Adsorption Behavior of Sodium Hydrogen Sulfate on Silica Gel

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Authors’ contributions

This work was carried out in collaboration among all authors. Author JX designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors ZJ and ZZ managed the analyses of the study. Author WX managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The adsorption behavior of sodium bisulfate on silica gel was studied. The adsorption isotherm of sodium hydrogen sulfate on silica gel were measured in the temperature range of 298.15 ~ 328.15 K, and the Langmuir model and the Dubini-Radushkevich (D-R) model were used to fit the experimental isotherm data. The average characteristic concentration (C_e') of NaHSO₄ was determined at different temperatures to distinguish chemisorption from physisorption. The values of the mean free energy (E) calculated from the D−R isotherm equation indicated that the adsorption of NaHSO₄ on silica gel occurs by sequential chemical and physical mechanisms.

Keywords: Adsorption; sodium bisulfate; silica gel; Langmuir; Dubini-Radushkevich.

1. INTRODUCTION

As a Lewis acid, sodium bisulfate is widely used as a catalyst for organic synthesis reactions such as esterification because of its low cost, environmental friendliness and insolubility in organic acids and alcohols [1]. However, it is difficult to separate sodium bisulfate from the
reaction system for recycling. In order to overcome the above drawbacks, an effective method is to load it on a porous solid medium. Generally available porous solid medium supports include activated carbon, silica gel, zeolite, molecular sieves and ion exchange resins [2,3]. The most commonly used carrier for sodium bisulfate is silica gel, which is mainly due to its low price and ease of availability [4,5]. Therefore, silica-supported sodium hydrogen sulphate (NaHSO₄/SiO₂) has been widely used as a new type of highly efficient heterogeneous catalyst and is commonly used in many organic reactions such as debenzylation [6], nitration [7], nitrosation [8], oxidation [9], esterification [10,11], alkylation [12], chemoselective protection and deprotection [13-15]. The advantages of using NaHSO₄/SiO₂ as a heterogeneous catalyst in these organic synthesis include short reaction time, mild reaction conditions [16], high catalytic activity and selectivity, good recyclability [17], easy operation and environmental protection [6]. NaHSO₄/SiO₂ is prepared by adsorbing sodium hydrogen sulfate in aqueous solution through silica gel. Therefore, it is necessary to study the adsorption behavior of sodium hydrogen sulfate on silica gel. However, there are no relevant reports in the literature.

In this paper, the adsorption isotherm of sodium hydrogen sulfate on silica gel were measured in the temperature range of 298.15 ~ 328.15 K, and two models (Langmuir model and Dubini-Radushkevich (D-R) model) were employed to fit the experimental isotherm data, and the adsorption mechanism of NaHSO₄ on silica gel will be discussed based on the fitting results of the above models. The effects of temperature and concentration of sodium bisulfate on the adsorption performance were investigated. The adsorption thermodynamics is also discussed.

2. EXPERIMENTAL SECTION

2.1 Materials

Sodium hydrogen sulphate (98.5 wt%) was purchased from Shanghai Lingfeng chemical reagent Co., Ltd. Silica gel was obtained from Tsingdao Shuoyuan Chemical Co., Ltd. (Tsingdao, China) with particle diameter of 0.20 ±0.02 mm and its detail physical parameters are listed in Table 1 [5].

2.2 Adsorption Experiment

Adsorption experiments were performed in glass flasks in a thermostatic water bath. In a temperature range of (298.15 to 328.15) K, 1.0 g of a silica gel sample was added to 10 mL of a sodium bisulfate aqueous solution having a concentration of 0.005 to 0.235 g/mL, and stirred for 3 h at a constant temperature, then left to stand for 2 h, and the supernatant was taken. The concentration of NaHSO₄ was measured by UV spectrophotometer (UV-PC754, APL Shanghai Co., Shanghai, China).

2.3 Adsorption Isotherm

The adsorption capacity at equilibrium per unit weight of adsorbent (qₑ) and equilibrium adsorption concentration in aqueous solution (Cₑ) were calculated from the adsorption data. The value of qₑ was calculated using Eq (2.1)

\[ qₑ = \frac{(C₀ - Cₑ)}{mₘ} \] (2.1)

where C₀ and Cₑ are the initial concentration of sodium hydrogen sulfate and equilibrium concentration of sodium hydrogen sulfate in aqueous solution respectively. V is the volume of aqueous solution, and mₘ is the weight of silica gel.

3. ADSORPTION MECHANISMS AND MODELS

3.1 Chemisorption

³¹P NMR MAS [18] technology showed that 12-phosphotungstic acid (12-HPW) has chemical interaction with the hydroxyl group (Si-OH) on the surface of silica gel. ¹H MAS NMR and microcalorimetry also showed [19] that a new type of proton was formed between 12-HPW and SiO₂, and the acidity of this proton was weaker than that of pure 12-HPW. Similarly, when silica gel is added to an aqueous solution of sodium hydrogen sulfate, chemical adsorption occurs, and a new proton is formed, that is, ionization of sodium hydrogen sulfate produces hydrogen ions (H⁺) and the hydrogen ions react with hydroxyl groups (Si-OH) on the surface of silica gel to form new protons (≡Si-OH₂⁺). The chemical equations are as follows:

\[ \text{NaHSO}_4 \rightarrow \text{Na}^+ + \text{H}^+ + \text{SO}_4^{2-} \] (3.1)

\[ \equiv\text{Si-OH} + \text{H}^+ \rightarrow (\equiv\text{Si-OH}_2)^+ \] (3.2)
Table 1. Physical parameters of silica gel

| Parameter               | BET surface area m²/g | Volume of pores cm³/g | Apparent density g/cm³ | Pore diameter Å |
|-------------------------|------------------------|------------------------|------------------------|-----------------|
| Values                  | 254.7                  | 0.68                   | 1.02                   | 97              |

3.2 Physisorption

Due to the van der Waals force between molecules, sodium bisulfate molecules can also be physically adsorbed on the surface of silica gel. Generally, the chemical force is greater than the van der Waals force, and chemical adsorption takes precedence over physical adsorption. It can be speculated that when sodium bisulfate concentration is low, chemisorption will occur preferentially. Because chemical adsorption is saturated and monolayered, physical adsorption occurs when the sodium bisulfate concentration reaches and exceeds a certain value. On the other hand, van der Waals force can exist not only between the sodium bisulfate molecules on the surface of silica gel, but also between the sodium bisulfate and sodium bisulfate molecules, so multilayer physical adsorption can occur.

3.3 Adsorption Isotherm Models

In this work, the Langmuir and the Dubinin-Radushkevich (D-R) model were employed to correlate the experimental data. As the most common adsorption isotherm model, the Langmuir model is suitable for monolayer homogeneous adsorption. The Langmuir equation can be represented as [5]

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_{\text{max}}} + \frac{C_e}{q_{\text{max}}}
\]

(3.3)

where \( q_{\text{max}} \) (g/g) is the maximum adsorption capacity of silica gel, \( K_L \) is the Langmuir adsorption constant (mL/g) related to the free energy of adsorption. The value of \( q_{\text{max}} \) and \( K_L \) were obtained from the slope (1/ \( q_{\text{max}} \)) and intercept (1/\( K_L \)) of the linear plot \( C_e/q_e \) vs. \( C_e \).

The Dubinin-Radushkevich (D-R) isotherm model can be described as follows [5]

\[
\ln q_e = \ln q_{\text{max}} - \beta \varepsilon^2
\]

(3.4)

where \( \beta \) is the affinity coefficient, which depends on the adsorptive and \( \varepsilon \) is the Polanyi potential and can be expressed as

\[
\varepsilon = RT \ln(1 + 1/C_e)
\]

(3.5)

The value of the mean free energy (\( E \)) can be obtained by Eq (3.6)

\[
E = \frac{1}{\sqrt{2\beta}}
\]

(3.6)

The value of \( E \) is useful in distinguishing between physical and chemical adsorption. When the \( E \) value is between 8 and 16 kJ/mol, the adsorption process is chemical adsorption. When the \( E \) value is smaller than 8 kJ/mol then the adsorption process is physical adsorption [20-23].

4. RESULTS AND DISCUSSION

4.1 Adsorption Isotherm

The isotherm data for the adsorption of sodium hydrogen sulfate on silica gel at sodium hydrogen sulfate concentrations range from 0 to 0.23 g/mL at 298 K, 308 K, 318 K and 328 K were shown in Fig. 1, and an enlargement of part A of Fig. 1 is presented in Fig. 2. It can be seen from Figs. 1 and 2 that \( q_e \) increases with the increase of \( C_e \). However, the variation of \( q_e \) with temperature is complicated.

4.2 Adsorption Mechanism and Model

Langmuir model: Fig. 3 shows the regression curve of Langmuir adsorption isotherm model for the adsorption of sodium hydrogen sulfate on silica gel at different temperatures (from 298.15K to 328.15K). From Fig. 3, it can be seen that there is a feature concentrate (\( C_eL \)) in the concentration range of 0.0049~0.202 g/mL, and the \( C_eL \) value at various temperatures is listed in Table 2. When \( C_e \leq C_{el} \), the function relationship between \( C_e \) and \( C_e/q_e \) is linear and when \( C_e > C_{el} \), there is another linear relationship between \( C_e \) and \( C_e/q_e \).
Fig. 1. Isothermal adsorption equilibrium lines of $q_e \sim C_e$ at 298.15–328.15 K

Fig. 2. Enlargement of part A of Fig. 1

Table 2. The parameters of Langmuir model for the adsorption of NaHSO$_4$ on silica gel at different temperatures

| $T$ (K) | $C_{el}$ (g/mL) | $C_e \geq C_{el.}$ | $C_e > C_{el.}$ |
|---------|-----------------|---------------------|-----------------|
|         | $q_{max}$ (g/g) | $K_{l}$ (mL/g)     | $R^2$           | $q_{max}$ (g/g) | $K_{l}$ (mL/g) | $R^2$           |
| 298.15  | 0.022           | 0.00772             | 81.12           | 0.990           | 0.0821         | 2.79             | 0.981            |
| 308.15  | 0.024           | 0.00747             | 118.58          | 0.990           | 0.0520         | 5.32             | 0.975            |
| 318.15  | 0.026           | 0.00739             | 139.33          | 0.993           | 0.0443         | 6.20             | 0.982            |
| 328.15  | 0.028           | 0.00697             | 194.11          | 0.994           | 0.0386         | 6.41             | 0.983            |

The Langmuir model parameters ($q_{max}$ and $K_{l}$) are calculated and listed in Table 2. The correlation coefficients ($R^2$) are also listed in Table 2. It can be seen from the $R^2$ values that the Langmuir model agrees well with the experimental values at lower NaHSO$_4$ concentrations, indicating that the adsorption of NaHSO$_4$ on silica gel occurs in a monolayer manner and is chemically adsorbed when $C_e \leq$...
$C_{el}$; while at higher NaHSO$_4$ concentrations, the model is not applicable, indicating that the multilayer adsorption may occur and it is physical adsorption when $C_e > C_{el}$.

**Dubinin-Radushkevich (D-R) model:** Fig. 4 shows the plots of $\ln(q_e)$ vs $\varepsilon^2$ for the adsorption of NaHSO$_4$ on silica gel at different temperatures (from 298.15K to 328.15K). It can be seen from Fig. 4 that there is a trait value ($\varepsilon_D^2$) on the abscissa. On both sides of the value ($\varepsilon_D^2$), the functional relationship between $\ln(q_e)$ and $\varepsilon^2$ can be described by two straight lines, respectively. According to Eq (3.5), a feature concentration value ($C_{e0}$) corresponding to $\varepsilon_D^2$ can be obtained and listed in Table 3. When $C_e \leq C_{e0}$ the function relationship between $C_e$ and $C_e/q_e$ is linear, and when $C_e > C_{e0}$, there is another linear relationship between $C_e$ and $C_e/q_e$.

![Fig. 3. The regression curve of Langmuir adsorption isotherm model at different temperatures](image)

(a) 298.15K; (b) 308.15K; (c) 318.15K; (d) 328.15K
Fig. 4. The regression curve of D-R adsorption isotherm model at different temperatures (a) 298.15K; (b) 308.15K; (c) 318.15K; (d) 328.15K

| T (K) | C_{eD} (g/mL) | C^e \leq C_{eD} | C^e > C_{eD} |
|-------|---------------|-----------------|---------------|
|       | q_{max} (g/g) | E (kJ/mol)      | R^2           | q_{max} (g/g) | E (kJ/mol) | R^2 |
| 298.15| 0.024         | 0.0095          | 8.22          | 0.995         | 0.0474     | 4.34 | 0.996 |
| 308.15| 0.023         | 0.0106          | 8.46          | 0.990         | 0.0412     | 4.83 | 0.994 |
| 318.15| 0.026         | 0.0109          | 8.83          | 0.998         | 0.0373     | 5.09 | 0.993 |
| 328.15| 0.029         | 0.0156          | 10.31         | 0.992         | 0.0324     | 5.33 | 0.996 |

Table 3. The parameters of Dubinin-Radushkevich model for the adsorption of NaHSO₄ on silica gel at different temperatures.

The D-R model parameters (q_{max} and E) are calculated and listed in Table 3. The correlation coefficients (R^2) are also listed in Table 3. It can be seen from the R^2 values that the D-R model
agrees well with the experimental values for all concentrations. However, when \( C_e \leq C_{ed} \), the average free energy of adsorption \( E \) (8.22~10.31 kJ/mol) is between 8 kJ/mol and 16 kJ/mol, indicating that the adsorption of NaHSO4 on silica gel is chemisorption, and when \( C_e > C_{ed} \), the \( E \) value (4.34~5.33 kJ/mol) is less than 8 kJ/mol, indicating the adsorption includes physical adsorption. The result is consistent to that obtained by the Langmuir model.

On the other hand, it can be seen from Tables 2 and 3 that the values of \( C_{ed} \) and \( C_{el} \) at the same temperature are very close. So we can define an average characteristic concentration (\( C'_e \)) as follow:

\[
C'_e = \frac{C_{el} + C_{ed}}{2}
\]  

(4.1)

The \( C'_e \) values at different temperatures and the relative errors are listed in Table 4.

From the Table 4, it is concluded that when the \( C_e \) value is less than \( C'_e \), the adsorption of sodium hydrogen sulfate on silica gel is chemisorption, and when it is greater than \( C'_e \), the adsorption also includes multilayer physical adsorption.

4.3 Adsorption Thermodynamics

It is significant to obtain the thermodynamic parameters including changes of enthalpy (\( \Delta H^0 \)), entropy (\( \Delta S^0 \)) and Gibbs free energy (\( \Delta G^0 \)) for a better understanding of the thermodynamic behavior of adsorption and they were determined by Eq (4.2) and Eq (4.3)

\[
\ln K_C = \ln \frac{C_{ae}}{C_{se}} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]  

(4.2)

\[
\Delta G^0 = -RT \ln K_C
\]  

(4.3)

where \( K_C \) is the thermodynamic equilibrium constant, \( C_{ae} \) is the solid-phase concentration at equilibrium and \( C_{se} \) is the equilibrium concentration of sodium hydrogen sulfate in the solution. The value of \( \Delta H^0 \) and \( \Delta S^0 \) can be calculated from the slope \((-\Delta H^0 / R\) \) and the intercept \((\Delta S^0 / R\) \) of the plot of \( \ln K_C \) versus \( 1/T \) [20]. A negative \( \Delta G^0 \) value indicates that the adsorption process is spontaneous and a negative \( \Delta H^0 \) value indicates the exothermic nature of this adsorption process.

Fig. 5 shows the relationship between \( \ln K_C \) and \( 1/T \) when silica gel adsorbs sodium bisulfate in different concentration ranges (\( C_e < C'_e \) and \( C_e > C'_e \)). It can be seen from Fig. 5 that the plots of \( \ln K_C \) and \( 1/T \) are linear. The values of \( \Delta H^0 \) and \( \Delta S^0 \) can be calculated from the slope and the intercept of the plots and listed in Table 5.

![Fig. 5. The linear relationship between In (Kc) and 1/T](image-url)
Table 4. The average characteristic concentration \( (C_e') \)

| \( T \) (K) | \( C_e' \) (g/mL) | Relative errors |
|------------|-----------------|----------------|
|            | \( C_e' - C_{el} \)/\( C_e' \) | \( C_e' - C_{eo} \)/\( C_e' \) |
| 298.15     | 0.0230          | 0.043          |
| 308.15     | 0.0235          | 0.022          |
| 318.15     | 0.0260          | 0.000          |
| 328.15     | 0.0285          | 0.018          |
|            | Average error   | 0.021          |

Table 5. Thermodynamic parameters of NaHSO\(_4\) adsorption on silica gel at different concentrations

| Parameters | \( C_e \leq C_e' \) | \( C_e > C_e' \) |
|------------|-----------------|-----------------|
| \( \Delta H^0 \) (kJ/mol) | 5.64            | -6.82           |
| \( \Delta S^0 \) (J/mol K) | 7.57            | -38.37          |

It can be seen from Table 5 that when \( C_e < C_e' \), the adsorption of sodium bisulfate on the surface of silica gel is an endothermic process, and when \( C_e > C_e' \), the adsorption is an exothermic process.

5. CONCLUSIONS

The adsorption isotherm of NaHSO\(_4\) on silica gel were measured in the temperature range of 298.15 ~ 328.15 K, and the Langmuir model and the Dubini-Radushkevich (D-R) model were used to fit the experimental isotherm data. The results are given below.

a. There is an average characteristic concentration \( (C_e' =0.0230-0.0285 \text{ g/mL}) \), and when the \( C_e \) value is less than \( C_e' \), the adsorption of NaHSO\(_4\) on silica gel is chemisorption, and when it is greater than \( C_e' \), the adsorption also includes multilayer physical adsorption.

b. The thermodynamic parameters \( (\Delta H^0 \text{ and } \Delta S^0)\) of NaHSO\(_4\) adsorption on silica gel at different concentrations were calculated, indicating that when \( C_e < C_e' \), the adsorption of sodium bisulfate on the surface of silica gel is an endothermic process, and when \( C_e > C_e' \), it is an exothermic process.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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