Transformation of amorphous aluminum oxide in the catalytic dehydration reaction of aromatic alcohol

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Research Article

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Abstract

The wide use of aluminum oxides as catalysts in petrochemicals and oil refining applications necessitates determination of factors affecting the catalytic systems efficiency. However, there are no studies showing the amorphous phase effect on the composition of aluminum oxide catalysts and the catalytic performance. At the same time, the uncontrolled presence of an amorphous phase in aluminum oxide catalyst can significantly worsen the catalyst efficiency. This paper shows for the first time, the transformation of amorphous aluminum oxide during the reaction of vapor-phase dehydration of aromatic alcohol, which leads to a decrease in conversion from 88 (for fresh) to 64% (after regeneration). Crystallization of amorphous aluminum oxide by high-temperature treatment may be impractical, due to a significant decrease in the catalyst textural characteristics.

1 Introduction

The implementation of catalytic processes in petrochemicals and oil refining fields is directly related to the usage of aluminum oxides adsorbents and catalysts [1–7].

Aluminum oxides have wide range of applications due to the existence of crystalline modifications with different textural characteristics, acid-base surface properties, crystal structure and thermal stability [8, 9].

Aluminum oxides can be transformed naturally from their hydroxides using heat treatment [10, 11]. Therefore, the aluminum oxides characteristics depend on the crystal structure and morphological properties of the initial aluminum hydroxide and the preparation method. Depending on the synthesis conditions, it is possible to form crystalline (boehmite, bayerite) and amorphous phases. At the same time, the amorphous phase in most cases is concomitant and its amount is variable from a synthesis to another. This significantly affects the reproducibility of such important indicators as textural, acidic and catalytic. However, these issues are not reflected in existing studies.

The synthesis of aluminum hydroxides is based on the hydrolysis reactions of the precursor aluminum compounds. The stepwise hydrolysis of aluminum salts leads to the formation of an amorphous phase stabilized by the incomplete hydrolysis products – the basic aluminum salts. Depending on the reaction conditions, the amorphous phase can be completely or partially transformed into crystalline hydroxides. The thermal decomposition of the basic salts during the conversion of hydroxide into oxide, can lead to the formation of amorphous aluminum oxide. It is quite difficult to control the content of the amorphous phase in an industrial scale. In turn, differences in the temperatures of amorphous aluminum hydroxide and boehmite phase transformations into γ-Al₂O₃ cause phase heterogeneity in low-temperature aluminum oxide forms. The amorphous phase transformation into a crystalline phase occurs at temperatures above 700°C [12]. When aluminum hydroxides are calcined in the range from 450 to 550°C, amorphous Al₂O₃ and γ-Al₂O₃ can be obtained. Amorphous aluminum oxide and γ-Al₂O₃ characterized by different textural and acid-base properties, which decrease the reproducibility of products based on them.
This defect worsens some processes, such as selective hydrogenation of pyrolysis fractions, dehydration of alcohols and skeletal isomerization of olefins.

The content of the amorphous phase was not studied in the accompanying documentation. One of the reasons is the lack of understanding of the contribution of amorphous aluminum compounds to the performance of the catalyst. It should be considered that the amorphous phase localized in the framework of the porous system of the crystalline phase, because of thermal decomposition, provides large shrinkages for granules. Another reason is the difficulty of identifying the amorphous component. Qualitatively, aluminum hydroxide can be determined on TEM images and by the halo in the XRD patterns. Also, the weight loss value in the (200–350 °C) region from TG analysis (in the absence of bayerite) or the exo-effect of phase transformation into γ-Al₂O₃ in temperature above 700°C on the DSC curve. However, it is quite difficult to detect amorphous aluminum oxide even qualitatively in the crystalline composition. It is manifested by the signal of a penta-coordinated aluminum sites in the ²⁷Al NMR spectra in the region of 32 ppm not in all systems [13–15]. Moreover, the exoeffect in the DSC curve may not be detected in the presence of an amorphous phase which less than 50 wt. % or a broadened effect of low intensity. Earlier, we proposed a method for identifying amorphous aluminum oxide in γ-Al₂O₃ [16] and showed the effect on the structure, electronic and catalytic properties of palladium particles in aluminum-palladium catalyst [17].

The purpose of this work is to study the properties and contribution of the amorphous phase to the textural and acidic properties of the surface, as well as the catalytic characteristics of aluminum oxide. For this purpose, amorphous aluminum compounds were studied. The differences of textural and acidic characteristics, thermal stability during the catalytic reaction of phase-inhomogeneous and monophase aluminum oxide were investigated. The catalytic reaction was the vapor-phase dehydration of 1-phenylethanol to styrene.

2 Materials And Methods

The target of the research and synthesis

Samples of Al-NA and Al-IP were studied as amorphous aluminum hydroxides. The Al-NA sample was obtained in laboratory conditions by precipitation technology from solutions of aluminum nitrate Al(NO₃)₃·9H₂O (125 g/l) and an aqueous solution of NH₄OH (25 wt. %). The deposition temperature was 20°C. An ammonia solution was injected into the aluminum nitrate solution to pH = 6.1. Then the gel was filtered using a vacuum pump and washed with distilled water at room temperature. The precipitate was dried at 105 °C for 2 hours. The Al-IP sample was obtained by hydrolysis of aluminum isopropylate (IPA) in an aqueous medium at room temperature. To obtain aluminum oxides, these compounds were calcined at temperatures of 550 and 750°C (heating rate of 3°C/min) for 2 hours in muffle furnaces (ambient atmosphere).

Methods
The element composition of the samples was made using a system for CHNS/O analysis of PE 2400-II (Perkin Elmer, USA) and an iCAP Q inductively coupled plasma mass spectrometer Thermo Fisher Scientific, Germany.

X-ray diffraction (XRD) studies of the samples were performed using the MiniFlex 600 diffractometer (Rigaku, Japan) equipped with a D/teX Ultra detector. Cu Kα radiation (40 kV, 15 mA) was used and the data were 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.

Simultaneous thermogravimetry and differential scanning calorimetry (TG/DSC) analysis of the samples were performed using the thermoanalyzer STA 449F1 Jupiter (Netzsch, Germany) at the temperature range from 30 to 1000°C (10°C/min) in Pt/Rh crucible and an argon atmospheric with a total flow rate of 75 ml/min.

The specific surface area \( S \) (calculated by the Brunauer–Emmett–Teller method) and the pore volume \( V \) (calculated by the Barrett–Joyner–Halenda method) 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 distributions of pore volume over the pore diameters were obtained from the curve of desorption isotherm.

The morphology of the samples was observed with a Hitachi HT7700 Exalens transmission electron microscope (TEM). 10 µl of the suspension with sample was placed on a carbon lacy 3 mm copper grid, drying was performed at room temperature. Analysis was held at an accelerating voltage of 100kV in TEM mode.

The quantity of acid centers of the synthesized aluminum oxides was determined using the AutoChem 2950 HP analyzer. 0.5 g of the samples were loaded into a quartz reactor with the following degassing of the instrument in an electric furnace at 550°C at a rate of 10°C/min. The flow rate of carrier gas (He) was 10 ml/min. The support was saturated with a mixture of 10% NH\(_3\) in He at room temperature for 1 h. Following that, the sample was purged with argon at 100°C to remove the physically adsorbed ammonia. Desorption spectra were recorded in the temperature range from 25 to 700°C. The amount of acidic centers was quantified by dividing the temperature-programmed desorption (TPD) profiles into the following temperature ranges (T.R.) : until 250°C (weak sites), \( 250 \leq T.R. < 350°C \) (medium), \( 350 \leq T.R. < 450°C \) (strong) and \( T.R. \geq 450°C \) (very strong) [18, 19].

\(^{27}\)Al solid state NMR measurements were performed on an Avance II 500 spectrometer at a frequency of 130,32 MHz. The spectra were recorded when the samples rotated at a magic angle with a frequency of 5 kHz. A capillary with an inner diameter of 0.8 mm and an outer diameter of 1.35 mm was filled with a standard solution (0.2 mol/l AlCl\(_3\)). The inner diameter of the ampoule is 4.2 m. The temperature is 25 °C. The pulses are rectangular, with a duration of 8 microseconds and a power of 80 W (rotation angle less than 90 °), the relaxation delay is 1 s. The number of accumulations is 400–800; the spectrum width is
504.8 ppm. The spectrum was processed using digital exponential filtering with a constant LB = 3 Hz. Error of chemical shift – ± 0.05 ppm.

Catalytic tests

The process of 1-phenylethanol (PE) dehydration was performed in an isothermal reactor at 250°C in the presence of water vapor (the PE:H₂O molar ratio was 1:10) under conditions of incomplete conversion because only in this case the activities of catalysts can be compared. The temperature was maintained to within ± 5°C; the space velocity of feed was 1.5 h⁻¹; the catalyst volume was 10 cm³. The catalyst activity was evaluated from the degree of PE conversion (X) and the selectivity to styrene formation (S). The feed and products of reaction were analyzed on a chromatograph.

\[
X = \left[ \frac{\left( \sum N_{PE, feed} - \sum N_{PE, product} \right)}{\sum N_{PE, feed}} \right] \cdot 100 \% \\
S = \left[ \frac{\left( \sum N_{styrene, product} - \sum N_{styrene, feed} \right)}{\sum N_{PE, feed} - \sum N_{PE, product}} \right] \cdot 100 \% ,
\]

N – concentration of substances, wt. %.

Oxidative regeneration of the spent catalysts was carried out in a reactor at 525°C in an air atmosphere for 1 hour.

3 Result And Discussion

3.1 Morphology, textural and acidic properties of amorphous aluminum compounds

In our study, we investigated the structure of the amorphous phase and its effect on the catalytic characteristics. The amorphous aluminum compounds were obtained from precipitation of aluminum nitrate (Al-NA) and hydrolysis of aluminum isopropylate (Al-IP).

For the obtained hydroxides, there is a pronounced amorphous halo in the region of 2θ from 10 to ~ 50 ° in the XRD patterns (Fig. 1a). The diffraction lines in the small-angle region (up to 12°) (Fig. 1b) are characteristic of particles with sizes significantly exceeding interatomic distances in various kinds of dispersed systems. At the same time, for the heat-treated samples Al-NA550 and Al-IP550, the intensity of the line decreases, which is a consequence of the formation of more ordered particles and/or an increase in their size.

The Al-NA sample, according to the elemental analysis results, contains 4.5 wt. % nitrogen in the composition of basic aluminum salts. The presence of the nitrogen may cause lines in the XRD pattern; however, this set of lines does not correspond to any compound in the card of X-ray diffraction method.
The amorphous phase of Al-NA is confirmed by TEM images and diffraction pattern of slow electrons (Fig. 2a).

According to the TEM image, the Al-NA sample is a non-porous material, probably due to the filling of the porous system with basic aluminum salts. According to the low-temperature nitrogen adsorption results, the specific surface area is less than 1 m$^2$/g, and the pore volume is less than 0.01 cm$^3$/g. As the sample dehydrates at 550 °C, the decomposition of the sample promotes the release of pores and the formation of a micro- and mesoporous system, which is characterized by an adsorption isotherm of type IV (Fig. 3a).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase content</th>
<th>$S$, m$^2$/g</th>
<th>$V$, cm$^3$/g</th>
<th>Pore size distribution, cm$^3$/g (%)</th>
<th>Maximum of pore size distribution, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-NA550</td>
<td>$\text{Al}_2\text{O}_3^{\text{Am}}$</td>
<td>175</td>
<td>0.18</td>
<td>0.20, 0.01 (96, 4)</td>
<td>3.7</td>
</tr>
<tr>
<td>Al-NA750</td>
<td>$\gamma\text{Al}_2\text{O}_3$</td>
<td>113</td>
<td>0.16</td>
<td>0.18, 0.01 (95, 5)</td>
<td>3.7</td>
</tr>
<tr>
<td>Al-IP</td>
<td>$\text{Al}_2\text{O}_3^{\text{Am}}$</td>
<td>322</td>
<td>0.38</td>
<td>0.27, 0.11 (73, 27)</td>
<td>3.8</td>
</tr>
<tr>
<td>Al-IP550</td>
<td>$\text{Al}_2\text{O}_3^{\text{Am}}$</td>
<td>277</td>
<td>0.40</td>
<td>0.13, 0.27 (32, 68)</td>
<td>5.1</td>
</tr>
<tr>
<td>Al-IP550 after regeneration</td>
<td>$\text{Al}_2\text{O}_3^{\text{Am}}$ $+$ $\gamma\text{Al}_2\text{O}_3$</td>
<td>181</td>
<td>0.31</td>
<td>0.19, 0.12 (61, 39)</td>
<td>3.7, 6.2</td>
</tr>
</tbody>
</table>

The hysteresis loop of type H2 is associated with ink-bottle-shaped pores with poor connectivity and uneven pore structure [20]. The horizontal section on the desorption branch of the adsorption isotherm indicates a narrow particle size distribution. It is clearly reflected on the curve of pore volume distribution (Fig. 3b) with a maximum at 3.7 nm. The intersection of a rectilinear section of the t-plot with a positive ordinate axis is due to the presence of micropores (Fig. 3c).

For a sample based on an organic precursor, Al-IP, randomly arranged needle-like and lamellar particles with a length of ~10–15 nm and plates with sides of 8–10 nm are noticeable in the TEM image (Fig. 2b). The isotherms for Al-IP and Al-IP550 are characterized by the type IV with a hysteresis loop of mixed type H1 and H2 (Fig. 3d, g) and correlated to cylindrical and bottle-shaped pores [21]. It should be noted that
the H2 loop is not always comparable to the shape of the pores. It is determined by the size ratio of the cavity and throat pores.

The particles formation of the IPA hydrolysis product is based on the nature of the aluminum hydroxide precursor. Thus, the substitution of functional groups during hydrolysis occurs through the formation of aluminoxanes, which are boehmite-like structures with rod-shaped particles or in the form of thin plates [22, 23]. This is confirmed by the high values of the specific surface area compared to Al-NA (Table 1).

The intersection of the t-graph (Fig. 3e) with the ordinate axis is due to the presence of micropores in Al-IP. Because of the amorphous aluminum hydroxide dehydration gives amorphous oxide at 550 °C, small pores close, which is observed in a decrease in intensity and a shift of the maximum on the curve of pore volume distribution towards large values (Fig. 3h). No carbon impurities were found in aluminum oxide. The decrease in the size of the surface is due to an increase in the particles size because of the small particles aggregation.

There are 6-coordinated aluminum sites characteristic of aluminum hydroxides in the region of chemical shifts $\delta = 8$ ppm and aluminum atoms in tetra- and penta-coordination in amorphous phase at $\delta = 41-43$ and $\delta = 62-68$ ppm, respectively in the $^{27}\text{Al}$ NMR spectra (Fig. 4a, c) [12]. The peaks intensity for 4 and 5-coordinated aluminum atoms increases in the corresponding aluminum oxides (Fig. 4b, d).

The presence of highly dispersed particles in aluminum oxide Al-IP500 contributes to a high concentration of acid sites according to the NH$_3$ TPD (Table 2). Thus, the total concentration of acid sites on the surface of this sample is 3 times greater than acid sites for Al-NA550, and reaches to 653 mmol/g. The predominant amount (65%) falls on acid sites of medium strength.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Distribution of a. s., $\mu$mol/g NH$_3$/g (fraction, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weak</td>
</tr>
<tr>
<td>Al-IP550</td>
<td>151 (23)</td>
</tr>
<tr>
<td>Al-IP550 after regeneration</td>
<td>63 (25)</td>
</tr>
<tr>
<td>Al-NA550</td>
<td>99 (50)</td>
</tr>
<tr>
<td>Al-NA750</td>
<td>53 (25)</td>
</tr>
</tbody>
</table>
3.2 Thermal stability of the aluminum oxide amorphous phase under catalytic reaction conditions

It is important to take into account stability of aluminum oxide catalysts in the conditions of the catalytic process. The use of amorphous aluminum oxide Al-IP550 in the vapor-phase dehydration reaction of 1-phenylethanol showed a decrease in alcohol conversion over time (Fig. 5). The decrease in conversion was due to the partial transformation of amorphous aluminum oxide in a vapor-phase conditions into boehmite as following:

\[
2\text{Al}_2\text{O}_3^{\text{Am}} + \text{H}_2\text{O} \rightarrow 2\gamma\text{-AlOOH} + \text{Al}_2\text{O}_3^{\text{Am}}.
\]

The oxidative regeneration reaction of the contributed sample to the formation of \(\gamma\text{-Al}_2\text{O}_3\):

\[
2\gamma\text{-AlOOH} \rightarrow \gamma\text{-Al}_2\text{O}_3 + \text{H}_2\text{O},
\]

which is confirmed by the XRD pattern (PDF card 00-029-0063) (Fig. 6a).

However, the amorphous halo in the XRD pattern is still present. The textural characteristics after regeneration for the catalyst, the specific surface area and pore volume decreased by 35 and 23%, respectively (Table 1). The proportion of pores with a size of 3–5 nm has increased. The maximum appeared at 3.7 nm on the pore volume distribution, probably as a result of \(\gamma\text{-Al}_2\text{O}_3\) small particles crystallization.

Alcohol conversion for the regenerated sample decreased significantly due to the low concentration of acid sites (Table 2), which usually cause the catalyst activity. At the same time, the conversion decreases due to the phase transformation continuation of the remaining amorphous aluminum oxide.

The heat treatment for fresh Al-NA at 750°C contributed to the formation of \(\gamma\text{-Al}_2\text{O}_3\) (Fig. 6b), an increase in alcohol conversion and an increase in selectivity for styrene (Fig. 7) compared to Al-NA550. The textural characteristics and total numbers of acidic sites decrease, and the proportion of medium strength sites increases for Al-NA750 (Table 2). Despite this, the values of conversion and selectivity for the Al-NA750 sample are higher than for Al-NA550.

However, it is worth noting that the highest alcohol conversion values are observed for Al-IP550, due to the high values of specific surface area, pore volume and the acid sites concentration. Therefore, in order to create a highly efficient catalyst, it is necessary to form a monophase \(\gamma\text{-Al}_2\text{O}_3\) with optimally high textural and acidic characteristics.

4 Conclusions

The amorphous phase in the composition of aluminum oxide undergoes phase transformations during the catalytic reaction and oxidative regeneration of the catalyst. These transformations reduce the
catalytic efficiency.

Crystallization of amorphous aluminum oxide by high-temperature treatment leads to a significant decrease in textural and acidic characteristics for the surface, which also worsens the catalyst performance. The development of monophase aluminum oxide with simultaneously high values of specific surface area and pore volume remains an interested research topic.

Declarations

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**Ethics approval and consent to participate**

Not applicable.

**Consent for publication**

All authors agree with the content, gave explicit consent to submit and obtained consent from the responsible authorities at the institute where the work has been carried out.

**Availability of data and materials**

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

**Competing interests**

Conflict of interest

The authors declare that they have no competing interests.

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Mostafa Esmail Farid: Investigation, Writing – correction of the text in English

Svetlana Egorova: Supervision

Alexander Lamberov: Resources, Supervision, Project administration, Funding acquisition.

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**Figures**

**Figure 1**

XRD patterns of amorphous aluminum hydroxides Al-NA and Al-IP and their oxides
Figure 2

TEM images and SAED patterns of Al-NA (a) and Al-IP (b)
Figure 3

$N_2$ adsorption/desorption isotherms (a, d, g), pore volume distribution (b, e, h) and t-plots (c, f, i) of Al-NA550, Al-IP, Al-IP550.
Figure 4

\(^{27}\)Al NMR spectra of Al-NA(a), Al-NA550(b), Al-IP(c) and Al-IP550(d)
Figure 5

Plots of performance of the catalysts against reaction time of fresh Al-IP550 and after regeneration

Figure 6

PXRD patterns of Al-IP550 after regeneration (a) и Al-NA750 (b)
Figure 7

Plots of performance of the catalysts against reaction time of Al-NA550 and Al-NA750

Supplementary Files

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