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Hydrogen generation by oxidation of coarse aluminum in low content alkali aqueous solution under intensive mixing

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ABSTRACT

Simple, safe, scalable and low-cost method of hydrogen production via aluminum-water reaction was proposed. Hydrogen generation method is based on oxidation of coarse aluminum of centimetric scale in alkali aqueous solution with alkali concentration of no more than 0.1 M under intensive mixing of reaction medium. In presented work aluminum conversion (hydrogen yield) was studied depending on the aluminum to solution mass ratio (α changed from 30.1 to 2.7), the concentration of alkali in aqueous solution, the mixing rate, the form of aluminum particles (granules or chips) and chemical purity of aluminum. It was shown that under implemented experimental conditions alkali is continuously regenerated during oxidation reaction and synergistic effect of low content alkali aqueous solution and intensive mixing works. Aluminum conversion degree after 5 h oxidation of aluminum chips at 90 °C in 0.1 M KOH aqueous solution with $\alpha = 4$ and mixing rate of 400 rpm was 75.4%. With alkali concentration increasing from 0.01 M to 0.3 M the conversion of aluminum increases from 20.7 to 95.7% (after 5 h at 90 °C, $\alpha = 4$). Proposed method was strongly affected by mixing of reaction medium inside the reactor while it didn't feel the difference between aluminum chips and granules having specific surface area of 22 and 5.5 cm²/g respectively. Chemical purity of aluminum had little effect on aluminum conversion as well. Generally, proposed method can be used for hydrogen generation, aluminum waste utilization and special-grade alumina production.

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Introduction

Hydrogen is a promising fuel, whose widespread use as energy carrier is expected in near future. This is due to the

absence of harmful emissions during hydrogen combustion, high energy content, easy conversion of its chemical energy into useful energy and almost unlimited resources (in bounded form). However, the problem of hydrogen storage and

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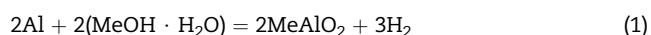
delivery to end users prevents its widespread use as a fuel up to now. Existing methods of hydrogen storage, such as high-pressure tanks or liquid are quite expensive and energy-consuming. There are also methods in which hydrogen is stored in a bounded state (chemisorption or physical adsorption), as well as ways in which the hydrogen is obtained from the intermediate materials such as metal hydride (NaBH_4 , AlH_3 etc.) or from water under the action of metals like Al, Mg, Fe, Si, etc.

There are a great number of studies devoted to hydrogen production from water via aluminum oxidation [1–4]. When aluminum reacts with water, 15–16 MJ of heat, 0.111 kg of H_2 and more than 1.9 kg of aluminum oxide/hydroxide are produced per a kg of aluminum. Due to high concentration in the earth's crust, easy storage and high industrial output aluminum is considered for both hydrogen production and energy generation. Its oxidation products (aluminum oxide or hydroxide) can be returned to the cycle of aluminum production or used as non-metallurgical aluminas, e.g. for the production of adsorbents, catalysts, special ceramics and other.

Aluminum oxidation in water under standard conditions is impossible due to formation on its surface of an oxide film. The problem of oxide film formation can be solved by aluminum powder oxidation under high temperatures and pressures [5–11], but the use of such oxidation processes reduces the economic efficiency. The search of ways of aluminum surface activation or oxide film destruction for low-temperature aluminum oxidation is an actual task.

A number of methods of aluminum activation have been already proposed. These methods include the mechanochemical preparation of highly reactive aluminum powder alloyed with gallams of various compositions including Ga, In, Sn, Zn and other additions [12–14]. Enhanced aluminum oxidation in water is observed after aluminum co-milling with graphite [15] and silicon [16]. Aluminum particle surface is activated by milling with different metal oxides such as Al_2O_3 , TiO_2 , Co_3O_4 , Cr_2O_3 , Fe_2O_3 , Mn_2O_3 , NiO, CuO, ZnO, MoO_3 , Bi_2O_3 and other [17–19]. Milling with salts was also proposed as perspective way of aluminum activation [20–24]; new aluminum surface created by milling is covered by salt during the storage of aluminum preventing its oxidation, such surface is revealed by salt dissolution in aqueous medium. There is also incalculable quantity of methods producing dispersed aluminum powder activated by mechanochemical pretreatment using different additional chemicals and its combinations. Mechanochemical pretreatment is certain to affect the aluminum hydrolysis activity even at room temperatures and undoubtedly it can be essential in some special applications but it suffer from its high cost because of using high power-consuming mixing process and additional valuable chemicals.

Aluminum oxidation in alkaline aqueous solutions is well-known method of simple rapid hydrogen production [25–28]. Aluminum can react with alkali aqueous solutions without any additional additives. Aluminum reacts with alkali forming aluminates in accordance with following equation:



The oxidation reaction of aluminum in aqueous solution, for example, of potassium hydroxide proceeds according to the following equation:



Produced aluminate is not stable and it can be decomposed into a more stable aluminum hydroxide and potassium hydroxide in accordance with the following equation:



Aluminum hydroxide is precipitated at relatively low temperatures. Such precipitation process is used for example in the Bayer process (industrial process producing alumina) when aluminum hydroxide at temperatures about 45–70 °C is precipitated from sodium aluminate aqueous solution. In case of aluminum oxidation in alkaline aqueous solution reaction (3) leads to the partial regeneration of alkali.

The reaction of aluminum oxidation was studied for different alkaline aqueous solutions, their concentrations and temperatures. Hydrogen production for air-hydrogen fuel cell has been studied putting 1 g of aluminum waste cans into 2 M NaOH aqueous solution [29]. Hydrogen generator has been proposed and tested when aluminum was putted into sodium hydroxide solution with concentration of 25 wt.%, 17 wt.% and 9 wt.% [30]. Waste aluminum in powdered form was recycled using special reactors filled with 5 M or 1 M NaOH solution at high pressures (up to 30 MPa) and relatively moderate temperatures (to 150 °C) to produce high-purity compressed hydrogen and marketable aluminum hydroxide [31–34]. In most studies devoted to hydrogen production by aluminum oxidation in alkaline aqueous solutions the excess of alkali was used, concentration of alkali usually exceeds 1 M while molar ratio of aluminum to alkali doesn't exceed 1. In most studies it is claimed that consumed alkali can be regenerated assuming a separate process and then it can be returned into the oxidation process. But generally the processes of aluminates decomposition may accompany the process of aluminum oxidation thus influencing on oxidation kinetics. And such mutual influence is not well studied yet.

The study of the aluminates decomposition directly at aluminum oxidation process is important in order to optimize the oxidation process conditions. Such optimization should be directed at the reduction of corrosive influence of alkali, at the scaling of hydrogen production method based on aluminum oxidation in aqueous medium and at the cost reduction of produced hydrogen.

Before we pose the aim of present study we want to mention about one more technique which is known to act on aluminum oxidation. It is a forced mechanical destruction of oxide film. It implies the obtaining of fresh (uncovered by oxide film) surface of aluminum and its immediate contact with oxidative environment. Such mechanical destruction can be caused by cutting, grinding, mixing, drilling or other. An example of mechanical destruction of oxide film and its influence on aluminum oxidation was demonstrated during the wet cutting of aluminum [35].

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