Boosting the activity of UiO-66(Zr) by defect engineering: efficient aldol condensation of furfural and MIBK for the production of bio jet-fuel precursors

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Electronic Supplementary Information

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Table ESI-1 Composition in the synthesis media for UiO-66(Zr) materials.

Sample Name	$ZrCl_4$ (mmol)	MOD (ml)	DMF (ml)	BDC (mmol)	C_{MOD} (mol/L)	MOD/DMF (mol)	MOD/BDC (mol)
UiO-66(Zr)-DF	16.2	-	100	32.4	-	-	-
UiO-66(Zr)	6	-	100	6	-	-	-
Modulator: Formic Acid (pKa = 3.77)							
UiO-66(Zr)-FA1	6	2	98	6	0.51	0.04	8.45
UiO-66(Zr)-FA2	6	8	92	6	2.04	0.17	33.82
UiO-66(Zr)-FA3	6	16	84	6	4.07	0.38	67.63
UiO-66(Zr)-FA4	6	20	80	6	5.09	0.49	84.54
Modulator: Trifluoroacetic acid (pKa = 0.23)							
UiO-66(Zr)-TFA1	6	2	98	6	0.26	0.02	4.30
UiO-66(Zr)-TFA2	6	8	92	6	1.03	0.09	17.19
Modulator: Hydrochloric acid (pKa = -6.3)							
UiO-66(Zr)-HCl1	6	2	98	6	0.24	0.02	4.05
UiO-66(Zr)-HCl2	6	8	92	6	0.97	0.08	16.19
UiO-66(Zr)-HCl3	6	16	84	6	1.95	0.18	32.37
UiO-66(Zr)-HCl4	6	20	80	6	2.44	0.24	40.46
UiO-66(Zr)-HCl5	6	24	76	6	2.92	0.30	48.56

MOD = modulator; DMF = N,N'-dimethyl formamide; BDC = benzene-1,4-dicarboxilate.

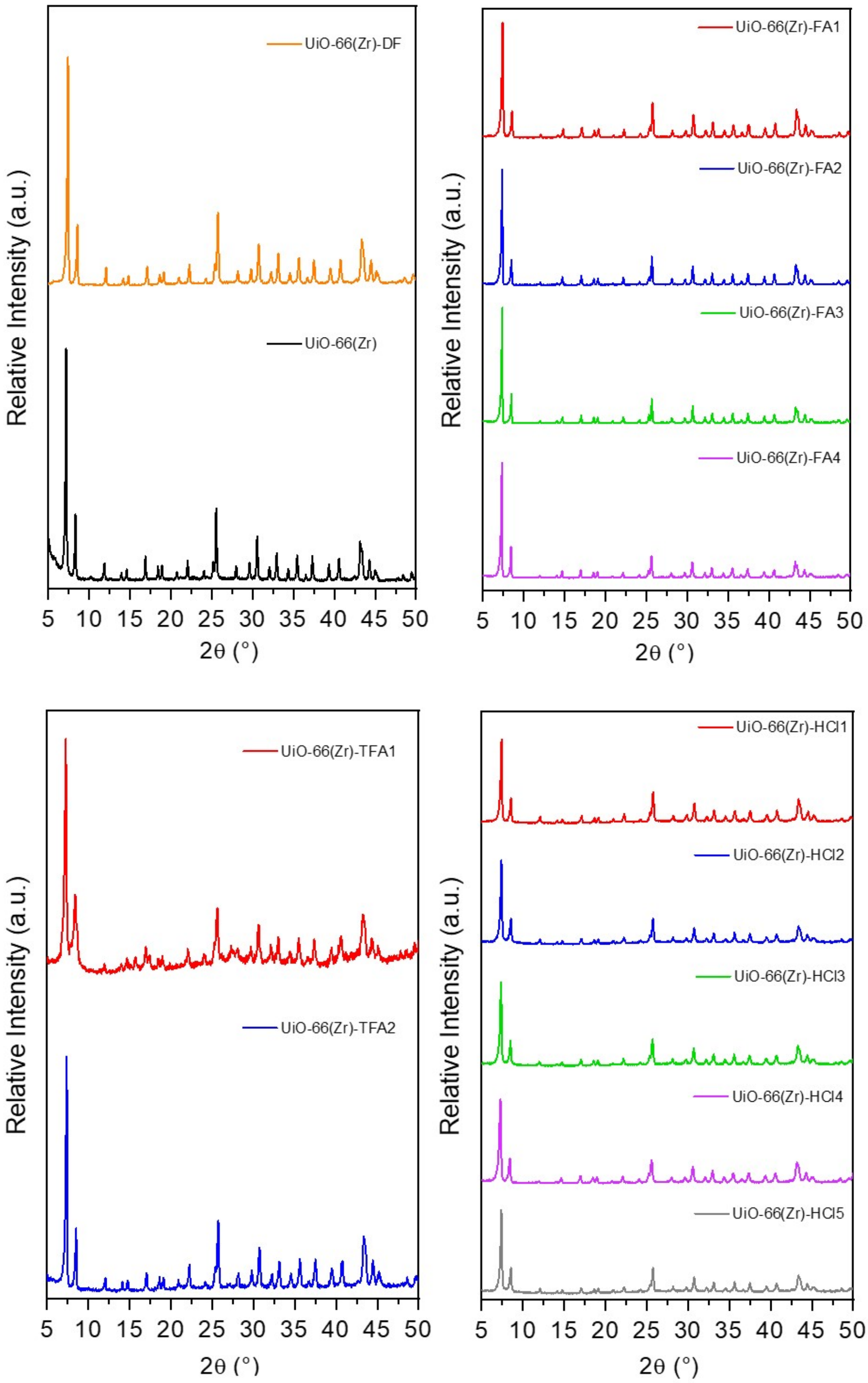


Fig. ESI-1 Powder X-ray diffraction patterns of UiO-66(Zr)-DF, UiO-66(Zr) parent and modulated UiO-66(Zr) series of materials.

Table ESI-2 Quantification of linker deficiencies in defective UiO-66 samples.

Sample	T_{plat} (°C)[a]	$W_{Exp\text{-}Plat}$ (%)[b]	NL_{Exp}[c]	x[d]	Composition at $W_{Exp.Plat}$[e]
UiO-66(Zr)-DF	370	220	6.00	0.00	$Zr_6O_6(BCD)_6$
UiO-66(Zr)	370	204	5.20	0.80	$Zr_6O_{6.8}(BCD)_{5.2}$
UiO-66(Zr)-FA1	370	199	4.95	1.05	$Zr_6O_{7.05}(BCD)_{4.95}$
UiO-66(Zr)-FA2	370	197	4.88	1.13	$Zr_6O_{7.13}(BCD)_{4.87}$
UiO-66(Zr)-FA3	370	192	4.60	1.40	$Zr_6O_{7.4}(BCD)_{4.6}$
UiO-66(Zr)-FA4	370	187	4.35	1.65	$Zr_6O_{7.65}(BCD)_{4.35}$
UiO-66(Zr)-TFA1	390	194	4.70	1.30	$Zr_6O_{7.3}(BCD)_{4.7}$
UiO-66(Zr)-TFA2	390	192	4.60	1.40	$Zr_6O_{7.4}(BCD)_{4.6}$
UiO-66(Zr)-HCl1	370	195	4.75	1.25	$Zr_6O_{7.25}(BCD)_{4.75}$
UiO-66(Zr)-HCl2	370	187	4.35	1.65	$Zr_6O_{7.65}(BCD)_{4.35}$
UiO-66(Zr)-HCl3	370	186	4.30	1.70	$Zr_6O_{7.7}(BCD)_{4.3}$
UiO-66(Zr)-HCl4	370	187	4.35	1.65	$Zr_6O_{7.65}(BCD)_{4.35}$
UiO-66(Zr)-HCl5	370	184	4.20	1.80	$Zr_6O_{7.8}(BCD)_{4.2}$

[a] Temperature of the plateau; [b] Experimental weight of the plateau; [c] Number of linkers per defective Zr_6 formula unit calculated as $(W_{Exp\text{-}Plat} – W_{End})/Wt.PL_{Theo}$ being $Wt.PL_{Theo}$=20 % when the end weight of the TGA run is normalized to 100 % (W_{End} = 100 %); [d] Number of linker deficiencies per Zr_6 formula unit calculated as 6 - NL_{Exp}; [e] Composition of the material assuming the following formula $Zr_6O_{6+x}(BDC)_{6\text{-}x}$

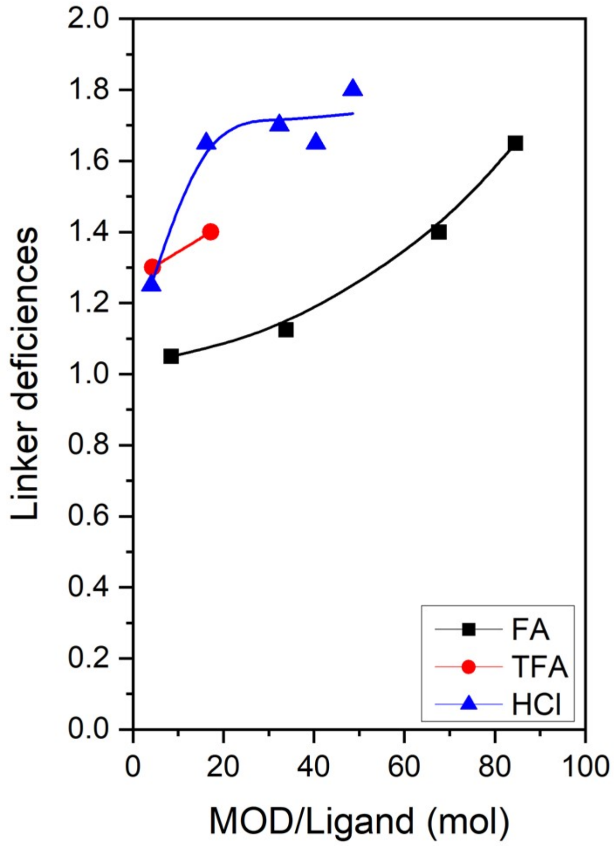


Fig. ESI-2. Linker deficiencies corresponding to modulated UiO-66(Zr) series of materials.

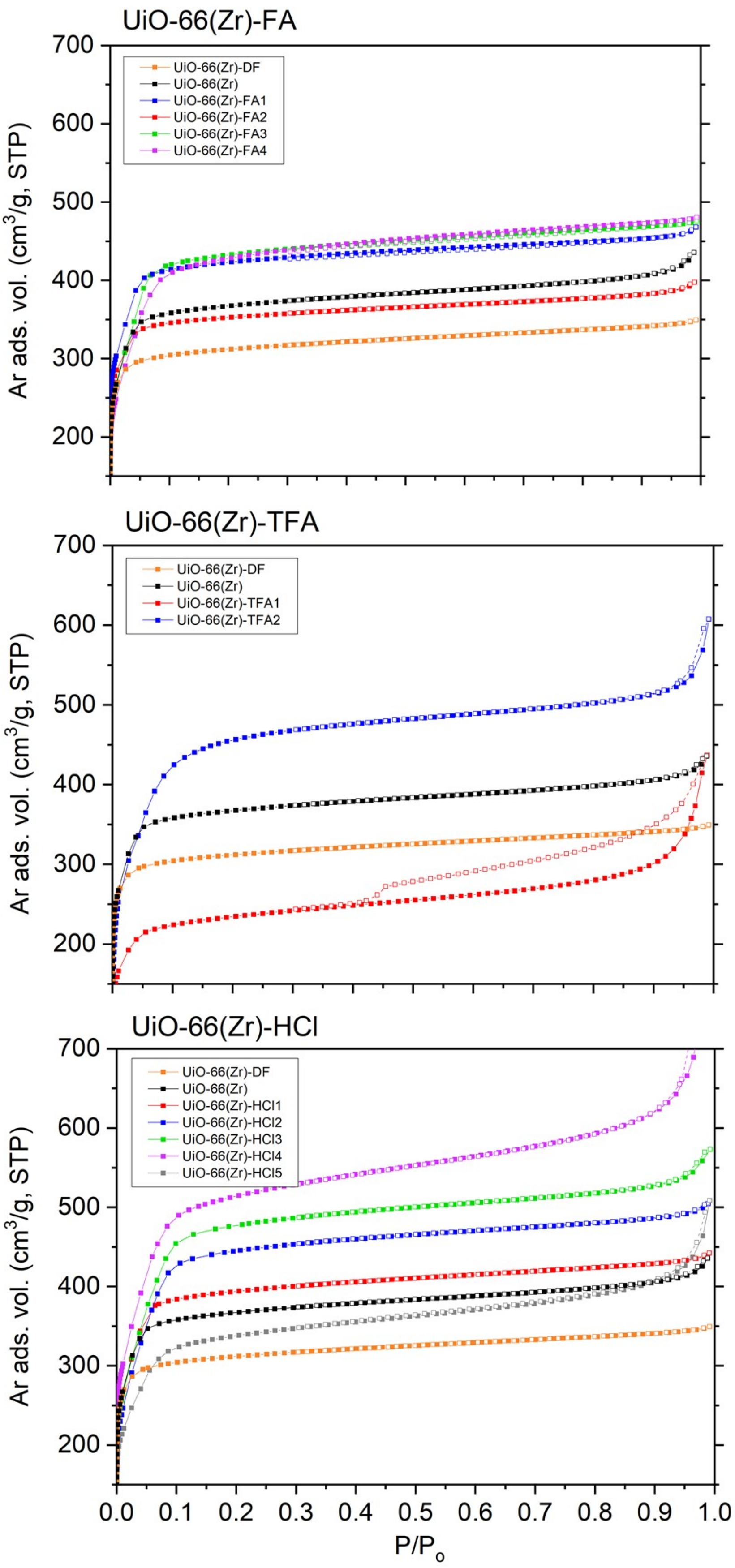


Fig. ESI-3 Argon adsorption-desorption isotherms of UiO-66(Zr)-DF, UiO-66(Zr) parent and modulated UiO-66(Zr) series of materials.

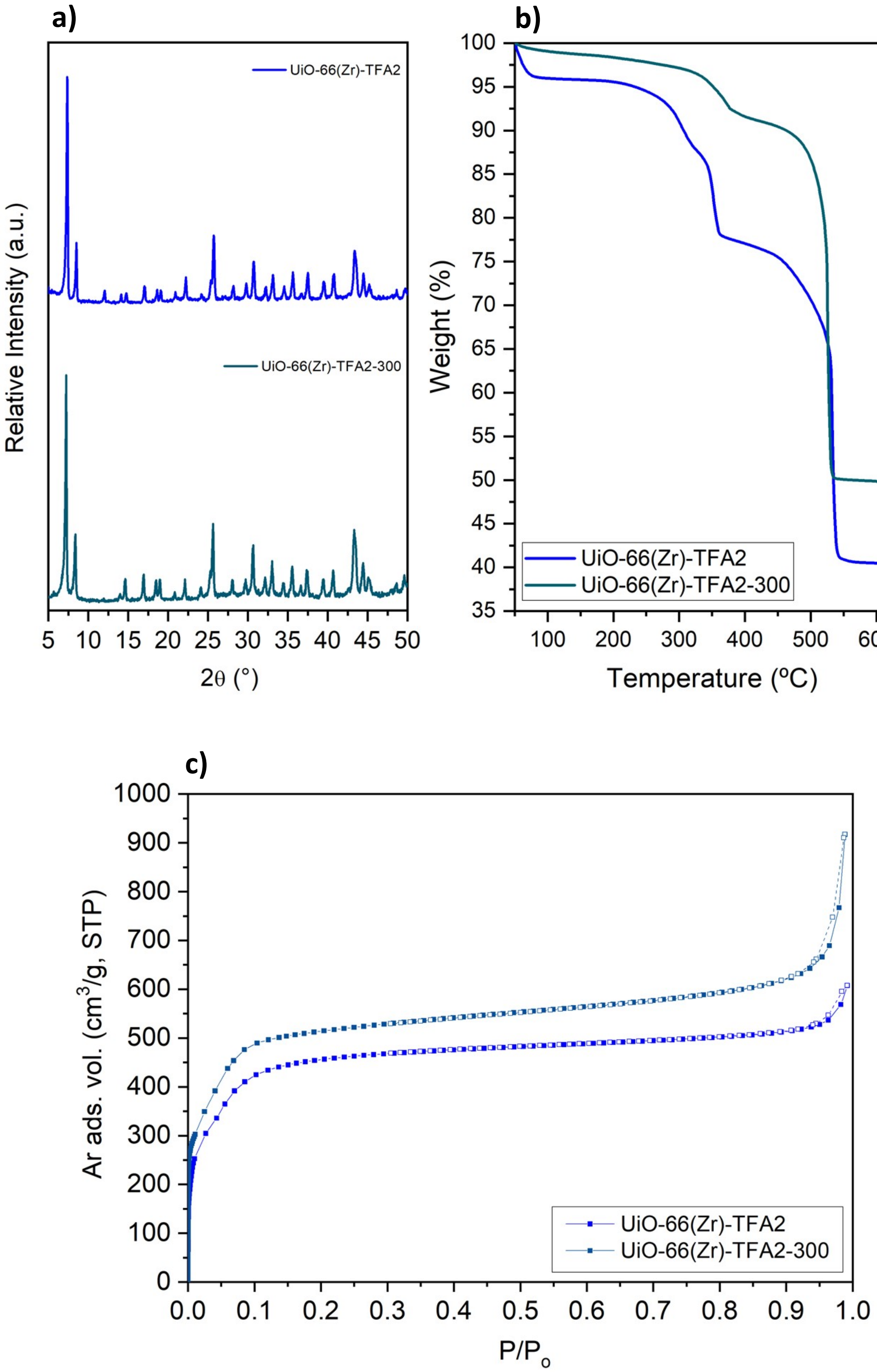


Fig. ESI-4 a) Powder X-ray diffraction patterns; b) Thermogravimetry analysis, and c) Argon adsorption-desorption isotherms of UiO-66(Zr)-TFA2 and UiO-66(Zr)-TFA2-300.

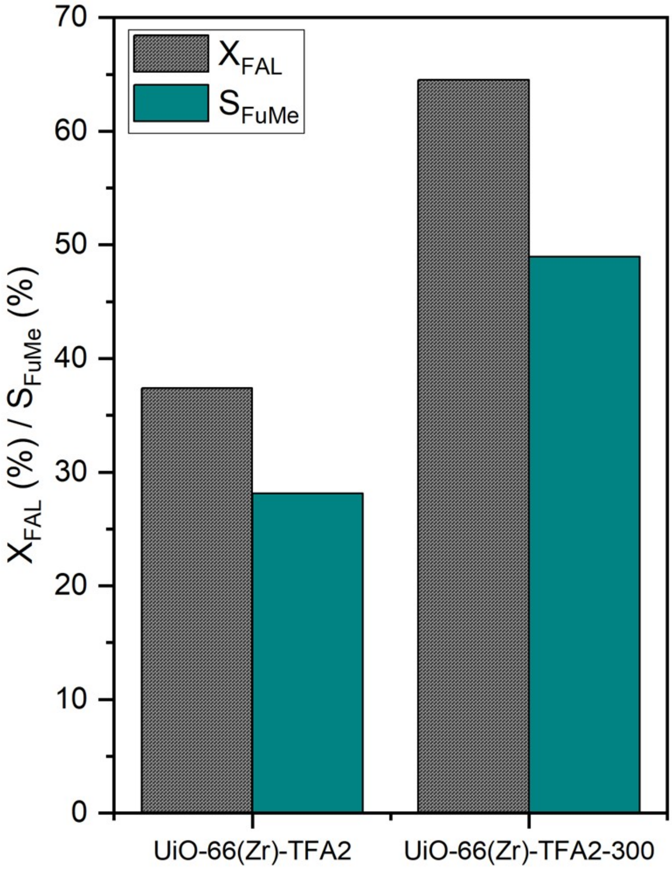
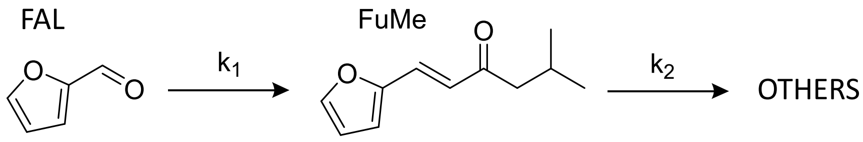


Fig. ESI-5 Catalytic activity of UiO-66(Zr)-TFA2 and UiO-66(Zr)-TFA2-300 in the aldol condensation of FAL and MIBK. Reaction conditions: time = 4 h; temperature = 130 °C; MIBK/FAL molar ratio = 4; FAL/Cat mass ratio = 10.



Scheme ESI-1. Transformations and constants considered for the kinetics analysis of the aldol condensation of FAL and MIBK.

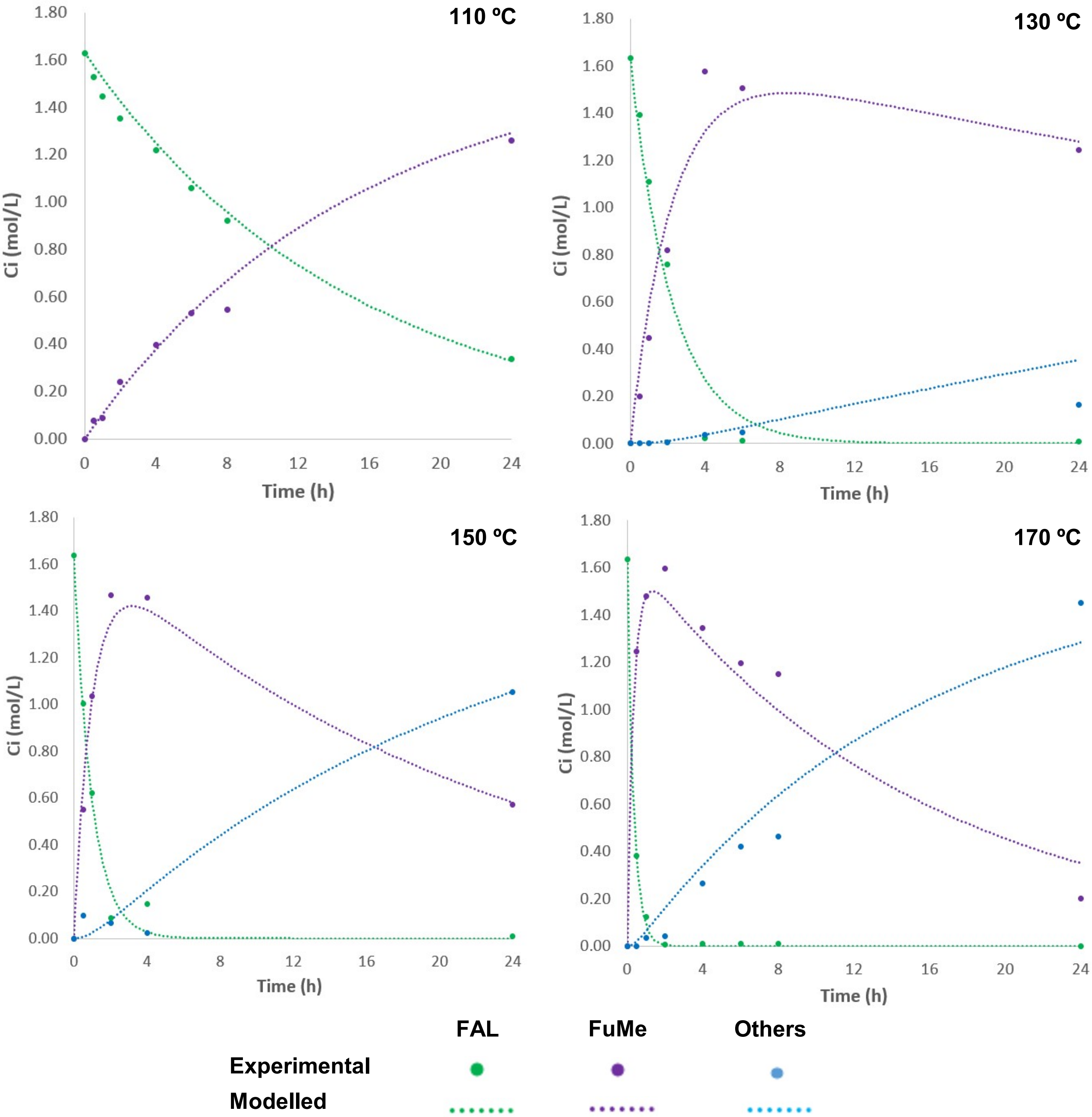


Fig. ESI-6. Experimental (symbols) and modelled (dash lines) concentrations of the compounds involved in the aldol condensation of FAL and MIBK over UiO-66(Zr)-HCl3. Reaction conditions: MIBK/FAL molar ratio = 4/1; FAL/Cat mass ratio = 10/1.

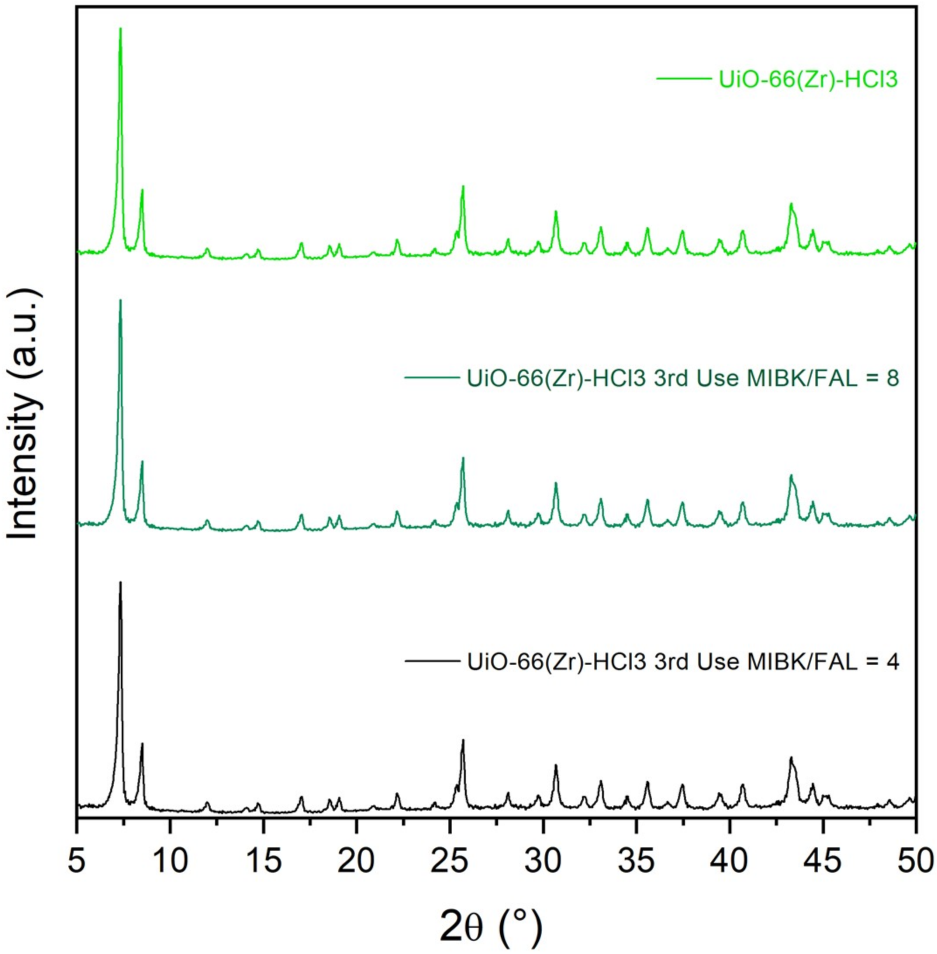


Fig. ESI-7. Powder X-ray diffraction patterns of the UiO-66(Zr)-HCl3, fresh and after three consecutive uses in reaction under different dilution. Reaction conditions: time = 3 h; temperature = 130 °C; MIBK/FAL molar ratio = 4 (FAL/Cat = 10) and 8 (FAL/Cat = 5).