Supporting Information

Adsorption of Butanol and Water Vapors in Silicalite-1 Films with Low Defect Density

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***In Situ* ATR-FTIR Experiments and Method.** At each partial pressure, the IR spectra were recorded continuously until equilibrium was reached. The Beer-Lambert law can be used to define a linear relationship between the absorbance and concentration of a sample. However, in order to calculate the amount of adsorbed species in ATR experiments, the Beer-Lambert law cannot be used directly. Mirabella[1] and Tompkins[2] have derived expressions to calculate concentrations of components adsorbed in a film on an ATR crystal:

$$\frac{A}{N} = \frac{n_{21} E_0^2 \varepsilon}{\cos\theta} \int_0^\infty C(z) e^{-2z/d_p} d_z \tag{S1}$$

Where A is the integrated absorbance, N is the number of reflections (here it is 20) inside the ATR element between the gaskets sealing the cell, n_{21} is the ratio of the refractive indices of the ATR element and zeolite film. The refractive index of ZnS is 2.25, whereas Nair et al.[3] reported the refractive index of empty MFI zeolite in the infrared range of 3000-1500 cm^{-1}. It was assumed that the refractive index of film would change linearly with the amount of adsorbed water and butanol. Furthermore, ε is the molar absorptivity which was previously determined[4] for water in a high-silica (Si/Al = 130) film. E_0 is the amplitude of the electric field at the interface between ATR element and zeolite film.[5-6] $C(z)$ is the concentration of adsorbate in the film, and θ is the angle of incidence (45°). Further, d_p is the penetration depth given by Eq. S2:

$$d_p = \frac{\lambda_1}{2\pi(\sin^2\theta - n_{21}^2)^{1/2}} \tag{S2}$$

where λ_1 is the wavelength of the infrared radiation inside the ATR element. The following equation (Eq. S3) was obtained by integrating over the film assuming a homogeneous concentration of the adsorbate in the film at equilibrium:

$$\frac{A}{N} = \frac{n_{21} E_0^2 d_p C}{2\cos\theta} \varepsilon\left(1 - e^{-2d_a/d_p}\right) \quad \text{(S3)}$$

d_a is the thickness of the film.

The molar absorptivity for butanol adsorbed in silicalite-1 is not reported yet; therefore, it was assumed that the silicalie-1 film had the same butanol uptake as silicalite-1 powder.[7-8] As Hammond et al. reported,[7] the adsorption behavior of MFI membrane is very similar to that of MFI powder. Besides, butanol uptake in MFI depends on the number of molecules that may fit per unit cell which would be very similar for both powder and film. Hence, it was assumed that the maximum absorbance determined for butanol from IR spectra of the silicalite-1 film loaded with butanol corresponds to the butanol uptake in silicalite-1 powder determined by the volumetric measurements (see figure 6). To avoid the contribution of capillary condensation of butanol in the powder grains, the uptake was measured below the mesoporous region (activity~ 12%).

Adsorption Selectivity: *The butanol/water adsorption selectivity of the silicalite-1(F^-) film was determined by using equation (S4):*

$$\alpha_{BuOH/H_2O} = \frac{X_{BuOH}/X_{H_2O}}{Y_{BuOH}/Y_{H_2O}} \quad \text{(S4)}$$

where X and Y are the mole fractions of an adsorbate in the film and feed respectively.

Sips and Langmuir Isotherms. Both of the Langmuir and Sips models were fitted to the butanol adsorption isotherms in silicalite-1(F^-) and silicalite-1(OH^-) films and presented in figures S1 and S2. It is clear that the Sips model fitted the isotherms better and could described the adsorption of butanol in both samples well.

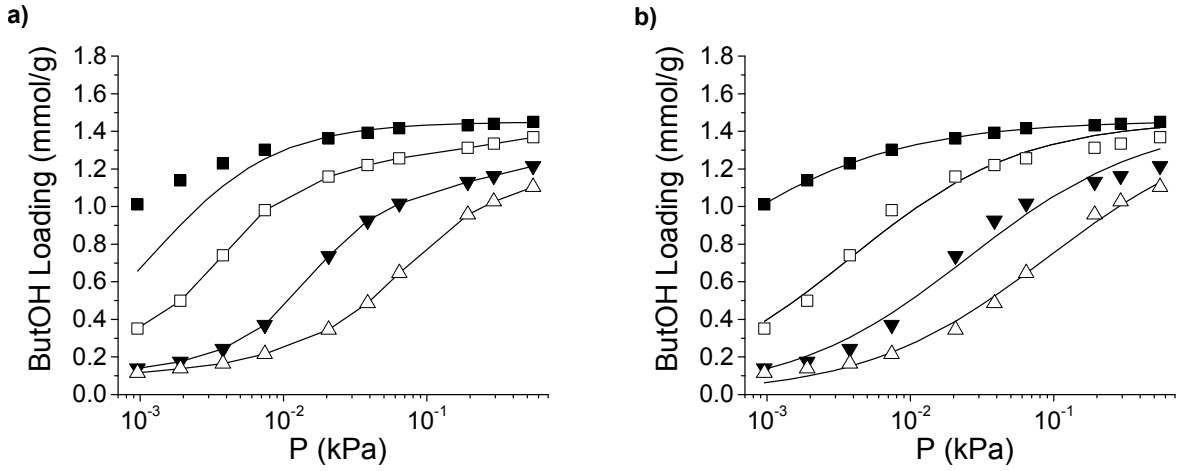

Figure S1. Adsorption isotherms for butanol in silicalite-1(F^-) film at (■) 35 °C, (□) 50 °C, (▼) 65 °C, and (△) 80 °C, obtained from FTIR experiments. Symbols and solid lines represent experimental data and the Langmuir (a) and Sips (b) models fitted to the experimental data, respectively.

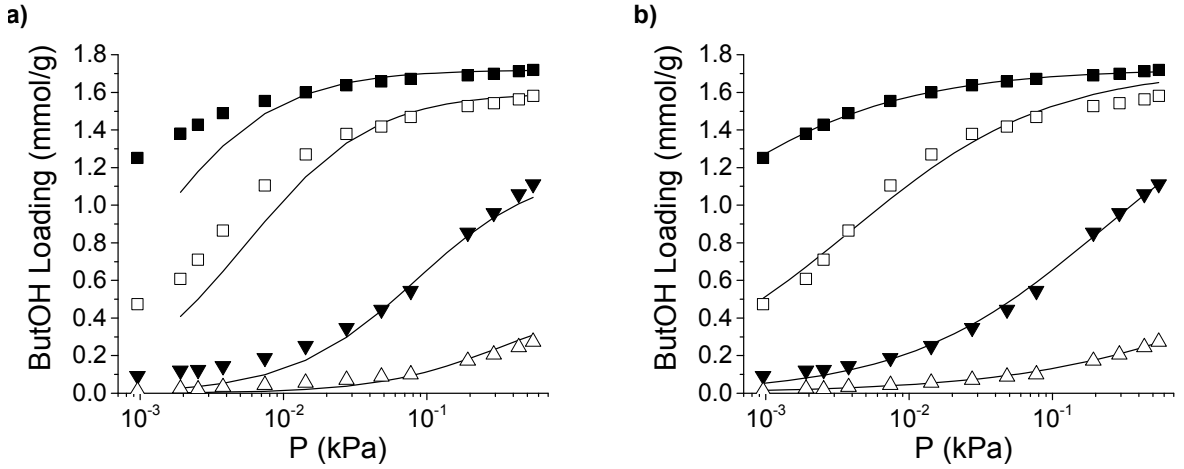

Figure S2. Adsorption isotherms for butanol in silicalite-1(OH^-) film at (■) 35 °C, (□) 50 °C, (▼) 85 °C, and (△) 120 °C, obtained from FTIR experiments. Symbols and solid lines represent experimental data and the Langmuir (a) and Sips (b) models fitted to the experimental data, respectively.

In Table S1, the Langmuir and Sips parameters and coefficient of determination (r^2) calculated for adsorption of butanol in silicalite-1(F^-) and (OH^-) films at different temperatures (the temperature ranges studied for two samples are also different) are presented. Based on the isotherms presented in figures S1 and S2, it is unsurprising that almost in all cases, the Sips model exhibits higher r^2 values indicating that it fits the experimental data better than the Langmuir model.

Table S1. Comparison of Linear Regression Coefficients of Determination, R^2 and Sips And Langmuir Parameters of Adsorption of Butanol in Silicalite-1(F^-) and Silicalite-1(OH^-) Films

Adsorbent	t (°C)	*Sips*				*Langmuir*		
		q(mmol/g)	b(kPa^n)	n	r^2	q(mmol/g)	b(kPa^{-1})	r^2
silicalite-1(F^-)	35	1.45	172.2	1.61	0.999	1.45	865.9	0.910
	50	1.45	57.0	1.34	0.989	1.45	226.0	0.978
	65	1.45	13.2	1.42	0.982	1.45	71.6	0.996
	80	1.45	5.2	1.46	0.991	1.45	35.0	0.944
silicalite-1(OH^-)	35	1.73	144.3	1.76	0.999	1.8	860	0.931
	50	1.73	32.5	1.59	0.987	1.8	267	0.930
	85	1.73	2.7	1.57	0.995	1.8	15.6	0.971
	120	1.73	0.2	2.08	0.998	1.8	2.6	0.929

Table S2. Heat of Adsorption of Butanol in Silicalite-1 Films

Adsorbent	ΔH_{ads}(kJ/mol)	
	Isosteric Heat of Adsorption at q= 0.5 q_{sat} (using b-values from the Sips model)	Heat of Adsorption (using b-values from Langmuir model)
silicalite-1(F^-)	-72	-67
silicalite-1(OH^-)	-74	-69

Refrences

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