Peptization Control of Aluminum Chloride-Containing Composites for Catalysts with Active Matrix

Aluminum-based composite particles are widely applied complex catalyst materials in oil refining. Due to their tunable shape, porosity, and acidity, they are commonly used for the production of cracking catalysts. Shaping of well-defined particles remains a challenge for industrial catalyst preparation by spray drying, because catalyst properties must satisfy local demands of a refinery. The selectivity can be modified and the cracking activity enhanced with acid binders, e.g., AlCl₃. Therefore, peptization of AlCl₃-containing suspensions with zeolite Y and kaolin was characterized by pH value, ²⁷Al NMR spectroscopy, and zeta potential. A new control strategy for binding of kaolin and zeolite Y in spray drying was developed by adjusting the pH and binder Al/Cl ratio.

Keywords: Aluminum chloride, Catalyst preparation, Catalysts, Porous materials, Spray drying

Received: January 10, 2021; revised: February 24, 2021; accepted: March 12, 2021

DOI: 10.1002/ceat.202100011

1 Introduction

Aluminum chloride is a substance that produces an acidic solution in water. During its hydrolysis, a solution of aluminum complexes can be formed as a reactive precursor. Its composition depends on the pH value. A concentrated slurry can be used as a binder for the production of cracking catalysts. After calcination, it decomposes to amorphous, partially halogenated alumina, which is an acidic and active material for cracking reactions at the matrix of the catalyst [1, 2].

The binding process with aluminum chloride complexes has been applied in industry for several years [3–5]. It is based on supersaturation of the solution during drying. At that point, the aluminum chloride starts to precipitate [6, 7] and forms solid bridges between the zeolite and kaolin particles. The agglomeration depends on the stability of colloidal particles in the slurry, which is defined by its surface and electrochemical properties.

To the best of the authors’ knowledge, there is no interdisciplinary approach to understand the basic surface chemistry of catalyst particle binding by alumina peptization in combination with considerations of solubility phenomena, complexation, and coverage of different aluminum-based species at the surface of zeolite Y. Therefore, the present study has three main aims. First, surface (electro)chemistry during agglomeration for multicomponent particles is explained through complex formation and coverage. Second, the correlation between agglomeration and slurry stability was adapted for mixtures containing zeolite HY and kaolin. Third, the binder Al/Cl ratio and the buffer capacity of the slurry were modified for corrosion control.

2 Materials and Methods

2.1 Raw Materials

The materials for the formulation and characterization were hydrated aluminum chloride from Alfa Aesar (99 wt % AlCl₃·6H₂O), HY zeolite CVB400 from Zeolyst, and kaolin from Sigma-Aldrich. In addition, HCl (37 wt %, BDH Chemicals), a solution of NH₄OH (25 wt %, Sigma-Aldrich) and amorphous aluminum hydroxide (51 wt % Al₂O₃ by EDTA complexation, Sigma-Aldrich) were applied for the formulations.

2.2 Preparation of Slurries and Spray Drying Process

Commercially available aluminum chloride was dissolved in deionized water and the solution was stirred at 700 rpm (ca 73 rad⁻¹). Afterwards, hydrochloric acid (8 M) or ammonium hydroxide (5 M) was added to adjust the desired pH value and the solution was stirred for 10 min. For experiments with aluminum hydroxide, the required amount of Al(OH)₃ was added and the
mixture was stirred for a few minutes. At this point, other components for the catalyst formulation (zeolite HY, kaolin) can be added and the mixture was stirred for a further 5 min. The slurries were spray dried with a Büchi B-290 mini spray dryer with a two-fluid nozzle. The conditions used for this process were 210°C (inlet temperature) and a volumetric gas-to-liquid ratio of 427 (liquid flow of 1.26 L h⁻¹). The produced powder was calcined at 650°C for 8 h.

Slurries for formulation contained 10 wt% of total solids with 1:1 mass ratio for binary mixtures (zeolite HY/aluminum chloride and kaolin/aluminum chloride) and 1:1:1 mass ratio for the ternary mixture zeolite HY/aluminum chloride/kaolin. In addition, the same mixtures were tested with addition of aluminum hydroxide. To obtain different mixtures of aluminum chloride and hydroxide as binder in the formulation, 16, 20, 25, 33, 50, and 100 mol% aluminum chloride was used.

2.3 Characterization of Slurry Properties

²⁷Al NMR spectra of the slurries were recorded with a Bruker 500 MHz Ascend, Advance III HDX spectrometer. This analysis was performed on the liquid phase of the slurries, which was separated by centrifugation and sedimentation of the slurry solids. Zeta potentials of slurries were determined with a Malvern Zeta-Sizer Nano instrument. The sample is exposed to an electrical field and the movement of the ions is quantified under these conditions. Depending on the parameters, zeta potentials ζ¹ were calculated for each system and pH value.

2.4 Characterization of Solid-State Materials After Spray Drying

Particle size distributions of spray-dried products were determined by laser scattering with a Bettersizer S3 plus instrument from 3P Instruments. The equipment performed a wet dispersion procedure at 2000 rpm (209 rad⁻¹) stirring and 200 W (26 kHz) ultrasonication for 120 s. Data acquisition and processing were carried out according to ISO 13320:2009. Mie theory was used for calculating particle size distribution from scattering data [8].

The specific surface area was quantified for these materials through nitrogen physisorption with a Horiba Scientific SA-9600 instrument. All samples were calcined at 200°C for 2 h. After calcination all samples were cooled in liquid nitrogen for physisorption.

Scanning electron microscopy (SEM) was performed with a SU8020 scanning electron microscope (Hitachi) equipped with a triple detector system for secondary and backscattered electrons (accelerating voltage: 2 kV). To acquire electron images, the samples were fixed directly on a double-sided adhesive carbon pad that was placed on an aluminum sample holder. To avoid any charge-up and chemical alteration during the measurements, the sample surface was coated with gold in an automatic rotary-pump coating system (Quorum Q150R ES).

3 Results and Discussion

A range of different slurries, i.e., aluminum chloride solutions and combinations with kaolin and zeolite HY, were studied in this work. The pH values of the slurries were chosen in accordance with the observed peptization results of the mixture. The pH value of 3 corresponds to dilute aluminum chloride. In addition, the slurry at pH 5 was analyzed due to the maximal colloidal behavior of the system. Finally, a pH value of 6 was chosen due to the observed precipitation of the binder in the system. Furthermore, these results are related to the particle size distribution of the samples after spray drying. As a separate experiment, zeta potentials of diluted slurries (1:100) with solutions of NH₄OH or HCl were quantified at a constant pH value to observe their peptization behavior and peptization regimes.

3.1 Properties of Aluminum Chloride

Aluminum chloride is hydrolyzed in water to form different complex species. The composition of the complex mixture formed depends on the pH value of the solution. At pH 3, the mixture mainly comprises mononuclear aluminum species (see Fig. 1), especially [Al(H₂O)₆]³⁺ and [Al(H₂O)₅(OH)]²⁺, which cause the acidity of the mixtures. After increasing the pH value to 4, dimeric and trimeric forms of these substances appear in the system. The polymerization continues at pH 5, at which the Keggin structure [AlO₄Al₁₂(OH)₂₄(H₂O)₁₂]³⁻ (K-Al₁₃) is observed. According to Bi et al. [9], the precipitation of the aluminum species starts with complexes of 30 aluminum atoms (Al₃₀) from pH 5 to 8 to finally form solid aluminum hydroxide.

The presence of multinuclear aluminum complexes at pH 5 is important, because these substances interact with the catalyst components at the surface, which includes a fast and uncontrollable binding process.

Figure 1. ²⁷Al NMR spectra of AlCl₃ solutions in water at pH values of 3, 4, and 5.
3.2 Properties of Binary Mixtures

For the mixture of zeolite HY with aluminum chloride, the pH increases to a value of 4. This can be attributed to proton coverage of the zeolite from the liquid phase due to the negative surface charge of zeolite Y, which has been documented in the literature for water slurries at a neutral pH value [10]. On contact with the binder solution, the total polarity of the particle surface adopts a positive value, which is confirmed by its observed zeta potential (see Fig. 2b). It can be attributed to the formation of soluble aluminum complexes (positively charged) and coverage of the zeolite surface by these substances. In the pH range between 4 and 5, the zeta potential of these particles reaches a maximum due to the higher complexation rate of the aluminum chloride. The partial precipitation of these complexes mainly occurs at the surface of the zeolite and not in the liquid phase, unless the pH value of the system reaches the precipitation range. The complexation was confirmed by $^{27}$Al NMR measurements, which mainly showed monomeric species (see Fig. 2c). This suggests that the particles are covered by aluminum complexes as a first step of binding. Similar coverage is documented in the literature for clays in the removal of aluminum from soils [11]. The proposed mechanism comprises the hydrolysis of superficial silanol groups of the zeolite and the acidic behavior of the aluminum chloride. On the one hand, there is a competitive coverage of protons on the zeolite and aluminum complexes at pH 3. Due to high ionic strength, the coverage rate is reduced for aluminum complexes. On the other hand, their coverage rate increases up to pH 5 due to the reduction of the ionic strength in the system. This produces an increase of the zeta potential. Beyond pH 5, the precipitation of aluminum species and the deprotonation of the zeolites reduce the surface coverage and binding efficiency [12].

Everything considered, the agglomeration is stable due to competitive proton coverage at pH 3. At pH 5, the average size is reduced due to the formation of a stable colloidal slurry, which is confirmed by a zeta potential beyond 30 mV [13]. Consequently, the binding is less stable due to repulsive forces of the particles at pH 5. Due to the reduction of the zeta potential at pH 6, the agglomeration is accelerated. However, the binding is not as effective as at pH 3 due to the fast precipitation of the aluminum from the liquid phase as aluminum hydroxide.

In the case of kaolin, heterogeneous agglomeration is observed. This is attributed to the structure of the kaolin particles, which are very compact with a low coverage capacity. In addition, kaolin is not covered by ions from the liquid phase of the slurry as efficiently as zeolite HY, so the pH of the system is not influenced by these particles. The mixture mainly comprises mononuclear aluminum species. The low phase contact between kaolin and binder promotes localized agglomeration of aluminum chloride on the surface of kaolin. These surface structures promote accelerated kaolin particle agglomeration, which leads to a broad particle size distribution (see Fig. 3).

3.3 Mixtures with Aluminum Chloride and Aluminum Hydroxide

Adding aluminum hydroxide to the system results in a higher rate of complex formation. This is useful to increase the binder concentration of slurries without further reducing the pH value. It helps to protect spray equipment from corrosion by very acidic slurries (pH < 3). At the interphase between the solution and particles, partial dissolution of the aluminum hydroxide into the liquid phase takes place, which increases the aluminum
content in the solution and promotes the formation of aluminum chloride complexes. This is confirmed by the $^{27}$Al NMR data of the liquid phase of these slurries (see Fig. 4), where the Keggin structure of aluminum (K-Al$_{13}$) is identified. The complexation takes place at a pH value of 4 and enhances the buffer effect of the AlCl$_3$ solution. Zeta potentials also confirm the formation of aluminum complexes in the surface of the particles with a maximum range at pH 3.5–4.5.

The coagulation behavior of hydrolyzed aluminum chloride leads to controlled agglomeration of particles at pH 3–3.5. Larger amounts of aluminum hydroxide increase the complexation rate in the system, whereby the agglomeration is less stable. In this case, the smallest amount tolerated for binding is 50 mol % of aluminum chloride in the binder (see Fig. 5). Nevertheless, the specific surface area of the particles is not significantly affected by complex formation. One possible reason for this behavior is the coverage of aluminum complexes as a thin layer on the surface. This coverage does not significantly alter the porosity of the particles. Furthermore, the pH value of the mixture is not influenced by the addition of Al(OH)$_3$, which also supports the explanation of particle surface coverage by aluminum complexes.

### 3.4 Complex Mixtures for Catalyst Preparation

The particles in the slurry have a positive surface charge due to coverage by aluminum complexes. In addition, the zeta potential of these particles again shows a maximum in the pH range between 4 and 6. At a higher pH value, the zeta potential is reduced due to precipitation of the aluminum species from the liquid phase. Bi et al. [9] mention the formation of aluminum hydroxide sediment in slightly acid solutions (pH 6–7). It is important to consider the addition of ammonium hydroxide for pH adjustment in this measurement (see Sect. 2.2). The slurry tends to be unstable again at pH 6. Consequently, the particle agglomeration is less stable at pH 5 (see Fig. 6).

Moreover, the addition of aluminum hydroxide was tested again (see Fig. 7). The results are similar to the system of zeolite HY with hydrolyzed aluminum chloride. The formation of the complexes is demonstrated without a significant change of the pH value. With larger amounts of Al(OH)$_3$ in the mixture, more aluminum complexes are formed and the rate of agglomeration is reduced. A tolerable addition of up to 50 mol % of Al(OH)$_3$ is again observed in the binder. Beyond this, excessive formation and deposition of aluminum complexes causes unstable particle binding. Furthermore, there is a minimum of the electrical conductivity at pH 5. This could be attributed to the enhanced coverage by the aluminum complexes at the zeolite surface [11] and the starting self-agglomeration of the binder.

To confirm the formation of the agglomerates from the catalyst components (zeolite HY, kaolin, and binder), SEM images were recorded for the studied mixtures of this work (see Fig. 8). The particles show coverage of the kaolin surface with zeolite crystals and a pastelike substance (binder) holding them together. The surfaces of the crystals are partially exposed and pores of different sizes are formed by their aggregation. This morphology is ideal for a catalyst, as the zeolites are not blocked and the pores are still accessible. The particles reached a size of up to 20 μm, which is the maximal drop size of the spray dryer nozzle. These results are complemented by analysis of porosity and specific surface area (Tab. 1 and Fig. S1 in the Supporting Information). Tab. 1 compares the porosity of a pure zeolite HY and an agglomerate formed from HY, kaolin, and binder.

**Figure 3.** Kaolin agglomeration with aluminum chloride; particle size distribution obtained by laser scattering.

**Figure 4.** (a) Zeta potential $\zeta$ and electric conductivity of HY/AlCl$_3$/Al(OH)$_3$ mixture at different pH values. (b) $^{27}$Al NMR spectrum of the liquid phase of the AlCl$_3$/Al(OH)$_3$ mixture at pH 3.

Chem. Eng. Technol. 2021, 44, No. 6, 1051–1057 © 2021 The Authors. Chemical Engineering & Technology published by Wiley-VCH GmbH www.cet-journal.com
The main difference is the reduction of the specific surface area, which is attributed to the increase of particle size and the combination of the zeolite with other particle components. In addition, the composite has lower pore volume, which is due to the binding coverage to form the composite. Due to the small change in the mesopore volume, the porosity reduction is attributed to coverage of micropores. This is confirmed by the observed adsorption equilibria and the pore size distribution (see Fig. S1).

Binder and kaolin partially cover the zeolite to form the composite. The zeolite crystals are exposed at the surface. In addition, kaolin and binder show compact structures. Further observation shows agglomeration of the zeolite crystals over the surface (see Fig. 8 and Fig. S3). Thus, the surface properties of the zeolite mainly contribute to the porosity and the specific surface area of the agglomerate.

Figure 5. Average particle size and specific surface area of formulations of zeolite HY with AlCl₃ and Al(OH)₃ at different AlCl₃ concentrations in the binder.

Figure 6. (a) Particle size distribution of formulations with HY/kaolin/aluminum chloride 1:1:1 (mass ratio). (b) Zeta potential $\zeta$ of the HY/kaolin/aluminum chloride system at different pH values.

Figure 7. (a) Average particle size of HY/kaolin/aluminum chloride formulations at different Al(OH)₃ additions. (b) pH dependence of zeta potential $\zeta$ for zeolite HY/kaolin/aluminum chloride after Al(OH)₃ addition.
Finally, the agglomeration can be summarized for the spray drying of the studied materials, whereby the slurry can be formed by dissolving aluminum chloride in water and adding aluminum hydroxide up to a minimum amount of 50 mol % AlCl$_3$ (cf. dry basis). It is important to maintain a pH value around 3. Thus, the disperse phase of the slurry will mainly contain monomeric aluminum chloride (see Fig. 2) and the binding would be more stable, controlled by competitive proton coverage. Following this preparation, the particle size of the spray-dried products can easily reach the nozzle limit of the equipment. This procedure is not limited by the equipment capacity, which should facilitate scale-up.

### 4 Conclusion

The consideration of interphase interactions of particles enables understanding and controlling the surface chemistry of particle binding for aluminum chloride-zeolite composites by coagulation. First, agglomeration of particles occurs if the zeta potential of the system is below a critical absolute value of 30 mV [13]. Beyond this point, the agglomeration is less stable due to an excess of surface charge and electrostatic repulsion. In addition, formation of smaller monomeric aluminum complexes supports the stability of the slurry. The nature and coverage of these complexes on the surface of the particles are dependent on the pH value. Finally, the complexation of the binder species can be enhanced in the presence of another alumina phase: Al(OH)$_3$. The formation of complexes enhances the buffer effect of the slurry, increases binder concentration, and protects spray equipment from corrosion by pH $< 3$. However, this process has to be limited to the formation of monomeric alumina species through adjusting the pH value and binder composition to maintain stable bonding.

The reported results combine fundamental approaches of aluminum complex formation with the binding of suspended particles to make the process scalable for equipment of higher capacity. The distinct novelty compared with classical solution chemistry is the control of the spray process only by the pH value and the broad variation of binder fraction in the slurry by the Al/Cl ratio to ensure reproducible binding with kaolin and zeolite HY.
Supporting Information

Supporting Information for this article can be found under DOI: 10.1002/ceat.202100011. This section includes an additional reference to primary literature relevant for this research [14].

Acknowledgment

The authors thank the German Federal Ministry for Education and Research (BMBF) for financial funding of this research within the directive Client-II "International Partnerships for Sustainable Innovation" by FONA³ (ReCaLi Project, funding code: 033R188A). In addition, the authors give special acknowledgment to Prof. Rainer Jordan and his co-workers Dr. Erik Wegener and Sarah Naumann from the Chair of Macromolecular Chemistry at Technische Universität Dresden for providing support with the sample characterization. Open access funding enabled and organized by Projekt DEAL.

The authors have declared no conflict of interest.

Symbols used

$D_{50}$ [μm] maximum particle size of the 50% smallest particles (relative frequency from Mie theory)

$\zeta$ [V] zeta potential

Abbreviation

EDTA ethylenediaminetetraacetic acid

NMR nuclear magnetic resonance

SEM scanning electron microscopy

References

[1] M. Hartman, O. Trnka, O. Šolcova, Ind. Eng. Chem. Res. 2005, 44 (17), 6591–6598. DOI: https://doi.org/10.1021/ie0508005y

[2] A. Sachse, C. Gérardin, G. Delahay, E. Belamie, K. L. Kostov, B. Alonso, Eur. J. Inorg. Chem. 2017, 2017 (17), 1516–1519. DOI: https://doi.org/10.1002/ejic.201700175

[3] V. Der Zon, E. J. Labeij, P. O. Connor (Albemarle Netherlands, B. V.), US Patent 7 160 830 B2, 2007.

[4] G. Pearson, S. Garcia (Inaeris Technologies LLC), US Patent 2019/0070595 A1, 2019.

[5] J. S. Magee, M. M. J. Mitchell, Fluid Catalytic Cracking: Science and Technology, 1st ed., Elsevier, Amsterdam 1993.

[6] N. T. K. Thanh, N. Maclean, S. Mahiddine, Chem. Rev. 2014, 114 (17), 7610–7630. DOI: https://doi.org/10.1021/cr400544s

[7] D. Erdemir, A. Y. Lee, A. S. Myerson, Acc. Chem. Res. 2009, 42 (5), 621–629. DOI: https://doi.org/10.1021/ar800217x

[8] ISO 13320:2020-01, Particle Size Analysis – Laser Diffraction Methods. International Organization for Standardization, Geneva 2020.

[9] S. Bi, C. Wang, Q. Cao, C. Zhang, Coord. Chem. Rev. 2004, 248 (5–6), 441–455. DOI: https://doi.org/10.1016/j.ccr.2003.11.001

[10] Y. H. Chen, S. J. Huang, B. Z. Wan, Ind. Eng. Chem. Res. 2016, 55 (7), 1921–1928. DOI: https://doi.org/10.1021/acs.iecr.5b04288

[11] W. J. Walker, C. S. Cronan, H. H. Patterson, Geochim. Cosmochim. Acta 1988, 52 (1), 55–62. DOI: https://doi.org/10.1016/S0016-7037(88)80056-7

[12] E. S. Hall, J. Appl. Chem. 1965, 15 (5), 197–205. DOI: https://doi.org/10.1002/jctb.2720150501

[13] W. K. Mekhamer, J. Saudi Chem. Soc. 2010, 14 (3), 301–306. DOI: https://doi.org/10.1016/j.jscs.2010.04.013

[14] F. Ambroz, T. J. Macdonald, V. Martis, L. P. Parkin, Small Methods 2018, 2 (11), 1800173.