EFFECT OF FIRING ON THE ADSORPTIVE CAPACITY OF TZK

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Fillers prepared from tripolite from the Zikeev pit (this tripolite type will further be referred to as TZK) and modified with vaseline oil are used mainly in the chromatographic separation of C_1-C_5 hydrocarbons boiling at low temperatures [1-3]. The amount of vaseline to be used in modifying a given TZK sample varies over a broad range and depends on the composition and the firing conditions.

TZK is a complex mineral whose origin is not clear yet. Most probably, tripolite is a biochemical product [4]. Tripolite is a soft rock which is readily ground to powder. However, hard stone-like particles (beads) are also found; these beads have the same composition as the soft mineral, but their adsorptive capacity is higher. The main component of TZK is silicon, which is present in the form of water-free quartz, chalcedony, and aluminum silicates. Hydrated quartz, titanium oxides, leucosene, ilmenite, rutile, epidote, turmaline, etc., are present in small amounts. The chemical composition of two TZK samples is given in the table.

Only fired TZK samples are used as carriers in gas-liquid chromatography. During the heat treatment of TZK the various mineral components undergo changes at different temperatures. Silica and aluminum silicates, which are the main components of TZK, are quite markedly altered.

TZK contains silica of various crystalline and amorphous structures. Studies by Boreskov, Kiselev and others [5] on various silica structures—chalky, glassy with narrow pores, large-pore silica gels – showed that the properties of the various SiO_2 structures change in different ways upon firing at temperatures from 115 to 1000°C for 12 h. Glassy SiO_2 with narrow pores has the lowest thermal stability. Samples containing large pores are stabler. Chalky SiO_2 has the highest thermal stability. Even at 1000°C a quite large surface area was preserved in this sample: The reported data demonstrate that it is very difficult to prepare TZK samples with previously fixed characteristics, as may be done for other adsorbents as are molecular sieves, silica gel, alumina. Firing is the only possible way of altering the adsorptive capacity of TZK. The effects of the temperature and duration of firing on the relative adsorptive capacity* of TZK [3] was studied in a sample (0.25-0.5 mm fraction) prepared in the Gor'kii experimental station (GOB) of the All-Union Scientific Research Institute of Oil Industry. This was done because nowadays a microspherical carrier —the adsorbent prepared and fired in the Gor'kii experimental station—has to be utilized instead of the raw material from the Zikeev pit. Moreover, the sample chosen for the test is a typical sample of average composition, for the amount of vaseline needed for modifying the microspherical TZK ranges from 7 to 10%.

The test procedure was as follows:

Samples taken from a fairly thoroughly mixed TZK batch were fired in a muffle furnace at 700, 750, 800, and 850° for 3 or 6 h. To prevent polymerization of branched unsaturated hydrocarbons, the TZK carriers were treated with soda (2%). To find the effect of soda on the value of a, the tested samples were treated with soda either before or after being fired at the above temperature for 3 h.

The effect of firing under the same conditions on the magnitude of a was studied also in TZK samples of various compositions prepared directly from soft and bead tripolite from the Zikeev pit. The samples were mixed with water, dried, and fired at temperatures from 700 to 800°C for 3 h. Soda was added to the fired samples in an amount of 2%.

Figure 1 shows the a values measured in one and the same sample fired and treated with soda under various conditions. The a value of the original sample without soda equaled 2.1.

* The relative adsorptive capacity a of TZK samples was determined from the volume of propane retained under strictly constant experimental conditions.

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TZK sample	Losses during firing	Oxide content, weight %								
		SiO_2	Fe_2O_3	CaO	MgO	Al_2O_3	SO_3	P_2O_5	MnO	Total
1	3,95	77,18	0,77	2,66	1,31	7,60	0,40	Traces	None	93,87
2	2,57	79,03	0,77	4,44	2,03	4,96	1,01	Traces	None	94,81

* Titanium oxides were not determined.

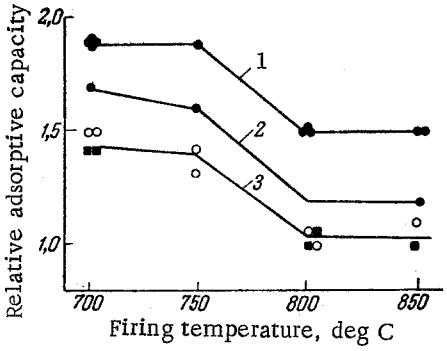

Fig. 1. Relative adsorptive capacity of TZK as a function of firing temperature and firing time, and the conditions of the treatment with soda: 1, 3) firing time 3 h; 2) 6 h; ●) fired without soda; ○) soda added after firing; ■) soda added before firing.

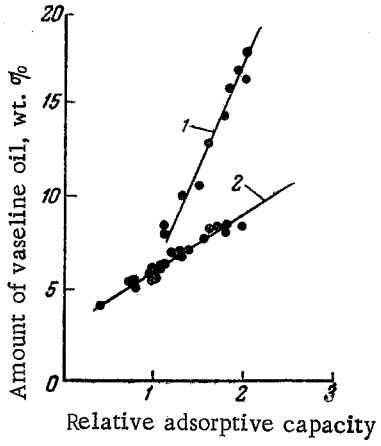

Fig. 2. The optimum amount of vaseline oil as a function of the relative adsorptive capacity: 1) TZK samples fired for 3 h; 2) TZK samples fired for more than 5 h.

It is remarkable that the curves are broken lines, and run parallel to the temperature axis in two definite ranges: 700-750°C and 800-850°C. In these temperature ranges evidently no noticeable changes take place in the samples tested. The curves of samples fired for 3 and 6 h have the same slope in the temperature range from 750-800°C; this points to changes in the structure of some minerals in the TZK.

Prolongation of firing from 3 to 6 h leads to a decrease of 0.2-0.3 in the adsorptive capacities of samples fired without soda at the same temperatures.

Upon a rise of the firing temperature from 700 to 800°C the adsorptive capacity decreases by 0.6 (from 2.1 to 1.5) upon 3 h firing, and by 0.9 upon 6 h firing. Admixture of soda decreases a by 0.4. From Fig. 1 it is evident also that the sorptive capacity a does not depend on whether soda is added before or after firing.

The TZK samples fired and treated with soda were modified with vaseline oil; for every sample we determined the amount of vaseline oil with which "optimum" separation of C_1-C_5 hydrocarbons was attained [3]. Figure 2 shows a plot of the optimum amount of vaseline oil versus the adsorptive capacity of TZK samples containing 2% soda and fired under various conditions. The adsorptive capacity was determined in a Fractovap device. Curve 1 represents samples directly prepared from Zikeev tripolite and fired for 3 h, and curve 2 represents samples prepared and fired at 700-780°C for 5-6 h in the Gor'kii experimental station and later fired again at 700-850°C for 3 or 6 h. The upper points of curve 1 correspond to fillers prepared from beads.

In paper [3] it was shown that modification with 5-11% vaseline oil yields the best fillers. As can be seen in Fig. 2, the adsorptive capacity of such samples equals 0.8-1.5.

It should be noted that the adsorptive capacity a is the sum of the adsorptive capacities of all TZK particles in the sample considered, in other words, it is an additive property; therefore, it is very important that all particles are sufficiently fired, since, otherwise, the peaks in the chromatogram will be diffuse.

SUMMARY

1. The effect of firing on the magnitude of the adsorptive capacity a of TZK has been studied. Firing of TZK samples at 750-800°C for 3 h reduces a by 0.6, and firing for 6 h reduces it by 0.9.

2. Plots representing the optimum amount of vaseline oil needed for modification as a function of the adsorptive capacity a are given for TZK samples fired under various conditions.

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