

Figure S2. *GC trace of the experiment of methane functionalization with PFOS*

3) Ethane, propane and butane functionalization in the water/SDS reaction medium.

The procedure described with methane was repeated with these alkanes, employing lower pressures (35 atm for ethane, 8 atm for propane and 2 atm for butane). After 14 h, depressurization of the vessel was performed by passing the gases throughout two consecutively connected traps cooled with liquid nitrogen. Additionally, the resulting, already depressurized reaction mixture was extracted with diethyl ether (3x10 mL). The organic phase and the collected material in the traps were mixed and diluted with more diethyl ether to an exact volume in volumetric flask. The final solution was analysed by GC using calibration curves, using in this case a CP-Sil 5CB 50 m 50 m x 0,32 mm x 1,2 µm. T_{iny} 200 $_{o}$C, T_{det} 250 $_{o}$C, ϕN_2 2.0 mL/min; program: 40 °C x 0,1 min 15 °C/min 200 °C x 7 min 20 °C/min 270 °C x 3,5 min.

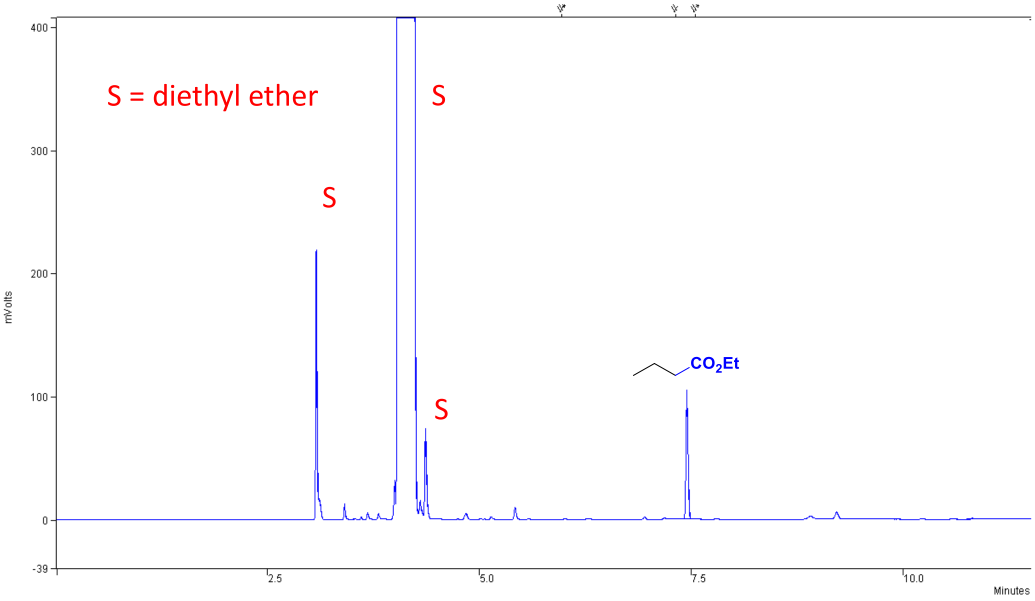

Figure S3. *GC trace of the experiment of ethane functionalization*

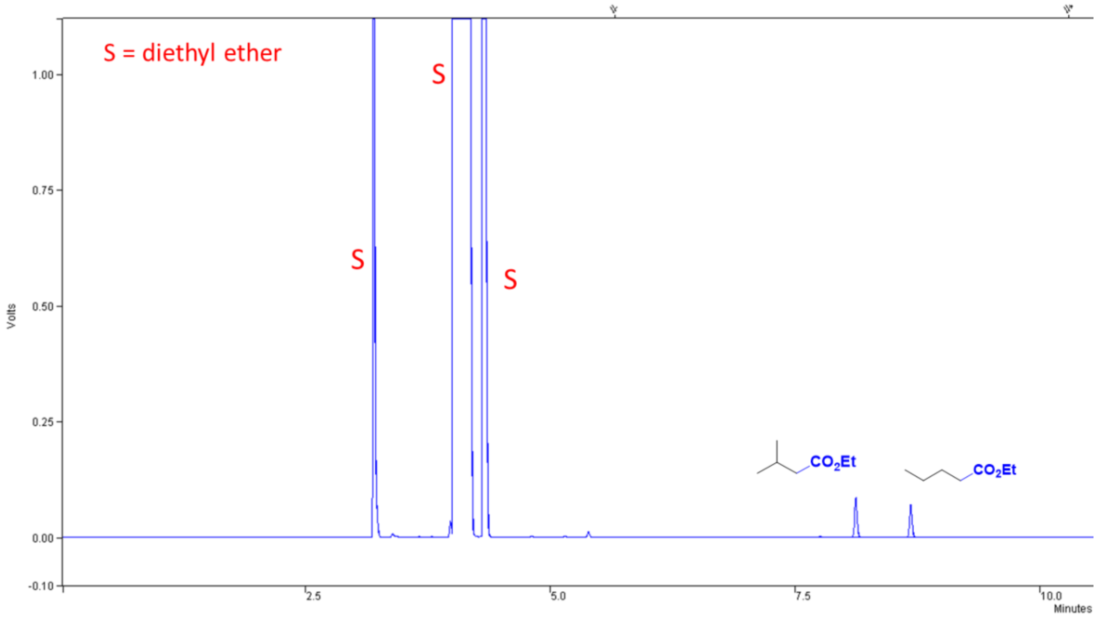

Figure S4. *GC trace of the experiment of propane functionalization*

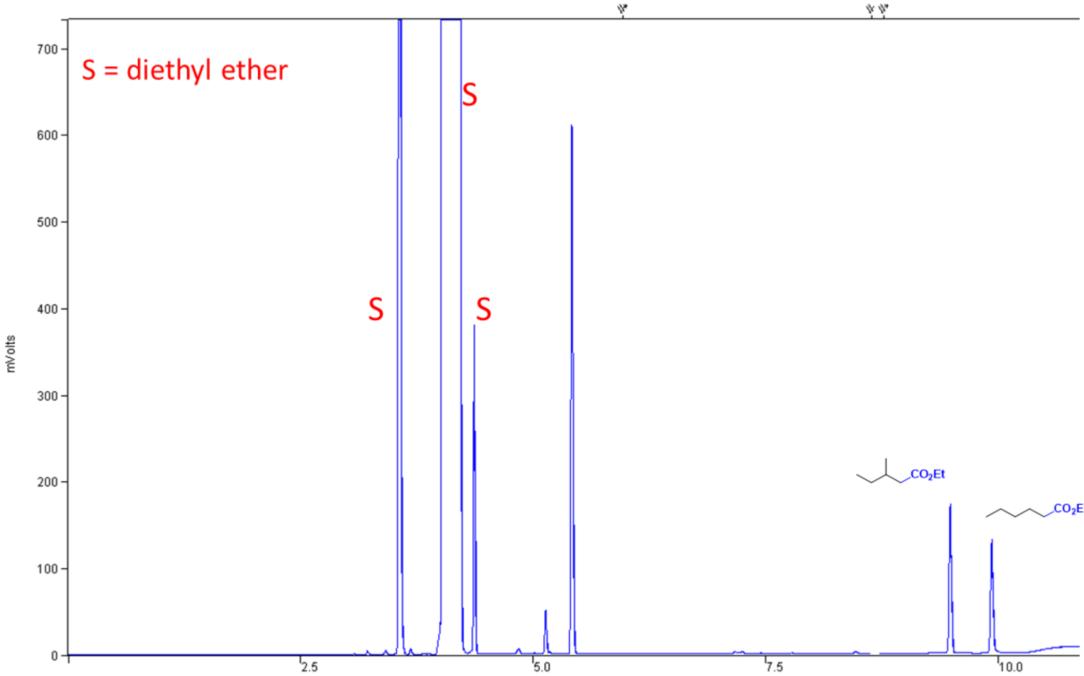

Figure S5. *GC trace of the experiment of butane functionalization*

4) Methane catalytic functionalization in D_2O at room temperature using SDS as surfactant.

Following the previous procedure, deuterium oxide was employed as the solvent to directly evaluate the composition of the reaction mixture. Figure S6 contain the region of the spectra where the representative resonances of the different products appear for the reactions of ethane or methane as the alkane. The identification of those resonances was performed with the aid of 2D-NMR experiments (Fig S7).

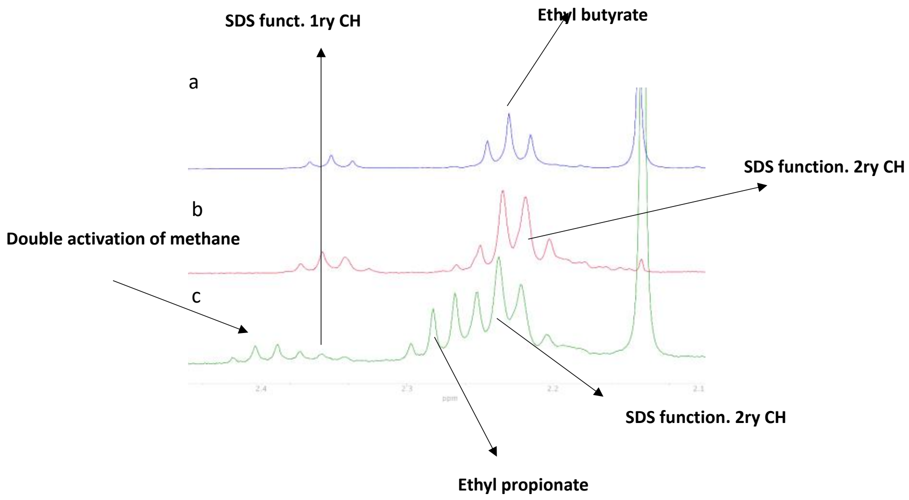

Figure S6. *^{1}H NMR (400 MHz, D_2O) spectra of the reactions of EDA in water with the silver catalysts and (a) ethane/SDS; (b) only SDS; (c) methane/SDS.*

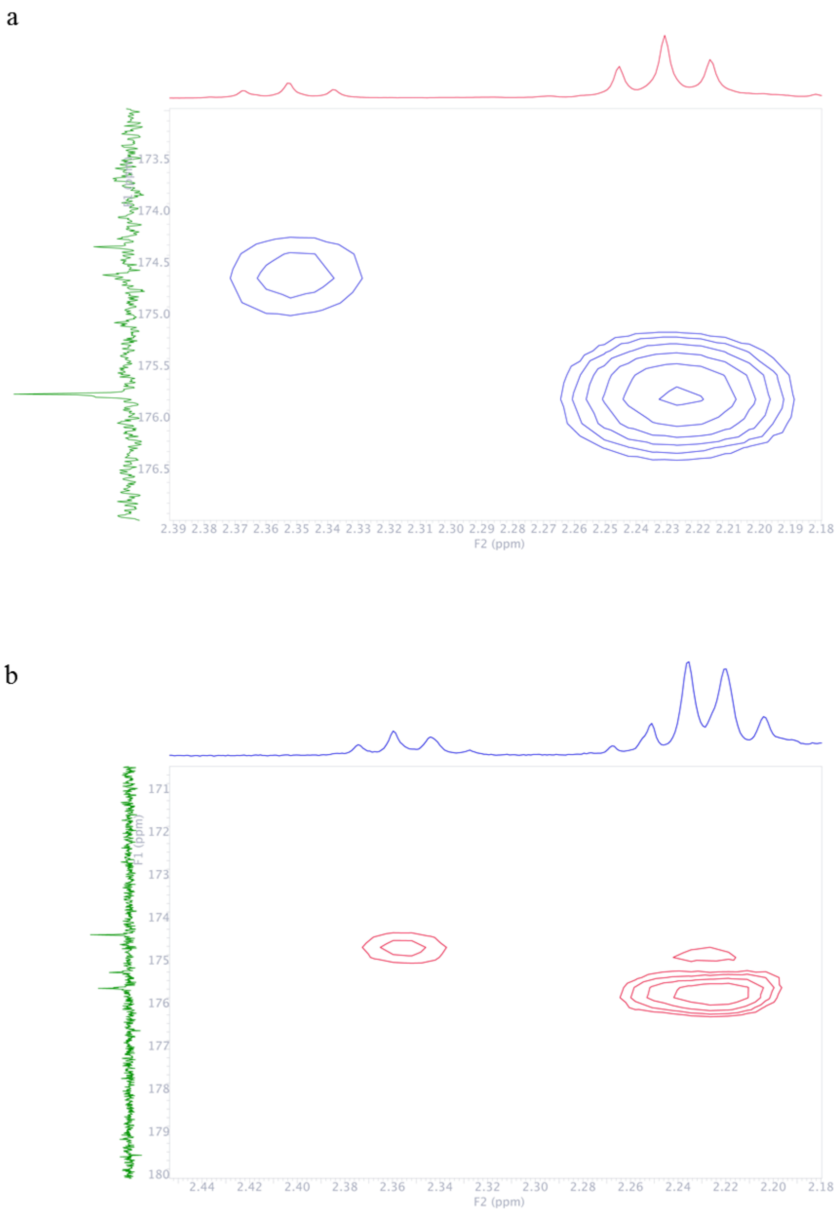

Figure S7. *(a) gHMBC- NMR region (2.18-2.44 ppm) of the reaction with ethane in D_2O-SDS. (b) gHMBC-NMR of reaction without ethane in D_2O-SDS*