

Fig. S1 Typical mass spectra of the alkylation products of α -pinene with Isobut-5
a, b- C_8H_{16} ; c, d- $C_{10}H_{16}$; e, f- $C_{12}H_{24}$; g, h- $C_{14}H_{24}$; i- $C_{15}H_{26}$; j- $C_{18}H_{28}$; k, l- $C_{20}H_{32}$

Table S1 Molecular size of reactants and products in alkylation system of α -pinene with Isobut-5



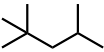


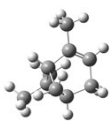


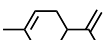
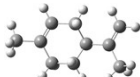

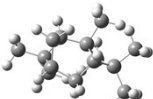
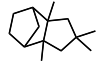
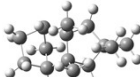
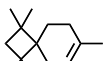
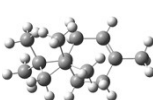
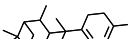
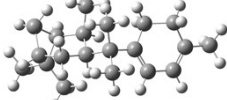
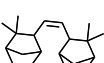
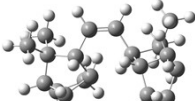
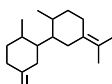
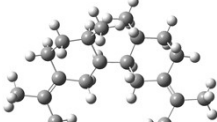
Typical chemical formula	Molecular formula	Optimized structure	Diameter/nm
	C_4H_8		0.40
	C_8H_{18}		0.52
	$C_{10}H_{16}$		0.58
	$C_{10}H_{16}$		0.56
	$C_{10}H_{14}$		0.56
	$C_{14}H_{24}$		0.61
	$C_{14}H_{24}$		0.61
	$C_{14}H_{24}$		0.63
	$C_{20}H_{32}$		0.73
	$C_{20}H_{32}$		0.69
	$C_{20}H_{34}$		0.71

Table S2 Physicochemical properties of various zeolites

Sample	Si/Al ^a	Acidity ^b (mmolNH ₃ /g)			120 °C ^c			180 °C ^c			250 °C ^c		
		Weak	Medium	Total	C _{BRONSTED} (μmol/g)	B/L	C _{LEWIS} (μmol/g)	C _{BRONSTED} (μmol/g)	B/L	C _{LEWIS} (μmol/g)	C _{BRONSTED} (μmol/g)	B/L	C _{LEWIS} (μmol/g)
Hβ-25n	14.0	0.46	0.17	0.63	102	2.6	39	90	3.3	27	68	3.6	19
HY	1.8	1.55	0.18	1.73	370	0.7	536	240	0.9	269	126	1.1	116
HZSM-5	7.7	0.78	0.31	1.09	166	7.5	22	135	20.2	7	94	27.7	3
HZSM-35	11.6	0.50	0.30	0.80	79	4.1	19	63	8.8	7	45	13.4	3
HSAPO-11	0.1	0.50	0.08	0.58	56	1.0	54	40	3.2	12	28	4.7	6

^a Determined by XRF.

^b Estimated from NH₃-TPD profiles.

^c Determined by FT-IR/pyridine desorption.

Table S3 Textural properties of various zeolites

Samples	V _{micro} ^a (cm ³ /g)	V _{meso} ^b (cm ³ /g)	V _{total} ^c (cm ³ /g)	S _{BET} ^d (m ² /g)	S _{micro} ^e (m ² /g)	S _{exter} ^f (m ² /g)
Hβ-25n	0.18	0.14	0.41	724.8	461.8	262.9
HY	0.31	0.05	0.40	951.6	812.6	139.0
HZSM-5	0.11	0.03	0.19	405.7	292.1	113.5
HZSM-35	0.10	0.06	0.18	313.4	267.8	45.5
HSAPO-11	0.02	0.12	0.15	90.9	58.7	32.2

^a V_{micro}, micropore volume.

^b V_{meso}, mesopore volume.

^c V_{total}, total pore volume measured at P/P₀=0.98.

^d S_{BET}, total specific surface area.

^e S_{micro}, micropore surface area.

^f S_{exter}, external and mesopore surface area.

Table S4 Structure properties of Hβ-25n, Hβ-25m, and Hβ-50m

Sample	Si/Al		Particle size ^b (nm)	D(4,3) ^c (μm)	D(3,2) ^d (μm)	S _{BET} (m ² /g)	S _{micro} (m ² /g)	S _{exter} (m ² /g)	V _{micro} (cm ³ /g)	V _{meso} (cm ³ /g)	V _{total} (cm ³ /g)
	Rational	Measured ^a									
Hβ-25n	12.5	14.0	88	1.29	0.06	724	461.8	262.9	0.18	0.14	0.41
Hβ-25m	12.5	12.0	103	0.56	0.06	572	454.6	117.8	0.17	0.14	0.35
Hβ-50m	25.0	19.2	100	0.93	0.06	623	492.7	134.1	0.19	0.15	0.38

^a Determined by XRF.

^b Median particle size: particles with a particle size distribution of 50%.

^c Volume average particle size: the weighted average of particle size versus volume;

^d Average particle size of surface area, which is the weighted average of particle size over surface area.

Table S5 Acid properties of Hβ-25n, Hβ-25m, and Hβ-50m

Sample	Acidity ^a (mmolNH ₃ /g)			120 °C ^b		
	Weak	Medium	Total	C _{BRONSTED} (μmol/g)	B/L	C _{LEWIS} (μmol/g)
Hβ-25n	0.63	0.23	0.86	102	2.6	39
Hβ-25m	0.55	0.20	0.75	80	0.4	178
Hβ-50m	0.47	0.20	0.67	43	0.2	311

^a Estimated from NH₃-TPD profiles.

^b Determined by FT-IR/pyridine desorption.

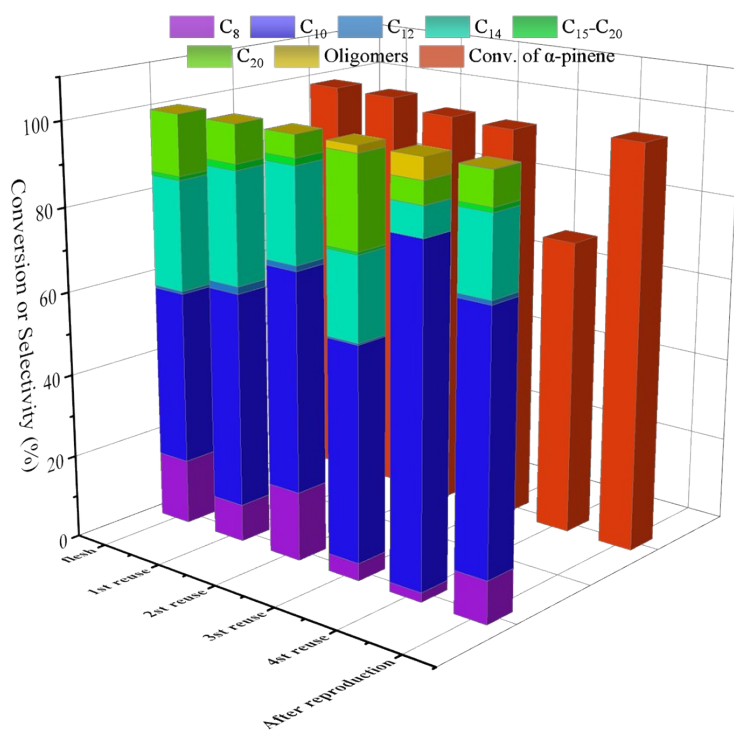


Fig S2 Reuse performance of Hβ-25n catalyst for the alkylation of α-pinene and Isobut-5