Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information:

Exploring the Potential and Design of Zeolite Nanosheets as Pervaporation Membranes for Ethanol Extraction

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1. Computational Details

MD simulations, implemented in the open-source LAMMPS package,[1] were employed to quantify the performance of zeolite nanosheets as pervaporation membranes to separate ethanol from ethanol/water mixtures at varying ethanol concentrations of 20 wt%, 40 wt%, and 80 wt%. The simulation system, as shown in Figure 1 of the manuscript, is consisted of three regions: feed (i.e., an ethanol/water mixture at a given concentration), membrane (i.e., a zeolite nanosheet as an active pervaporation layer), and permeate (i.e., a large vacuum space). The ethanol/water mixture at a given concentration in the feed side is bounded by a graphene sheet as a piston to modulate the pressure at one atm. The vacuum condition of the permeate side was also maintained using a graphene sheet as an adsorbing plate to capture all permeated molecules. In these calculations, to describe intermolecular and intramolecular interactions, both non-bonded and bonded potentials were used. For non-bonded contributions, we used 12-6 Lennard-Jones (L-J) potential for van der Waals interactions, while point charge models were employed for describing Coulombic contributions. The L-J potential was truncated and shifted to zero at a cutoff radius of 12 Å, and the long-range electrostatic interactions were computed using the particle-particle particle-mesh (pppm) method. The force field developed by Emami et al.,[2] a potential that has been shown to describe the interface between aqueous liquids and siliceous materials well, was adopted for zeolite nanosheets. The OPLS-AA force field[3] and the TIP4P/2005 model[4] were used to model ethanol and water molecules, respectively. The carbon atoms of the piston were also described by the OPLS-AA force field. For the carbon atoms in the adsorbing plate, to ensure all of the permeated molecules during the simulations were captured by the plate, larger values were assigned to their ε and σ parameters (i.e., 10 kcal/mol and 5 Å, respectively). We have also applied a permeant force on the molecules in a region with 15 Å from the adsorbing plate to help capture all permeated molecules. The geometric mixing rule was applied for estimating the pair-wise L-J parameters of dissimilar atoms, per the OPLS-AA force field. However, since the zeolite membranes should not be influenced by the piston as well as the adsorbing plate, their L-J pair-wise coefficients (i.e., piston-membrane and plate-membrane) were set to zero. All the non-bonded potential parameters including L-J coefficients and atomic partial charges are summarized in Tables S1-S5 below, and the definition of each atom type assigned for nanosheets and ethanol molecules can also be seen respectively in Figures S1 and S2. For bonded interactions, harmonic models were used to describe bonding and bending with the OPLS style for dihedral contributions. All non-bonded parameters are given in Tables S6-S8. We note that intra-vdW interactions were included with a 1-4 scaling factor of 0.5.

To investigate the separation performance of each membrane candidate studied in this work, simulations in the canonical ensemble were carried out using the Nosé-Hoover thermostat with a timestep of 1 fs and a damping factor of 100 fs. In these calculations, the bulk part of nanosheet (i.e., non-surface portion), as well as the piston and adsorbing plate, were assumed to be rigid, whereas the surface silanol groups and ethanol molecules were fully flexible. At least four simulation replicas with different initial configurations were conducted to ensure statistically accurate results. We note

that, before sampling the membrane's separation performance, at least 20 ns equilibration simulations were first performed to saturate the membranes.

Table S1. L-J parameters for atoms in zeolite nanosheets. The definition of each atom type can be seen in Figure S1.

Atom type	ε (kcal/mol)	σ (Å)
Ho	0.015	0.9666
Oh	0.122	3.0914
Osi	0.054	3.0914
Si	0.093	3.6972
Sioh	0.093	3.6972

Table S2. L-J parameters for water molecules, as given from the TIP4P/2005 model.[4]

Atom type	ε (kcal/mol)	σ (Å)
O (H_2O)	0.1852	3.1589
H (H_2O)	0	0

Table S3. L-J parameters for ethanol molecules, as given from the OPLS-AA force field.[3] The definition of each atom type can be seen in Figure S2.

Atom type	ε (kcal/mol)	σ (Å)
Ch/Coh	0.066	3.5
Hc	0.03	2.5
Oh_e	0.17	3.12
Ho_e	0	0

Table S4. Pair-wise L-J parameters for pair-wise interactions between ethanol molecules and the carbon atoms in the piston or the adsorption plate.

Atom type	Piston		Adsorbing plate	
	ε (kcal/mol)	σ (Å)	ε (kcal/mol)	σ (Å)
OT	0.096	3.325	1.36	3.98
HT	0	0	0	0
Ch/Coh	0.0574	3.5	0.8124	4.2
Hc	0.0387	2.96	0	0
Oh_e	0.092	3.3	1.303	3.95
Ho_e	0	0	0	0

Table S5. Partial charges of all atom types defined in this study

Atom type	q (e)
Ho	0.4
Oh	-0.675
Osi	-0.55
Si	1.1
Sioh	1.1

OT	-1.1128
HT	0.5564
Coh	0.145
Ch	-0.18
Hc	0.06
Oh_e	-0.6830
Ho_e	0.4180
C (Piston/Plate)	0

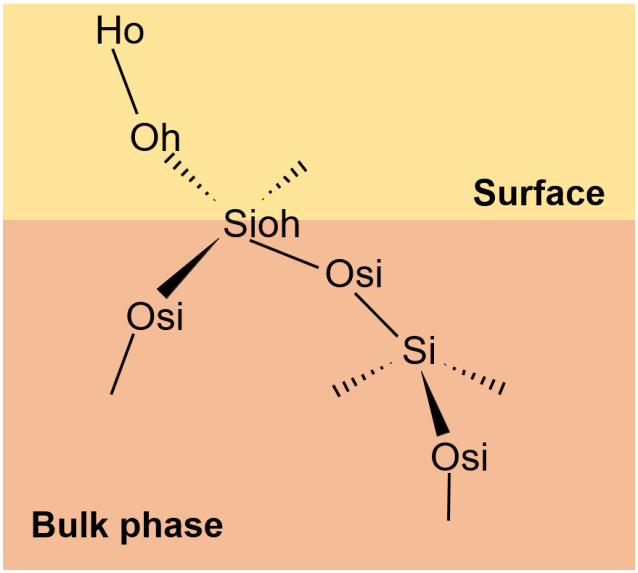

Figure S1. A schematic diagram of the atom types defined for nanosheet zeolites. Ho, Oh and Sioh respectively refer to the hydrogen, oxygen, and silicon of the surface silanol groups, while Osi and Si respectively represent the bridging oxygen and silicon in the bulk phase.

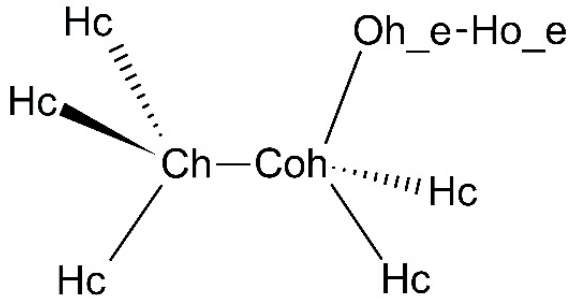

Figure S2. A schematic diagram of the atom types defined for ethanol molecules.

Table S6. Potential coefficients for bond stretching.

Bond type	K (kcal/mol-Å ^{2})	r_0 (Å)
Ho-Oh	495	0.945
Oh-Sioh	285	1.68
Osi-Si	285	1.68
Osi-Sioh	285	1.68
Oh_e-Ho_e	553	0.945
Coh-Oh_e	320	1.41
Coh-Ch	268	1.529
Ch-Hc	340	1.09

Table S7. Potential coefficients for angle bending.

Angle type	K (kcal/mol)	θ (degrees)
Ho-Oh-Sioh	50	115
Oh-Sioh-Osi	100	109.5
Osi-Si-Osi	100	109.5
Osi-Sioh-Osi	100	109.5
Si-Osi-Si	100	149
Si-Osi-Sioh	100	149
Sioh-Osi-Sioh	100	149
Coh-Oh_e-Ho_e	55	108.5
Ch-Coh-Oh_e	50	109.5
Hc-Coh/Ch-Hc	33	107.8
Hc-Hoh-Oh_e	35	109.5
Coh-Ch-Hc/Ch-Coh-Hc	37.5	110.7

Table S8. Potential coefficients for dihedral torsion.

Dihedral type	K1 (kcal/mol)	K2 (kcal /mol)	K3 (kcal /mol)	K4 (kcal /mol)
Ch-Coh-Oh_e-Ho_e	-0.356	-0.174	0.492	0
Hc-Ch-Coh-Oh_e	0	0	0.468	0
Hc-Coh-Oh_e-Ho_e	0	0	0.450	0
Hc-Ch-Coh-Hc	0	0	0.318	0

2. Additional Figures and Tables Referred in the Manuscript

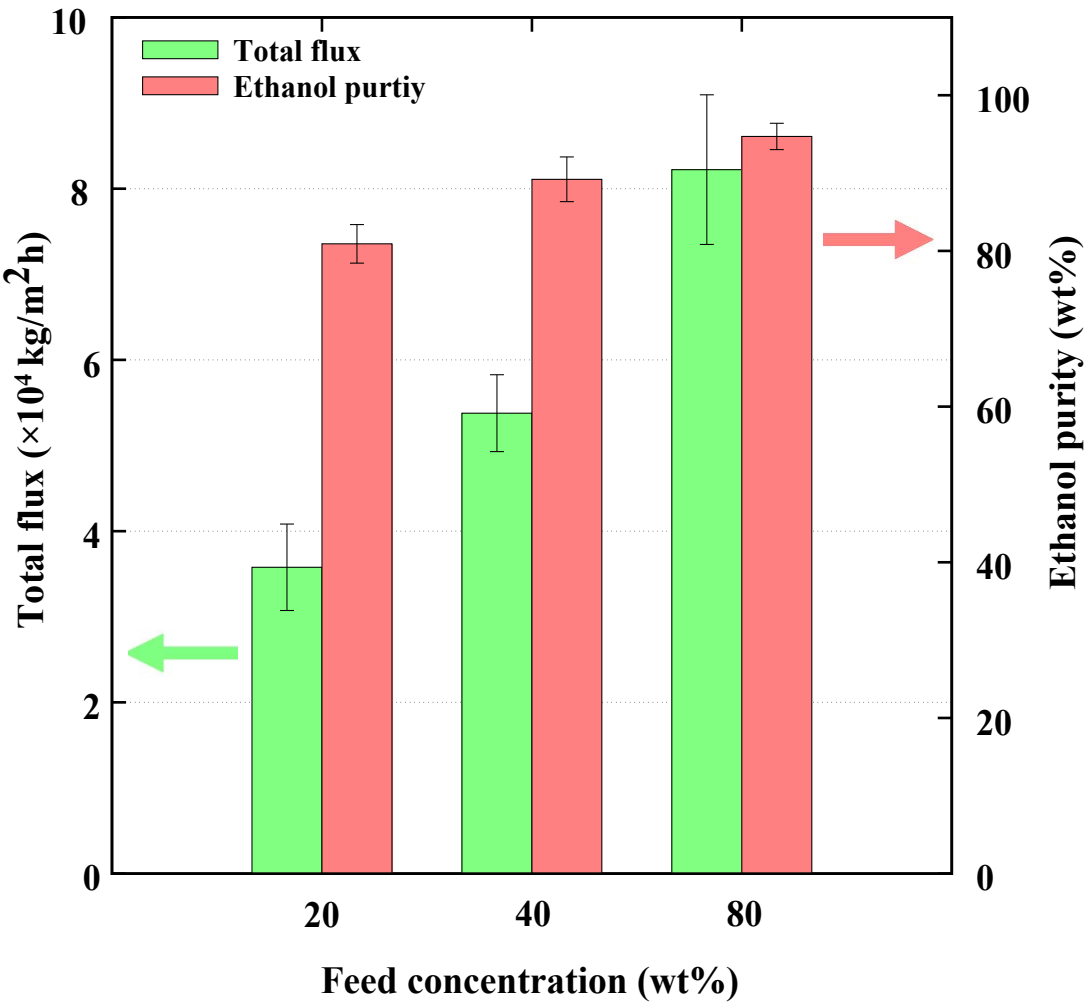

Figure S3. The product purity and total flux predicted for the MFI nanosheet membrane with feed concentrations of 20 wt% 40 wt% and 80 wt% at 353 K.

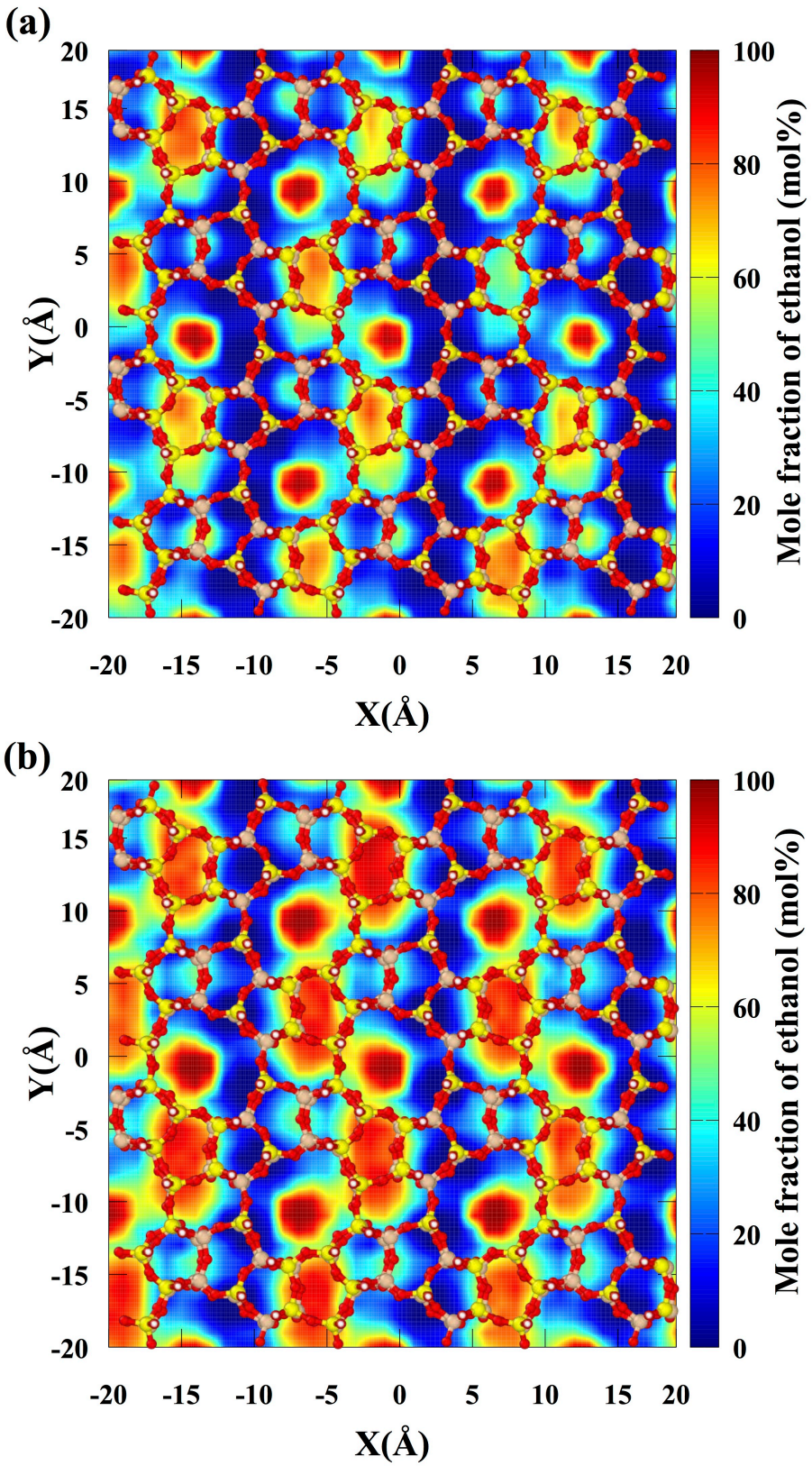

Figure S4. Density plots of ethanol adsorbed on the membrane surface for (a) MFI_1 and (b) MFI_2. Color bar indicates the mole fraction of ethanol (mol%) with warmer colors representing a higher mole fraction.

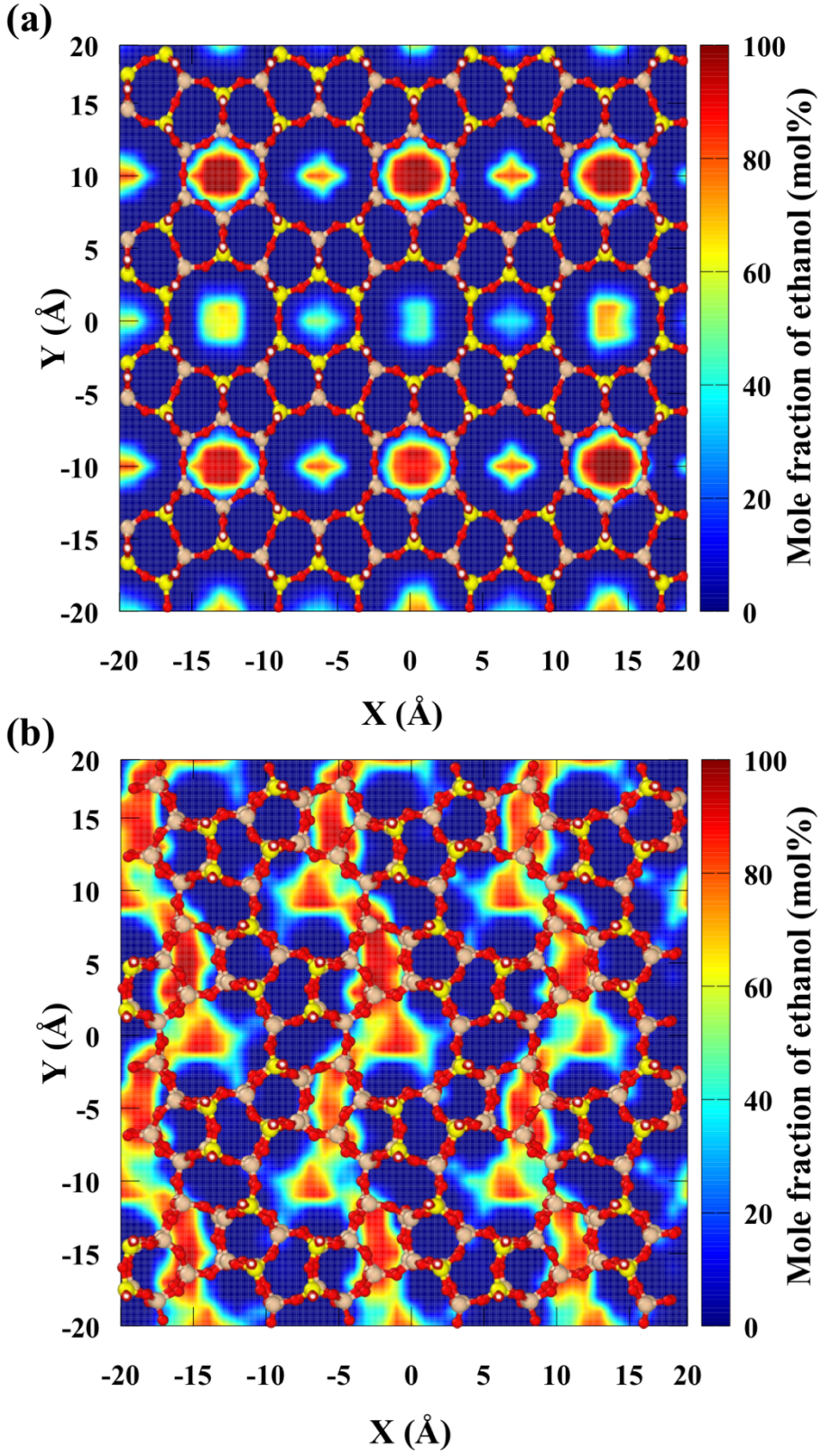

Figure S5. Density plots of ethanol adsorbed on the membrane surface for (a) FER and (b) MFI-zigzag. Color bar indicates the mole fraction of ethanol (mol%) with warmer colors representing a higher mole fraction.

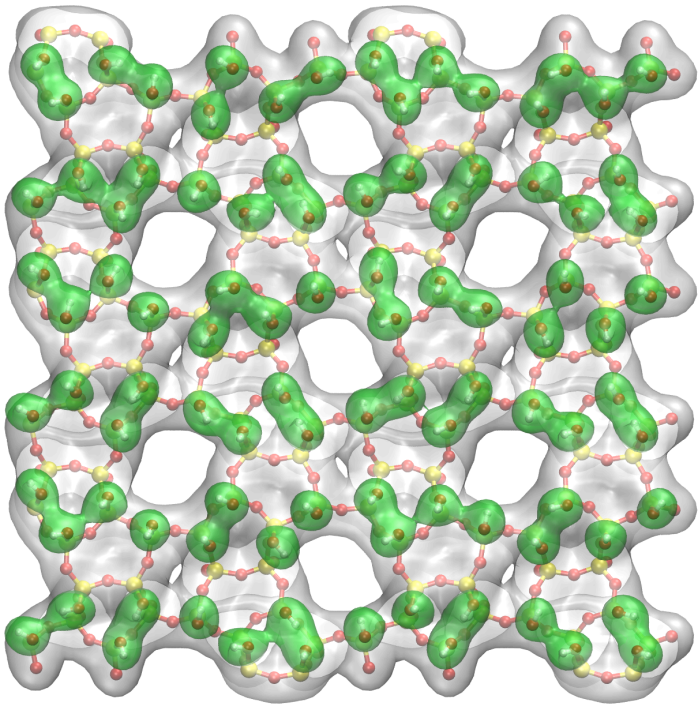

Figure S6. The top view of the MFI nanosheet surface. The structure is presented by sticks and balls with van der Waals surfaces highlighted in transparent grey, and the surface silanol groups are highlighted in green. Color code for the structure: yellow-silicon, red-oxygen, white-hydrogen.

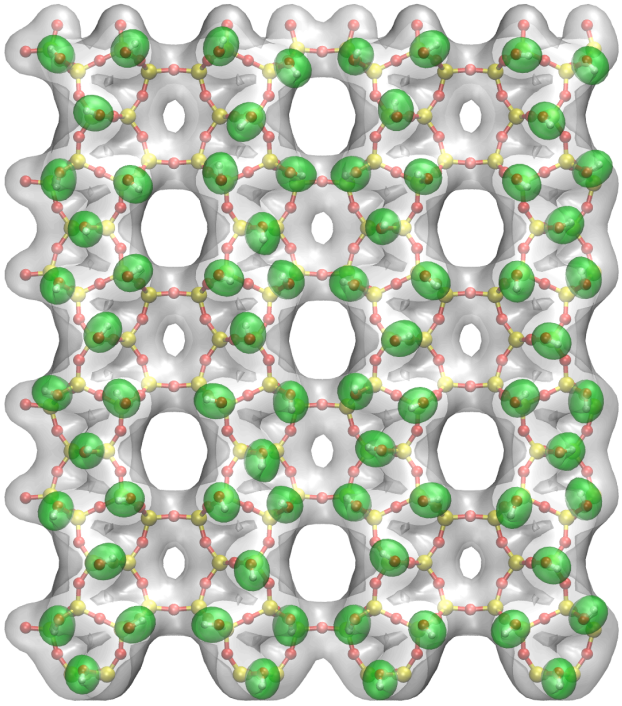

Figure S7. The top view of the FER nanosheet surface. The structure is presented by sticks and balls with van der Waals surfaces highlighted in transparent grey, and the surface silanol groups are highlighted in green. Color code for the structure: yellow-silicon, red-oxygen, white-hydrogen.

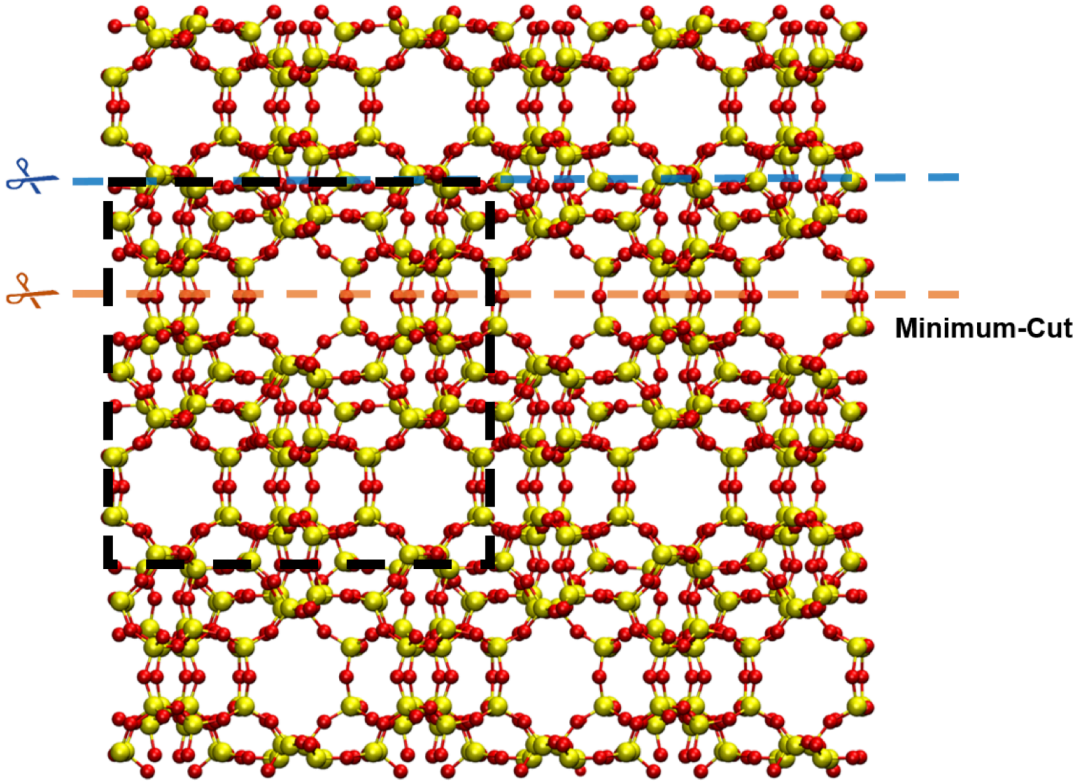

Figure S8. A schematic representation of two different surface terminations: the blue dashed line and the orange dashed line indicate to the surface cuts for the MFI membrane and the MFI-zigzag membrane, respectively. The unit cell of MFI structures is presented by a black dashed rectangle. The structure is presented by sticks and balls. Color code: yellow-silicon, red-oxygen, white-hydrogen.

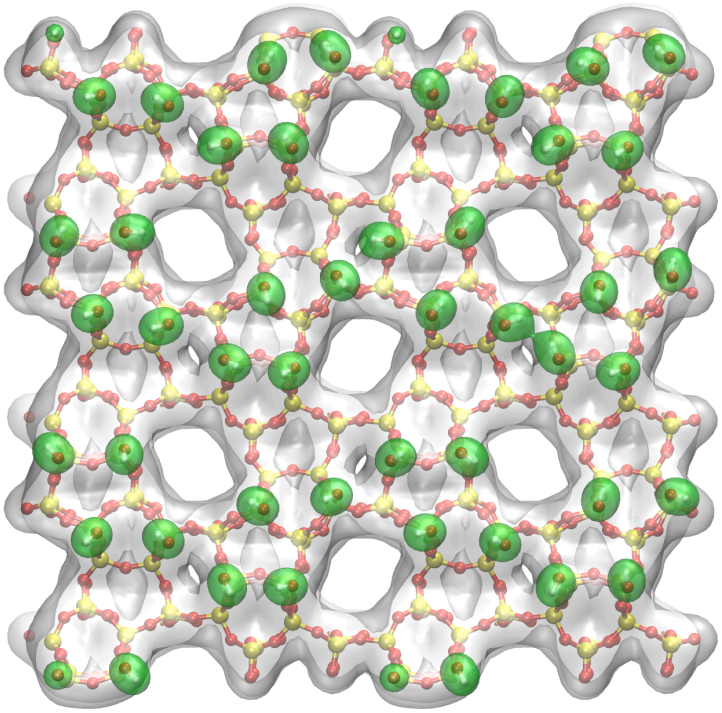

Figure S9. The top view of the MFI-zigzag nanosheet surface. The structure is presented by sticks and balls with van der Waals surfaces highlighted in transparent grey, and the surface silanol groups are highlighted in green. Color code for the structure: yellow-silicon, red-oxygen, white-hydrogen.

References

1 S. Plimpton, *J. Comput. Phys.*, 1995, **117**, 1–19.

2 F. S. Emami, V. Puddu, R. J. Berry, V. Varshney, S. V. Patwardhan, C. C. Perry and H. Heinz, *Chem. Mater.*, 2014, **26**, 2647–2658.

3 W. L. Jorgensen, D. S. Maxwell and J. Tirado-Rives, *J. Am. Chem. Soc.*, 1996, **118**, 11225–11236.

4 J. L. Abascal and C. Vega, *J. Chem. Phys.*, 2005, **123**, 234505.