

Preparation and characterization of high efficient ion-sieve $\text{H}_8\text{Nb}_{22}\text{O}_{59} \cdot 8\text{H}_2\text{O}$

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Keywords: Na^+ ; K^+ ; ion sieve; $\text{H}_8\text{Nb}_{22}\text{O}_{59} \cdot 8\text{H}_2\text{O}$; high-purity sodium chloride.

Abstract. The adsorbent $\text{H}_8\text{Nb}_{22}\text{O}_{59} \cdot 8\text{H}_2\text{O}$ and its precursor $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ were prepared to produce high-purity NaCl. Their characteristics were studied by X-ray diffraction (XRD), thermogravimetric and differential scanning calorimetry (TG-DSC) and scanning electron microscope (SEM). Two main calcinations factors of calcinations time and temperature were investigated. Results suggest that calcination time rarely influenced the crystal structure probably owing to the high calcination temperature. Furthermore, the high calcination temperature contributed to the stronger crystallinity of precursor $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$, which shows that the structure of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ was not changed by the extraction of Rb^+ from $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ and this process is topotactical. Finally, the present adsorbent of $\text{H}_8\text{Nb}_{22}\text{O}_{59} \cdot 8\text{H}_2\text{O}$ exhibited the excellent selectivity for K^+ ion, indicating that it can be considered as a promising adsorbent for the selective removal of K^+ from sodium chloride solutions.

1. Introduction

High-purity sodium chloride (99.99%) could be extensively applied in food industry, medicine, the medical field, etc. The similar properties for Na^+ and K^+ results in the difficulty for separation of K^+ from their mixed solution. In order to obtain high-purity sodium chloride, more attention is focused on the ion-sieve compound with high selectivity for K^+ in recent decades [1]. Ion-sieve compound is a metal oxide porous crystals (MOPCS), which is usually synthesized through the template method. And the ion-sieve compound can be obtained by topotactically removing the template ions from inorganic compound with the template ions, which is calcined at the high temperature. The ion-sieve compound shows a high selectivity for specific ion depending on the template ion [1,2].

$\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ was synthesized since 1960s, and more attention was paid for the structure and physico-chemical properties of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ [4,5]. However, Yang et al. [6] suggested $\text{H}_8\text{Nb}_{22}\text{O}_{59} \cdot 8\text{H}_2\text{O}$ obtained from $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ should be a new type of ion-sieve exchanger owing to its excellent ion-exchange properties with different affinity for alkali metal at different pH values.

In this study, the ion-sieve adsorbent $\text{H}_8\text{Nb}_{22}\text{O}_{59} \cdot 8\text{H}_2\text{O}$ was synthesized by removing Rb^+ from $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ at high temperature. The characteristics of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ and $\text{H}_8\text{Nb}_{22}\text{O}_{59} \cdot 8\text{H}_2\text{O}$ were studied by X-ray diffraction (XRD), Thermogravimetric and differential scanning calorimetry (TG-DSC), and scanning electron microscope (SEM), respectively. Furthermore, the removal efficiency of K^+ by the adsorbent was tested.

2. Materials and methods

Compound containing Rb_2CO_3 (99.9%, m.p. 723 °C, Gracia Chengdu chemical Technology Co. Ltd., China) and Nb_2O_5 (99.99%, m.p. 1520 °C, Gracia Chengdu chemical Technology Co. Ltd., China) were completely mixed with the $\text{Rb}_2\text{CO}_3/\text{Nb}_2\text{O}_5$ mole ratio of 4/11. Then the mixture was calcined to obtain $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$.

The XRD patterns of different $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ samples were carried out on a XD-3 X-ray powder diffractometer (Purkinje, China). TG-DSC analysis was performed by using a TGA/DSC1/1100

instrument (Mettler Toledo Co. Ltd., Sweden). The morphology of various samples was obtained using a scanning electron microscope (SU-1510, Hitachi, Japan).

3. Results and discussion

3.1 XRD patterns

In order to investigate the effect of the calcination time on the $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ crystallinity, the XRD patterns of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ samples calcined at 1200 °C for different time (5 h, 8 h, 12 h, and 16 h) were investigated (Fig. 1). The intensities of the characteristic peaks of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ were not obviously strengthened with the increase of calcination time, suggesting that the calcination time rarely influenced the crystal structure. Generally, the calcination time influences the crystallinity of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$, and the crystal grain size continues to grow with the increase of calcination time (Dewan and others 1978). But the obvious effect of the calcination time on the structure of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ was not observed in this study, probably owing to the high calcination temperature.

Wang et al. [7] studied by the XRD patterns for Nb_2O_5 , Rb_2CO_3 , and $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ calcined for 8 hours at different temperatures. The XRD results show that the high calcination temperature contributed to the stronger crystallinity of precursor $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ and it indicated the curve of $\text{H}_8\text{Nb}_{22}\text{O}_{59} \cdot 8\text{H}_2\text{O}$ was identical to that of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$, which suggests that the structure of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ is not changed by the extraction of Rb^+ from $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ and this process is topotactical.

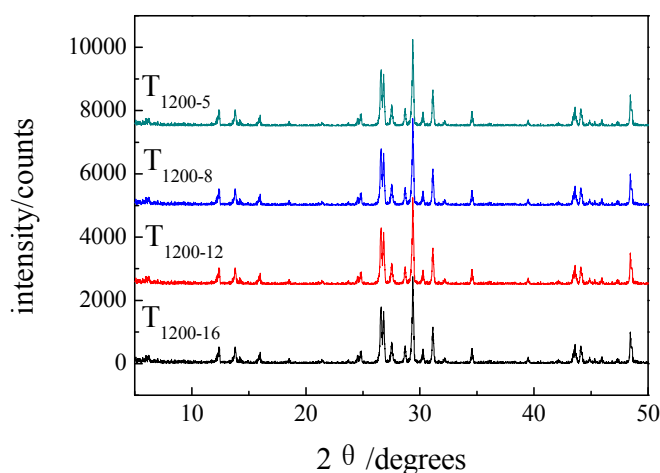


Fig. 1. XRD patterns of the $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ samples calcined at 1200 °C for different time.

3.2 SEM results

The SEM images of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ and $\text{H}_8\text{Nb}_{22}\text{O}_{59} \cdot \text{H}_2\text{O}$ calcined at 1200 °C for 16 hours are showed in Fig. 2. The similar morphology of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ and $\text{H}_8\text{Nb}_{22}\text{O}_{59} \cdot \text{H}_2\text{O}$ was observed, which are 1 μm flaky crystal, suggesting that the morphology was not changed by the extraction of Rb^+ .

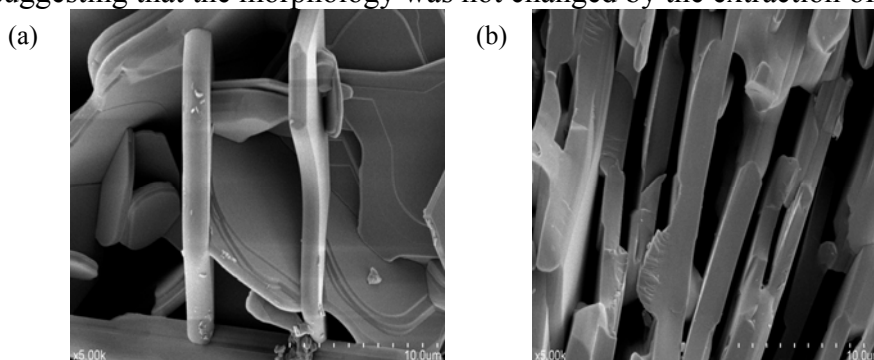


Fig. 2. SEM images of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ (a) and $\text{H}_8\text{Nb}_{22}\text{O}_{59} \cdot \text{H}_2\text{O}$ (b) calcined at 1200 °C for 16 hours

3.1 XRD patterns

Fig. 3 shows the TG-DSC curves of the $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ and $\text{H}_8\text{Nb}_{22}\text{O}_{59}\cdot 8\text{H}_2\text{O}$ calcined at 1200 °C for 16 h. The TG curve of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ exhibited no change without any peak observed in the corresponding DSC curve. In contrast, the TG curve of $\text{H}_8\text{Nb}_{22}\text{O}_{59}\cdot 8\text{H}_2\text{O}$ showed two stages of weight loss. And the first large weight loss of 4.31% between 50 °C and 340 °C was due to the evaporation of lattice water, which was close to the weight loss of 4.58 % for the crystal-structure model of $(\text{H}_3\text{O})_8\text{Nb}_{22}\text{O}_{59}$. The second weight loss of 2.16 % and 0.19 % were corresponding to 380 °C endothermic peak and 445 °C exothermic peak of DSC cure, respectively. This process was caused by the release of lattice proton and oxygen between 340 °C and 450 °C. The hexagonal symmetry ($\text{H}_8\text{Nb}_{22}\text{O}_{59}\cdot 8\text{H}_2\text{O}$) was transformed to Nb_2O_5 at 380 °C with the release of oxygen and hydrogen, which was similar with the transformation of the HolMO (Hollandite-Type Manganese Oxide) to Mn_2O_3 with the weight loss of oxygen at 480 °C. The exothermic peak at 445 °C might be caused by the continuing transformation of $\text{H}_8\text{Nb}_{22}\text{O}_{59}\cdot 8\text{H}_2\text{O}$ to Nb_2O_5 with the release of oxygen [8].

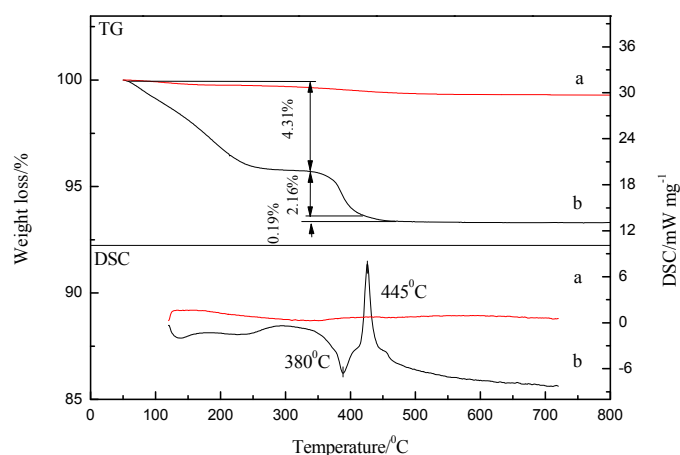


Fig. 3 TG-DSC curves of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ (a) and $\text{H}_8\text{Nb}_{22}\text{O}_{59}\cdot 8\text{H}_2\text{O}$ (b) calcined at 1200 °C for 16 hours

3.4 Removal efficiency of K^+

The influence of Na^+/K^+ on K^+ removal efficiency was investigated in different solution, and the results are showed in Table 1. In the low Na^+/K^+ (mole ratio) solution, K^+ can be efficiently removed by the adsorbent, whereas the removal efficiency decreased obviously at the high Na^+/K^+ mole ratio. Wang et al. [7] studied the removal efficiency was up to 93.0 % in the mixture solution with Na^+/K^+ mole ratio of 50. However, the removal efficiency was only 43.3 % in the mixture solution with Na^+/K^+ mole ratio of 10000. These results indicate that the concentration of sodium chloride solutions significantly influences the removal of K^+ ion. Nevertheless the present adsorbent of $\text{H}_8\text{Nb}_{22}\text{O}_{59}\cdot 8\text{H}_2\text{O}$ exhibited the excellent selectivity for K^+ ion, indicating that it can be considered as a promising adsorbent for the selective removal of K^+ from sodium chloride solutions.

Table 1. Effect of Na^+/K^+ (mole ratio) in mixed solutions on K^+ removal efficiency

Na^+/K^+	Concentration /mM			pH values after adsorption
	K^+ (before adsorption)	K^+ (after adsorption)	Remove efficiency/%	
50	0.94	0.07	93.0	2.00
500	0.94	0.33	65.0	1.91
1000	0.92	0.38	58.4	1.76
2000	0.46	0.21	54.6	1.78
10000	0.095	0.05	43.3	1.78

4. Summary

The synthesis of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ and its ion-exchange properties for Na^+ and K^+ are studied. The structural characteristics are studied by XRD, TG-DSC, and SEM, respectively. It is found that the crystallinity of $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ increases with the increase of the calcination temperature. However, the calcination time slightly influence the crystal structure. Overall, the obtained ion-sieve exchanger $\text{Rb}_8\text{Nb}_{22}\text{O}_{59}$ is a promising adsorbent for K^+ for purification from sodium chloride solution.

Acknowledgements

This work was supported by the Projects (201404140) supported by Agricultural Commission of Tianjin, China; Project (14ZCDGNC00097) supported by the science and Technology Commission of Tianjin, China.

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