Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information

Kinetic Modeling of H_2S Adsorption and Desorption on NiO Surfaces in Resistive MEMS Gas Sensor: Coupling Mass Transfer, Multisite Adsorption, and Surface Interactions

S1. Reaction Mechanism and Kinetic Scheme

The interaction of hydrogen sulfide with the surface involves sequential molecular adsorption and dissociation:

$H_2S(g) \rightleftharpoons H_2S(ads) \rightleftharpoons 2H(ads) + S(ads)$

The chemical reaction with nickel oxide proceeds as follows:

$NiO + H_2S \rightarrow NiS + H_2O$

From a kinetic perspective, this corresponds to sequential molecular adsorption and dissociation. A specific feature of the interaction between hydrogen sulfide and nickel oxide is that it is partially irreversible.

S2. Analytical Kinetic Model

Consider the adsorption of substance A from the gas phase onto surface P (molecular adsorption):

$$A^{gas} + P \leftrightarrow B_s$$

$$[B_s] = C_s * \theta$$

This yields a first-order linear differential equation (LDE):

$$\frac{d\theta}{dt} = k^+ C(1-\theta) - k^- C_s \theta$$

Then:

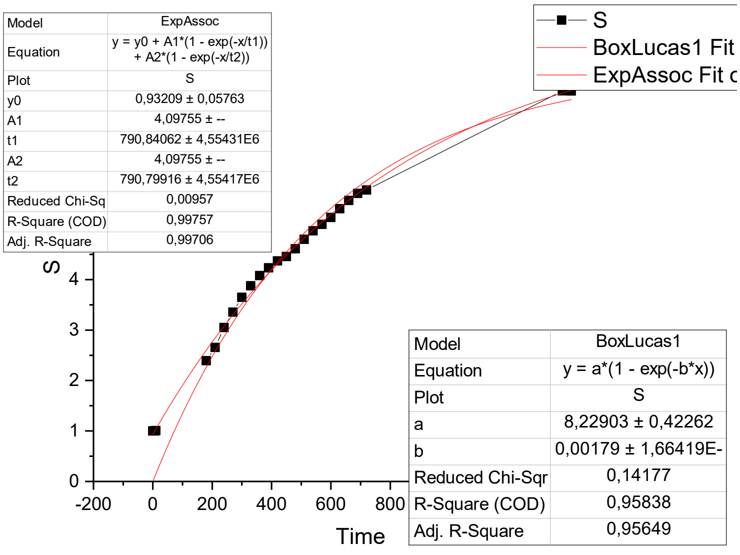
$$\theta(t) = \frac{k^+ * C}{k^+ * C + k^- * C_s} * \left(1 - e^{-\left(k^+ * C + k^- * C_s\right) * t}\right) = \theta_{eq} * \left(1 - e^{-\left(\right.}\right.$$

$$\left(1 - e^{-B * t}\right)$$

$$\theta_\infty = \frac{k^+ * C}{k^+ * C + k^- * C_s} = A$$

$$B = k^{+} * C + k^{-} * C_s$$

The equilibrium degree of coverage θ_{eq} corresponds to filling at t →∞.



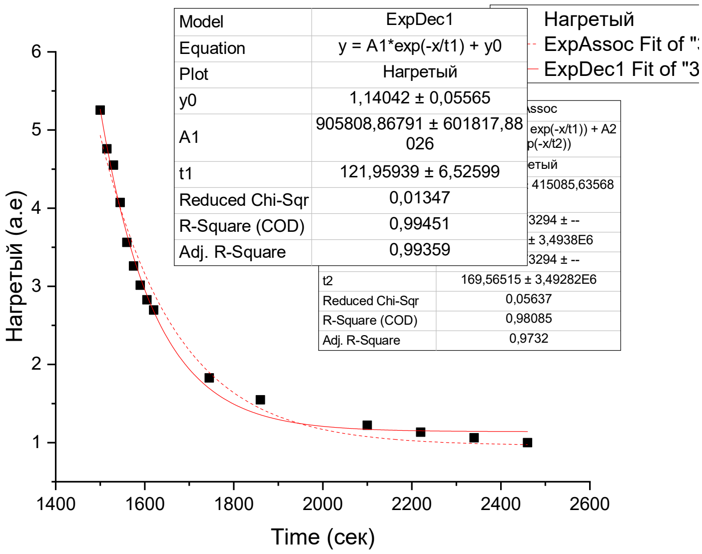
Model	ExpAssoc
Equation	y = y0 + A1*(1 - exp(-x/t1)) + A2*(1 - exp(-x/t2))
Plot	S
y0	0,93209 ± 0,05763
A1	4,09755 ± --
t1	790,84062 ± 4,55431E6
A2	4,09755 ± --
t2	790,79916 ± 4,55417E6
Reduced Chi-Sq	0,00957
R-Square (COD)	0,99757
Adj. R-Square	0,99706

Model	BoxLucas1
Equation	y = a*(1 - exp(-b*x))
Plot	S
a	8,22903 ± 0,42262
b	0,00179 ± 1,66419E-
Reduced Chi-Sqr	0,14177
R-Square (COD)	0,95838
Adj. R-Square	0,95649

Figure 1. NiO-MEMS type sensor response to 100 ppm of H_2S

The kinetics of the real response to hydrogen sulfide are described by the molecular adsorption equation with a high correlation coefficient (fig.1). However, a second process is additionally mixed in. Including dissociation in the consideration increases the correlation coefficient.

Including the sensor cleaning region (fig.2) allows modeling the recovery curve under the condition of an exponential decrease in the amount of analyte in the gas phase.



Model	ExpDec1
Equation	y = A1*exp(-x/t1) + y0
Plot	Нагретый
y0	1,14042 ± 0,05565
A1	905808,86791 ± 601817,88026
t1	121,95939 ± 6,52599
Reduced Chi-Sqr	0,01347
R-Square (COD)	0,99451
Adj. R-Square	0,99359

Figure 2. NiO-MEMS type sensor recovery to 100 ppm of H_2S

For the *competitive adsorption model* with *concentration-dependent desorption* and *exponential decrease in gas phase concentration*, desorption will have a *double exponential character*:

Formulation:

1. Exponential decrease in gas concentration:

$C\_gas(t) = C_0 \times \exp(-t/\tau\_gas)$
where τ_{gas} is the relaxation time of the gas phase.

2. Concentration-dependent desorption:

$k\_d\textasciicircum eff(t) = k\_d \times (1 + \alpha \times C\_gas(t)) = k\_d \times (1 + \alpha \times C_0 \times \exp(-t/\tau\_gas))$

3. Site occupancy equation:

$d\theta/dt = k\_a \times C\_surface \times (1-\theta) - k\_d\textasciicircum eff(t) \times \theta$

Analytical solution for one substance:

$\theta(t) \approx K\_eff(t) / (1 + K\_eff(t))$, где $K\_eff(t) = k\_a \times C_0 \times \exp(-t/\tau\_gas) / k\_d\textasciicircum eff(t)$
This creates a characteristic "hump" on the desorption curve.

S3. Numerical Solution Model

The system describes the kinetics of H_2S adsorption on NiO, concentration-dependent desorption, and chemical reaction in the gas phase.

Coverages:

θ_A: Adsorbed H_2S

θ_R: NiS product

$\theta_{free} = 1 - \theta_A - \theta_R$:Free NiO centers

P_{H2S}: Partial pressure of H_2S (atm)

α: Lateral interaction coefficient

Initial and Boundary Conditions:

Initial: $t=0$, $\theta_A(0)=0$, $\theta_R(0)=0$ (clean NiO surface).

Boundary: $t \to \infty$., $d\theta_A/dt \to 0$, $d\theta_R/dt \to 0$ (equilibrium: $\theta_A^{eq} = K P / (1 + K P)$), where K = k_{ads} / k_{des}^{eq}).

Physical constraints: $0 \leq \theta_A + \theta_R \leq 1 \ \forall \ t \geq 0$

Without accounting for concentration-dependent desorption, the model corresponds to *Langmuir-Hinshelwood with interaction*.

S4. Kinetic Parameters

Estimated Constants (250°C = 523 K, NiO + H_2S)

Constant	Value	Unit	Comment
k_{ads}	1.2	s^{-1}	H_2S dissociation on NiO, E_a approx 120 kJ/mol
k_{des}	0.08	s^{-1}	Base desorption, $A = 10^{12}\ s^{-1}$, E_{des} approx 14\$ kJ/mol
α	2.5	-	Lateral interaction ~10-15 kJ/mol per pair
k_{rxn}	0.03	s^{-1}	Sulfidation, E_a approx 130 kJ/mol by CLC analogy
P_{H2S}	0.01	atm	Experimental