

Supplementary Information

1) Molecular adsorption with internal and external limitations

$\varepsilon_p \frac{\partial C_A}{\partial t} = \frac{1}{y^2 r_p^2} D_{effA} \frac{\partial(y^2 \frac{\partial C_A}{\partial y})}{\partial y} - C_{NM}(k_1 C_A \theta^* - k_{-1}(1 - \theta^*))$	Equation 1
$\frac{\partial \theta^*}{\partial t} = -k_1 C_A \theta^* + k_{-1}(1 - \theta^*)$	Equation 2
$\varepsilon \frac{C_A^g}{\partial t} = -v_{sg} \frac{\partial C_A^g}{\partial z} - k_{gs}(C_A^g - C_{A(y=1)}) \frac{3}{r_p} (1 - \varepsilon)$	Equation 3

The first step is to express those expressions by replacing the fractional surface coverage and the concentration by their steady state value in addition to the perturbation performed.

$$\theta_* = \theta_*^{ss} + \Delta\theta_*(t) \quad \text{Equation 4}$$

$$C_A = C_A^{ss} + \Delta C_A(t) \quad \text{Equation 5}$$

Those expressions are first used in the mass balances at the pellet scale yielding Equation 6 and Equation 7.

$$\varepsilon_p \frac{\partial \Delta C_A}{\partial t} = \frac{1}{y^2 r_p^2} D_{effA} \frac{\partial(y^2 \frac{\partial \Delta C_A}{\partial y})}{\partial y} - C_{NM}(k_1 C_A^{ss} \Delta\theta^* + k_1 \Delta C_A \theta^{*ss} + k_{-1} \Delta\theta^* + o(\Delta^2)) \quad \text{Equation 6}$$

$$-\frac{\partial \Delta\theta^*}{\partial t} = k_1 C_A^{ss} \Delta\theta^* + k_1 \Delta C_A \theta^{*ss} + k_{-1} \Delta\theta^* + o(\Delta^2) \quad \text{Equation 7}$$

with boundary conditions:

$$y = 0; \quad \frac{d\Delta C_A}{dy} = 0$$

$$y = 1; \quad \frac{d\Delta C_A}{dy} = Bi(\Delta C_A^g - \Delta C_{A(y=1)}) \quad \text{where } Bi = \frac{k_{gs} r_p}{D_{effA}}$$

Then Laplace transform is used:

In Equation 7: $-s\Delta\theta^* = k_1 C_A^{SS} \Delta\theta^* + k_1 \Delta C_A \theta^{*SS} + k_{-1} \Delta\theta^*$ Equation 8

Thus: $\Delta\theta^* = -\frac{k_1 \theta^{*SS} T_1}{sT_1 + 1} \Delta C_A$ with $T_1 = \frac{1}{k_1 C_A^{SS} + k_{-1}}$

In Equation 6: $\varepsilon_p s \Delta C_A = \frac{1}{y^2 r_p^2} D_{effA} \frac{\partial(y^2 \frac{\partial \Delta C_A}{\partial y})}{\partial y} - C_{NM} \frac{k_1 \theta^{*SS} T_1}{sT_1 + 1} s \Delta C_A$ Equation 9

Resolution of Equation 6 (accounting for boundary conditions) leads to:

$$\Delta C_A = \Delta C_A^g y^{-1/2} \frac{Bi \times I_{1/2}(\sqrt{\tau_D s} y)}{\sqrt{\tau_D s} I_{3/2}(\sqrt{\tau_D s}) + Bi \times I_{1/2}(\sqrt{\tau_D s})}$$
 Equation 10

where

$$\tau_D = \frac{r_p^2}{D_{effA}} \left(\varepsilon_p + C_{NM} \frac{k_1 \theta^{*SS} T_1}{sT_1 + 1} \right)$$

A similar method applied to the mass balance at the reactor scale leads to:

$$\varepsilon s \Delta C_A^g = -\frac{v_{sg}}{L_R} \frac{\partial \Delta C_A^g}{\partial x} - k_{gs} \frac{3}{r_p} (1 - \varepsilon) B(s) \Delta C_A^g$$
 Equation 11

with $B(s) = \frac{Bi^{-1}(F(s) \coth(F(s)) - 1)}{1 + Bi^{-1}(F(s) \coth(F(s)) - 1)}$ and $F(s) = \sqrt{\tau_D s}$

The transfer function of the whole reactor is thus:

$$H(s) = \frac{\Delta C_A^{g.out}}{\Delta C_A^{g.in}} = e^{(-t_R s - t_{R2} k_{gs} \frac{3}{r_p} (1 - \varepsilon) B(s))}$$
 Equation 12

with $t_R = \varepsilon \frac{L_R}{v_{sg}}$ and $t_{R2} = \frac{L_R}{v_{sg}}$

The expression of B(s) is then developed in the frequency domain (with $s = jw$). The calculation steps are detailed below.

$$\tau_D jw = \frac{r_p^2}{D_{effA}} \left(\varepsilon_p jw + C_{NM} \frac{k_1 \theta^{*SS} T_1 (1 - jw T_1) jw}{w^2 T_1^2 + 1} \right) = a + bj$$
 Equation 13

with $a = C_{NM} \frac{k_1 k_{-1} T_1^3 w^2}{1 + w^2 T_1^2} \frac{r_p^2}{D_{effA}}$ and $b = \left(\varepsilon_p + C_{NM} \frac{k_1 k_{-1} T_1^2}{1 + w^2 T_1^2} \right) \frac{w r_p^2}{D_{effA}}$

As $\sqrt{z} = \sqrt{r} \frac{z+r}{|z+r|}$ with $r = |z| = \sqrt{a^2 + b^2}$ and $z = a + jb$, it follows:

$$\sqrt{\tau_D j\omega} = (a^2 + b^2)^{1/4} \frac{(a + \sqrt{a^2 + b^2}) + bj}{\sqrt{(a + \sqrt{a^2 + b^2})^2 + b^2}} = a' + jb' \quad \text{Equation 14}$$

$$\text{with } a' = (a^2 + b^2)^{1/4} \frac{(a + \sqrt{a^2 + b^2})}{\sqrt{(a + \sqrt{a^2 + b^2})^2 + b^2}} \text{ and } b' = (a^2 + b^2)^{1/4} \frac{b}{\sqrt{(a + \sqrt{a^2 + b^2})^2 + b^2}}$$

As $\coth(x + jy) = \frac{j\sin(2y) - \sinh(2x)}{\cos(2y) - \cosh(2x)}$, it follows:

$$\coth(F(j\omega)) = \frac{j\sin(2b') - \sinh(2a')}{\cos(2b') - \cosh(2a')} = c + jd \quad \text{Equation 15}$$

$$\text{with } c = \frac{-\sinh(2a')}{\cos(2b') - \cosh(2a')} \text{ and } d = \frac{\sin(2b')}{\cos(2b') - \cosh(2a')}$$

Accounting for Equation 14 and Equation 15:

$$F(j\omega) \coth(F(j\omega)) = (a' + jb')(c + jd) = (a'c - b'd) + j(b'c + a'd) = c + jd' \quad \text{Equation 16}$$

Thus:

$$B(j\omega) = \frac{Bi^{-1}(c' - 1) + Bi^{-1}d'j}{1 + Bi^{-1}(c' - 1) + Bi^{-1}d'j} \quad \text{Equation 17}$$

Setting $a_1 = Bi^{-1}(c' - 1)$, $a_2 = Bi^{-1}(c' - 1) + 1$ and $b_1 = Bi^{-1}d'$, then :

$$B(j\omega) = \frac{a_1 + jb_1}{a_2 + jb_1} = \frac{(a_1 + jb_1)(a_2 - jb_1)}{a_2^2 + b_1^2} = \frac{(a_1a_2 + b_1^2)}{a_2^2 + b_1^2} + j \frac{(b_1a_2 - a_1b_1)}{a_2^2 + b_1^2} \quad \text{Equation 18}$$

$$B(j\omega) = \frac{(a_1a_2 + b_1^2)}{a_2^2 + b_1^2} + j \frac{b_1}{a_2^2 + b_1^2} \text{ because } a_2 - a_1 = 1 \quad \text{Equation 19}$$

The expression of $B(j\omega)$ can finally be written as:

$$B(j\omega) = \alpha + j\beta \quad \text{Equation 20}$$

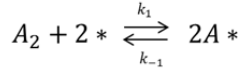
Thus the gain and phase shift can be expressed respectively as:

$$|H(w)| = e^{\left(-\frac{3k_{gs}}{r_p}(1-\varepsilon)t_{R_2}\alpha\right)}$$

$$\phi = -t_{RW} - \frac{3k_{gs}}{r_p}(1-\varepsilon)t_{R_2}\beta$$

2) Dissociative adsorption without internal and external limitations

The following reaction is considered:



The mass balance for the reactant in the gas phase is given by combining equations (2), (3) and (4) and neglecting concentration gradients in the film and inside the pores ($\forall r, C_i = C_i^g$):

$$(\varepsilon + (1 - \varepsilon)\varepsilon_p) \frac{\partial C_{A_2}}{\partial t} = -v_{sg} \frac{\partial C_{A_2}}{\partial z} - C_{NM}(1 - \varepsilon)(k_1 C_{A_2} \theta^{*2} - k_{-1}(1 - \theta^*)^2) \quad \text{Equation 21}$$

$$\frac{\partial \theta^*}{\partial t} = -2k_1 C_{A_2} \theta^{*2} + 2k_{-1}(1 - \theta^*)^2 \quad \text{Equation 22}$$

The inlet and outlet concentrations of A_2 oscillate around the steady state. The concentration and the fractional surface coverage are expressed as their value at the steady state plus a perturbation term.

$$\theta_* = \theta_*^{ss} + \Delta\theta_*(t) \quad \text{Equation 23}$$

$$C_{A_2} = C_{A_2}^{ss} + \Delta C_{A_2}(t) \quad \text{Equation 24}$$

Amplitudes for the oscillations are supposed to be small to comply with linear conditions. As a consequence, terms in Δ^2 are neglected.

A Laplace transform is performed on the mass balances in adsorbed phase and in the fluid phase (external + internal), respectively:

$$-s\Delta\theta_* = 2k_1\theta_*^{ss2}\Delta C_{A_2} + 4k_1C_{A_2}^{ss}\theta_*^{ss}\Delta\theta_* + 4k_{-1}(1 - \theta_*^{ss})\Delta\theta_* \quad \text{Equation 25}$$

leading to:

$$\Delta\theta_* = -\frac{2k_1\theta_*^{SS2}T_1\Delta C_{A_2}}{sT_1 + 1} \quad \text{Equation 26}$$

$$\text{with } \theta^{*SS} = \frac{1}{1 + \sqrt{KC_{A_2}^{SS}}} \text{ and } T_1 = \frac{1}{4k_1C_{A_2}^{SS}\theta_*^{SS} + 4k_{-1}(1-\theta_*^{SS})} = \frac{1}{4k_{-1}\sqrt{KC_{A_2}^{SS}}}$$

$$\text{And } (\varepsilon + (1 - \varepsilon)\varepsilon_p)s\Delta C_{A_2} = -v_{sg} \frac{\partial \Delta C_{A_2}}{\partial z} - C_{NM}(1 - \varepsilon) \left(-\frac{s\Delta\theta_*}{2} \right) \quad \text{Equation 27}$$

By replacing $\Delta\theta_*$ by its expression, one obtains:

$$\Delta C_{A_2}^{out} = \Delta C_{A_2}^{in} e^{(-T_{R1} - T_{R2} C_{NM} \frac{k_1 \theta_*^{SS2} T_1}{sT_1 + 1})s} \quad \text{Equation 28}$$

$$\text{with } T_R = (\varepsilon + (1 - \varepsilon)\varepsilon_p) \frac{L_R}{v_{sg}} \text{ and } T_{R2} = (1 - \varepsilon) \frac{L_R}{v_{sg}}$$

The transfer function of the whole reactor system in the frequency domain becomes:

$$H(j\omega) = \frac{\Delta C_{A_2}^{out}}{\Delta C_{A_2}^{in}} = e^{\left(\left(-T_R - T_{R2} C_{NM} \frac{k_1 \theta_*^{SS2} T_1}{T_1^2 \omega^2 + 1} \right) j\omega \right)} e^{\left(-T_{R2} C_{NM} \frac{k_1 \theta_*^{SS2} T_1^2 \omega^2}{T_1^2 \omega^2 + 1} \right)} \quad \text{Equation 29}$$

Then the expressions for the gain and the phase lag are:

$$\phi = -\omega \left(T_R + \frac{4T_{R2} C_{NM} k_1 k_{-1} (\theta^{*SS})^2 \sqrt{KC_{A_2}^{SS}}}{16k_{-1}^2 KC_{A_2}^{SS} + \omega^2} \right) \quad |H(\omega)| = e^{\left(-T_{R2} \omega^2 \frac{k_1 C_{NM} (\theta^{*SS})^2}{16k_{-1}^2 KC_{A_2}^{SS} + \omega^2} \right)}$$

3) Dissociative adsorption with internal and external limitations

The mass balances in this case are the following:

$\varepsilon \frac{\partial C_{A_2}^g}{\partial t} = -\frac{v_{sg}}{L_R} \frac{\partial C_{A_2}^g}{\partial x} - k_{gs}(C_{A_2}^g - C_{A_2(y=1)}) \frac{3}{r_p} (1 - \varepsilon)$	Equation 30
$\varepsilon_p \frac{\partial C_{A_2}}{\partial t} = \frac{1}{y^2 r_p^2} D_{eff A_2} \frac{\partial \left(y^2 \frac{\partial C_{A_2}}{\partial y} \right)}{\partial y} - C_{NM} (k_1 C_{A_2} \theta^{*2} - k_{-1} (1 - \theta^*)^2)$	Equation 31
$\frac{\partial \theta^*}{\partial t} = -2k_1 C_{A_2} \theta^{*2} + 2k_{-1} (1 - \theta^*)^2$	Equation 32

The same development as for molecular adsorption is performed, but:

$$\text{with } a = C_{NM} \frac{k_1 T_1^2 w^2 \theta^{*SS2}}{1 + w^2 T_1^2} \frac{r_p^2}{D_{eff A_2}} \text{ and } b = \left(\varepsilon_p + C_{NM} \frac{k_1 T_1 \theta^{*SS2}}{1 + w^2 T_1^2} \right) \frac{w r_p^2}{D_{eff A_2}}$$

$$\text{and } T_1 = \frac{1}{4k_{-1} \sqrt{K C_{A_2}^{SS}}} \text{ and } \theta^{*SS} = \frac{1}{1 + \sqrt{K C_{A_2}^{SS}}}$$

4) Effect of the individual rate constants for reversible molecular adsorption

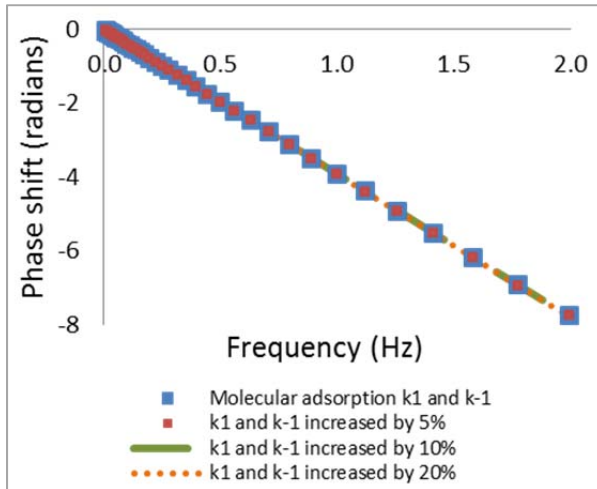


Fig. S1. Sensitivity of the phase shift vs. frequency curves (analytical solution with input data of Table 3). The adsorption and desorption rate constants are increased by 5, 10 and 20%. K remains constant.

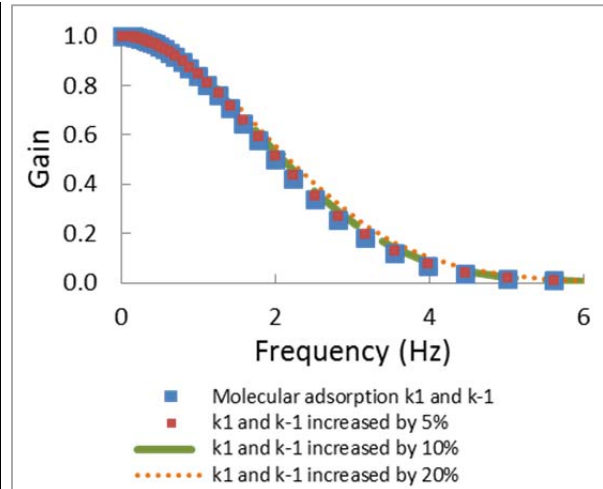


Fig. S2. Sensitivity of the gain vs. frequency curves (analytical solution with input data of Table 3). The adsorption and desorption rate constants are increased by 5, 10 and 20%. K remains constant.

5) Effect of the particle radius for several effective diffusivity values

The effect of the particle radius, in the case of a molecular adsorption with internal diffusion limitation, has been studied. Three values of the diffusion coefficient (in the classical range) have set to thoroughly analyze the effect of grinding the catalyst on the dynamic reactor response. The corresponding plots are displayed in Figure S3 to Figure S8. In those cases, the gas-solid mass transfer coefficient has been settled to 10 m s^{-1} in order to neglect the influence of this parameter.

With $D_{eff} = 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$:

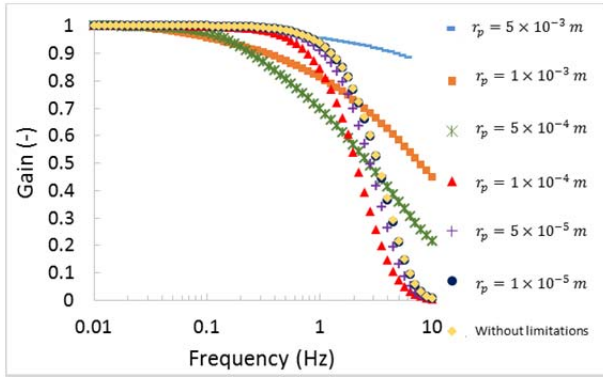


Fig. S3. Evolution of the gain as a function of the frequency for conditions of Table 3, but variable particle radius and $D_{eff} = 10^{-6}m^2 \cdot s^{-1}$.

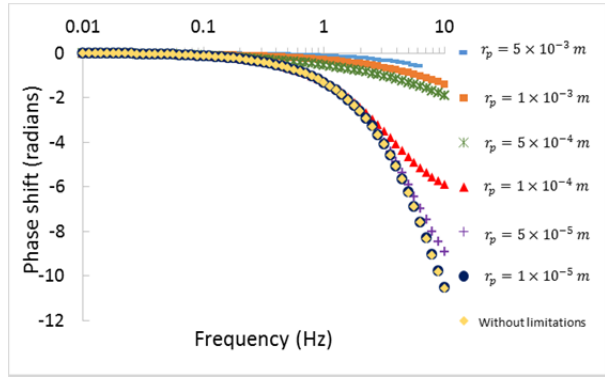


Fig. S4. Evolution of the phase shift as a function of the frequency for conditions of Table 3, but variable particle radius and $D_{eff} = 10^{-6}m^2 \cdot s^{-1}$.

With $D_{eff} = 10^{-7}m^2 \cdot s^{-1}$:

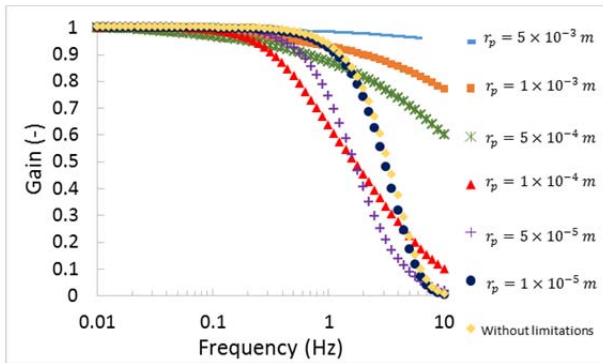


Fig. S5. Evolution of the gain as a function of the frequency for conditions of Table 3, but variable particle radius and $D_{eff} = 10^{-7}m^2 \cdot s^{-1}$.

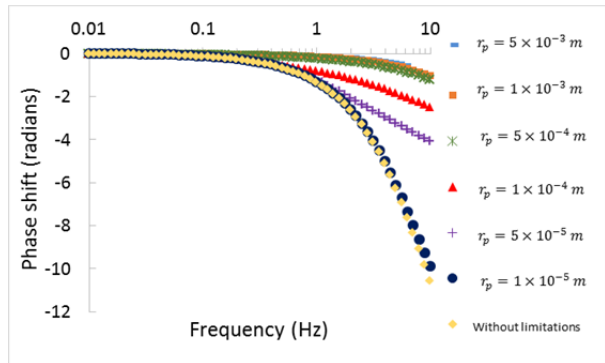


Fig. S6. Evolution of the phase shift as a function of the frequency for conditions of Table 3, but variable particle radius and $D_{eff} = 10^{-7}m^2 \cdot s^{-1}$.

With $D_{eff} = 10^{-8}m^2 \cdot s^{-1}$:

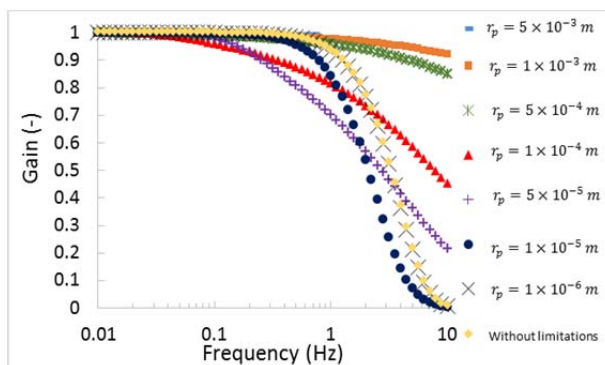


Fig. S7. Evolution of the gain as a function of the frequency for conditions of Table 3, but variable particle radius and $D_{eff} = 10^{-8}m^2.s^{-1}$.

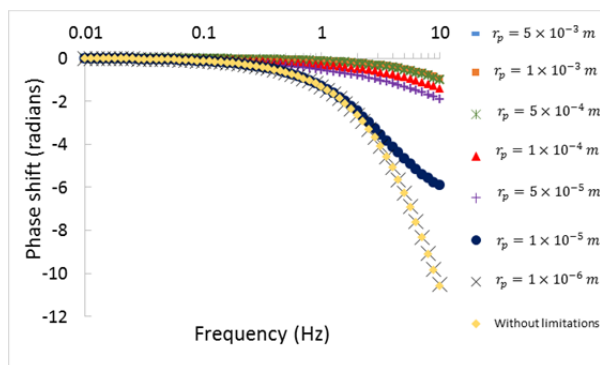


Fig. S8. Evolution of the phase shift as a function of the frequency for conditions of Table 3, but variable particle radius and $D_{eff} = 10^{-8}m^2.s^{-1}$.

6) Step response experiments for ethylene adsorption

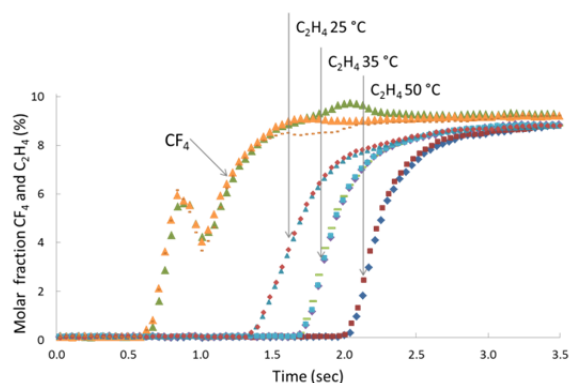


Fig. S9. Step responses from pure Ar to a mixture of Ar, CF₄, C₂H₄ at 25, 35 & 50°C. The tests were performed three times at each temperature.

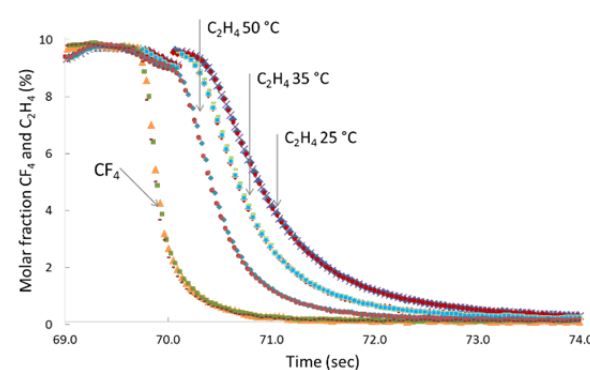


Fig. S10. Back-switch of step-response experiments in Fig. S9. The tests were performed three times at each temperature.

Temperature	Moles of C ₂ H ₄ adsorbed	K (Pa ⁻¹)	Moles of C ₂ H ₄ desorbed	K (Pa ⁻¹)
25°C	2.9×10^{-5}	9.5×10^{-6}	2.4×10^{-5}	7.6×10^{-6}
35°C	1.8×10^{-5}	5.7×10^{-6}	1.7×10^{-5}	5.5×10^{-6}
50°C	1.5×10^{-5}	4.6×10^{-6}	1.1×10^{-5}	3.3×10^{-6}

From the adsorption equilibrium constants given above an adsorption enthalpy of -19.5 and -24.1 kJ/mol is obtained for the forward and backward switch respectively.