Supporting Information

Methanol-to-Olefins Conversion over Small-Pore DDR Zeolites: Tuning the Propylene Selectivity *via* the Olefins-Based Catalytic Cycle

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Table S1. Textural properties of DDR zeolites with different Si/Al ratios.

Catalyst	Si/Al ratio [a]	S_{BET} [b] m^2/g	Total Volume [c] cm^3/g	$V_{Micpore}$ [d] cm^3/g	V_{Ext} [e] cm^3/g	$S_{Micpore}$ [f] m^2/g
DDR_22	22	276	0.147	0.088	0.059	230
DDR_43	43	296	0.173	0.097	0.076	234
DDR_87	87	263	0.140	0.085	0.055	228
DDR_172	172	248	0.148	0.078	0.070	189
DDR_172*	168	213	0.138	0.053	0.085	143

[a] Si/Al ratio was tested by ICP-OES
[b] BET surface area
[c] Total pore volume determined at the absorption pressure P/P_0 = 0.95.
[d] The volume of micropores (< 1.5 nm) calculated by the NLDFT method.
[e] The external pore volume cauculated from the total volume and the volume of micropores.
[f] Surface area of micropores calculated by the NLDFT method.

Table S2. Reaction conditions used for DDR zeolites.[#]

DDR samples	**DDR_22**	**DDR_43**	**DDR_87**	**DDR_172**	**DDR_172***
MeOH flow rate (mL/min)	0.0016	0.002	0.0011	0.001	0.0012
Carry gas (He) flow rate (mL/min)	20	20	20	20	20
Catalyst weight (mg)	11	15	20	30	50
SiC weight (mg)*	110	100	105	95	80
WHSV (g_{MeOH} g_{Cat}^{-1} h^{-1})	6.9	6.3	2.6	1.6	1.1
MeOH conversion (%)	51.2	51.6	46.4	47.1	52.9

[#] The reactions are performed at 400 °C and 10 mins on stream
[*] SiC is added to dilute the catalyst and its amount is adjusted to keep the length of catalyst bed identical

Table S3. Reaction conditions used for HZSM-5 zeolites.[#]

Si/Al in the HZSM-5 samples	**55**	**115**	**651**	**1119**	**1580**
DME pressure /kPa	55	57	54	51	49
Total feed pressure /kPa	104	105	106	103	104
Space-velocity /mol C (mol Al-s)$^{-1}$	0.36	2.40	3.98	3.23	2.80
Net carbon converted /%	47	48	48	46	52

[#] Crystallite size of HZSM-5: 150–240 nm; reaction temperature: 350 °C. See more details in reference 31.

Table S4. Conversion-weighed average selectivity over the entire deactivation cycle.

DDR samples	**DDR_22**	**DDR_172**	**DDR_172***
Amount of converted MeOH (mmol)	19.38	10.33	17.38
Yield of $C_2^=$ / $C_3^=$ / $C_4^=$ / C_{5+} / C_{1-4}^- (mmol C)	6.88 / 7.23 / 1.79 / 0.74 / 2.75	2.75 / 5.17 / 1.02 / 0.48 / 0.90	4.04 / 9.32 / 1.89 / 0.77 / 1.36
Selectivity of $C_2^=$ / $C_3^=$ / $C_4^=$ / C_{5+} / C_{1-4}^- (C%)	35.48 / 37.28 / 9.23 / 3.84 / 14.17	26.64 / 50.07 / 9.91 / 4.64 / 8.74	23.27 / 53.64 / 10.85 / 4.43 / 7.81

Table S5. Quantification of residual species (overall aliphatics and MBs) analyzed in Figure 5 by integrating their peak areas in the GC profiles.

DDR samples	**Area of Aliphatics**	**Area of MBs**	**MBs/Aliphatics**
DDR_22	268775	480579	1.788
DDR_172	345415	406185	1.176
DDR_172*	278593	113327	0.407

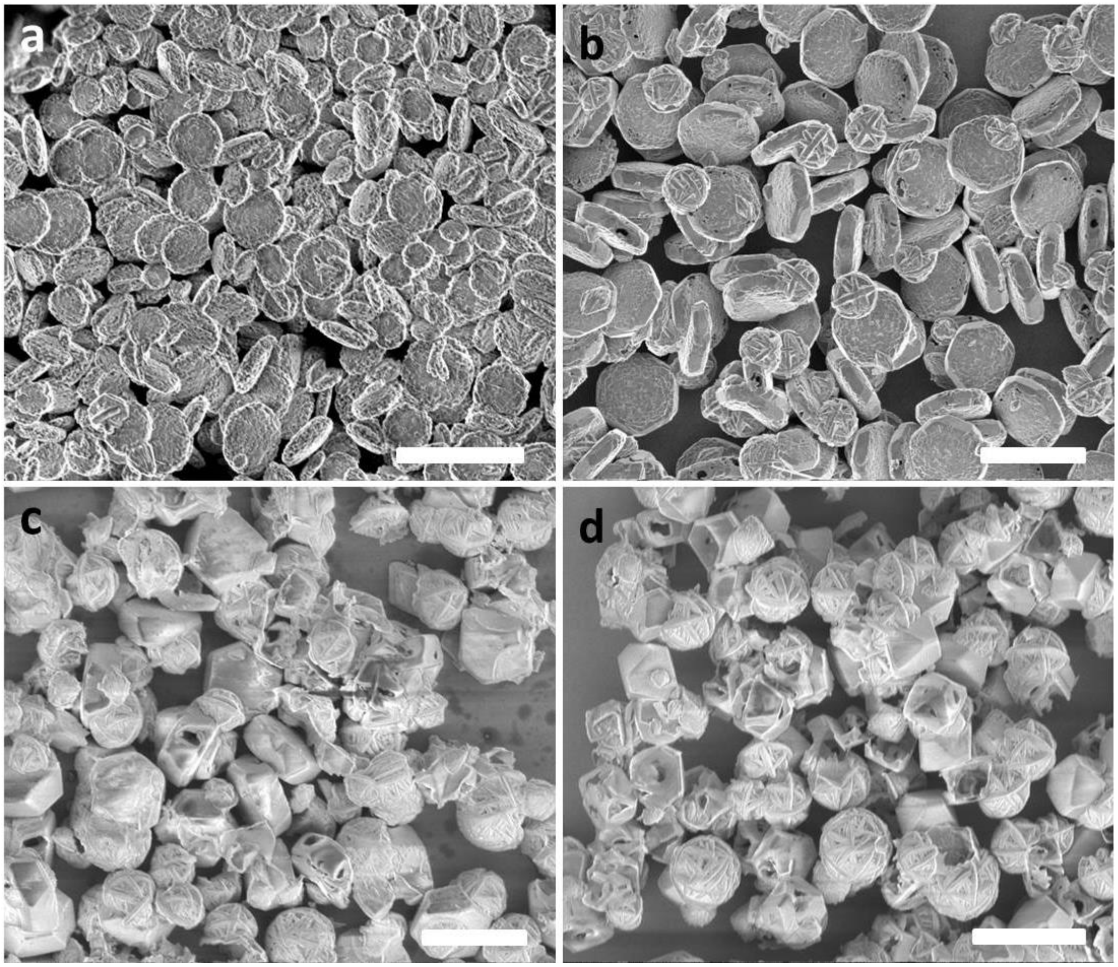

Figure S1. SEM images of as-synthesized DDR zeolites with different Si/Al ratios: (a) Si/Al = 22; (b) Si/Al = 43; (c) Si/Al = 87; (d) Si/Al = 172. The scale bars represent 10 μm.

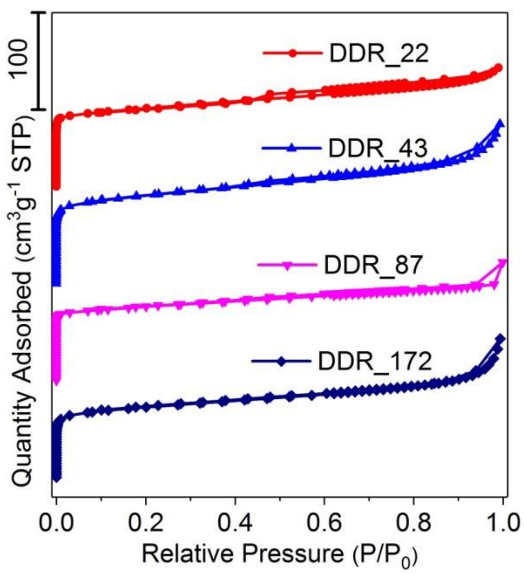

Figure S2. Ar adsorption isotherms of DDR zeolites with different Si/Al ratios.

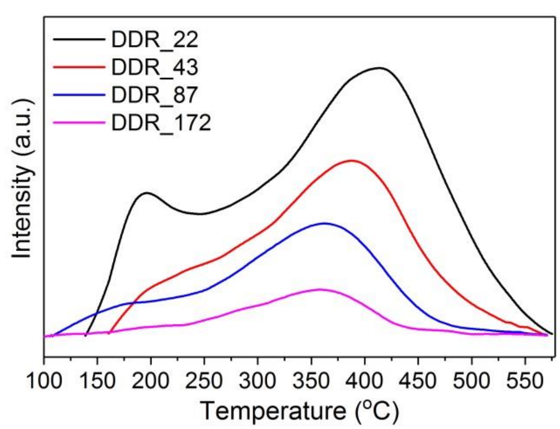

Figure S3. NH_3-TPD profiles of the as-synthesized DDR zeolites with different Si/Al ratios.

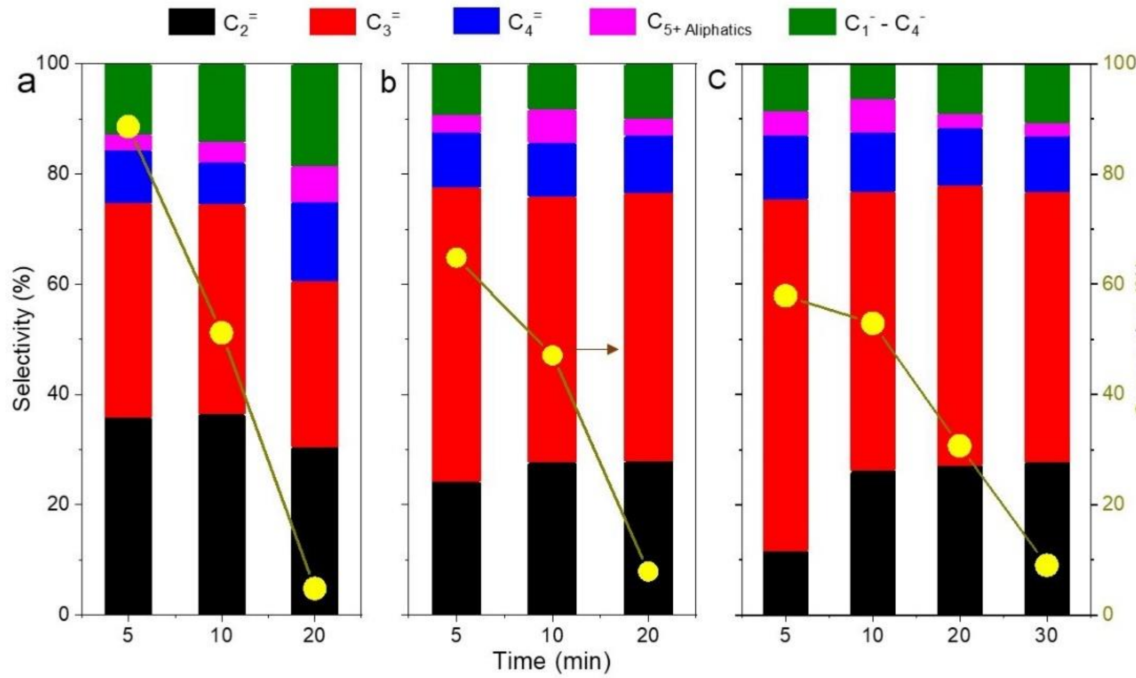

Figure S4. Conversion of methanol and effluent hydrocarbon product selectivity versus time-on-stream during the reaction of MTO over DDR_22 (a), DDR_172 (b) and DDR_172* (c).

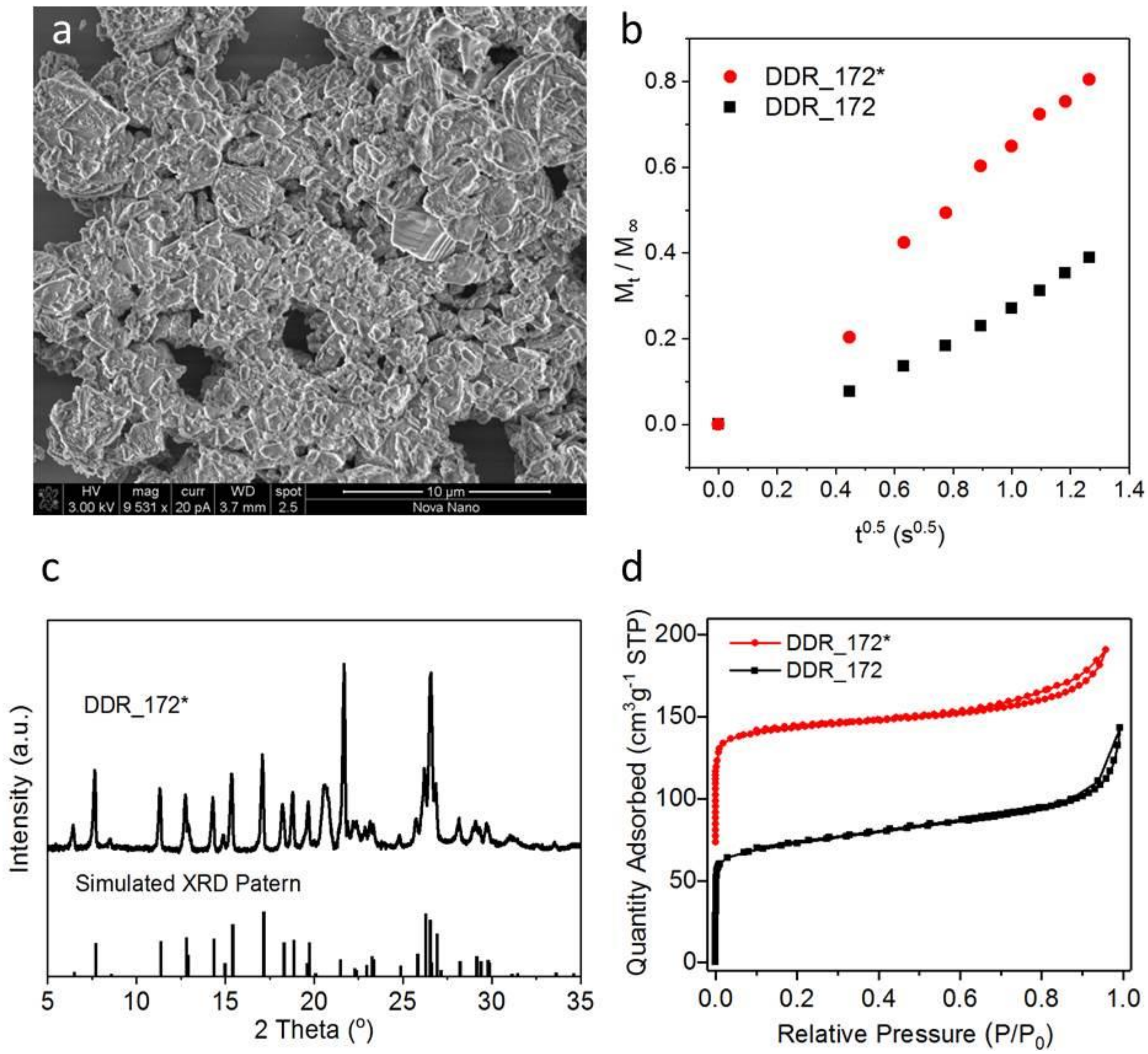

Figure S5. (a) SEM image of DDR_172*. (b) Adsorption uptake of propylene on DDR_172* in comparison with that of DDR_172. (c) PXRD pattern of DDR_172*. (d) Ar adsorption isotherms of DDR_172* in comparison with that of DDR_172.

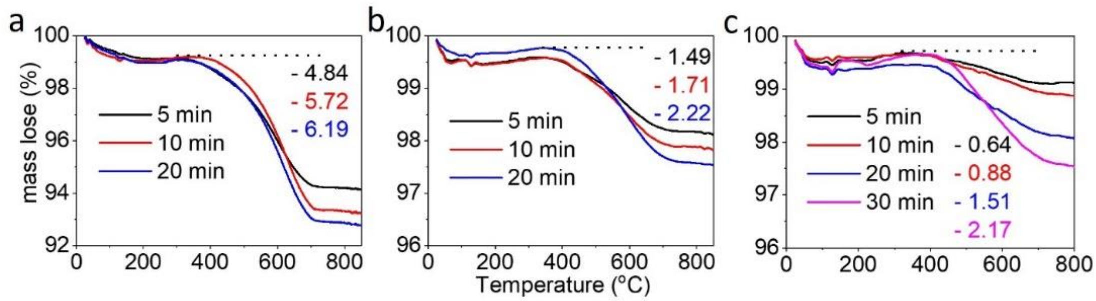

Figure S6. Thermogravimetric analysis of used catalysts (a, DDR_22; b, DDR_172; c, DDR_172*) at different reaction times.

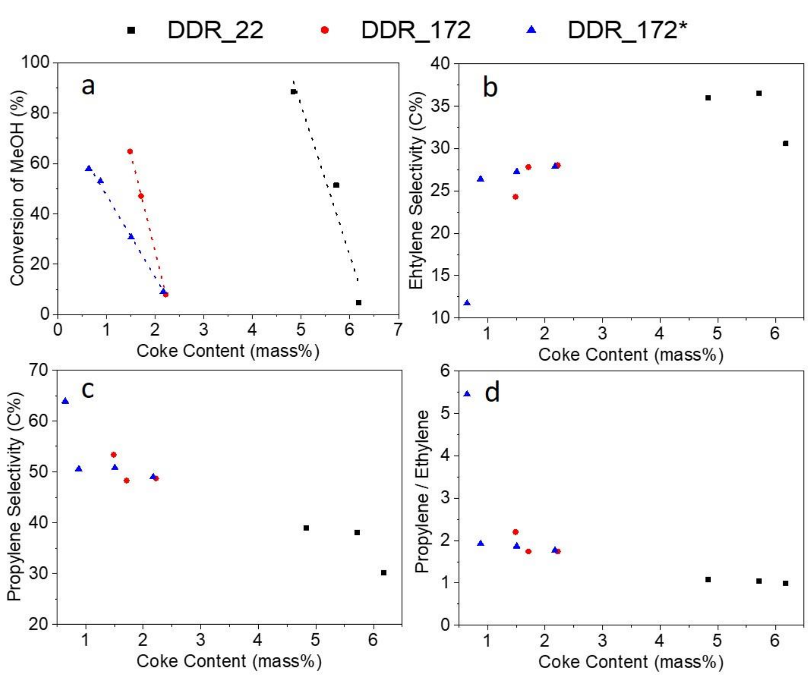

Figure S7. Plots of conversion of methanol (a), Ethylene selectivity (b), Propylene selectivity (c), and Propylene/Ethylene ratio (d), as a function of the coke content in used DDR zeolites.

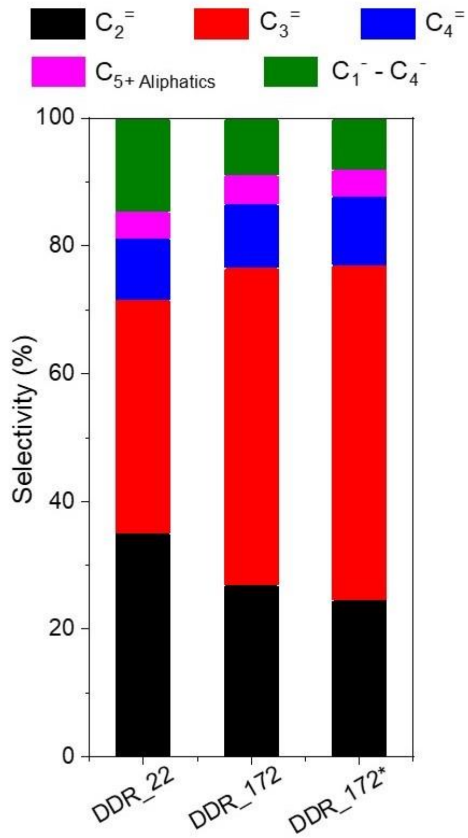

Figure S8. Conversion-weighed averaged selectivity over the entire reaction on DDR_22, DDR_172, and DDR_172*, as labelled.

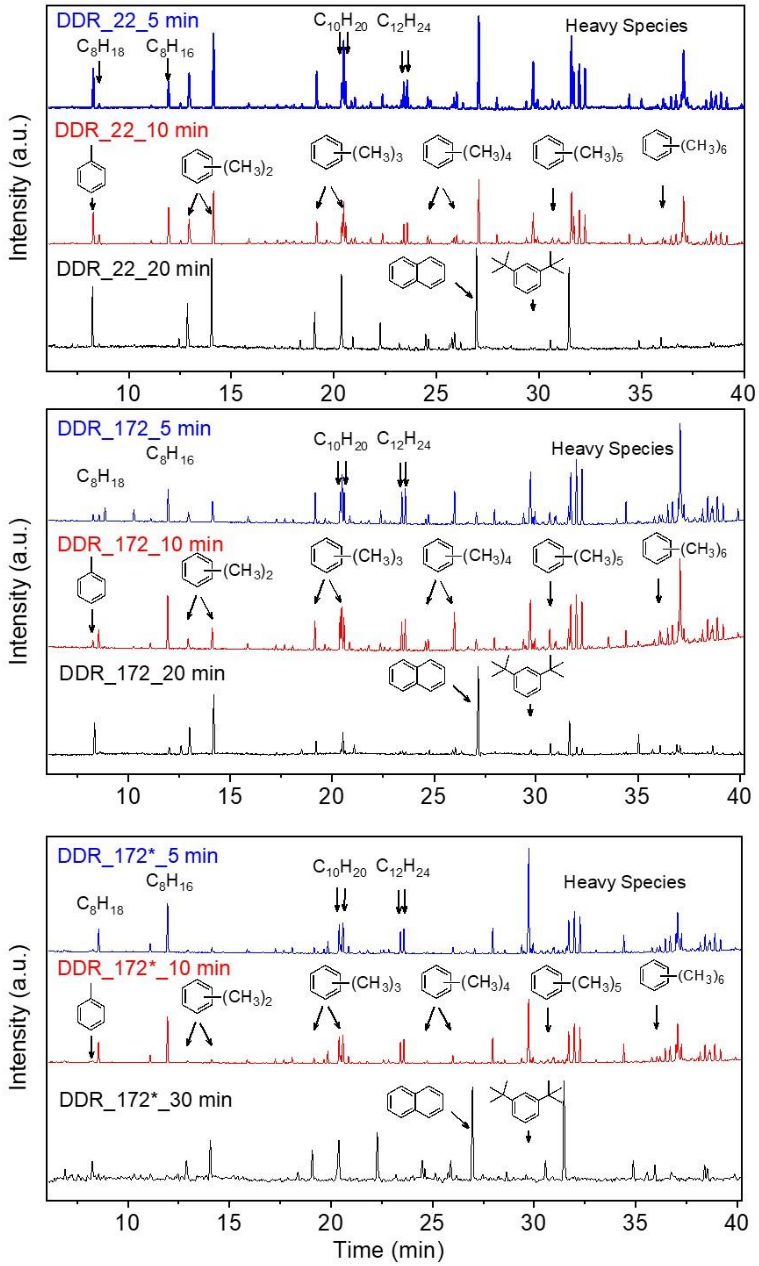

Figure S9. GC analysis of the residual hydrocarbon species extracted from used DDR catalysts (DDR_22, DDR_172 and DDR_172* from top to down) at different reaction times.

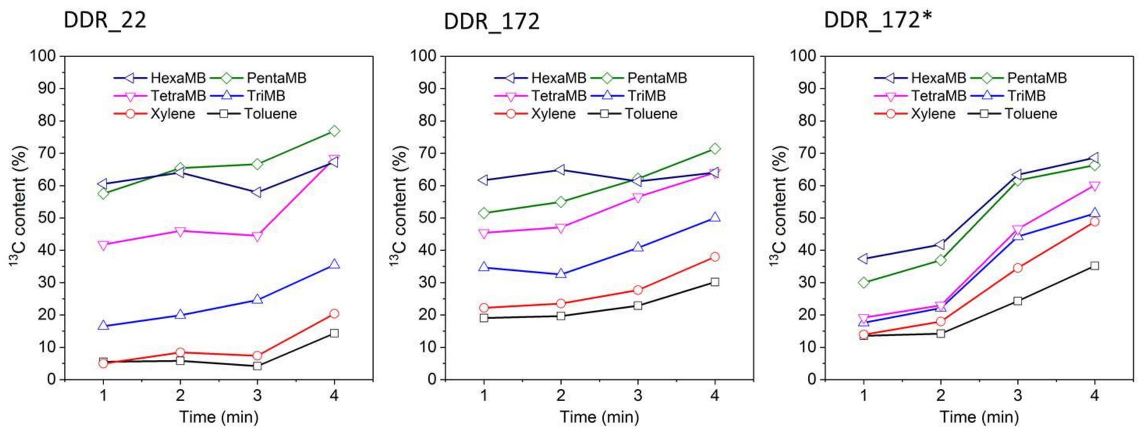

Figure S10. Evolution of ^{13}C content in the residual species in the used catalysts after ^{12}C/ ^{13}C-methanol feed switch over different DDR zeolites.