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Abstract

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OZONATION OF KOH IN A “FLUIDIZED”BED

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In 1949 (^1) it was shown for the first time that ozonation of calcined potassium hydroxide at −10–15° is accompanied by the formation of an orange-colored substance, soluble in liquid ammonia at −60 and −70°. This substance was named potassium ozonide, KO_3, and assigned to a new class of higher oxygen compounds—ozonides, whose individuality was subsequently proved by experimental studies carried out in this field over the past decade (^2–7).

Proceeding from the fact of the existence of potassium ozonide, it seemed of interest to determine the possibility of its formation over a broader temperature range, and also by using not only anhydrous caustic potash but also its hydrated compounds.

No such data are available in the literature. To this end we carried out the synthesis of potassium ozonide in the temperature range −65 to +60°.

For ozonation, chemically pure caustic potash was used, both calcined (97% KOH; 2.45% K_2CO_3) and uncalcined (83.48% KOH; 2.24% K_2CO_3; 14% H_2O). Ozonation was carried out at temperatures −65; −53; −35; −20; −10; 0; +10; +30; +40; +48; +50; +57°.

Since the reaction of ozone with KOH proceeds in a heterogeneous medium, the degree of comminution and mixing of the reacting substances is of great importance.

To intensify mixing and ensure the most complete mass and heat exchange, the method of the so-called fluidized bed was employed; at present this method has found wide application in industry and laboratory practice.

The experiments were carried out in a glass reactor in the form of a U-shaped tube, one arm of which, equipped with a dust trap, narrowed into a cone and passed into a tube for introducing ozone. The simple design of the apparatus proved very convenient and made it possible to observe the course of the process directly. The completeness of mixing was confirmed visually and by comparison with the hydrodynamic criterion for the formation of a fluidized bed. The use of a fluidized bed in turn required the use of alkali ground to a particle size of 0.25 mm. The use of finer alkali caused the formation of “flame-like” gas breakthrough channels, with a sharp decrease in mixing. In addition, fine alkali

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

was very readily carried out by the gas stream from the reaction zone in the form of dust.

The following ratios were found to be the most favorable aerodynamically and were used in the work: 35 g of KOH with a particle size of 0.25 mm and a flow rate of ozonized oxygen of not less than 100 l per hour. Taking these requirements into account, a battery of tubular ozonizers connected in parallel in the direction of gas flow was assembled, providing the possibility of obtaining (at 20 kV) not less than 13.5 g of ozone per hour, with a content of about 4-5% by weight and a throughput of more than 200 l/hour. The ozone-oxygen mixture was fed into the reactor at a rate of 200 l per hour.

In experiments at temperatures from -20° to $+50^\circ$, the reactor was placed in an ultrathermostat, which maintained the specified temperature with an accuracy of $\pm 0.1^\circ$. Under subzero-temperature conditions ($-20^\circ, -65^\circ$), cooling was achieved by using a mixture of acetone or ethyl alcohol with dry ice.

Owing to the heat of reaction, the temperature in the fluidized bed of alkali, determined by thermocouples, in all experiments remained 5–6° higher than in the thermostat. The specified temperature regime was reached in the reactor within 1–2 min after the start of ozonation. Over the height of the fluidized bed, the temperature gradient did not exceed 1–2°. Periodically withdrawn samples were analyzed for active oxygen content by decomposition with a 0.5% solution of $CuSO_4$ and volumetric measurement of the oxygen evolved. Kinetic curves for the increase in oxygen content in the samples with time were constructed from the average results of 2–3 series of measurements and, for 30°, are shown in Fig. 1 for calcined and uncalcined alkali. The character of the curves at other temperatures is similar to those shown. The presence of $\sim 14\%$ water of crystallization in the alkali reduces ozone assimilation by approximately a factor of three. An equilibrium stationary state was reached in all experiments no later than 50–60 min after the start of ozonation.

Fig. 1

Fig. 2

Figure 2 shows curves characterizing the dependence of the active oxygen content in the products of ozonation of caustic potash (anhydrous and containing $\sim 14\%$ H_2O) on temperature for the established state. The curve of maximum oxygen yields (Fig. 2) has clearly expressed maxima at $+40^\circ$ for calcined alkali and +50° for uncalcined alkali.

A further increase in temperature leads to a sharp decrease in oxygen content, and at +47° and +58° the ozonation products begin to decompose vigorously; in the lower part of the reactor, sintering of them into a dense mass is observed over the entire cross section. The ozonated alkali above the sinter becomes noticeably lighter; its oxygen content falls to 0.9—1.0%. In the sintered part, the O_2 content fluctuates within 0.5—0.7%, irrespective of the type of alkali.

The ozonation products obtained at +40, +50° were extracted with liquid ammonia and, after evaporation of the latter at −40°, analyzed for KO_3 content. In this case, the KO_3 content from calcined alkali proved to be 93% KO_3, while from uncalcined alkali it was somewhat lower, 91.0% KO_3.

After extraction of potassium ozonide with ammonia, the alkali retained a yellow color for 7—8 days, and volumetric analysis established a residual content of up to 0.8% active oxygen.

Thus, the use of the fluidized-bed method makes it possible to substantially broaden the temperature interval for ozonation of caustic potash not only in the anhydrous state, but also for its hydrated form. For practi-

for practical purposes, carrying out the ozonation process of caustic potash at positive temperatures is of substantial importance.

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