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Research article
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Investigation of the conditions (nature) of pentacoordinated aluminum oxide formation

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Abstract: Aluminum oxide is widely used as a catalyst carrier, including in internal combustion engine systems, where operating temperatures exceed 1000 °C. As such, aluminum oxide must exhibit enhanced thermal stability. This property is linked to the presence of pentacoordinated centers on the surface of the γ-phase of Al_2O_3. This paper examines the effect of the pH during aluminum hydroxide precipitation on the formation of pentacoordinated centers on the surface of aluminum oxide. The samples of aluminum hydroxide were synthesized via controlled double-jet precipitation, followed by thermal decomposition into oxides. Precipitation was carried out at constant pH levels, and for comparison, parallel samples were synthesized at pH values of 5, 6, 7, 8, and 9. The precursors for precipitation were a 1 M aluminum nitrate solution (Al^{3+}) and a 10 wt. % ammonia solution (NH_4OH). The solutions were introduced into the reactor in a dropwise mode with continuous stirring. The resulting aluminum oxide samples were analyzed using *X*-ray diffraction and nuclear magnetic resonance techniques. The data show a direct correlation between the pH of aluminum hydroxide precipitation and the presence of pentacoordinated centers on the aluminum oxide surface: the higher the pH, the lower the content of pentacoordinated atoms. Additionally, a relationship was observed between the pH value and the size of the coherent scattering region, with an increase in coherent scattering observed at higher pH levels.

Keywords: pentacoordinated aluminum oxide, thermostability, controlled double-jet precipitation.

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Исследование условий (природы) образования пентакоординированного оксида алюминия

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Аннотация: Оксид алюминия находит широкое применение в качестве носителя катализаторов, в том числе в системах двигателей внутреннего сгорания автомобилей, где рабочие температуры достигают свыше 1000 °C, в связи с чем он должен обладать повышенной термической устойчивостью, или термостабильностью. Данный параметр связывают с наличием пентакоординированных центров на поверхности γ-фазы Al_2O_3. В настоящей работе описано влияние pH осаждения гидроксида алюминия на присутствие пентакоординированных центров на поверхности оксида алюминия. Методом контролируемого двухструйного осаждения синтезировали образцы гидроксида алюминия с его последующим термическим разложением до оксидов. Осаждение проводили при поддержании постоянного значения pH, и для сравнения были синтезированы параллели при постоянных значениях pH = 5, 6, 7, 8 и 9. Исходные реагенты для осаждения представляли собой раствор нитрата алюминия (Al^{3+} = 1 M) и раствор аммиака (10 мас. % NH_4OH). Растворы подавали в реактор в капельном режиме при постоянном перемешивании. Полученные образцы оксида алюминия исследовали методами рентгенофазового анализа и ядерного магнитного резонанса. Полученные данные свидетельствуют о прямой зависимости между значением pH осаждения гидроксидов алюминия и образованием пентакоординированых центров на поверхности получаемых оксидов алюминия: чем выше значение pH осаждения, тем меньше содержание пентакоординированных атомов. Кроме того, была обнаружена зависимость между значением pH осаждения и размерами области когерентного рассеяния – наблюдался ее рост с увеличением pH.

Ключевые слова: пентакоординированный оксид алюминия, термостабильность, контролируемое двухструйное осаждение.

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Introduction

Aluminum oxide is widely used in industry due to its highly developed specific surface area, which is significantly influenced by the synthesis method and conditions [1—13]. Aluminum oxide powder is a key component of automotive catalysts, serving as a carrier for precious metal particles on its surface [7—9; 11]. For automotive catalysts, aluminum oxide powders must exhibit a stable structure, high specific surface area, and developed porosity, while being resistant to extreme operating temperatures up to 1100 °C. These properties largely depend on the presence of pentacoordinated aluminum oxide atoms (Al^V), also known as penta-centers [13—17].

Precipitation is the most common method for synthesizing pentacoordinated aluminum oxide due to the process's simplicity from a technological perspective. Aluminum salt solutions are often used as the precursor, with the choice of precipitant solution depending on the pH. A specific case is the controlled double-jet precipitation (CDJP) method, where the process is conducted at a constant pH with discrete dropwise addition of solutions into the reactor. After precipitation, the resulting suspension undergoes various processing steps, including filtration, drying, and calcination, producing aluminum oxide [18; 19].

The calcination temperature significantly affects the structure of the resulting oxide [18]. For instance, low-temperature phases of aluminum oxide form at temperatures up to 700 °C, while high-temperature phases form at temperatures above 700 °C [20].

Particular attention is given to the γ-phase of aluminum oxide, which is a metastable, transitional, structurally polymorphic form [21—26]. The bulk and surface structures of γ-aluminum oxide, along with its formation and thermal stability, have been the subject of numerous studies [21—26]. However, due to the low crystallinity and corresponding small particle size of γ-aluminum oxide, traditional analytical methods for determining its surface structure are significantly limited.

Several authors have reported that pentacoordinated Al^{3+} atoms are present on the surface of the γ-phase of aluminum oxide [13—17], which affect the material's thermal stability by interacting with the catalytically active phase. The detection of coordination centers (tetra-, penta-, or octa-) is possible using nuclear magnetic resonance (NMR).

It should be noted that the literature lacks data on the influence of the synthesis pH on the formation of pentacoordinated centers, as well as on the relationship between the presence of pentacoordinated centers and the crystallite characteristics of aluminum oxide obtained at various pH levels.

The aim of this study is to investigate the effect of the synthesis pH of aluminum hydroxide on the formation of pentacoordinated Al^{3+} atoms in its oxide.

Materials and method

Controlled double-jet precipitation of aluminum hydroxides at constant pH in batch mode was selected as the synthesis method for the samples. After precipitation, the samples were dried and calcined, resulting in aluminum oxide.

The synthesis of the samples was conducted as follows: aluminum nitrate and ammonia solutions were added dropwise while maintaining a constant pH throughout the precipitation process. The selected pH values were 5, 6, 7, 8, and 9.

The concentrations of the precipitation solutions were as follows: $C(Al^{3+})$ = 1 M and 10 wt. % NH_4OH. To produce 100 g of aluminum oxide, 2 L of aluminum nitrate solution was used. The process was carried out at room temperature, with the stirrer set at 500 rpm, and aluminum nitrate solution was fed at a rate of 10 mL/min. Drying was conducted in an oven for

4 h at 130 °C. The thermal treatment involved heating at a rate of 500 °C/h to 500 °C, holding at 500 °C for 4 h, followed by cooling in the furnace to room temperature.

After synthesis, the content of pentacoordinated aluminum oxide atoms was determined by nuclear magnetic resonance (NMR), and the values of the coherent scattering region (CSR) were calculated after conducting *X*-ray phase analysis.

^{27}Al NMR spectra were recorded at room temperature using an "Agilent VNMR 400" pulsed spectrometer (USA) at a frequency of 104.23 MHz with magic angle spinning (MAS). The rotor spinning frequency was 10 kHz. The spectra were processed using the "Dmfit" program.

The phase composition of the samples was determined using *X*-ray diffraction analysis. Measurements were performed over angles ranging from 10° to 80°. The *X*-ray patterns were processed using the "OriginPro" software, with baseline subtraction and smoothing of the peaks.

Results and discussion

The obtained nuclear magnetic resonance (NMR) results are presented in Fig. 1. Data are shown for the two samples that differ most significantly in terms of penta-center content, synthesized at pH = 5 and pH = = 9. The samples were labeled accordingly. NMR spectrum analysis revealed that the sample labeled pH = 9 does not have pentacoordinated aluminum atoms on its surface, as indicated by the absence of the corresponding peak. In contrast, the sample labeled pH = 5 is characterized by the presence of a peak, which corresponds to the presence of pentacoordinated centers.

Figure 2 presents the *X*-ray diffraction patterns for the same samples. The *X*-ray diffractograms show that the degree of crystallization of the samples varies depending on the pH of the precipitation, and all samples consist of γ-Al_2O_3 (JCPDS, 10-0425). No impurities of aluminum hydroxide or high-temperature phases of aluminum oxide were detected. As the precipitation pH increases, a decrease in peak width at half maximum is observed, indicating an increase in crystallite size. The *X*-ray diffractograms of the sample at pH = 9 are characterized by sharp peaks, with the pH = 9 sample exhibiting higher crystallinity than the pH = 5 sample. Additionally, the pH = 5 sample shows the highest number of defects.

The crystallite sizes of the aluminum oxide samples were calculated using the Scherrer method. It was found that the crystallite size increases with the rise in the pH

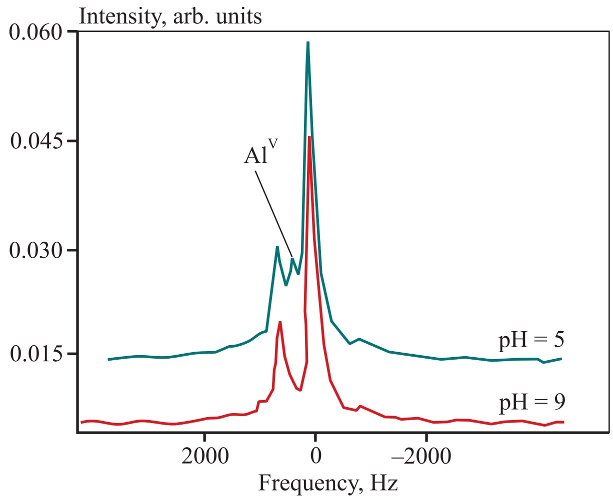

Fig. 1. NMR spectra of aluminum oxide samples

Рис. 1. ЯМР-спектры образцов оксида алюминия

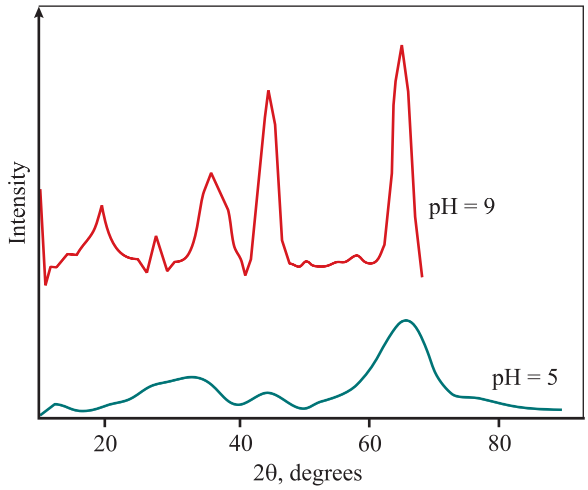

Fig. 2. XRD diffractograms of aluminum oxide samples

Рис. 2. Рентгенограммы образцов оксида алюминия

of the precipitation process. The data obtained are presented below:

Sample	Al-5	Al-6	Al-7	Al-8	Al-9
Size, nm	1,17	1,71	2,52	3,31	3,67

Based on the research results, correlations were established between the pH values of the precipitation and the proportion of pentacoordinated Al^{3+} atoms, as well as the size of the coherent scattering region (CSR). A dependence of the studied parameters on the pH of precipitation was demonstrated: the proportion of pentacoordinated Al^{3+} atoms decreases with increasing synthesis pH (Fig. 3), while the crystallite size, on the other hand, increases (Fig. 4).

The sample labeled pH = 5 exhibits the highest number of defects and the greatest proportion of pentacoordinated aluminum atoms, while the sample labeled pH = 9 is characterized by the fewest defects and a significantly lower content of pentacoordinated atoms. Overall, as the pH of precipitation and the size of the CSR increase, the content of penta-centers in aluminum oxides decreases significantly.

Conclusion

The study demonstrated that the pH of aluminum hydroxide precipitation has a substantial effect on the content of pentacoordinated atoms in the resulting oxides. As the pH of precipitation and the size of the CSR increase, the proportion of pentacoordinated atoms on the surface of aluminum oxide decreases. These findings can be applied in further research into the mechanism of pentacoordinated atom formation on the surface of aluminum oxide, which holds practical value in the production of catalyst supports and adsorbents.

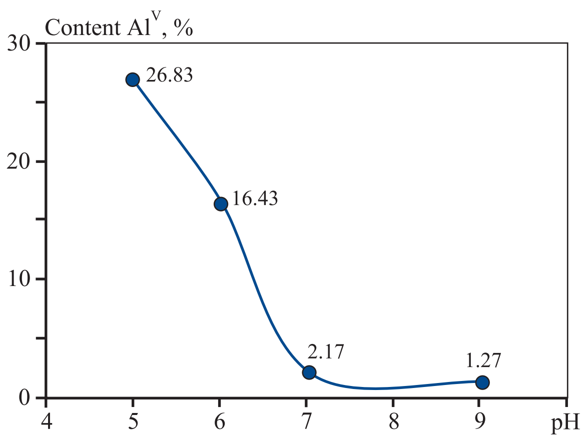

Fig. 3. Correlation between pH value and Al^V content

Рис. 3. Корреляция между значением pH и содержанием Al^V

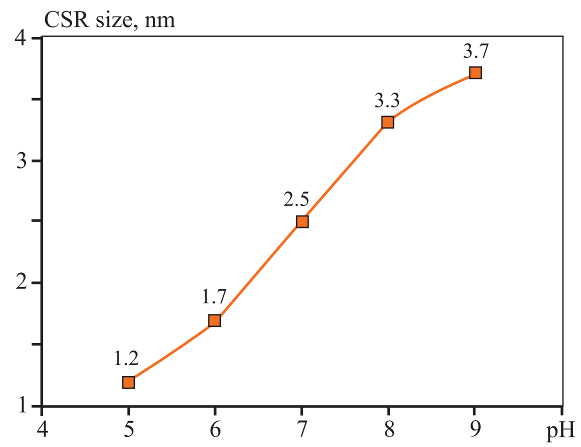

Fig. 4. Correlation between pH value and CSR size

Рис. 4. Корреляция между значением pH и размерами ОКР

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V.N. Rychkov – participation in the discussion of results, consulting.

G.V. Ginko – synthesis of samples at a constant pH = 5, 6, 7, and 8.

T.E. Telegin – synthesis of samples at a constant pH = 9.

M.V. Ugrumova – analysis of the synthesized samples.

Вклад авторов

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Г.В. Гинько – синтез образцов при постоянном pH = 5, 6, 7 и 8.

Т.Е. Телегин – синтез образцов при постоянном pH = 9.

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