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Investigation of the catalytic properties in the dehydration of 1-phenylethanol in styrene process of an amorphous aluminum hydroxyl gel after its heat treatments

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Abstract. Styrene is the widely used as a monomer, which is produced by PO-technology using γ-alumina catalyst. It is mainly synthesized by the precipitation of aluminum nitrate solution by ammonia. However, amorphous aluminum compounds are formed after synthesis with pseudoboehmite, which is a precursor of the alumina. Therefore, the product of precipitation and the alumina derived by its heat treatment at the 550 and 750°C were synthesized and investigated. Starting product consists ~86 wt.% of amorphous aluminum compounds and 14 wt.% of pseudoboehmite. These substances transform into amorphous alumina from and γ-Al_2O_3 (1) after calcination at 550°C and show low catalytic characteristics in vapor-phase of 1-phenylethanol into styrene. However, after heat treatment at 750°C, when amorphous alumina transform in γ-Al_2O_3 (2), the conversion, selectivity and styrene yield increase by 10-20%.

1. Introduction

Styrene is the widely used as a monomer in the world, which is produced by PO-SM technology [1-3]. The technology includes stadiums of a propane oxide and styrene production last of which is carried out by using of zeolite or metal oxides as a catalyst. γ-alumina (γ-Al_2O_3) catalyst for the styrene production is cheapest and its precursor is obtained by different methods. There are a hydrolysis of aluminum alkoxide, a precipitation of Al-containing ions by base or hydrothermal treatment aluminum oxides and hydroxides [4-7].

The most common used method of boehmite or pseudoboehmite synthesis, which are alumina precursors, is the precipitation of aluminum nitrate solution by ammonia [8-10]. Variating of pH, temperature and time condition allows to regulate porous and surface structure properties of aluminum hydroxide. However, amorphous aluminum compounds such as an amorphous aluminum hydroxide (am-$Al(OH)_3$) and the basic aluminum salts ($Al(NO_3)_x(OH)_y$) are obtained after synthesis with main product pseudoboehmite [9,10].

Currently, the amorphous aluminum compounds have been studied poorly and they are described in a small amount of research works. However, these compounds affect the properties of γ-Al_2O_3 catalysts. The amorphous compound is reduced the filterability of the precipitation product and complicated the washing of Na, Fe, etc. ions from pseudoboehmite. It decreases styrene yield in the dehydration reaction. Also, the amorphous component has a low specific surface area due to basic aluminum salts [11]. Therefore, the manufacturing tries to reduce the amount of the amorphous component in the pseudoboehmite at the synthesis process. However, the amorphous component has a positive effect on the catalyst after some modification. In our previous works [13], we have already

shown that it is possible to improve the properties of catalyst for skeletal isomerization of n-butenes to isobutylene by transforming the amorphous component. Besides, the heat treatment at the different temperature could be formation a new binding phase after the calcination and improving catalyst properties [12].

Therefore, the purpose of our research was an investigation of the catalytic properties in the dehydration of 1-phenylethanol in styrene process of an amorphous aluminum hydroxyl gel after its heat treatments at the 550 and 750°C.

2. Materials and methods

The amorphous aluminum compound was carried out by the precipitation from 0.25 g/mL $Al(NO_3)_3 \cdot 9H_2O$ (analytically pure, according to the State standard GOST 3757-75 contains <0.004 wt.% Fe, <0.05 wt.% K + Na) solution by ammonia water (chemically pure, according to the State standard GOST 3760-79 contains <0.0001 wt.% Fe, <0.0001 wt.% Mg + Ca, <0.001 wt.% CO_3^{2-}) at pH = 6.2 and the room temperature without the stabilization and aging stages. The obtained gel-like product was centrifuged 20 min in 700 ml of H_2O 4 times to remove the ammonium nitrate formed during the precipitation. Subsequently, the sample was drying during 2 h at the 100-105°C. A precipitate with the maximum amount of basic salt was obtained.

Heat treatment was carried out at the 550°C during 3 hours (Catalyst 1) and 750°C during 2 hours (Catalyst 2).

The phase composition of the samples was determined using X-ray powder diffraction (XRPD) by a MiniFlex 600 diffractometer (Rigaku, Japan) equipped with a D/teX Ultra detector. In this experiment, Cu K_α-radiation (40 kV, 15 mA) was used and data was collected at room temperature in the range of 2θ from 2° to 100° with a step of 0.02° and exposure time at each point of 0.24 s without sample rotation. The phase concentrations were determined using the thermal analysis (TA; Netzsch STA-449C Jupiter, Selb, Germany). The TA was carried out in a way that is capable of recording the thermogravimetric (TG), derivative thermogravimetric (DTG), and differential thermal analysis (DTA) curves simultaneously. The samples were heated in the temperature range of 30-1000°C at the uniform heating rate of 10 °C/min in an argon flow. Concentrations of aluminum hydroxides were calculated from the amount of the water that was released during the aluminum hydroxides dehydration and dehydroxilation. Mass spectrometry (MS) analysis was carried out at the heating of samples at the same rate in He current using of a ThermoStar GSD 320 T gas analyzer (Pfeiffer Vacuum, Nashua, New Hampshire, USA).

The specific surface area S_{BET} (calculated with the Brunauer-Emmett-Teller method [14]) and the pore volume V (calculated by the last point of isotherm [14]) were determined using a multipurpose Autosorb-iQ analyser (Quantachrome Instruments, USA). Adsorption isotherms were obtained at −196°C (77 K) after the degassing of samples at 150°C under the residual pressure of 0.013 Pa.

The surface acidity of samples analyzed by the method of temperature-programmed desorption of ammonia (TPD-NH_3) on a flow-type instrument with a thermal conductivity detector ChemBet Pulsar (Quantachrome Instruments, USA). Before ammonia adsorption, the sample was degassed by heating up to 550°C in a helium flow. The adsorption step was carried out in a stream of ammonia for 30 min at a temperature of 100°C. The physically adsorbed ammonia was removed by helium flow at 100°C for 30 min. After analysis, the sample was cooled to room temperature in a helium flow. Temperature programmed desorption of ammonia was carried out from room temperature to 700°C at a rate of 10°C/min. Calculations of TPD-NH_3 data on the distribution of acid sites were performed according to the method that is given in the research [15].

Catalytic tests were carried out on the laboratory unit in the vapor-phase of the 1-phenylethanol into styrene at the 250°C during 300 min with feed: water vapor ratio 1:10. Feed composition includes 83.4 wt.% 1-phenylethanol, 12.5 wt.% acetophenone, 2.7 wt.% C_{9+} fraction, 0.8 wt.% C_1-C_3 fraction and 0.1 wt.% styrene.

3. Results and discussion

The diffraction pattern of starting sample (an amorphous aluminum hydroxide gel) is characterized by wide, blurred lines at angles $2\theta = 20\text{-}45°$ which are typical of the amorphous aluminum compound [4-8], and diffraction lines of psuedoboehmite (PB) (JCPDS Card 00-021- 1307) (figure 1a). The diffraction line at $2\theta = 8°$ characterizes of the aluminum complex $Al_a(OH)_b(H_2O)_c(NO_3)_d(NH_4)_e$ (JCPDSCard 01-080-7534). The starting sample is described in detail in our previous publication [15].
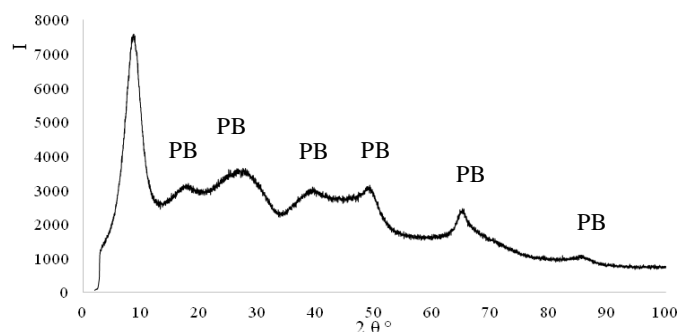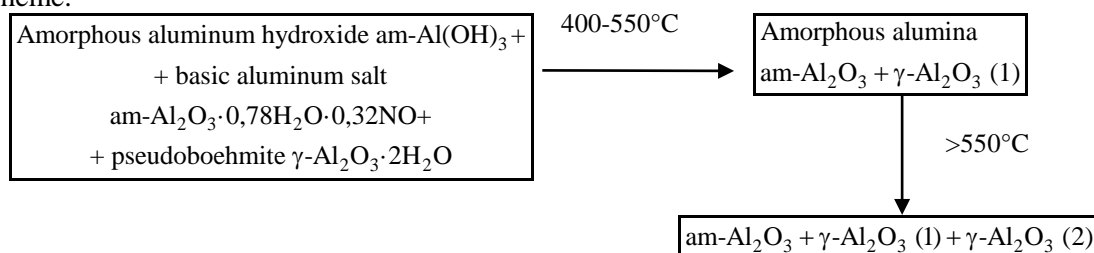

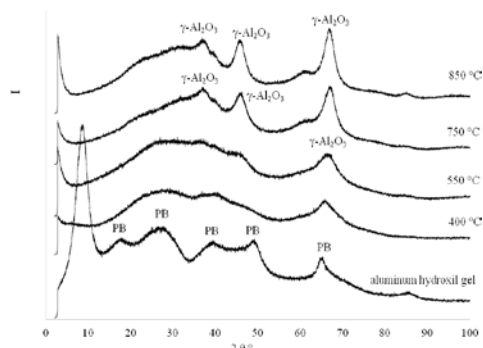**Figure 1**. Diffractogram of the precipitation product (aluminum hydroxyl gel).

According to the mass-spectrometry (MS), thermogravimetry and differential scanning calorimetry (TG-DSC), the synthesized amorphous aluminum hydroxide gel (figure 2a, b) is a mixture of 20 wt.% of amorphous aluminum hydroxide (am-Al(OH)$_3$), 66 wt.% of basic aluminum nitrate salt (Al$_2$O$_3$·xH$_2$O·yNO) and 14 wt.% of pseudoboehmite (γ-Al$_2$O$_3$·2H$_2$O) [16].

a   *b*
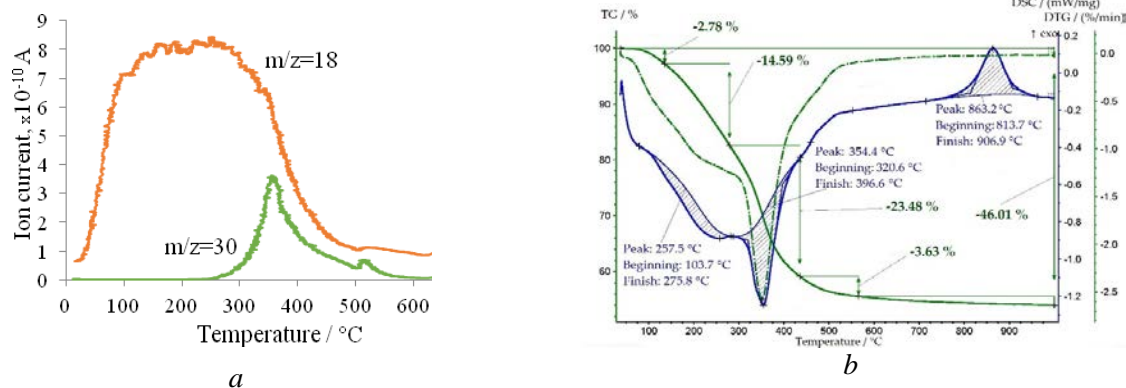
Figure 2. MS (a) and TG-DSC (б) results of starting aluminum hydroxide gel.

After heat treatment at $T = 400\text{-}550°C$ of the aluminum hydroxide gel, the aluminum basic salt and amorphous aluminum hydroxide are transformed into amorphous aluminum oxide. It is evidenced by the disappearance of the high-intensity diffraction line at an angle of $2\theta = 8°$ of the nitrogen-containing aluminum complex. The pseudoboehmite, which is also contained in the gel, forms γ-Al$_2$O$_3$ (1) which does not appear on the diffraction pattern due to its low content (10.2 wt.%) (figure 3). At the temperatures >550°C, amorphous alumina also undergoes a phase transformation in γ-Al$_2$O$_3$ (2) which is identified in diffractograms by a characteristic diffraction lines (figure 3) according to the scheme:

Amorphous aluminum hydroxide am-Al(OH)$_3$+ + basic aluminum salt am-Al$_2$O$_3$·0,78H$_2$O·0,32NO+ + pseudoboehmite γ-Al$_2$O$_3$·2H$_2$O

→ 400-550°C →

Amorphous alumina am-Al$_2$O$_3$ + γ-Al$_2$O$_3$ (1)

↓ >550°C

am-Al$_2$O$_3$ + γ-Al$_2$O$_3$ (1) + γ-Al$_2$O$_3$ (2)

Figure 3. Diffractograms of aluminum hydroxyl gel and its heat treating products.

According to the results of low-temperature nitrogen adsorption, starting amorphous hydroxyl gel is a non-porous compound which is characterized by specific surface area <0.1 m^2/g and pore volume <0.01 cm^3/g.

After heat treatment of starting amorphous gel at the 550°C during 3 h (Catalyst 1) and 750°C during 2 h (Catalyst 2), catalytic tests in the vapor-phase of 1-phenylethanol were carries out. The conversion of the Catalyst 1, which contains ~86 wt.% the amorphous alumina, is less than 40% (figure 4a). However, after increasing the temperature of its calcination to 750°C, which leads to the complete transformation of amorphous to gamma alumina, the conversion, selectivity and styrene yield values increase in ~2 times (figure 4a-c).
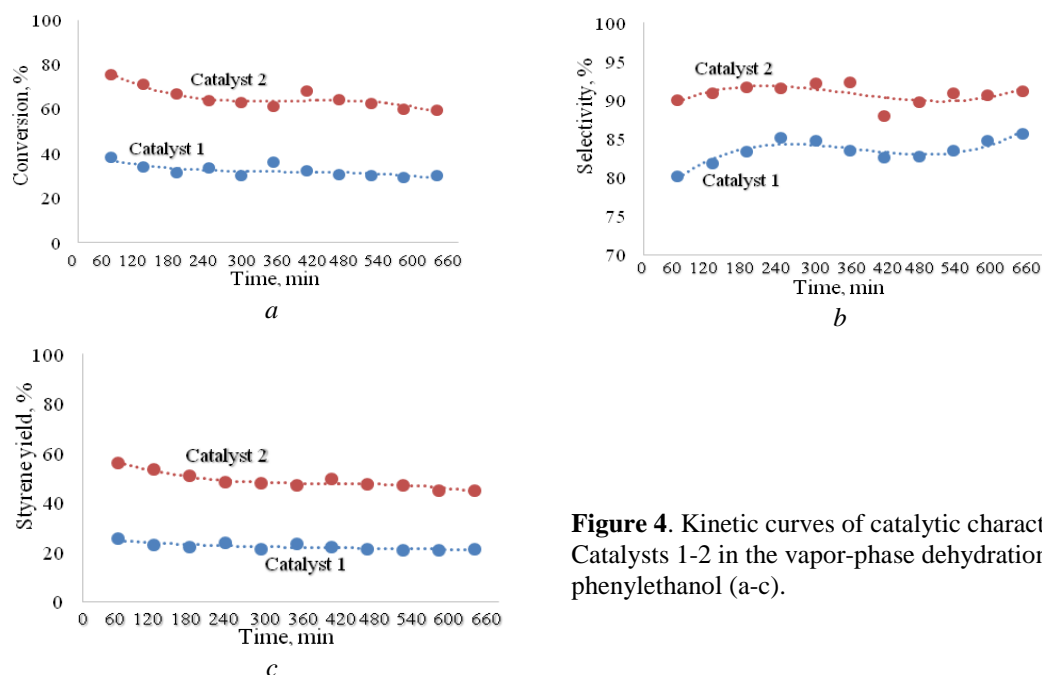
Figure 4. Kinetic curves of catalytic characteristic Catalysts 1-2 in the vapor-phase dehydration of 1-phenylethanol (a-c).

4. Conclusions

Products of the precipitation of aluminum nitrate solution by ammonia at the pH = 6.2 and alumina derived by its heat-treatment at the 550 and 750°C were synthesized and investigated. Starting product of precipitation is characterized by low specific surface area and pore volume. It consists ~86 wt.% of amorphous aluminum compounds (aluminum hydroxide and basic salts) and 14 wt.% of psuedoboehmite. These substances transform into amorphous alumina and γ-Al$_2$O$_3$ (1) after calcination at 550°C and show low catalytic characteristics in vapor-phase of 1-phenylethanol into

styrene (30% of conversion, 84% of selectivity and 21% of styrene yield). However, after heat treatment at 750°C, amorphous alumina transform in γ-Al$_2$O$_3$ (2) and the conversion, selectivity and styrene yield increase by 10-20%.

Acknowledge

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