

Intelligent Catalyst Shaping: Effect of Binders on the Physicochemical and Catalytic Properties of Zeolite-Based Catalysts

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ARTICLE INFO	ABSTRACT
<p>Article History: Received: 15 May 20223 Revised: 29 January 2024 Accepted: 30 January 2024</p> <p>Article type: Research</p> <p>Keywords: Additives, Extrudates, Industrialization, Mechanical strength, Scale up</p>	<p>Today, zeolitic catalysts play an important role in catalytic processes such as cracking, alkylation, etc. However, shaping these catalysts for industrial applications remains a challenge. Despite extensive research in this area in recent years, the number of studies is limited, and detailed information is scarce. Consequently, this study aims to increase awareness of the challenges associated with catalyst shaping and to contribute to the body of knowledge in this field. Following an introduction to the fundamental concepts and shaping techniques, our focus in this review has been on the binder agent, whereby we have categorized the effects of binders that can influence catalyst performance. We demonstrate that while binders may not necessarily possess catalytic properties, the chemical interaction between the binder and the catalyst, as well as the extrusion process, can significantly impact the physicochemical characteristics of the final catalyst, including its acid characteristics, pore characteristics, distribution of loaded metals, and so on. Moreover, depending on the desired properties of the catalyst, different sequences can be employed to utilize the binder. Finally, we identify research gaps in this domain and present recommendations for future studies.</p>

Introduction

The catalytic processes employed in the oil and gas, petrochemical, pharmaceutical, environmental, and other industries are considered to be among the most critical and essential industrial processes of today. Among the noteworthy catalysts utilized in these processes are zeolitic catalysts, which assume a critical role in the production of diverse fuels and a range of products that are needed by society. Zeolites are three-dimensional networks comprising SiO₄ and AlO₄ tetrahedral [1]. These materials possess channels and pores or interconnected cages, along with cations and water molecules that can move and occupy the space within the zeolite pores. The presence of ion-exchangeable cations in their structure, adjustable acidity, high hydrothermal stability, and other characteristics has piqued the interest of many researchers in zeolites [2]. Despite their numerous advantages, catalysts cannot be employed directly after synthesis and in the form of powder, as their use can result in drawbacks such as pressure drop, dust production, insufficient strength, bed clogging, etc. Fig. 1 provides a clear depiction of the

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gap between the production of a zeolite catalyst and its industrial application. According to this figure, to transform these particles into compounds with wider applications and higher added value, shaping is necessary. Arvela et al. studied the shaping of catalysts, with an emphasis on understanding the effects of extrusion on the properties of the final shaped catalyst. They acknowledged that the extrusion method provides higher throughput at lower costs compared to other catalyst shaping methods [3]. Yang et al. reviewed catalyst shaping with a focus on studying the zeolite-extrudate catalysts. They believed that extrudate is the most suitable shape for processes in fixed-bed reactors due to its simplicity in preparation and operation compared to other shapes [4]. Mendes et al. examined HUSY zeolite catalysts for the hydroisomerization process. The objective of the study was to bridge the gap between the formulations that have been explored in the literature and the hydroisomerization catalysts used in industry. The researchers highlighted that the properties of the binder and the shaping process have a significant impact on the final properties of the catalyst [5]. Bingre et al. conducted a study on zeolite shaping technology to overcome problems that arise during shaping and the addition of additives. They created meso and/or macro pores to address issues related to acidity and textural characteristics [6]. Devyatkov et al. studied catalyst shaping and pointed out its importance. Whereas academic research focuses on small quantities of powders and do not consider the influence of scale-up. They raised some points about the compounds that are added to the powdered catalysts during shaping. Rheology improver, peptizing agents, binder, etc. are among the additives used for this purpose [7].

Binders are one of the most crucial materials utilized during catalyst shaping, acting as a bridge between particles, and increasing the strength of the obtained bodies based on their type and function. However, to date, limited academic studies have addressed the effects of binders and their applications. The reason that the knowledge about binders is small, from one point of view, is because of the manufacturers of heterogeneous catalysts who do not disclose its recipe. On the other hand, few scientific efforts have been made to understand the preparation method of these catalytic bodies [5]. During the shaping process, the mechanical resistance of the catalysts must increase, while their properties should not undergo negative changes compared to their powdered state [8]. Of course, when shaping with a binder causes negative effects on the characteristics of zeolite, it is recommended to use binder-free methods for zeolite shaping. Since the binder is removed from the zeolite structure through calcination, it is possible to create a binder-free catalyst. Various methods have been utilized for zeolites shaping without a binder, such as hard templating, hydrothermal transformation, etc. [9]. However, it is worth noting that the final shape of zeolites formed using these methods may resemble the shape of zeolite created with the binder. For example, in the hard templating method, carbon materials, aerogels, and other hard templates are used to structure zeolites. After the templates are removed through calcination, porous particles with spherical shapes are obtained. However, since the focus of this study is on the zeolites shaping in the presence of a binder, we will not be discussing this topic any further. Given the significance of catalyst shaping and binder agents in the final catalysts' quality, and little information about binders in the literature, both of these categories are thoroughly addressed in this study.

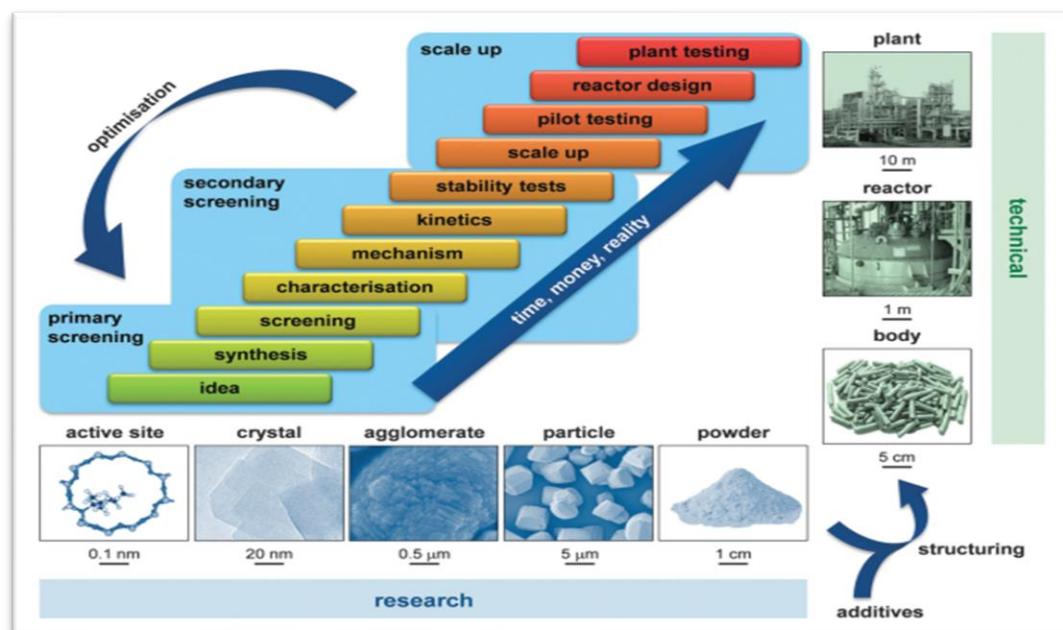


Fig. 1. The stages of industrialization of a catalyst [10]

Catalyst Shaping

Catalyst shaping has advantages compared to the case where catalytic powder is used, like:

- Increasing particle resistance
- Reduce pressure drop
- Control of final particle size
- Create less dust
- Easier transportation
- etc.

Therefore, in the following, we have discussed the process of catalyst shaping in more detail.

Shaping Methods

Heterogeneous catalysts, depend on the type of reactor, the type of reaction, what conditions, what feeds, etc. to be used, they must have a certain size and shape so that have a high activity and mechanical resistance to erosion, corrosion, breaking, etc. Shaped catalysts are often in the form of granules, pellets, tablets, and extrudate [11]. For example, the catalysts used in the hydrocracking process are mainly USY extrudates zeolite with a diameter of 2 mm. In the catalytic reforming process, mini ZSM-5 spheres with a diameter of 2 mm are mainly used, and in the fluidized bed catalytic cracking process, zeolite Y micro spheres with a diameter of 70 micrometers are used [12]. Accordingly, depending on the conditions, there are different methods for heterogeneous catalysts shaping. These methods can be placed in four main categories including spray drying, extrusion, tableting and granulation. For the catalysts that are used in the fluid bed reactor, the spray drying method is usually used, and for the catalysts that are used in the fixed bed reactor, the tableting and extrusion method is mainly used. In the spray drying method, a slurry containing solid catalyst and some additives is sprayed inside the dryer chamber with the help of a nozzle. During the pouring of the slurry, the materials in it are exposed to hot drying gas with a temperature of 150-200°C. In this way, particles with an average size of 100 micrometers are produced [13].

The tableting method is mostly used in the pharmaceutical industry, however, it is also used for the catalysts shaping. In this method, the dry catalyst is first made into a powder and after

adding the necessary additives such as lubricants and binders, the resulting paste is compressed between two movable steel pieces. For the particles produced in this method, to have proper resistance, uniform pressure is applied to the material from all three directions. Although it is easier to move catalysts in the form of tablets and catalyst tablets have good resistance to scratches and pressure, but the operation of making tablets and making cylinders with molds and pistons to produce pressure is very expensive in most cases [14].

In the extrusion method, which is the most important technique in the production of fixed bed catalysts, the catalyst powder is first mixed with a binder and some lubricants. Then, the materials enter the extruder, during which the paste passes through a steel piece, such as a meat grinder, and another device cuts these bodies to the desired length. In this way, cylinders with desired dimensions are obtained, which are calcined in the furnace after drying [15]. Although the tableting method is easier than the extrusion method and tablets with more regular shapes are created, but the extrusion method is considered a better method due to the protection of the surface area and porosity of the catalyst [16]. In addition, the extrusion method has a lower cost [3]. Therefore, the most widely used method today is the extrusion, which is widely used in the production of monolithic catalysts used in purification of cars exhaust gas. Fig. 2 shows how the extruder works to produce catalytic extrudates.

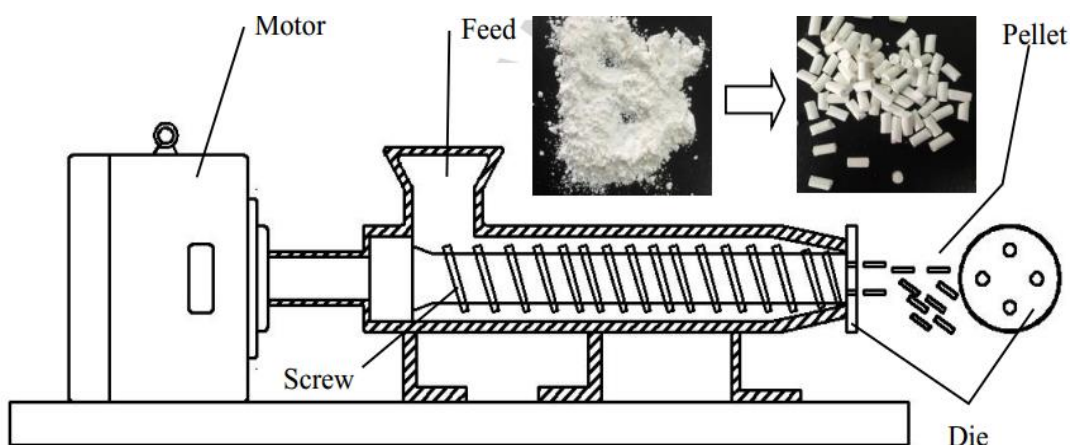


Fig. 2. Extrusion process by an extruder [15]

Factors Affecting the Properties of the Shaped Catalyst

Several factors effect on the final properties of the shaped catalysts, some of the most important ones are mentioned below:

Mold Shape and Machine Pressure

One of the important factors which effect on the final properties of the shaped catalyst is the type of mold used for shaping. For example, the resistance of the catalyst shaped in the form of a solid cylinder is much higher than that of the catalyst in the form of a hollow cylinder. Because the holes of hollow cylinder reduce the resistance of the catalyst against pressure. In addition, for these hollow forms, when the pins are pulled out, the edges of the holes are damaged. Also, catalysts such as alumina, which are often made spherical, have advantages such as reducing the pressure drop along the bed, less damage during handling (because they do not have sharp corners), etc. Ren et al. investigated the effect of molding method on the catalytic performance of MoO₃/ZSM-5 zeolite in the aromatization of methane in the absence of oxygen. Comparing

the laminar catalyst obtained by spraying ZSM-5 zeolite suspension on an inert silica ball and the extruded catalyst obtained from the combination of ZSM-5 catalyst and colloidal silica, the results of various analyzes showed that the laminar catalyst performed better than the extruded catalysts. Laminar catalysts, due to their lower thickness, had a higher degree of diffusion, which reduced the resistance of mass transfer and caused the easier and faster release of aromatic species from the zeolite channels [17]. Keep in mind, in addition to the structure of the mold used for shaping, the pressure applied by the pressing and shaping devices also affects the porosity, the resistance of the shaped catalyst, etc. By changing the pressure of the press machine and comparing the results, the optimal value for the reaction and the desired conditions can be obtained.

Amount of Added Additives

To achieve a mixture that has the necessary characteristics for shaping, compounds such as binders (to establish connection and increase mechanical strength), clay and starches (to create better rheological behavior), organic polymers (to reduce shape changes), Anti-flocculation agents (to break solid masses), progens (to increase porosity), lubricants, water, etc. are added to the catalyst [3]. Determining the proper combination of these materials is very important and affects the ability of the catalyst to form and its resistance to pressure [18]. This is while a specific theoretical approach has not been presented in this field. As a concrete example, during extrusion, if the amount of water that is added is small, it leads to the production of a paste with high viscosity, brittle and unsustainable, which cannot be easily fed into the extruder and be shaped. But if the amount of water is high, the extruded particles stick together after exiting the nozzle and cannot maintain their shape. Therefore, in the production of paste for extrusion, there must be a balance between these two factors [16]. Fig. 3 shows this very well.

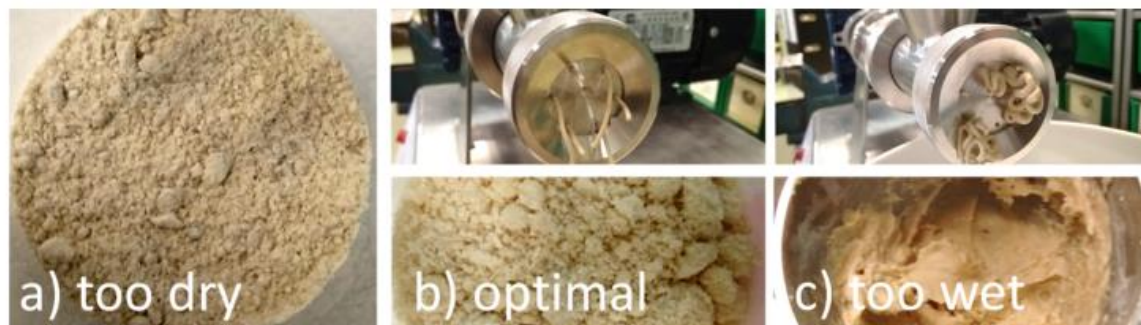


Fig. 3. The effect of water amount on the morphology of the shaped catalytic material [16]

Almeida et al. studied the effect of the number of additives on the integrity of extrudates. The results showed that for a sample with a high content of polyvinyl alcohol, after heat treatment, the sample with low mechanical strength and irregular shape was obtained. However, for the sample with the lowest amount of polyvinyl alcohol (2% polyvinyl alcohol and 14% silica), extrusions with regular shape and diameter as well as high mechanical strength were obtained [19]. Kantarelis et al. used bentonite as a binder to form transition metal modified ZSM-5 catalyst in converting biomass to liquids. In this research, the effect of zeolite to binder ratio on product yield was studied. The results showed that the sample with more bentonite content had less coke production due to the decrease in the amount of strong acid sites. In addition, this sample had a higher liquid production efficiency [20].



Type of Binder

Many catalytic materials do not have enough resistance after shaping and turn into sand. In this case, materials called binders are added to the catalyst composition so that the catalyst has a suitable mechanical resistance after shaping. Binders are divided into two categories, organic (like methylcellulose, polyethylene glycol, and polyvinyl alcohol) and inorganic (like alumina, silica, silica-alumina, zirconia, titania, pseudo-boehmite, and clays) binders which inorganic binders generally show better performance. The following list, in Table 1, presents a list of these organic and inorganic binders.

Table 1. A list of some organic and inorganic binders and their applications

Zeolite	Organic binder	Inorganic binder	Application	Ref.
13X/activated carbon	Carboxymethylcellulose	-	CO ₂ capture	[21]
Y	-	A mixture of colloidal silica with aluminum dihydrogen phosphate	Hydrocarbon Cracking	[22]
MCM-41 /ZSM-5	-	Boehmite	Hydroisomerization of C-8	[23]
5A	Carboxymethylcellulose	Kaolin	Adsorption of saturated linear hydrocarbon	[24]
Fe-ZSM-5	-	Alumina	NO _x conversion	[25]
13X	Polyvinyl alcohol and polyethylene glycol	-	CO ₂ adsorption	[26]

Different binders give different resistances to the catalyst under different conditions. Ren et al. investigated the effect of binder type (silica, alumina and silica-alumina) on the performance of MoO₃/ZSM-5 shaped catalyst. The results showed that silica binder was more suitable for methane aromatization over this catalyst. Because the silica binder has the lowest strong acid content. While for alumina binder, with the introduction of aluminum species into the structure of ZSM-5, strong acid sites are produced, which themselves cause adverse side effects. Of course, from the point of view of mechanical strength, silica binder has the lowest mechanical strength. But in general, the sample prepared with silica binder had more selectivity to aromatic compounds, and at the same time, less coke deposited on it [17].

Calcination After Catalyst Shaping

Additives that were added to the catalyst during shaping must be removed from the catalyst after shaping, which is done during the thermal process of calcination. Calcination is a heat process that is carried out in the presence of air, oxygen or other gases. Calcination is usually done at temperatures below the melting point and increases mechanical strength and resistance, and also affects the physical properties of materials [27]. The purpose of catalyst calcination after the drying stage is to remove volatile substances from solid materials, to simultaneously regulate texture, surface and volume of porosity, and to achieve a suitable mechanical strength. Depending on the intensity of calcination, a transverse connection is created at the junction of hydroxyl groups and other groups, thus increasing the mechanical resistance [28]. Keep in mind, the furnace temperature and heat treatment time should be such that the additives are removed from the catalyst, while the catalyst with greater resistance is produced. However, the optimal calcination temperature may vary depending on the specific catalyst, the kind of binder and the desired reaction. Therefore, it is advisable to conduct experimental tests to determine the best calcination conditions for each case. When the calcination process creates many

irregularities in the catalyst structure, the initial formation is lost. In this case, it is better to perform an initial calcination operation first, then to shape the catalyst, and then to perform the calcination operation again to remove volatile substances and optimize mechanical resistance. But if calcination does not change the tissue, calcination can be done only after shaping.

Ebrahimi et al. investigated the effect of calcination temperature, ranging from 450°C to 650°C, on the spray-dried SAPO-34/ kaolin catalyst in the MTO process. The study found that at temperatures exceeding 550°C, the kaolin binder was transformed into metakaolin, creating new Brønsted acid sites in the catalyst. As a result, the catalyst had a life time of over 900 minutes in the MTO process. However, at a reaction temperature of approximately 450°C, the catalyst had low methanol conversion and was rapidly deactivated [29]. Tian et al conducted a study on the impact of calcination process variables, such as calcination temperature, time, and heating rate, on the mechanical strength of ZSM-extruded catalysts. The extrusion process consisted of five stages: first, mixing ZSM-5 with pseudo boehmite; then, kneading, extrusion, drying, and finally, calcination in a muffle furnace at varying temperatures, times, and heating rates. Results indicate that the average strength decreased as the heating rate increased from 5 to around 10 °C/min, but then enhanced as the heating rate increased further up to 15 °C/min. In addition, increase in calcination temperature up to 600 °C enhanced the mean strength, beyond which it decreased. This is due to the fact that as the calcination temperature increases, the sintering phenomenon of small particles becomes more prominent, causing significant changes in properties such as specific surface area and mesopore volume, which may influence the strength and stability of the catalyst [30].

Employing Binders

As mentioned, one of the important parameters affecting the properties of the shaped catalyst is the binder, which can have a very important effect on the properties of the final catalyst. Be careful that the binder usually does not have a catalytic role by itself, but the relationship between the binder and the zeolite as well as the shaping process can have an important effect on the physicochemical characteristics of the final catalyst and, as a result, on its stability, activity and selectivity [31]. A suitable binder should have the following properties:

It can be easily removed from the texture at low temperature

- It should not be toxic, abrasive, corrosive, etc
- Leave the least amount of ash after heating
- Increase the mechanical strength of particles
- Cheap and available
- Disperse easily

Following is the introduction of a number of commonly used binders:

Alumina: Aluminum oxide with the chemical formula of Al_2O_3 has a very high melting point and is chemically very stable. This feature allows this material to be used in applications that require high temperature tolerance. The hardness, strength and wear resistance of alumina is the highest among oxides. This issue causes this material to be used as a binder and a material to increase stability [32].

Bentonite: It is one of the main minerals of the montmorillonite group, which is characterized by its swelling when in contact with water. This material has an aluminosilicate structure and is included in the category of three-layer silicates [33]. Bentonite has two tetrahedral layers and one octahedral layer, which increase mechanical strength and do not migrate during drying. Fig. 4 depicts the structure of bentonite.

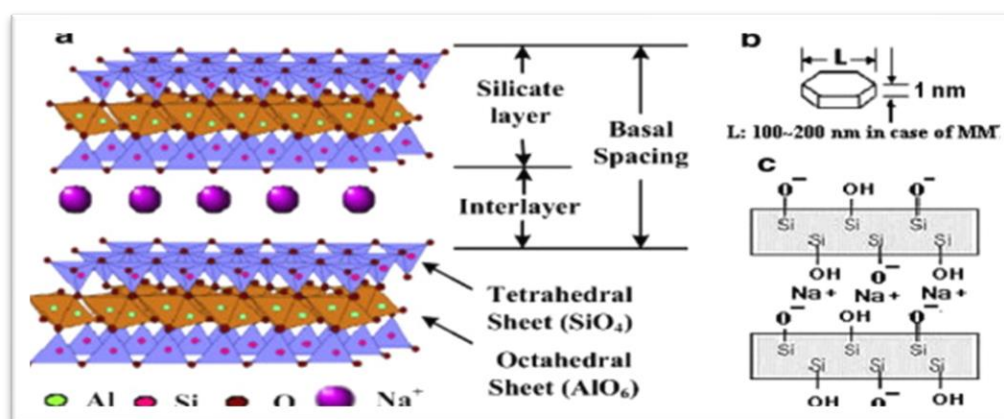


Fig. 4. The structure of bentonite as a binder [33]

Kaolin: This semi-crystalline material, which belongs to the family of clays, its structure consists of tetrahedral layers of silicon and octahedral layers of aluminum, which Fig. 5 shows the image of these layers well. Kaolins have characteristics such as stickiness, colloidity, impermeability, high water absorption, low heat and electricity conductivity, etc. [34]. By heating kaolin in the temperature range of 500-900 °C, it is possible to achieve an amorphous structure containing silicon and tetrahedral aluminum, which is known as metakaolin.

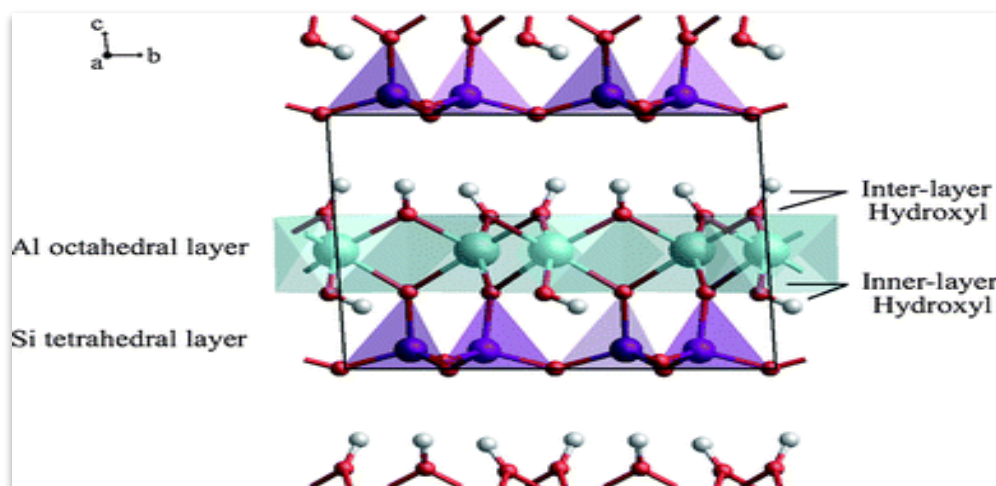


Fig. 5. Silicon tetrahedral and aluminum octahedral layers in kaolin [34]

The process of fluid catalytic cracking (FCC) is one of the important processes in the production of liquid hydrocarbons such as gasoline. The catalysts used in this process are a typical example of catalysts that need to be shaped with a binder and generally the mentioned binders are used in their production [35].

Effects of the Presence of Binder

In addition to the general benefits of the shaping process and binders, such as establishing connection, binders can leave special and unique effects in catalytic matters. When a binder is added to the catalyst, the relationship between the binder and the catalyst affects the diffusion characteristics and pore structure, the acidic characteristics of the catalyst, the distribution of loaded metals, and in general, the stability, activity, and selectivity. For example, Wang et al.'s research showed that alumina acts as a pre-cracking catalyst in breaking large molecules, which in addition to the pre-conversion of bulky molecules, causes easier entry of reactants into the

catalyst pore structure [36]. Saavedra et al., also confirmed the role of the matrix, consisting of binder and filler, in the pre-cracking of molecules, so, increasing the contact of molecules with catalytic active sites [22]. Or, the research showed that the use of binders has been effective in improving the coking characteristics of the shaped catalyst by changing the acidic characteristics, changing the diffusion characteristics, and also trapping the coke precursors [28]. Liu et al. used cylindrical H-ZSM-5 catalysts extruded with gamma-alumina binder to perform the process of methanol to hydrocarbon. The gamma alumina binder used in this study, while creating a very good mechanical resistance compared to other binders, with the introduction of aluminum species led to the creation of some additional catalytic properties such as reducing the rate of coke production [11]. Therefore, by engineering this issue, it is possible to provide much more benefits of increasing the resistance of particles for the catalyst. In the following, some of the most important effects of binder's presence are mentioned.

Change in Diffusion Characteristics

The process of producing pellets from zeolite powders is mainly associated with the production of meso and macro pores, after which the diffusion characteristics change. Du et al. have acknowledged that when a binder such as alumina is used, which mainly contains mesopores, a mesopore structure is formed on the catalyst, which can help mass transfer during the reaction. In the study of the effect of alumina, silica gel and kaolin binders on the performance of Ni/HZSM-5 catalyst in the hydrodeoxygenation of cyclohexanone, they observed that in the case of using alumina binder, the total pore volume was the largest and 80% of the pores were mesopores. Also, the highest catalytic activity was obtained on the sample that was shaped with alumina binder, the conversion of cyclohexanone and selectivity of cyclohexane were 97.3% and 88.3%, respectively [37].

Kim et al also encountered this issue while investigating the performance of synthesized samples for the methanol to dimethyl ether process. They observed that when the binder was not used, the size of the pores was not in the meso range, but by adding gamma alumina, which had mesopores in the range of 10-5 nm, mesopores were formed, and the volume of these pores increased with the increase in the amount of binder [38].

Lakiss et al, in the study of hydroisomerization of octane and dialkylation of triisopropylbenzene in the presence of boehmite-like binder, observed the production of additional mesopores and also new catalytic sites near the external surface of zeolite, which improved the catalytic performance in cracking of triisopropylbenzene molecules [12].

Change in Acidic Properties

In addition to playing its main role, which is creating a connection between zeolite components, the binder can also be a source of mobile species and cause the transfer of chemical species to/from the active sites [28]. For example, in a binder like alumina, the migration of aluminum from the binder to the catalyst has occurred, which causes the formation of new acid sites, and as a result, the concentration of acid sites increases compared to the case without a binder. Zeolites contain two types of acid sites: Brønsted acid sites and Lewis acid sites. Brønsted acidity in zeolites arises from a hydroxyl group that originates from the aluminum atoms. On the other hand, Lewis acidity in zeolites can be created by removing some of the framework aluminum and forming extra-framework species [39]. The catalytic activity of zeolite can be influenced by these two acid sites, which affect the strength of the zeolite acid sites. Therefore, a binder like alumina, can be suitable for processes that require a high concentration of acid sites. Alumina has the capability of moving aluminum to the zeolite and producing extra-framework aluminum, which generates new acid sites for the zeolite. However, the presence of silicon in the silica binder and the presence of sodium in the bentonite binder neutralize the acidic sites and reduce the concentration of these sites. So, binders such as silica, bentonite, etc. are suitable for processes that require a low concentration of acid sites.



Of course, the type of zeolite that is placed next to such binders is also important [28]. For example, Dorado et al. when studying the effect of bentonite binder on the activity of pd/ZSM-5 and pd/Beta zeolites in the hydroisomerization of n-butane, although the ion exchange between protons of zeolite and sodium in bentonite neutralize the number and concentration of strong acid sites and so decreased the conversion of n-butane, but the negative effect was compensated by the selectivity of zeolite ZSM-5 to the iso-butane. As a result, the presence of bentonite improved the catalytic performance. But for zeolites with beta base, the presence of bentonite decreased the catalytic performance due to the reduction of strong acid sites [40].

Therefore, this rule as a rule of thumb is generally accepted, but it may not be true in some cases. In addition, Zhou et al. showed that the amount of aluminum that migrates from the alumina binder and the place where it settles depends on the size of the alumina particles used. As the size of alumina particles is smaller and in nano dimensions, the migration of alumina and as a result the acidity increased more and more new acidic sites were produced. It was also observed that nano-alumina species with a higher diffusion coefficient compared to micro-sized alumina, tended more to migrate to the ionic position, from where the migration of aluminum species to the zeolite structure will occur [41].

Better Distribution of Loaded Metals

If metal is used, in the case where a binder is used, the metal particles may block the pores of catalyst. However, in the presence of the binder, the metal particles are placed in the mesopores formed between the binder and the zeolite, and so, the available surface for the reaction does not become inaccessible. During the investigation of PtSnNa/AlSBA-15 catalyst for propane dehydrogenation, Duan et al noticed that the dispersion of platinum on the shaped catalysts was improved. So that, PtSnNa/AlSBA-15 catalyst mixed with 20 wt% alumina showed the highest catalytic performance in terms of propane conversion and platinum distribution. It was observed that in the content of 20% by weight of alumina binder, alumina species on the surface of the catalyst isolated the metal components and prevented their accumulation during calcination and caused the best dispersion. But, at content more than 20%, the opposite happened. In fact, the aluminum species deposited on the surface of the catalyst and covered the platinum and reduced the dispersion of platinum [42].

Buttignol et al., while investigating the performance of Fe-ZSM-5 catalyst, found out that the agglomeration of iron species in extruded catalysts was significantly less than powdered catalysts. Because the binder prevented the agglomeration of iron species during calcination. This problem caused the extruded catalysts to show a better performance than the powder catalysts in the NOX conversion process [43].

In addition to the above effects, a number of studies have mentioned the role of binder as a heat sink in exothermic reactions. As you know, proper heat transfer is effective in preventing hot spots. Otherwise, excessive heating will cause sintering and destruction of the active site of the catalyst. The use of a suitable binder by diluting the active phase can significantly increase the thermal stability of catalysts and by reducing the possibility of agglomeration, it can protect the integrity of the active phase of the catalyst [44]. Also, it has been mentioned in some studies that the binder can increase the catalyst's resistance to structural changes by trapping the poisons in the feed. In petroleum feed, there are metals such as vanadium, nickel, sodium, iron, etc., which cause contamination and poisoning of the catalyst. Meanwhile, the effect of vanadium and sodium is very strong, in such a way that zeolite is completely deactivated by the formation of metavanadic acid and sodium hydroxide. The binder can increase the resistance of catalysts to poisoning by trapping these poisons and compounds such as nitrogenous compounds [28].

Binder Addition Order

The review of the literature has shown that the effects of the binder on the catalytic characteristics of the shaped catalyst can be investigated in three cases. In the following, each of these items is discussed in more detail:

- a) First, make the necessary modifications on the powdered catalyst and then mix this catalyst with the binder
- b) The powdered catalyst is mixed with the binder and then the necessary modifications are made on the extrudates
- c) The binder should be modified and then mixed with the powdered catalyst

In fact, the stage at which the binder addition is performed, significantly effects on results.

Modifying the Catalytic Powder and Mixing with the Binder

In this case, any operations and modifications that are needed are first performed on the powdered catalyst and then this catalyst is mixed with the binder.

To investigate the role of the matrix on the activity of the catalyst, Saavedra et al. used ZSM-5 zeolite shaped with three binders of sodium metasilicate, aluminum chloride and a composite binder of aluminum phosphate and colloidal silica. Catalytic tests were performed in the cracking of trimethylpentane and n-hexane. The results showed that the sodium metasilicate binder, with its low porosity, caused non-selective cracking. Besides, this catalyst was quickly deactivated due to the coke deposition. Aluminum chloride binder was more active than sodium methasilicate, but had similar selectivity to olefin. This is while the aluminum phosphate binder combined with colloidal silica, due to its lower acidity and the large pores it created, prevented the quick blocking of the pores due to coke deposition and showed better performance than the other two catalysts [22].

Bertolini et al., after synthesizing zeolite A, shaped it using bentonite, kaolin and a combination of these two binders. Binders were used from 5 to 10 wt% compared to the weight of zeolite. The results showed that the highest mechanical strength was achieved with the sample containing 10% by weight of bentonite binder. To break such a granule, a force of 32.7 N and a pressure of 2.9 MPa were calculated [45].

Honda et al. compared the dehydroaromatization activity of methane over MoO₃/HZSM-5 catalyst prepared by three different methods. These three methods are:

- a) Mixing ZSM-5 with binder, then impregnating molybdenum on the extrudate and finally carburizing in the presence of methane flow to convert molybdenum oxide into molybdenum carbide.
- b) impregnating molybdenum on ZSM-5 and then mixing it with binder and finally carburization of the mixture
- c) Molybdenum doping on ZSM-5, then carburizing MOO₃/ZSM-5 and finally mixing these samples with binder

The results showed that in the first case, due to the distribution of molybdenum on the silica surface, this sample had no significant activity. In the second case, due to the migration of molybdenum oxide from the support to the binder, the catalytic activity was low. However, in the third method, where the carburization of the sample was done before any binder was added, high activity was obtained. Because carburization, which had converted most of the molybdenum oxide into molybdenum carbide, prevented molybdenum from migrating from the support to the binder [46].

Mixing the Catalyst Powder with Binder and Modifying the Extrudates

In this case, the catalyst is shaped first, and then modifications are carried out on these shaped catalysts. Beheshti et al. studied the extrusion of zeolite H-[B]-ZSM-5 with alumina binder and then steaming it. The results showed that during this operation, single and narrow mesopores were formed without destroying the crystal structure. Also, the catalytic lifetime of this sample



was 750 hours, while it was 520 hours for the extruded sample without steaming and 580 hours for the powdered sample. This improvement in the lifetime can be related to the created mesopores and also to the synergistic effects of extrusion and steaming operations, which lead to a decrease in the strength of acid sites and a decrease in the ratio of strong to weak acid sites [47].

Huang et al. considered Molybdenum oxide supported on mordenite zeolite-alumina composite ($\text{MoO}_3/\text{mordenite-alumina}$), and then subjected this catalyst to nitric acid leaching. During the calcination operation, molybdenum oxide has migrated to mordenite channels. During the migration, the molybdenum oxide encountered extraframework aluminum (EFAL), which led to the formation of aluminum molybdate ($\text{Al}_2(\text{MoO}_4)_3$). In the following, it was assumed that some of these aluminum molybdate species were located in the pores or inside the zeolite channels, and after acid leaching, these species were extracted and disappeared. The results of the analyzes confirmed the formation of aluminum molybdate and then its extraction during acid leaching. This structural change made the aforementioned catalyst show good stability in *n*-butene metathesis reactions due to the transfer of coke species [48].

Song et al. investigated the effect of treatment with organic bases, such as tetraethylammonium hydroxide, etc., on the catalytic characteristics of TS-1/ SiO_2 extrudate in propylene epoxidation [49]. In their recent study, this research team concluded that if TS-1/ SiO_2 extrudates are used, it is better than using titanium silicalite powder. Finally, it turned out that different organic bases have shown different results. In such a way that the best results in terms of conversion percentage and stability were obtained with the sample that was treated with tetrapropylammonium hydroxide. Such an improvement in performance is due to the improvement in diffusion characteristics, increase in acidity, widening of pore opening and optimal distribution of titanium and silicon [50].

Klimov et al. considered two different methods to introduce "boron" into hydroprocessing catalysts. In one, boron was added to the alumina support during the kneading of the paste, and in the other one, extruded alumina was first doped with cobalt and molybdenum, and then boric acid was used for impregnation. The results showed that the introduction of boron increased the catalytic activity in desulfurization and denitrogenation. In fact, this increase in activity with the addition of boron was greater for the case when boron was added to the solution. Because in this case, boron is located on the surface of the alumina particles, while when boron is present in the support, it is like the boron is inside the chamber and capsule, which does not have any effect on the characteristics of the catalyst [51].

Zhang et al. subjected ZSM-5 powders and its extrudates to steaming by changing the temperature and time, then these materials were used in the methanol to propylene reaction. The results showed that during the time on stream, the extruded catalysts that were subjected to steaming had a longer life time (89 hr) than the non-extruded catalysts (57 hr) and the extrudates that were not subjected to steaming (45 hr). The improvement in catalytic performance can be attributed to the appropriate ratio and number of Lewis and Bronsted acid sites in combination with the meso structure, which are required to reduce hydrogen transfer reactions and prevent coke deposition. It was found that although the total number of acid sites and acid strength decreased during steaming, this decrease was more for the steamed extrudates than the one that ZSM-5 powder steamed. This prevented the creation of coke precursors and increased the catalyst lifetime [52].

Using alkaline treatment is one of the simplest methods of creating mesopore. In the control of desilication, the amount of aluminum and Si/Al ratio of zeolite is a very important parameter, so that its optimal ratio is usually between 25-50. But there is still the question whether extraframework aluminum (EFAL), for example, due to the presence of alumina binder, affects the desiliconization process? To answer this question, Li et al. investigated the effect of alkali

treatment on structural characteristics and catalytic performance of ZSM-5/ZSM-11, shaped with alumina binder, in 1-hexane isomerization and aromatization reactions. They observed that although binders such as silica and alumina are considered neutral for the reactions, but during the alkaline treatment, the alkaline solution interacted with the binder and the catalyst. In such a way that, for the alkali-washed sample after extrusion, the highest activity and stability were observed. This is due to the distribution of acidic sites due to the dissolution of part of the alumina binder in the alkaline solution and the creation of more mesopores due to the cooperation of the alumina binder in the production of mesopores [53]. So, the sequence of alkaline treatment has been effective not only in acidity but also in the number of created mesopores.

Modifying the Binder and Mixing with the Catalytic Powder

One of the interesting discussions in the field of using binders can be dedicated to the issue that we first make changes in the structure of the binder and then mix this new binder with catalytic powders. In this context, Gao et al obtained a new porous binder with the help of acid-treated kaolin, and then extruded ZSM-5 zeolite with this binder. The results showed that the catalyst used with this binder had less corrosion, less zeolite consumption and higher stability. In addition, the conversion and total liquid yield increased by 0.73% and 0.95%, respectively over this shaped catalyst [54].

In another study, Lee et al. treated the pseudo-boehmite binder with phosphoric acid, then ZSM-5 was extruded with this new binder. As you know, during calcination, boehmite turns into gamma-alumina [47]. The results showed that in the presence of phosphorus, the unfavorable characteristics of the pseudo-boehmite binder such as self-catalytic activity, the reaction between the aluminum in the binder and zeolite and the creation of additional acid sites were neutralized. Aluminophosphate binder showed no acidity increase and even caused a decrease in strong acidity. Finally, this extrudate showed high mechanical strength, resistance to coke, stability up to 150 hours, etc. in the conversion of methanol to propylene, and these positive effects were more evident with the increase of phosphorus content. So that, in the ratio of phosphorus to aluminum equal to 0.8, the yield to olefins was 80% and the conversion of methanol was 100% [55].

But finally, the order of adding the binder depends on the expectation from the binder. For example, during the upgrading of heavy fuels, since large molecules can hardly enter the openings of the pores and the blocking of the pores and the deactivation of the catalyst are dominant, the addition of binder can make the situation worse and as a result, large molecules cannot access the active sites. To solve this problem, by creating meso and/or macro pores in the alumina binder, Bingre et al. reduced the negative effects of the binder on the surface area, resulting in a better mass transfer and even like powder [6]. Therefore, in these cases, using the third method can be effective.

Summary and Future Prospects

Although shaped catalysts have been used in the industry for many years, less attention has been paid to this field. In this regard, in this study by reviewing the previous literature, it has been tried to deal with the basic concepts of catalyst shaping and specifically to the investigation of the effect of binder on the Physico-chemical and Catalytic Properties of shaped catalysts. The results showed that the shaping method and the materials used during this work highly effect on the final characteristics of the catalyst such as acidity, pore characteristics, mechanical stability, thermal stability, etc. One of the important agents that is added to the catalyst during shaping is the binder, which affects the physico-chemical and catalytic properties of extruded catalysts. Therefore, by engineering various shaping methods and additives that are added during shaping, it is possible to create the desired catalytic properties.



Generally, the results obtained from reviewing the literature show that the catalyst shaping process is still at the initial development level. So, for future studies, the scale up of zeolitic catalysts shaping, improving the performance of shaped catalyst by using methods such as plasma and ultrasound irradiation, designing new and efficient binders, etc. is an exciting research topic that seems attractive.

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How to cite: Mirshafiee F, Karimzadeh R. Intelligent Catalyst Shaping: Effect of Binders on the Physicochemical and Catalytic Properties of Zeolite-Based Catalysts. *Journal of Chemical and Petroleum Engineering* 2024; 58(1): 131-147.