ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 7, pp. 1200−1204. © Pleiades Publishing, Ltd., 2009.
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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Effect of Some Ammonium Salts on Thermal Decomposition of Impregnated Wood and Properties of Activated Carbons

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Received January 28, 2008

Abstract—Methods of chemical, thermal, IR spectral, and X-ray phase analysis were used to study the effect of ammonium additives NH_4Cl + NH_4NO_3 introduced into a phosphorus-nitrogen formulation on the thermal decomposition of impregnated wood in the temperature range 20–700°C and on adsorption characteristics of the resulting activated carbon.

DOI: 10.1134/S1070427209070088

Activated carbons are widely used in solution of various ecological, technological, and chemical problems, power engineering, and manufacture of various materials. Wide industrial application of activated carbons requires not only their high sorption parameters, porous structure with pore size comparable with the diameter of sorbate molecules, and acceptable kinetic parameters of sorption, but also their low cost.

As a rule, activated carbons are produced from wood in two stages: pyrolysis of wood to give a raw carbon at 500°C and its further activation at 850–950°C with steam or another oxidizing agent [1, 2]. Recently, activated carbons have been increasingly frequently produced by a single-stage process including thermal treatment of raw materials impregnated with zinc chloride, Lewis acids, and potassium sulfate, followed by washing of carbonized wood [3, 4]. The carbons produced by the methods described above are rather expensive, which strongly hinders their use.

It has been shown previously that a low-cost activated carbon can be produced by single-stage pyrolysis of impregnated sawdust. Readily soluble phosphorus-nitrogen formulations with addition of nitrate compounds (NH_4NO_3, $CsNO_3$, $LiNO_3$) have been used as impregnating agents [5].

The aim of this study was to examine the process in which activated carbon is formed in thermal decomposition of wood impregnated with a phosphorus-nitrogen decomposition catalyst to which ammonium salts NH_4Cl + NH_4NO_3 are added in various ratios and to analyze the adsorption properties of the resulting carbons.

EXPERIMENTAL

We studied the thermal decomposition of waste produced by wood-processing industries: sawdust with a particle size of 1–3 mm, impregnated with a phosphorus-nitrogen formulation $CO(NH_2)_2$–H_3PO_4 (formulation B) [5] with addition of ammonium salts (5 wt %) NH_4Cl + NH_4NO_3 at additive ratios of 1 : 2, 1 : 1, or 2 : 1, and examined the adsorption properties of the resulting activated carbons. The weight increment the impregnating formulation was 170% relative to dry sawdust. The thermal studies of impregnated samples were performed with an MOM instrument (Hungary) at a heating rate of 20 deg min^{-1} and a sample mass of 200 mg. The initial and thermally treated samples were analyzed for the content of phosphorus and nitrogen. Phosphorus was determined photocolorimetricaly by formation of a Phosphorus-molybdenum Blue [6], and nitrogen, by the procedure described in [7] in a Kjeldahl apparatus upon wet burning of the samples in concentrated sulfuric acid. X-ray diffraction patterns of the samples were obtained using a Dron-3 instrument with $Cu_{K\alpha}$ radiation (Ni filter) at angles $2\theta = 2–60°$. IR spectra of the samples with a KBr immersion medium were measured on a Perkin–Elmer instrument in the frequency range 400–3900 cm^{-1}. To obtain activated carbons upon a thermal treatment of

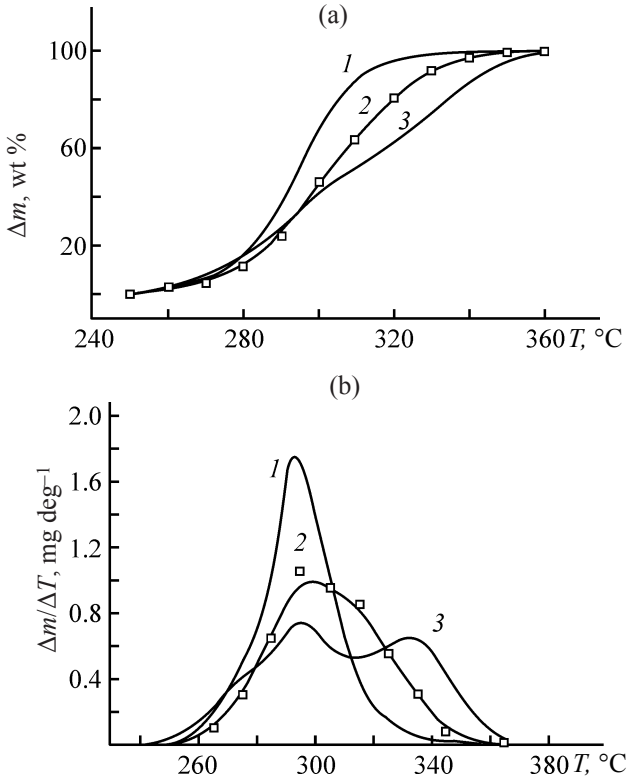

Fig. 1. (a) TG and (b) DTG curves of (*1*) 1 : 2, (*2*) 1 : 1, and (*3*) 2 : 1 $NH_4Cl + NH_4NO_3$ mixtures. (Δm) Mass loss, ($\Delta m/\Delta T$) rate of change in mass, and (T) temperature; the same for Fig. 2.

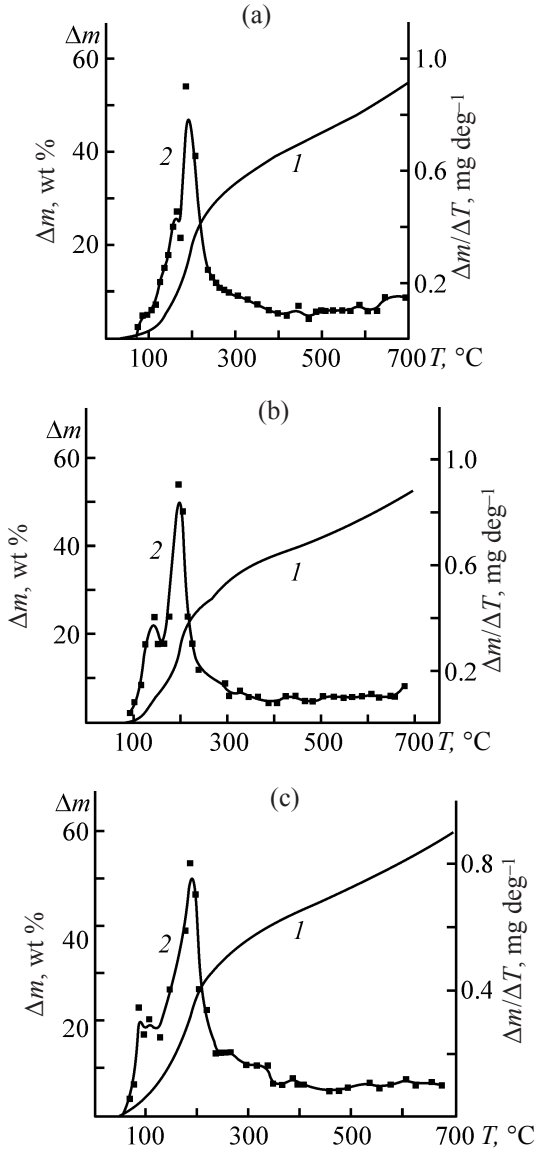

Fig. 2. Curves for impregnated sawdust. Addition of a $NH_4Cl + NH_4NO_3$ mixture: (a) 2 : 1, (b) 1 : 1, and (c) 1 : 2.

impregnated sawdust in the temperature range 20–550°C, the carbon residue was thoroughly washed to remove water-soluble pyrolyzed products by submerging the samples in boiling water, with the subsequent by squeezing. The washing was continued to neutral pH of washing water, and the samples were dried at 20°C for 24 h and then at 45°C in a drying box for 2 h. The activity of the carbons toward iodine was determined in accordance with GOST (State Standard) 17218–74, and the bulk density, in accordance with GOST 14922–77. The static ion-exchange capacity was analyzed using the procedure described in [8]. The sorption of benzene was determined by the desiccator method using the procedure described in GOST 17218–71.

A DTA study of the thermal stability in air of a mixture of salts $NH_4Cl + NH_4NO_3$, used as additives to the phosphorus-nitrogen formulation B, demonstrated that their thermal decomposition begins above 250°C (Fig. 1). The highest decomposition intensity is observed at 295°C for all the ratios of the ammonium salts. As the fraction of NH_4NO_3 is raised from 1.3 to 3.7 wt %, the thermal decomposition intensity is 0.8–1.0, and 1.8 mg deg^{-1}, respectively, with their complete decomposition occurring at 350°C.

For wood impregnated with a phosphorus-nitrogen catalyst with addition of these salts, the mass loss on heating in the range 20–200°C depends on the ratio between the ammonium salts (Fig. 2). Upon an increase in the fraction of NH_4NO_3 in the mixture of the additives to 3.3 wt %, the loss of mass by wood in the temperature range 20–200°C grows to 26 wt %, being 17–20 wt % at a NH_4NO_3 content of 1.7–2.5 wt %. According to chemical analysis data, the content of phosphorus in products of thermal decomposition at 20–250°C is almost the same as that in a sample before its heating, and the amount of

Table 1. Results of a chemical analysis of unwashed carbons produced by heating of impregnated wood

NH_4Cl : NH_4NO_3 ratio	T, °C	Mass loss Δm, %	Found, wt %	
			nitrogen	phosphorus
1:1	20	0	3.6	11.4
	180	13.5	4.2	13.2
	250	28.2	4.4	15.9
	450	44.5	5.7	20.6
	550	57.6	4.2	27.0
2:1	20	0	3.6	11.3
	180	10.3	4.0	12.6
	250	35.2	5.0	17.4
	450	45.2	5.6	20.7
	550	56.5	4.4	25.7
1:2	20	0	3.6	11.2
	180	14.9	3.3	13.1
	250	29.2	4.0	15.7
	450	44.4	4.7	19.9
	550	57.5	4.2	26.1

nitrogen decreases from 88.9 to 77.%, depending on the ratio of the ammonium salts in the additive (Tables 1, 2). According to DTG data, two processes are observed in this temperature range (20–200°C). The first process occurs at 70–175°C with a maximum intensity of 0.5–0.3 mg deg^{-1} and, depending on the ratio between the additive components, shifts to higher temperatures. For example, upon introduction of an additive containing 3.3 wt % NH_4NO_3 into the phosphorus-nitrogen formulation, the highest intensity of the first process in decomposition of impregnated wood is observed at 85°C. Upon a decrease in the fraction of NH_4NO_3 to 2.5 or 1.7 wt%, the maximum process rate is observed at 145 and 165°C, respectively. For the second process occurring in the temperature range 175–200°C, the additives do not strongly affect the maximum decomposition intensity of 0.8–0.9 mg deg^{-1} (at 185–195°C).

The thermal decomposition of wood at these and higher temperatures yields condensed phosphates, which is confirmed by X-ray diffraction and IR spectral data. The IR spectra of samples obtained at 250–550°C show absorption bands (cm^{-1}): 980 γ_{as} (POP), 680 γ_s (POP), 640 δ (PO_2), and 625 γ_{as} (PO_3), which are characteristic of vibrations of phosphate groups in chain polyphosphates. According to the results of the X-ray phase analysis, the phosphorus compounds introduced are reconstructed in the course of heating to give crystalline compounds (NH_4PO_3) in wood. Similar crystalline phases have been found in a phosphorus-nitrogen system with other nitrate additives [5]. Crystalline ammonium polyphosphates were found in a sample thermally treated at 550°C; at lower heating temperatures, no diffraction peaks of crystalline phases were observed in X-ray diffraction patterns. Above 250°C, ammonium additives have no significant effect on the rate (0.2–0.1 mg deg^{-1}) of thermal decomposition of impregnated wood, and the yield of the product at 700°C varies within the range 41–47 wt %, depending on the ratio between the salts taken as additives.

Table 2. Retention of phosphorus and nitrogen in samples of thermally treated impregnated wood

NH_4Cl : NH_4NO_3 ratio	T, °C	Unwashed		Washed	
		nitrogen, %	phosphorus, %	nitrogen, %	phosphorus, %
1:1	180	100.0	100	36.1	7.0
	250	88.9	100	50.0	15.8
	450	88.9	100	55.6	9.6
	550	50.0	100	50.0	13.2
1:2	180	100	100	22.2	4.2
	250	77.8	99.1	52.8	15.2
	450	77.8	99.1	38.8	11.6
	550	50.0	99.1	30.6	7.4
2:1	180	100.0	100	44.4	10.6
	250	88.9	100	55.6	17.7
	450	86.1	100	52.8	10.6
	550	52.8	99.9	41.7	13.3

Table 3. Adsorption characteristics of activated carbons

Impregnating agent[a]	Iodine number, %	Bulk density, g dm^{-3}	Sorption of benzene, %	Sorption of Methylene Blue, mg g^{-1}	Static ion-exchange capacity, mg-equiv g^{-1}
B + *a*	33.0	303	30	45	0.8
B + *b*	45.0	232	36	14	0.7
B + *c*	54.0	190	49	17	0.9

[a] Ratio between additive components, see Fig. 2.

Production of activated carbons by the method under consideration requires a thorough washing of pyrolysis products to remove water-soluble salts and thermal decomposition products. However, the high solubility of the impregnating agent introduced in wood results in that, in contrast to the industrial technique employing zinc chloride, the washing process is considerably simpler and consumes a 2–2.55 times smaller amount of water. Table 2 lists data on the retention of nitrogen and phosphorus in samples before and after washing of a thermally treated impregnated wood, obtained at different temperatures. To evaluate the influence exerted by various impregnating agents on the process of wood carbonization, we present conditional criteria of nitrogen and phosphorus retention (for unwashed samples, ratio of the actual content of an element, with its mass loss taken into account, to its initial value before heating; for washed samples, the ratio of the amount of phosphorus found, with the mass loss upon heating and washing taken into account, to its content in the samples before heating). As follows from these results, the lowest retention of phosphorus (7.4%) and nitrogen (30.6%) is observed in a washed samples with an impregnating agent with NH_4Cl : NH_4NO_3 = 1 : 2 additive, heated in the temperature range 20–550°C. At other ratios between ammonium chloride and nitrate, the retention of phosphorus in the polymer increases to 13.3–13.2%, and that of nitrogen, to 41.7 or 50.0% (NH_4Cl : NH_4NO_3 = 2 : 1 or 1 : 1, respectively). It should be noted that, at almost equal contents of phosphorus and nitrogen in unwashed carbons (thermal treatment temperature 550°C) obtained at various ratios between the additives introduced, the contents of phosphorus and nitrogen in washed pyrolyzed residues become substantially lower upon an increase in the fraction of NH_4NO_3 (up to 2 mass parts in a mixture): by factors of 1.8 and 1.4–1.6, respectively.

The adsorption characteristics of carbons produced by pyrolysis (at 550°C) of wood with various impregnating agents and subsequent washing are listed in Table 3. It follows from the data obtained that sorption capacity for benzene and iodine grows, respectively, from 30 to 49% and from 33.0 to 54.0% upon an increase in the fraction of ammonium nitrate in the impregnating agent from 1.7 to 3.3 wt %. The highest sorption activity toward benzene (49%) and iodine (54.0%) was observed for a sample impregnated with a phosphorus-nitrogen formulation with a NH_4Cl : NH_4NO_3 = 1 : 2 additive. The activated carbons produced by the single-stage method under consideration are, as regards their adsorption characteristics, microporous sorbents with a cation-exchange capacity of 0.7–0.9 mg-equiv g–1 for Na^+. The sorption of Methylene Blue (volume of supermicropores and mesopores) grows by a factor of 3.2–2.6 upon an increase in the fraction of NH_4Cl in the mixture of additives to 2 mass parts.

CONCLUSIONS

(1) In thermal decomposition of wood impregnated with a phosphorus–nitrogen formulation with addition of a mixture of ammonium salts NH_4Cl + NH_4NO_3 in the temperature range 20–550°C, the additives introduced strongly affect the thermal decomposition of the impregnated wood at 20–200°C. Two processes are observed, with the maximum intensities of the first and second processes equal to 0.3–0.4 (85–165°C) and 1.8–1.9 mg deg^{-1} (185–195°C), respectively. As the fraction of ammonium nitrate introduced into the phosphorus-nitrogen formulation increases, the maximum intensity of the first process of thermal decomposition of impregnated wood shifts to lower temperatures.

(2) In the temperature range 250–700°C, the additives introduced do not affect significantly the thermal decomposition rate of impregnated wood and the yield of the solid product (41–47%).

(3) Addition of ammonium salts NH_4Cl + NH_4NO_3 affects the adsorption properties of the activated carbons obtained. An increase in the fraction of ammonium nitrate results in that the sorption capacities for benzene and iodine grow from 30 to 49% and from 33 to 54%,

respectively. The activated carbons can be classed with microporous sorbents, they can be recommended for use to absorb vapors of benzene, carbon tetrachloride, hydrogen sulfide, and oil products. An increase in the fraction of NH_4Cl in the mixture of additives leads to a higher sorption of Methylene Blue by the carbon.

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