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Supplementary Information

Surfaces, Silica and Semivolatile Organics — Limonene Uptake and Desorption Indoors and Outdoors

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Figure S1. Schematic diagram of experimental setup in a) side-on perspective and b) top-down perspective. (Reproduced from Ref. 1 with permission from the Royal Society of Chemistry.)

Kinetic Model Description and Table of Parameters

The kinetic model used in this work has been described in detail in a previous publication and is summarized below.¹ Processes in the kinetic model include flows in and out of the chamber, vertical diffusion of limonene through pores which exist between the silica particles, and reversible adsorption of limonene to the silica particle surfaces. The silica particles and pores are treated using a multi-layer approach with the same silica surface area being assumed in each layer. Transport fluxes between each layer are calculated by assuming Fickian diffusion and constant diffusion coefficients. Reversible adsorption fluxes of limonene to the silica particles in each layer are consistent with Langmuir's theory of adsorption. Simulations were performed with 500 layers which enabled convergence in the results and vertical concentration gradients of limonene throughout the silica to be determined. Parameters used in the model are summarized in Table S1 alongside explanations of their values. Most parameters were known and set to be consistent with

experimental values or values determined from previous work or other methods. The only unknown parameter in the model was the diffusion coefficient of limonene through the pores which was determined for each individual temperature by varying the value until the best visual fit to the measurements could be achieved. The flow of limonene molecules was set to be constant throughout each experiment and small drifts in the signal or pressure were not treated.

Parameter	Description	Value	Additional information		
k	First order removal rate	0.416 s ⁻¹	Experimental value (k_{esc}),		
out	coefficient of molecules from		see SI of Johnson, et al.		
	the chamber.		20241		
k.	First order rate coefficient of	0.416 s ⁻¹	Same as kout		
in	molecules entering the chamber.				
Т	Temperature	210 – 250 K	Experimental value		
-	Surface area of 1 molecule	0.79 nm^2	$\frac{1}{2}$		
$\sigma_{_{ m limonene}}$	Surface area of T molecule	0.79 mm	The model outputs are		
			insensitive to small changes		
			in this parameter		
1	Geometric surface area of the	3.14 cm^2	Experimental value		
sil	spot that the particles form	5.14 em	Experimental value		
S	Total surface area of the silica	2000 cm^2	Experimental value		
Ssil	narticles	2000 em	determined from Na		
	particles		adsorption		
V	Volume of the shamher	5260 am^2	Experimental value		
V		5200 cm-			
$\delta_{_{ m sil}}$	I nickness of the deposited	1.77 µ m	A nexagonal closed packing		
	particles	0.74	structure is assumed.		
$P_{\rm sil}$	Volume fraction of silica in the	0.74			
	layers of deposited silica				
	particles.				
<i>F</i> _{pores}	Volume fraction of gas (or	0.26			
	pores) in the layers of deposited				
	silica particles.				
$\alpha_{s,0}$	Surface accommodation	1	Typical value		
	coefficient on an adsorbate free				
	silica surface				
k_{d}^{*}	Desorption rate coefficient of	$6.5 \times 10^{12} \times \exp(-$	The desorption energy is		
	molecules from the silica	46.6/RT) s ⁻¹	fixed to 46.6 kJ mol ⁻¹ for		
	surface.		consistency with the average		
			value determined by		
			inversion analysis and		
			Arrhenius fit methods		
			detailed in the main text.		
			The pre-exponential factor is		
			fixed to 6.5×10^{12} s-1 for		
			consistency with the		
			desorption rate determined		
			in Eang et al 2 at 296 K (3.9		
			\times 10 ⁴ s ⁻¹). 296 K is the		
			temperature at which most		
			of the experiments in Fang		
			et al. ² were performed.		
			$R = 0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1}$		
$D_{p}*$	Diffusion coefficient through the	$0.0048 \text{ cm}^2 \text{ s}^{-1} (210 \text{ K})$	These values resulted in the		
-	gas-phase pores.	$0.0052 \text{ cm}^2 \text{ s}^{-1} (220 \text{ K})$	best visual fit to the		
		$0.0053 \text{ cm}^2 \text{ s}^{-1} (222 \text{ K})$	measurements. Higher		
		$0.0061 \text{ cm}^2 \text{ s}^{-1}(230 \text{ K})$	diffusion coefficients with		
		$0.0072 \text{ cm}^2 \text{ s}^{-1} (240 \text{ K})$	increasing temperature are		
		$0.0083 \text{ cm}^2 \text{ s}^{-1} (250 \text{ K})$	consistent with the expected		
			behavior. Note that pore		
			diffusion is slower than gas-		
			phase diffusion indicating		
			that other interactions or		
			processes may be occurring,		
			which could also be		
			temperature dependent.		
			1 1		

Table S1	: I	Parameters	used	in	the	kinetic	model.
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* Note that there is a degree of co-dependency between k_d and D_p . Sensitivity tests indicated that similar fittings to the measurements could be achieved if k_d and D_p were both decreased by the same factor. This was tested up to a factor of 3.5. Increasing k_d and D_p leads to a worse fit to the measurements if equilibrium between the surface and gas phase is achieved too rapidly.



Figure S2. (a) Dependence of $\theta/(1-\theta)$ on the initial concentration of gaseous limonene. At each temperature, colored solid shapes represent experimental values and the dashed lines the corresponding data fit. (b) Temperature dependence of the ratio of the rate constants for adsorption to desorption as a function of T⁻¹.

Derivation of Equation IV

Considering only loss of the gas G due to adsorption, in general, at a fixed temperature,

$$\frac{d[G]}{dt} = -k_{ads} \left[G\right](1-\theta)\left[S\right] + k_{des}\theta\left[S\right]$$

where [G] is the gas-phase concentration of limonene in the sample chamber in molec. cm⁻³, [S] is surface binding site density in molec. cm⁻², and θ is the fractional coverage of the silica surface binding sites by adsorbed limonene.

Once the uptake lid has been opened and the experiment has reached steady-state conditions, the change in the gas-phase concentration should be 0, and rearranging of the above equation yields

$$k_{ads}[G](1-\theta)[S] = k_{des}\theta[S]$$

$$\frac{k_{ads}}{k_{des}}[G] = \frac{\theta}{1-\theta}$$

Thus a plot of $\frac{\theta}{1-\theta}$ vs. [G] should yield a straight line with slope $\frac{k_{ads}}{k_{des}}$, as shown in Fig. 7 (Main Text). Again neglecting the effects of variable surface area and gas-phase diffusion into the pores, kinetic molecular theory states that the adsorption rate, $k_{ads}[G]$, should be proportional to the collision frequency of gases, given by

$$\frac{Collisions}{cm^2s} = \frac{1}{4}N\bar{c} = \frac{N}{4}\sqrt{\frac{RT}{2\pi m}}$$

where N is the gas-phase concentration of the adsorbing molecule (limonene) in molec. cm⁻³, \bar{c} is the mean molecular speed in cm/sec, R is the ideal gas constant, T is the temperature of the adsorbing molecules (assumed to be 298 K or room temperature) in the sample chamber, and *m* is the molar mass of the adsorbing molecule (136.24 g/mol for limonene). This is the origin of the T^{0.5} temperature dependence in k_{ads}/k_{des} accounted for in Fig. S2b.

Deriving Fractional Coverage (θ) from Uptake Profiles

The typical fractional coverage achieved during a single uptake experiment, θ , was determined by fitting an asymptote-shifted biexponential decay function to I₀ – I(t), the change in the uptake signal after the initial drop, which has the form

$$I(t) = \frac{C - D}{2} \cdot (e^{-k_1 \cdot t} + e^{-k_2 \cdot t}) + D$$

where *C* and *D* are the scale factor and horizontal asymptote, respectively, and k_1 and k_2 are decay constants with units of s⁻¹. The faster decay component, arbitrarily set to be k_1 , is attributed to the desorption process, while the slower component is attributed to effective diffusion (including the effects of re-adsorption). The area corresponding to the integral of the fast component (corresponding to C/k₁) is computed, and divided by the integrated signal area corresponding to a monolayer from TPD experiments to yield a fractional coverage achieved during the given uptake condition. An example fit is shown in Figure S3 below.



Figure S3. Example fit of the shifted biexponential model (red dashed line) to uptake profile data (blue line) taken at 230 K, showing the extracted desorption component of the fit (green dotted line). The area under the green dotted line is integrated and divided by the monolayer signal area to compute the fractional coverage after uptake in each experiment.

Comparison of Effective Langmuir Coefficients (k_{ads}/k_{des} **) from Uptake Experiments** The effective Langmuir coefficient measured by Fang et al.³ at 296 K was 0.032 mTorr⁻¹, or 9.9 ×10⁻¹⁶ cm³ molec.⁻¹. Fitting an Arrhenius form to the values of k_{ads}/k_{des} reported in Table 2 (Main Text) and extrapolating to 298 K yields a value of 3.92×10^{-15} cm³ molec.⁻¹ (Figure S4), roughly 4 times larger than the effective equilibrium coefficient reported by Fang et al.³ Given the different experimental designs and temperature ranges, with a long extrapolation from our lower temperatures to room temperature, the agreement is reasonable.



Figure S4. Temperature dependence of Effective Langmuir Coefficients (k_{ads}/k_{des}) from uptake experiments, and extrapolation to value at 298 K assuming Arrhenius behavior.



Additional Uptake Experiments and Model Outputs

Figure S5. Experimental uptake profile (black lines) and corresponding model output (red curve) at 210 K.



Figure S6. Additional experimental uptake profile (black lines) and corresponding model output (red curve) at 210 K.



Figure S7. Additional experimental uptake profile (black lines) and corresponding model output (red curve) at 210 K.



Figure S8. Additional experimental uptake profile (black lines) and corresponding model output (red curve) at 210 K.



Figure S9. Experimental uptake profile (black lines) and corresponding model output (red curve) at 220 K.



Figure S10. Experimental uptake profile (black lines) and corresponding model output (red curve) at 222 K.



Figure S11. Experimental uptake profile (black lines) and corresponding model output (red curve) at 230 K.



Figure S12. Additional experimental uptake profile (black lines) and corresponding model output (red curve) at 230 K.



Figure S13. Experimental uptake profile (black lines) and corresponding model output (red curve) at 240 K.



Figure S14. Experimental uptake profile (black lines) and corresponding model output (red curve) at 250 K.



Figure S15. Additional experimental uptake profile (black lines) and corresponding model output (red curve) at 250 K.



Figure S16. Additional experimental uptake profile (black lines) and corresponding model output (red curve) at 250 K.



Figure S17. Additional experimental uptake profile (black lines) and corresponding model output (red curve) at 250 K.



Figure S18. Contour plots of adsorbed limonene concentration profiles (in molec. cm⁻²) in the particle bed.



Figure S19. Contour plots of the concentration profiles (in molec. cm⁻³) of gas-phase limonene in pores in the particle bed.

References

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