Supplementary Information for *RSC Advances*.

Hydrolytically stable ZIF-8@PDMS Core–Shell Microspheres for Gas-Solid Chromatographic separations

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Effect of particle dimensions on pressure drop

The pressure drop associated with a gas flowing through packed tubes, decreases with the voidage in the tube (ε) as well as the length of the tube. The relation between these properties and Pressure drop is expressed by a correlation equation

$$\Delta P = \frac{2 f_m \times G_i{}^2 \times L_t (1-\varepsilon)^{3-n}}{D_P \rho_f \phi_s{}^{3-n} \times \varepsilon^3} \qquad \text{......Eq-1}$$

Where, ΔP = pressure drop, psi

L_t = depth of the packed bed, ft.

G = ρV = mass velocity, lb $h^{-1}ft^2$

ρ = fluid density, lb ft^{-3}

D = effective particle diameter, ft.

ε = interparticle void fraction, dimensionless

$f_{m=}$ modified friction factor

n = Reynolds number

f_s = shape factor

φ_s = sphericity of the particle

By assuming a modified friction factor ($f_m = 2$), Reynolds number ($n = 2$), and a shape factor ($f_s = 1$) for a perfect sphere, the pressure drops were calculated as a function of microsphere diameter and the resultant plots are presented in Fig. 1 The expanded portion is presented in the inset.

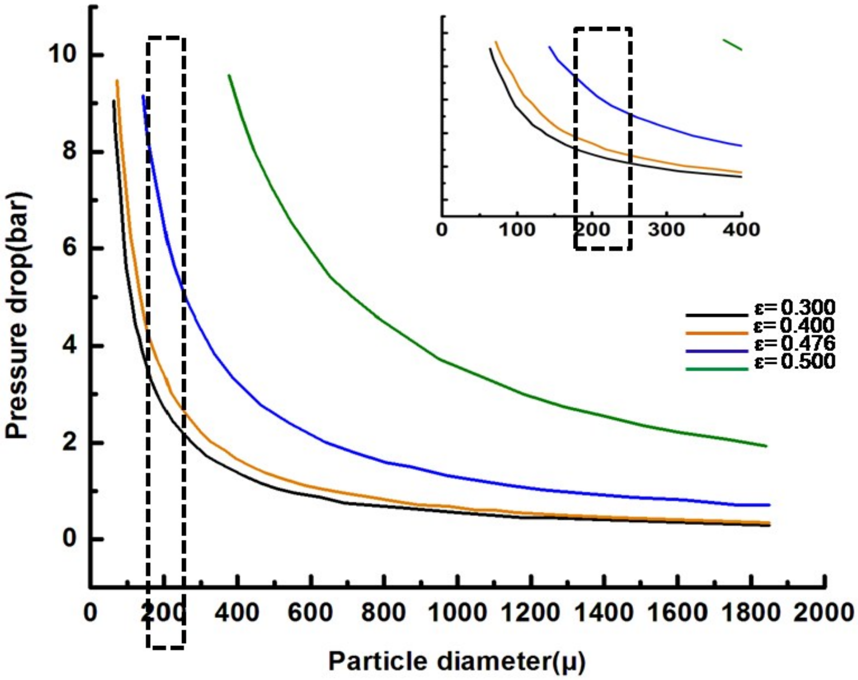

Fig. S1 : Pressure drops through a packed tube with a particle diameter (D_P) and voidage (ε) by equation 1. Inset shows an expanded view.

It can be seen that the pressure drop increases steeply with decreasing particle dimensions. The pressure drop associated with the particle range used in the present study is presented in the dashed box (250-177 µm). As is apparent, further decrease in the particle size would lead to extremely high pressure drops which in turn would lead to operability issues in the gas chromatographic column. Further increase in packing efficiency (lower voidage) would further aggravate the pressure drop issue. It is for this reason, that chromatographic separations were performed on stationary phase with these dimensions (250-177 µm).

Preparation of core microspheres

The poly (dimethylsiloxane) (PDMS) core was prepared using a batch suspension polymerization process. A feed solution was prepared by dissolving vinyl terminated siloxane macromonomer (Elastosil M4644) in chloroform (60 % v/v) followed by the addition of requisite amounts of platinum based hardener (resin :hardener=10:1). The feed solution was introduced into a 1 L four-necked RB flask containing the suspending agent, PVA (1.5% w/v) through a rubber septum and was constantly stirred (600 rpm) at 45 ^oC. The polymerisation reaction was allowed to continue for 8 h. The reaction mixture was cooled and the microspheres were filtered, washed with water and dried under vacuum at 80 ^oC for 2 h. The extent of conversion was measured gravimetrically as the ratio of mass of microspheres to the amount of liquid macromonomer used for its preparation.

The effect of increasing the feed macromonomer solution concentration on the particle size distribution of the resultant microspheres is presented in Figure S2. As is evident, the distribution shifts towards larger sized microspheres as the concentration of siloxane in the feed increases, which can be attributed to the increased polymerisable content in the hydrophobic dispersed droplets. Morphological investigations reveal the smooth texture of the siloxane microspheres (Figure S2, Inset). In all cases, complete conversion (> 98%) could be achieved, as evidenced by gravimetric analysis.

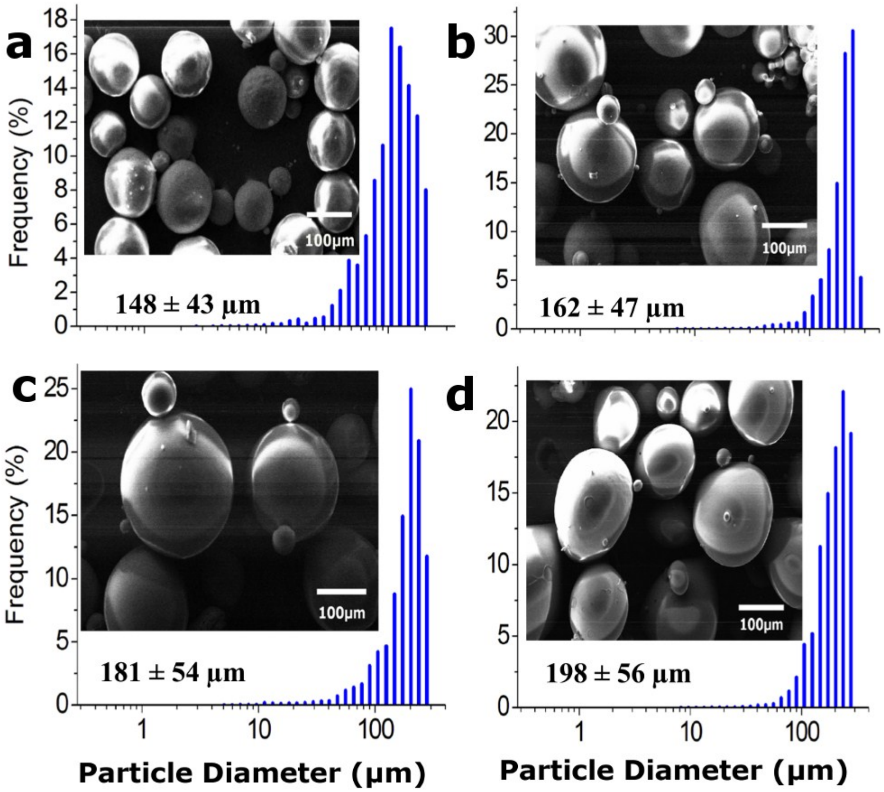

Fig. S2. Effect of feed concentration on the particle size distribution and surface morphology of PDMS microspheres (stirring speed 600 rpm). a) 30% b) 40% c) 50% d) 60%

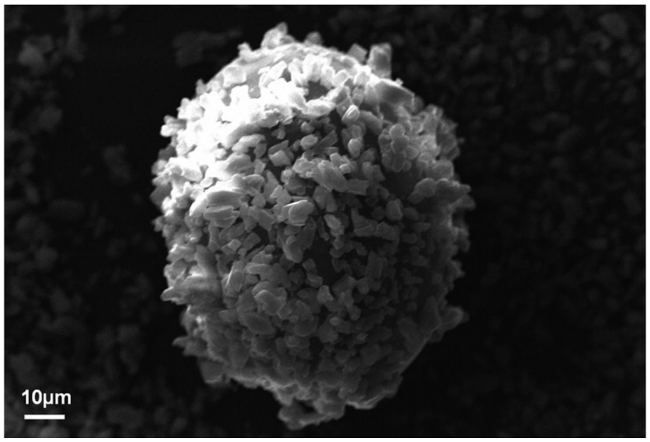

Fig S3: SEM image of a single core-shell microsphere

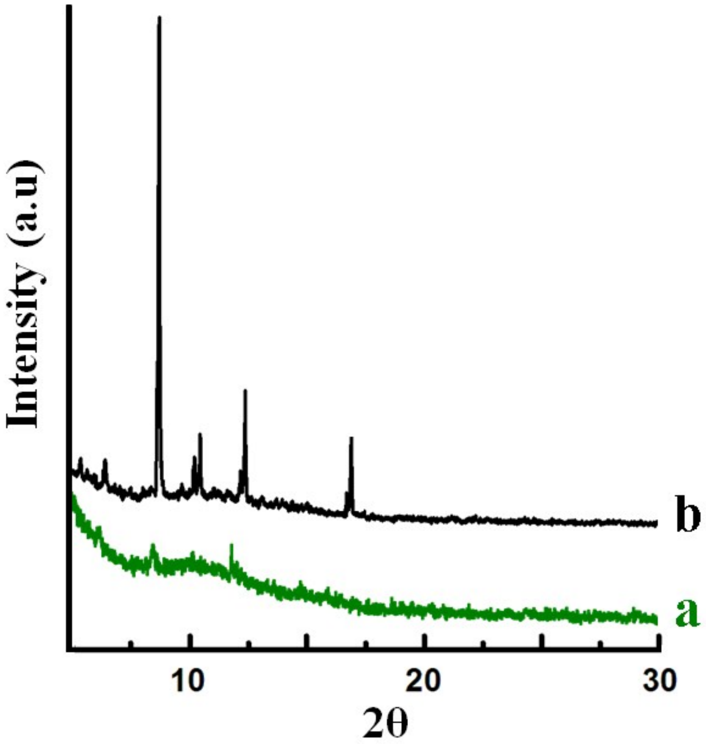

Fig. S4: PXRD pattern of a) PDMS, b) ZIF8@PDMS

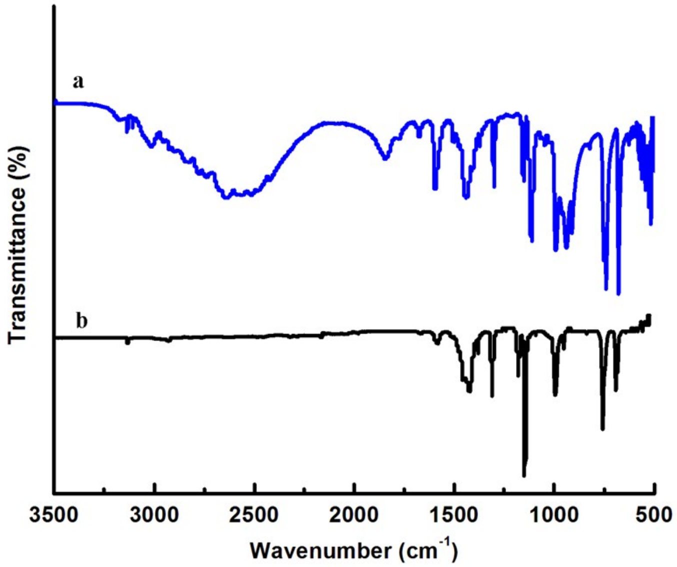

Fig. S5: FT-IR spectra of a) organic linker (2 methyl imidazole) and b) ZIF -8

Table S1: GC conditions for analysis of natural gas

Reference in main text	Natural gas mixture		
Figure 6	Composition	Amount (% v/v)	Retention time (min)
	Methane	79.37	0.6
	Ethane	6.72	1.7
	Propane	8.09	3.6
	Carbon dioxide	5.04	4.3
	Iso-Butane	6.72	4.9
	n-Butane	1.31	9.4
	iso-Pentane	0.53	12.0
	n-Hexane	0.19	15.2
Injector Temperature : 60 °C, Oven Temperature: 70°C, Detector temperature: 110°C			

Table S2: GC conditions for analysis of xylene mixtures

Reference in main text	Separation of xylene mixtures		
Figure 7	Composition	Amount (%)	Retention time (min)
	o- xylene	28.5	1.2
	m- xylene	57.2	2.2
	p- xylene	14.3	4.4
Injector Temperature : 150 °C, Oven Temperature: 140°C, Detector temperature: 150°C			

Table S3: GC conditions for analysis of ethanol-water solution

Reference in main text	Separation of ethanol water mixture		
Figure 8	Composition	Ethanol concentration (% v/v)	Retention time (min)
	Ethanol-water	4	1.2
	Ethanol-water	8	1.2
	Ethanol-water	12	1.2
	Ethanol-water	16	1.2
Injector Temperature : 150 °C, Oven Temperature: 110 °C, Detector temperature: 150 °C			

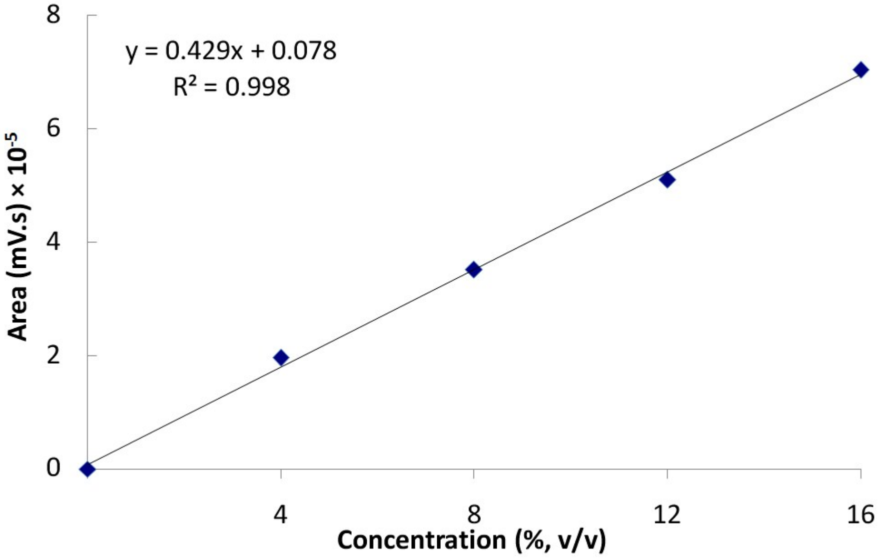

Fig. S6: Ethanol- water solutions:- FID response Area vs concentration plot.

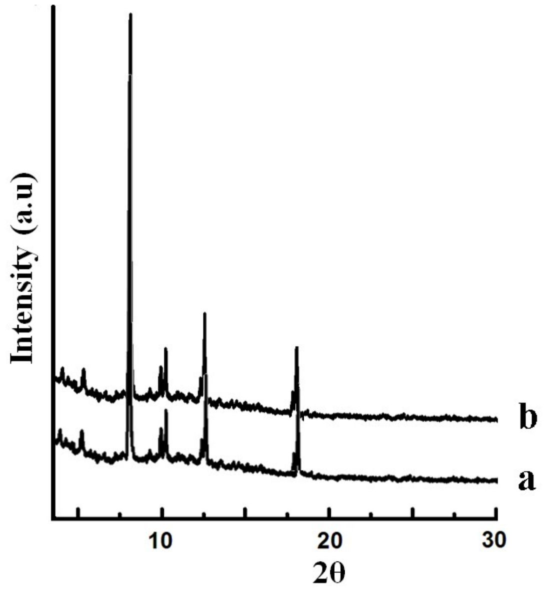

Fig. S7: PXRD of ZIF 8 a) as prepared b) after placing in ethanol-water mixture (16% v/v).

Table S4: GC conditions for analysis of hexane-octane solution

Reference in main text	Separation of hexane- octane solution		
Figure 9a	Composition	Concentration (% v/v)	Retention time (min)
	Hexane (b.pt 68°C)	75	1.4
	Octane (b.pt 125°C)	25	3.7
Injector Temperature : 170 °C, Oven Temperature: 160°C, Detector temperature: 170°C			

Table S5: GC conditions for separation of benzene-toluene

Reference	Separation of benzene-toluene solution

in main text			
Figure 9b	Composition	Concentration (% v/v)	Retention time (min)
	Benzene(b.pt 80°C)	66.7	1.2
	Toluene (b.pt 110°C)	33.3	1.9
Injector Temperature : 150 °C, Oven Temperature: 140°C, Detector temperature: 150 °C			

Table S6: GC conditions for separation of benzene-toluene-m-xylene

Reference in main text	Separation of Hexane and Petroleum ether solution		
Figure 9c	Composition	Concentration (% v/v)	Retention time (min)
	Benzene (b.pt 80°C)	25	1.0
	Toluene(b.pt 110°C)	50	1.8
	m-xylene (b.pt 138°C)	25	3.0
Injector Temperature : 140 °C, Oven Temperature: 130°C, Detector temperature: 140°C			