



Adsorption Behavior of Sodium Hydrogen Sulfate on Silica Gel

Jumei Xu¹, Zhongkai Jiang¹, Zuoxiang Zeng^{1*} and Weilan Xue¹

¹School of Chemical Engineering, East China University of Science and Technology, Shanghai, 200237, China.

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.

Article Information

DOI: 10.9734/AJOCS/2020/v7i319024

Editor(s):

(1) Dr. Sung Cheal Moon, Korea Institute of Materials Science, Republic of Korea.

Reviewers:

(1) John Onyatta, University of Nairobi, Kenya.

(2) Manohar V. Lokhande, Sathaye College, India.

Complete Peer review History: <http://www.sdiarticle4.com/review-history/56220>

Received 06 February 2020

Accepted 12 April 2020

Published 21 April 2020

Original Research Article

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 NaHSO_4 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 NaHSO_4 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

*Corresponding author: E-mail: zengzx@ecust.edu.cn;

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 ($\text{NaHSO}_4/\text{SiO}_2$) has been widely used as a new type of highly efficient heterogeneous catalyst and is commonly used in many organic reactions such as debenzoylation [6], nitration [7], nitrosation [8], oxidation [9], esterification [10,11], alkylation [12], chemoselective protection and deprotection [13-15]. The advantages of using $\text{NaHSO}_4/\text{SiO}_2$ 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]. $\text{NaHSO}_4/\text{SiO}_2$ 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 NaHSO_4 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 \pm 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 NaHSO_4 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 (q_e) and equilibrium adsorption concentration in aqueous solution (C_e) were calculated from the adsorption data. The value of q_e was calculated using Eq (2.1)

$$q_e = (C_0 - C_e) \frac{V}{m_s} \quad (2.1)$$

where C_0 and C_e 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 m_s is the weight of silica gel.

3. ADSORPTION MECHANISMS AND MODELS

3.1 Chemisorption

^{31}P 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 SiO_2 , 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 ($\equiv\text{Si-OH}_2^+$). The chemical equations are as follows:

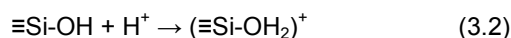
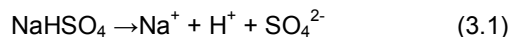


Table 1. Physical parameters of silica gel

Parameter	BET surface area m ² /g	Volume of pores cm ³ /g	Apparent density g/cm ³	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 Dubini-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]

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \quad (3.3)$$

where q_{\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_{\max} and K_L were obtained from the slope ($1/q_{\max}$) 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]

$$\ln q_e = \ln q_{\max} - \beta \varepsilon^2 \quad (3.4)$$

where β is the affinity coefficient, which depends on the adsorptive and ε is the Polanyi potential and can be expressed as

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (3.5)$$

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

$$E = \frac{1}{\sqrt{2\beta}} \quad (3.6)$$

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 .

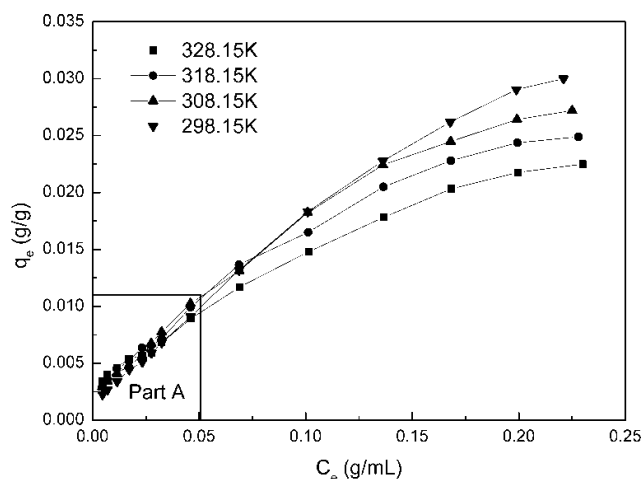


Fig. 1. Isothermal adsorption equilibrium lines of $q_e \sim C_e$ at 298.15~328.15 K

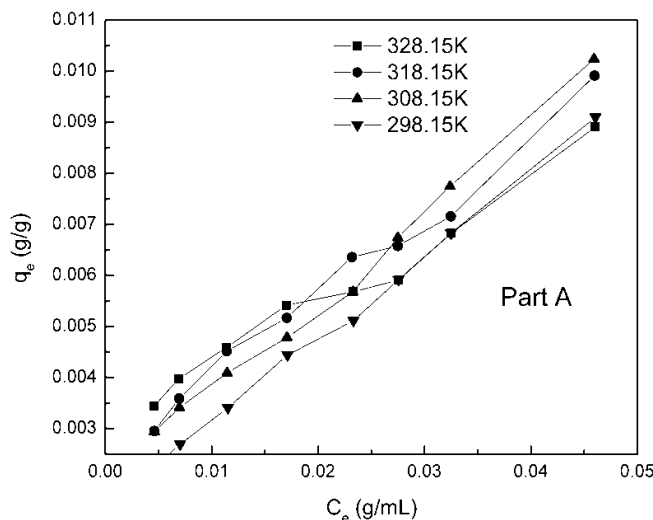


Fig. 2. Enlargement of part A of Fig. 1

Table 2. The parameters of Langmuir model for the adsorption of NaHSO₄ on silica gel at different temperatures

T (K)	C _{eL} (g/mL)	C _e ≤ 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 NaHSO₄ concentrations, indicating that the adsorption of NaHSO₄ 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 ϵ^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 (ϵ_D^2)

on the abscissa. On both sides of the value (ϵ_D^2), the functional relationship between $\ln(q_e)$ and ϵ^2 can be described by two straight lines, respectively. According to Eq (3.5), a feature concentration value (C_{eD}) corresponding to ϵ_D^2 can be obtained and listed in Table 3. When $C_e \leq C_{eD}$ the function relationship between C_e and C_e/q_e is linear, and when $C_e > C_{eD}$, there is another linear relationship between C_e and C_e/q_e .

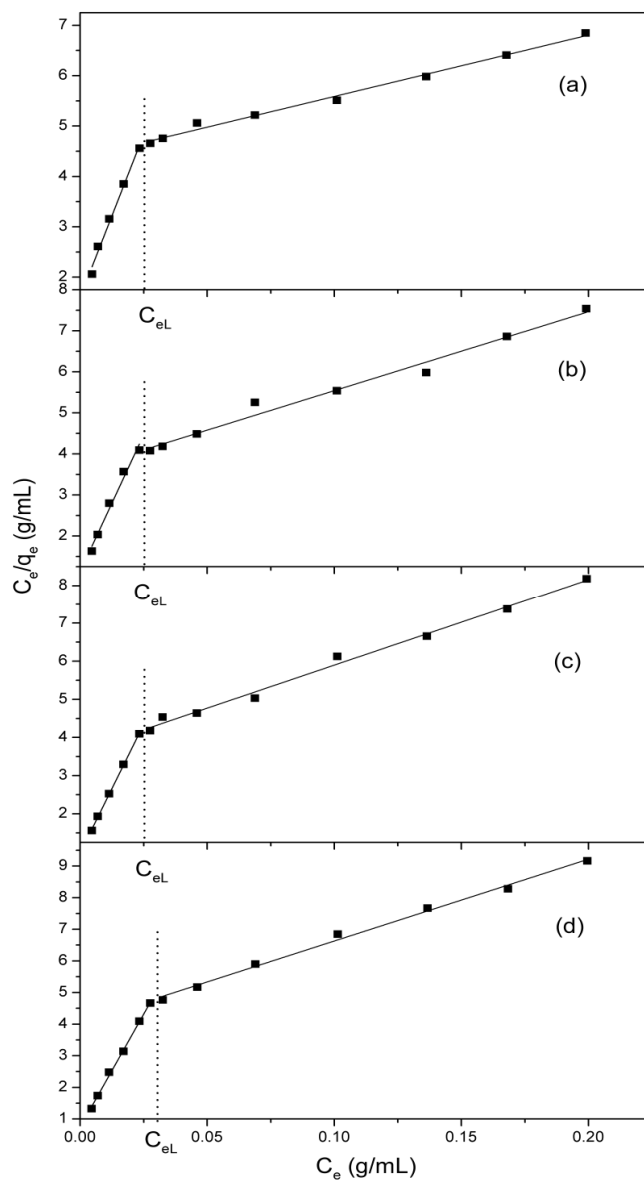


Fig. 3. The regression curve of Langmuir adsorption isotherm model at different temperatures (a) 298.15K; (b) 308.15K; (c) 318.15K; (d) 328.15K

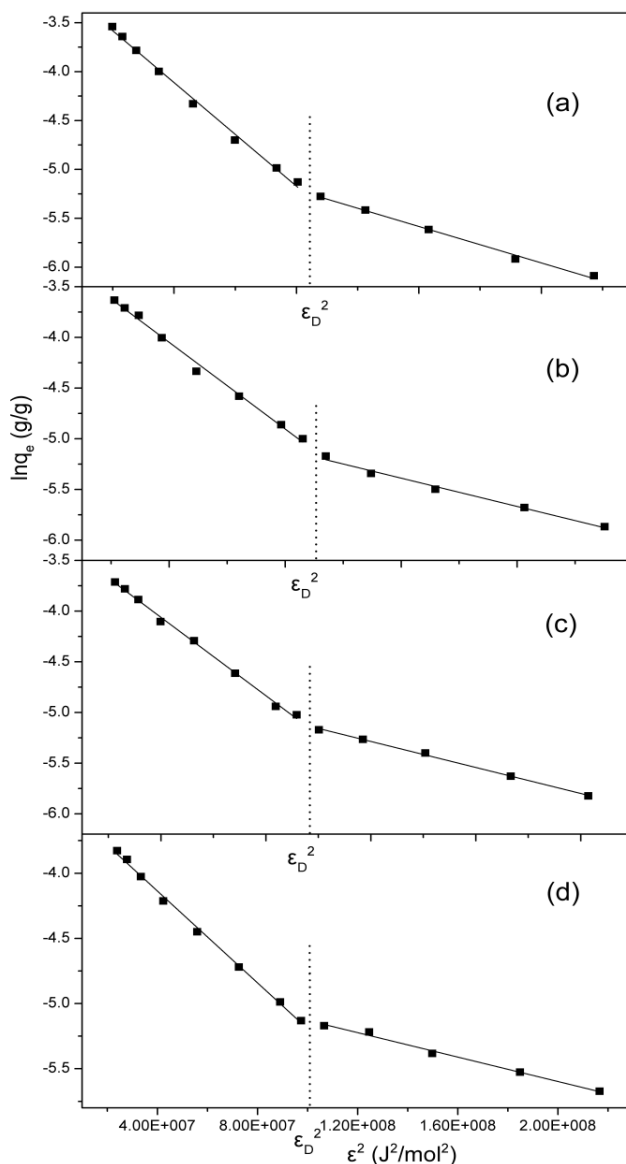


Fig. 4. The regression curve of D-R adsorption isotherm model at different temperatures (a) 298.15K; (b) 308.15K; (c) 318.15K; (d) 328.15K

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

T (K)	C _{eD} (g/mL)	C _c ≤ C _{eD}			C _c > 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

The D-R model parameters (q_{max} and E) are calculated and listed in Table 3. The correlation coefficients (R²) are also listed in Table 3. It can be seen from the R² 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:

$$C_e' = (C_{eL} + C_{eD})/2 \quad (4.1)$$

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 (ΔH^0), entropy (ΔS^0) and Gibbs free energy

(ΔG^0) for a better understanding of the thermodynamic behavior of adsorption and they were determined by Eq (4.2) and Eq (4.3)

$$\ln K_C = \ln \frac{C_{Ae}}{C_{Se}} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (4.2)$$

$$\Delta G^0 = -RT \ln K_C \quad (4.3)$$

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 ΔH^0 and ΔS^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 ΔG^0 value indicates that the adsorption process is spontaneous and a negative ΔH^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 ΔH^0 and ΔS^0 can be calculated from the slope and the intercept of the plots and listed in Table 5.

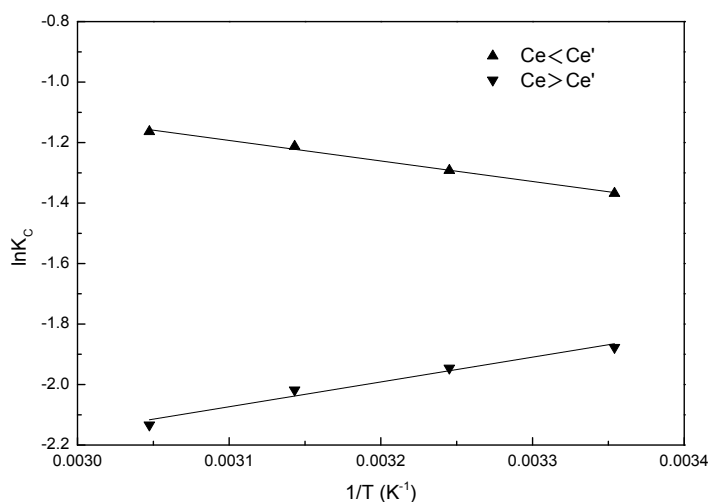


Fig. 5. The linear relationship between $\ln(K_C)$ and $1/T$

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_{eD} /C_e'$
298.15	0.0230	0.043	0.043
308.15	0.0235	0.022	0.022
318.15	0.0260	0.000	0.000
328.15	0.0285	0.018	0.018
	Average error errors	0.021	0.021

Table 5. Thermodynamic parameters of NaHSO₄ adsorption on silica gel at different concentrations

Parameters	$C_e \leq C_e'$	$C_e > C_e'$
ΔH^0 (kJ/mol)	5.64	-6.82
ΔS^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 NaHSO₄ 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 ($C_e' = 0.0230 \sim 0.0285$ g/mL), and when the C_e value is less than C_e' , the adsorption of NaHSO₄ on silica gel is chemisorption, and when it is greater than C_e' , the adsorption also includes multilayer physical adsorption.

b. The thermodynamic parameters (ΔH^0 and ΔS^0) of NaHSO₄ 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.

REFERENCES

1. Kukharev BF, Stankevich VK, Klimenko GR. Hydrolysis of 2-[2-(vinylloxy)

ethoxymethyl] oxirane in the presence of sodium hydrogen sulfate. *Russ. J. Org. Chem.* 2009;45:1123-1124.

2. Bhure MH, Kumar I, Natu AD, Chikate RC, Rode CV. Phosphotungstic acid on silica with modified acid sites as a solid catalyst for selective cleavage of tert-butyl dimethylsilyl ethers. *Catal. Commun.* 2008;9:1863.

3. Kukovecz Á, Balogi Z, Kónya Z, Toba M, Lentz P, Niwa SI, Mizukami F, Molnár Á, Nagy JB, Kiricsi I. Synthesis, characterisation and catalytic applications of sol-gel derived silica-phosphotungstic acid composites. *Appl. Catal. A: Gen.* 2002;228:83.

4. Kolvari E. Sodium hydrogen sulfate: Safe and efficient. *Synlett.* 2006;12:1971-1972.

5. Zeng ZX, Cui L, Xue WL, Ma NK. Study on adsorption behavior of 12-phosphotungstic acid on silica gel. *Ind. Eng. Chem. Res.* 2013;23:8070-8078.

6. Zhou LN, Wang WJ, Zuo L, Yao SY. Selective debenylation of aromatic benzyl ethers by silica-supported sodium hydrogen sulfate. *Tetrahedron Letters.* 2008;49:4876-4878.

7. Zolfigol MA, Madrakian E, Ghaemi E. Nitration of phenols under mild and heterogeneous conditions. *Molecules.* 2001;6:614-620.

8. Zolfigol MA, Madrakian E, Ghaemi E, Kiani M. An efficient method for N-nitrosation of secondary amines under mild and heterogeneous conditions. *Synth. Comm.* 2000;30(11):2057-2060.

9. Shirini F, Zolfigol MA, Torabi S. Chromium trioxide supported on NaHSO₄ center dot H₂O: Simple oxidation of alcohols in

- solution and solvent free conditions. Lett. Org. Chem. 2005;2:544-546.
10. Das B, Venkataiah B, Madhusudhan P. A simple and efficient selective esterification of aliphatic carboxylic acids in the presence of aromatic carboxylic acids. Synlett. 2000;1:59-60.
 11. Das B, Venkataiah B. Selective transesterification of aliphatic acids in the presence of aromatic acids using silica gel supported NaHSO₄ catalyst. Synthesis. 2000;12:1671-1672.
 12. Aoyama T, Miyota S, Takido T, Kodomari M. Direct carbon-carbon bond formation from alcohols and active methylenes using NaHSO₄/SiO₂. Synlett. 2011;20:2971-2976.
 13. Ravindranath N, Ramesh C, Reddy MR, Das B. Studies on novel synthetic methodologies - Part 19. Selective removal of n-boc protecting group from aromatic amines using silica gel-supported sodium hydrogen sulfate and HY-zeolite as heterogeneous catalysts. Adv. Synth. Catal. 2003;345:1207-1208.
 14. Ramesh C, Ravindranath N, Das B. Simple, efficient, and selective deprotection of phenolic methoxymethyl ethers using silica-supported sodium hydrogen sulfate as a heterogeneous catalyst. J. Org. Chem. 2003;68:7101-7103.
 15. Ramesh C, Mahender G, Ravindranath N, Das B. A simple, mild and efficient procedure for selective cleavage of prenyl esters using silica-supported sodium hydrogen sulphate as a heterogenous catalyst. Tetrahedron Lett. 2003;44:1465-1467.
 16. Das B, Mahender G, Kumar VS, Chowdhury N. Chemoselective deprotection of trityl ethers using silica-supported sodium hydrogen sulfate. Tetrahedron Lett. 2004;45:6709-6711.
 17. Dabiri M, Azimi SC, Bazgir A. An efficient and rapid approach to quinolines via friedlander synthesis catalyzed by silica gel supported sodium hydrogen sulfate under solvent-free conditions. Monatshefte fur Chemie. 2007;7:659-661.
 18. Lefebvre F. ³¹P MAS NMR study of H₃PW₁₂O₄₀ supported on silica: Formation of (-SiOH₂⁺) (H₂ PW₂O₄₀⁻). J. Chem. Soc., Chem. Commun. 1992;756-757.
 19. Kozhevnikov IV, Kloetstra KR, Sinnema A, Zandbergen HW, van Bekkum H. Study of catalysts comprising heteropoly acid H₃PW₁₂O₄₀ supported on MCM-41 molecular sieve and amorphous silica. J. Molecular Catal. A: Chem. 1996;114:287-298.
 20. Qu RJ, Niu YZ, Sun CM, Ji CN, Wang CH, Cheng GX. Syntheses, characterization, and adsorption properties for metal ions of silica-gel functionalized by ester- and amino-terminated dendrimer-like polyamidoamine polymer. Microporous Mesoporous Mater. 2006;97:58-65.
 21. Dubinin MM, Zaverina ED, Radushkevich LV. Sorption and structure of active carbons. I. Adsorption of organic vapors. Zh. Fiz. Khim. 1947;21:1351-1362.
 22. Helfferich F. Ion exchange. McGraw-Hill. New York; 1962.
 23. Kiran I, Akar T, Ozcan AS, Ozcan A, Tunali S. Biosorption kinetics and isotherm studies of acid red 57 by dried *Cephalosporium aphidicola* cells from aqueous solutions. Biol. Chem. Eng. J. 2006;31:197-203.

© 2020 Xu et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

The peer review history for this paper can be accessed here:
<http://www.sdiarticle4.com/review-history/56220>