

Amoxidized Active Carbons as Adsorbents for Pollution from Liquid and Gas Phases

Robert Pietrzak*, Piotr Nowicki, Helena Wachowska

Laboratory of Coal Chemistry and Technology, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

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Abstract

The influence of modification by pre- and post-treatment of active carbons with ammonia on adsorption abilities from liquid and gas phases has been tested. Carbon materials with different surface chemistry were obtained by chemical activation of Polish brown and subbituminous coal. The products were microporous active carbon samples of well developed surface area (S_{BET} from 1579 to 2,922 m²/g), containing from 0.3 to 7.4 wt% of nitrogen. The results obtained in our study have, moreover, proven that a suitable choice of the modification procedure for coals can produce activated carbons with high capacity of iodine adsorption (to 2,100 mg/g) and high nitrogen dioxide adsorption ability, reaching to 55.1 mg NO₂/g.

Keywords: active carbons, amoxidation, chemical activation, NO₂ adsorption

Introduction

The increased emission of toxic gases being a consequence of rapid and uncontrolled development of industry and progress in civilization has recently become a serious threat to the natural environment. Particularly dangerous gases emitted by electric power plants, industrial production plants and motor vehicles are nitrogen oxides, contributing to the appearance of acid rains and to destruction of the ozone layer. The problem is tackled in two different ways. The first approach is to improve the technological processes by e.g. proper choice and preliminary purification of the raw products, and tight sealing of the process chambers. The second approach is to purify the waste gases.

In this approach of post-production gas purification, of great importance are active carbons that can be used as adsorbents, catalysts, catalyst supports or ion-exchangers [1, 2]. This wide spectrum of use of the active carbons is related to their unique physical and chemical properties

determined by their well-developed porous structure and the presence of heteroatoms built into their structure. Recently, much attention has been paid to active carbons enriched in nitrogen as – because of the basic character of their surface – they show enhanced sorption ability toward the compounds of acidic character, e.g. SO₂, H₂S or CO₂ [3, 4]. Active carbons have also been successfully used for low temperature selective catalytic reduction of NO [5] and for removal of inorganic and organic contaminants from the liquid phase [6, 7].

The problem of restriction of NO_x emission with the help of nitrogen-enriched active carbons is studied at many research centres in the world, but the majority of the hitherto published results concern adsorption or catalytic reduction of nitrogen oxide with ammonia [5, 8, 9]. Much fewer papers have been devoted to the problems of removal of NO₂ [10].

The main aim of our study was to test the suitability of active carbons enriched in nitrogen by amoxidation (simultaneous oxidation and nitrogenation of fossil coals) for removal of nitrogen dioxide and contaminants of the liquid phase.

*e-mail: pietrob@amu.edu.pl

Table 1. Physicochemical characteristics of active carbons obtained.

Sample	N content [wt.%]	S _{BET} [m ² /g]	V _T [cm ³ /g]	Acidic groups [mmol/g]	Basic groups [mmol/g]	pH	Iodine number [mg/g]
KA	0.5	2,156	1.05	1.36	0.70	5.20	1,970
KNA	3.8	2,922	1.72	1.98	0.77	5.36	2,010
KAN	6.5	1,877	0.91	0.97	1.22	8.35	1,790
KJA	0.3	1,973	0.97	1.71	0.42	4.18	1,900
KJNA	1.7	2,819	1.60	1.62	0.52	4.66	2,100
KJAN	7.4	1,579	0.77	1.02	0.89	7.60	1,680

Experimental Procedures

The starting raw samples were prepared from a Polish brown coal (K – the Konin mine) and subbituminous coal (KJ – the Kazimierz-Juliusz mine). All measurements were carried out on samples demineralized according to the Radmacher and Mohrhauer method. The nitrogen-enriched active carbon samples were prepared by two procedures differing in the order of the technological processes:

- ammonoxidation of the precursor at 350°C followed by carbonization and activation by KOH (KNA and KJNA),
- ammonoxidation after activation (KAN and KJAN). The non-ammonoxidized samples (KA and KJA) served as references.

The sample preparation, detail procedure of their carbonization, activation, ammonoxidation and characterisation of the initial samples and products is given in our earlier work [11].

Nitrogen content was determined by the Kjeldahl method (according to Data National Standards ISO 333:1996). Characterization of the pore structure of activated carbons was performed on the ground of low-temperature nitrogen adsorption-desorption isotherms measured on a sorptometer ASAP 2010 (Micrometrics Instrument Corp. USA), following BET and BJH techniques.

The pH of active carbons was measured using the following procedure: a portion of 0.2 g the sample of dry char powder was added to 10 ml of distilled water and the suspension was stirred overnight to reach equilibrium. Then pH of the suspension was measured.

The iodine sorption ability of the active carbon samples was determined according to the ASTM Standard D4607-94 (2006).

The evaluation of NO₂ sorption capacity was carried out according to the procedures described in [12] with some modifications. The samples were packed into a glass column (length 300 mm, internal diameter 9 mm, bed volume between 1-1.5 cm³). Dry or moist (75% humidity) air with 0.1% of NO₂ was passed through the column with the adsorbent at 450 ml/min for NO₂. The breakthrough of NO₂ was monitored using Q-RAE PLUS PGM-2000/2020 with an electrochemical sensor.

Results and Discussion

Physicochemical Properties of Active Carbons Obtained

As follows from the data collected in Table 1, the ammonoxidation and chemical activation of brown and subbituminous coal give active carbons significantly enriched in nitrogen. The content of nitrogen in the final product highly depends on the sequence of the processes of carbonization, activation and ammonoxidation to which the precursor is subjected. The samples ammonoxidized after activation (KAN and KJAN) have much higher content of nitrogen than those ammonoxidized prior to activation (KNA and KJNA). Much lower content of nitrogen in the samples ammonoxidized prior to activation is a result of low thermal stability of the nitrogen groups built in the carbon structure upon ammonoxidation and their resistance to potassium hydroxide. The content of nitrogen introduced into the active carbon depends also on the degree of the precursor metamorphism, although the influence of this parameter is less pronounced.

The data presented in Table 1 also imply that the sequence of the processes of ammonoxidation, carbonization and activation influences the development of porous structure. The active carbons ammonoxidized prior to activation (KNA and KJNA) have much better developed surface area and greater pore volume than non-ammonoxidized samples. Ammonoxidation of the active carbons KA and KJA leads to significant worsening of the textural parameters. The differences follow from the fact that the coals ammonoxidized at the stage of precursor in the process of activation show much higher reactivity toward the activating agent than the unmodified samples, which leads to more effective development of the porous structure. The deterioration of the textural parameters of the samples ammonoxidized after activation can result from blocking of some pores by oxygen and nitrogen functional groups formed upon ammonoxidation or from partial oxidation of the active carbon surface area, leading to destruction of walls between some pores.

Analysis of Table 1 data also proves that the introduction of nitrogen into the structure of active carbon samples changes significantly the acid-base properties of their surface.

The samples ammoxidized prior to activation (KNA and KJNA), similar the non-ammoxidized ones (KA and KJA), show high content of surface oxygen functional groups of acidic character and pH value between 4.2 and 5.4. Performance of ammoxidation after activation leads to a significant increase in the content of oxygen groups of basic character accompanied by a significant decrease in the content of acidic groups and an increase in the pH value to about 8.

Sorption Properties of Active Carbons Obtained

As follows from the results collected in Table 1, the ammoxidized active carbons can be successfully used for removal of substances of the particle size close to that of iodine molecules so of a diameter close to 1nm, from the liquid phase. The best adsorption abilities from the liquid

phase (iodine number above 2,000 mg/g) have active carbons ammoxidized at the precursor stage (KNA and KJNA) showing highly developed porous structure. Poorer adsorption properties show the non-ammoxidized samples KA and KJA, while the least effective sorbents are the samples ammoxidized after activation by KAN and KJAN, showing also the poorest textural parameters. The above observations imply a correlation between the number of iodine adsorption and the structural parameters of the active carbons. All active carbon samples obtained have much better sorption capacity than the commercial products whose iodine number varies from 600 to 1,200 mg/g.

According to the data shown in Fig. 1A, the active carbons obtained are characterized by diverse sorption capacities of NO₂. However, they are always better than those of the commercially available carbons such as Norit® RKD-3 or Norit® SX-2, whose sorption capacity of NO₂

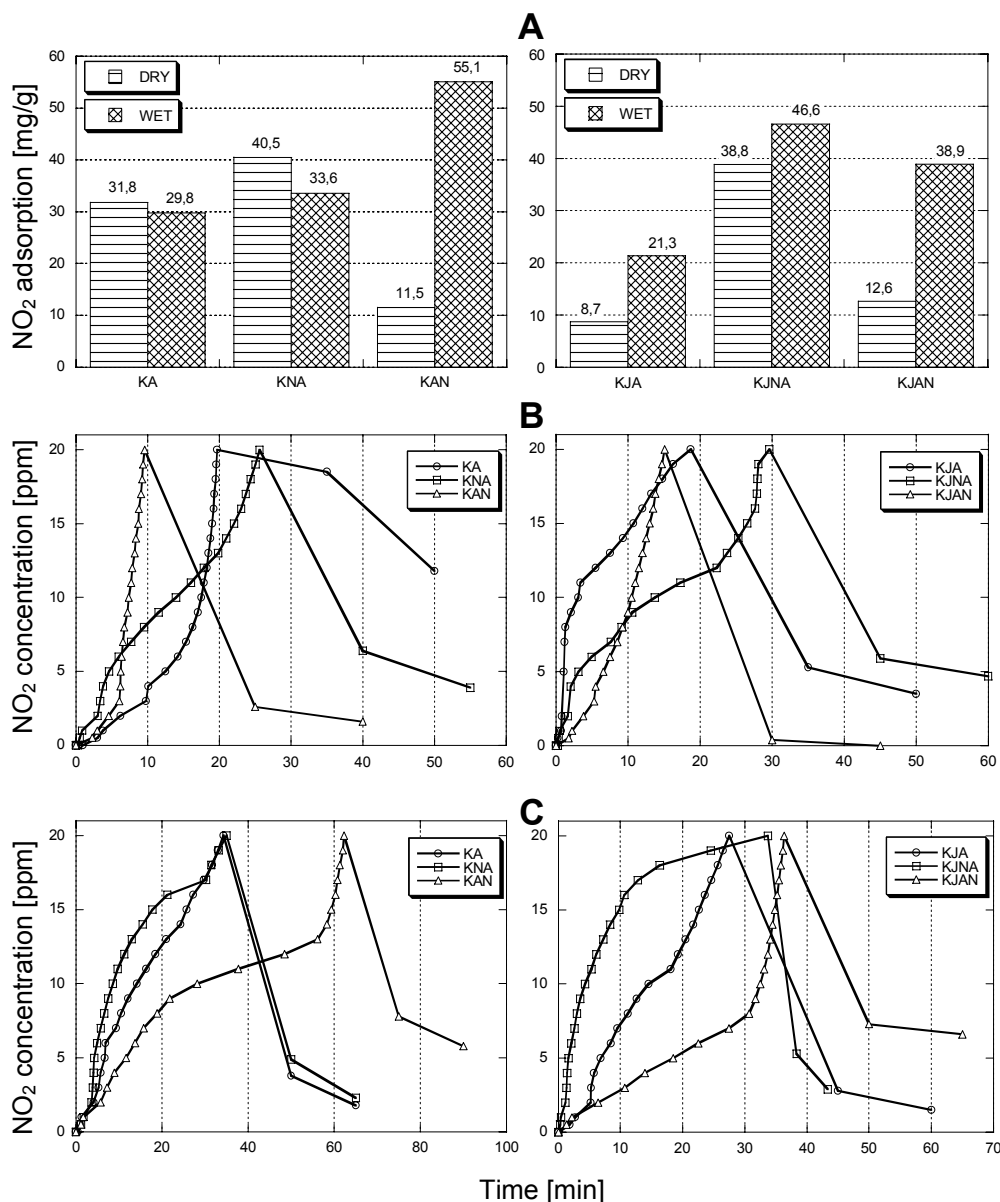


Fig. 1. NO₂ breakthrough capacities (A), NO₂ breakthrough curves in dry conditions (B) and in wet conditions (C) of samples obtained.

on dry conditions is: 24 and 11.5 mg/g, and in wet conditions: 27 and 2.8 mg/g, respectively. The highest NO₂ sorption capacity of 55.1 mg/g was obtained for sample KAN in wet conditions, while the lowest of 8.7 mg/g for sample KJA in dry conditions. The majority of active carbon samples studied in our experiments showed much better sorption abilities in wet conditions. The difference was particularly pronounced for samples KJAN and KAN ammoxidized after activation, their sorption capacity in wet conditions was 3 and 5 times, respectively, greater than that in dry conditions. Only for samples KA and KNA was the adsorption capacity of NO₂ a bit higher in dry conditions.

Analysis of the data presented in Table 1 and in Fig. 1A reveals that the sorption abilities of the nitrogen-enriched active carbon depend significantly on the acid-base character of their surface. Samples KAN and KJAN, having comparable contents of functional groups of acidic and basic character, show very good sorption capacity of NO₂ in wet conditions, while in dry conditions their sorption properties are similar (KJAN) or much worse (KAN) than the non-ammoxidized samples (KJA and KA). The samples ammoxidized prior to activation have much greater content of acidic oxygen groups on the surface and show high adsorption capacities in wet and in dry conditions (in particular the KJNA sample), much greater than those of the non-ammoxidized samples.

Different behaviour of these two groups of carbon samples suggests that adsorption of nitrogen dioxide on them takes place according to different mechanisms. This thesis is supported by the character of the NO₂ breakthrough curves presented in Figs. 1B and 1C. The shape of these curves for samples KNA and KJNA (in particular in wet conditions – Fig. 1C) is much different from those observed for the other samples. Exact determination of the mechanisms of NO₂ adsorption on the nitrogen-enriched active carbons requires further study.

Conclusions

The above presented and discussed results have shown that the ammoxidized active carbons can be successfully used as adsorbents for removal of contaminants from the liquid and gas phases. The sorption properties of the active carbons can be regulated by the proper choice of the precursor as well as parameters of ammoxidation, carbonisation and activation processes to meet specific needs.

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