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CATALYSTS FOR SORPTION ENHANCED DME SYNTHESIS (SEDMES)

ICP CSIC

CSIC Consejo Superior de Investigaciones Científicas

MADRID-SPAIN

&

THE NETHERLANDS

TNO

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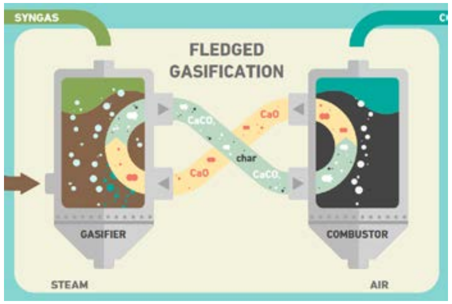
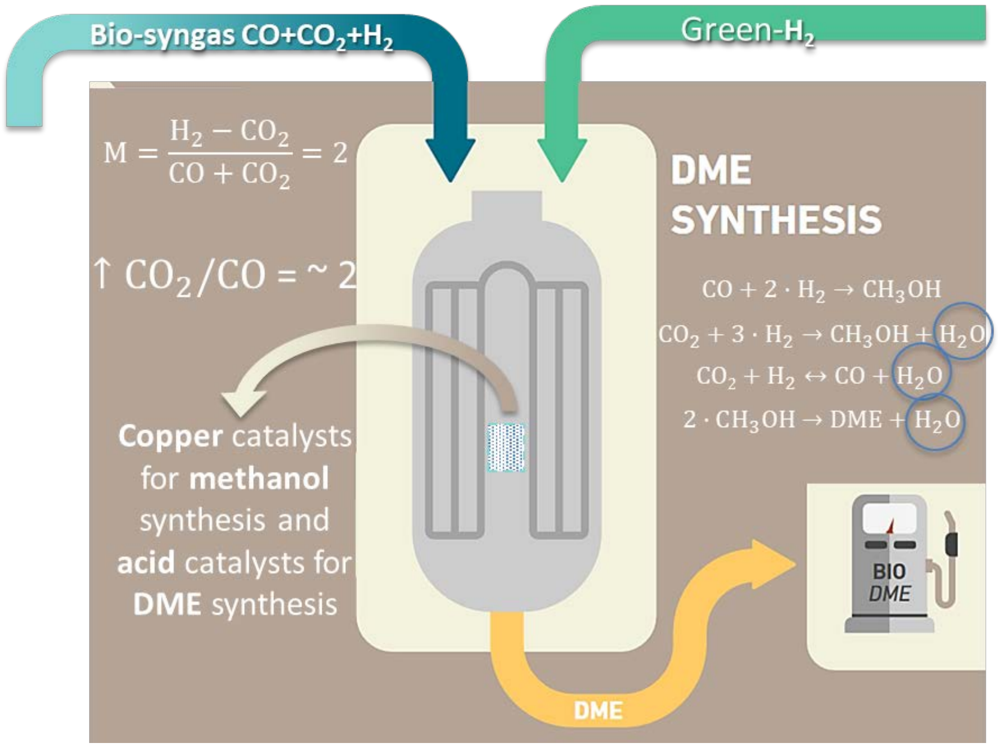
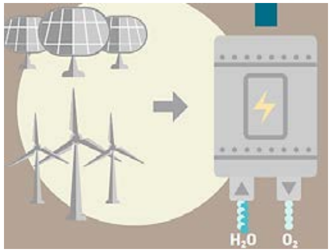
Introduction

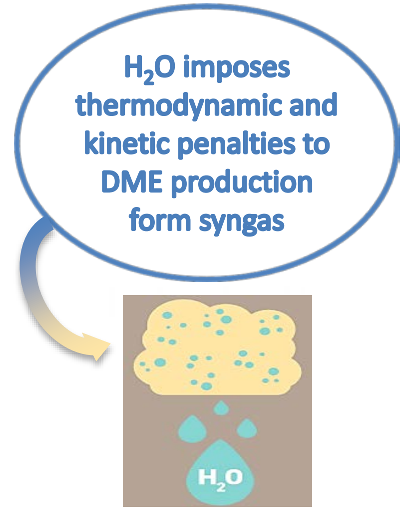
SEDMES process



Biomass gasification produces a CO_2 rich syngas with high CO_2 /CO ratio





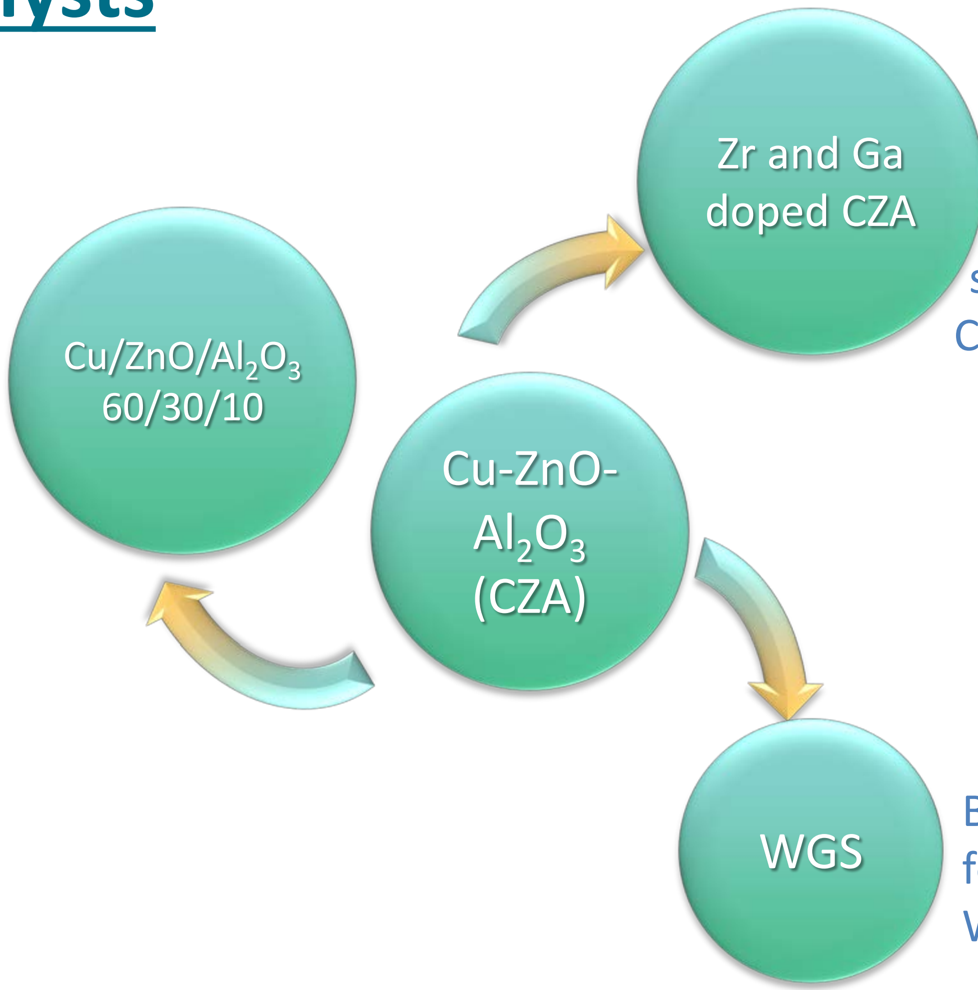


Sorbents for *in situ* water removal

Catalysts to adjust the CO_2/CO ratio
Sorbents for in situ water removal

Methanol catalysts

- Benchmark catalysts syngas → methanol
- syngas with 2-5% CO_2
- Higher CO_2 content lower methanol productivity
- Higher production of H_2O (lower DME productivity)
- Water removal strategies

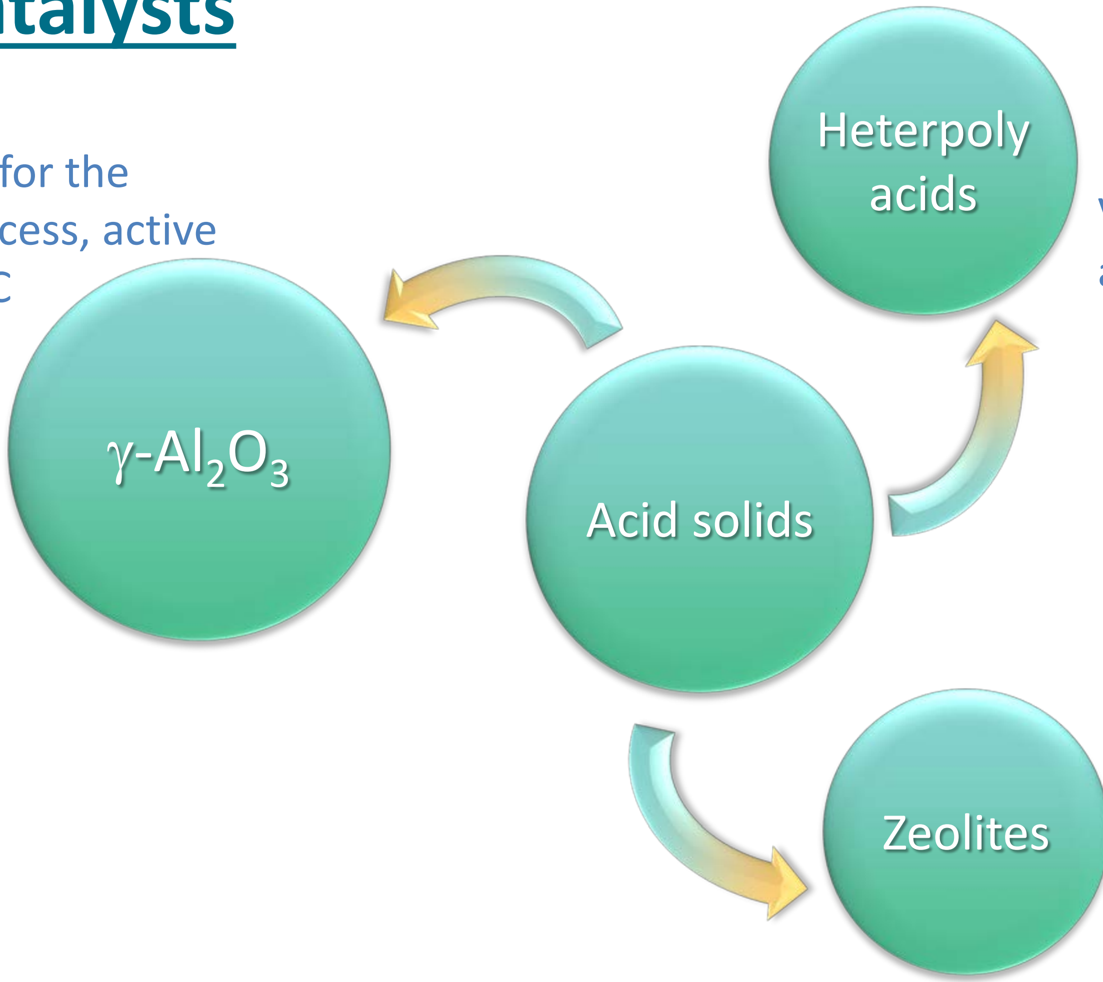


Methanol synthesis from CO_2 or CO_2-rich syngas

Benchmark catalyts for low temperature WGS reaction

DME catalysts

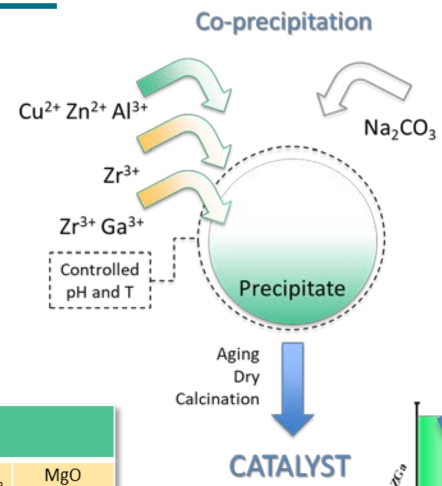
SoA catalyst for the industial process, active above 250 ºC



Very active and selective at low temperatures

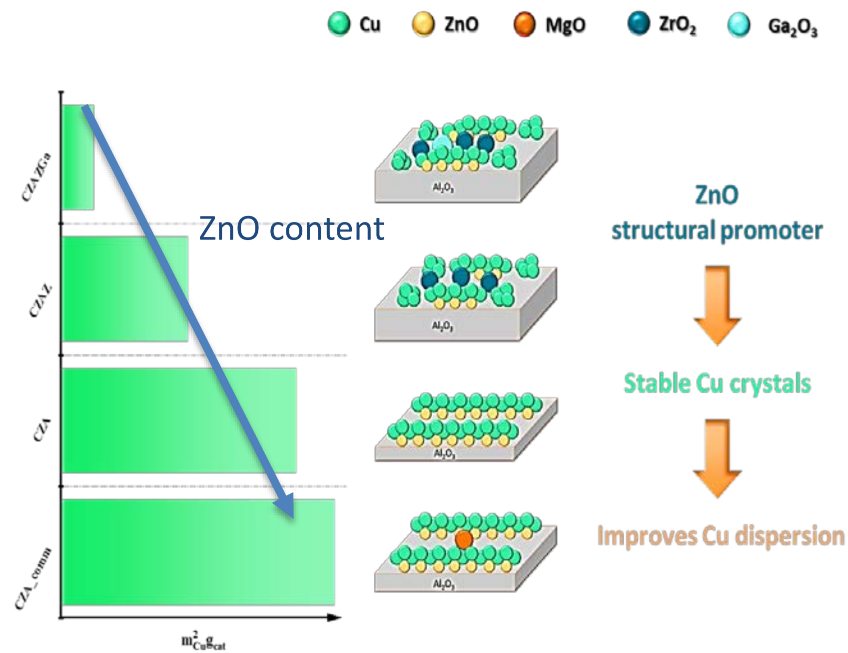
Very active at high temperatures

Methanol catalysts



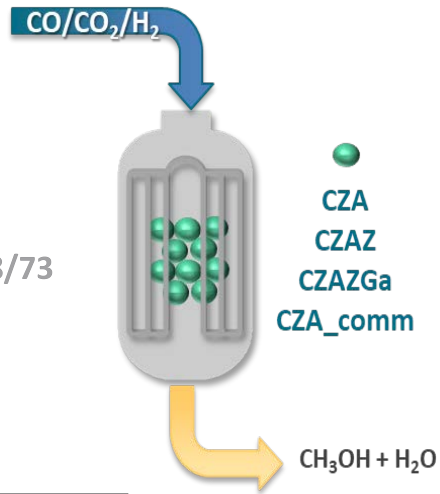
Catalyst	Surface area	Pore diameter	Composition (wt %)					
	$m^2 g^{-1}$	nm	Cu	ZnO	Al_2O_3	ZrO_2	Ga_2O_3	MgO
CZA	38	12. 4	67	29	5	-	-	-
CZAZ	88	6.5	67	10	15	8	-	-
CZAZGa	28	13-50	63	16	13	6	1	-
CZA_comm	97	7.0	59	27	11	-	-	2

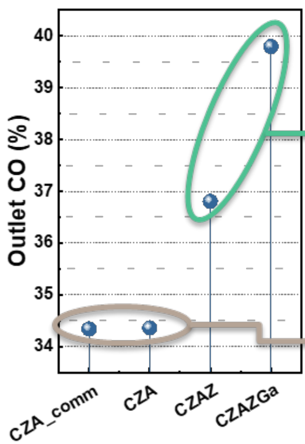
	ps_{Cu}	S_{Cu} (XRD)	D_{Cu}	S_{Cu} (chem N_2O)
	nm	$m^2_{Cu}\ g_{cat}^{-1}$	%	$m^2_{Cu}\ g_{cat}^{-1}$
CZA	11	41	7.8	34
CZAZ	8	56	5.8	25
CZAZGa	9	47	-	-
CZA_comm	6	66	13.7	52



MeS Methanol Synthesis

270 ºC; 25 bar;
7500 h^{-1};
$CO_2/CO=1.9$;
$CO/CO_2/H_2$: 9/18/73





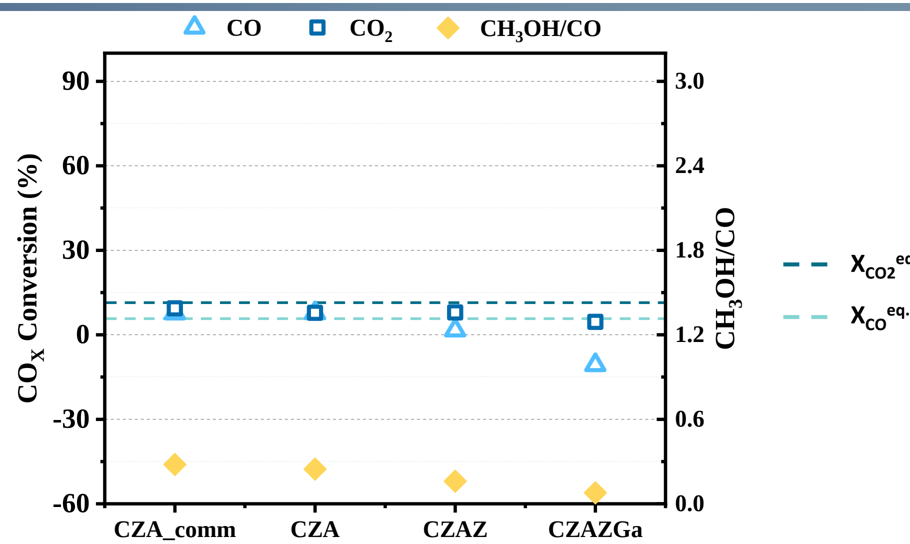
$(-3)\ CO_2 + H_2 \leftrightarrow CO + H_2O$

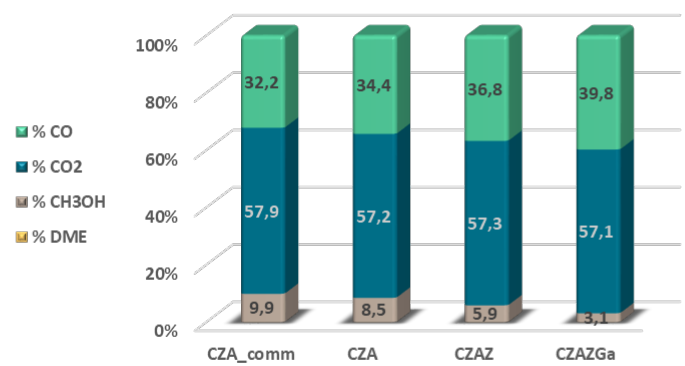
%mol $_{CO2}$ $^{opt.}$
2.4 %

$(1)\ CO + 2H_2 \leftrightarrow CH_3OH$

$(2)\ CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$

$(3)\ CO + H_2O \leftrightarrow CO_2 + H_2$



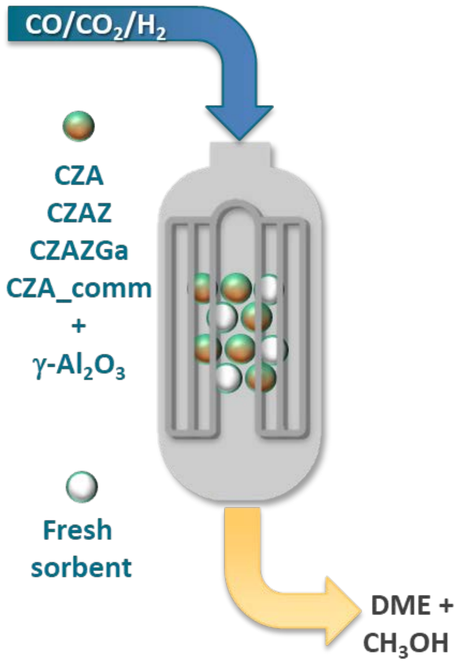


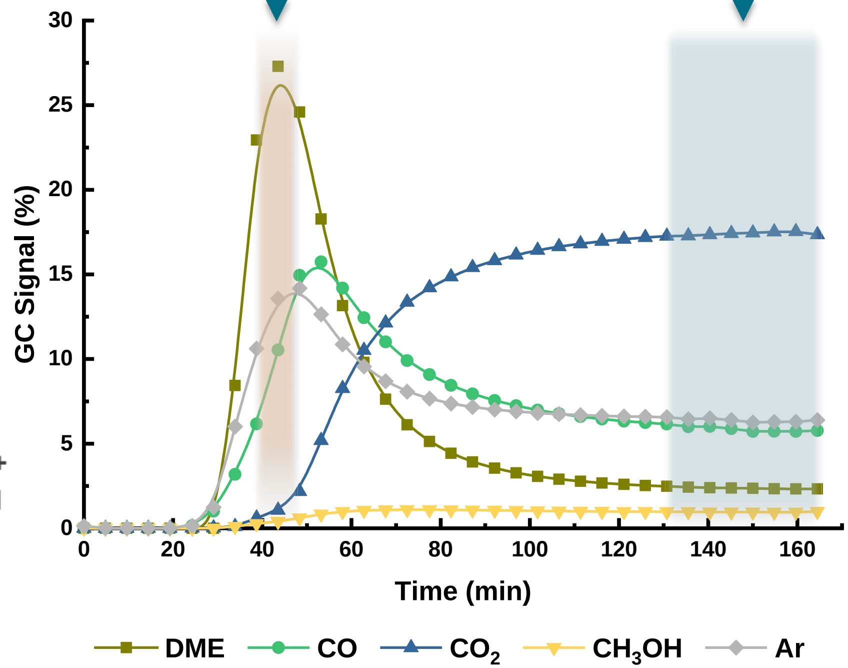
SEDMES
Sorption Enhanced DME Synthesis

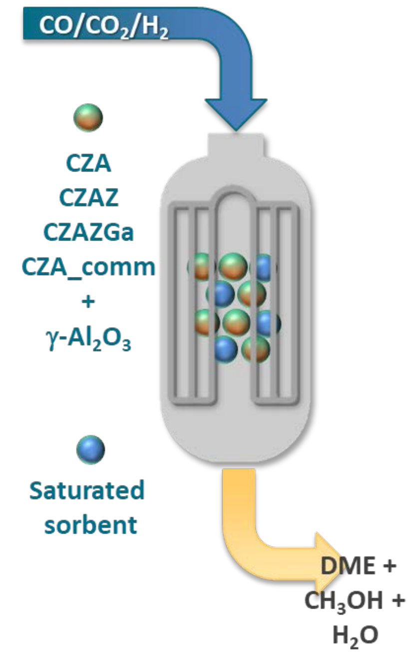
Pre-breakthrough
Fresh sorbent 3A

DDMES
Direct DME Synthesis

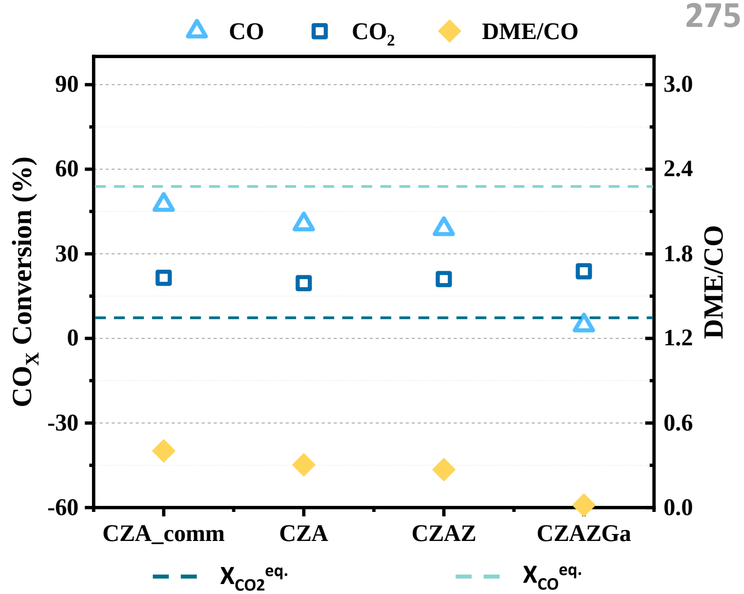
After complete
saturation 3A



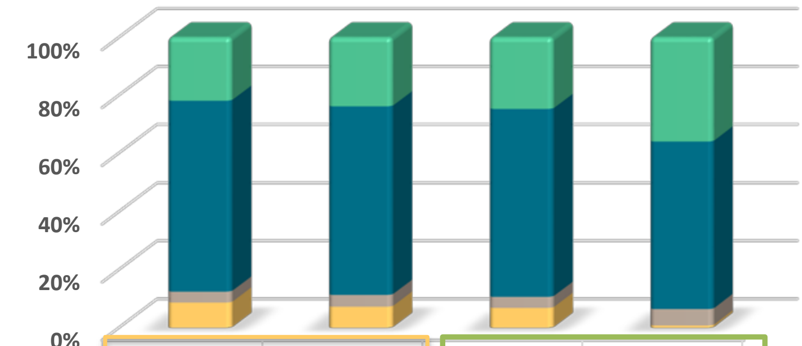




DDMES Direct DME Synthesis



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

Higher DME production

High CO production

(1) $CO + 2H_2 \leftrightarrow CH_3OH$

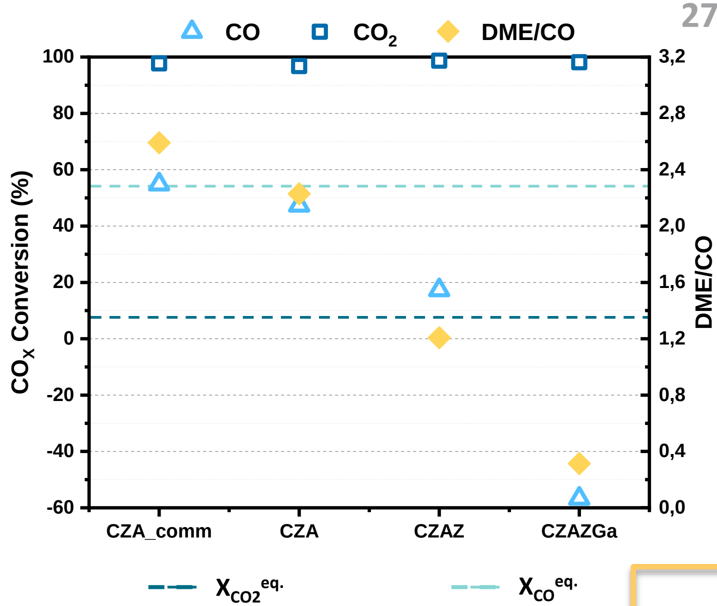
(2) $CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$

(3) $CO + H_2O \leftrightarrow CO_2 + H_2$

(4) $2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$

CH_3OH dehydration to DME → shift of (eq. 2) equilibrium towards more CH_3OH and H_2O

SEDMES Sorption Enhanced DME Synthesis



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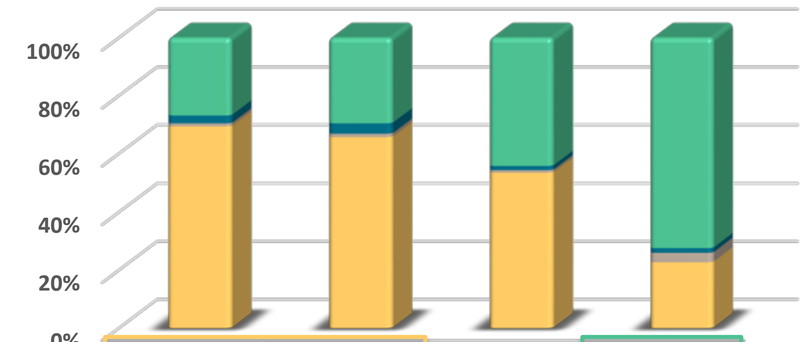

	CZA_comm	CZA	CZAZ	CZAZGa
% CO	26.8	29.5	44.2	72.4
% CO2	2.7	3.6	1.4	1.6
% CH3OH	1.0	1.2	0.9	3.3
% DME	69.5	65.7	53.5	22.8

Very high DME production

Low CO_2 in products

Easier separation DME/CO_2 downstream

R-wGS

Highest CO production

Highest non converted CH_3OH

Lowest DME production

$$(1)\ CO + 2H_2 \leftrightarrow CH_3OH$$

$$(2)\ CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$$

$$(3)\ CO + H_2O \leftrightarrow CO_2 + H_2$$

$$(4)\ 2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$$

Removing H_2O results in high CO_2 conversion and DME production

- **SEDMES approach, based in the in situ removal of H_2O** during the direct synthesis of DME from CO_2 rich syngas by using a water sorbent, **lead to higher carbon conversions and higher DME** productions

- In situ increasing **r-WGS activity** by using of promoters increases CO content (lower CO_2/CO ratio) but due to H_2O production affects negatively catalyst performance for methanol production

Thanks for your attention

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