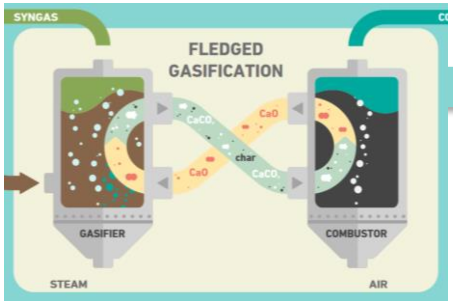
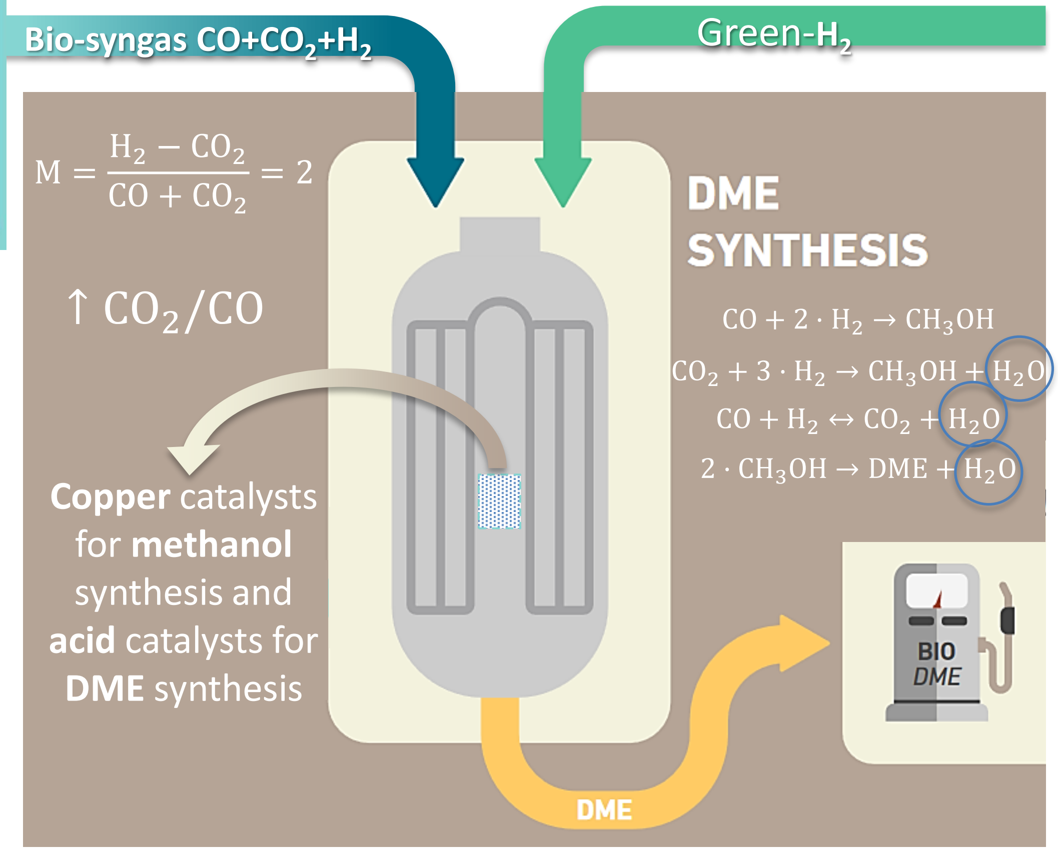
CATALYST/SORBENT MIXTURES DEVELOPMENT FOR SORPTION ENHANCED OPERATION

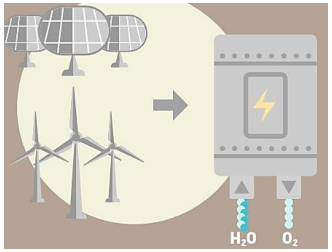
MADRID-SPAIN

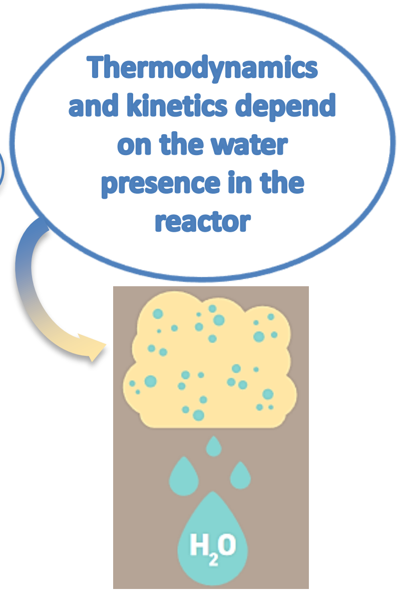
Dalia Liuzzi - *Cristina Peinado* - *Sergio Rojas*

SEDMES process









Sorbent for *in situ* water removal

Catalytic process and assessment of their physicochemical characteristics and activity by ICP-CSIC

ICP-CSIC → *Catalyst development & laboratory scale DME from syngas performance*

Syngas to methanol

$Cu/ZnO/Al_2O_3$-based

CZAx (*x (wt% Al_2O_3): 5, 11, 20, 30, 40, 50*)

CZAY (*Y: Pd, Zr a/o Ga*)

CZA_comm (*ICI Katalco™ 51-8*)

Methanol to DME

γ-Al_2O_3

H-ZSM-5

Heteropolyacids

$H_4[W_{12}SiO_{40}]/S$

$H_3[PW_{12}O_{40}]/S$

(S: Al_2O_3; SiO_2; ZrO_2; TiO_2; CeO_2; BN)

Syngas to DME

CZA-based : γ-Al_2O_3

DDMES^A

230-240-250-270-290 ^{0}C;
25-50 bar;
5000-7500 h^{-1};
CO_2:CO=1.9; M= 2
m:a=9:1; 1:1; 1:9

CZA-based : γ-Al_2O_3 + 3A

SEDMES^A

275 ^{0}C; 25 bar; 1080 h^{-1}; CO_2:CO=2
290 ^{0}C; 50 bar; 5000 h^{-1}; CO_2:CO=1.9
m:a=1:1; M= 2

CZA_comm : HPA

DDMES^HPA

200-240-270 ^{0}C; 25-40-50 bar;
7500-15000 h^{-1}; m:a= 9:1; 1:1
180 to 300 ºC; 50 bar; 7500 h^{-1};
m:a= 1:1
CO_2:CO=1.9; M= 2

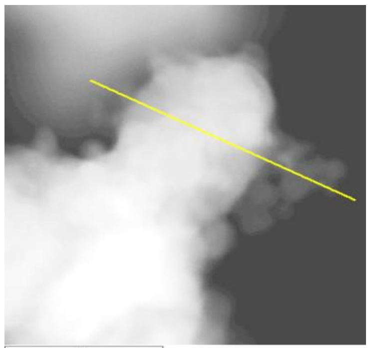
CZA_comm : HPA + 3A

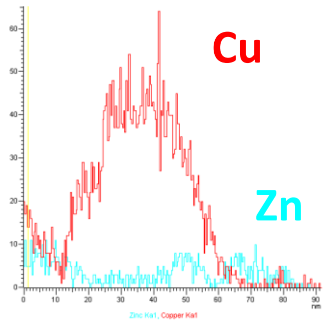
SEDMES^HPA

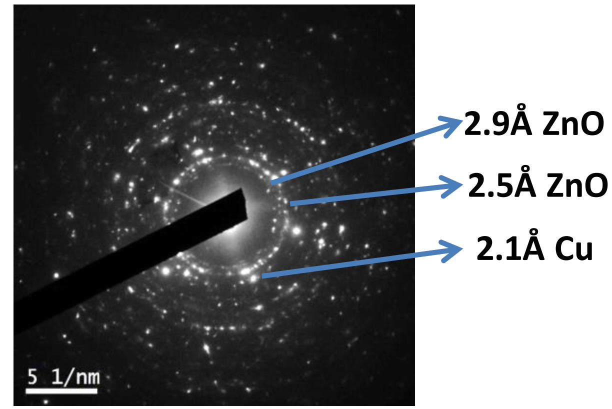
220-240-280-300 ^{0}C; 50 bar;
7500 h^{-1}; CO_2:CO=1.9
m:a=1:1; M= 2

Catalysts characterization: *ICP-OES, XRD, XPS, N_2-Isotherms, SEM, TEM/STEM/HAADF, TPR, H_2-TGA, N_2O-Chemisorption, NH_3-TPD, Raman spectroscopy, ^{1}H-NMR*

HR-TEM CZA







Catalyst	Surface area	Pore diameter	Composition (wt %)					
	$m^2\ g^{-1}$	nm	Cu	ZnO	Al_2O_3	ZrO_2	Ga_2O_3	MgO
CZA	38	12, 36	67	29	5	-	-	-
CZAZ	88	6, 48	67	10	15	8	-	-
CZAZGa	28	13-50	63	16	13	6	1	-
CZA_comm	97	7	59	27	11	-	-	2

	ps_{Cu}	S_{Cu} (XRD)	D_{Cu}	S_{Cu} (chem N_2O)
	nm	$m^2_{Cu}\ g_{cat}^{-1}$	%	$m^2_{Cu}\ g_{cat}^{-1}$
CZA	11	41	7.8	34
CZAZ	8	56	5.8	25
CZAZGa	9	47	-	-
CZA_comm	6	66	13.7	52

CZA_comm:γ-Al_2O_3 mixtures

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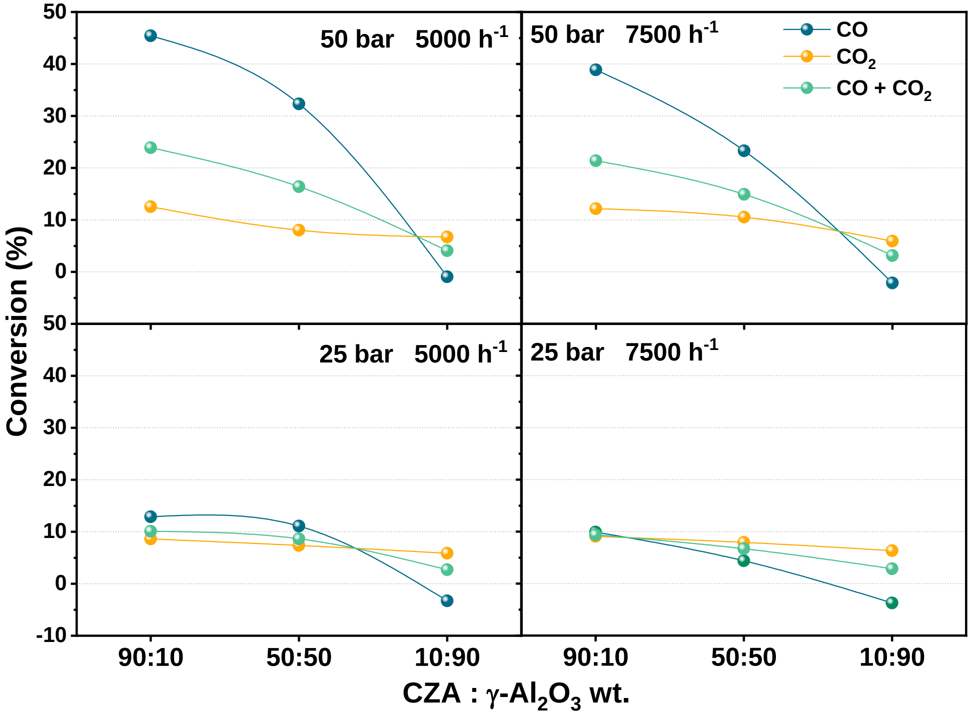

270 °C, 25 and 50 bar, and 5000 and 7500 h^{-1}.

10:90

r-WGS, since CO conversion < 0 (CO formation)

50:50

Optimum; DME selectivity is higher than mixture 90:10

90:10

Highly active in WGS instead of methanol production @ 50 bar

Optimum mixture 50:50

	DME selectivity (%)			
	50 bar; 5000 h^{-1}	50 bar; 7500 h^{-1}	25 bar; 5000 h^{-1}	25 bar; 7500 h^{-1}
90:10	*1*	*1*	*2*	*1*
50:50	*23*	*17*	*30*	*35*
10:90	*70*	*43*	*68*	*43*

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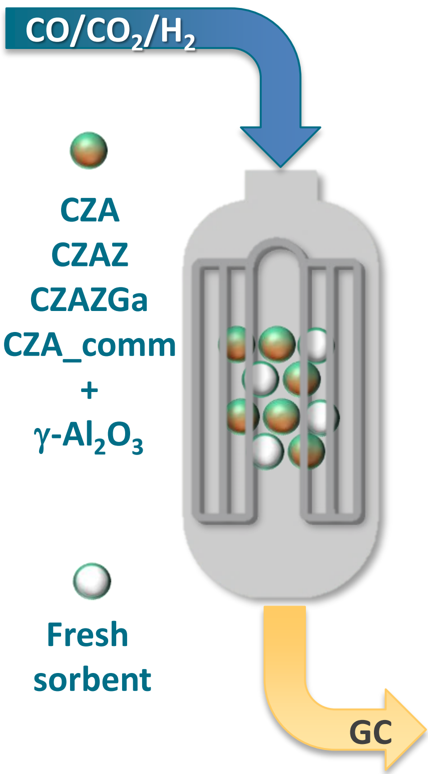
DDMES vs SEDMES with γ-Al_2O_3

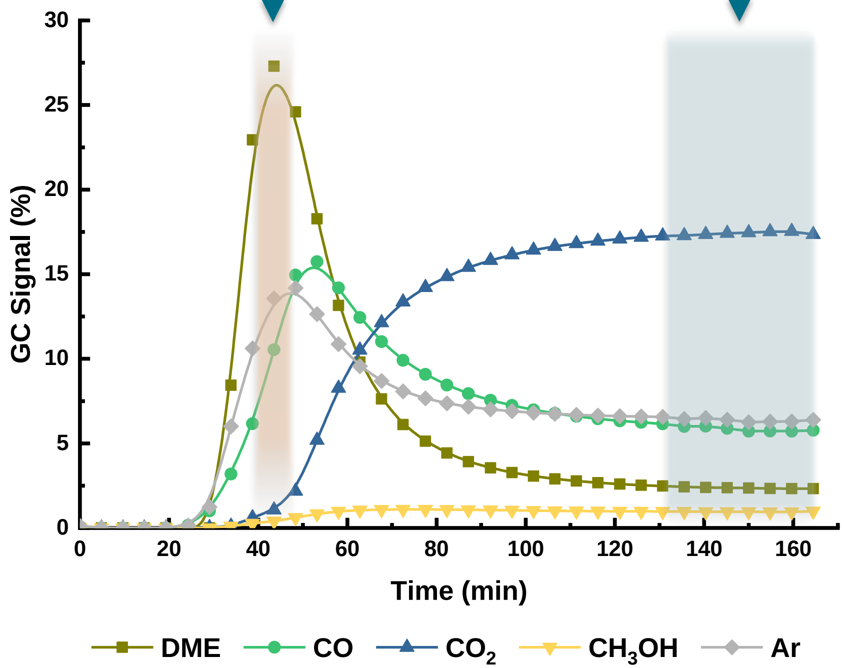
SEDMES
Sorption Enhanced DME Synthesis

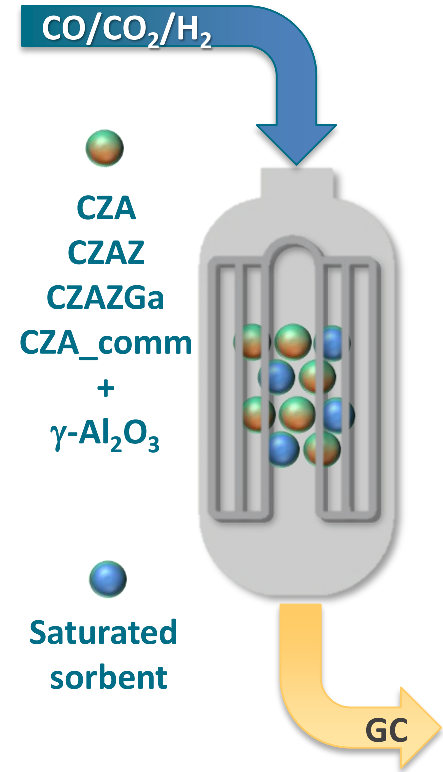
Pre-breakthrough
Fresh sorbent 3A

DDMES
Direct DME Synthesis

After complete
saturation 3A







Experiments performed at TNO facilities, Petten, The Netherlands

DDMES vs SEDMES with γ-Al_2O_3

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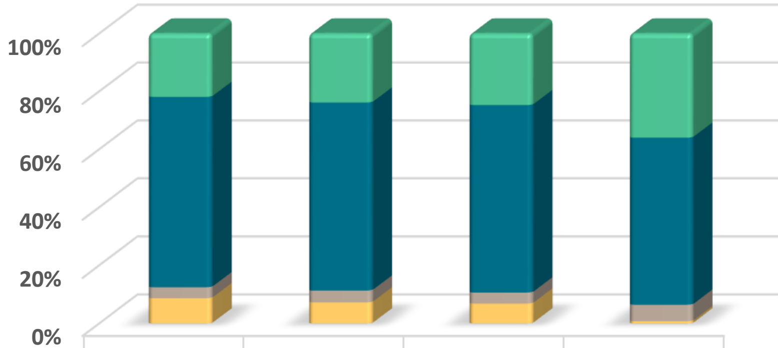
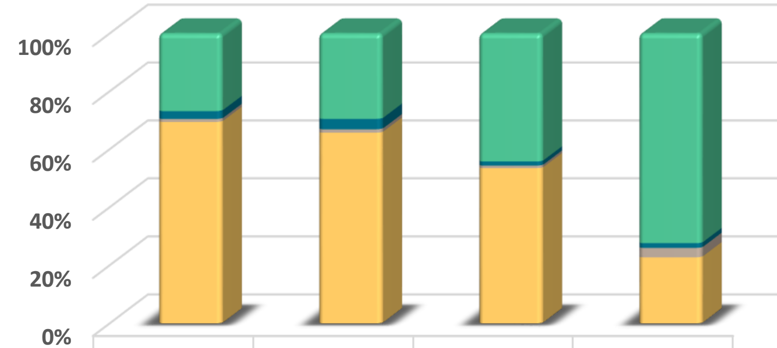
DDMES[A]
Direct DME Synthesis

SEDMES[A]
Sorption Enhanced DME Synthesis

CZA:γ-Al_2O_3= 1:1 + 3A (3A:Catalysts= 4:1)
275 ºC; 25 bar; 1080 h^{-1}; CO_2/CO=1.9; CO/CO_2/H_2= 9/18/73 (v/v)



	CZA_comm	CZA	CZAZ	CZAZGa
% CO	21,9	23,8	24,7	36,0
% CO2	65,7	64,9	64,6	57,6
% CH3OH	3,8	4,1	3,8	5,7
% DME	8,7	7,2	6,8	0,8



	CZA_comm	CZA	CZAZ	CZAZGa
% CO	26,8	29,5	44,2	72,4
% CO2	2,7	3,6	1,4	1,6
% CH3OH	1,0	1,2	0,9	3,3
% DME	69,5	65,7	53,5	22,8

In situ water removal enhances DME production

- Catalyst with higher ZnO loading and surface Cu area: improved methanol performance → enhanced DME
- Catalyst with lower ZnO loading surface Cu area: rWGS performance → poor DME production

CZA_comm	27% ZnO	52 $m^2_{Cu}\,g_{cat}^{-1}$
CZA	29% ZnO	34 $m^2_{Cu}\,g_{cat}^{-1}$
CZAZ	10% ZnO	25 $m^2_{Cu}\,g_{cat}^{-1}$
CZAZGa	16% ZnO	--

D. Liuzzi, C. Peinado, M.A. Peña, J. van Kampen, J. Boon, S. Rojas, Sustain. Energy Fuels. (2020)

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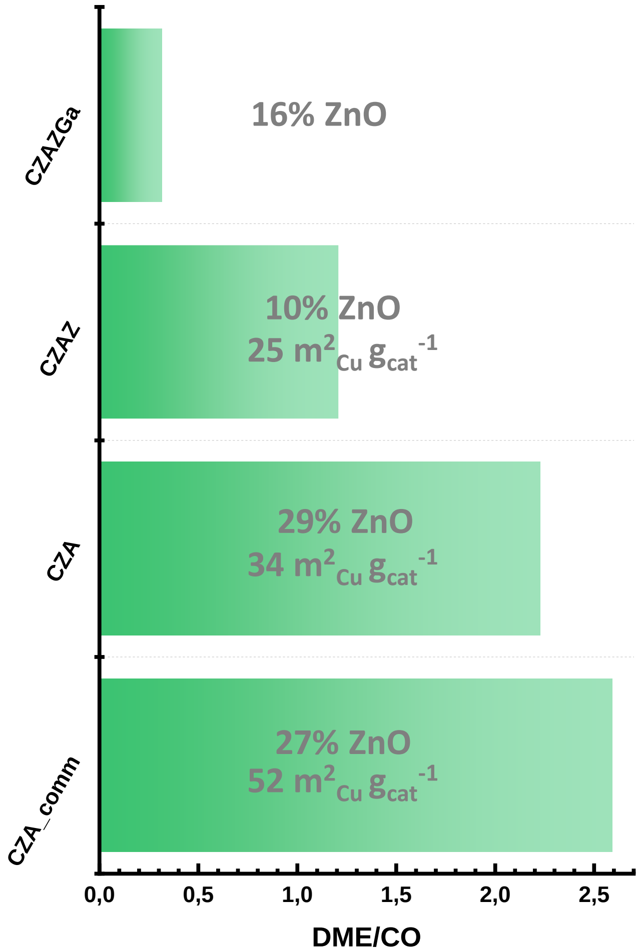
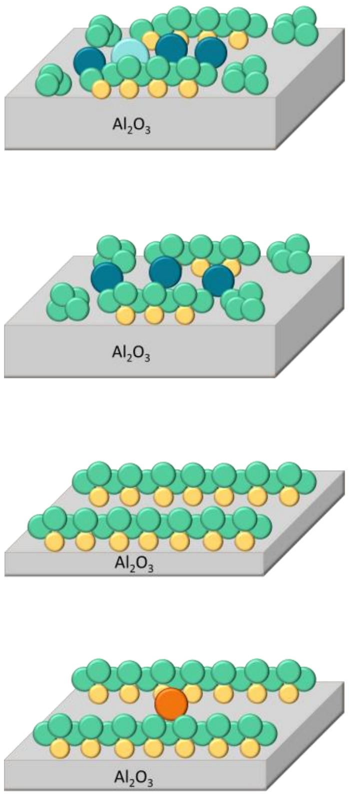
DDMES vs SEDMES with γ-Al_2O_3

Structure & activity

Cu ZnO MgO ZrO_2 Ga_2O_3





ZnO structural promoter

Stable Cu crystals

Improves Cu dispersion

DDMES with $H_4[W_{12}SiO_{40}]/TiO_2$ ($HWSi/TiO_2$), CZA:HPA = 1:1

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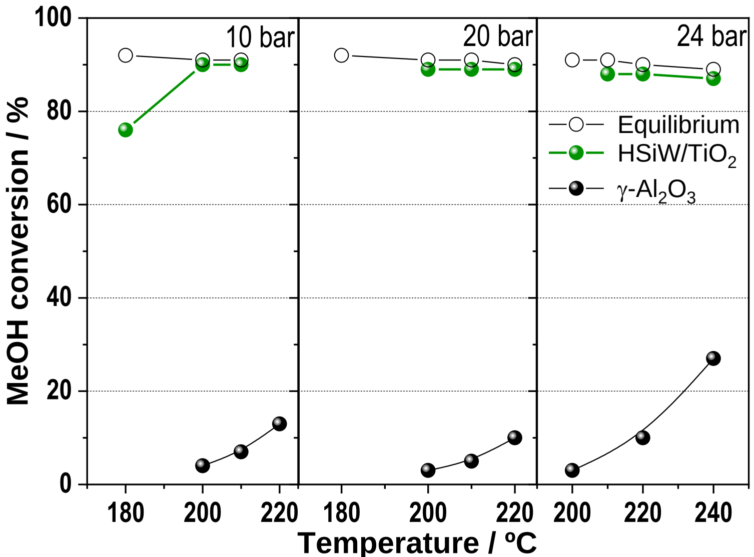


LHSV= 1.1 h^{-1}

Methanol conversion

Higher with $HWSi/TiO_2$ than with γ-Al_2O_3 @ low T

Follows pseudo-liquid catalysis:

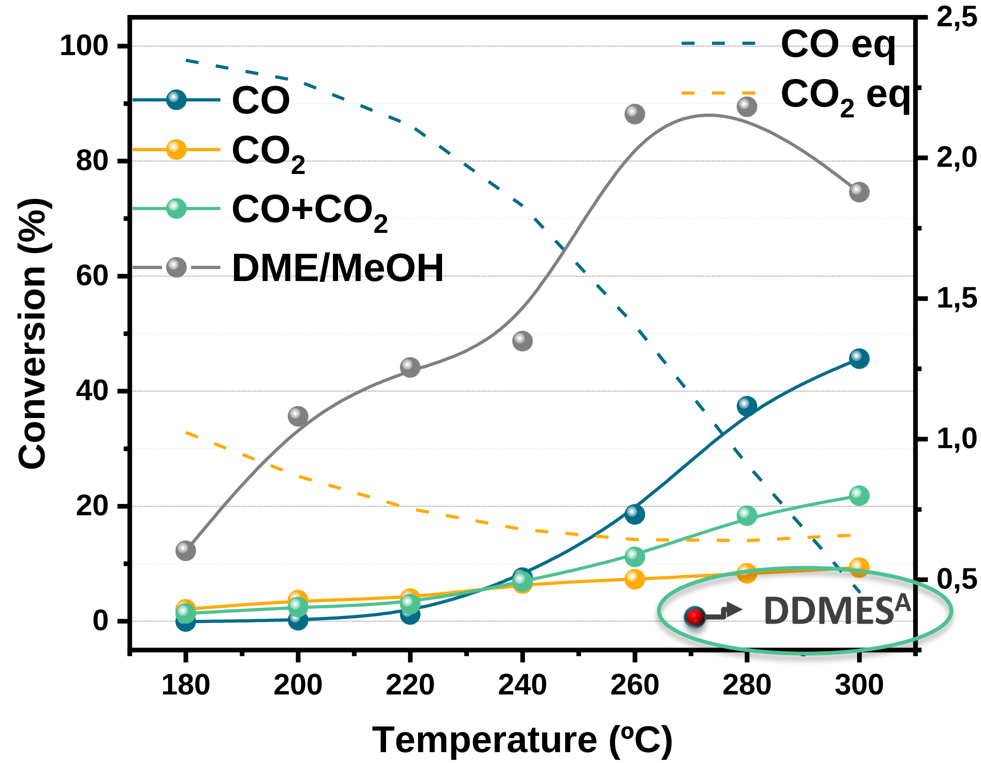
Decreases with T from 200 ^0C

Increases with P

DDMES^{HPA} 50 bar; 7500 h^{-1}; CO_2/CO=1.9

DME/MeOH increases with T up to a maximum (c.a. 270 ºC)

DME/MeOH is 21 times higher with HPA than with γ-Al_2O_3



C. Peinado, D. Liuzzi, R.M. Ladera-Gallardo, M. Retuerto, M. Ojeda, M.A. Peña, S. Rojas, Sci. Rep. 10 (2020) 8551.

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Conclusions

- The optimal **m:a-ratio** for the DDMES from syngas is **1:1**
- Using m:a mixtures with **heteropolyacids improves** the **DME** selectivity in DDMES, compared with the mixture of catalysts using the benchmark catalyst γ-Al_2O_3
- The use of promoters (Zr a/o Ga) promotes the r-WGSR
- The **in situ water removal** results in **higher DME productivity** employing CZA catalyst
- The ZnO is a structural promoter. Higher ZnO loading enhances the DME production with m:a mixtures

Thanks for your attention

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