Electronic Supplementary Material (ESI) for ChemComm.

Exfoliation of two-dimensional zeolites in liquid polybutadienes

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Experimental:

Synthesis of MCM-22(P)

MCM-22 precursor, MCM-22(P), was synthesized using a reported method.[1] 0.072 g of sodium aluminate (Sigma Aldrich) and 0.248 g of sodium hydroxide (Fisher Scientific) were dissolved in 31.1 g of distilled water. 1.91 g of hexamethyleneimine (HMI) (Sigma Aldrich) and 2.36 g of fumed silica (Cab-O-Sil M5) were then added to the mixture. The resulting gel composition was 100 SiO_2: 50 HMI: 2.2 $NaAlO_2$: 15.8 NaOH: 4400 H_2O. The mixture was stirred at room temperature for 5 h, followed by hydrothermal synthesis in a Teflon-lined stainless steel autoclave with a rotation of 8 rpm at 135 °C for 11 days. The obtained crystalline product was collected by centrifugation and repeatedly washed by distilled water until the pH of supernatant solution was reduced to 9.

Swelling of MCM-22(P)

MCM-22(P) was swollen with cetyl trimethyl ammonium bromide (CTAB) at room temperature following a reported procedure.[2] 9.0 g of aqueous slurry of MCM-22(P) (20 wt% solids) was mixed with 35.0 g of an aqueous solution of 29 wt% CTAB (Research Organics Inc.) and 11.0 g of an aqueous solution of 40 wt% tetrapropyl ammonium hydroxide (Alfa Aesar). The mixture was stirred at room temperature for 16 h. The particles were then recovered by 15 cycles of centrifugation and washing with distilled water so that the pH of the supernatant solution was gradually reduced to 9. The resulting swollen material, MCM-22(S), was dried overnight in an oven at 70 ^{o}C.

Synthesis of multilamellar MFI

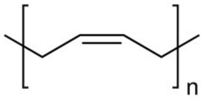
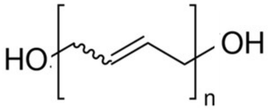
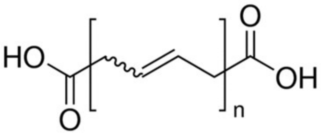
Multilamellar MFI (ml-MFI) was synthesized using a reported procedure.[3] $[C_{22}H_{45}\text{-}N^+(CH_3)_2\text{-}C_6H_{12}\text{-}N^+(CH_3)_2\text{-}C_6H_{13}]Br_2$, $C_{22\text{-}6\text{-}6}Br_2$, was synthesized by alkylation of N,N,N',N'-tetramethyl-1,6-hexanediamine (TCI Chemicals) with 1-bromodocosane (TCI chemicals) at 70 °C. The resultant product was alkylated by 1-bromohexane (Alfa Aesar) at 85 °C. $C_{22\text{-}6\text{-}6}Br_2$ was ion-exchanged with Amberlyst A-26(OH) resin (Alfa Aesar) to obtain $C_{22\text{-}6\text{-}6}(OH)_2$. Ml-MFI was synthesized by hydrolyzing tetraethyl orthosilicate (Alfa Aesar) in presence of $C_{22\text{-}6\text{-}6}(OH)_2$ and distilled water to obtain a gel composition of 100 SiO_2: 15 $C_{22\text{-}6\text{-}6}(OH)_2$: 4000 H_2O: 400 C_2H_5OH. The gel was stirred at room temperature for 24 h and then transferred to a Teflon-lined stainless steel autoclave. Crystallization was carried out at 150 °C for 5 days. The product obtained by centrifugation was washed with distilled water until the pH of supernatant solution was reduced to 9, and then dried overnight in an oven at 70 ^oC.

Exfoliation of MCM-22 (S) and ml-MFI

Hydroxyl-terminated polybutadiene (HTPB, Average M_n =2800 g/mol), carboxyl-terminated polybutadiene (CTPB, Average M_n = 4200 g/mol) and polybutadiene (PB, Average M_n = 5000 g/mol) from Sigma Aldrich were used. 10 wt% zeolite was first mixed with each of the polybutadienes above forming zeolite/polymer suspension. The exfoliation of MCM-22(S) and ml-MFI was achieved by either chaotic flow or sonication. The zeolite/polymer suspension was subjected to chaotic flow treatment in a planetary mixing system (FlackTek SpeedMixer DAC 150). The combination of gravitational forces in different planes enables efficient shearing and mixing of the suspension. The chaotic flow is achieved by adding four cylindrical ceramic pebbles (h =10.0mm, r= 4.80mm) into the zeolite/polymer suspension. A rotational speed of

3000 rpm was used in 2 min cycles followed by a 1 min cooling. For exfoliation using sonication, the zeolite/polymer suspension was subjected to sonication in a bath sonicator (Branson 3510) at room temperature for different time periods.

Table S1: Structures of the polymers used

Polymer	Structure
Polybutadiene (PB)	
Hydroxyl-terminated polybutadiene (HTPB)	
Carboxyl-terminated polybutadiene (CTPB)	

Characterization

The small-angle X-ray (SAXS) scattering data was obtained using a SAXSLAB's Ganesha instrument with a Cu-Kα radiation source and a sample-to-detector distance of 441 mm. Powder X-ray diffraction patterns were collected on a PANalytical X'Pert Pro instrument with a Cu-Kα radiation source in the 2θ range of 4° to 32°. Transmission electron microscope (TEM) images of the zeolite nanosheets were obtained using a JEOL JEM-2200FS instrument operated at 200 kV. 0.3 g of the zeolite/polybutadiene mixture after exfoliation was dissolved in 5 mL of toluene, and centrifuged for 10 min at 6000 rpm. The supernatant was collected for the TEM observation. To prepare the TEM samples, a drop of the supernatant was deposited on a copper grid (Lacey carbon film, Cu 300 mesh, Electron Microscopy Sciences), and dried in air. Scanning electron microscope (SEM) images were collected using FEI Magellan 400 XHR-SEM operated at 3.0 kV. The samples were sputter-coated with platinum before imaging. Atomic force microscopy (AFM) measurements on the nanosheets were performed on an Asylum Research Cypher ES (Oxford instruments) using a non-contact cantilever (BudgetSensors Tap300Al-G; k = 40 N/m, f = 300 kHz) in tapping mode. To prepare the samples, a drop of the nanosheet suspension in toluene was deposited on a mica disc (MTI Corporation, 9.9 mm diameter). The polymer was removed from the sample by calcining at 540 °C for 6 h in air flow with a flow rate of 472 mL/min.

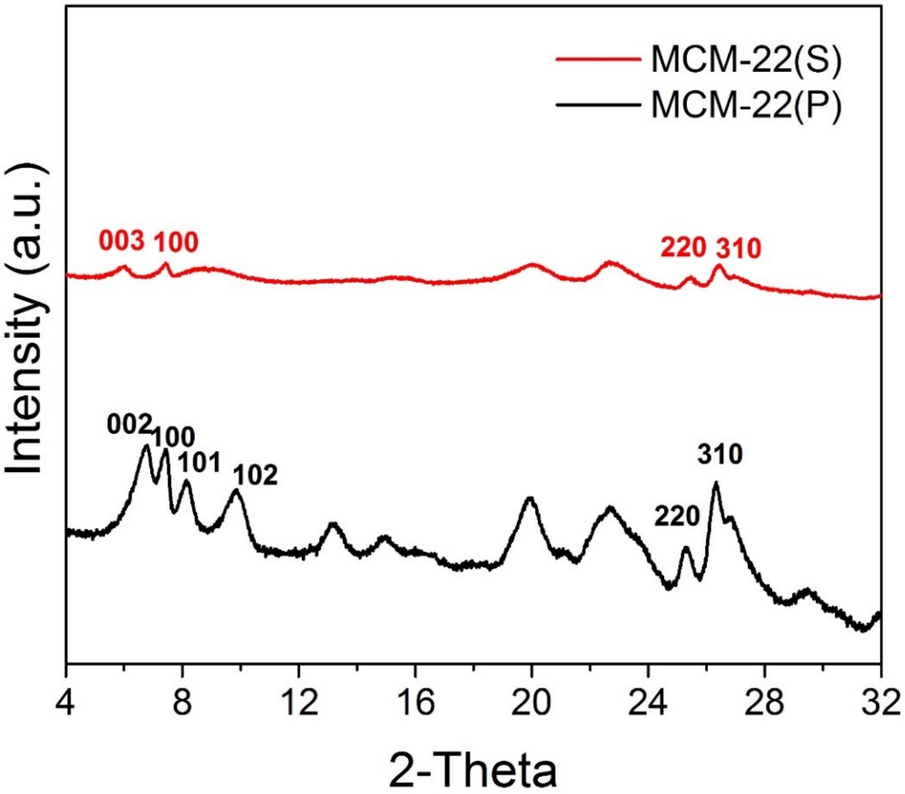


Figure S1: XRD patterns of MCM-22(P) and MCM-22(S). The diffraction peaks associated with the MWW framework are not changed during the swelling process (from MCM-22(P) to MCM-22(S)), indicating the crystalline structure of layered precursor was retained.

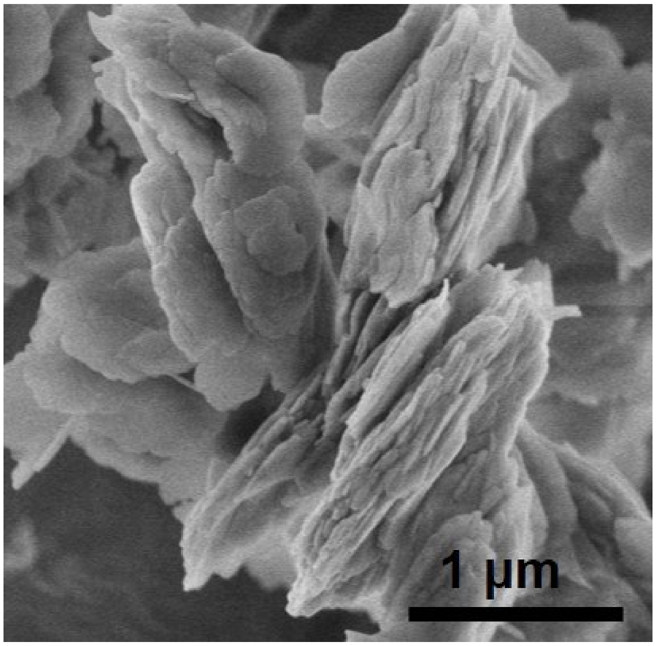


Figure S2: SEM image of MCM-22(S) shows the layered structure of the material.

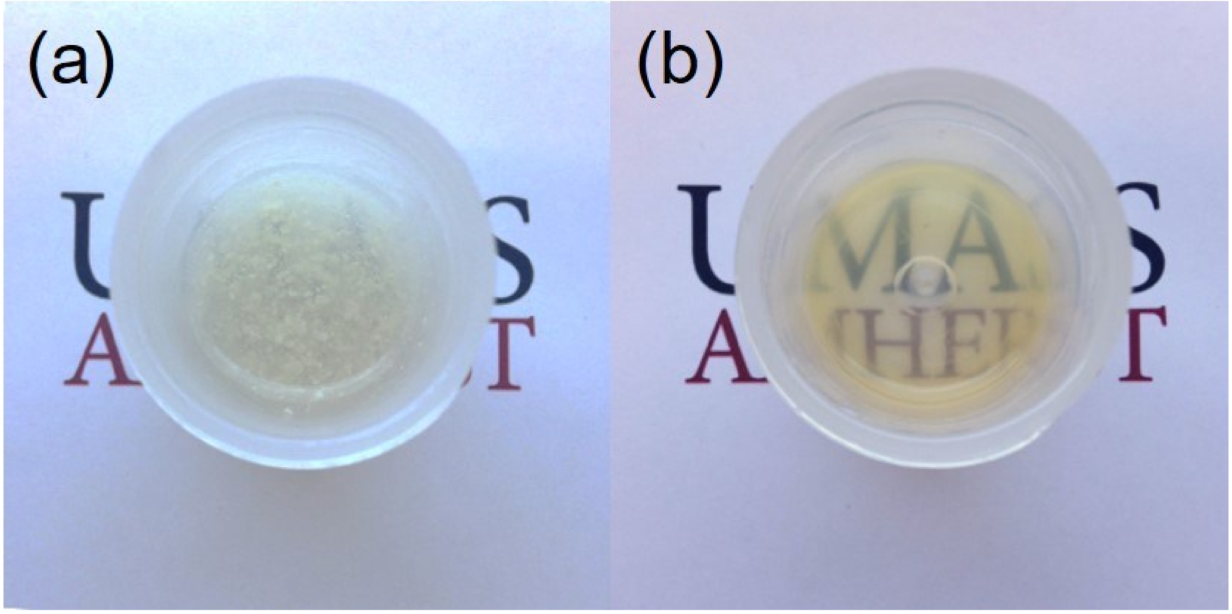


Figure S3: MCM-22(S)/HTPB mixture **(a)** manually mixed with a slight stir, and **(b)** after 36 min of chaotic-flow treatment. After the chaotic-flow treatment, the mixture transformed from a dispersion of visual aggregates to a transparent mixture.

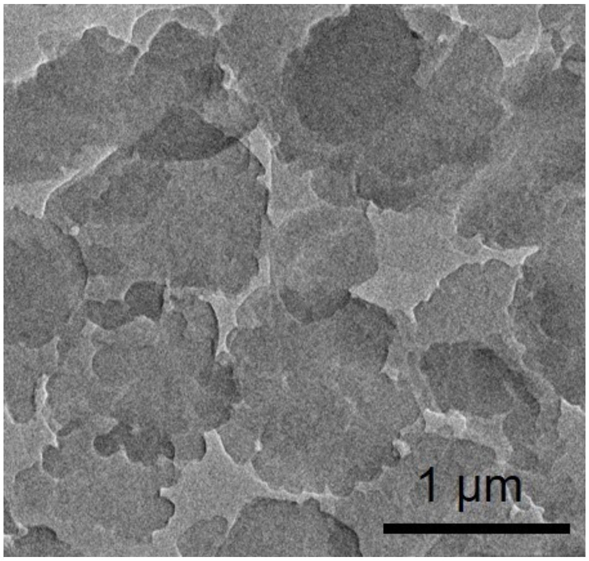


Figure S4: TEM image showing the presence of partially-exfoliated particles. The exfoliated MCM-22(S) with HTPB was dispersed in toluene and the resultant dispersion was used for the TEM imaging.

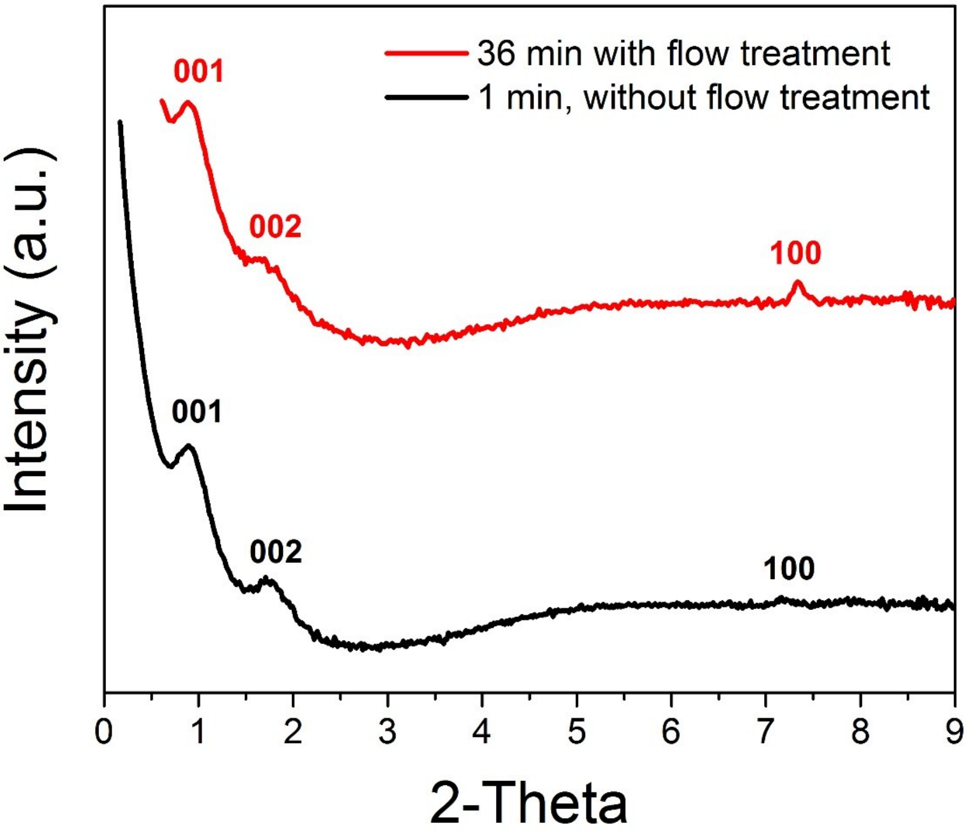


Figure S5: SAXS patterns of MCM-22(S)/CTPB mixture after 1 min of mixing without flow treatment and after 36 min of mixing with flow treatment. Mild mixing of MCM-22(S) with CTPB increases the d-spacing to 9.8 nm. Chaotic flow treatment for 36 min, however, does exfoliate the zeolite any further.

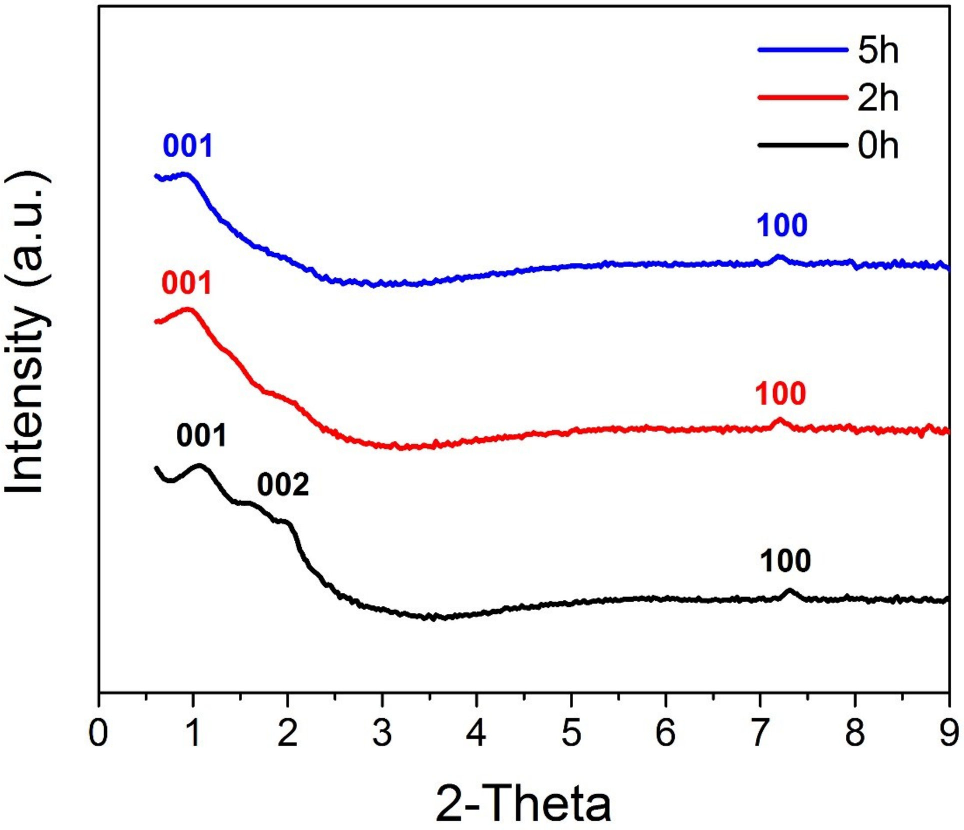


Figure S6: SAXS patterns of MCM-22(S/HTPB mixture after slight manual stirring and no sonication (0 h) and of MCM-22(S)/HTPB mixture after 2 and 5 hours of sonication respectively. The intensities of (001) and (002) reflections decrease with increasing sonication time.

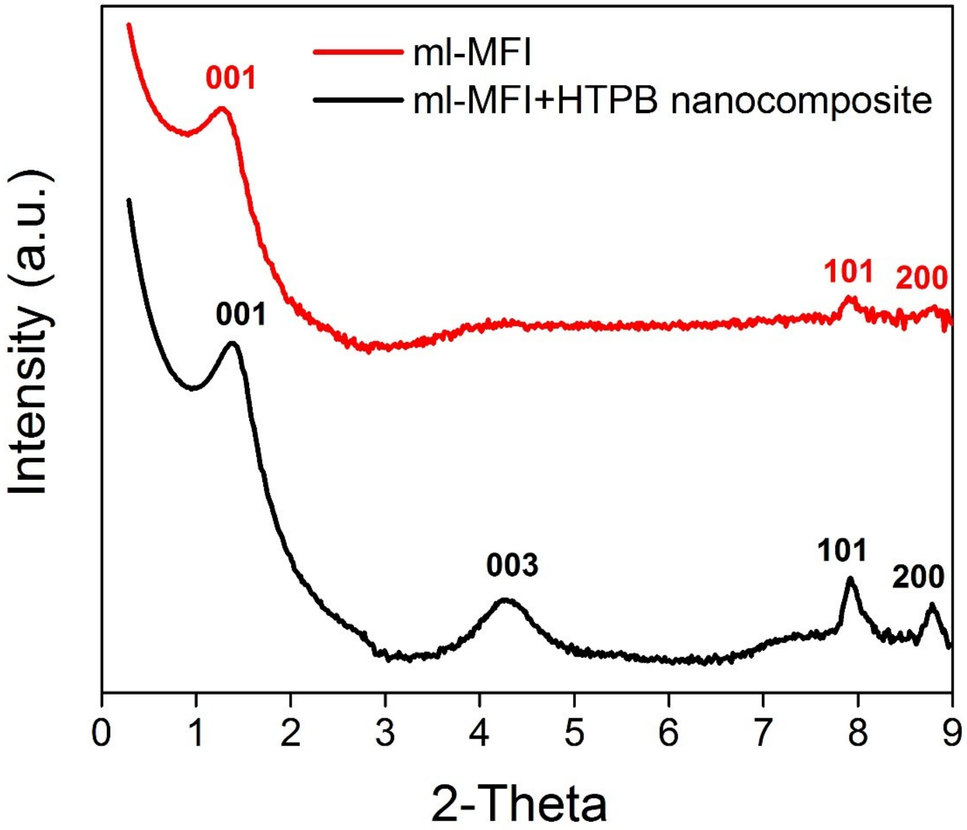


Figure S7: SAXS pattern of ml-MFI and the ml-MFI/HTPB nanocomposite after 36 min of chaotic flow treatment.

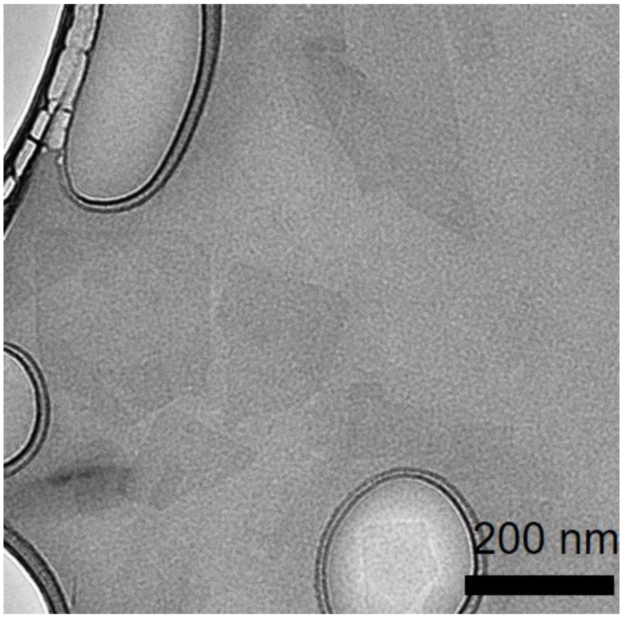


Figure S8: TEM image showing MWW nanosheets. The exfoliated MCM-22(S)/HTPB mixture was dispersed in toluene and further centrifuged. The supernatant was collected and used for TEM imaging.

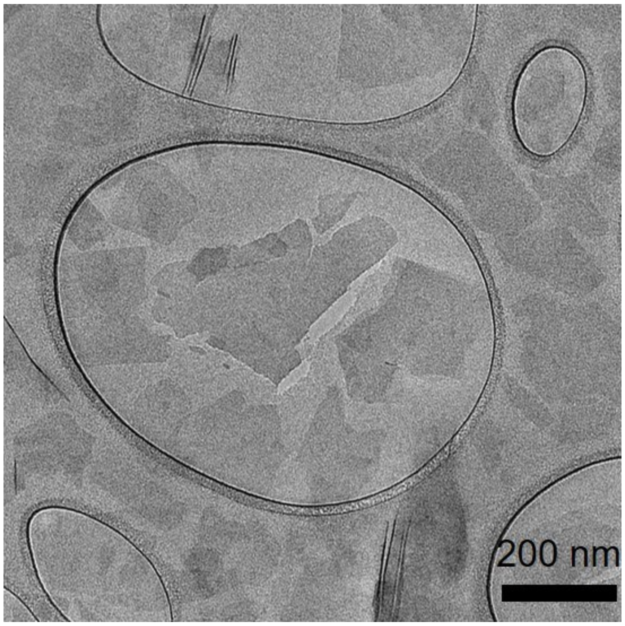


Figure S9: TEM image showing MFI nanosheets. The exfoliated ml-MFI/HTPB mixture was dispersed in toluene and further centrifuged. The supernatant was collected and used for TEM imaging.

Radius of gyration of polymer and its effect on exfoliation

$$R_g \cong C_\infty N^{\frac{1}{2}} \quad (1)$$

Equation 1 is used to understand the effect of polymer molecular weight on the size and conformation of the polymer, in which R_g is the radius of gyration of the polymer and N is the degree of polymerization.[4]

$$N = \frac{M_n}{M_o} \quad (2)$$

Where M_n = Number average molecular weight
M_o = Molecular weight of the monomer unit

$$\Rightarrow \frac{(R_g)_{CTPB}}{(R_g)_{HTPB}} = \frac{(C_\infty)_{CTPB}(M_n)_{CTPB}{}^{1/2}}{(C_\infty)_{HTPB}(M_n)_{HTPB}{}^{1/2}}$$

Assuming the C_∞ for HTPB and CTPB are the same,

$$\frac{(R_g)_{CTPB}}{(R_g)_{HTPB}} = \frac{4200^{1/2}}{2800^{1/2}} = 1.22$$

Table S2: d-spacing of MCM-22(S) after mixing with various polybutadienes

Polymer	M_n (g/mol)	d-spacing after 1 min mixing without flow treatment (nm)	d-spacing after 36 min mixing with flow treatment (nm)
HTPB	2800	9.4	Exfoliated
CTPB	4200	9.8	9.9
PB	5000	4.7	4.9

The interlayer d-spacing of MCM-22(S) powder is 4.6 nm. PB has no end-groups and does not intercalate the zeolite layer. Thus, PB doesn't change the d-spacing of MCM-22(S), highlighting its inability to intercalate the zeolite.

HTPB and CTPB possess functional end-groups that can intercalate the zeolite only after mild mixing. The radius of gyration of CTPB is 1.22 times larger than that of HTPB. Hence, CTPB increases the d-spacing slightly more (9.8 nm) than HTPB (9.4 nm).

However, after application of flow treatment, only HTPB is able to exfoliate the zeolite. On the other hand, CTPB increases the interlayer d-spacing only to 9.9 nm on application of flow treatment. This highlights the critical role of the polymer end-groups on exfoliation.

References

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