Effect of pre-adsorbed water in zeolites with different pore structures on acetone adsorption performance

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Abstract: Zeolites with uniform pore structures are potential adsorbents for the volatile organic compounds (VOCs) adsorption. The pore structures of zeolites and the pre-adsorbed water contained in the adsorbents all affected VOCs adsorption performance. In this work, we investigated the acetone adsorption performance of four zeolites with different pore structures and studied the effect of pre-adsorbed water vapor on the adsorption performance of acetone. The results showed that the acetone adsorption performance was affected by the specific surface area, pore size and pore volume of zeolite. The pre-adsorbed water had a negative influence on acetone adsorption capacities, which formed competitive adsorption between water vapor and acetone molecular. In addition, we measured and analyzed the difference between the ideal specific surface area and the actual specific surface area, which will provide a reference for actual industrial applications in the future.

1. Introduction

Acetone is a representative of volatile organic compounds (VOCs), which is seriously harmful to human health and the environment [1-2]. Various techniques have been used to remove acetone, and the adsorption technique is a promising method because of its simple operation, low cost and high efficiency. Zeolites are aluminosilicate crystalline materials with unique two- or three-dimensional structural patterns, which are widely used as adsorbents [3-4]. The specific surface area, pore structure and chemical functional groups are three crucial factors for adsorbents, which directly determine their VOCs adsorption performance [5]. It is significant to compare and analyze the influence of zeolites with different pore structures on the adsorption performance. Steam heating regeneration is one of the commonly used desorption methods. However, the adsorbent bed always contains some residual water during the regeneration step, which can compete with VOCs adsorption [6-7]. Consequently, understanding the influence of moisture retained in the adsorbent bed on VOCs adsorption is important to optimize the adsorption process.

In this paper, we chose four zeolites (Y, Beta, ZK-5 and SSZ-13) with different pore structures to adsorption acetone, and investigated the influence of pre-adsorbed water on the acetone adsorption capacity. Then the specific surface area was tested by N₂ and acetone, which was analyzed the theoretical specific surface area and the real specific surface area. The results would be beneficial to the practical application of industry, and better understand the adsorption of VOCs in the real world.
2. Experimental

2.1. Materials and Characteristics
ZK-5 zeolite was synthesized using the method reported by Schwarz S [8]. Various commercially available zeolites (Y zeolite, Beta zeolite and SSZ-13 zeolite) were used as adsorbents. These zeolites were activated in the air at 773 K for 4 hours for further use.

2.2. Characterization
X-ray diffraction (XRD) was measured by the D8-Focus (BRUKER AXS GMBH) with Cu Kα radiation. Nitrogen adsorption and desorption isotherms of samples were measured with the Quantachrome Autosorb iQ system.

2.3. Adsorption experiment
The sorption of acetone and acetone/water sorption isotherms were measured using a dynamic gravimetric vapor sorption analyzer. Before adsorption, samples were degassed in-situ under high vacuum at 150°C for 120 min.

3. Results and discussion

3.1. Characteristics
The XRD patterns of zeolites were shown in Figure 1, which were all in good agreement with the standard spectrum in the database of zeolite structures [9]. This result indicated that the zeolites had the high purity phase and well crystalline structure. The pore structure parameters of these samples tested by N2 adsorption-desorption were shown in Table 1. All samples demonstrated the presence of micro- and textural mesoporosity.

![Figure 1. The XRD patterns of four zeolites](image)

| Sample | BET (m². g⁻¹) | Micropore volume (cm³.g⁻¹) | Mesopore volume (cm³.g⁻¹) | Total pore volume (cm³. g⁻¹) |
|--------|---------------|----------------------------|--------------------------|-------------------------------|
| H-ZK-5 | 590           | 0.286                      | 0.182                    | 0.454                         |
| H-SSZ-13 | 415          | 0.235                      | 0.159                    | 0.367                         |

Table 1. Pore structure parameters of samples.
### 3.2. Acetone adsorption by ZK-5, SSZ-13, Y and Beta zeolite

The acetone adsorption and desorption isotherms of samples were shown in Figure 2. Y zeolite showed the highest acetone adsorption capacity (17%), whereas SSZ-13 showed the lowest (4.5%), and the adsorption mass change of Beta and ZK-5 was almost 15% and 14%. Compared adsorption capacity under different pressures, the mass of Y zeolite increased to 15% at the 10-relative pressure. The mass change of Y zeolite only increased by 2% when the relative pressure increased from 10 to 50, and Beta and SSZ-13 zeolite had the consistent trend with Y zeolite. However, the mass change of ZK-5 was changed from 5-6% to 12%, nearly increased by 6%. It was shown that ZK-5 was more suitable for acetone adsorption under high pressure.

The acetone adsorption properties of zeolites were affected by their diverse structural characteristics. Y zeolite and beta zeolite with pores diameter of 0.74 nm and 0.595 nm are formed by the 12-member oxygen rings. The pores diameter of ZK-5 and SSZ-13 zeolite is 0.404 nm and 0.38 nm, which are formed by 8-member oxygen rings. Acetone with kinetic diameters of 0.46 nm could easily adsorb into Y and beta zeolite, while had difficulty being adsorbed into the ZK-5 and SSZ-13 zeolite. The pore volume of zeolite was also a key diameter for acetone adsorption. The mesoporous volume was beneficial to diffusion and adsorption, while narrow pore necks could lead to lower adsorption rates. Y zeolite with large pore size, large specific surface area and high mesoporous volume had the high acetone adsorption capacity, which could adsorb quickly in the low pressure.

The actual working capacity was of great significance for adsorption, which was evaluated by the changes between the amounts of adsorption and desorption. The mass change of ZK-5 increased to 14% by adsorption whereas residual mass was nearly 11% by desorption, and the actual working capacity was just 3%. The Beta, Y and SSZ-13 actual working capacity was 11%, 16% and 2.3%. More acetone molecular was difficult to desorb in the small pore zeolite and occupied in the zeolite channel, which led to the actual working capacity decreased and influenced the next adsorption.

|    | Y  | 511 | 0.288 | 0.269 | 0.518 |
|----|----|-----|-------|-------|-------|
| Beta | 445 | 0.217 | 0.214 | 0.421 |

3.3. Effect of pre-adsorbed water on the acetone adsorption performance of four zeolites

Figure 3 shows the acetone adsorption isotherms of samples under dry and wet conditions. The results showed that ZK-5 and SSZ-13 zeolite hardly adsorbed acetone in the presence of water. As for Y and
Beta zeolite, the adsorption of acetone decreased sharply after pre-adsorbed water vapor. They possessed large pore size, high specific surface area and pore volume, while pre-adsorbed water vapor took over more space sites, and only little acetone molecular could be adsorbed. Besides, the surface of zeolites has polarity, which is easier to adsorb polar molecules [10]. The polarity of acetone was weaker than water molecular, which was difficult to replace the water molecular.

The specific surface area of samples tested by nitrogen (N2) was regarded as the ideal specific surface area, and that tested by acetone could obtain the real conditions results (Table 2). SSZ-13 zeolite had the lowest real specific surface area and ZK-5 zeolite was the highest, which was consistent with the ideal specific surface area. According to the real specific surface area, we could intuitively see the positive correlation between the acetone adsorption performance of zeolites and the specific surface area. Therefore, it was necessary to test the real specific surface area, which was more instructive for industrial applications.

### Table 2. Comparison of BET results between N2 adsorption-desorption and acetone

| Samples   | N2 BET (m². g⁻¹) | Acetone BET (m². g⁻¹) | Micropore volume (cm³.g⁻¹) |
|-----------|------------------|------------------------|-----------------------------|
| H-ZK-5    | 590              | 493                    | 0.286                       |
| H-SSZ-13  | 415              | 61                     | 0.235                       |
| Y         | 511              | 436                    | 0.288                       |
| Beta      | 445              | 261                    | 0.217                       |

3.4. Dynamic

To explore the adsorption mechanism of samples, the Langmuir model and the Freundlich model were analyzed (Figure 4). The Langmuir model was more suitable for the adsorption process of Y, ZK-5 and Beta zeolite, indicating that acetone adsorption was monolayer adsorption. The isotherm of SSZ-13 zeolite appeared an inflection point when the relative pressure was 10, indicating that monolayer adsorption reached saturation, and multilayer adsorption and capillary condensation occurred, and the Freundlich model better fitted the acetone adsorption of SSZ-13.
4. Conclusion
This study discussed the acetone adsorption performance of four zeolites with different pore structures and investigated the effect of pre-adsorbed water on the adsorption of acetone. The specific surface area, pore volume and pore size of samples all affected the adsorption performance. Y zeolite with large pore size, high specific surface area and large mesoporous volume had the highest acetone adsorption capacity. The ideal specific surface area and the real specific surface area of zeolites were measured by N2 and acetone. They were quite different but had the same arrangement. The actual specific surface area was more suitable for practical application. The presence of water vapor could decrease the acetone adsorption capacity due to the competitive adsorption. Therefore, the hydrophobic zeolite should be considered to increase the acetone adsorption capacity and reduce the water vapor adsorption.

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