NOx 흡착용 알칼리성 탄소재료의 경제적인 제조/ 공정 운영 및 타 사용 재료/기술과의 비교

이영환, 김현진, 손승준, 박진원*, 최대기,
한국과학기술연구원 환경공정연구부, 연세대학교 화학공학과*

Comparison Summaries with Other Commercial Materials & Technologies and Low Cost Preparation & Efficient Operation on NOx Adsorption of Alkaline Carbonaceous Materials

Young-Whan Lee, Hyun-Jin Kim*, Seung-Jun Son*, Dae-Ki Choi*, Jin-Won Park
Environment and Process Technology Div., KIST
Dept. of Chemical Engineering, Yonsei University*

Summaries

We judge that alkaline activated carbon holds high research value since it possesses numerous advantages as shown below.

First, simultaneous adsorption of SO_2 and NO_x using alkaline activated carbon in comparison with general activated carbon are distinguished as follows:

1. Problem for the process that simultaneously removes SO_2 and NO_x using general activated carbon is that if NH_3 is added when there is high concentration of SO_2 in the combustion flue gas, it reacts with SO_2 and produces ammonium salt, which leads to consumption of NH_3, and unable to result in effective removal of NO_x. Accordingly, only the addition of NH_3 to waste gas that contains low concentration of SO_2 will result in the most favorable performance and enhance the deNOx while consuming small amount of NH_3. However, controlling the concentration of SO_2 that is brought in as adsorber is not easy in the actual field application. Furthermore, addition of NH_3, which is essential, is becoming a cause that induces secondary pollution.
2. A great progress has been made by many researchers to date on the subject of adsorption of organic compounds, which are formed of weak acidity, weak basicity and neutrality, using general activated carbon. In particular, a significant progress has already been made on commercial technology for treating volatile organic compounds. However, treatment of various gases in the inorganic compound group with strong acidity and strong basicity, including NO_x, SO_2, HCl and offensive odor types (H_2S, NH_3), with general activated carbon fails to exhibit proper adsorption capacity, thus, inadequate for commercial application in terms of removal efficiency. Since separate addition of H_2O, a reducing agent like NH_3, is needed to enhance removal efficiency, the multi-use application is limited. This has been widely known through numerous literatures. Therefore, alkaline activated carbon, which provides selective adsorptivity for toxic gases by enabling chemical activation on the general activated carbon to supplement the weakness of general activated carbon, has attracted major attention in recent years. Our group, also, starting several years ago, began to manufacture alkaline activated carbons, applied to the acidic gas of inorganic compounds and succeeded in achieving high adsorptivity compared to general activated carbon, and continues to make efforts for establishment of optimal conditions. With regard to SO_2 and NO_x studied in the following literatures, the research attempted simultaneous adsorption after ample experience in single component adsorption.
3. Alkaline activated carbon can carry out simultaneous adsorption of various gases depending on acid/base of the adsorbate, as well as characteristics of functional groups that exist on the surface that is modified by the impregnant.
4. General activated carbon is expected to display greater adsorptivity in the moving bed adsorber than in the fixed bed adsorber; however, alkaline activated carbon can use the fixed bed absorber, which requires a relatively simple design and auxiliary facilities.

In addition, utilization of alkaline activated carbon holds the following advantages over the materials/processes currently in commercial use.

1. SCR catalyst, which is the most widely applied catalyst for commercial use today for controlling NO_x, also requires a reducing agent, is expensive, and requires much energy cost for maintaining high temperature. In addition, there still exists the issue of regeneration.
2. Although wet alkali absorption is used often in the case of SO_2 control, this process is also known to accompany the issues of cost and serious secondary pollution.
3. With regard to treatment process such as incinerator, which treats SO_2/NO_x that are emitted in high concentration, if alkaline activated carbon adsorber is put into use in combination with the existing process rather than replacing the existing process altogether, we can expect significant reduction in cost for such as catalyst, secondary pollution treatment and energy loss.
4. Fixed bed adsorber packed with alkaline activated carbon exhibits good adsorption capacity between 373-473K, where no cooling or heating apparatus is needed, for combustion flue gas. Moreover, it is desorbed in temperature below 700K, which is lower compared to other processes, and can be regenerated. In particular, alkaline activated carbon is not deactivated by O_2, which stands out as the biggest problem for today's commercial catalysts, but rather, it brings forth an increase in activity. Furthermore, it does not require addition of reducing agent and costs considerably less. With low energy consumption and no use of expensive catalyst, it is known that operating expenses and secondary waste treatment expenses can be reduced to one-tenth of those for the existing facility.
5. Alkaline activated carbon can save energy cost since adsorption and desorption temperatures are lower than other commercial processes, and active carbon used in the research, as well as KOH, an impregnant, also belong in the group of low cost chemicals. And since we chose the wet impregnation method under 373K for manufacturing alkaline activated carbon, the cost for manufacturing was significantly lower than the existing commercial catalysts. Furthermore, compared to SCR catalyst that is relatively difficult to regenerate, alkaline activated carbon can be put into wide use, such as for air purification filter, gas mask and treatment of combustion flue gas if proper desorption conditions and regeneration method can be established (research is currently in progress and have produced optimistic results.)
6. Additionally, the results on desorption and regeneration is as follows. Temperature of optimum regeneration is 600-700K. This temperature range is lower than commocial catalyst. As a result of EPMA/EDS and ToF-SIMS, it was confirmed that potassium after desorption of KOH-IAC adsorbed NOx remain without loss in surface. The desorption depends significantly on the composition of the impregnant and the nature of the reacting carbon. The major factors that influence the rates of desorption with K-IAC are "The concentration of impregnant on the carbon surface", "The crystallinity and the structure of the carbon" and " The diffusion of reactive gases to selective adsorption sites". Thus, regeneration of alkaline (KOH impregnated) activated carbon.

Results and Discussion

Figure 1 shows the process involving several steps, as expected, from the manufacture of alkaline-AC to adsorption of NO_2, which manifests electrochemical status of the surface of alkaline-AC. The degree and the scope of modification of the surface vary depending on surface properties of GAC, serving as a support, and chemical state of impregnant.

Figure 2 shows results of DSC analysis on KOH (i.e. used as reagent for modifying the surface), GAC and alkaline-AC. KOH showed an endothermic reaction at 114°C, and found an exothermic reaction of a relatively sharp peak at 142°C and a broad peak at 297°C. GAC showed a high peak of an exothermic reaction at temperature hovering over 500°C. In comparison, alkaline-AC displayed high peaks at 349°C and 427°C, where exothermic reactions occurred. The difference in the TGA and DSC trends of the three samples are attributable to functional groups and chemical structures existing on surface, or interaction and physical-and-chemical bonds between the surface-modifying samples and the surface, which occurred in the process of chemical modification of the surface.

Figure 3 shows the TGA curves measured in air ambience against the sample adsorbed and desorbed, respectively. The sample adsorbed by NOx showed a drastic reduction by 80.3 % until the temperature reached 380°C. This is the same temperature when the very strong bond zone reached its maximum peak. On the other hand, against the sample desorbed, 50% of the weight decreased until temperature reached 380°C, and 80% fell subsequently when the temperature rose up to 950°C. This matches with approx. 380°C, i.e. a temperature at which VSB in the desorbed state showed its peak as confirmed in NOx adsorption-desorption. This can be analyzed that the gap between TGA patterns against the sample adsorbed, and the desorption is attributable to a weight decrease as NOx is desorbed from the surface due to decomposition of KNO_2 and KNO_3 upon desorption. The post-desorption sample showed a pattern very similar to TGA curve of alkaline-AC.

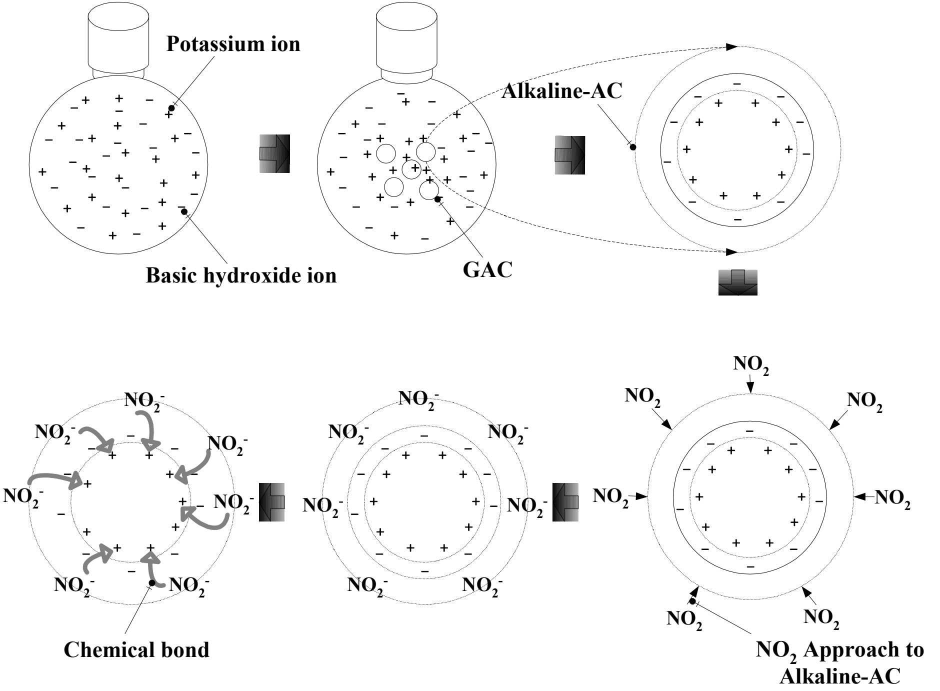
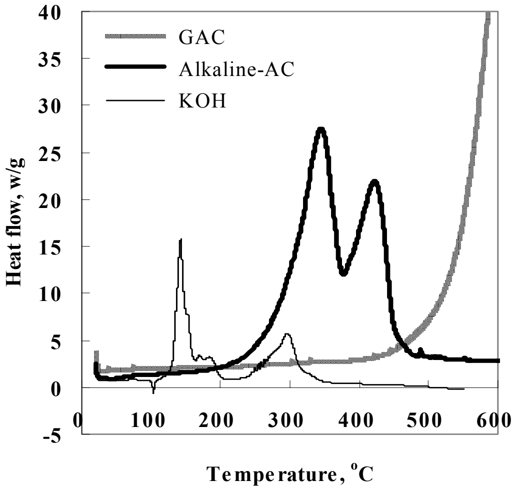


Figure 1. Predicted electrochemical status of surface from the manufacture of alkaline-AC to adsorption of NO_2.



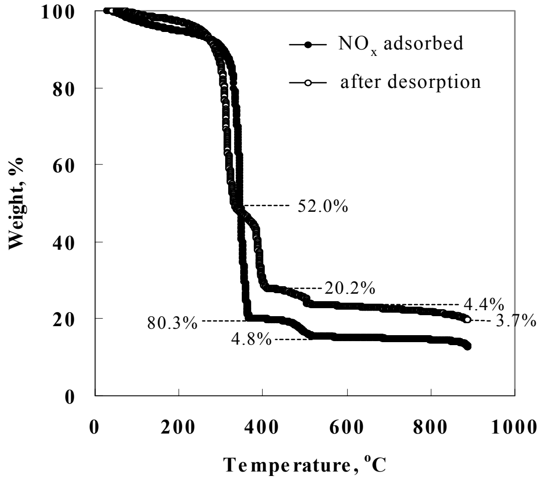


Figure 2. DSC analysis on KOH, GAC and alkaline-AC.

Figure 3. TGA curves after adsorption and desorption on alkaline-AC**Referenece**

Refferences

[1] Lee, Y. W., Choi, D. K., Park, J. W.: *Ind. Eng. Chem. Res*. 40, 3337 (2001).
[2] Lee, Y. W., Choi, D. K., Park, J. W.: *Sep. Sci. Technol*. 37, 1 (2002).
[3] Lee, Y. W., Park, J. W., Choi, D. K.: *Carbon* 40, 1409 (2002)
[4] Lee, Y. W., Choung, J. H., Choi, D. K., Park, J. W.: *Fundamentals of Adsorption*, IK Int. Ltd. 154-161 (2002)
[5] Lee, Y. W., Park, J. W., Choung, J. H., Choi, D. K.: *Environ. Sci. Technol.* 36, 1086 (2002).
[6] Lee, Y. W., Park, J. W., Yun, J. H., Lee, J. H., Choi, D. K.: in press, *Environ. Sci. Technol.*
[7] Lee, Y. W., Park, J. W., Kim, H. J., Park, J. W., Choi, B. W, Choi, D. K.: submitted to *Carbon*.
[8] Lee, Y. W., Kim, H. J., Choi, D. K., Yie, J. E., Park, J. W.: submitted to *Environ. Sci. Technol.*
[9] Kim, H. J., Lee, Y. W., Choi, D. K., Na, B. K., Lee, E. I., Park, J. W.: accepted in *J. Korean Society of Environmental Engineers.*

[10] Thomas, W. J.; Crittenden, B. *Adsorption Technology and Design*, Butterworth Heinmann: Oxford, 1998.

[11] Ościk, J., Cooper, I. L. *Adsorption*, John Wiley & Sons: New York, 1982.
[12] Yang, J., Mestl, G., Herein, D., Shlögl, R., Find, J. *Carbon* 38, 729 (2000).
[13] Illán-Goméz, M. J., Linares-Solano, A., Radovic, L. R., Salinas-Martínez de Lecea, C. *Energy Fuels* 9, 104 (1995).
[14] Huang, H. Y., Yang, R. T. *J. Catal.* 1999, 185, 286 (1999).
[15] Mehandjiev, D., Bekyarova, E., Khristova, M. *J. Colloid Interface Sci.* 192, 440 (1997).
[16] Márquez-Alvarez, C., Rodríguez-Ramos, I., Guerrero-Ruiz, A. *Carbon* 34, 1509 (1996)
[17] Carabineiro, S.A., Fernandes, F. B., Vital, J. S., Ramos, A. M., Silva, I. F., *Catal. Today*. 54, 559 (1999).
[18] Bereznitski, Y., Gangoda, M., Jaroniec, M., Gilpin, R. K. *Langmuir 14,* 2485 (1998).
[19] de la Puente, G.., Gil, A., Pis, J. J., Grange, P. *Langmuir 15,* 5800 (1999).
[20] Dandekar, A., Baker, R. T. K., Vannice, M. A. *J. Catal* 183, 131 (1999).

[21] Greenwood, N. N., Earnshaw, A. *Chemistry of the Elements* Butterworth Heinmann: Oxford, 1984.
[22] Chan, L.K, Sarofim, A. F. Beér, J. M. *Combust Flame* 52, 37 (1983).
[23] Mochida, I., Kuroda, K., Miyamoto, S., Sotowa, C., Korai, Y., Kawano, S., Sakanishi, K., Yasutake, A., Yoshikawa, M. *Energy Fuels* 11, 272 (1997).