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Supplementary Material (ESI) for Chemical Communications

Mesoporous silica-supported zirconocene catalysts for highly isotactic polypropylene

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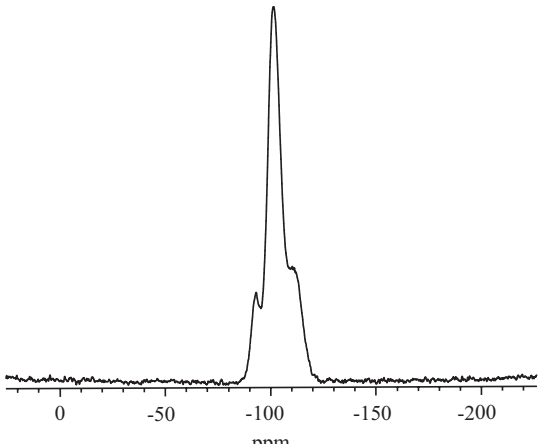
Supplementary information:

Table 1 BET surface areas of and C values of the BET(2) equation for mesoporous materials and supported zirconocenes

Material	**BET surface area (m^2g^{-1})**	**% reduction in surface area**	**C value of BET(2) equation**
MCM-41	820.56		97.67
2	558.93	31.9	19.57
SBA-15	706.45		113.13
3	558.55	20.9	106.67
MCM-48	641.84		66.13
4	597.19	7.0	38.86
DMS-150	672.58		36.08
5	367.89	45.3	40.64
Amorphous silica	316.53		224.26
6	244.77	20.7	21.58
MCM-41[1]	1139		80
MCM-41/$HN(SiMe_3)_2$[1]	851	25.3	26
MCM-41[42]	930		
MCM-41/TMSCl[42]	660	29.0	
MCM-41/$BuMe_2SiCl$[42]	550	40.9	
MCM-41/ $OctylMe_2SiCl$[42]	440	52.7	
MCM-41[13]	1140		
MCM-41/Cp_2ZrCl_2[13]	1106	3.0	
Grace Silica[13]	372		
Grace Silica/Cp_2ZrCl_2[13]	346	7.0	
SBA-15[20]	910		
MCM-48[23]	1100		

29Si Solid State NMR Spectra of silica substates and zirconocene functionalsed supports

MCM-41



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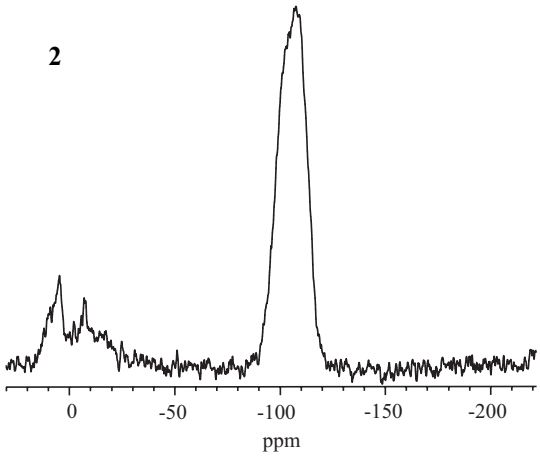
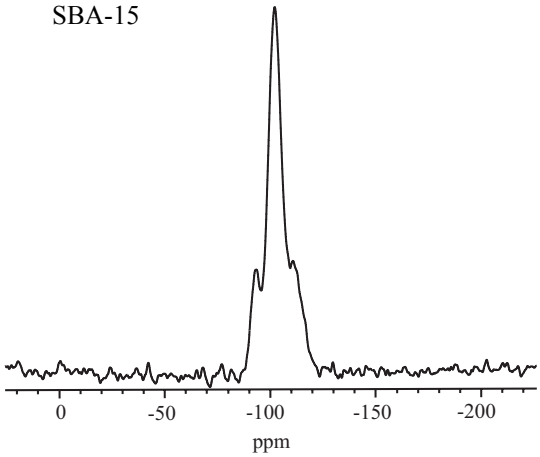


SBA-15



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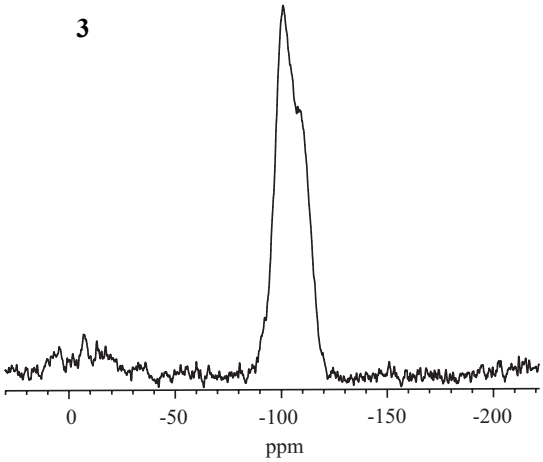
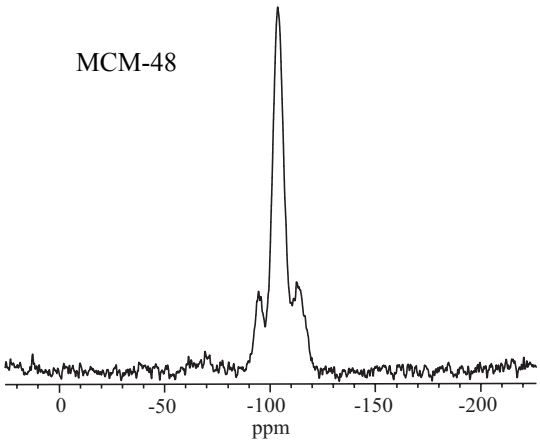


MCM-48



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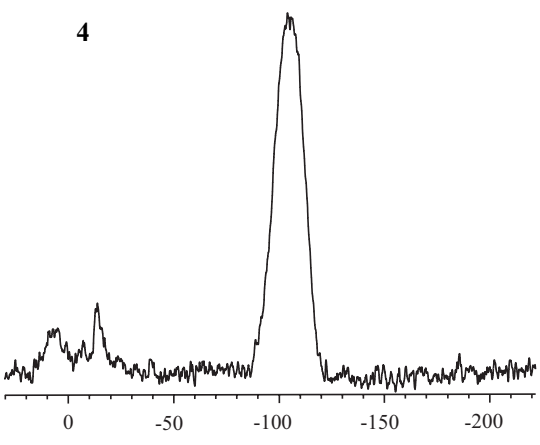
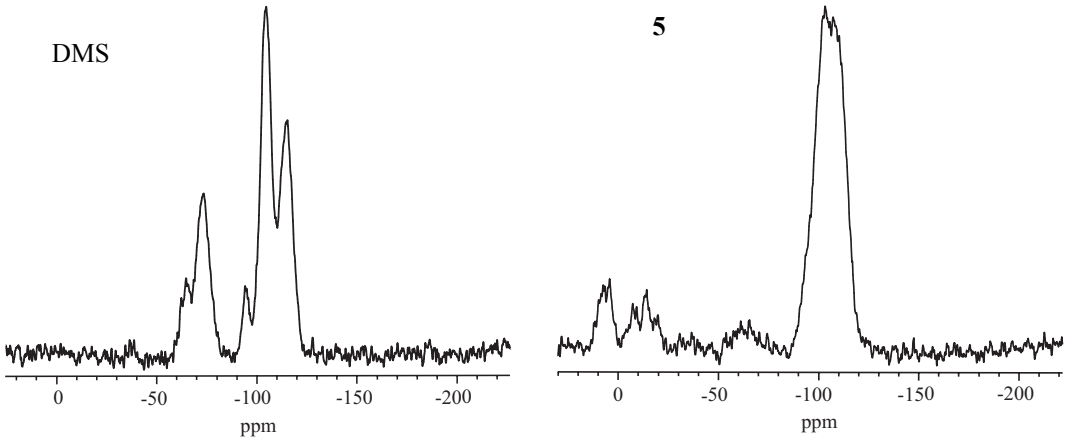




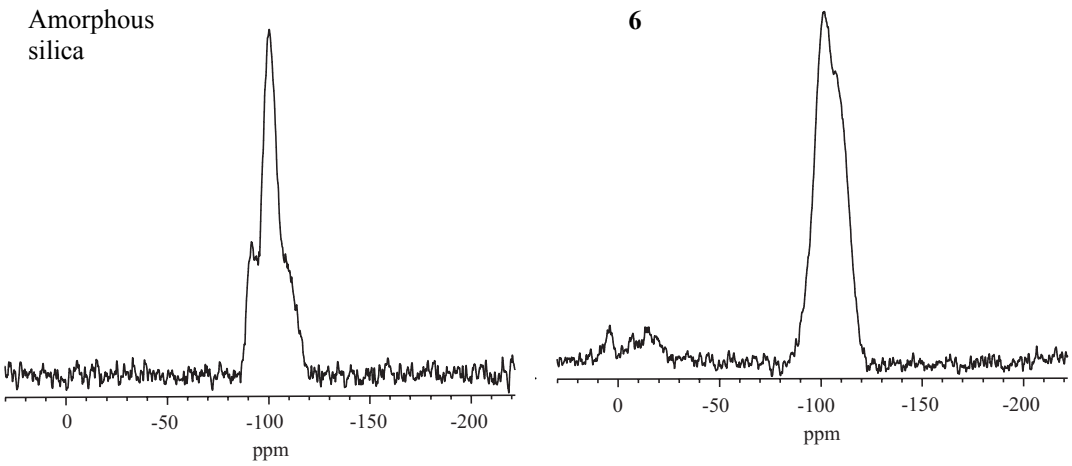


Table 2 ^{29}Si chemical shifts for materials studied and comparative literature materials

Material	^{29}Si chemical shifts (ppm)				Assignment of Si sites
	Q^2	Q^3	Q^4	other Si sites	
1	-	-	-	32.3[a] (36.47)[b] -13.0[a] (-16.52)[b]	Cl_2MeSiR[c] *ansa* Si
MCM-41[d]	-93.4	-101.8	-110.8	-	-
2	-	-107.2[e]		5.2 -6.9 -15.7	M^{Cl} D^1 *ansa* Si
MCM-41[17]	-92	-101	-110	-	-
MCM-41-TMS[17]	-92	-101	-110	14	M
SBA-15[d]	-93.7	-102.9	-110.0	-	-
3	-	-101.4	-108.0	4.8 -7.0 -12.9	M^{Cl} D^1 *ansa* Si
SBA-15[67]	-92	-101	-110	-	-
MCM-48[d]	-94.7	-101.4	-112.6	-	-
4	-	-104.4[e]		7.5 -6.8 -13.6	M^{Cl} D^1 *ansa* Si
MCM-48[71]	-91.3	-100.6	-109.6	-	-
DMS[d]	-93.9	-104.4	-114.6	-65.3 -73.7	T^2 T^3
5	-	-102.6	-106.7	7.7, 4.7 -7.0, -8.8 -13.7 -18.0, -19.5	M^{Cl} D^1 *ansa* Si D^2
Cyanoethyl-HMS[35]	-96.4	-102.0	-109.8	-63.1 -68.7	T^2 T^3
amorphous silica[d]	-91.9	-100.9	-108.3	-	-
6	-	-101.9	-107.6	3.1 -6.8 -14.0 -18.2	M^{Cl} D^1 *ansa* Si D^2
silica gel[56,58]	-90.6	-99.8	-109.3	-	-
silica gel-TMS[57,58]	-91	-100	-109	13	M
silica gel-Me_2SiCl_2[57,61]	-91	-100	-109	9.4 -4.1 -14.2	M^{Cl} D^1 D^2

[a] solid-state ^{29}Si CP MAS, as for heterogenised Zc, 75 MHz; [b] solution ^{29}Si NMR, 56 MHz, in CD_2Cl_2; [c] R = $(CH_2)_3Si(C_9H_6)_2ZrCl_2$; [d] this work; [e] convoluted Q^3 and Q^4 peaks not possible to assign separately.

^{13}C CP MAS NMR experiments were carried out on the five supported zirconocenes **2** - **6**, and the resulting spectra are shown in Figs. 1 - 5.

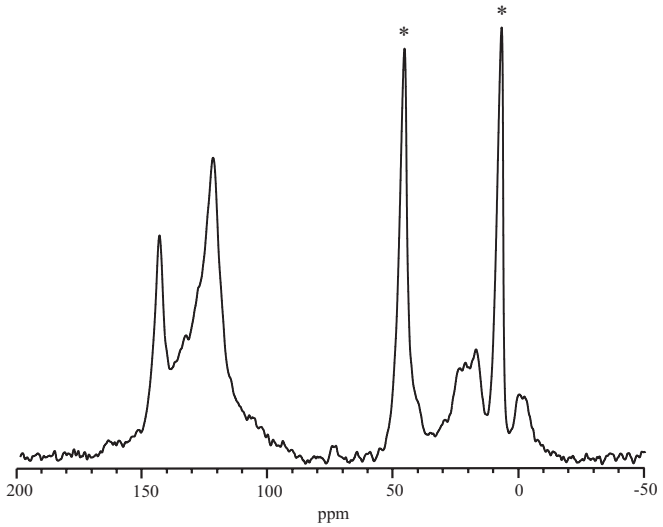


Fig. 1 ^{13}C CP MAS NMR spectrum of **2** (Et_3N peaks are marked with asterisks)

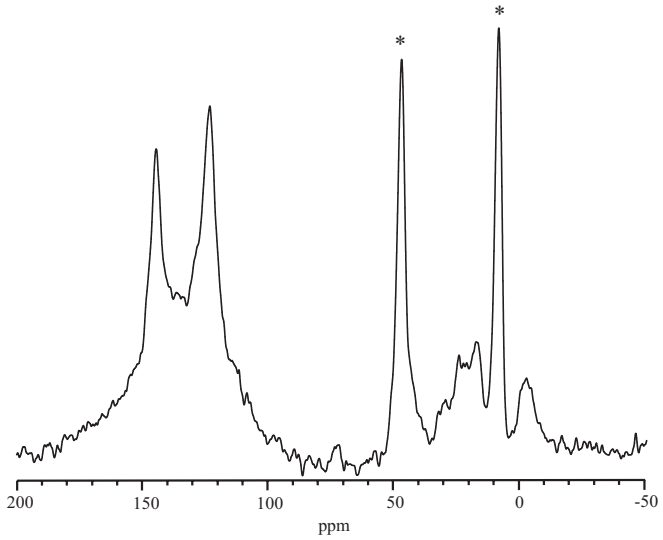


Fig. 2 ^{13}C CP MAS NMR spectrum of **3** (Et_3N peaks are marked with asterisks)

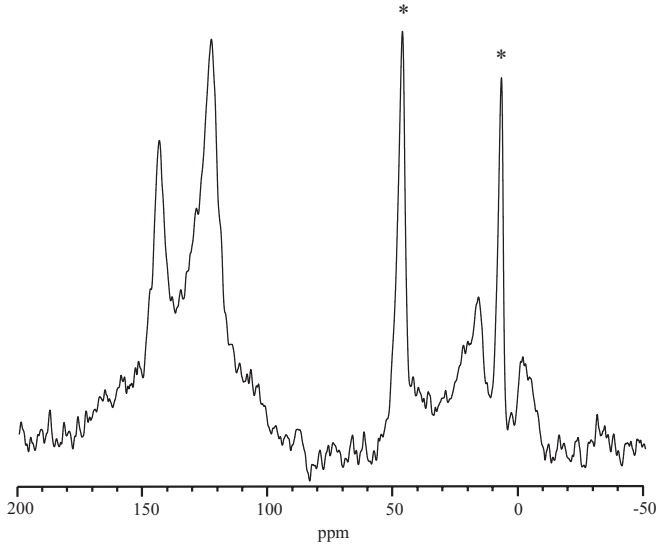


Fig. Error! No text of specified style in document. ^{13}C CP MAS NMR spectrum of **4** (Et_3N peaks are marked with asterisks)

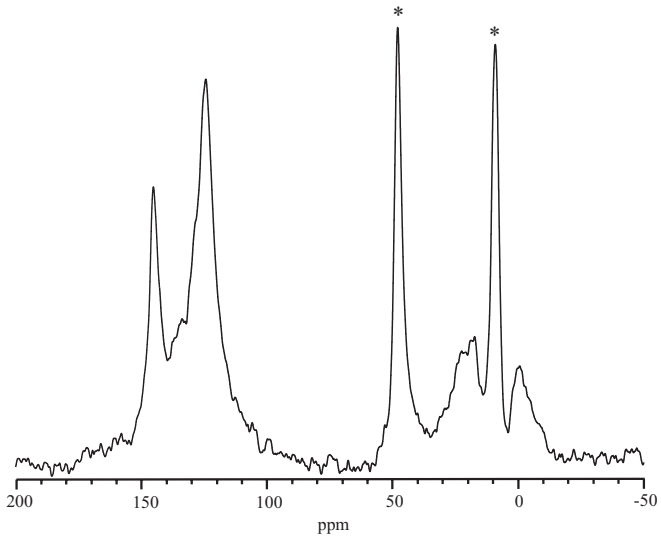


Fig. 4 ^{13}C CP MAS NMR spectrum of **5** (Et_3N peaks are marked with asterisks)

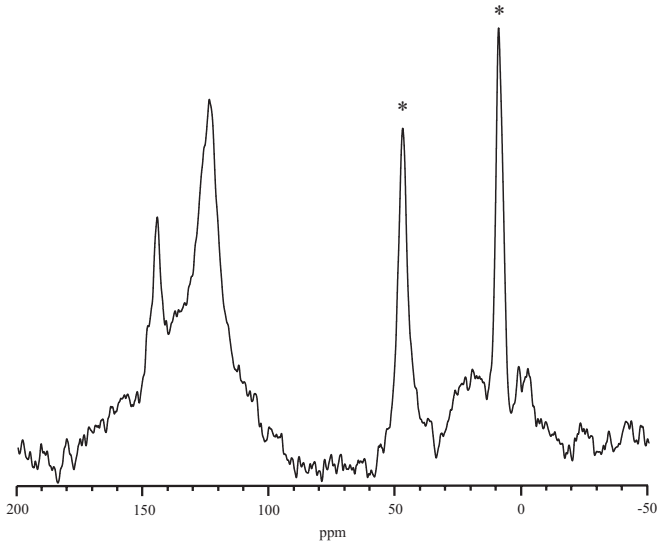
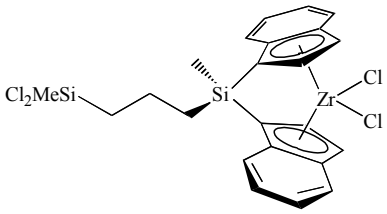
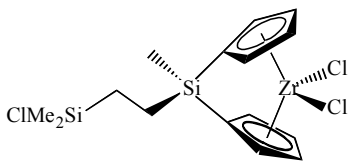
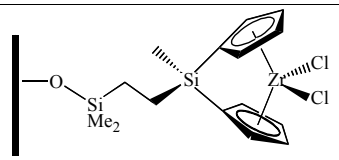


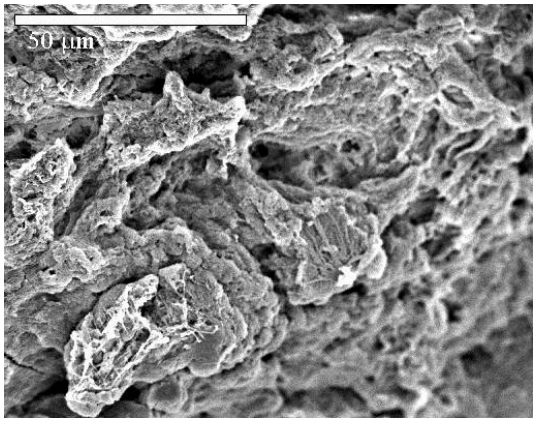
Fig. 5 ^{13}C CP MAS NMR spectrum of **6** (Et_3N peaks are marked with asterisks)

Table 3 ^{13}C NMR chemical shifts and proposed assignments for **1** and supported zirconocenes **2 - 6** and related compounds of interest (spectra were recorded at 100 MHz unless otherwise stated)

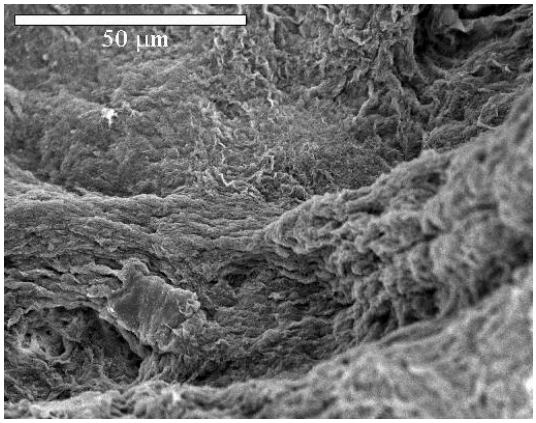
Compound/Material	^{13}C chemical shift (ppm)			Assignment
 **1**[a]	135.00 128.36		127.39 126.48	q, Ind
	126.10		125.98	CH, Ind
	119.98		119.81	CH 'Cp' Ind
		90.05		q, 'Cp' Ind (*ipso*)
	25.64	18.23	17.22	CH_2
		5.46		Cl_2MeSi-
		-5.51		SiMe (*ansa*)
2	145.6 133.9		129.1 123.6	Ind
	24.2	20.9	17.9	CH_2
	0.6		-1.5	SiMe
3	144.6	135.5	123.5	Ind
	30.6	24.6	17.7	CH_2
		-2.0		SiMe
4	144.4	129.5	123.8	Ind
		16.9		CH_2
		-0.8		SiMe
5	144.7	133.5	123.7	Ind
	21.8		17.7	CH_2
		-0.8		SiMe
6	144.8		124.1	Ind
	23.0		19.3	CH_2
	1.6		-2.0	SiMe
 Collins *et al.*[15,b]	129.8 128.2 116.0		114.0 109.3	Cp
		10.5		**-C**H_2SiMe_2Cl
		2.8		$SiMe_2$
		1.1		**-C**$H_2SiMeCp_2ZrCl_2$
		-7.7		SiMe (*ansa*)
 Collins *et al.*[15,c]	128.0		112.0	Cp
	9.8		7.4	CH_2
		2.6		$OSiMe_2$
		-9.6		SiMe (*ansa*)

[a] data recorded at 75 MHz in solution (CD_2Cl_2); [b] data recorded at 75 MHz in solution ($CDCl_3$); [c] data recorded at 125 MHz (CP MAS).

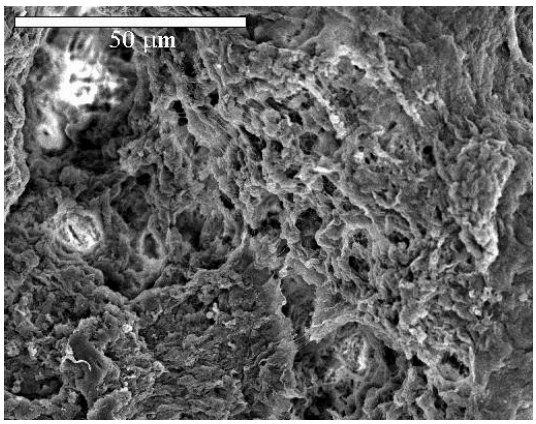
SEM micrographs (× 900 magnification) of polyethylenes (catalysts named below):



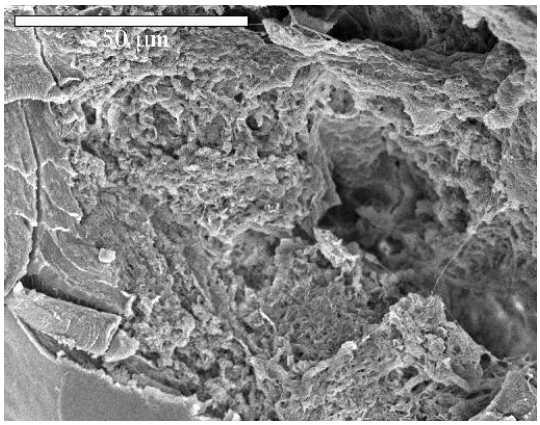
2 (MCM-41 host)



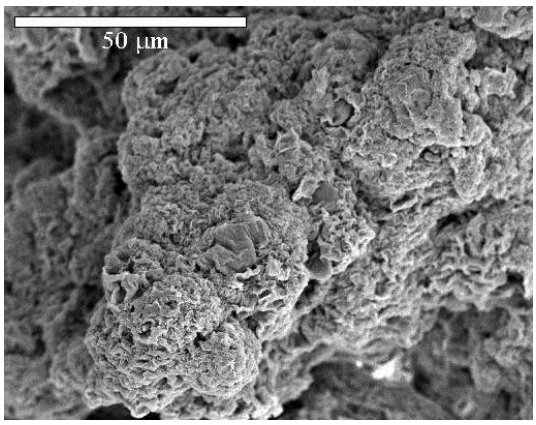
3 (SBA-15 host)



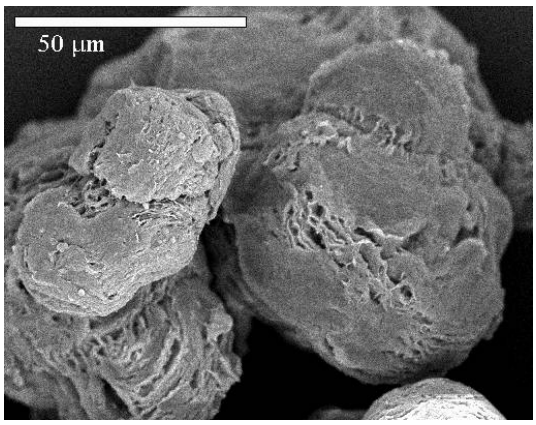
4 (MCM-48 host)



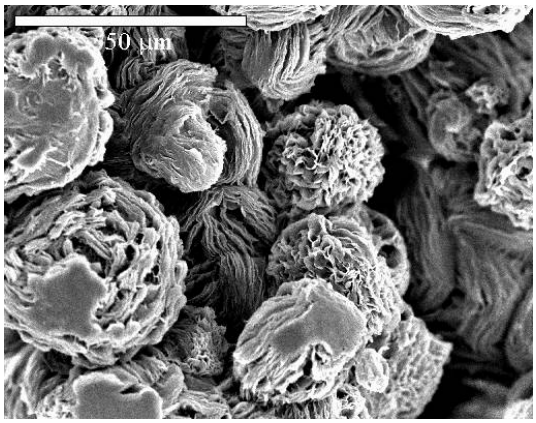
5 (DMS host)



1

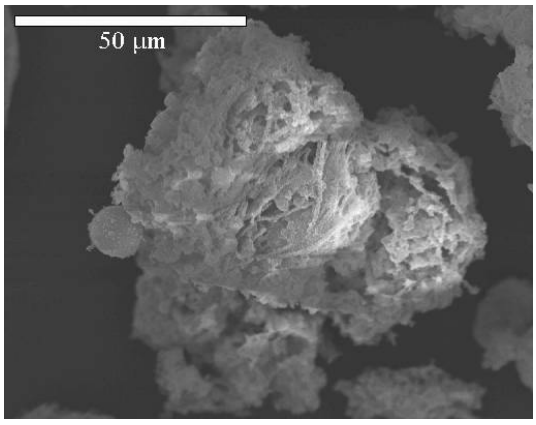


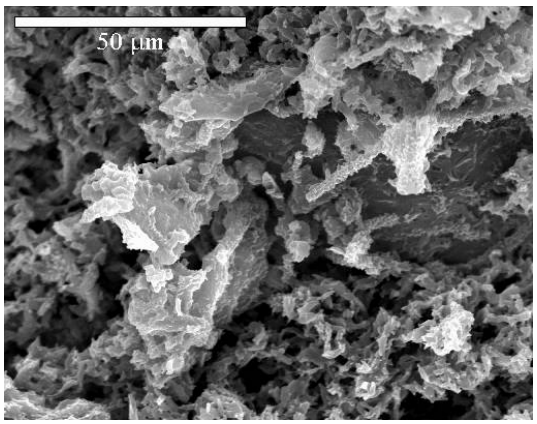
6 (SiO_2 host)



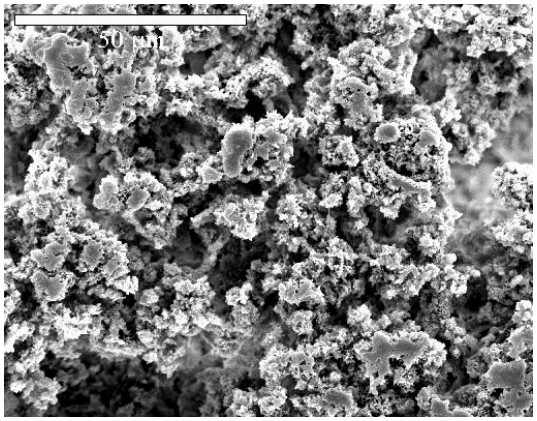
7

SEM micrographs (× 900 magnification) of polypropylenes (catalysts named below):

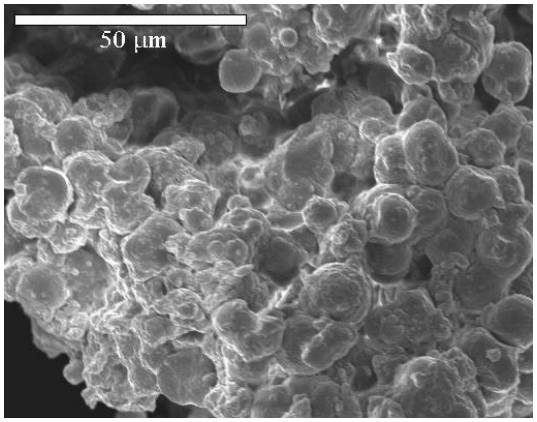




4 (MCM-48 host)



6 (SiO_2 host)



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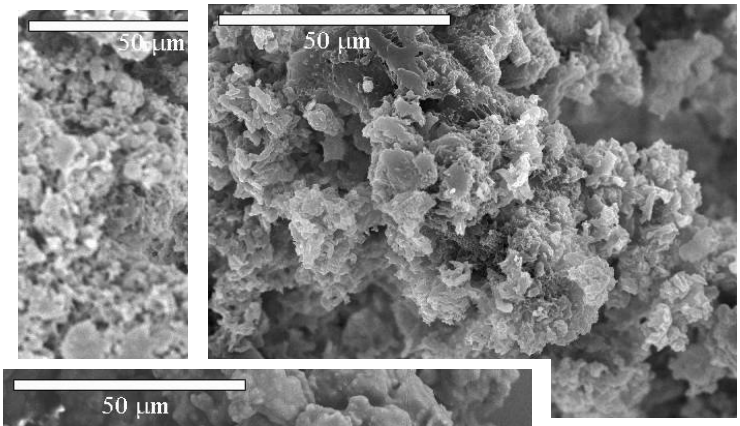
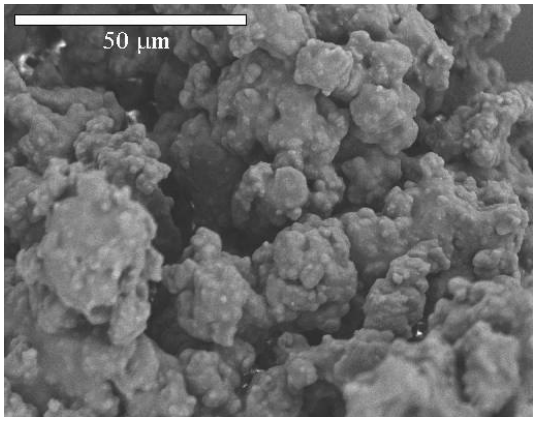
2 (MCM-41 host)

3 (SBA-15 host)





1