

Review

# A Review on the Role of Amorphous Aluminum Compounds in Catalysis: Avenues of Investigation and Potential Application in Petrochemistry and Oil Refining

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**Abstract:** Aluminum oxides and hydroxides are widely applied because of the great variety of their modifications. In particular, aluminum oxides and hydroxides are used in petrochemistry and oil refining. However, amorphous aluminum compounds have not been sufficiently studied due to the complexity of their synthesis and the problems encountered during their study. The study of amorphous aluminum compounds is hindered by the ambiguity of terminology. In this work, the structures of amorphous aluminum compounds prepared by different methods and the properties that determine their applications have been highlighted in detail. Amorphous aluminum compounds play both positive and negative roles in petrochemistry; however, in petroleum refining, amorphous compounds (without promoters and transition metal salts) demonstrate a promising catalytic performance in oil upgrading.

**Keywords:** heavy oil; asphaltenes; amorphous alumina; amorphous aluminum hydroxide; amorphous aluminum gel



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## 1. Introduction

Aluminum oxide is widely used in the global petrochemical industry due to the diverse physical and chemical properties of its surface formed during synthesis. It is an adsorbent-catalyst and also a catalyst support for various petrochemical and oil refining processes [1–8]. Alumina is used as a support for oxide catalysts applied in the neutralization of industrial emissions, as well as in hydrogenation, hydrogenolysis, reforming, and hydrotreating catalysts, where the active components are Cr, Mo, Ni, W oxides or metals (Pt, Pd, Ni, etc.) [2–4,6,7]. In the hydrogenation processes, in case of nickel catalysts, the thermal stability of alumina increases up to 600–700 °C which significantly expands the range of its applications [5].

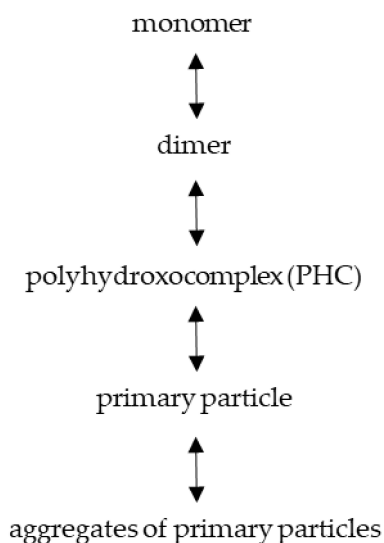
The supports in the composition of hydrotreating catalysts act not only as inert diluent, but also participate in the formation of active phases. Moreover, the supports serve as structural promoters that create specific porous structures—optimum for the processing of the certain crudes [3]. So far, various materials with high specific surface area have been used as supports for hydrotreating catalysts, such as activated carbon, aluminosilicates, silica gel, oxides of Mg, Ti and other metals, and zeolites. However,  $\gamma$ -alumina is considered as an effective catalyst support that provides a combination of high performance and selectivity of hydrotreating processes. The supports have significant influence on the properties of the catalysts, and modification of the supports can improve the potential and efficiency of the catalysis [4]. The widespread use of  $\gamma$ -alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) is due to the different surface properties, which depend on the synthesis conditions of aluminum oxide.

The synthesis of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and its crystalline precursors—boehmite (Bm) and pseudo-boehmite (Pb)—are well studied because they have been known for ages. In industry,

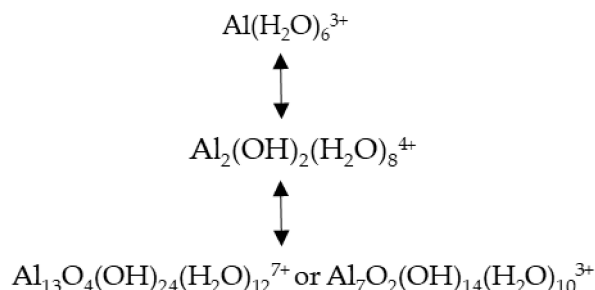
the synthesis of monohydroxides is mainly carried out by the hydrolysis of organic and inorganic aluminum salts, the sol-gel technology (hydrolysis of aluminum alcoholates), and the precipitation of hydroxides from Al-containing acidic solutions by base. However, all boehmite and pseudoboehmite synthesis methods yield amorphous aluminum compounds, which are the products of incomplete hydrolysis. During calcination, amorphous aluminum compounds are transformed into alumina with a disordered structure (amorphous alumina), the stability of which under the conditions of a catalytic reaction and regeneration is poorly studied. At the same time, the properties of amorphous alumina (am- $\text{Al}_2\text{O}_3$ ) are very different from the properties of crystalline  $\gamma\text{-Al}_2\text{O}_3$ . If the alumina precursors contain amorphous compounds, part of the alumina becomes unpredictable during catalytic reactions, which leads to the nonreproducibility of the catalytic properties and, consequently, to the loss of its efficiency. Therefore, amorphous aluminum is considered an undesirable compound in the petrochemical industry. However, the selective synthesis and modification of amorphous aluminum compounds can yield a new type of non-crystalline water-soluble catalyst. Amorphous aluminum compounds, like all compounds with an amorphous structure, have a high reactivity. Gelatinous structures of aluminas open up new application potentials. Such catalysts modified with cobalt salts can be applied in petroleum refining, particularly for upgrading of heavy oil and natural bitumen [9]. This review paper examines some aspects of the amorphous aluminum compounds, unique properties and methods of synthesis, the influence of amorphous aluminum compounds on catalysis of various processes (hydrothermal treatment of catalyst precursors particularly), and the role of amorphous aluminum compounds in petrochemistry and their potential application in oil refining. The aim of this review is to summarize the current state of research on amorphous aluminum compounds in the field of catalysis, to highlight the problems encountered in their study, and to consider possible applications of them in petroleum refining.

## 2. Some Aspects of the Synthesis of Amorphous Aluminum Compounds: Unique Properties and Problems of Study

Amorphous aluminum hydroxide has a disordered structure and a large intrinsic volume due to the high content of water ( $\text{H}_2\text{O}/\text{Al}_2\text{O}_3 \geq 3$ ). It is finely dispersed, the particle size of which does not exceed 0.3 nm [10]. The disordered structure of amorphous aluminum hydroxide can be formed by the interaction of Al (III) ions during the precipitation of condensed aggregates. The formation of amorphous precipitates consists of the following stages:



In this case, the structure of the short-range order of the amorphous precipitates can be very different depending on the condition, which can form primary particles of two types [11]:



where the minimum sizes reach 1.2–1.6 nm.

In literature, aluminum hydroxide is usually described as amorphous phase [5–11]. However, there are some organic and inorganic aluminum salts, which contain radical ( $R^-$ ) and acidic ( $A^{-y}$ ) residues ( $\text{Al(OH)}_l(\text{OR})_m$  or  $\text{Al(A)}_x(\text{OH})_y$ ) in their structure. They replace one or more hydroxyl groups in aluminum trihydroxide [12,13]. Hence, it is important to distinguish the influence of amorphous alumina hydroxide and its main salts on the characteristics of amorphous alumina compounds.

There are many methods for the synthesis of aluminum hydroxides, such as mechanochemical and thermochemical activation, precipitation, calcination of aluminum salts, hydrothermal treatment of aluminum oxides and hydroxides, and hydrolysis of organoaluminium compounds. Each method has its own advantages and disadvantages, which are described in detail in numerous scientific papers [1–14]. However, the problem of formation of amorphous alumina compounds, which inevitably arise during the synthesis by all the given methods except hydrothermal treatment, has not yet been sufficiently investigated. It is well known [12,13] that amorphous aluminum compounds decrease the permeability of precipitates and the washing of aluminum hydroxides from catalytic poisons. Moreover, they unpredictably affect the properties of the alumina catalyst due to the lack of data about their thermal stability and other properties. Therefore, the study of aluminum hydroxides with emphasis on the formation of amorphous aluminum compounds is of great scientific interest.

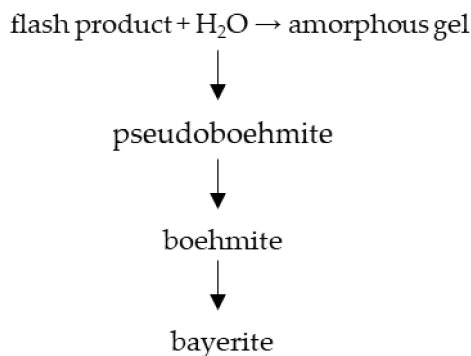
### 2.1. Mechanochemical Activation (MCA), Thermochemical Activation (TCA), and Thermal Centrifugal Activation (CTA)

Pulse activation methods such as mechanochemical activation (MCA), thermochemical activation (TCA), and thermal centrifugal activation (CTA) are widely used for the synthesis of alumina supports and catalysts [15,16]. The common characteristic of all activation methods is a short exposure time on the initial aluminum hydroxide (1–1.5 s), the aim of which is to destroy its crystal structure and form X-ray amorphous products (amorphous phase). The phase transformations during mechanical and chemical activation are due to high pressure and temperature or significant heating of the whole system during grinding [15]. The dehydration of the activation products occurs at lower temperatures than dehydration of the initial substances due to the destruction of the three-dimensional structure. However, mainly  $\chi\text{-Al}_2\text{O}_3$  oxides without  $\gamma\text{-Al}_2\text{O}_3$  impurities are formed from X-ray amorphous aluminum oxides during calcination of mechanical and chemical activation products. That is also accompanied by certain disadvantages, such as high energy consumption and poor resulting products [16].

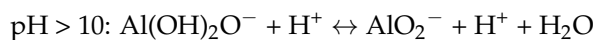
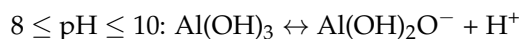
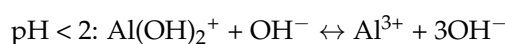
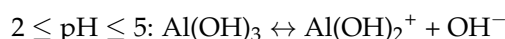
The amorphous aluminum hydroxide obtained by heating of gibbsite (aluminum trihydroxide) at high speed owing to thermo-chemical activation and followed by rapid cooling is highly reactive. The structural elements are close to initial hydroxide (gibbsite), but the composition is similar to that of alumina. The flash product of thermochemical activation (TCA product) calcined at 400 °C is an amorphous aluminum hydroxide with a

small amount of crystallized boehmite. Increasing the processing temperature  $> 600\text{ }^{\circ}\text{C}$  promotes crystallization of the amorphous component, which transforms into  $\eta\text{-Al}_2\text{O}_3$ , and  $\chi\text{-Al}_2\text{O}_3$  at  $T > 900\text{ }^{\circ}\text{C}$  as well [16]. The content of amorphous aluminum hydroxide exceeds 50%wt. of CTA product. It appears on the DSC curves as an exothermic reaction in the high temperature range (peak temperature  $800\text{--}810\text{ }^{\circ}\text{C}$ ) due to its crystallization into high-temperature aluminum oxides [17]. The thermal treatment of the CTA-product at  $400\text{ }^{\circ}\text{C}$  promotes its crystallization into  $\gamma\text{-Al}_2\text{O}_3$ , the amount of which increases with temperature. The low-temperature forms of aluminum oxides are related to the size and shape of the primary particles and the way they docked. The similarity of the CTA-product structure to  $\gamma\text{-Al}_2\text{O}_3$  indicates specific structural changes of the gibbsite during its nonequilibrium treatment. However,  $\gamma\text{-Al}_2\text{O}_3$  product contains a critical amount of  $\text{Na}_2\text{O}$  for the catalyst and a large particle size ( $\sim 80\text{ }\mu\text{m}$ ), which complicates its formation, as in the case of the TCA product. In this context, the products of thermochemical and centrifugal-chemical activation were hydrated in order to obtain pseudoboehmite (aluminum mono-hydroxide) and reduce the amount of undesirable impurities.

The hydration of the TCA product was carried out by hydrothermal treatment method or at atmospheric pressure, and depending on the temperature, time, and pH of the medium, was carried out according to the scheme [17]:



Depending on the pH of the medium, ionization of molecules occurred as follows [17]:



If hydration is carried out in alkaline medium, Bayerite or gibbsite (aluminum three-hydroxides) may be formed. Pseudoboehmite can be obtained under hydrothermal conditions in an acid medium ( $\text{pH} = 1.5\text{--}3.5$ ). Even in case of maximum pseudoboehmite content, up to 20%wt. of the amorphous phase still remains in the composition of hydrothermal products, which is explained by the absence of phase homogeneity of alumina oxides [17].

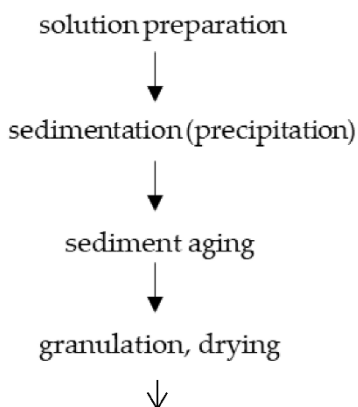
Activation products have certain advantages, such as the possibility of excluding “wet” operations from the technological scheme, but at the same time have a number of similar disadvantages. The most important one is a high heterogeneity of phases, largely due to the complexity of the impulse impact (significant parameters in the activation conditions).

## 2.2. Precipitation Method

Precipitation is one of the widely used methods of obtaining aluminum hydroxides, which are used for the production of alumina supports and catalysts ( $\gamma$ - and  $\eta\text{-Al}_2\text{O}_3$ ) [18–29]. It is well known that acid (nitrate) and alkaline (aluminate) methods of precipitation have great practical importance, and as a result of which it is possible to synthesize crystalline hydroxides such as bayerite, pseudoboehmite, or boehmite. The

acid method is carried out by precipitating aluminum salts from acid solutions with base solutions and the alkaline vice versa. However, in case of aluminate method, significant concentration of Na is observed in the products as aluminum hydroxide is precipitated from sodium aluminate ( $\text{NaAlO}_2$ ). Na poisons the alumina catalysts, and hereby a large number of flushing operations are required. Thus, acid precipitation method is usually preferred to obtain aluminum hydroxide.

The precipitation method consists of the following steps. Each step has a certain effect on the physical and chemical properties of the synthesized aluminum hydroxide [21,22]:



The determining characteristics of the products are precipitation, aging, and washing stages. The conditions of precipitation have a great influence on the phase composition, which was evaluated by the pH value, temperature, concentration of solvents, and their mixing rate. The aging time determines crystal sizes and porosity of aluminum hydroxide [21].

Aluminum salts and alkali aluminates dissolved in water are easily hydrolyzed and then condensed. Therefore, mono-, di-, and polymeric aluminum ions such as  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  or  $\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}$ ,  $\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8^{4+}$ ,  $\text{Al}_8(\text{OH})_{20}(\text{H}_2\text{O})_x^4$ , or  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  can be found in solution [21]. At the same time, authors [23] show that formation of crystalline aluminum hydroxide is determined by the structure of amorphous polyhydroxo-complex (crystallization precursor) produced during the hydrolysis of aluminum salts at the precipitation stage. Thus, boehmites or pseudoboehmites are formed from  $\text{Al}_7\text{O}_2(\text{OH})_{14}(\text{H}_2\text{O})_{10}^{3+}$  and bayerites with boehmites impurity are formed from  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  (Table 1) [21].

**Table 1.** Influence of precipitation conditions (pH, T, and  $\tau$ -aging duration) on the phase composition of the products and their morphology [20]. Copyright Elsevier, 2021.

Initial Compounds	Precipitation Conditions			Morphology	Phase Composition
	pH	T, °C	$\tau$ , h		
$\text{Al}(\text{NO}_3)_3$	7	20	0	spheres irregular shape	amorphous phase
	7	70	1	small spheres	pseudoboehmite
	7	70	36	needles	pseudoboehmite
$\text{NaAlO}_2$	7	70	100	needles	pseudoboehmite
$\text{Al}(\text{NO}_3)_3$	11	20	96	rods and prisms	bayerite
$\text{NaAlO}_2$	11	20	100	rods and prisms	bayerite

Initially, small particles of amorphous phase with the size of 0.3 nm are formed on the stage of precipitation at low pH values and temperatures. Pseudoboehmite needles (aluminum mono-hydroxide) are formed with increasing temperature and pH. The length of chains reaches up to 60–100 nm. In case of high pH values and room temperature, the main

precipitation product after transformation of amorphous phase more than 50%wt. is a large rod of bayerite (200 nm) with pseudoboehmite impurity, the amount of which decreases with increasing aging time [20]. During the aging process, oriented accretion of many primary particles occur, as a result of which the outer surface of the given intergrowths forms the inner surface of aluminum hydroxides.

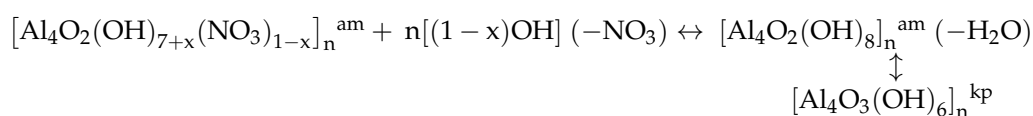
In case of bayerite formation, the structural elements are high order particles, which can be visually observed by electron microscope [7,10,19]. The duration of aging, which also leads to washing of the aluminum hydroxides from impurity ions, determines the size of the crystals and the porous structure of the obtained hydroxides. The synthesis of pseudoboehmite and boehmite is carried out mainly by nitrate-ammonia technology in continuous precipitation mode. Then, the obtained products are used for the synthesis alumina supports and catalysts. In the continuous precipitation mode, all the parameters of the system remain constant because of the installation, where the product is constantly drained from the buffer solution. It provides enhancement in the surface of aluminum hydroxide by reducing aging of the formed precipitates in mother liquor.

Aluminum hydroxides obtained just after precipitation (without aging) and washed out from the soluble ammonium nitrate salts contain up to 20%wt. nitrates, which are considered in the structure of the main salts  $(OC) Al(NO_3)_x(H_2O)_y$ . The content of main salts decreases with increasing pH, temperature, and aging time.

In all cases, hydrolysis can be divided into three steps [20]. At the first step, upon reaching a required condition (pH = 6 and a temperature of 20 °C), a stable basic salt with amorphous structure  $Al_2O_3 \cdot 1.75H_2O \cdot 0.5NO_3$  or  $Al_4O_2(OH)_7(NO_3)$  is formed when the solutions of ammonia and aluminum nitrate are drained. The given amorphous structures are rapidly hydrolyzed with raising pH up to 11 and temperature above 50 °C, where the content of  $NO_3^-$  in its structure is significantly reduced—from 19 to 0.6%wt.



In the second step, the amount of main salts can remain constant at room temperature as long as the pH is low. At pH > 9 the amount of  $OH^-$  ions (x) and the depth of hydrolysis increases, while the amount of  $NO_3^-$  is further reduced. At temperatures < 50 °C and prolonged aging the third stage initiates, where the system loses its stability and complete hydrolysis occurs, i.e., initiation of hydroxide crystallization:



At  $T > 50$  °C hydrolysis is carried out immediately after the first stage, i.e., the amount of main salts in the precipitates is not stabilized [1,3,21]. The existence of the second stage of hydrolysis, i.e., the stability of the main salts under certain conditions in the precipitate is explained by the fact that the structure of the main salts  $[Al_4O_2(OH)_{7+x}(NO_3)_{1-x}]_n^{am}$  is in equilibrium with the amorphous hydroxide  $[Al_4O_2(OH)_8]_n^{am}$  in the first stage of hydrolysis. It maintains its structure until the concentration of  $[Al_4O_2(OH)_8]_n^{am}$  in the sediment is constant and equal to the concentration of hydroxyl ions in the environment [1,2,5,15,22]. At the same time, the depth of polymerization is increased, forming one or another crystalline aluminum hydroxide. The processes of hydrolysis and polymerization at the stage of precipitation are carried out simultaneously, as a result of which the achieved precipitate of aluminum hydroxide will contain a certain amount of the main salts (Table 2) [15]. Crystallization begins in case of high hydrolysis degree. Therefore, initiation of the process requires dehydration of 20–40%wt. of amorphous alumina hydroxide, while there is no need in complete hydrolysis of the main alumina salts.

**Table 2.** Chemical and phase composition of aluminum hydroxides obtained under different precipitation conditions [15]. Copyright Springer Nature, 2021.

pH	Aging, h (hour)	Chemical Composition	Phase Composition
6	0 or 240	$\text{Al}_2\text{O}_3 \cdot 1.77 \text{H}_2\text{O} \cdot 0.50 \text{NO}_3$	Amorphous
7	0 or 100	$\text{Al}_2\text{O}_3 \cdot 1.80 \text{H}_2\text{O} \cdot 0.35 \text{NO}_3$	Amorphous
9	0	$\text{Al}_2\text{O}_3 \cdot 2.00 \text{H}_2\text{O} \cdot 0.15 \text{NO}_3$	Amorphous
	20	$\text{Al}_2\text{O}_3 \cdot 1.60 \text{H}_2\text{O} \cdot 0.02 \text{NO}_3$	Boehmite
	70	$\text{Al}_2\text{O}_3 \cdot 2.20 \text{H}_2\text{O}$	Boehmite/Bayerite
10	0	$\text{Al}_2\text{O}_3 \cdot 2.00 \text{H}_2\text{O} \cdot 0.06 \text{NO}_3$	Amorphous
	1.5	$\text{Al}_2\text{O}_3 \cdot 1.80 \text{H}_2\text{O} \cdot 0.05 \text{NO}_3$	Boehmite
	70	$\text{Al}_2\text{O}_3 \cdot 2.40 \text{H}_2\text{O}$	Boehmite/Bayerite
11	0	$\text{Al}_2\text{O}_3 \cdot 2.00 \text{H}_2\text{O} \cdot 0.01 \text{NO}_3$	Amorphous
	3	$\text{Al}_2\text{O}_3 \cdot 1.70 \text{H}_2\text{O} \cdot 0.003 \text{NO}_3$	Boehmite
	70	$\text{Al}_2\text{O}_3 \cdot 2.50 \text{H}_2\text{O}$	Boehmite/Bayerite

Hydrolysis of the main salts does not end at the precipitation formation stage, but continues during washing stage. Hence, the industrial precipitation product in addition to crystalline aluminum hydroxide usually contains amorphous aluminum compounds, main salt, and amorphous aluminum hydroxides [5,15,22,30] (Table 3).

**Table 3.** Phase composition of industrial aluminum hydroxides and the obtained textural characteristics of aluminum oxides [5,15,22,30], where Pb—pseudoboehmite, Gb—gibbsite, Br—bayerite, Am—an amorphous aluminum compound (S—specific surface area, V—total pore volume, D—pore diameter).

Mode of Production	Phase Composition, %			S, m <sup>2</sup> /g	V, sm <sup>3</sup> /g	D, nm
	Pb	Gb (Br)	Am			
Aluminate-nitrate (Angarsk)	85	5	10	255	0.58	4.6
Nitrate (Novokuibyshevsk)	95	15	-	190	0.36	7.7
Nitrate (Ryazan)	100	-	-	240	0.45	3.8
Aluminate-sulfate (Angarsk)	70	15	15	247	0.60	4.8
Aluminate-sulfonic acid (Omsk)	75	10	15	220	0.58	5.3

The formation of pseudoboehmite is carried out by dehydration of amorphous aluminum hydroxide due to condensation and polymerization processes in which water is released from a highly hydrated gel. However, the formation of bayerite occurs through the dissolution of pseudoboehmite, where the limiting stage is its nucleation [15,30].

The amorphous aluminum compounds obtained by precipitation methods are currently poorly studied. However, they strongly influence the porous properties of the resulting aluminum hydroxide surface. The authors [31] have shown that an intense decrease in the specific surface area was observed with an increase in the content of  $\text{NO}_3^-$  in the structure of the main salts. Amorphous basic aluminum salts have a specific surface area (S) of 5–10 m<sup>2</sup>/g. The reason for this is the coalescence of the primary particles during drying with the formation of large secondary aggregates, the size of which increases with increasing the content of  $\text{NO}_3^-$  groups. Therefore, the specific surface area is determined only by the outer surface of the aggregates [31,32]. With increasing hydrolysis degree of the main aluminum salt in the precipitate, the specific surface area increases to a maximum value, which is characteristic for the given pH and temperature. The maximum specific surface area corresponds to the minimum amount of  $\text{NO}_3^-$  in the composition of the precipitates and reaches 500 m<sup>2</sup>/g. The size of obtained particles is ~4 nm. The decrease in the surface area with the increase in the content of the main salts in the composition of the

precipitates is not only because of the primary particle sizes, but also due to their accretion, which makes the surface inaccessible to the molecules of adsorbed gas [15].

The study of amorphous aluminum compounds by physical and chemical methods is complicated because of their disordered structure. Thus, the diffraction patterns of amorphous aluminum compounds are usually characterized by a broad halo in the range of  $2\theta$  20–40° [33,34]. At the same time, the authors [34] pointed out a diffuse intense peak at  $2\theta = 8^\circ$ , which appears in the diffractograms of the gel-like precipitated products using nitrate-ammonia technology at a low pH = 5. Moreover, infrared spectroscopy (IR) identifies amorphous aluminum compounds by broad absorption bands of the deformation vibrations Al-O of a hexacoordinated aluminum atom in an oxygen environment ( $\text{AlO}_6$ ) and OH-groups at 530–570 and 3470  $\text{cm}^{-1}$ , respectively [35–40].

The phase transformations of amorphous aluminum compounds during thermal decomposition differ from the transformations of crystalline hydroxides by the intermediate stage—a formation of stable phase of amorphous alumina before crystallization into  $\gamma\text{-Al}_2\text{O}_3$  [33,34]. However, the temperature ranges of phase transitions from amorphous aluminum compounds into amorphous oxide and further into  $\gamma\text{-Al}_2\text{O}_3$  have not been clearly determined. Thus, it was shown in [33] (Table 4) that amorphous aluminum hydroxide and basic salt transformed into amorphous alumina at temperatures above 400 °C, which remains stable up to 750 °C. The stability of the amorphous structure of the oxide is due to the presence of residual acid anions (e.g., nitrates) in the samples, which stabilizes it.

**Table 4.** Thermal decomposition of amorphous aluminum compounds (S—specific surface area) [33,34].

$T_{\text{calcination}}, ^\circ\text{C}$	Phase Composition	S, $\text{m}^2/\text{g}$	Content of $\text{NO}_3^-$ , %
400	Amorphous oxide	80	4.0
700	Amorphous oxide	80	1.0
750	$\gamma\text{-Al}_2\text{O}_3$	60	<0.1
800	$\eta\text{-Al}_2\text{O}_3$	60	–
1000	$\eta$ - + traces $\alpha\text{-Al}_2\text{O}_3$	50	–
1100	$\alpha\text{-Al}_2\text{O}_3$	10	–

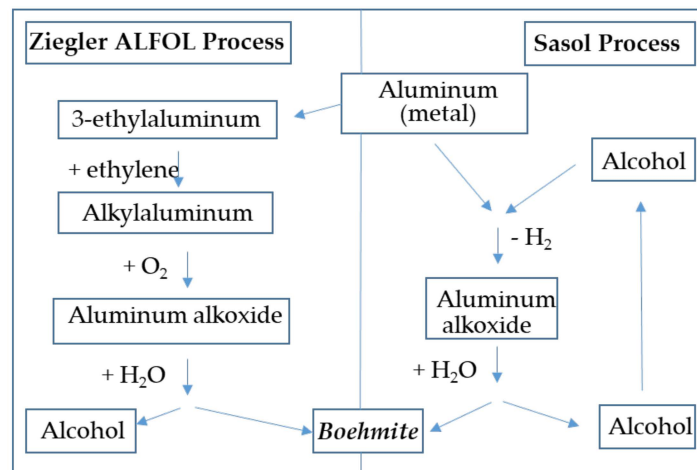
Some other researchers [33,41–46] identified the transformation of amorphous aluminum compounds into amorphous alumina by differential scanning calorimetry (DSC). An endothermic peak of water was observed in the curve, in the temperature range of 250–500 °C, which was due to the slow dehydration of hydroxide to oxide due to the disordered structure. The stability of amorphous alumina was recorded by the same authors [33,46], which was up to a calcination temperature of 700 °C. The transformation in this high temperature range ( $T = 850\text{--}900^\circ\text{C}$ ) was accompanied by an exothermic effect on the DSC curve.

### 2.3. Sol-Gel Process (Alcoholate Technology)

High-purity aluminum hydroxides with a large surface area, which are used for the preparation of catalysts and supports, are synthesized mainly by the expensive but very efficient sol-gel method (alcoholate technology) [41–46]. This technology allows for the achievement of high purity boehmite and bayerite. There are two important industrial synthesis processes: Ziegler ALFOL and Sasol (Figure 1) [46].

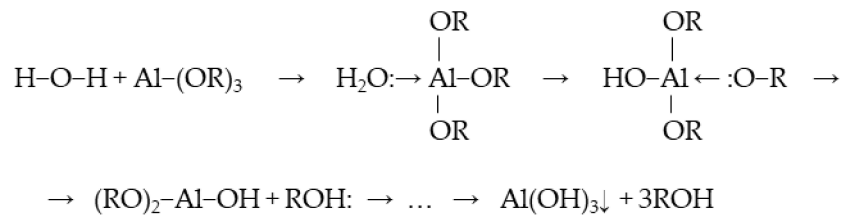
The first method is based on the Ziegler reaction, which is applied in production of higher linear alcohols. However, the second hydrolysis method of aluminum alkoxides, which was developed by Condea (Sasol) company, is preferable due to the absence of by-products except the easily utilizable hydrogen.



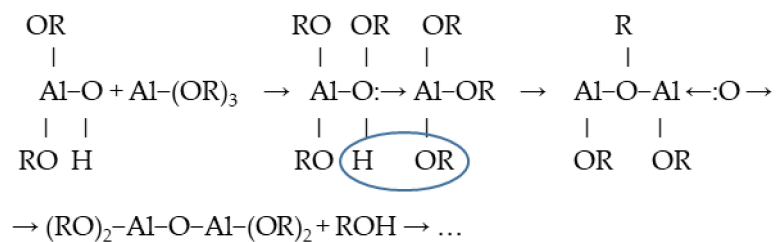


**Figure 1.** Scheme of boehmite synthesis using alcoholate technology [42,46].

Hydrolysis of aluminum alcoholates is carried out by nucleophile substitution mechanism as the relatively high electronegativity of the alkoxy -OR group makes the Al atom available for nucleophilic attack [47]. Alkoxy groups have a significant effect on the rate of hydrolysis. The substitution of any further -OR group of the alcoholate may be associated with steric hindrances or the mesomeric effect, as a result of which the replacement of the second and third alkoxy-groups by the hydroxyl group is always slower [46–53]:



In the phase of hydrolysis of aluminum alcoholates, formation of boehmite was preceded by formation of amorphous gel, which was transformed into more stable forms during further heat treatment. Oligomeric particles (aluminoxanes) were also formed during the synthesis of aluminum monohydroxide by the hydrolysis of aluminum alcoholates:



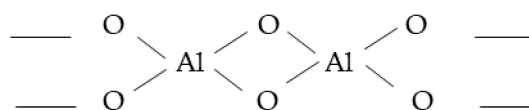
Aluminoxanes contain an -O- group linked by two aluminum atoms—[>Al-O-Al<]<sub>n</sub> and form supramolecular three-dimensional clusters with the indicated structural element [46,50]. The final products of hydrolysis are highly reactive, form stable hydrogels, and dehydrate at lower temperatures to form finely divided oxides [51].

In order to synthesize homogeneous aluminum hydroxides, precipitate was peptized by adding strong acids (HNO<sub>3</sub>) after the hydrolysis of aluminum alcoholates. In this case, the peptization was comparable to the aging during production of aluminum hydroxides by precipitation method. Similarly, during the hydrolysis of aluminum alcoholates the degree of hydrolysis increased with the temperature of hydrolysis [49–52].

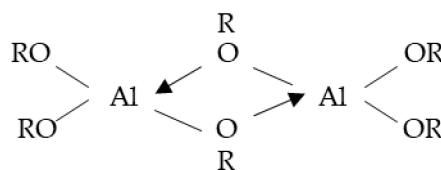
The phase composition and the properties of obtained aluminum hydroxide strongly depend on the conditions of hydrolysis: alkoxy types, pH of medium, concentration of

compounds, and temperature. However, the conditions for obtaining boehmite structured hydroxides is the excess of water ( $H/Al = 0.07\text{--}0.10$ ), the pH of the boehmite suspension equal to 4.0, and the hydrolysis temperature around  $80\text{--}100\text{ }^{\circ}\text{C}$  [51,53].

One of the disadvantages of this method of aluminum hydroxide production is the formation of aluminoxanes due to the hydrolysis organoaluminum compounds. Aluminoxanes form from oligomers of alcoholate molecules during substitution of one or more groups of OR- to OH-. The further polycondensation of aluminoxane clusters can be carried out with formation of one-dimensional, planar, and volumetric forms that bring some difficulties with determining their structural formula. Most aluminum alcoholates are characterized by association in vapors and solutions, where each aluminum atom coordinates at least four oxygen atoms with formation of oxide bridges:



Aluminum alkoxides are multinuclear particles or solvate complexes of  $Al(RO)_3$ . Aluminum isopropoxide, which has been most commonly used in the synthesis of aluminum hydroxides, forms a dimer in the gas phase [46,50,51,53]:



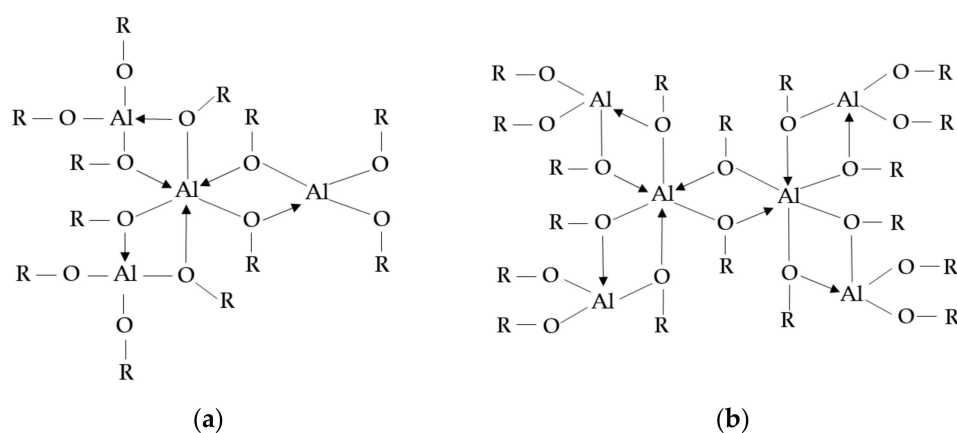
Aluminum isopropoxide in the liquid state is a pseudo two-component system, which transforms into a tetramer by time.

The synthesis of aluminum hydroxides by hydrolysis is carried out immediately after obtaining aluminum alkoxides because of the increase in their degree of association with time, which is called “aging phenomenon” [46,50,51,53]. Immediately after their formation, the molecules of aluminum alcoholates are dimers and octamers, in which the coordination number of Al was 4 and 6 respectively. When they are mixed in the ratio of 3:1, a tetramer is formed (Figure 2a), which appears in the first stage of aging. The second stage ends with the formation of a hexamer (Figure 2b) and the third with octamer. This association scheme is applicable only for derivatives of primary alcohols, since the aging process of secondary and tertiary alcohols is strongly inhibited or completely absent due to steric barriers [46,50,51,53].

During hydrolysis, the three-dimensional structures of aluminum alcoholates can form three-dimensional clusters that combine 12 aluminum atoms. The structure of the hybrid aluminoxane core coincide with the structure of boehmite, i.e., the aluminoxane centers are also found in a six-coordinated medium [46,50,53]. The structure of aluminoxanes is nearly amorphous and could be identified by the appearance of a  $\delta = 50$  ppm signal of the pentacoordinated aluminum atom  $[AlO_5]$  in the  $^{27}\text{Al}$  nuclear magnetic resonance (NMR) spectra [53].

The thermal decomposition of aluminoxanes has not yet been studied thoroughly, which is probably due to the formation of various polymeric and oligomeric structures. However, many authors [46–53] agree that the decomposition of aluminoxanes with the formation of  $\gamma$ -modification alumina occurs via the stage of formation of a hydroxide with boehmite structure. For example, it was shown in [53] that an amorphous aluminum compound obtained by hydrolysis of aluminum isopropoxide loses 44.03% of mass as a result of thermal analysis due to the release of water and organic gases, but exhibits

only two endothermic effects. The first with  $T = 110\text{ }^{\circ}\text{C}$  is in a wide temperature range of  $30\text{--}300\text{ }^{\circ}\text{C}$  and is accompanied by mass loss ( $\Delta m$ )~40% of mass, and the second peak with  $T = 350$  and  $378\text{ }^{\circ}\text{C}$  in the range of  $300\text{--}400\text{ }^{\circ}\text{C}$  with  $\Delta m$  about 4%. The first endothermic effect is due to the release of physically adsorbed water and water molecules as a result of dehydration of amorphous aluminum hydroxide, and the second effect is due to thermal decomposition of aluminoxanes. Moreover, an exothermic effect is observed at high temperatures ( $\sim 850\text{ }^{\circ}\text{C}$ ), which is due to the phase transformation of  $\gamma\text{-Al}_2\text{O}_3$  to  $\alpha\text{-Al}_2\text{O}_3$ .



**Figure 2.** Tetrameric (a) and hexameric (b) structures of aluminum alcoholate.

Thus, the problem of the formation of amorphous aluminum compounds arises in the synthesis of aluminum hydroxides by activation methods (mechanochemical, thermochemical, and centrifugal activation) and as a result of the hydrolysis of inorganic (precipitation) and organic (hydrolysis of alcoholates) aluminum salts. The formed amorphous compounds combine disorder of their structures, while their other properties are different. Amorphous aluminum compounds, which are synthesized by activation method, are crushed fragments of hydroxide precursors and with increasing depth of bond cleavage their properties change to a greater extent after peptization and thermal treatment. At the same time, amorphous aluminoxanes and basic aluminum salts formed by hydrolysis of alcoholates and precipitation, respectively, have certain similarities, probably due to their synthesis by hydrolysis and polycondensation processes.

### 3. The Effect of Amorphous Aluminum Compounds on Catalysts in Different Processes: The Introduction of Hydrothermal Treatment of Catalyst Precursors

Aluminum oxide is widely used in petroleum chemistry and oil refining [1–8]. The most commonly used aluminum oxide is  $\gamma\text{-Al}_2\text{O}_3$  as a catalyst or a catalyst support. Aluminum oxide is applied in the neutralization of industrial emissions as a support, while as a catalyst it is used in hydrogenation, hydrogenolysis, reforming, and hydrotreating processes, where the active components are Cr, Mo, Ni, W oxides or metals (Pt-, Pd-, Ni-, etc.). During hydrogenation, aluminum oxide increases the thermal stability of the nickel catalyst up to  $600\text{--}700\text{ }^{\circ}\text{C}$ . The supports in the composition of hydrotreating catalysts act as structural promoters in the formation of active phases. Platinum aluminum oxides are considered as bifunctional reforming catalysts. The metal (Pt, Pt-Re or three-component metal alloys of noble metals) catalyzes hydrogenation-dehydrogenation reactions, while alumina accelerates isomerization reactions. Moreover, aluminum oxide is often used as a catalyst in acidic reactions. For example, the dehydration of alcohols is a typical acidic process and is accelerated by the following oxides:  $\text{Al}_2\text{O}_3$ ,  $\text{WO}_3$ ,  $\text{ThO}_2$ ,  $\text{TiO}_2$ , etc., aluminosilicates, aluminophosphates, etc. The active centers of the catalyst in the reaction are Lewis acid centers. The catalysts are insensitive to the action of poisons and are easily regenerated. The process of ethanol dehydration to produce ethylene proceeds at  $300\text{--}400\text{ }^{\circ}\text{C}$  on  $\gamma\text{-Al}_2\text{O}_3$  with a selectivity almost reaching 100%. On other oxides, the selectivity is shifted towards the formation of aldehyde [8].

The widespread use of aluminum oxides even within a single modification ( $\gamma$ - $\text{Al}_2\text{O}_3$ ) is due to variation of its surface properties, which are achieved by changing the conditions of aluminum oxide synthesis. The homogeneity of alumina precursors ensures the efficiency of catalysts and it is one of the most important requirements for their synthesis. However, this condition is often not met due to the formation of amorphous aluminum compounds. Therefore, it is necessary to modify amorphous aluminum compounds to forcibly complete the hydrolysis reaction and obtain crystalline aluminum hydroxides. A simple and effective method for such modification is hydrothermal treatment (HTT).

A growing body of literature has studied the hydrothermal treatment of amorphous aluminum compounds due to the properties of final products and surface properties of phase compositions, which can be modified toward the crystallization [46,54–66]. The main conditions that affect the phase composition of the obtained products are saturated vapor temperature and pressure. However, the formation of the porous system and the morphology also depend on the pH of the medium and the hydrothermal treatment duration.

Phase diagrams of aluminum oxides and hydroxides are evaluated after the hydrothermal treatment of crystalline aluminum oxides and hydroxides [46,64]. However, the disordered structure of amorphous aluminum compounds may lead to a change in the boundary conditions of crystalline aluminum hydroxides ( $T$ , °C and  $P$ , MPa), which are formed as a result of hydrothermal modification.

Transformation of the crystalline structured compounds into another crystalline structures compounds requires energy both for the destruction of the initial crystal structure and for the subsequent formation of a new crystal structure. The formation of crystalline aluminum hydroxides by the mechanism of dissolution and precipitation from amorphous compounds under hydrothermal conditions suggests lower energy consumption during crystallization due to the absence of long-range order in the arrangement of atoms of the amorphous phase [56]. The rate of boehmite formation from crystalline aluminum hydroxide under hydrothermal conditions is higher than its transformation from amorphous hydroxides [54,55]. Probably, the formation of crystalline boehmite from an amorphous aluminum compound under low temperature hydrothermal treatment is thermodynamically possible but kinetically difficult, which is of great scientific interest.

Thus, amorphous aluminum compounds are formed during the synthesis of boehmite or pseudoboehmite as activation products (MCA, TCA, CTA), as products of incomplete hydrolysis due to precipitation of inorganic aluminum salts with a base or as products of polycondensation of aluminum alcoholates and aluminoxanes. The mechanism of crystal rise in boehmite under hydrothermal impact depends on the initial pH of the aqueous suspension. Small embryos are formed in the acidic environment, which form a fibrillar structure after coagulation [58]. The particle size of aluminum monohydroxide depends on the rate of nucleation. The authors in [59] showed that the morphology of the particles changes with the solubility of the ions ( $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Al}(\text{OH})^{4-}$ ,  $\text{NO}_3^-$ ). The morphology of boehmite particles is determined by the selective adsorption of positively charged  $\text{Al}(\text{OH})^{2+}$  particles on the negatively charged faces of boehmite particles. Additionally, the properties of boehmite, such as porosity and the amount of connate water, as well as the temperature of phase transformation into  $\gamma$ - $\text{Al}_2\text{O}_3$ , affect the size of boehmite crystallites [60].

The amorphous product of mechanical activation of gibbsite forms boehmite crystals under the hydrothermal treatment, the size of which is very small (~100 nm) [56]. The amorphous gel obtained as a result of precipitation of  $\text{Al}(\text{NO}_3)_3$  and  $\text{NH}_3$  solutions after hydrothermal modification at 150 °C was pseudoboehmite with crystals of 2.5–3.0 nm. The crystal size increases with hydrothermal processing duration. A strong sensitivity of obtained boehmite to the deposition of gel conditions and the presence of external ions was noted [61].

The hydrothermal treatment of gels at temperature more than 150 °C, which is synthesized by the mixture of  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{NH}_3$  solutions, produces boehmite, the crystallinity of which increases with temperature [62]. The products of hydrothermal treatment at

lower temperatures are crystal boehmite and amorphous phase. Pseudoboehmites with a crystal size of 4.9 nm are formed after neutralization of aluminum salts solutions by urea in hydrothermal conditions ( $T = 160\text{ }^{\circ}\text{C}$ ). In case of higher processing temperature we obtain boehmite [63]. The hydrolysis product of aluminum acetate under hydrothermal impact for 2 h was transformed to boehmite at  $200\text{ }^{\circ}\text{C}$  [64].

In [65], the authors showed the formation of a fine fibrous boehmite (10–20 nm) with a high specific surface area ( $400\text{ m}^2/\text{g}$ ) at a drastically low hydrothermal treatment temperature— $105\text{ }^{\circ}\text{C}$ . The initial compounds were suspensions of aluminum sulfate and nitrate with neutralized  $\text{pH} = 7$ . The aqueous suspensions of samples obtained by hydrothermal treatment had low  $\text{pH}$  values, which are explained by the result of hydrolysis, since the protons are evolved during the conversion of the metastable polymer Al13 to aluminum hydroxide.

We have previously described in [66] the positive effect of hydrothermal treatment on the alumina catalyst for the skeletal isomerization of *n*-butylenes to isobutylene due to the conversion of the amorphous component. The hydrothermally modified alumina was obtained by calcination of boehmite from Pural SB, SASOL (Germany), synthesized by the method of hydrolysis of aluminum alcoholates. It was found that an increase in the acidity and surface area of the alumina due to the formation of boehmite with needle morphology from the amorphous phase of the initial aluminum hydroxide during hydrothermal treatment in water at  $150\text{ }^{\circ}\text{C}$  for 3 h increased the catalyst conversion by 4%.

#### 4. The Role of Amorphous Aluminum Compounds in Petrochemistry

Currently, amorphous compounds play an ambiguous role in petrochemistry [4–11,14–17,19,26–29,41–49,54,62,66–79]. They are often considered as an undesirable component of heterogeneous alumina catalysts, since they are inevitably formed during the synthesis methods of aluminum hydroxides (precipitation and alcohol technology) [6,9,11,17,37,45,58,67,68,70]. Amorphous aluminum compounds are gel-like, therefore, it complicates the washing and filtration phases of aluminum hydroxides synthesized by precipitation [11,43]. Moreover, amorphous compounds differ in their thermostability from crystalline hydroxides (different temperatures of phase transformation), which is important for the phase inhomogeneity of the obtained catalyst [7,12,25,32,33]. This leads to an uncontrolled effect of amorphous aluminum compounds on the transformation and selectivity of the alumina catalyst [27,29,31,42,47,48,64,70].

At the same time, some authors [34,55,66] show a positive effect of heterogeneous catalysts during hydrothermal treatment of amorphous aluminum. For example, the hydrothermal treatment of pseudoboehmite, which contains the amorphous aluminum, significantly increases the selectivity and conversion of the alumina catalyst for skeletal isomerization of *n*-butylene to isobutylene [66]. Taking into account the formation influence of crystalline aluminum hydroxide from amorphous aluminum compounds at lower temperatures (in comparison with crystalline hydroxides) [54,55,61,62], it is possible to estimate the contribution of amorphous aluminum compounds to the composition of the synthesized crystalline aluminum hydroxide pseudoboehmite using hydrothermal treatment [73]. The dual position of amorphous aluminum compounds in petrochemistry is thus due to a number of problems in the study of amorphous aluminum compounds.

The application of amorphous aluminum in petrochemistry and their study are limited by numerous factors. Thus, the study of crystallization of amorphous aluminum compounds under hydrothermal conditions is at a high level, but the knowledge gained is not systematized. Often, hydrothermal modification is carried out with a minimal examination of the phase composition and precursor properties, which does not allow an accurate observation of the transformations that occur in the process. At the same time, hydrothermal treatment as a tool for forced completion of hydrolysis for basic aluminum salts and amorphous aluminum hydroxide is a promising method to achieve phase homogeneity of the obtained boehmite or pseudoboehmite. Simultaneously, the influence of preliminary heat treatment of the amorphous aluminum compound on the product

phase transformations under hydrothermal conditions without any additives is also of great scientific interest. Thus, an intermediate conclusion can be made about the following current problems in this area:

1. Ambiguous terminology.

Many fundamental researches on the structure of aluminum oxides and hydroxides and on methods for their synthesis were developed more than 50 years ago. These researches use outdated terms such as “gelled boehmite” and “amorphous phase”. The term ‘amorphous phase’ can also be misleading as it can be a mixture of amorphous aluminum compounds from several phases, e.g., a basic salt together with amorphous aluminum hydroxide or amorphous aluminum hydroxide together with aluminoxanes.

2. Ignoring the formation of amorphous aluminum compounds.

Due to the terminological ambiguities, insufficient knowledge, and difficulties in identification of industrial samples, the formation of amorphous aluminum compounds as a result of synthesis of boehmite mono-hydroxides or pseudoboehmite structures are ignored. At the same time, after calcining such samples, a serious problem arises in the phase homogeneity of the obtained aluminum oxides, which negatively affects their efficiency.

3. Crystallization of amorphous aluminum compounds.

Amorphous aluminum compounds are mainly products of incomplete hydrolysis, which can be forcibly completed by hydrothermal modifications. The systematization of phase transformations of amorphous aluminum compounds obtained by various methods under hydrothermal conditions is of great scientific interest, as well as the study of phase transformations of amorphous alumina without impurities of basic aluminum salts or aluminoxanes and the change of the obtained products properties during hydrothermal treatment. An important applied problem is to fill the gap in scientific research on the crystallization effect of amorphous aluminum compounds on the efficiency of the alumina catalyst in the industrial processes.

4. Potential application amorphous aluminum compounds in oil refining

Application of amorphous aluminum compounds in the field of petroleum refining is a promising method. In contrast to the conventional methods of processing heavy oils by thermal cracking and hydrocracking, the mechanisms of processing hydrocarbons with the presence of catalysts are more complex and still largely disputed in the scientific arena. For example, the alumina support plays an important role in the catalyst, which can also participate in the reactions at the catalyst active sites [67–81].

The nature and strength of the interaction between the promoter, molybdenum, acting as the active site, and the support or alumina support are largely dependent on its structure. A major problem in the applying of heterogeneous catalysts is removing the active component from the support surface as a result of catalyst operation over long periods of time. The solution to this problem may be the synthesis of the support, i.e., the alumina, from weak crystallized aluminum hydroxide—pseudoboehmite. A small part of the amorphousness allows the chemical bonds formation between the promoter, molybdenum, and the carrier precursor, aluminum hydroxide, which prevents the removal of the active component and its incorporation into the oil.

Amorphous aluminum compounds have a gel-like state after synthesis, which also allows them to be used as a water-soluble catalyst for oil refining. Unfortunately, there are currently few examples of such work in the literature, but there are many prerequisites for this type of research. For example, the authors of [82] describe the use of alumina as a catalyst for the upgrading of gasoline distillates. The proposed method is intended for the upgrading of distillates containing unsaturated and aromatic hydrocarbons in addition to sulfur compounds and can be used as well in the petrochemical and coke industries. A process of upgrading gasoline distillates is proposed in which the initial petroleum feedstock is first contacted with alumina at a temperature of 50–160 °C, which is added to the total charge of hydrogenation catalysts in an amount of 5–30% by volume.

This is followed by a two-stage hydrogenation in the presence of an aluminum-cobalt-molybdenum catalyst at a temperature of 200–280 °C in the first stage and at a temperature of 260–380 °C in the second stage. Then, the hydrogenation is carried out at a pressure of 3–5 MPa and the volumetric feed rate of the feedstock is 0.5–3.0 h<sup>-1</sup> in each phase. The process is suitable for refining of gasoline distillates containing unsaturated and aromatic hydrocarbons and can be used in petrochemical and coke chemical industries.

Research on different types of catalysts for oil refining is being carried out worldwide. In [83–88], the authors describe the use of catalysts based on transition metals (Co, Ni, Fe, Cu) in combination with the action of water steam, which allow the creation of conditions for the underground refining of heavy oil (partial processing of heavy fractions in the reservoir), reducing the viscosity of the produced oil and improving its qualitative composition. This can increase the oil production rate and reduce the steam to oil ratio. The proposed technologies can be used in fields that are already developed with steam injection processes without the need to significantly change the infrastructure based on the existing equipment. As a basis for the tested catalysts, we used molecular precursors synthesized in one step by the exchange reaction of inorganic salts of the studied metals with the sodium salt of tall oil. Under reservoir conditions, the catalyst precursors exist in an inactive form prior to steam injection, whereas during steam injection they transform into an active form (nanoscale particles of transition metal oxides and sulfides) and begin to catalyze the aquathermolysis reactions. Thus, the promotion of an amorphous aluminum compound with salts of transition metals (Co, Ni, Fe, Cu) can lead to the creation of a potentially new type of catalysts for the refining of viscous oils and natural bitumens. In addition, aluminum compounds can act as hydrogen donors during aquathermolysis. The addition of hydrogen donors during aquathermolysis has a positive effect on the overall reaction. In the absence of hydrogen donors, the compounds obtained may react with each other to form a high molecular weight chain. The aluminate structures of zeolite, which have the shape of a tetrahedron and represent Bronsted acid sites, are hydrogen donors under the conditions of aquathermolysis [89].

## 5. Concluding Remarks

Amorphous aluminum compounds have not been adequately studied and are poorly addressed in the literature. Despite the many gaps in their study, the use of these compounds has great potential due to their amorphous structure:

- The role of amorphous aluminum compounds in the field of petrochemistry is currently ambiguous as their positive and negative sides are described. A negative effect is the impeded filtration during the synthesis of the alumina catalyst precursor, the increased coke formation at the active sites of the amorphous alumina as a consequence of the catalytic reaction. A positive effect is possible by introducing hydrothermal treatment of the amorphous aluminum compounds in the catalyst synthesis phase. The hydrothermal treatment promotes the forced crystallization of the amorphous compounds into aluminum hydroxides with the desired properties.
- However, the role of amorphous aluminum compounds in oil refining is also controversial due to the lack of knowledge on the subject. At the same time, the possibilities of using amorphous aluminum compounds represent a great potential due to the low cost of the initial reagents. The Bronsted acid sites on the surface of the aluminum compounds can act as proton donors in the aquathermolysis reaction. The aggregate state and structure of the gel enables the use of amorphous aluminum compounds as water-soluble catalysts for oil refining. Thus, amorphous aluminum compounds can play the role of a catalyst in oil refining under aquathermolysis conditions, which opens up new opportunities in the field of their potential applications.

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