

## TiCl<sub>4</sub>/MgCl<sub>2</sub>/MCM-41 Bi-supported Ziegler–Natta Catalyst: Effects of Catalyst Composition on Ethylene/1-Hexene Copolymerization

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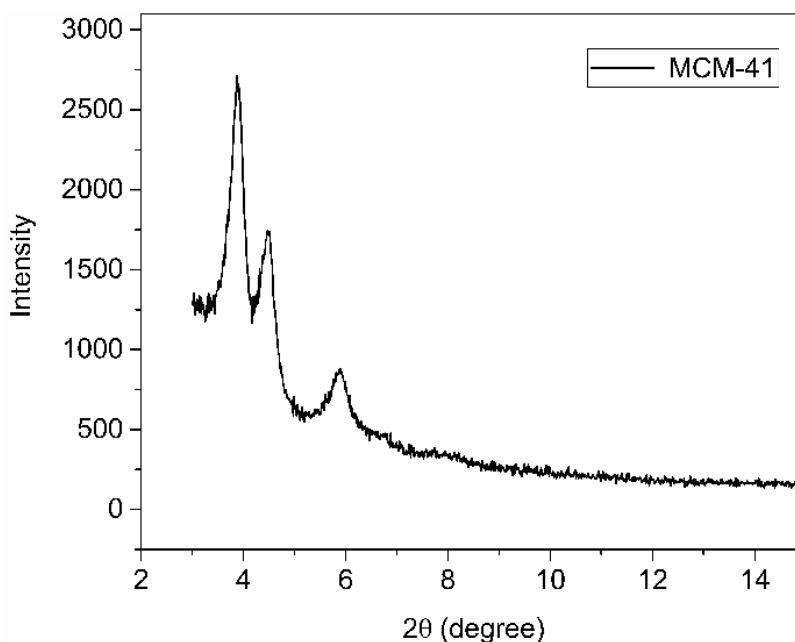


Figure S1. XRD curve of MCM-41.

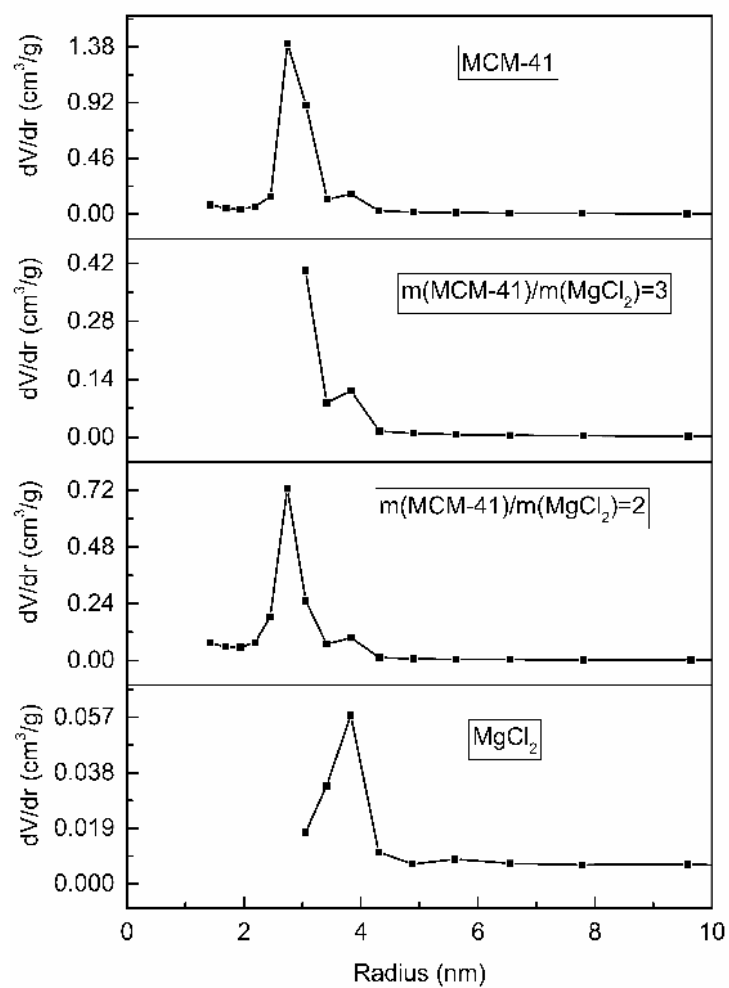


Figure S2. Pore size distribution of MgCl<sub>2</sub>, MCM-41 and two composite supports.

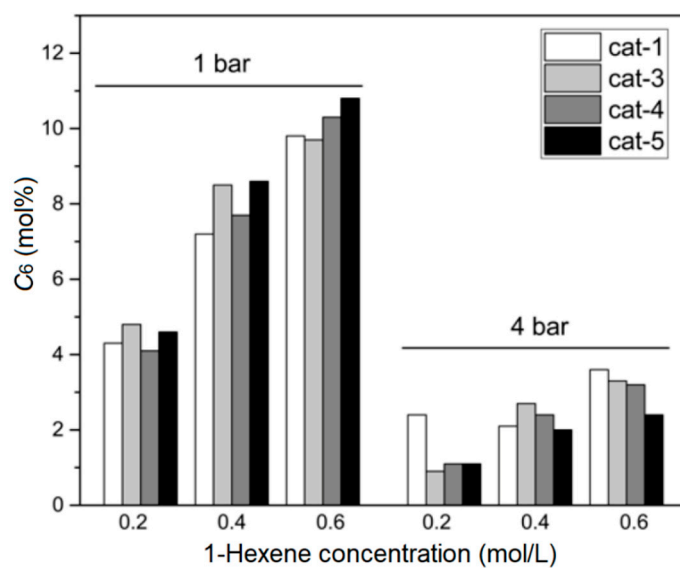


Figure S3. 1-Hexene content of ethylene/1-hexene copolymer produced under 1 bar and 4 bar.

Table S1. Boiling *n*-heptane extraction results of copolymer catalyzed by cat-1, cat-3, cat-4 and cat-5 under 1 bar.

Entry	Catalyst	[H] (mol/L)	C <sub>6</sub> <sup>a</sup> (mol%)	Conv. <sup>b</sup> (%)	C7-s		C7-in	
					Fraction (wt%)	C <sub>6</sub> <sup>a</sup> (mol%)	Fraction (wt%)	C <sub>6</sub> <sup>a</sup> (mol%)
2	cat-1	0.2	4.3	36.2	43.5	8.3	56.5	1.6
3	cat-1	0.4	7.2	33.9	61.4	10.6	38.6	2.5
4	cat-1	0.6	9.8	31.6	68.2	13.6	31.8	3.1
10	cat-3	0.2	4.8	47.4	42.7	8.9	57.3	2.0
11	cat-3	0.4	8.5	40.4	63.6	12.9	36.4	2.5
12	cat-3	0.6	9.7	39.4	67.9	15.1	32.1	3.0
14	cat-4	0.2	4.1	28.7	40.7	8.6	59.3	1.6
15	cat-4	0.4	7.7	28.5	62.6	12.0	37.4	3.0
16	cat-4	0.6	10.3	30.2	69.1	15.2	30.9	3.1
18	cat-5	0.2	4.6	29.1	38.3	9.8	61.7	1.6
19	cat-5	0.4	8.6	28.4	56.5	12.9	43.5	2.1
20	cat-5	0.6	10.8	24.2	64.6	14.1	35.4	2.3

<sup>a</sup> C<sub>6</sub> indicates 1-hexene content in copolymer determined by FTIR. <sup>b</sup> Conversion rate of 1-hexene.

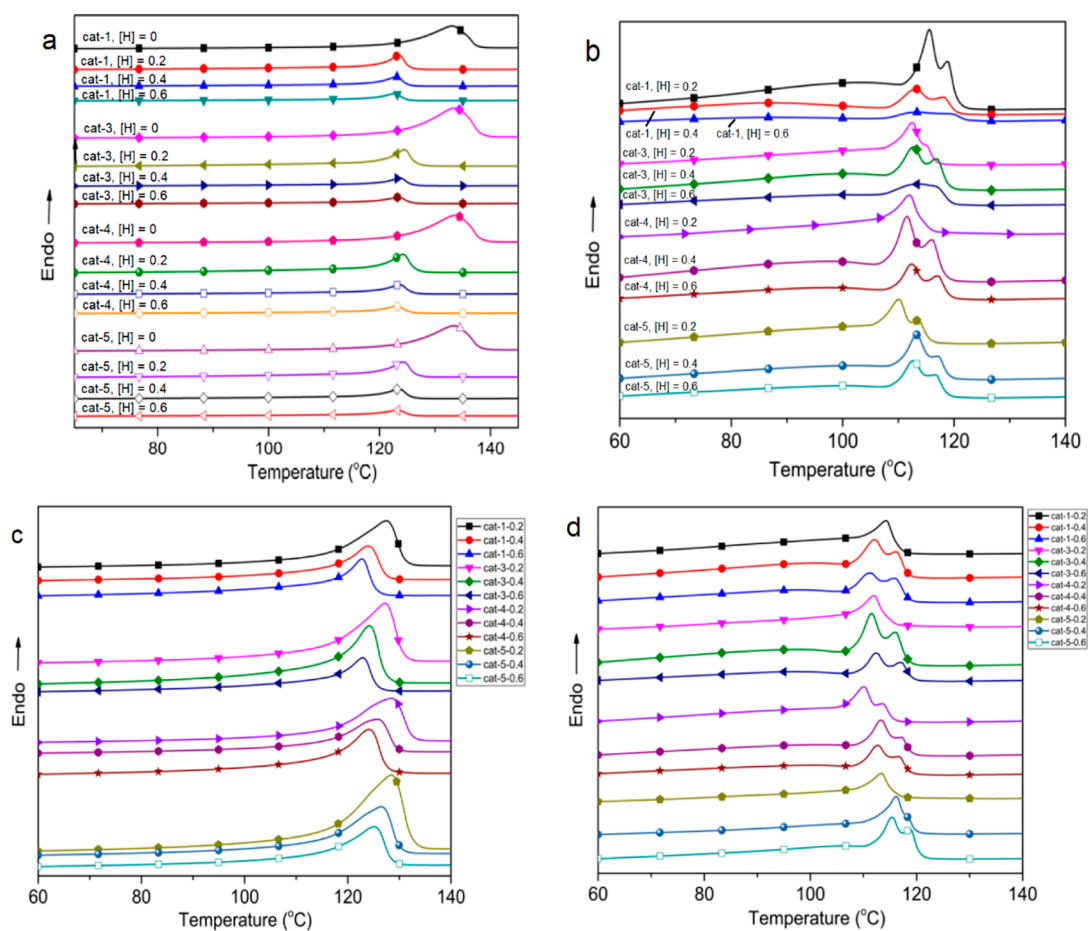


Figure S4. DSC traces of unfractionated (co)polymers produced under (a) 1 bar and (c) 4 bar, and their C7-s fractions produced under (b) 1 bar and (d) 4 bar.

Table S2. Thermal properties of copolymer and C7-sol fraction produced by cat-1, cat-3, cat-4 and cat-5 under 1 bar.

Entry	Catalyst	[H] (mol/L)	C7-s		C7-in	
			$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_m$ (°C)	$\Delta H_m$ (J/g)
2	cat-1	0.2	114	49.4	125	118.2
3	cat-1	0.4	112	28.7	125	103.5
4	cat-1	0.6	111	12.6	125	98.5
10	cat-3	0.2	114	47.9	125	115.8
11	cat-3	0.4	111	17.6	124	105.9
12	cat-3	0.6	114	7.1	124	98.0
14	cat-4	0.2	115	8.6	125	115.3
15	cat-4	0.4	113	12.0	125	105.1
16	cat-4	0.6	111	15.2	124	99.8
18	cat-5	0.2	115	9.8	125	120.9
19	cat-5	0.4	114	12.9	125	108.4
20	cat-5	0.6	113	14.1	125	100.8

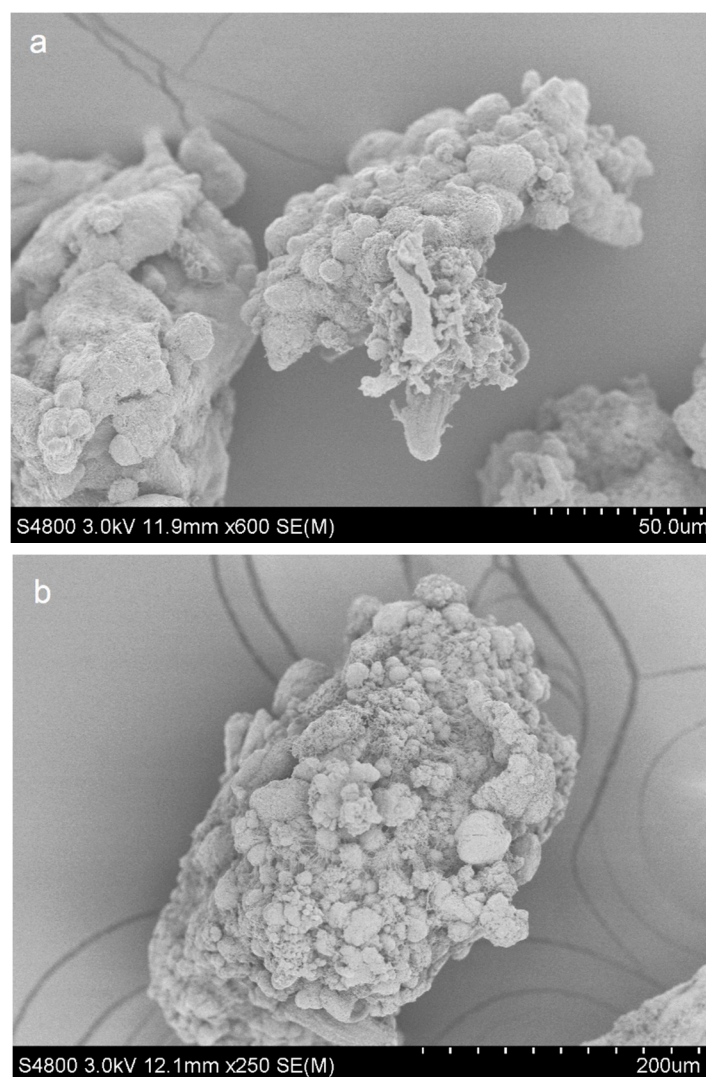


Figure S5. Morphology of nascent copolymer particles synthesized under 4 bar ethylene pressure and [H] = 0.2 mol/L with cat-4 and cat-5.

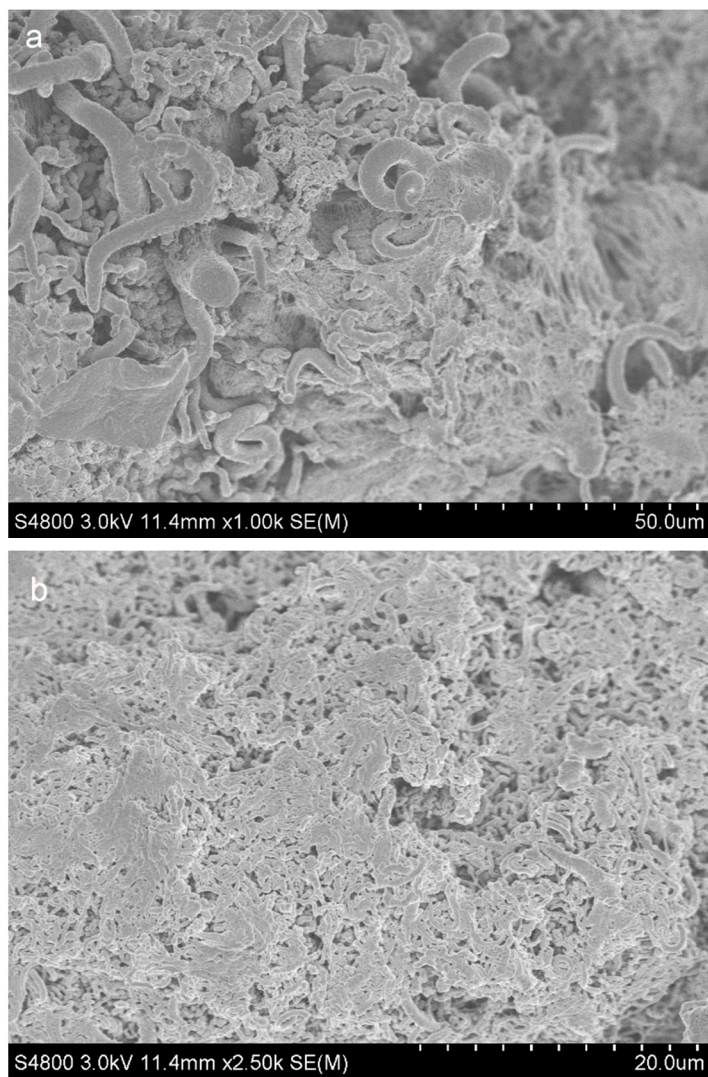


Figure S6. Morphology of nascent copolymer particles synthesized under 4 bar ethylene pressure and  $[H] = 0.2 \text{ mol/L}$  with cat-1.