

## Electronic Supplementary Information

### The Effect of Structure Directing Agents on the Ordering of Fluoride Ions in Pure Silica MFI Zeolites

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#### 1. Experimental Details

##### 1.1 Syntheses

The structure directing agents used in the preparation of the pure silica MFI type zeolites were synthesised via the exhaustive alkylation of tributylamine (Alfa Aesar, 98%) or tripropylamine (Sigma Aldrich  $\geq 98\%$ ) using iodomethane (Acros Organics, 99%) or iodoethane (Acros Organics, 99%) as necessary. The products of the reactions were recrystallized using ethyl acetate and ethanol and the structures and purities verified using solution  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. Tetrapropylammonium bromide (Acros Organics, 98%) was used as supplied.

The pure silica MFI zeolite samples were prepared by dissolving the SDAs in deionised water with fumed silica (Sigma Aldrich, 0.007  $\mu\text{m}$  powder) and ammonium fluoride (Acros Organics, 98+) in 40 mL Teflon-lined, stainless steel autoclaves. The resulting gels with a molar ratio of  $1\text{SiO}_2:0.08\text{SDA}:1\text{NH}_4\text{F}:20\text{H}_2\text{O}$  were heated in a forced air oven at 180 °C for 5-8 days. The MFI crystals were recovered by repeated centrifugation and washing with deionised water before being dried at 60 °C overnight.

##### 1.2 Powder X-ray Diffraction

Powder X-Ray diffraction patterns were collected on all zeolite samples using a Bruker D8 Advance diffractometer operating with Cu  $K\alpha$  radiation. The obtained patterns were compared to those previously published to confirm the materials as the MFI framework type.<sup>1</sup>

##### 1.3 $^{29}\text{Si}$ NMR

$^{29}\text{Si}\{^1\text{H}\}$  CP MAS spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer operating at 79.47 MHz for  $^{29}\text{Si}$  and 400.13 MHz for  $^1\text{H}$  using 2.5 mm rotors. Experiments were conducted using a 7 ms contact time, a linear ramp on the  $^1\text{H}$  contact pulse (30% slope),  $^1\text{H}$  decoupling (SPINAL-64, nutation frequency of 50 kHz), recycle delay of 3 s and a 6 kHz spinning rate.  $^{29}\text{Si}$  chemical shifts were referenced to TMS using Q8M8 as an external secondary standard.

##### 1.4 $^{13}\text{C}$ NMR

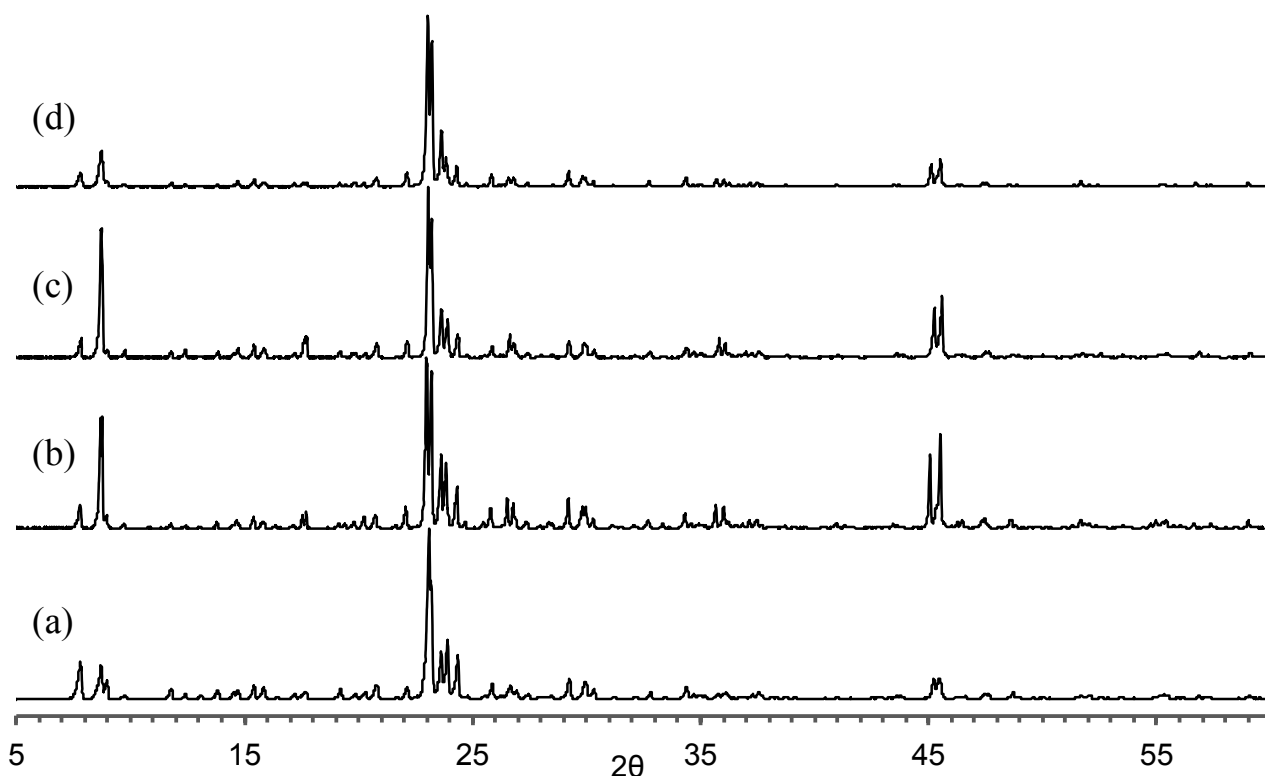
$^{13}\text{C}\{^1\text{H}\}$  CP MAS spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer operating at 100.59 MHz for  $^{13}\text{C}$  and 400.13 MHz for  $^1\text{H}$  using 2.5 mm rotors. Experiments were conducted using a 3 ms contact time, a linear ramp on the  $^1\text{H}$  contact pulse (30% slope),  $^1\text{H}$  decoupling (SPINAL-64, nutation frequency of 50 kHz), recycle delay of 3 s and a 6 kHz spinning

rate.  $^{13}\text{C}$  chemical shifts were referenced to TMS using adamantane as an external secondary standard.

### 1.5 $^{19}\text{F}$ NMR

$^{19}\text{F}$  MAS spectra were recorded on a Bruker Avance III 400 MHz spectrometer operating at 376.49 MHz for  $^{19}\text{F}$  using 1.9 mm rotors. Experiments were conducted at 280 K using a spin echo, recycle delay of 20 s and a 30 kHz spinning rate.  $^{19}\text{F}$  chemical shifts were referenced to a replacement sample of  $\text{C}_6\text{F}_6$  ( $\delta_{\text{F}} = -166.4\text{ppm}$  with respect to the signal for  $\text{CFCl}_3$ ).

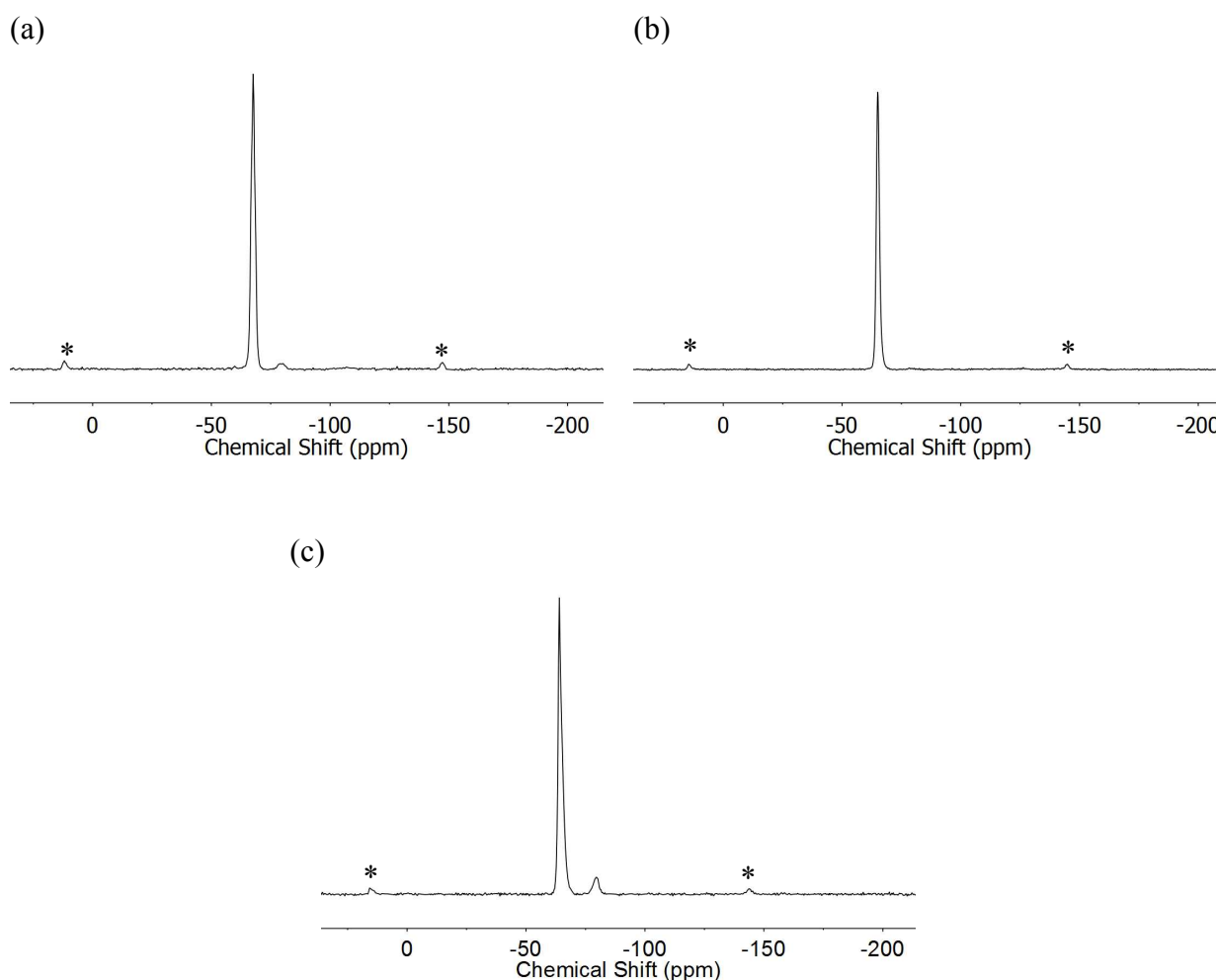
## 2. Powder X-ray Diffraction Patterns



**Figure S1.** Room temperature powder X-ray diffraction patterns of (a) [TPA]-F,MFI, (b) [MTBA]-F,MFI, (c) [MTPA]-F,MFI and (d) [ETBA]-F,MFI

Powder X-ray diffraction patterns were compared to published results and confirmed that all the SDAs produce phase pure MFI materials with no signs of MEL intergrowths, as confirmed by the lack of the additional peaks at  $6.2$  and  $18.7^\circ$   $2\text{-theta}$ . Initial analysis of the patterns show that all the materials can be described in the orthorhombic  $\text{Pnma}$  spacegroup and show no observable additional peaks and/or splitting to suggest the monoclinic spacegroup  $\text{P}2_1/\text{n}$  or an intergrown material. This confirms the theory that statically disordered fluoride ions only occupy one site within the  $[4^15^26^2]$  cage and hence on a local scale shows 24 tetrahedral sites whilst still displaying  $\text{Pnma}$  symmetry by powder X-ray diffraction.

### 3. $^{19}\text{F}$ MAS NMR Spectra



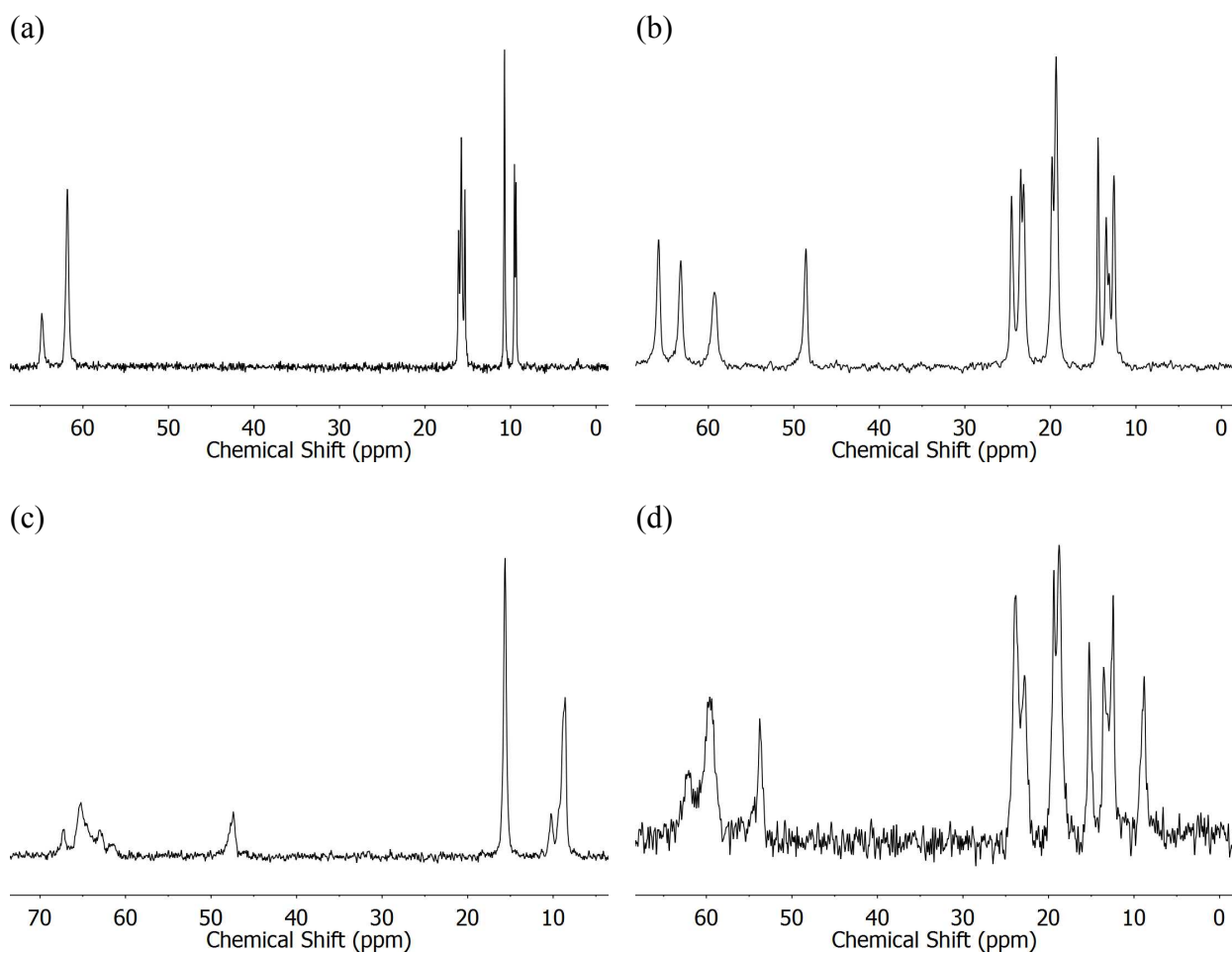
**Figure S2.**  $^{19}\text{F}$  MAS NMR spectra of (a) [MTBA]-F,MFI, (b) [MTPA]-F,MFI, (c) [ETBA]-F,MFI collected at 30 kHz spinning rate. Spinning sidebands are indicated with an asterisk (\*).

The  $^{19}\text{F}$  MAS spectra for all samples showed an isotropic peak with a chemical shift consistent with those previously reported for other fluoride containing zeolites., including [TPA]-F,MFI.<sup>2</sup> Both [MTBA]-F,MFI and [ETBA]-F,MFI showed a small additional peak at -79.5 ppm, which has been previously observed, and is currently subject to further investigation.<sup>3</sup>

**Table S1.**  $^{19}\text{F}$  isotropic chemical shifts of the  $[\text{SiO}_{4/2}\text{F}]^-$  peak in MFI zeolites

Sample	$\delta_{\text{iso}}$ / ppm
[MTBA]-F,MFI	-67.68
[MTPA]-F,MFI	-65.09
[ETBA]-F,MFI	-63.97

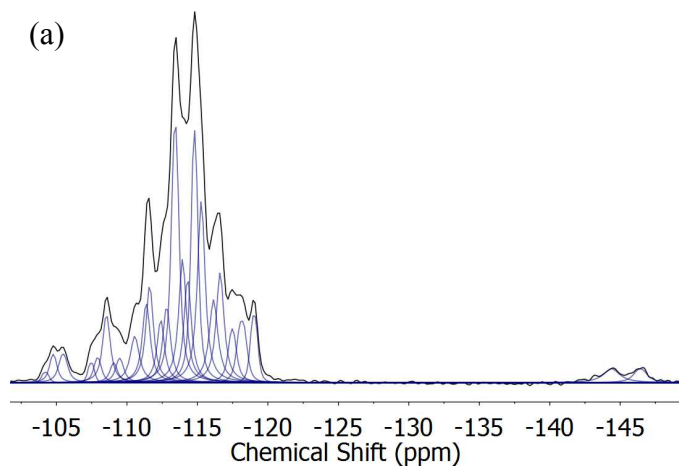
#### 4. $^{13}\text{C}\{^1\text{H}\}$ CP MAS NMR Spectra



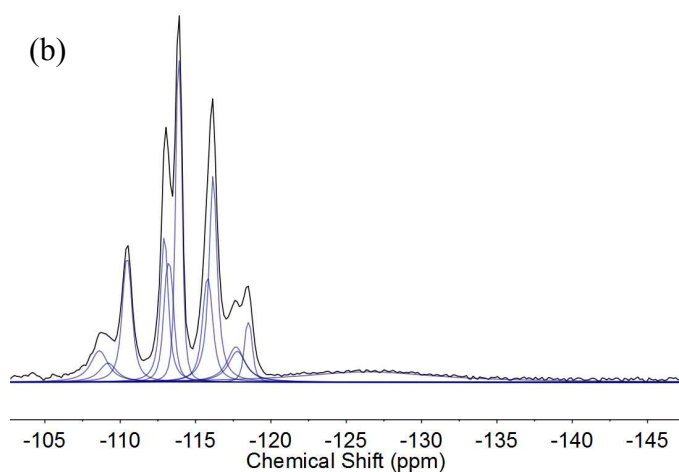
**Figure S3.**  $^{13}\text{C}\{^1\text{H}\}$  CP MAS spectra of (a) [TPA]-F,MFI, (b) [MTBA]-F,MFI, (c) [MTPA]-F,MFI and (d) [ETBA]-F,MFI at 6 kHz spinning rate.

The  $^{13}\text{C}\{^1\text{H}\}$  CP MAS spectra of all the MFI samples show that the SDAs have been successfully incorporated in to the zeolite frameworks and further work to correlate the  $^{13}\text{C}$  spectra with the fluoride disorder is currently underway.

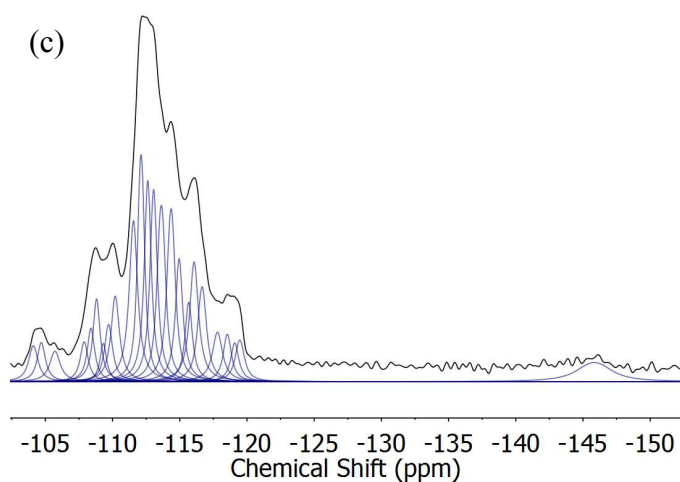
## 5. Deconvoluted $^{29}\text{Si}\{^1\text{H}\}$ CP MAS NMR Spectra



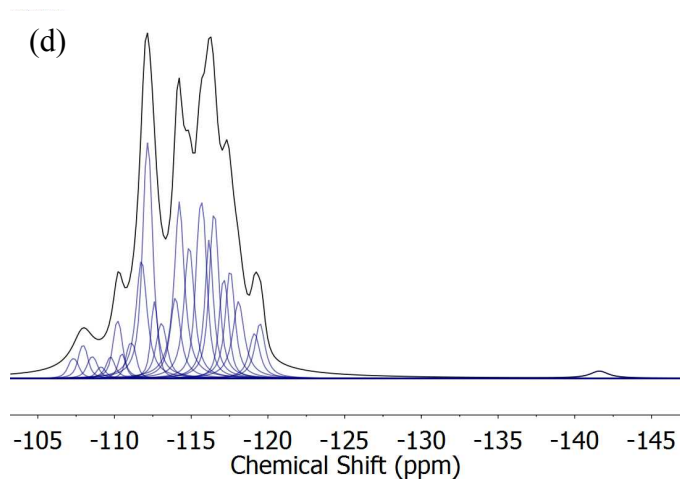
Peak	$\delta_{\text{iso}}$ /ppm	FWHM / Hz	Peak	$\delta_{\text{iso}}$ /ppm	FWHM / Hz
1	-104.21	48	13	-112.81	51
2	-104.77	50	14	-113.42	51
3	-105.47	60	15	-113.94	51
4	-107.46	43	16	-114.31	50
5	-107.92	50	17	-114.79	46
6	-108.54	51	18	-115.28	51
7	-109.06	50	19	-116.14	59
8	-109.48	54	20	-116.61	53
9	-110.55	61	21	-117.48	54
10	-111.37	53	22	-118.15	64
11	-111.61	50	23	-119.02	49
12	-112.40	49	24	-144.38	110
				-146.43	90



Peak	$\delta_{\text{iso}}$ /ppm	FWHM / Hz
1	-108.61	110
2	-109.19	110
3	-110.46	60
4	-112.93	48
5	-113.22	61
6	-113.89	40
7	-115.80	63
8	-116.16	49
9	-117.77	110
10	-117.68	110
11	-118.50	49
12	-126.42	882



Peak	$\delta_{\text{iso}}$ /ppm	FWHM /Hz	Peak	$\delta_{\text{iso}}$ /ppm	FWHM /Hz
1	-104.10	66.4	13	-113.05	51.2
2	-104.69	57.8	14	-113.62	58.6
3	-105.71	73.9	15	-114.95	52.3
4	-107.88	55.6	16	-114.35	58.5
5	-109.31	46.6	17	-115.66	52.2
6	-108.80	51.1	18	-116.65	62.4
7	-108.39	53.1	19	-117.80	72.0
8	-109.70	56.6	20	-116.06	62.5
9	-110.19	59.7	21	-119.09	57.5
10	-112.11	49.0	22	-118.53	57.8
11	-111.55	59.5	23	-119.46	65.0
12	-112.61	49.2	24	-145.84	243.0



Peak	$\delta_{\text{iso}}$ /ppm	FWHM /Hz	Peak	$\delta_{\text{iso}}$ /ppm	FWHM /Hz
1	-	50	13	-	51
2	-	68	14	-	58
3	-	46	15	-	51
4	-	54	16	-	56
5	-	57	17	-	49
6	-	64	18	-	50
7	-	47	19	-	53
8	-	68	20	-	46
9	-	53	21	-	54
10	-	65	22	-	59
11	-	47	23	-	63
12	-	50	24	-	110

**Figure S4.** Deconvoluted  $^{29}\text{Si}\{^1\text{H}\}$  CP MAS spectra of (a) [MTBA]-F,MFI, (b) [TPA]-F,MFI, (c) [MTPA]-F,MFI and (d) [ETBA]-F,MFI at 6 kHz spinning rate.

Deconvolution of the  $^{29}\text{Si}\{^1\text{H}\}$  CP MAS spectra for [MTBA]-F,MFI, [ETBA]-F,MFI and [MTPA]-F,MFI at 233 K, all showed 24 Si sites consistent with that previously reported for [TPA]-F,MFI at 223 K where fluoride motion had been frozen out.

## 6. References

1. Robson, H., *Verified Syntheses of Zeolitic Materials*. Elsevier: Amsterdam, 2001.
2. H. Koller, A. Wolker, L. A. Villascusa, M. J. Diaz-Cabanas, S. Valencia and M. A. Camblor, *J. Am. Chem. Soc.*, 1999, **121**, 3368-3376.
3. C. A. Fyfe, R. J. Darton, H. Mowatt and Z. S. Lin, *Micropor. Mesopor. Mat.* 2011, **144**, 57-66.