

MODIFICATION OF CARBONACEOUS ADSORBENTS WITH MANGANESE COMPOUNDS

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Abstract. Four series of samples containing manganese supported carbonaceous adsorbents were prepared. Samples of series AC-B, synthesised from the carbonaceous support with basic surface, were obtained with a yield of 50-60%, while manganese was loaded in amount of 1.44-1.65 % depending on applied method. The samples of series AC-A, synthesised from the carbonaceous support with acidic surface, were obtained with a higher yield (92-98%), but with small quantities of loaded manganese. Obtained results reveal the importance of surface chemistry of carbonaceous adsorbents on the manganese loading.

Keywords: active carbon, modification, manganese, surface chemistry, thermal treatment.

Received: October 2015/ Revised final: October 2015/ Accepted: November 2015

Introduction

It is well known that modification of carbonaceous adsorbents with metal oxides improves their physico-chemical characteristics, influencing the catalytic activity in redox reactions. A number of catalysts consisted of various transition metal oxides (Co, Ni, Mn, Fe, Cu etc.) on active carbons have been studied for removal/oxidation of hydrogen sulphide, ammonium ions, dyes etc. [1-5]. Among these catalysts, manganese oxides supported on active carbons have attracted much interest due to their high catalytic activities.

Various active manganese state and dispersion of particles can be obtained using different precursors and preparation methods [2,6,7]. Different quantities of loaded manganese on active carbon have been obtained depending on initial concentration of the precursor solution [7]. Thermal treatment (autoclave or furnace, under oxic or anoxic conditions) also are important parameters exploited by researchers [2,6]. However, any reports about the dependence between the surface chemistry of carbonaceous adsorbents and amount of loaded manganese are not presented in the literature.

The aim of this work was to highlight the influence of surface chemistry of carbonaceous adsorbents on the manganese oxides loading.

Experimental

Materials

In this study a commercially available activated carbon with basic surface (Norit®), designated as AC-B, and a sample of active carbon with acidic surface obtained by chemical activation method [8], designated as AC-A, have been used. All the chemical reagents used in this study were of analytical grade.

Samples

Four series of samples containing manganese were prepared, supported on carbonaceous adsorbents (particle size 0.8-1.3 mm). The carbonaceous adsorbents were impregnated with an aqueous solution of manganese salt (at a solid/liquid ratio equal to 10) for ca. 24 h, followed by treatment with an alkaline solution to generate manganese hydroxide within carbon pores. Dried samples (110°C) were subjected to thermal treatment at different temperatures (300, 450, 600°C) to obtain manganese oxides. Obtained samples were washed several times with distilled water to remove soluble species and dried at 110°C.

Characterization methods

Prior characterization measurements the active carbon samples were dried at 110°C for 3 h.

Elemental analysis (C, H, N, Cl, S) was carried out by the Elemental Analysis group of the Institute of Chemistry of Academy of Sciences of Moldova.

The **content of metals** was determined by atomic absorption spectroscopy (AAS-IN, Laboratory of Atomic Spectroscopy of the Institute of Chemistry of A.S.M.).

The **ash content** of the samples was determined by burning off the carbon at 700°C for 2 h.

The **pH of the samples** has been evaluated by determination of pH value of active carbon suspension (10 g of dried sample/100 mL of distilled water) equilibrated for 24 h [9].

Thermal analysis measurements were performed using a Derivatograph Q-1000 analyzer. The samples were heated from room temperature up to 1000 °C in a flowing air atmosphere (100 mL/min) at a heating rate of 10 °C/min.

Results and discussion

Active carbons used for impregnation with manganese ions are very different concerning surface chemistry and ash content. Sample AC-B has higher content of ash due to compounds of calcium, magnesium and iron, and has a basic surface pH (9.5) (Table 1). Sample AC-A has only traces of ash (0.29%, Table 1) and an acidic surface (pH 4.0).

Table 1

Humidity, ash content and analyses of mineral matters of initial active carbon samples.

| Sample | Humidity, wt% | Ash, wt% | Constituents in mineral matter (wt%) | | | | | | | |
|--------|---------------|----------|--------------------------------------|------|--------------------------------|------------------|-------|--------------------------------|-------|-------|
| | | | CaO | MgO | Fe ₂ O ₃ | MnO ₂ | CuO | Cr ₂ O ₃ | NiO | ZnO |
| AC-B | 4.09 | 7.24 | 3.34 | 0.85 | 0.490 | 0.016 | 0.002 | 0.001 | 0.001 | 0.001 |
| AC-A | 10.72 | 0.29 | - | - | 0.004 | 0.001 | 0.001 | 0.001 | 0.001 | - |

The initial samples, as well as the modified by impregnation with manganese salts were subjected to thermal analysis in order to choose the treatment temperatures. Initial sample AC-B is quite stable till around 450 °C and then the sample buns out (Figure 1). TGA curves of the modified samples (AC-B-0, AC-B-A) show an initial weight loss of about 10-14% around 100 °C, which is related to thermo-desorption of physically adsorbed water. For series of AC-B samples, impregnation with manganese salts leads to the decomposition of the carbonaceous support. Above 325 °C TGA curves show a drastic decrease in weight of these samples (Figure 1).

Thermo-gravimetric curves (TGA) of AC-A series samples are presented in Figure 2. All samples show generally similar thermal behaviour: weight losses of ca. 7-15 % around 100 °C, most probably due to thermo-desorption of physically adsorbed water; above ca. 450 °C the burning of the carbon skeleton occurs.

Summarizing, the temperatures of 300, 450 and 600 °C have been chosen for thermal treatment of impregnated samples. After thermal treatment obtained samples were washed. Thermal treated samples of series AC-B were obtained with a yield of 50-60% and manganese was loaded in amount of 1.44-1.65 % depending on applied method (Table 2). The samples of series AC-A were obtained with a higher yield (92-98 %), but with small quantities of loaded manganese, and don not contain chloride ions (Table 3).

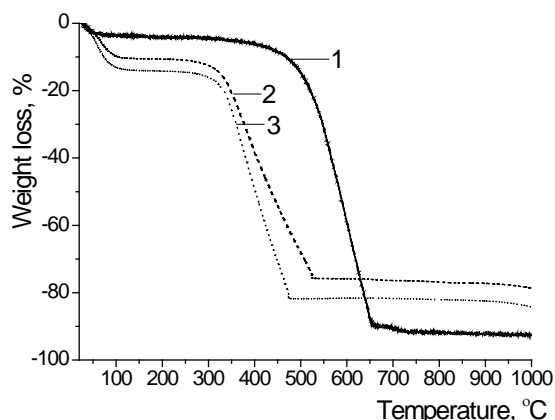


Figure 1. TGA curves measured in air for unmodified AC-B (1) and modified AC-B-0 (2), AC-B-A (3) samples.

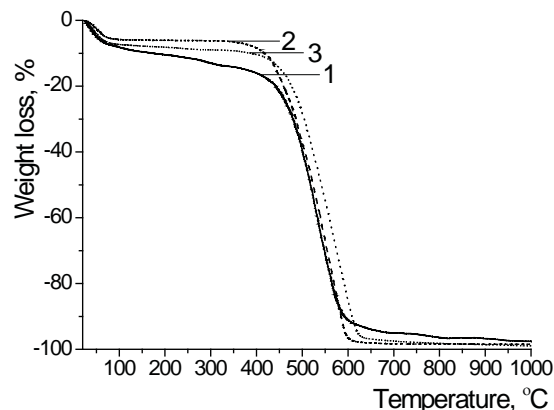


Figure 2. TGA curves measured in air for unmodified AC-A (1) and modified AC-A-A (2), AC-A-Ac (3) samples.

Table 2

Physical-chemical characteristics of manganese modified samples.

| Sample | Description | η , % | Humidity, % | Ash, % | Mn, % |
|---------|---|------------|-------------|--------|-------|
| AC-B-0 | Obtained by impregnation with manganese (ii) chloride solution, followed by treatment at 300 °C. | 56.33 | 8.65 | 7.08 | 1.65 |
| AC-B-A | Obtained by impregnation with acidulated manganese (ii) chloride solution, followed by treatment at 300 °C. | 56.00 | 7.00 | 4.57 | 1.44 |
| AC-A-A | Obtained by impregnation with acidulated manganese (ii) chloride solution, followed by treatment at 300 °C. | 96.40 | 5.86 | 0.81 | 0.51 |
| AC-A-Ac | Obtained by impregnation with manganese (ii) acetate solution, followed by treatment at 300 °C. | 97.20 | 5.65 | 0.54 | 0.22 |

Table 3

Elemental analyses of active carbon samples (wt%, determined on dry and ash free basis).

| Sample | C | H | N | S | Cl |
|---------|-------|------|---|------|--------|
| AC-B | 91.34 | 1.90 | - | 2.57 | traces |
| AC-B-0 | 90.56 | 1.83 | - | - | - |
| AC-B-A | 85.62 | 1.49 | - | - | - |
| AC-A | 89.60 | 3.06 | - | - | - |
| AC-A-A | 88.28 | 2.28 | - | - | - |
| AC-A-Ac | 88.63 | 2.51 | - | - | - |

Present work highlights the influence of surface chemistry of carbonaceous adsorbents on the manganese oxides loading. Following researches will be focused on the determination of the oxidation state of the supported manganese phases Mn_xO_y , dispersion of the manganese oxide particles, and evaluation of physical-chemical characteristics of modified adsorbents.

Conclusions

Obtained results reveal the importance of surface chemistry of carbonaceous adsorbents on the manganese loading. Samples of series AC-B, synthesised from the carbonaceous support with basic surface, were obtained with a yield of 50-60% while manganese was loaded in amount of 1.44-1.65% depending on applied method. The samples of series AC-A, synthesised from the carbonaceous support with acidic surface, were obtained with a higher yield (92-98%), but with small quantities of loaded manganese.

Acknowledgements

The present work was performed within Joint Moldova-Belarus Project "Supported catalysts for underground water treatment: synthesis, properties and using" (No. 15.820.18.02.04/B, 2015-2016).

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