INVESTIGATION OF THE VAPOR-PHASE HYDROLYSIS OF CHLOROBENZENE
IN PRESENCE OF A PHOSPHATE CATALYST

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The choice of catalysts for the vapor-phase hydrolysis of aryl halides has been the subject of many investigations. Dozens of substances have been tested as catalysts — metals, their oxides, salts and acids. It was found that in the absence of promoters silica gel is the only substance that accelerates this reaction. The activity of some of the substances mentioned in the literature is undoubtedly also due to their content of polysilicic acid [1]. Only a few other substances manifest catalytic activity in this reaction. Small and short-lived activity is exhibited, for example, by stannic [2], titanic [2, 3] and aluminate acids [4]. In their presence the yield of phenol from chlorobenzene at 450-500° is less than 1% of the theoretical but can be slightly increased by promotion with copper chloride. The selectivity of these catalysts is also poor (the yield of hydrochloric acid considerably exceeds the yield of phenol). In the absence of catalysts, however, chlorobenzene generally does not react with water under the same conditions.

All these and a number of other facts are satisfactorily explained by our earlier theory to the effect that in the process of vapor-phase hydrolysis on silica gel there is surface interaction of the aryl halide with the silica gel which then functions as a weak but thermally stable acid [5]. This theory also accounts for the difficulty of selection of catalysts for this reaction. It appears that hardly any compounds are known that resemble silica gel in exhibiting weakly acidic properties, in being stable under the conditions of a high-temperature reaction and in satisfying the theoretical requirements of a catalyst in this reaction. Detailed consideration of a model of a catalyst for the vapor-phase hydrolysis of aryl halides has appeared in previous publications [1, 5].

It is therefore natural that interest should be aroused by the reports of the catalytic activity of phosphate catalysts whose composition and properties are only briefly described in the literature. Catalysts for vapor-phase hydrolysis of chlorobenzene at 350-700° recommended in patents are neutral and acid manganese pyrophosphates and their mixtures with copper [6], calcium phosphate [7] and other phosphates of the alkaline-earth metals on which are deposited Cu, Ni, Co, Ag, Au or metals of the Pt group [8], salts, oxides or hydroxides of metals on which copper phosphate or zinc phosphate is deposited [9]. It is claimed that the yield of phenol in the reaction reaches 90% of the theoretical. In the same manner as chlorobenzene, chloro derivatives of toluene, naphthalene, diphenyl, etc. are hydrolyzed on phosphate catalysts. Phosphate catalysts have been tested in a pilot plant in Germany [10].

Our investigations show that tricalcium phosphate is likewise an active catalyst for this reaction and is comparable with silica gel. The probable similarity in the mechanism of their activating action may be attributed to the acidic character of both catalysts.

EXPERIMENTAL

The experimental procedure for this investigation was the same as that formerly employed with a silica gel catalyst [11]. The reaction was carried out by a flow method. An approximately 1:1 ratio (by weight) of water to chlorobenzene was maintained in all of the experiments. The duration of an experiment was 1-2 hrs. The space velocity was 300 g of chlorobenzene per liter of catalyst per hr. Yields of acid and phenol are given in percentages of the theoretical, reckoned on the chlorobenzene introduced.
Preliminary experiments established that metaphosphoric acid, copper phosphate and dicalcium phosphate are inactive in this reaction. Commercial grades of tricalcium phosphate (Russian and Kahlbaum) evidently contain impurities; these, too, had poor activity and were unstable. Unlike them, the tricalcium phosphate that we prepared from soluble calcium salts and phosphoric acid or by neutralization of calcium hydroxide with acid had high activity and stability. This is illustrated by Figs. 1-3 in which curves characterizing the activity of silica gel at various temperatures and its deactivating mineral impurities are compared with curves for phosphate on the basis of our previously published data.

It follows from Table 1 and Fig. 1 that in presence of phosphate catalyst the vapor-phase hydrolysis of chlorobenzene takes place with measurable velocity in the same temperature range as with silica gel (450-600°C). The activity of phosphate catalyst is lower than that of silica gel. In order to obtain the same yield of phenol as on silica gel, it is necessary to raise the reaction temperature by approximately 100°C. Using freshly prepared phosphate catalyst at 450°C, the yield of hydrochloric acid is seen to be lower than that of phenol. In the subsequent experiments at 500 and 550°C, with a longer duration, the yields of acid and phenol are equal. With phosphate catalyst the reaction goes with a high degree of selectivity up to 550°C. At higher temperatures the yield of hydrochloric acid sharply exceeds the phenol yield (evidence of secondary reactions). The results of our experiments confirm that the phosphate catalyst itself (in the absence of promoters) is active in the investigated reaction.

Table 2 contains the data for the influence of calcination on the activity of phosphate catalyst. We see that the yield of phenol in the experiment at 500°C (carried out over the catalyst after an experiment at 650°C followed by regeneration for 2 hrs) was nearly the same (4%) as before the experiment at 650°C (4.4%). Similar data were obtained in the last two experiments (Table 1) at 500°C which were likewise performed after experiments at 650°C. It follows from the other experiments of Table 2 that over a catalyst calcined for 2 hrs in air at 850°C, the phenol yield in the 500°C experiment is 0.9%, and in the 550°C experiment 2.2%.

The catalyst accordingly nearly fully retained its activity after the 650°C experiment followed by regeneration. Only after calcination at 850°C did the catalytic activity of the phosphate fall by a factor of 4 to 5. Comparison of these results with previous ones shows that the thermal stability of phosphate catalyst is higher than that of silica gel [11].

We established earlier that inorganic impurities such as NaCl and lead acetate, added in the proportion of 1%, nearly completely deactivate a silica gel catalyst [12]. The phosphate catalyst behaves differently.