

ADSORPTION OF AMMONIA ON OXYGEN - CONTAINING ACTIVATED CARBONS

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Introduction

NH₃ is one of the most common nitrogen compounds, and is used for producing basic chemical products and manure. NH₃ is usually emitted during various industrial processes; rubber processing, animal husbandry and wastewater treatment process. Activated carbon (AC) is a widely used adsorbent for NH₃. The increase in amount of NH₃ adsorption is found on oxidized ACs. There is proportional relation between the amount of NH₃ adsorbed and oxygen surface functional groups, especially acidic oxygen groups on the carbon surfaces [1]. However, it is unknown what specific acidic functional group plays an important role in NH₃ adsorption. Adsorption of NH₃ in wet atmosphere involves competitive adsorption with moisture or water. There are diverse results reported in literature; one of oxidized ACs increased NH₃ adsorption capacity by the presence of water, while the other carbon did not affect the adsorption capacity [2]. The mechanism for water adsorption occurring in oxidized ACs differs when relative water pressure is changed [3]. Therefore, it is important to evaluate NH₃ adsorption on the carbons containing various amounts of water.

In this study, NH₃ adsorption capacity was analyzed in terms of the type of surface oxygen functional groups under various amounts of pre-adsorbed water in the carbons.

Experimental

Materials

The samples of ACs used in this study were derived from phenolic resin. The AC was firstly treated with 6N-HCl to remove metallic impurities and then washed thoroughly with distilled water. The AC was heat-treated at 1273K for 30 minutes in a flowing Ar. The AC thus prepared denoted BEL in this study. The BEL was oxidized further by either HNO₃ or atmospheric air in order to introduce surface oxygen complexes on the carbon surfaces. The BEL oxidized in HNO₃ was denoted as N-BEL and oxidized in air was denoted as A-BEL.

Characterization

The physicochemical characterization was made on the AC samples. The NaOH neutralization known as Boehm titration was used to estimate the amount of acidic functional groups present on the carbon surfaces. The concentrations of gas evolving during TPD runs were measured by gas chromatographs (GC-8A, SHIMADZU). Nitrogen adsorption isotherms were obtained at 77K by gas adsorption apparatus (BELSORP18-PLUS, BEL Japan inc.). The BET surface area

was calculated from BET method. Water vapor adsorption on the sample was also measured by BELSORP18-PLUS at 298K. NH₃ adsorption

Dynamic adsorption experiments were performed at 303K to estimate the amount of NH₃ adsorbed on the dry ACs of BEL, N-BEL and A-BEL. Known amount of the carbon sample was packed in a glass tube (7mm in diameter) and Ar containing 1% of NH₃ was passed through the sample bed at 60 ml/min. The breakthrough curve for NH₃ was obtained by monitoring the amount NH₃ dissolved into NaOH solution with an ammonia electrode (AE-2041, TOA-DKK). The dynamic adsorption runs were also carried out on selected samples of BEL, N-BEL and A-BEL, which had contained various amount of water.

Results and Discussion

Generally, adsorption phenomena are governed by the physical and chemical properties of an adsorbent. However, there was no correlation found between NH₃ adsorption and BET specific surface area, indicating that the chemical property of ACs is important for NH₃ adsorption. Fig.1 shows the correlation between NH₃ adsorption capacity and the concentration of acidic functional groups. The NH₃ adsorption capacity increased proportionally with the concentration of acidic site that exists on AC surfaces, suggesting that the NH₃ adsorption capacity depends on the chemical property of ACs.

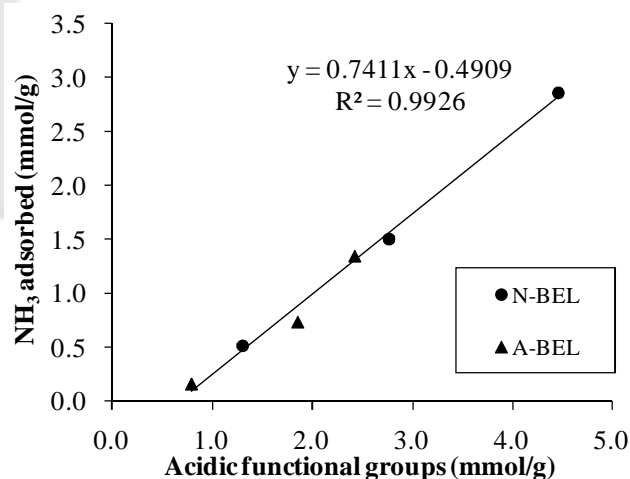


Fig. 1 Relationship between the amounts of NH₃ adsorbed and the site concentration of acidic functional groups on the AC surfaces.

The acidic functional groups consist of several functional groups. In this study, oxygen functional groups are categorized into two types. One is the complex containing one oxygen atom; C(O), and the other is that containing two oxygen atoms; C(O)₂. The concentration of these two oxygen functional groups are estimated from the amount of CO and CO₂ evolved during the TPD [4]. The relation between the amount of NH₃ adsorption and the concentration of oxygen functional groups is shown in Fig.2. The NH₃ adsorption capacity increased with

the concentration of both C(O) and C(O)₂. In terms of R² values, the approximate curve of C(O)₂ shows better linearity than that of C(O). This suggests that C(O)₂ is important for NH₃ adsorption.

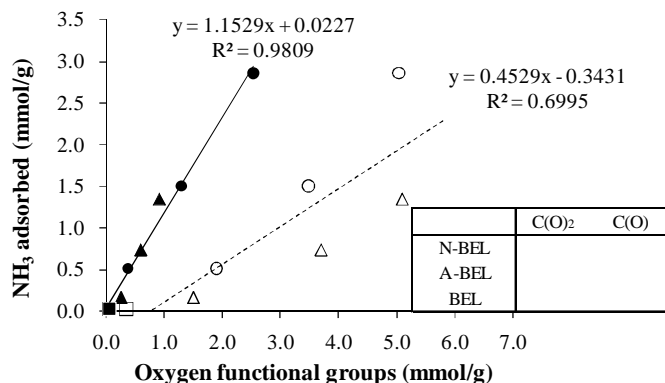


Fig. 2 Relationship between the amount of NH₃ adsorbed and the concentration of oxygen functional groups on the ACs.

In order to prepare the AC samples that contain different amounts of pre-adsorbed water, the water adsorption isotherms were obtained (Fig. 3). At the first stage of water adsorption with p/p_0 less than 0.2, the amount of water increased due to the presence of oxygen functional groups, which attract water molecules through hydrogen bonding [3]. The amount of water adsorption increased rapidly at the second stage adsorption of $p/p_0 > 0.2$ for N-BEL and A-BEL. The rapid adsorption of water above this relative pressure occurs mainly by physical adsorption into micro pores [3]. However, since BEL possesses small amount of functional groups, water adsorption does not occur at the first stage of water adsorption. Fig.4 presents the relationship between the amount of NH₃ adsorbed and the amount of water pre-adsorbed. The values by the curves of

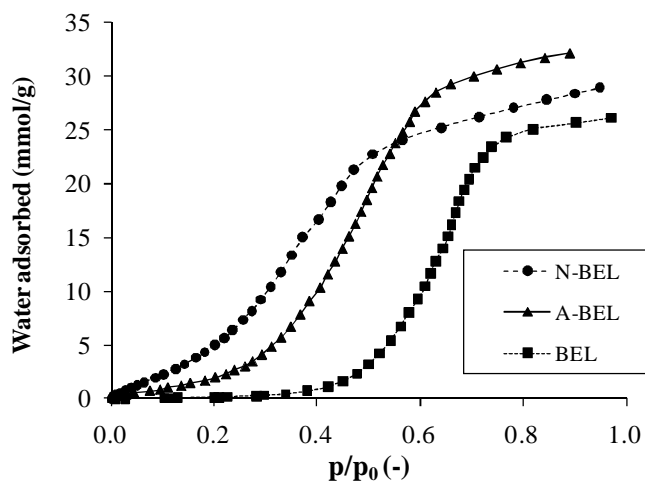


Fig.3 Adsorption isotherms of water vapor on the ACs.

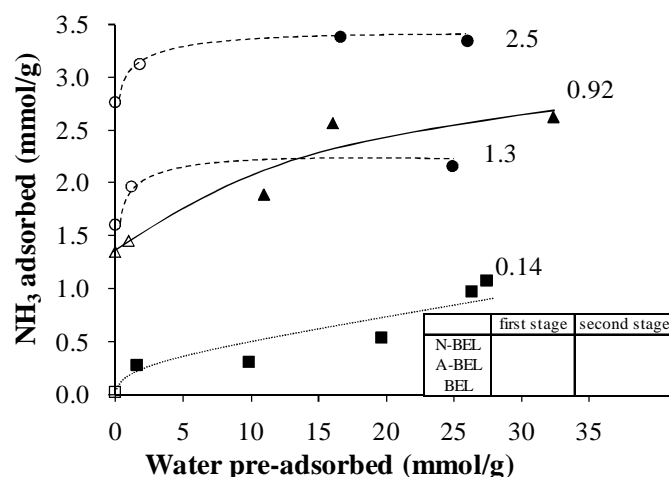


Fig.4 NH₃ adsorption capacity on the ACs containing various amount of water.

Fig.4 are the amounts of C(O)₂ with a unit of mmol/g. The water, associated with oxygen groups at the first stage of water adsorption, leads to NH₃ adsorption for all four samples used in this study. A close examination indicates that BEL and A-BEL carbons, possessing more water in pores at the second stage of water adsorption, continue to adsorb NH₃. However, a different behavior is seen for NH₃ adsorption on N-BEL samples; that is, the amount of NH₃ adsorbed becomes constant at the second stage of water adsorption.

Conclusions

The chemical property on the carbon surfaces, especially acidic functional groups, has a strong influence to NH₃ adsorption. The oxygen complex of C(O)₂ is more effective to NH₃ adsorption than that of C(O). A small addition of water to oxidized carbons increases the amount of NH₃ adsorbed. However, the water that adsorbed further in pore does not necessarily increase the amount of NH₃ adsorption.

References

- [1] Chen CH, Hong SL, Chien HC. Effect of surface acidic oxides of activated carbon on adsorption of ammonia. *Journal of Hazardous Materials* 2008;1595:523–527
- [2] Leuch LML, Bandosz TJ. The role of water and surface acidity on the reactive adsorption of ammonia on modified activated carbons. *Carbon* 2007;45:568–578
- [3] Do DD, Junpirom S, Do HD. A new adsorption-desorption model for water adsorption in activated carbon. *Carbon* 2009;47 1466-1473
- [4] Yoshinobu O, Robert GJ. Characterization of oxygen-containing surface complexes created on a microporous carbon by air and nitric acid treatment. *Carbon* 1993;31 109-121