Supporting Information

Selective Linear Ethylene Oligomerization over Nickel-Containing Zeotypes with Tetravalent Framework Heteroatoms

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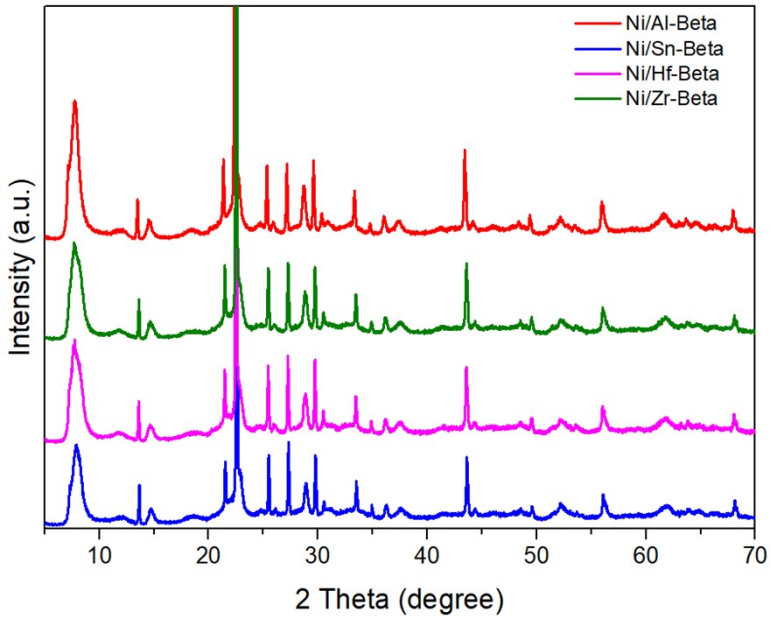

Figure S1 XRD patterns of representative nickel loaded Beta zeotypes.

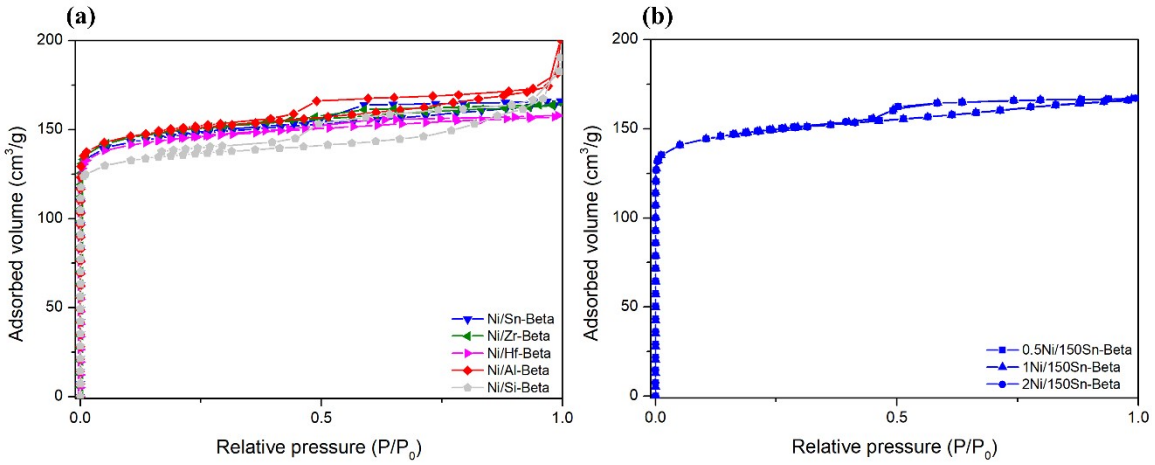

Figure S2 N_2-adsorption/desorption isotherms for: (a) different heteroatom-incorporated Beta zeotypes with 1 wt% nickel loading; and (b) tin-incorporated Beta zeotypes with various nickel loadings.

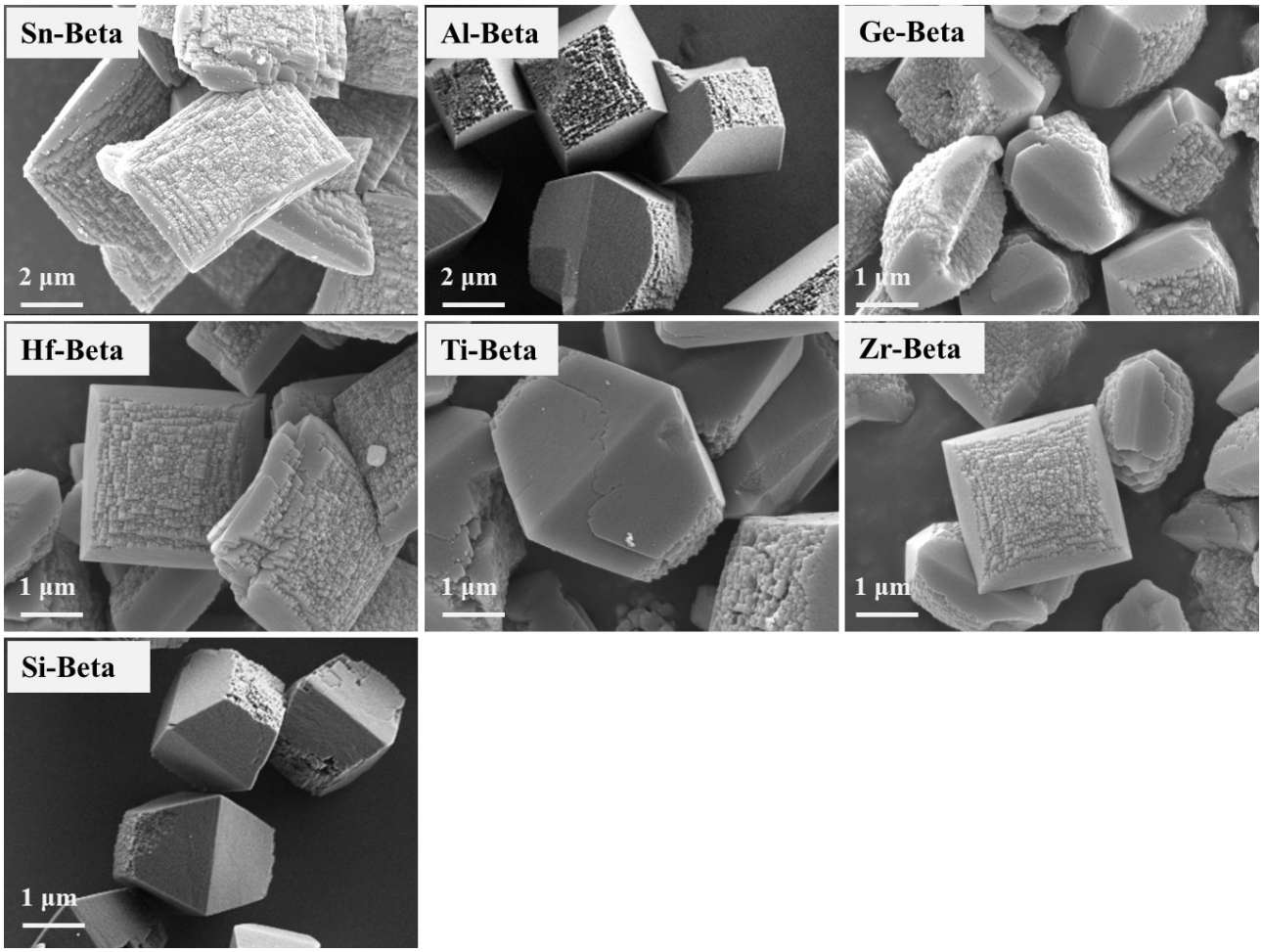

Figure S3 SEM images of representative Beta zeotype supports.

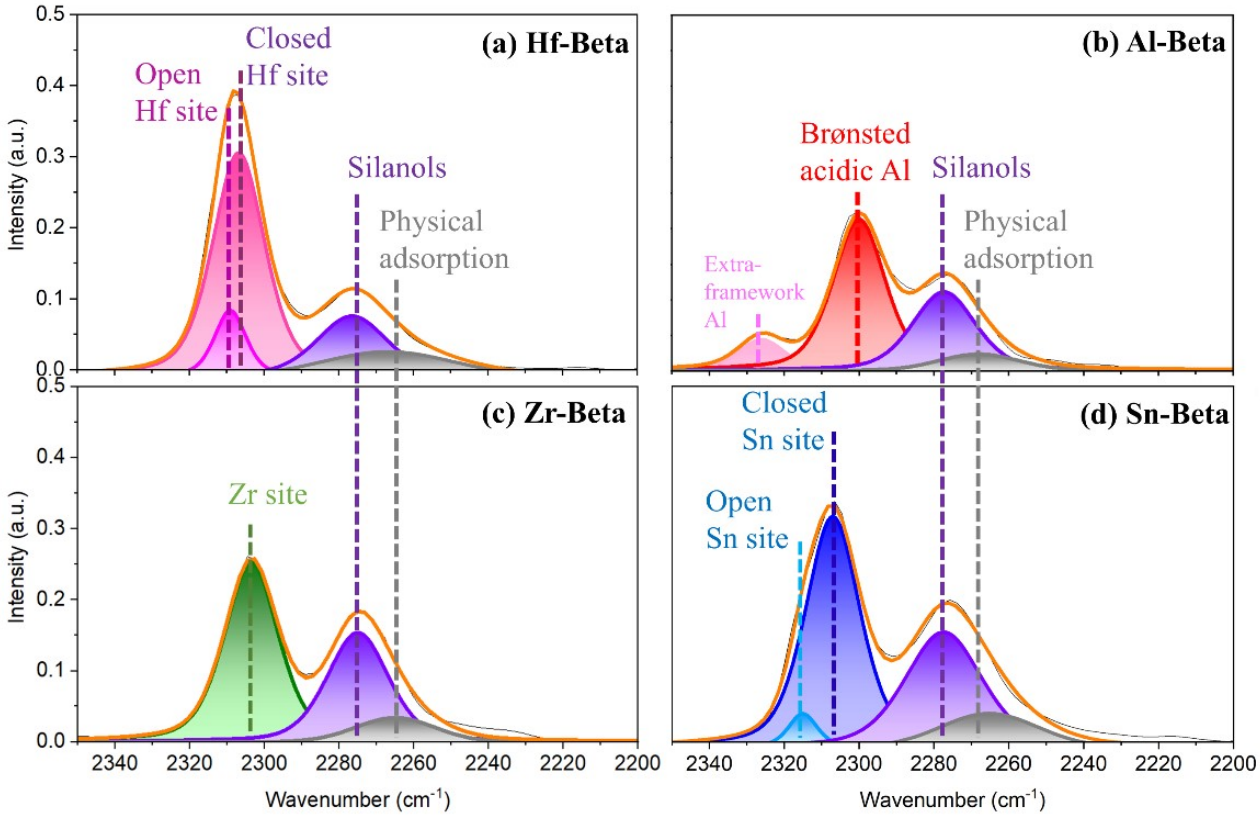

Figure S4 IR spectra within C≡N stretching region for CD_3CN adsorbed over M-Beta zeotypes.

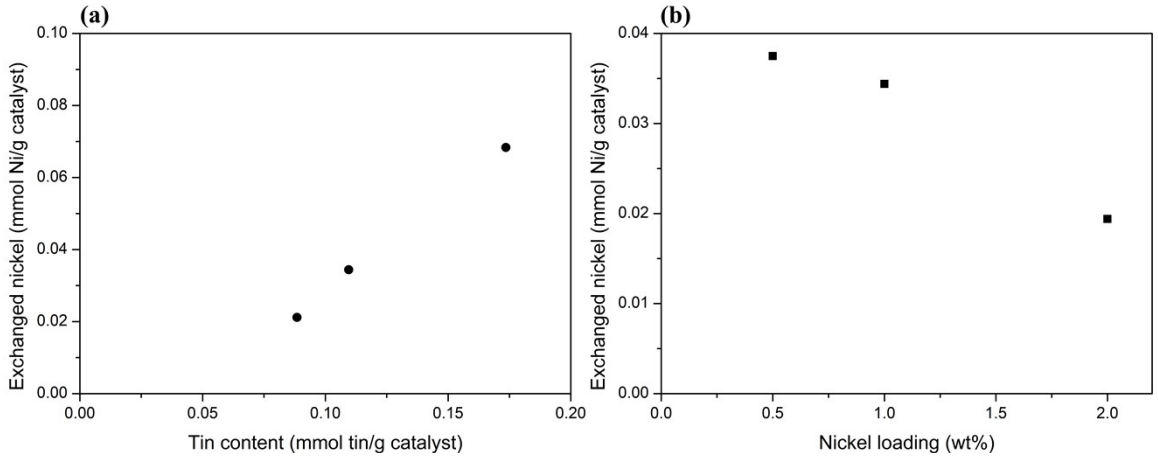

Figure S5 Correlation between exchanged nickel content and (a) tin content of Sn-Beta support, as well as (b) nickel loading of Ni/Sn-Beta catalysts.

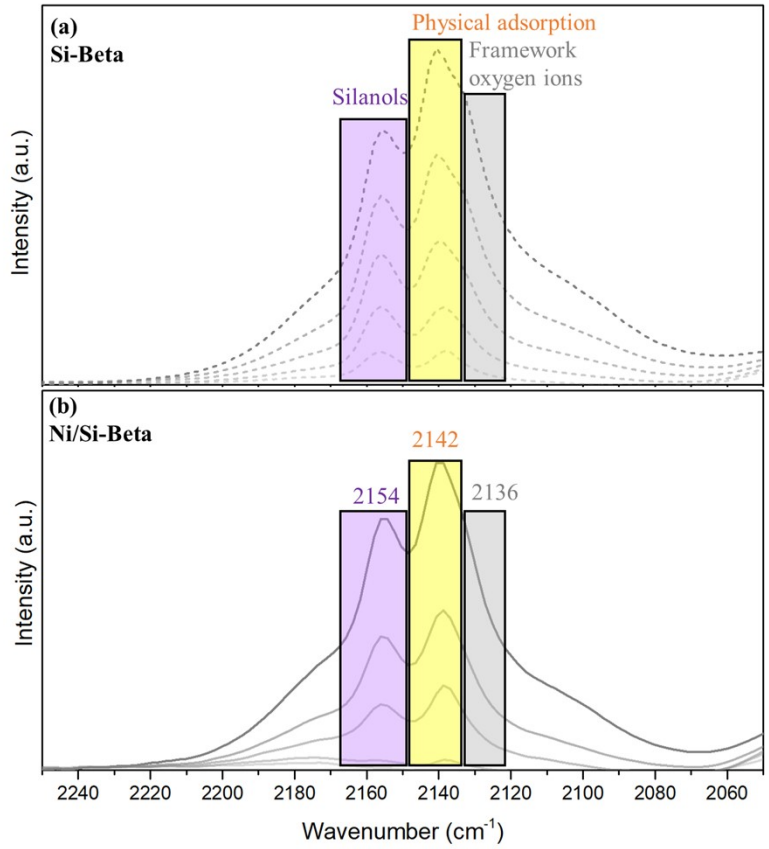

Figure S6 FTIR CO vibration region of Si-Beta (heteroatom-free) with and without nickel loading upon CO adsorption at liquid nitrogen temperature.

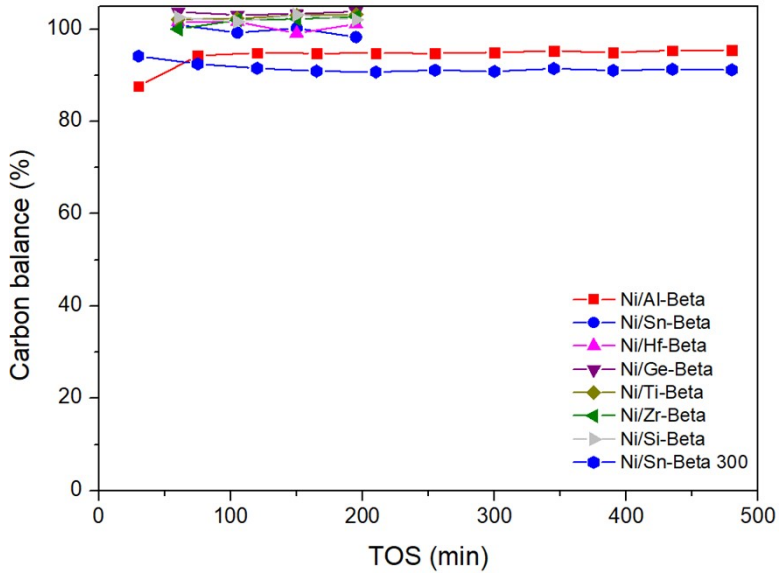

Figure S7 Carbon balance calculated based on carbon atoms.

Reference reaction conditions: 30 bar total pressure, $P_{ethylene}$ =10 bar, T= 250 °C and contact time of 0.017 min g_{cat}/mL.

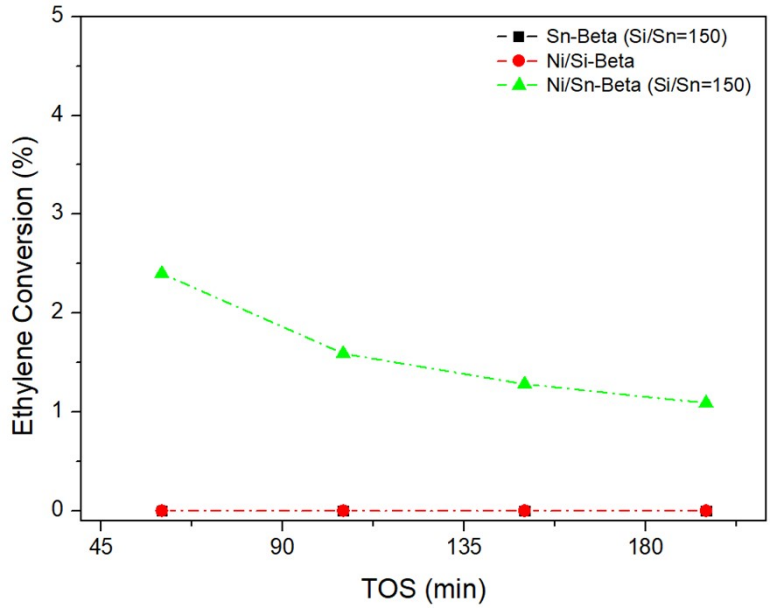

Figure S8 Ethylene conversion over Sn-Beta (nickel-free), Ni/Si-Beta (heteroatom free) and Ni/Sn-Beta catalysts.

Reference reaction conditions: 30 bar total pressure, $P_{ethylene}$ =10 bar, T= 250 °C and contact time of 0.017 min g_{cat}/mL.

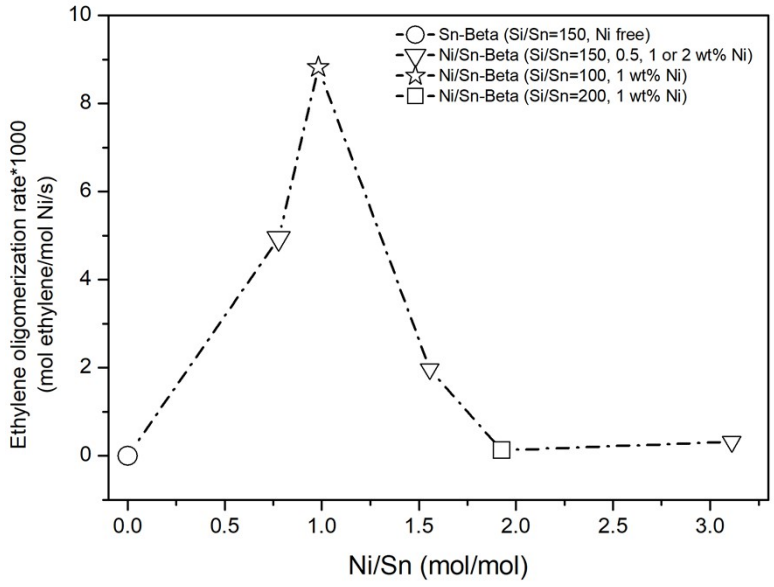

Figure S9 TOF comparison of Ni/Sn-Beta with various nickel to tin ratios with TOS=60 min.

Reference reaction conditions: 30 bar total pressure, $P_{ethylene}$ =10 bar, T= 250 °C and contact time of 0.017 min g_{cat}/mL.

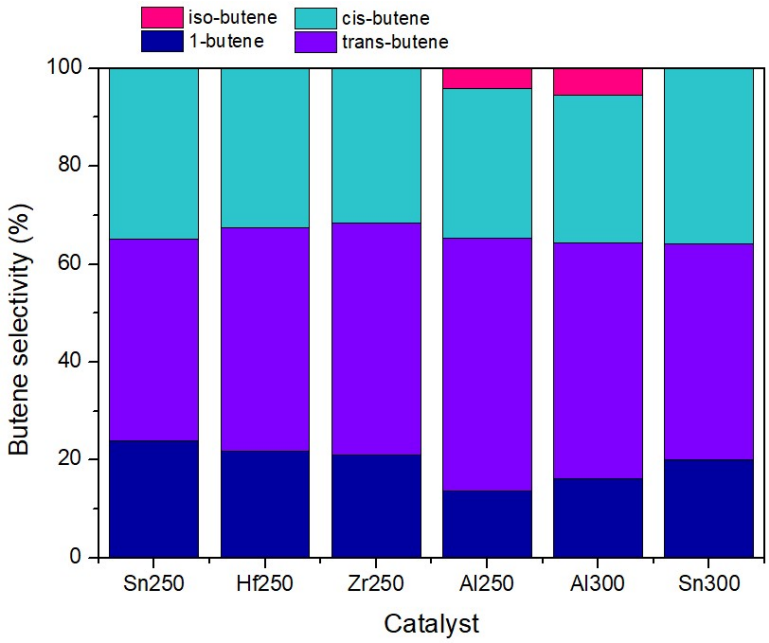

Figure S10 Butene product distribution obtained from ethylene oligomerization over Ni/M-Beta catalysts.

Reference reaction conditions: 30 bar total pressure, $P_{ethylene}$ =10 bar, T= 250 °C and contact time of 0.017 min g_{cat}/mL.

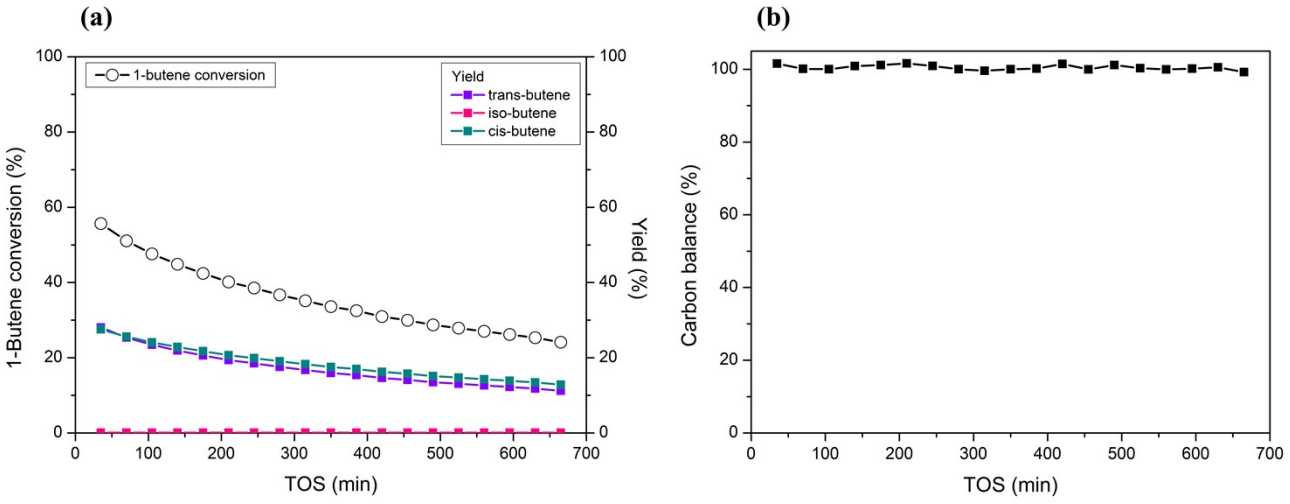

Figure S11 Results of 1-butene isomerization experiment.

(a) 1-butene conversion and yield of butene isomers; (b) carbon balance of the reaction. Reference reaction conditions: atmospheric pressure, T= 250 °C and contact time of 0.0083 min g_{cat}/mL.

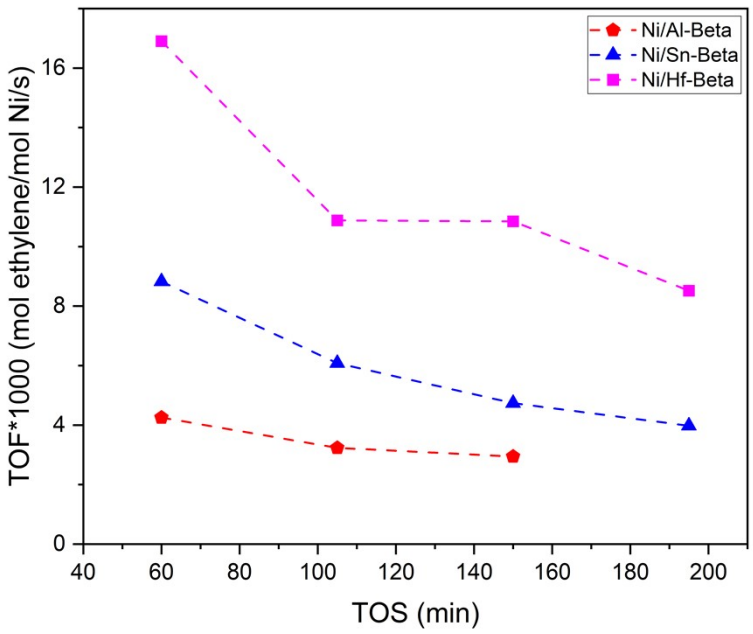

Figure S12 TOF-TOS profiles of catalysts for TPO experiments.

Reference reaction conditions: 30 bar total pressure, $P_{ethylene}$ =10 bar, T= 250 °C and contact time of 0.017 min g_{cat}/mL.

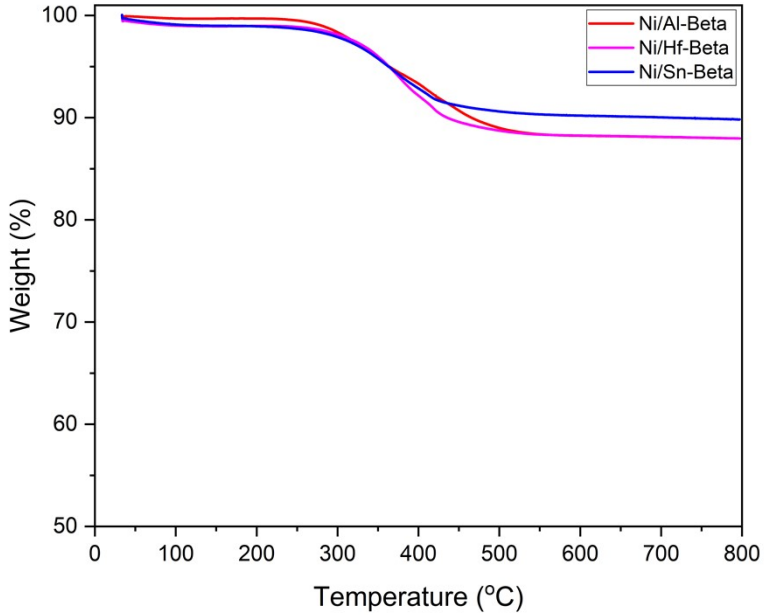

Figure S13 Weight change profile of TPO experiments.

Table S1 Textural properties of representative Ni/M-Beta catalysts.

Entry	Sample	Nominal Ni loading (wt%)	Surface Area (m^2/g)	Micropore volume (cc/g)
1	0.5Ni/150Sn-Beta	0.5	579	0.21
2	1Ni/150Sn-Beta	1	583	0.21
3	2Ni/150Sn-Beta	2	583	0.21
4	1Ni/100Sn-Beta	1	578	0.21
5	1Ni/100Zr-Beta	1	587	0.22
6	1Ni/100Hf-Beta	1	573	0.21
7	1Ni/100Al-Beta	1	591	0.21
8	1Ni/Si-Beta	1	537	0.20

Table S2 Ion exchange capacity of different zeotype supports.

Entry	Catalyst	Heteroatom	Silicon to M	Nominal Ni loading	Exchanged	Exchanged

		content	ratio			Ni	Ni/heteroatom
		mmol/g		wt%	mmol/g	mmol/g	
1	Ni/Sn-Beta	0.174	94	1	0.170	0.068	0.39
2	Ni/Zr-Beta	0.143	110	1	0.170	0.044	0.31
3	Ni/Ti-Beta	0.131	123	1	0.170	0.008	0.06
4	Ni/Al-Beta	0.110 (nominal)	150 (nominal)	1	0.170	0.043	0.39
5	Ni/Si-Beta	0	-	1	0.170	0.008	-
6	Ni/Sn-Beta	0.088	185	1	0.170	0.021	0.24
7	Ni/Sn-Beta	0.110	150	0.5	0.085	0.037	0.34
8	Ni/Sn-Beta	0.110	150	1	0.170	0.034	0.31
9	Ni/Sn-Beta	0.110	150	2	0.341	0.019	0.18
10	NiO/Sn-Beta	0.110	150	1	0.170	0.002	0.02

Table S3 Total mass loss of catalyst samples after TPO experiments under air atmosphere.

Entry	Sample	Mass loss (%)
1	Ni/Al-Beta (300 °C, used)	12.0
2	Ni/Al-Beta (250 °C, used)	11.6
3	Ni/Hf-Beta (250 °C, used)	12.0
4	Ni/Sn-Beta (250 °C, used)	10.2
5	Ni/Sn-Beta (Fresh)	0.4