Supporting Information

Table. S1 Catalytic evaluation of regenerated catalysts at 310 °C, WHSV of 1.8 h^{-1} and ethanol/acetaldehyde mole ratio of 3.5 for 10 h.

Catalyst	Con.(%)	Selectivity (C mol%)							
		EL	PL	BL	BD	DE	EA	BU	C6+
Fresh	33.5	4.9	1.4	0.4	84.2	3.3	1.5	0.5	3.8
1st regeneration	32.6	3.8	1.9	0.5	85.0	3.8	0.9	1.1	3.3
2nd regeneration	33.2	3.0	1.5	0.4	85.8	4.5	1.0	1.2	2.6

Table. S2 The influence of different addition amount of water on the catalytic activity at 310 °C, WHSV of 1.8 $h^{-1}$and ethanol/acetaldehyde mole ratio of 3.5 for 10 h.

H_2O content (vol%)	Con./%	Selectivity (C mol%)							
		EL	PL	BL	BD	DE	EA	BU	C6+
0	33.5	4.9	1.4	0.5	84.2	3.3	1.5	0.5	3.8
5	38.1	4.4	1.6	1.3	85.0	2.7	1.7	0.4	3.1
10	34.2	3.1	2.0	1.5	86.6	1.9	1.3	0.4	3.2
15	31.8	2.9	3.0	1.6	85.3	1.5	1.5	0.5	3.9

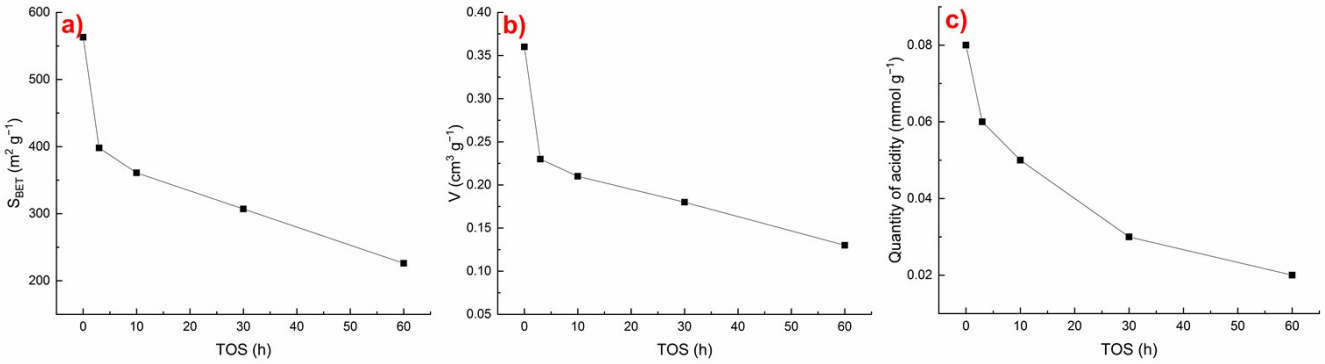


Fig. S1 Change of (a) specific surface area, (b) pore volume and (c) the total amount of acid sites with increasing of TOS.

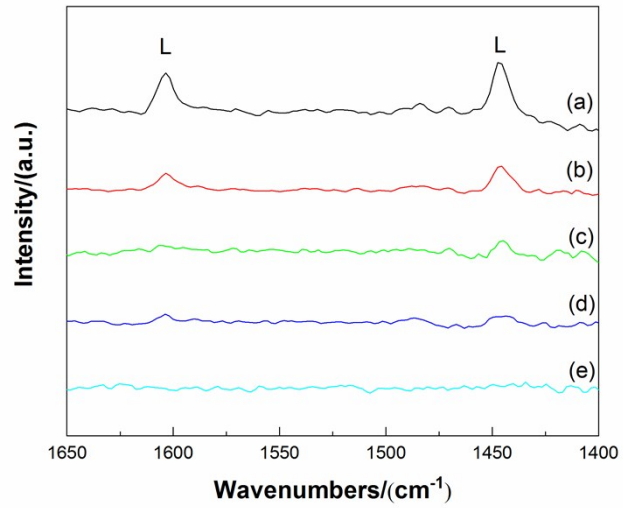


Fig.S2 Py-IR spectra of catalysts with different TOS. (a) 0 h; (b) 3 h; (c) 10 h; (d) 30 h; (e) 60 h.

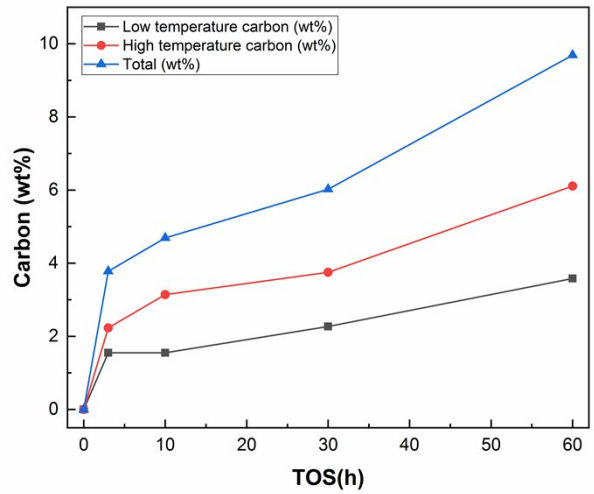


Fig. S3 Accumulation rate of two type carbon deposit

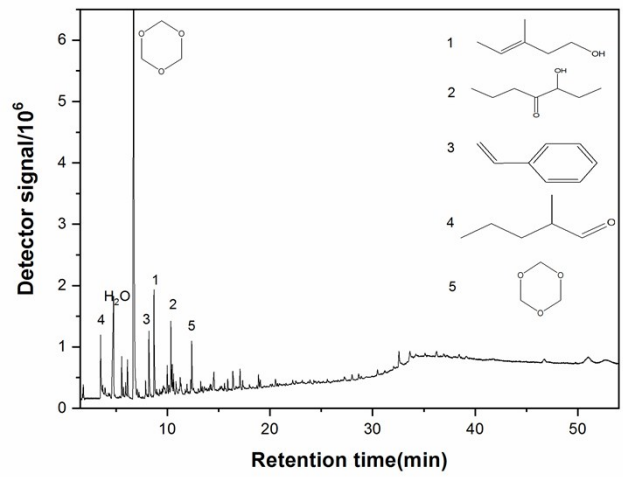
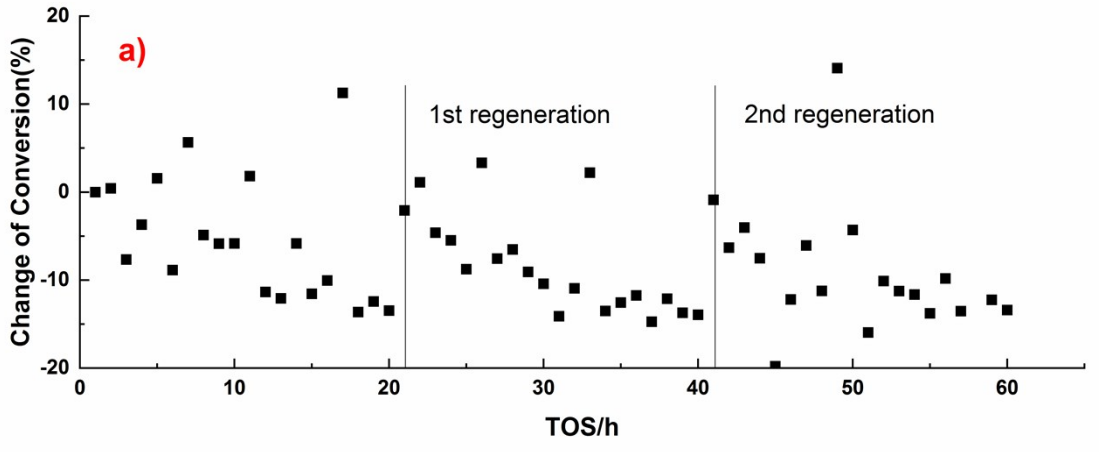


Fig. S4 GC-MS spectroscopy of extraction raffinate in the CH_2Cl_2 extraction of the used catalysts



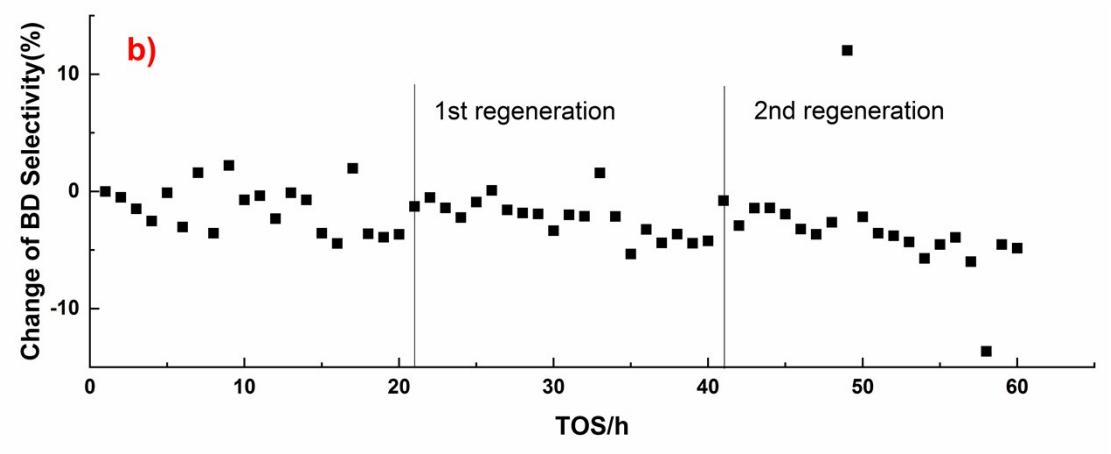


Fig. S5 Changes of Conversion and BD Selectivity. a) Conversion; b) BD Selectivity

The catalyst was regenerated insitu in the reactor and the run-time for tests with catalyst after first and second regeneration was recorded. The regeneration cycles were conducted under flowing synthetic air at 650 °C for 6 h. Due to the change of conversion and BD selectivity was not obvious, we processed the data and change of conversion or selectivity was calculated as follows:

$$Change\ of\ \ Conversion = \frac{C_n - C_1}{C_1} \times 100\%;$$

$$Change\ of\ \ Selectivity = \frac{S_n - S_1}{S_1} \times 100\%$$

C1, S1 means conversion or BD selectivity of 1 h of TOS;
Cn, Sn means conversion or BD selectivity of 1 h of TOS (n≤60).