ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 6, pp. 1053–1055. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © M.Kh. Annagiev, R.S. Safarov, S.S. Bairamova, G.N. Mamedova, Dzh.T. Rustamov, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 6, pp. 883–885.

Study of Phenol and Carbon Dioxide Adsorption by the Sorbents Based on Montomorillonite and Diatomite

M. Kh. Annagiev, R. S. Safarov, S. S. Bairamova, G. N. Mamedova, and Dzh. T. Rustamov

Institute of Chemical Problems of National Academy of Sciences of Azerbaijan,
pr. G. Dzhavida 29, Baku, 1143 Azerbaijan
e-mail: annagiyem@gmail.com

Received January 13, 2010

Abstract—The nature, concentration and strength of the basic sites on the outer and inner surfaces of diatomite and bentonite toward adsorption of carbon dioxide and phenol was studied by derivatographic methods in respect of the conditions of processing the samples.

DOI: 10.1134/S1070363210060022

To meet the needs of different branches of chemical, oil and gas industry in the sorbents and catalysts effective sorbents should be created based on the natural aluminosilicates by processing them with salts of various metals and controlling the nature, concentration, and strength of active adsorption sites on their surface.

On the basis of zeolite type raw materials montomorillonite and diatomite effective sorbents were created by processing them with the salts of various metals and acids of different concentrations. The nature, strength, number of acidic and basic adsorption sites toward various molecular probes like ammonia, acetone, *n*-butylamine, and carbon dioxide were studied using the methods of spectroscopy and derivatography [1–3].

The purpose of this work was the study of the basic sites in the natural and modified forms of diatomite and bentonite in respect to adsorption of carbon dioxide and phenol using the derivatography method.

Figure 1 shows a derivatogram of natural diatomite after adsorption on the surface of carbon dioxide. As is evident from the derivatogram, in the DTA curve there is one exothermic effect with a peak at 460°C, and an endothermic effect with maximum at 120°C, while in the DTG curve are observed minima at temperatures 120, 360, and 500°C.

The first endothermic effect with maximum at 120°C characterizes desorption of carbon dioxide weakly bound with the basic sites on the sample surface. The endothermic effect at 360°C corresponds to the desorption of carbon dioxide from a strong basic site on the sample. The appearance of a minimum in the DTG curve centered at 500°C indicates that on the sample surface there is a strong basic site. It should be noted that the value of critical diameter of carbon dioxide molecule provides opportunity to interact with the basic sites located both on the inner and outer surfaces of the sample.

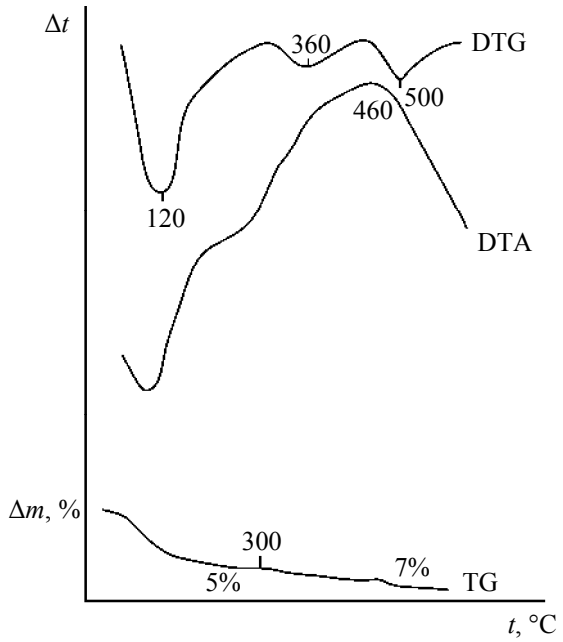

Fig. 1. Derivatogram of natural diatomite after adsorption of carbon dioxide.

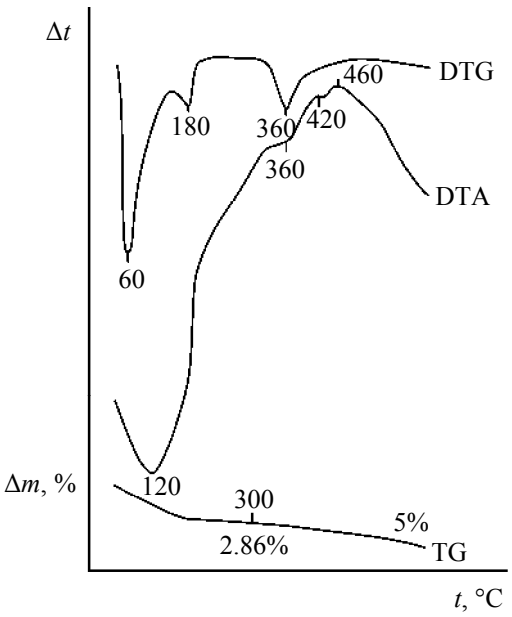

Fig. 2. Derivatogram of natural diatomite after adsorption of phenol.

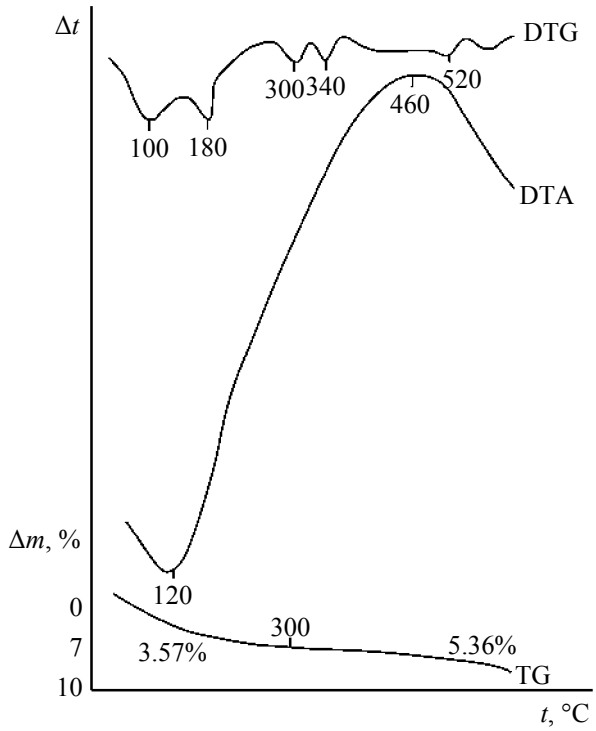

Fig. 3. Derivatogram of diatomite after treatment with hydrochloric acid and adsorption of phenol.

After adsorption of phenol on the surface of a sample of natural diatomite, the DTA curve exhibits three endothermic effects with maxima at 120, 360, and 420°C, and one exothermic effect with a maximum at 460°C (Fig. 2). The first endothermic effect (with a maximum at 120°C) corresponds to the desorption of physically adsorbed molecules of phenol from the surface of the sample. It should be noted that the critical diameter of the phenol molecule (d_{cr} = 6.6 Å) does not allow it to penetrate diatomite and to reach its inner surface, and adsorption occurs only on the outer surface. The appearance of endothermic effects with the maxima at 180, 360, and 470°C indicates the existence on the surface of the weak, medium and strong basic sites.

After processing the natural diatomite with hydrochloric acid and adsorbing phenol on its surface, in the DTA and DTG curves appeared only endothermic effects of a very low intensity, with minima at 120°C in the DTA, and 100, 180, 300, 340, and 520°C in the DTG, and one exothermic effect with a maximum at 460°C in the DTA (Fig. 3).

Reduction in the intensity of endothermic effects of the phenol molecules adsorbed of diatomite treated with hydrochloric acid shows that the concentrations of basic sites on the outer and inner surfaces of the sample decreased. The strong endothermic effects that was observed in DTA curve after adsorption of the phenol molecules were defined by gradual oxidation of the phenol molecules located on the outer surface.

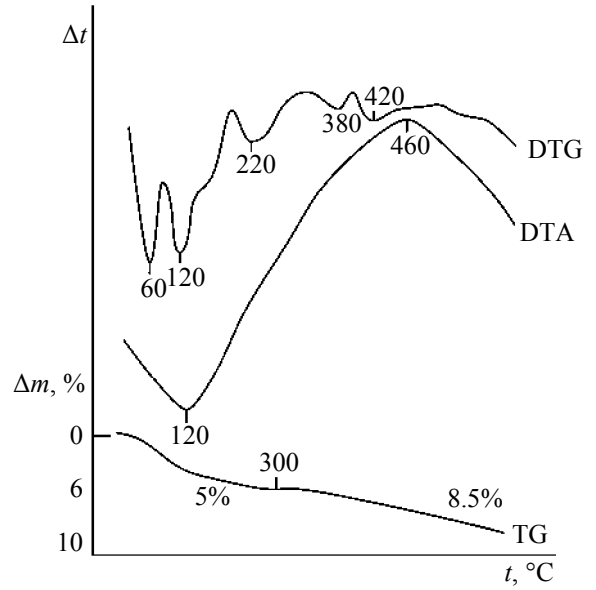

Fig. 4. Derivatogram of natural diatomite after treatment with an aqueous solution of sodium hydroxide and adsorption of phenol.

Figure 4 shows a derivatogram of natural diatomite treated with aqueous solution of sodium hydroxide after adsorption of phenol on its surface. As seen, there are minima in the DTG curve at 60, 120, 220, and 380°C. In the DTA curve one endothermic effect is observed with a maximum at 120°C and one exothermic effect at 460°C.

It should be noted that after processing diatomite with aqueous solution of sodium hydroxide the intensity of the endothermic effects increased due to the desorption of phenol molecules and simultaneously the minima were shifted to the high-temperature region indicating the growing strength of the basic sites toward the phenol molecules.

Thus, after processing diatomite with a solution of sodium hydroxide the strength and number of basic sites on the surface increases compared with the untreated sample. As is evident from the derivatograms, the intensity of endothermic effects in the temperature range 60–300°C increases, which is mainly due to the increase in the concentration of the basic sites of the medium strength.

Comparison of derivatograms (Figs. 1 and 2) of the diatomite after adsorption of carbon dioxide and phenol showed that 2.0–3.0% of the basic sites are located on the inner surface of the sample inaccessible to phenol molecules. Comparing the mass loss after the adsorption of phenol on the natural and modified diatomite at heating to 600°C as a dependence on the type of treatment gave the following sequence of activity: natural diatomite < diatomite + HCl < diatomite + NaOH. We found that, depending on the conditions of processing the diatomite samples, the basic sites formed on the surface differ from each other in energy.

Thus, we studied the strength, concentration, and nature of the basic sites of the obtained sorbents by adsorption of phenol and carbon dioxide. The critical diameter of a molecule of carbon dioxide allows it to penetrate the micropores of the sorbent, while the critical diameter of phenol molecule does not allow it to interact with the basic sites on the inner surface of micropores. In the case of phenol the adsorption occurs in the secondary pores. As a result of studying the concentration of basic sites on the surface of sorbents based on montomorillonite and diatomite we found that their number is greater in the samples synthesized on the basis of montomorillonite [3].

The prepared sorbents were tested in the process of purifying air from the phenol vapor. The tests showed that air was purified completely.

EXPERIMENTAL

The diatomite samples were treated with 10% solution of sodium hydroxide and 25% solution of hydrochloric acid at 90°C with strong shaking. The mass ratio of liquid to solid phase was L:S = 10: 1.

The duration of treatment of diatomite samples with alkali was 4 h, and with acid, 6 h. After filtration, the samples were washed with distilled water and dried at room temperature. In order to study the nature of the basic sites on the surface of the synthesized samples adsorption of carbon dioxide and phenol was carried out, and then the compositions obtained were studied by derivatography. The methodology of the experiments has been described in detail in [4–6].

REFERENCES

1. Annagiev, M.Kh., Alidzhanova, S.M., Imanova, N.A., Alieva, S.G., and Agdamskii, T.A., *Fiziko-khimicheskii analiz i neorganicheskoe materialovedenie* (Physico-Chemical Analysis and Inorganic Materials Science), Baku: Gos. Univ., 2007, p. 230.
2. Annagiev, M.Kh., Imanova, N.A., Alieva, S.G., and Kuliev, T.M., *Sorbenty na osnove prirodnykh tseolitov* (Sorbents Based on Natural Zeolites), Baku: Elm, 2007, p. 40.
3. Annaqiev, M.Kh., Rustamova, J.T., Akhmedova, A.N., and Mamedov, I.Kh., *J. Chem. Problems*, 2004, no. 4, p. 103.
4. Han, P. and Zin, Z.Y., *Appl. Surface Sci.*, 2004, vol. 227, no. 4, p. 30.
5. Annagiyev, M.Kh., Aliyeva, S.G., and Kuliyev, T.M., Abstracts of Papers, *13th Int. Zeolite Conf.*, Montpellier, France, 2001, Stnd. Surf. Ser. Catal., p. 5170.
6. Annagiyev, M. Kh., Yagubov, A.I., Alekperova, G.F., and Mamedov, G.Kh., *Azerb. Khim. Zh.*, 2002, no. 3, p. 35.