Effect of aluminium oxide contaminants on the process of ozone decomposition in water

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ABSTRACT

In the recent years a number of publications have appeared on Al_2O_3 as ozonation catalyst. The results, however, raise many controversies. Adsorption of ozone on a surface of the catalyst and subsequent decomposition of O_3 molecule leading to formation of OH radicals is one of the possible mechanism of catalytic activity of alumina. However such the activity sometimes is observed while in other reports alumina does not show an ability to generate the radicals. As formation of the radicals depends strongly on pH controversial effects observed in the published papers may result from the lack of proper pH control. Aluminas are contaminated with alkali metals and the contaminants may cause unwanted (unexpected) changes in pH of ozonated solutions. The pH is a key factor responsible for the process of ozone decomposition in water. Therefore the purity of Al_2O_3 must be considered as an important parameter that can influence the process of ozone decomposition. This paper aims at showing that in the processes of catalytic ozonation special attention should be given to precise pH control. Commercially available aluminum oxides, purified by an extraction do not show the abilities to decompose ozone in water.

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1. Introduction

Catalytic ozonation is the area of science that has recently attracted a lot of attention and that results in numerous publications [1,2]. Aluminum oxide is one of the most often used catalyst or catalyst supports as its catalytic activity was shown in one of the first papers on catalytic ozonation [3]. However, many of the presented results may be considered controversial: in some papers catalytic activity was observed, [4–7], while in some reports alumina has not caused decomposition of ozone [8–10]. The controversies must have their reasons. There are three possible catalytic mechanisms in heterogeneous catalysis: i) ozone adsorbs on the catalyst surface and decomposes into the radicals, ii) organic compound adsorbs on the surface and adsorbed species are attacked by ozone molecules and iii) both ozone and organic molecules adsorb on the catalyst surface and react there. In this paper we discuss solely the first mechanism.

Decomposition of ozone in water strongly depends on pH. Therefore to assess the ability of a catalyst to decompose of ozone molecule it is absolutely necessary to compare ozone stability in water with and without catalyst at exactly the same Ph. However,

in many of the papers on catalytic properties of Al_2O_3 published to date not enough attention was paid to pH control [3,8,11,12], which is crucial particularly at high catalyst concentrations [13].

In the majority of published papers concerning the alumina as the catalyst there are no data on pH control not only after the catalyst introduction to the ozonated solution, but also during and after the completion of catalytic process. In the papers published to date pH value has been usually controlled at the beginning of the process (although in some papers [3,8] it was not controlled at all), and relatively rarely after the catalyst introduction and after the completion of the process. Controlling this parameter allows for the differentiation between the effect caused by pH increase and true catalytic effect.

Commercially available aluminum oxides are produced using the Bayer process, and then they are subjected to calcination in order to obtain the desired crystal phase [14]. Oxides produced in this way contain alkaline residues after the bauxite extraction as well as other contaminants remaining after the careless rinsing of ore. In most cases, available literature on the alumina as an ozonation catalyst either lacks information on the method of oxide purification or the data are scarce. It is therefore expected that alkaline contaminants of alumina may significantly change the pH of water after introduction of the catalyst to the ozonated solution. This paper aims at showing that mineral contaminants of aluminum oxide significantly affect the process of ozone decomposition because they are responsible for pH changes following the introduction of catalyst to water.

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2. Experimental

2.1. Materials and analytical methodology

Three commercially available aluminum oxides have been used in this study: activated aluminum oxide (AA – Nanning Elaiter Environmental Technologies Co. Ltd.), SAS 200 (SAS - BASF) and CDO Selexsorb® (CDO–BASF). The oxides have been used as unpurified and purified materials. The purification of oxides was conducted by: rinsing them first with 200 mL with HCl (0.1 M Chempur) and then with water to neutrality. Another portions of the oxides were extracted with high purity water (Millipore) in Soxhlet apparatus. Aqueous extracts used in the ozone decomposition experiments were obtained by 5 h continuous extraction of oxides in the apparatus similar to that described elsewhere [15]. The extracts were subjected to elemental analysis using ICP-OES (Varian ICP-OES Vista-MPX, Varian, Australia).

Specific surface area (Quantachrome Autosorb iQ) and phase composition using X-ray diffraction XRD (Bruker, AXS D8 Advance) were determined for all the oxides. Isoelectric point of oxides (pH_{pzc}) was determined by a slightly modified method proposed by Faria et al. for active carbons [16]. The amounts of electrolyte and oxide were doubled, while the time of pH equilibration was 24 h [6].

Simultaneously, the method accuracy was verified by comparison with mass titration method [6]. No significant differences were observed in pH_{pzc} values. The pHpzc values were determined with an accuracy of 0.15 pH unit.

Ozone in gaseous phase was determined by iodometric method, while ozone in water–by indigo method. Both methods have been described in Standard Methods [17].

2.2. Measurements of ozone decomposition

Experiments in ozone decomposition in water were conducted at room temperature, in high purity unbuffered water (Millipore), whose pH was corrected to 5.0 with hydrochloric acid (10 μM HCl). In each experiment, 200 ml water with appropriate pH was introduced to 250 ml glass reactor. Ozone was produced from pure oxygen using the Crystal ozone generator (Canada). Water was saturated with ozone for 20 min, after the time the concentration of ozone in the aqueous phase was approximately $5.82 \pm 0.64 \, mgO_3/l$. After switching off the ozonator, a zero sample was immediately taken and 0.5 g of appropriate oxide was introduced. Ozone concentration was measured at specified time intervals. Before each series of experiments, in order to ensure zero demand for ozone, the reactor was saturated with ozone for 20 min. Similar experiments were also done introducing instead of the appropriate oxide, equivalent amount of its aqueous extract. Another set of experiments was carried out in 0.01 M phosphate buffer. All the experiments were repeated three times, in general the precision of ozone determination was better than ±2%.

3. Results and discussion

3.1. Characteristics of aluminum oxides

Chemical and physical properties of aluminum oxides used in this study were measured. Table 1 presents the properties of the oxides. The oxides differ in terms of phase composition and specific surface area. The observed pH_{pzc} values are within the range of 7.9–8.8 (non-purified oxides), and following the extraction with water–within the range 7.4–8.8.

In order to identify the contaminants in samples of examined aluminum oxides, qualitative and quantitative analyses of aqueous
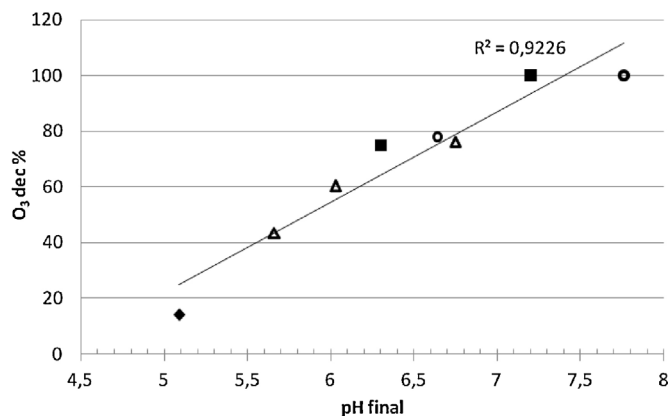

Fig. 1. Relationship between degree of ozone decomposition and pH after introducing different quantities of different aluminas to 200 ml ozone solution with pH 5.0 (adjusted with acid), after 30 min. (♦- O_3; △- SAS (0.5 g; 1 g and 2 g); ■- AA (0.5 g and 1 g); ○-CDO (0.5 g and 1 g)).

extracts of all the oxides were conducted. The results have been listed in Table 2.

Chromium, iron, magnesium and manganese were also found, but in insignificant quantities.

Major contaminant of aluminum oxides is sodium, which constitutes from 77% to over 82% of the total amount of oxide contaminants. This is not surprising as sodium hydroxide is used as the leaching agent in the industrial production of aluminum oxide in the Bayer process [14]. The content of sodium in the studied aluminum oxides ranged from about 13 to over 34 μmol/g. Such the amount of sodium easily affects pH after suspension of the oxide in water for e.g. ozone decomposition studies. The increase of pH will be higher when the experiments are carried out at pH close to neutral. It is also worth to emphasize that high purity water used in many research papers does not have any buffer capacity and subsequently is prone to pH changes.

The other elements: Ca, K, Si are also the post-production material and they are the main component of so called "red mud" remaining after the leaching of bauxite ore [14]. In turn, B is characteristic for bauxite rich in this element [18]. However, it is mainly sodium, as alkaline element, that is responsible for the increase in water pH in contact with aluminum oxide and consequently, for ozone decomposition.

3.2. The pH control

In the first experiments, ultrapure water with pH corrected by hydrochloric acid to pH 5.0 was saturated with ozone, different quantities of different aluminum oxides were introduced and disappearance of ozone was observed within 30 min. The rates of ozone disappearance varied for different oxides. Solutions pHs after the process of ozone decomposition were measured and the analysis revealed that pH values also varied and depended not only on the type of oxide but also on its quantity. The dependence between the degree of ozone decomposition and final solution pH was plotted. It turned out that the varied degree of ozone decomposition is highly dependent on pH changes. The results are shown in Fig. 1. The question should be answered what was the reason of pH changes following the introduction of Al_2O_3 to water.

It seems obvious that ozone decomposition after the introduction of aluminum oxides to water was affected by the pH changes and not by catalytic activity of the oxides. Mineral contaminants of aluminum oxides must be considered responsible for the pH changes. Changing the pH of pure water to pH 5.0 requires about 10 μmol/l HCl, while the amount of sodium in oxides can be as high as 35 μmol/g (Table 1).