Supplementary Materials: Enhanced Direct Dimethyl Ether Synthesis from CO_2-Rich Syngas with $Cu/ZnO/ZrO_2$ Catalysts Prepared by Continuous Co-Precipitation

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1. N_2 Physisorption Isotherms.
2. XRD of the Spent Catalysts.
3. Catalytic Activity in the Direct DME Synthesis.

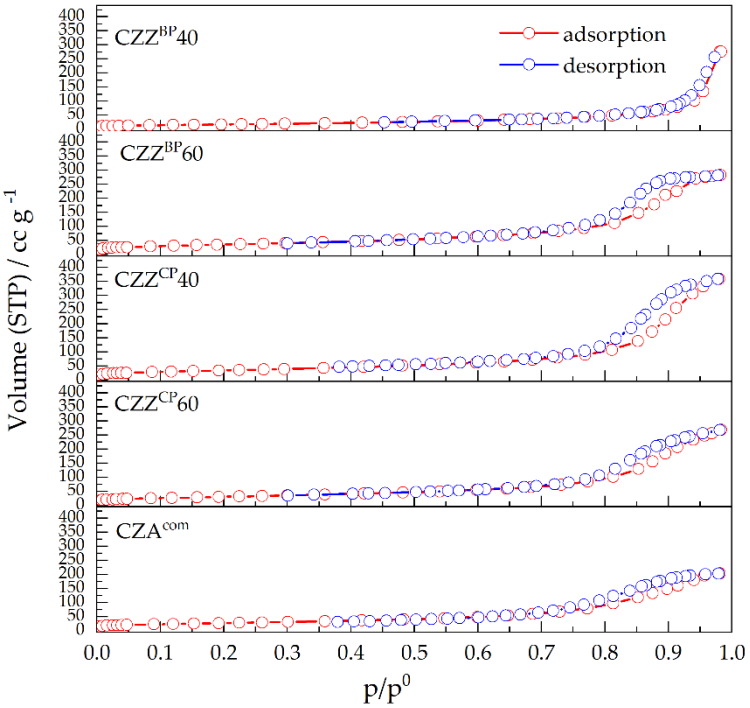

Figure 1. N_2 physisorption isotherms of the calcined CZZ pre-catalysts and CZA^{com}.

The sorption isotherms (except $CZZ^{BP}40$) match with type IVa according to IUPAC classification, which is typically associated to partial porous structures. The shape of the hysteresis loop for these pre-catalysts is of the H1 type, typically present in materials with a narrow range of uniform mesopores [1]. The comparative sample from the semi-batch co-precipitation $CZZ^{BP}40$ however, shows a reversible type II isotherm, typically indicating nonporous or microporous structure [1].

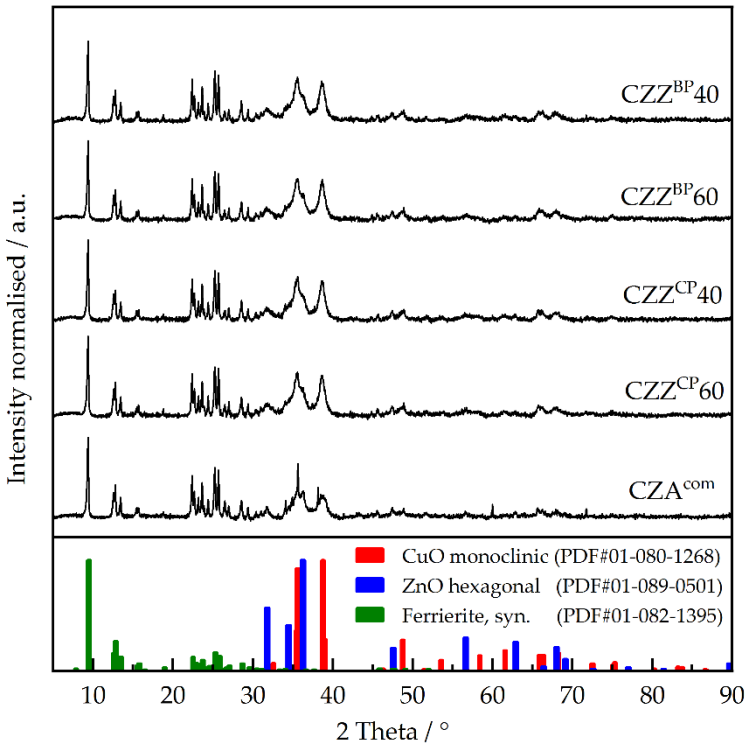

Figure 2. X-ray diffraction patterns of the spent CZZ and CZA^{com} catalysts. It should be noted that the XRD measurements were carried out after several weeks of storage, what effect the re-oxidation process.

Catalytic Activity in the Direct DME Synthesis

CO (99.97%), Ar, (99.9999%), N_2 (99.9999%), H_2 (9.9999%) and CO_2/N_2, (50:50±1.0 vol.%) (Air Liquid Germany GmbH) were used as reactant gases. The feed compositions for "CO-rich" ($CO_2/(CO+CO_2)$=0.2) and "CO_2-rich" ($CO_2/(CO+CO_2)$=0.8) synthesis gas can be found in Table S1. Time on stream (ToS) ranges can be found in Table S2.

Table S1 Feed compositions.

$CO_2/(CO+CO_2)$ ratio	H_2/ vol%	CO/ vol%	CO_2/ vol%	N_2/ vol%	Ar/ vol%
0.2	37.5	12	3	15	32.5
0.8	46.5	3	12	15	23.5

Table S2 Time on stream (ToS) ranges in which the inlet feeds (Table S1) were measured.

Catalyst	ToS range / h	
	$CO_2/(CO+CO_2)$=0.2	$CO_2/(CO+CO_2)$=0.8
$CZZ^{BP}40$/FER	37–39	41–43
$CZZ^{BP}60$/FER	37–39	41–43
$CZZ^{CP}40$/FER	35–37	39–41
$CZZ^{CP}60$/FER	37–39	41–43
CZA^{com}/FER	62–64	66–68

ToS ranges for CZA/FER are slightly higher because as our reference material it was investigated in more detail. The differences are rather small, so it is still suitable for comparison of the different materials.

Equations

The conversion of CO and CO_2 is expressed in the CO_x conversion X_{CO_x}:

$$X_{CO_x} = \frac{\dot{n}_{CO,in} - \dot{n}_{CO,out} + \dot{n}_{CO_2,in} - \dot{n}_{CO_2,out}}{\dot{n}_{CO,in} + \dot{n}_{CO_2,in}} \cdot 100\ [\%] \quad \text{(S1)}$$

DME productivity P_{DME} is related to mass of the MeOH catalyst and defined as following:

$$P_{DME} = \frac{\dot{m}_{DME,out}}{m_{MeOH\ cat.}} \left[\frac{g}{kg \cdot h}\right] \quad \text{(S2)}$$

Productivity of not converted MeOH is related to the mass of MeOH catalyst and defined as following:

$$P_{MeOH} = \frac{\dot{m}_{MeOH,out}}{m_{MeOH\ cat.}} \left[\frac{g}{kg \cdot h}\right] \quad \text{(S3)}$$

The mass specific cumulative MeOH productivity $P_{MeOH,\ cum.}$ is defined as following:

$$P_{MeOH,cum.} = \frac{2\,\dot{n}_{DME,out} + \dot{n}_{MeOH,out}}{m_{MeOH\ cat.}} \left[\frac{mol}{kg \cdot h}\right] \quad \text{(S4)}$$

References

1. Thommes, M.; Kaneko, K.; Neimark, A.V.; Olivier, J.P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K.S.W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051-1069, doi:10.1515/pac-2014-1117.