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Adsorption and Desorption Properties of Several Molecular Sieves on Formaldehyde Gas

Wenqin Zeng[1], Yuhui Du[2], Zhouke Kang[3], Bohao Zhao[4], Guanbo Wang[5]

[1]Yongzhou Vocational Technical College, Yongzhou, China

[2]Engineering University of PAP, Xi’an, China

[3]Army Engineering University of PLA, Nanjing, China

[4]Rocket Force University of Engineering, Xi’an, China

[5]Xi’an Jiaotong University, Xi’an, China

Abstract

Static formaldehyde adsorption experiments were conducted on three types of molecular sieves(3A, 13X, and beta) made in the laboratory. The BET specific surface area and adsorption desorption isotherm curves of the samples were measured using low-temperature nitrogen adsorption method. BET specific surface area and adsorption desorption isotherm curves of the samples were measured using low-temperature nitrogen adsorption method. The pore volume and pore size distribution of each sample was calculated using density function theory. The effects of specific surface area, pore Size, and skeleton structure on the formaldehyde and nitrogen adsorption of the samples were measured using low-temperature nitrogen adsorption method. The effects of specific surface area, pore size, and skeleton structure on the formaldehyde adsorption performance of beta and 13X molecular sieves were emphatically investigated. that the skeleton structure had a significant impact on the formaldehyde adsorption performance of beta and 13X molecular sieves. The thermal desorption experiment found that the greater the surface area, pore size, and skeleton structure, the greater the formaldehyde adsorption performance. desorption experiment found that the greater the heating rate, the greater the weight loss ratio of molecular sieve thermal desorption. more easily desorbed on beta molecular sieve than on 13X molecular sieveand 3A molecular sieve.

Keywords

Molecular sieves, Formaldehyde gas, Adsorption, Desorption.

1. INTRODUCTION

With the improvement of people's living standard, the indoor air pollution problem generated by home decoration is inevitable. Formaldehyde(HCHO) is one of the most common and harmful pollutants released indoors, which mainly comes from pressed wood products bonded with HCHO-based resins[1], such as particle boards, plywoods, fiber boards and adhesives[2] . Studies have shown that chronic and acute inhalation of HCHO can easily lead to inflammation of the throat, nose and eyes, and may cause nasopharyngeal cancer and cancer, which are very harmful to human beings.

Plant absorption, biotechnological decomposition, photocatalytic oxidation, thermocatalytic oxidation, and chemical absorption[3]have been recently widely used for formaldehyde degradation, but there are still limitations such as low adsorption efficiency, high energy

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consumptio, and long adsorption treatment cycle. Therefore, applications based on the above methods are difficult to apply in real life. The adsorption method uses adsorbents to selectively adsorb components of the exhaust gas to achieve purification, which is a mature process and high purification efficiency, and is suitable for low concentration VOCS gas treatment. Traditional commercially available activated carbon is a commonly used material for formaldehyde adsorption, but it is not easy to desorb after adsorption, has poor recyclable performance, the absorbent needs to be replaced frequently, and improper maintenance is prone to secondary pollution[4], so it is of great practical significance to explore a kind of adsorbent with strong adsorption performance and good recyclable performance.

The pore structure of adsorbents such as zeolite molecular sieves includes regular arrays of uniform channels of molecular size, thus offering the possibility of size-selective(molecular sieve) separation with strong selective adsorption and good adsorption of molecules with strong polarizability[5]. Formaldehyde is a polar molecule and is easily polarized and adsorbed by molecular sieves. In this thesis, three kinds of representative molecular sieves were manufactured, and the main factors of the adsorption of formaldehyde by different molecular sieves were analyzed from the aspects of specific surface area, pore size and crystal type; thermal desorption method was adopted to desorb the molecular sieves, to explore the more economic and efficient desorption conditions, and to provide a theoretical basis for the industrial use of molecular sieve adsorbents.

2. EXPERIMENTAL SECTION

2.1. Experimental reagents and apparatus

3A molecular sieve, homemade; 13X molecular sieve, homemade; beta molecular sieve, homemade; formaldehyde, Tianjin Hengxing Chemical Reagent Co; JW-ZQ200 static volumetric vapor adsorption meter, Beijing Jingwei GaoBo Science and Technology Co. ; TGA-1250A Thermogravimetri Analyzer, from Shanghai Yingnuo Precision Instrument Co.

Preparation of 13X molecular sieves:With reference to the properties of commercial X molecular sieves(i.e., molar ratios of SiO_2:Al_2O_3=3.0, Na_2O:SiO_2=1.8, and H_2O:Na_2O=40), 13X molecular sieves were prepared by a hydrothermal method. All the chemicals used in this experiment(including Na_2O, SiO_2, Al_2O_3) were supplied by Beijing Chemical Factory. Firstly, the chemicals and selected samples were mixed and heated for 24h. Secondly, the reactants were transferred to are actor and then the reactor was heated using a muffle furnace at a heating rate of 2°C/min. Finally, the synthesized samples were refrigerated to room temperature and leached with distilled water until their pH was neutral and then dried (i.e., the purification process). Beta molecular sieves were prepared similarly to 3A molecular sieves.

2.2. Static adsorption method[4]

The three kinds of molecular sieves we replaced in an oven at 200°C for 5h of activation to remove the organic impurities adsorbed on the surface of the adsorbent and inside the pore size as well as the interference of moisture. Prepare four clean and dry desiccators, weigh 10g of each of the activated three molecular sieves on a balance, place the mona surface dish of the same size, put the surface dish containing the molecular sieves into the four desiccators, measure 150ml of formaldehyde in four dry 200ml beakers, and put them into the four desiccators. Seal the desiccator lid by evenly applying petroleum jelly on the edge of the lid. The four desiccators were kept under the same conditions to ensure that the volatilization and adsorption of formaldehyde solution were carried out under the same conditions. Samples were taken and weighed every 1h. When the weighed mass no longer changed(the adsorption capacity of the molecular sieve was saturated), the molecular sieve was removed and sealed in a Ziploc bag, and the adsorption capacity was calculated.

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2.3. Thermal Desorption

Thermal desorption of adsorption-saturated molecular sieves was carried out using a thermogravimetric analyzer, which was heated from room temperature to 500°C under the protection of high-purity nitrogen with the heating rates of 5K/min, 10K/min, and 15K/min, respectively.

3. RESULTS AND DISCUSSION

3.1. Effect of time on adsorption amount

Figure 1 shows the static adsorption curves of formaldehyde by 3A, 13X and beta zeolite molecular sieves, from the figure it can be seen that after 20h of adsorption, he formaldehyde adsorption of beta molecular sieve can reach a maximum of 197.6mg/g, the adsorption of 13X is 126mg/g, and the adsorption of 3A molecular sieve is 84.95mg/g. From the Fig.1, it can be seen that the three kinds of molecular sieves reached adsorption equilibrium at 20h.

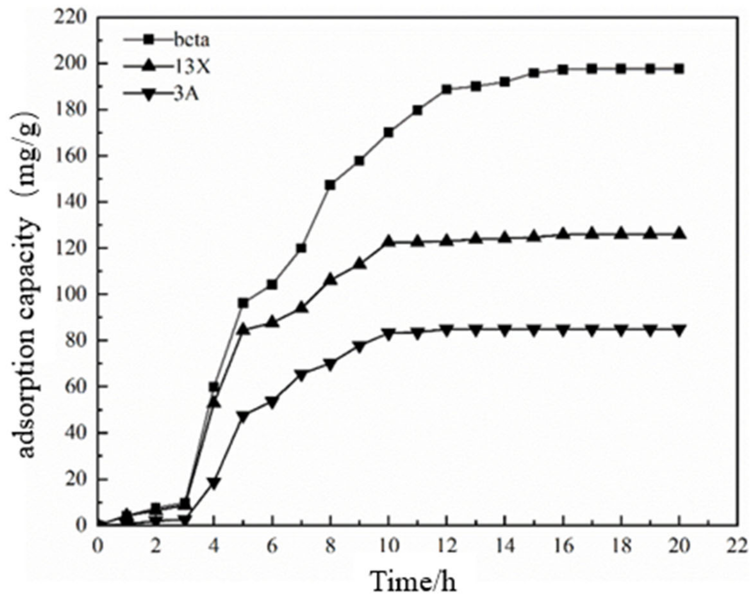

Figure 1. Static adsorption curves of several molecular sieves

3.2. Molecular sieve characterization

3.2.1 Specific surface area and pore structure parameters of samples tested by JW-ZQ 200 static volumetric vapor adsorption meter

Table 1. Parameters of molecular sieves

molecular sieve	Effective Pore size(nm)	Specific surface area(m^2/g)	Pore volume (cm^3/g)
beta	0.745	566.32	0.329
13X	0.723	587.56	0.259
3A	0.313	152.26	0.014

As shown in Table 1, 3A molecular sieve has a small specific surface area and effective pore size, the effective pore size is 0. 313nm, less than the molecular diameter of formaldehyde molecules 0. 33nm, Knudsen diffusion occurs[5], formaldehyde gas molecules and molecular sieve pore wall frequent collision, it will produce strong site resistance effect, so the

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formaldehyde adsorption amount is the smallest. 13X molecular sieve specific surface area and effective pore size is similar to beta molecular sieve, and the amount of formaldehyde adsorption is higher than 13X molecular sieve. formaldehyde adsorption of beta molecular sieve is higher than that of 13X molecular sieve, indicating that the specific surface area and pore size are not the only determining factors.

3.2.2 Poresizeanalysisof13X molecular sieves and beta molecular sieves

Figures 2 and 3 show the pore volume-pore size distribution of beta molecular sieve and 13X molecular sieve, respectively. As can be seen from the figures, the pore size peak of beta molecular sieve is around 0.74nm, and that of 13X molecular sieve is around 0.73nm, and the effective pore sizes of the pore sieves are larger than that of formaldehyde's molecular diameter of 0.33nm, so the two have small adsorption site-barrier effects and better adsorption effects.

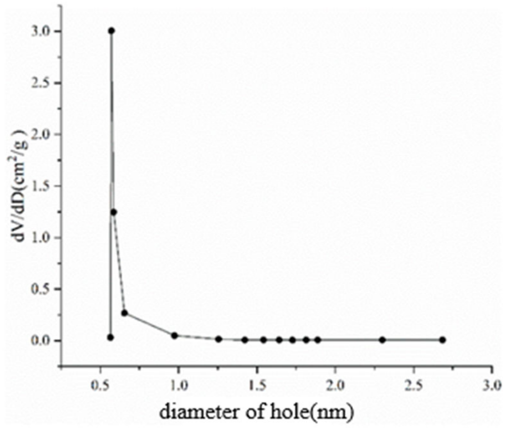

Figure 2. Pore size distribution of beta molecular sieve

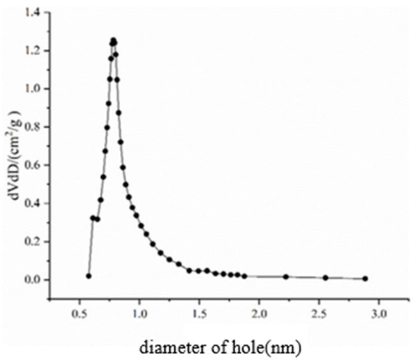

Figure 3. Pore size distribution of 13X molecular sieve

3.2.3 Low-temperature nitrogen adsorption and desorption isotherm testing of 13X molecular sieves and beta molecular sieves

From Fig.4 and Fig.5, it can be seen that the low temperature nitrogen adsorption and desorption curves of 13X and beta molecular sieves are I-type adsorption isotherms with typical microporous adsorption type characteristics, and the nitrogen adsorption amount of increased steeply with the increase of the pressure as the relative pressure P/Po was increased from 0 to 0.1, and the samples reached the saturation of the adsorption at the lower pressure, and the adsorption isotherms of the molecular sieves of 13Xandbetao were in the range from 0 to 1. The adsorption and desorption isotherms of the molecular sieves were basically coincident. and desorption isotherms basically coincide, indicating that the two selected zeolite molecular

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sieves have relatively uniform pore size distribution, rich microporous structure and good adsorption effect on formaldehyde.

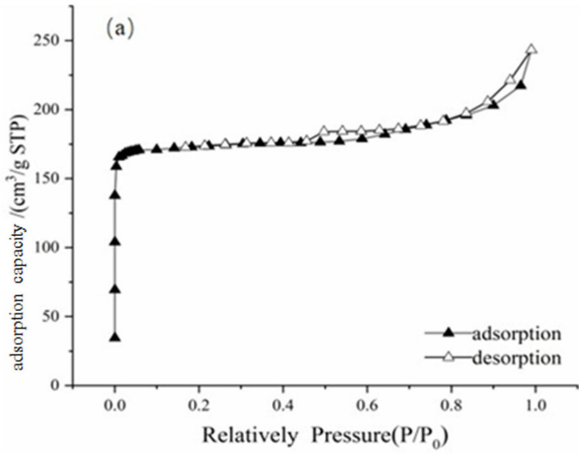

Figure 4. N_2 adsorption and desorption of 13X

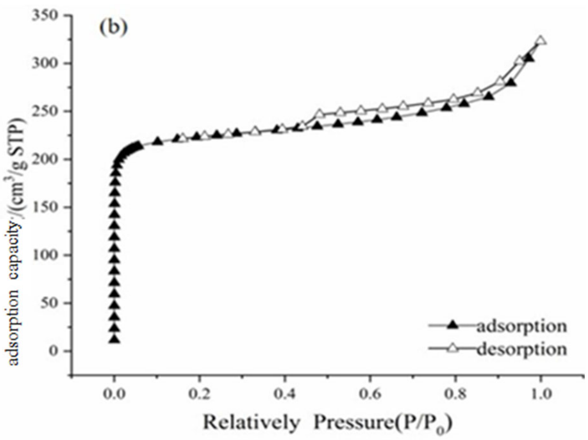

Figure 5. N_2 adsorption and desorption of beta

3.3. Skeletal structure analysis of 13X molecular sieves and beta molecular sieves

13X molecular sieve is a synthetic NaX type molecular sieve, its structural unit isβ-cage, neighboring β-cage is connected by hexagonal column cage[6]. Each β-cage is interconnected with other β-cages with T-O-T bonds in tetrahedral direction using four hexagonal rings to form a three-dimensional skeleton. After formaldehyde molecules enter the molecular sieve through the twelve-membered rings of the main pore channel, the three-dimensional pore system existing inside the molecular sieve maybe unfavorable to the diffusion of formaldehyde molecules into theβ-cages that enter the pore channel, which prevents more formaldehyde molecules from entering into the pore channel.

3.4. Thermal desorption

Thermal desorption of beta, 13X, 3A molecular Sieves, the temperature range of 20 to 500℃, heating rate were 5k/min, 10k/min, 15/min, the results are shown in Table 2 below. The heating rate of the larger the effect of removal, the larger the heating rate, the larger the weightloss ratio, the weightloss ratio of the average sizeof the beta(17.29%) >13X(10.71%) ≈3A(10.38%), this shows that formaldehyde is more susceptible to desorption in beta molecular sieves than 13X and 3A molecular sieves.

Table 2. The weightlessness ration of dichloromethane on molecular sieves

Molecular sieve	Heating rate(k/min)			Mean of Weight lost raito
	5	10	15	
13X	7.52%	10.18%	14.41%	10.71%
beta	12.59%	17.45%	21.84%	17.29%
3A	6.32%	8.84%	15.98%	10.38%

4. CONCLUSION

(1) The static adsorption of formaldehyde by 3A, 13X, and beta molecular sieves was determined by static adsorption method, and the results showed that the adsorption performance of 13X and beta molecular sieves on formaldehyde was larger than that of 3A, indicating that the high specific surface area and large pore size were favorable for the adsorption of formaldehyde gas.

(2) Beta molecular sieve and 13X molecular sieve have similar specific surface area and pore size, and the adsorption amount of formaldehyde of beta molecular sieve is larger than that of 13X molecular sieve, so it is hypothesized that the molecular sieve's skeleton structure has a certain influence on the adsorption.

(3) All three molecular sieves show that the higher the rate of temperature rise, the higher the weightloss ratio of thermal desorption of molecular sieves in desorption. Formaldehyde is more easily desorbed in beta molecular sievethan13Xand3A molecular sieve, and the desorption effect is better.

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