Supplementary information of

Shape Selective Cracking of Polypropylene on H-MFI Type Zeolite Catalyst with Recovery of Cyclooctane Solvent

Tomohiro Fukumasa¹, Yuya Kawatani¹, Hiroki Masuda¹, Ikuto Nakashita¹, Ryusei Hashiguchi¹,

Masanori Takemoto², Satoshi Suganuma³, Etsushi Tsuji¹, Toru Wakaihara⁴ and Naonobu Katada¹*

1 Center for Research on Green Sustainable Chemistry, Faculty of Engineering, Tottori University,

4-101 Koyama-cho Minami, Tottori 680-8552, Japan

2 Department of Chemical System Engineering, School of Engineering, the University of Tokyo, 7-

3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

3 Institute for Catalysis, Hokkaido University, Kita21, Nishi10, Kita-ku, Sapporo, Hokkaido, Japan

4 Institute of Engineering Innovation, School of Engineering, the University of Tokyo. Department

of Project, 2-11-16 Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan

* Corresponding author: katada@tottori-u.ac.jp

Entry	aatabiat	aabiant	n e hume n	town on at the / K	Yield / C-mol								
Entry	catalyst	solveni	polymer	temperature / K	C1 aliphatic	C2 aliphatic	C3 aliphatic	C4 aliphatic	C5 aliphatic	C6 aliphatic	C7 aliphatic	C8 aliphatic	
1	No	cyclooctane	No	673	0.0000000	0.0000000	0.0000000	0.0000000	0.0000040	0.0000009	0.0003461	0.0002787	
2	No	cyclooctane	PP	673	0.0000051	0.000088	0.0000989	0.0000413	0.0003424	0.0000690	0.0004905	0.0000000	
3	Parent MFI	cyclooctane	No	673	0.0000103	0.0000064	0.0000479	0.0000144	0.0008564	0.0000223	0.0000043	0.0000021	
4	Parent MFI	No	PP	673	0.0000182	0.0000572	0.0006078	0.0002514	0.0003073	0.0001026	0.0000066	0.0000000	
5	Parent MFI	cyclooctane	PP	673	0.0000001	0.000003	0.0000019	0.0000045	0.0005841	0.0000000	0.0000563	0.0005282	
6	Parent MFI	hexadecane	PP	673	0.0000212	0.0000350	0.0001738	0.0002744	0.0054377	0.0024777	0.0010178	0.0005029	
7	Beta	cyclooctane	PP	673	0.0000043	0.0000597	0.0005628	0.0001583	0.0089914	0.0246989	0.0146217	0.0025716	
8	Amorphous silica-alumina	cyclooctane	PP	673	0.0000189	0.0000261	0.0001201	0.0001370	0.0017003	0.0011054	0.0023550	0.0008058	
9	Silica alkali-treated MFI	cyclooctane	PP	673	0.0001435	0.0005811	0.0002027	0.0001587	0.0007827	0.0002602	0.0001966	0.0001724	
10	Silica alkali-treated MFI	cyclooctane	PP	693	0.0000704	0.0009877	0.0026827	0.0007547	0.0038291	0.0003152	0.0014880	0.0000048	
11	Silica alkali-treated MFI	cyclooctane	LLDPE	673	0.0000338	0.0000617	0.0003629	0.0001078	0.0062396	0.0004769	0.0003378	0.0002531	
12	Silica alkali-treated MFI	cyclooctane	GPPS	673	0.0000399	0.0000623	0.0002187	0.0000500	0.0032509	0.0001136	0.0012741	0.0004661	
13	Silica alkali-treated MFI	No	PP	673	0.0000456	0.0001804	0.0020112	0.0007248	0.0008467	0.0001453	0.0000000	0.0000000	

Table S1: Compositions of solutions after polymer cracking experiments Entries 1–13.

Enter	Yield / C-mol											
Entry	C9 aliphatic	C10 aliphatic	C11 aliphatic	C12 aliphatic	C13 aliphatic	C14 aliphatic	C15 aliphatic	C16 aliphatic	C17 aliphatic	C18 aliphatic	C19 aliphatic	C20 aliphatic
1	0.0000000	0.0000854	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
2	0.0001782	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
3	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000005	0.0000004	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
4	0.0000186	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
5	0.0001113	0.0001110	0.0000000	0.0000000	0.0000000	0.0000000	0.0000729	0.0001660	0.0000000	0.0000000	0.0000000	0.0000000
6	0.0001681	0.0000924	0.0000319	0.0000171	0.0000190	0.0000193	0.0000407	0.0000010	0.0000096	0.0000221	0.0000148	0.0000036
7	0.0003976	0.0006142	0.0002283	0.0001449	0.0000172	0.0000000	0.0000093	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
8	0.0003890	0.0002594	0.0003847	0.0003467	0.0000000	0.0000000	0.0004044	0.0004041	0.0003173	0.0002650	0.0001439	0.0000987
9	0.0001401	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0014911	0.0000000	0.0000000	0.0000000	0.0000000
10	0.0004088	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000610	0.0000788	0.0000000	0.0000000	0.0000000	0.0000000
11	0.0000660	0.0000649	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
12	0.0003529	0.0000341	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
13	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000410	0.0000000	0.0000000	0.0000000	0.0000000

Entry		Yield / C-mol												
Entry	C21 aliphatic	C22 aliphatic	C23 aliphatic	C24 aliphatic	C25 aliphatic	C26 aliphatic	C27 aliphatic	C28 aliphatic	C6 monocycli	C7 monocycli	8 monocycli	C9 monocycli		
1	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000118	0.0000000	0.0000000	0.0000000		
2	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000704	0.0000000	0.0001276	0.0000899		
3	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000290	0.0002202	0.0002346	0.0000329		
4	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000147	0.0001320	0.0002404	0.0000823		
5	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0005953	0.0002915	0.0005559	0.0002527		
6	0.0000025	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0004443	0.0004201		
7	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0043743	0.0032450	0.0044834	0.0034927		
8	0.0000526	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0006889	0.0002416	0.0009808	0.0002832		
9	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0001525	0.0000000	0.0000992	0.0001281	0.0003242	0.0007181		
10	0.0000836	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0004919	0.0005142	0.0014908	0.0014644		
11	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0005219	0.0015825	0.0011242		
12	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0006427	0.0012086	0.0016623	0.0005601		
13	0.0000450	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0004680		

Entry	Yield / C-mol												
C	10 monocycl	11 monocycl	12 monocycl	13 monocycl	14 monocycl	15 monocycl	l6 monocycli	17 monocycl	C10 dicyclic	C11 dicyclic	C12 dicyclic	C13 dicyclic	
1	0.0000000	0.0000000	0.0000040	0.0000000	0.0000000	0.0000000	0.0000000	0.0000070	0.0000000	0.0000000	0.0000000	0.0000000	
2	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	
3	0.0000073	0.0000018	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000185	0.0000684	0.0000270	0.0000055	
4	0.0000317	0.0000047	0.0000018	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000290	0.0000604	0.0000541	0.0000162	
5	0.0000412	0.0005137	0.0000000	0.0001369	0.0000000	0.0000000	0.0000000	0.0000000	0.0000784	0.0002797	0.0002218	0.0000484	
6	0.0001565	0.0000874	0.0000248	0.0000026	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000047	0.0000000	0.0000000	
7	0.0006065	0.0000000	0.0012862	0.0000000	0.0000000	0.0001666	0.0000000	0.0000000	0.0000000	0.0000000	0.0006372	0.0000000	
8	0.0001544	0.0000000	0.0001393	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	
9	0.0000000	0.0000000	0.0000613	0.0000000	0.0000000	0.0001049	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	
10	0.0000000	0.0000000	0.0003298	0.0000000	0.0000000	0.0001635	0.0000000	0.0000000	0.0001295	0.0007709	0.0008444	0.0000000	
11	0.0006856	0.0006364	0.0005168	0.0001871	0.0002831	0.0001169	0.0000550	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	
12	0.0004989	0.0007198	0.0008518	0.0002027	0.0005789	0.0003340	0.0003962	0.0006078	0.0000000	0.0000000	0.0000000	0.0000000	
13	0.0000000	0.0000000	0.0000250	0.0000000	0.0000000	0.0001560	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	

Entry	Yield / C-mol											
	C14 dicyclic	C15 dicyclic	C14 tricyclic	C15 tricyclic	C16 tricyclic	C17 tricyclic	C18 tricyclic	C19 tricyclic	18 tetracyclic			
1	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000			
2	0.0000000	0.0000779	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000			
3	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000			
4	0.0000044	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000			
5	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000			
6	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000			
7	0.0000000	0.0015704	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000			
8	0.0000000	0.0003584	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000			
9	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000			
10	0.0000000	0.0003585	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000			
11	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000			
12	0.0004675	0.0006547	0.0011963	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0001688			
13	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000			



Figure S1: Nitrogen adsorption (solid line) / desorption (dotted line) isotherms of employed (A) zeolite samples and (B) amorphous silica Reolosil at 77 K. The digit in (A) shows the amount of NaOH used for the silica-alkali treatment in the unit of mol kg_{zeolite}⁻¹. V_a shows the amount of adsorbed nitrogen under equilibrium for gaseous nitrogen with p of the pressure at 77 K, expressed by the volume of gas at 101 kPa and 273 K. p_0 shows the vapor pressure of nitrogen at 77 K (101 kPa).



Figure S2: ²⁹Si NMR spectra. The digit shows the amount of NaOH used for the silica-alkali treatment in the unit of mol $kg_{zeolite}^{-1}$.



Figure S3: Full width at half maximum of diffraction ascribed to **MFI** (0 5 1) plane ($2\theta = 23.1^{\circ}$) observed by X-ray diffraction (Figure 1).



Figure S4: Molecular weight distribution of (A) PP, (B) LLDPE and (C) GPPS used in this study determined by the gel permeation chromatography (GPC). For each polymer sample, the experiment was repeated, and two curves overlapped. In each case, the repeated experiments gave almost identical results that looked like one distribution curve. The measurements were performed using a Tosoh HLC-8321GPC/HT chromatograph, a gel guard column HHR(30)HT (inner diameter: 7.5 mm,

length: 7.5 cm), three columns GMHHR-H(20)HT (inner diameter: 7.8 mm, length: 30 cm), and a refractive index detector, with eluent [1,2,4-trichlorobenzene (99.5%) + 2,6-di-*tert*-butyl-*p*-cresol (0.05%), 1.0 cm³ min⁻¹] at 413 K.