

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

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Abstract:

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

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10 necessarily possess catalytic properties, the chemical interaction between the binder and the
11 catalyst, as well as the extrusion process, can significantly impact the physicochemical
12 characteristics of the final catalyst, including its acid characteristics, pore characteristics,
13 distribution of loaded metals, and so on. Moreover, depending on the desired properties of the
14 catalyst, different sequences can be employed to utilize the binder. Finally, we identify research
15 gaps in this domain and present recommendations for future studies.

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22 **Keywords:** Additives, Extrudates, Mechanical strength, Scale up, industrialization.

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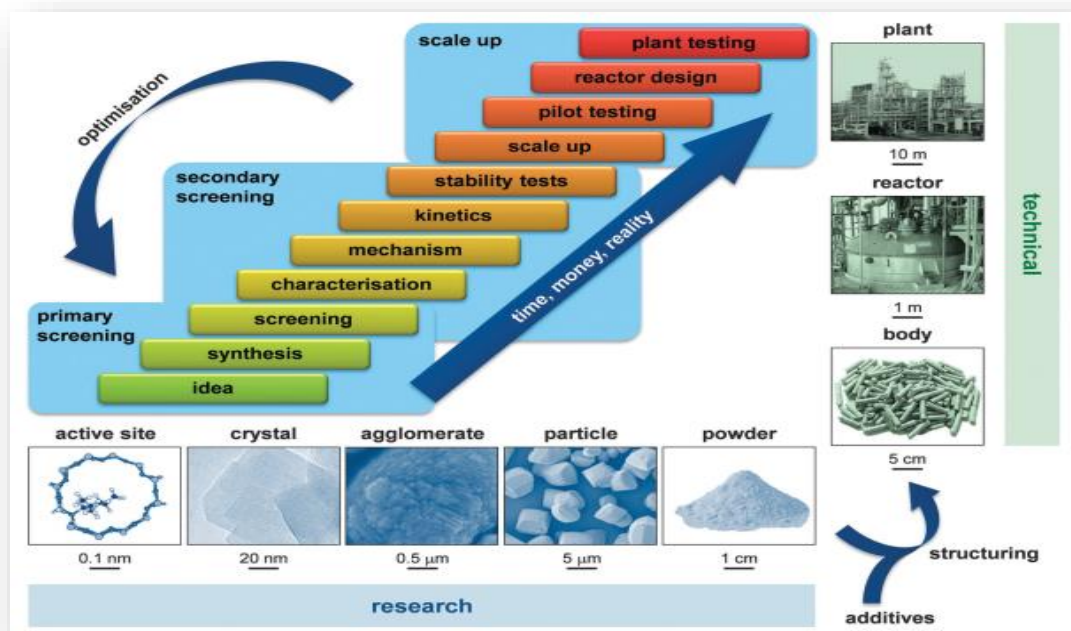
25 **1 Introduction**

26 The catalytic processes employed in the oil and gas, petrochemical, pharmaceutical,
27 environmental, and other industries are considered to be among the most critical and essential
28 industrial processes of today. Among the noteworthy catalysts utilized in these processes are
29 zeolitic catalysts, which assume a critical role in the production of diverse fuels and a range of
30 products that are needed by society. Zeolites are three-dimensional networks comprising SiO_4
31 and AlO_4 tetrahedral [1]. These materials possess channels and pores or interconnected cages,
32 along with cations and water molecules that can move and occupy the space within the zeolite
33 pores. The presence of ion-exchangeable cations in their structure, adjustable acidity, high
34 hydrothermal stability, and other characteristics has piqued the interest of many researchers in

30 zeolites [2]. Despite their numerous advantages, catalysts cannot be employed directly after
36 synthesis and in the form of powder, as their use can result in drawbacks such as pressure drop,
37 dust production, insufficient strength, bed clogging, etc. Figure 1 provides a clear depiction of
38 the gap between the production of a zeolite catalyst and its industrial application. According to
39 this figure, to transform these particles into compounds with wider applications and higher
40 added value, shaping is necessary. Arvela et al. studied the shaping of catalysts, with an
41 emphasis on understanding the effects of extrusion on the properties of the final shaped
42 catalyst. They acknowledged that the extrusion method provides higher throughput at lower
43 costs compared to other catalyst shaping methods [3]. Yang et al. reviewed catalyst shaping
44 with a focus on studying the zeolite-extrudate catalysts. They believed that extrudate is the
45 most suitable shape for processes in fixed-bed reactors due to its simplicity in preparation and
46 operation compared to other shapes [4]. Mendes et al examined HUSY zeolite catalysts for the
47 hydroisomerization process. The objective of the study was to bridge the gap between the
48 formulations that have been explored in the literature and the hydroisomerization catalysts used
49 in industry. The researchers highlighted that the properties of the binder and the shaping
50 process have a significant impact on the final properties of the catalyst [5]. Bingre et al.
51 conducted a study on zeolite shaping technology to overcome problems that arise during
52 shaping and the addition of additives. They created meso and/or macro pores to address issues
53 related to acidity and textural characteristics [6]. Devyatkov et al. studied catalyst shaping and
54 pointed out its importance. Whereas academic research focuses on small quantities of powders
55 and do not consider the influence of scale-up. They raised some points about the compounds
56 that are added to the powdered catalysts during shaping. Rheology improver, peptizing agents,
57 binder, etc. are among the additives used for this purpose [7].
58 Binders are one of the most crucial materials utilized during catalyst shaping, acting as a bridge
59 between particles, and increasing the strength of the obtained bodies based on their type and

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

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2 Catalyst shaping

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

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- Increasing particle resistance

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- Reduce pressure drop

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- Control of final particle size

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- Create less dust

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- Easier transportation

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- etc.

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

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2.1 Shaping methods

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Heterogeneous catalysts, depend on the type of reactor, the type of reaction, what conditions,

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what feeds, etc. to be used, they must have a certain size and shape so that have a high activity

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and mechanical resistance to erosion, corrosion, breaking, etc. Shaped catalysts are often in the

98 form of granules, pellets, tablets, and extrudate [11]. For example, the catalysts used in the
99 hydrocracking process are mainly USY extrudates zeolite with a diameter of 2 mm. In the
100 catalytic reforming process, mini ZSM-5 spheres with a diameter of 2 mm are mainly used,
101 and in the fluidized bed catalytic cracking process, zeolite Y micro spheres with a diameter of
102 70 micrometers are used [12]. Accordingly, depending on the conditions, there are different
103 methods for heterogeneous catalysts shaping. These methods can be placed in four main
104 categories including spray drying, extrusion, tableting and granulation. For the catalysts that
105 are used in the fluid bed reactor, the spray drying method is usually used, and for the catalysts
106 that are used in the fixed bed reactor, the tableting and extrusion method is mainly used. In the
107 spray drying method, a slurry containing solid catalyst and some additives is sprayed inside the
108 dryer chamber with the help of a nozzle. During the pouring of the slurry, the materials in it
109 are exposed to hot drying gas with a temperature of 150-200°C. In this way, particles with an
110 average size of 100 micrometers are produced [13].

111 The tableting method is mostly used in the pharmaceutical industry, however, it is also used
112 for the catalysts shaping. In this method, the dry catalyst is first made into a powder and after
113 adding the necessary additives such as lubricants and binders, the resulting paste is compressed
114 between two movable steel pieces. For the particles produced in this method, to have proper
115 resistance, uniform pressure is applied to the material from all three directions. Although it is
116 easier to move catalysts in the form of tablets and catalyst tablets have good resistance to
117 scratches and pressure, but the operation of making tablets and making cylinders with molds
118 and pistons to produce pressure is very expensive in most cases [14].

119 In the extrusion method, which is the most important technique in the production of fixed bed
120 catalysts, the catalyst powder is first mixed with a binder and some lubricants. Then, the
121 materials enter the extruder, during which the paste passes through a steel piece, such as a meat
122 grinder, and another device cuts these bodies to the desired length. In this way, cylinders with

123 desired dimensions are obtained, which are calcined in the furnace after drying [15]. Although
124 the tableting method is easier than the extrusion method and tablets with more regular shapes
125 are created, but the extrusion method is considered a better method due to the protection of the
126 surface area and porosity of the catalyst [16]. In addition, the extrusion method has a lower
127 cost [3]. Therefore, the most widely used method today is the extrusion, which is widely used
128 in the production of monolithic catalysts used in purification of cars exhaust gas. Figure 2
129 shows how the extruder works to produce catalytic extrudates.

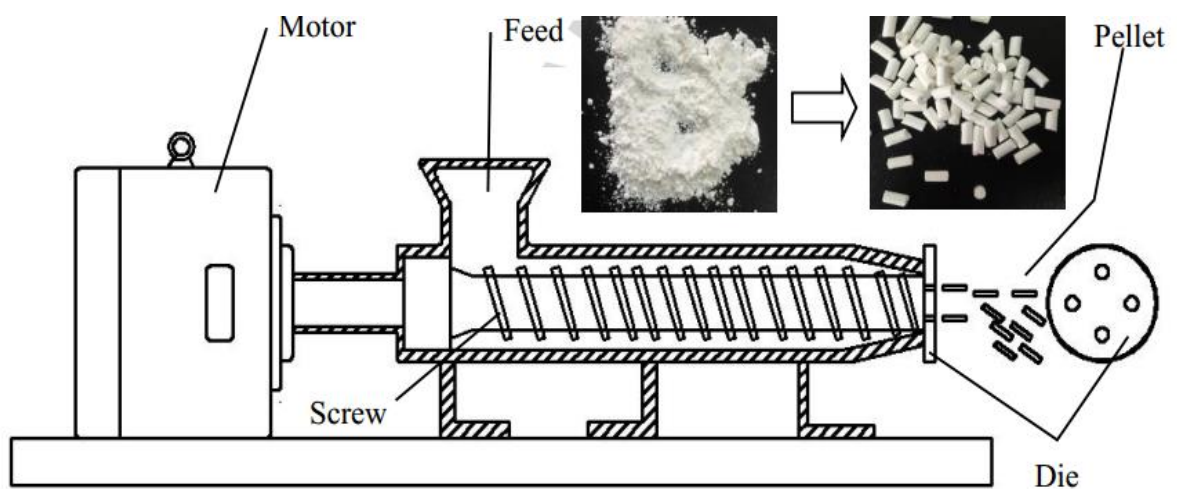


Figure 2: Extrusion process by an extruder [15]

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133 2.2 Factors affecting the properties of the shaped catalyst

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

136 2.2.1 Mold shape and machine pressure

137 One of the important factors which effect on the final properties of the shaped catalyst is the
138 type of mold used for shaping. For example, the resistance of the catalyst shaped in the form
139 of a solid cylinder is much higher than that of the catalyst in the form of a hollow cylinder.
140 Because the holes of hollow cylinder reduce the resistance of the catalyst against pressure. In
141 addition, for these hollow forms, when the pins are pulled out, the edges of the holes are dam-
142 aged. Also, catalysts such as alumina, which are often made spherical, have advantages such

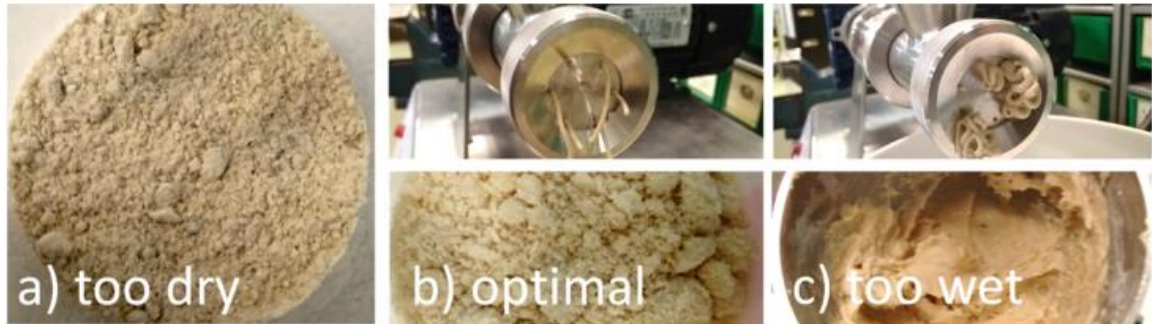
1 4 3 as reducing the pressure drop along the bed, less damage during handling (because they do not
1 4 4 have sharp corners), etc. Ren et al. investigated the effect of molding method on the catalytic
1 4 5 performance of MoO₃/ZSM-5 zeolite in the aromatization of methane in the absence of oxygen.
1 4 6 Comparing the laminar catalyst obtained by spraying ZSM-5 zeolite suspension on an inert
1 4 7 silica ball and the extruded catalyst obtained from the combination of ZSM-5 catalyst and col-
1 4 8 loidal silica, the results of various analyzes showed that the laminar catalyst performed better
1 4 9 than the extruded catalysts. Laminar catalysts, due to their lower thickness, had a higher degree
1 5 0 of diffusion, which reduced the resistance of mass transfer and caused the easier and faster
1 5 1 release of aromatic species from the zeolite channels [17]. Keep in mind, in addition to the
1 5 2 structure of the mold used for shaping, the pressure applied by the pressing and shaping devices
1 5 3 also affects the porosity, the resistance of the shaped catalyst, etc. By changing the pressure of
1 5 4 the press machine and comparing the results, the optimal value for the reaction and the desired
1 5 5 conditions can be obtained.

1 5 6 **2.2.2 Amount of added additives**

1 5 7 To achieve a mixture that has the necessary characteristics for shaping, compounds such as
1 5 8 binders (to establish connection and increase mechanical strength), clay and starches (to create
1 5 9 better rheological behavior), organic polymers (to reduce shape changes), Anti-flocculation
1 6 0 agents (to break solid masses), progens (to increase porosity), lubricants, water, etc. are added
1 6 1 to the catalyst [3]. Determining the proper combination of these materials is very important and
1 6 2 affects the ability of the catalyst to form and its resistance to pressure[18]. This is while a
1 6 3 specific theoretical approach has not been presented in this field. As a concrete example, during
1 6 4 extrusion, if the amount of water that is added is small, it leads to the production of a paste with
1 6 5 high viscosity, brittle and unsustainable, which cannot be easily fed into the extruder and be
1 6 6 shaped. But if the amount of water is high, the extruded particles stick together after exiting

167 the nozzle and cannot maintain their shape. Therefore, in the production of paste for extrusion,
168 there must be a balance between these two factors [16]. Figure 3 shows this very well.

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Figure 3: The effect of water amount on the morphology of the shaped catalytic material [16]

173 Almeida et al. studied the effect of the amount of additives on the integrity of extrudates. The
174 results showed that for a sample with a high content of polyvinyl alcohol, after heat treatment,
175 the sample with low mechanical strength and irregular shape was obtained. However, for the
176 sample with the lowest amount of polyvinyl alcohol (2% polyvinyl alcohol and 14% silica),
177 extrusions with regular shape and diameter as well as high mechanical strength were obtained
178 [19]. Kantarelis et al. used bentonite as a binder to form transition metal modified ZSM-5 cat-
179 alyst in converting biomass to liquids. In this research, the effect of zeolite to binder ratio on
180 product yield was studied. The results showed that the sample with more bentonite content had
181 less coke production due to the decrease in the amount of strong acid sites. In addition, this
182 sample had a higher liquid production efficiency [20].

183 2.2.3 Type of binder

184 Many catalytic materials do not have enough resistance after shaping and turn into sand. In this
185 case, materials called binders are added to the catalyst composition so that the catalyst has a
186 suitable mechanical resistance after shaping. Binders are divided into two categories, organic
187 (like methylcellulose, polyethylene glycol, and polyvinyl alcohol) and inorganic (like alumina,
188 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].

2.2.4 Calcination after catalyst shaping

۲۰۳ Additives that were added to the catalyst during shaping must be removed from the catalyst
۲۰۴ after shaping, which is done during the thermal process of calcination. Calcination is a heat
۲۰۵ process that is carried out in the presence of air, oxygen or other gases. Calcination is usually
۲۰۶ done at temperatures below the melting point and increases mechanical strength and resistance,
۲۰۷ and also affects the physical properties of materials [27]. The purpose of catalyst calcination
۲۰۸ after the drying stage is to remove volatile substances from solid materials, to simultaneously
۲۰۹ regulate texture, surface and volume of porosity, and to achieve a suitable mechanical strength.
۲۱۰ Depending on the intensity of calcination, a transverse connection is created at the junction of
۲۱۱ hydroxyl groups and other groups, thus increasing the mechanical resistance [28]. Keep in
۲۱۲ mind, the furnace temperature and heat treatment time should be such that the additives are
۲۱۳ removed from the catalyst, while the catalyst with greater resistance is produced. However, the
۲۱۴ optimal calcination temperature may vary depending on the specific catalyst, the kind of binder
۲۱۵ and the desired reaction. Therefore, it is advisable to conduct experimental tests to determine
۲۱۶ the best calcination conditions for each case. When the calcination process creates many irreg-
۲۱۷ ularities in the catalyst structure, the initial formation is lost. In this case, it is better to perform
۲۱۸ an initial calcination operation first, then to shape the catalyst, and then to perform the calcina-
۲۱۹ tion operation again to remove volatile substances and optimize mechanical resistance. But if
۲۲۰ calcination does not change the tissue, calcination can be done only after shaping.
۲۲۱ Ebrahimi et al. investigated the effect of calcination temperature, ranging from 450°C to 650°C,
۲۲۲ on the spray-dried SAPO-34/ kaolin catalyst in the MTO process. The study found that at tem-
۲۲۳ peratures exceeding 550°C, the kaolin binder was transformed into metakaolin, creating new
۲۲۴ Brønsted acid sites in the catalyst. As a result, the catalyst had a life time of over 900 minutes
۲۲۵ in the MTO process. However, at a reaction temperature of approximately 450°C, the catalyst
۲۲۶ had low methanol conversion and was rapidly deactivated [29]. Tian et al conducted a study

۲۲۷ on the impact of calcination process variables, such as calcination temperature, time, and heat-
۲۲۸ ing rate, on the mechanical strength of ZSM-extruded catalysts. The extrusion process con-
۲۲۹ sisted of five stages: first, mixing ZSM-5 with pseudo boehmite; then, kneading, extrusion,
۲۳۰ drying, and finally, calcination in a muffle furnace at varying temperatures, times, and heating
۲۳۱ rates Results indicate that the average strength decreased as the heating rate increased from 5
۲۳۲ to around 10 °C/min, but then enhanced as the heating rate increased further up to 15 °C/min. In
۲۳۳ addition, increase in calcination temperature up to 600 °C enhanced the mean strength, beyond
۲۳۴ which it decreased. This is due to the fact that as the calcination temperature increases, the
۲۳۵ sintering phenomenon of small particles becomes more prominent, causing significant changes
۲۳۶ in properties such as specific surface area and mesopore volume, which may influence the
۲۳۷ strength and stability of the catalyst [30].

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۲۳۹ **3 Employing binders**

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

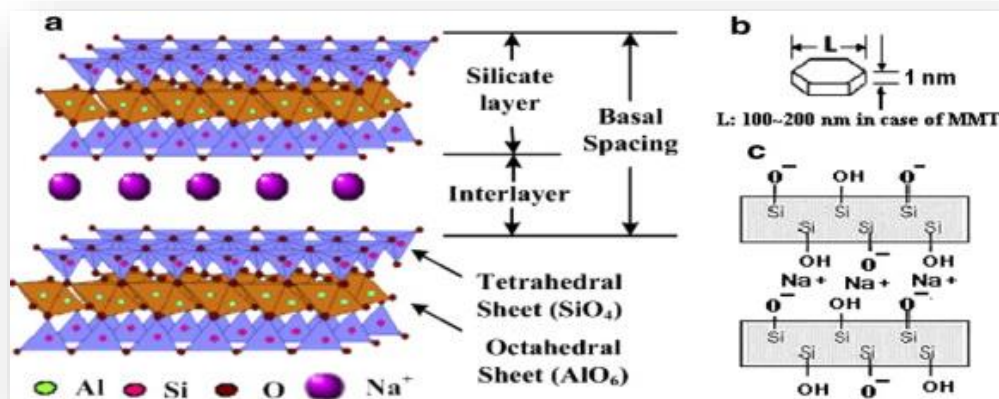
- ۲۴۶ • It can be easily removed from the texture at low temperature
- ۲۴۷ • It should not be toxic, abrasive, corrosive, etc
- ۲۴۸ • Leave the least amount of ash after heating
- ۲۴۹ • Increase the mechanical strength of particles
- ۲۵۰ • Cheap and available
- ۲۵۱ • Disperse easily

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

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

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

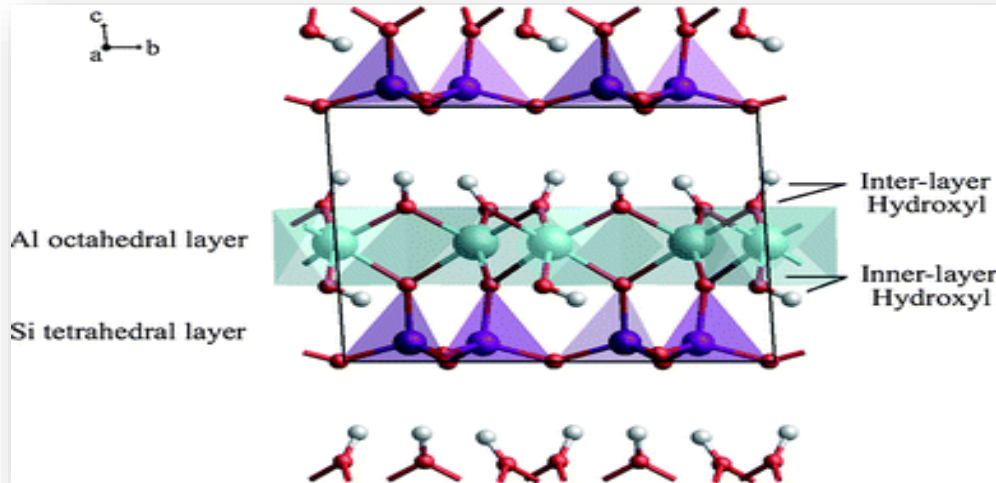
212 Figure 4 depicts the structure of bentonite.



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214 Figure 4: The structure of bentonite as a binder [33]

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216 **Kaolin:** This semi-crystalline material, which belongs to the family of clays, its structure con-
217 sists of tetrahedral layers of silicon and octahedral layers of aluminum, which Figure 5 shows
218 the image of these layers well. Kaolins have characteristics such as stickiness, colloidity, im-
219 permeability, high water absorption, low heat and electricity conductivity, etc. [34]. By heating

270 kaolin in the temperature range of 500-900 °C, it is possible to achieve an amorphous structure
271 containing silicon and tetrahedral aluminum, which is known as metakaolin.



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Figure 5: Silicon tetrahedral and aluminum octahedral layers in kaolin [34]

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

279

280 3.1 Effects of the presence of binder

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

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

300 **3.1.1 Change in diffusion characteristics**

301 The process of producing pellets from zeolite powders is mainly associated with the production
302 of meso and macro pores, after which the diffusion characteristics change. Du et al. have
303 acknowledged that when a binder such as alumina is used, which mainly contains meso-pores,
304 a mesopore structure is formed on the catalyst, which can help mass transfer during the reaction.
305 In the study of the effect of alumina, silica gel and kaolin binders on the performance of
306 Ni/HZSM-5 catalyst in the hydrodeoxygenation of cyclohexanone, they observed that in the
307 case of using alumina binder, the total pore volume was the largest and 80% of the pores were
308 mesopores. Also, the highest catalytic activity was obtained on the sample that was shaped
309 with alumina binder, the conversion of cyclohexanone and selectivity of cyclohexane were
310 97.3% and 88.3%, respectively [37].

311 Kim et al also encountered this issue while investigating the performance of synthesized samples
312 for the methanol to dimethyl ether process. They observed that when the binder was not

۳۱۳ used, the size of the pores was not in the meso range, but by adding gamma alumina, which
۳۱۴ had mesopores in the range of 10-5 nm, mesopores were formed, and the volume of these pores
۳۱۵ increased with the increase in the amount of binder [38].

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

۳۲۰ **3.1.2 Change in acidic properties**

۳۲۱ In addition to playing its main role, which is creating a connection between zeolite components,
۳۲۲ the binder can also be a source of mobile species and cause the transfer of chemical species
۳۲۳ to/from the active sites [28]. For example, in a binder like alumina, the migration of aluminum
۳۲۴ from the binder to the catalyst has occurred, which causes the formation of new acid sites, and
۳۲۵ as a result, the concentration of acid sites increases compared to the case without a binder.

۳۲۶ Zeolites contain two types of acid sites: Brønsted acid sites and Lewis acid sites. Brønsted
۳۲۷ acidity in zeolites arises from a hydroxyl group that originates from the aluminum atoms. On
۳۲۸ the other hand, Lewis acidity in zeolites can be created by removing some of the framework
۳۲۹ aluminum and forming extra-framework species [39]. The catalytic activity of zeolite can be
۳۳۰ influenced by these two acid sites, which affect the strength of the zeolite acid sites. Therefore,
۳۳۱ a binder like alumina, can be suitable for processes that require a high concentration of acid
۳۳۲ sites. Alumina has the capability of moving aluminum to the zeolite and producing extra-frame-
۳۳۳ work aluminum, which generates new acid sites for the zeolite. However, the presence of
۳۳۴ silicon in the silica binder and the presence of sodium in the bentonite binder neutralize the
۳۳۵ acidic sites and reduce the concentration of these sites. So, binders such as silica, bentonite,
۳۳۶ etc. are suitable for processes that require a low concentration of acid sites. Of course, the type
۳۳۷ of zeolite that is placed next to such binders is also important [28]. For example, Dorado et al.

338 when studying the effect of bentonite binder on the activity of pd/ZSM-5 and pd/Beta zeolites
339 in the hydroisomerization of n-butane, although the ion exchange between protons of zeolite
340 and sodium in bentonite neutralize the number and concentration of strong acid sites and so
341 decreased the conversion of n-butane, but the negative effect was compensated by the selectiv-
342 ity of zeolite ZSM-5 to the iso-butane. As a result, the presence of bentonite improved the
343 catalytic performance. But for zeolites with beta base, the presence of bentonite decreased the
344 catalytic performance due to the reduction of strong acid sites [40].

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

353 **3.1.3 Better distribution of loaded metals**

354 If metal is used, in the case where a binder is used, the metal particles may block the pores of
355 catalyst. However, in the presence of the binder, the metal particles are placed in the mesopores
356 formed between the binder and the zeolite, and so, the available surface for the reaction does
357 not become inaccessible. During the investigation of PtSnNa/AlSBA-15 catalyst for propane
358 dehydrogenation, Duan et al noticed that the dispersion of platinum on the shaped catalysts was
359 improved. So that, PtSnNa/AlSBA-15 catalyst mixed with 20 wt% alumina showed the highest
360 catalytic performance in terms of propane conversion and platinum distribution. It was ob-
361 served that in the content of 20% by weight of alumina binder, alumina species on the surface

362 of the catalyst isolated the metal components and prevented their accumulation during calcina-
363 tion and caused the best dispersion. But, at content more than 20%, the opposite happened. In
364 fact, the aluminum species deposited on the surface of the catalyst and covered the platinum
365 and reduced the dispersion of platinum [42].

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

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

384

3.2 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.

3.2.1 Modifying the catalytic powder and then mixing it 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.

410 The results showed that the highest mechanical strength was achieved with the sample contain-
411 ing 10% by weight of bentonite binder. To break such a granule, a force of 32.7 N and a pres-
412 sure of 2.9 MPa were calculated [45].

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

415 a) Mixing ZSM-5 with binder, then impregnating molybdenum on the extrudate and finally
416 carburizing in the presence of methane flow to convert molybdenum oxide into molybdenum
417 carbide.

418 b) impregnating molybdenum on ZSM-5 and then mixing it with binder and finally carburiza-
419 tion of the mixture

420 c) Molybdenum doping on ZSM-5, then carburizing MOO₃/ZSM-5 and finally mixing these
421 samples with binder

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

429 **3.2.2 Mixing the catalyst powder with the binder and then modifying the extrudates**

430 In this case, the catalyst is shaped first, and then modifications are carried out on these shaped
431 catalysts. Beheshti et al. studied the extrusion of zeolite H-[B]-ZSM-5 with alumina binder and
432 then steaming it. The results showed that during this operation, single and narrow mesopores
433 were formed without destroying the crystal structure. Also, the catalytic lifetime of this sample
434 was 750 hours, while it was 520 hours for the extruded sample without steaming and 580 hours

430 for the powdered sample. This improvement in the lifetime can be related to the created meso-
436 pores and also to the synergistic effects of extrusion and steaming operations, which lead to a
437 decrease in the strength of acid sites and a decrease in the ratio of strong to weak acid sites
438 [47].

439 Huang et al. considered Molybdenum oxide supported on mordenite zeolite-alumina composite
440 (MoO₃/mordenite-alumina), and then subjected this catalyst to nitric acid leaching. During the
441 calcination operation, molybdenum oxide has migrated to mordenite channels. During the mi-
442 gration, the molybdenum oxide encountered extraframework aluminum (EFAL), which led to
443 the formation of aluminum molybdate (Al₂(MoO₄)₃). In the following, it was assumed that
444 some of these aluminum molybdate species were located in the pores or inside the zeolite chan-
445 nels, and after acid leaching, these species were extracted and disappeared. The results of the
446 analyzes confirmed the formation of aluminum molybdate and then its extraction during acid
447 leaching. This structural change made the aforementioned catalyst show good stability in a-
448 butene metathesis reactions due to the transfer of coke species [48].

449 Song et al. investigated the effect of treatment with organic bases, such as tetraethylammonium
450 hydroxide, etc., on the catalytic characteristics of TS-1/SiO₂ extrudate in propylene epoxidation
451 [49]. In their recent study, this research team concluded that if TS-1/SiO₂ extrudates are used,
452 it is better than using titanium silicalite powder. Finally, it turned out that different organic
453 bases have shown different results. In such a way that the best results in terms of conversion
454 percentage and stability were obtained with the sample that was treated with tetrapropylammo-
455 nium hydroxide. Such an improvement in performance is due to the improvement in diffusion
456 characteristics, increase in acidity, widening of pore opening and optimal distribution of tita-
457 nium and silicon [50].

458 Klimov et al. considered two different methods to introduce "boron" into hydroprocessing cat-
459 alysts. 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 desilication 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

480 that although binders such as silica and alumina are considered neutral for the reactions, but
486 during the alkaline treatment, the alkaline solution interacted with the binder and the catalyst.
487 In such a way that, for the alkali-washed sample after extrusion, the highest activity and stabil-
488 ity were observed. This is due to the distribution of acidic sites due to the dissolution of part of
489 the alumina binder in the alkaline solution and the creation of more mesopores due to the co-
490 operation of the alumina binder in the production of mesopores [53]. So, the sequence of alka-
491 line treatment has been effective not only in acidity but also in the number of created meso-
492 pores.

493 **3.2.3 Modifying the binder and then mixing it with the catalytic powder**

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

501 In another study, Lee et al. treated the pseudo-boehmite binder with phosphoric acid, then
502 ZSM-5 was extruded with this new binder. As you know, during calcination, boehmite turns
503 into gamma-alumina[47]. The results showed that in the presence of phosphorus, the unfavor-
504 able characteristics of the pseudo-boehmite binder such as self-catalytic activity, the reaction
505 between the aluminum in the binder and zeolite and the creation of additional acid sites were
506 neutralized. Aluminophosphate binder showed no acidity increase and even caused a decrease
507 in strong acidity. Finally, this extrudate showed high mechanical strength, resistance to coke,
508 stability up to 150 hours, etc. in the conversion of methanol to propylene, and these positive

009 effects were more evident with the increase of phosphorus content. So that, in the ratio of phos-
010 phorus to aluminum equal to 0.8, the yield to olefins was 80% and the conversion of methanol
011 was 100% [55].

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

020 021 **4 Summary and future prospects**

022 Although shaped catalysts have been used in the industry for many years, less attention has
023 been paid to this field. In this regard, in this study by reviewing the previous literature, it has
024 been tried to deal with the basic concepts of catalyst shaping and specifically to the investiga-
025 tion of the effect of binder on the Physico-chemical and Catalytic Properties of shaped cata-
026 lysts. The results showed that the shaping method and the materials used during this work
027 highly effect on the final characteristics of the catalyst such as acidity, pore characteristics,
028 mechanical stability, thermal stability, etc. One of the important agents that is added to the
029 catalyst during shaping is the binder, which affects the physico-chemical and catalytic proper-
030 ties of extruded catalysts. Therefore, by engineering various shaping methods and additives
031 that are added during shaping, it is possible to create the desired catalytic properties.
032 Generally, the results obtained from reviewing the literature show that the catalyst shaping
033 process is still at the initial development level. So, for future studies, the scale up of zeolitic

034 catalysts shaping, improving the performance of shaped catalyst by using methods such as
035 plasma and ultrasound irradiation, designing new and efficient binders, etc. is an exciting re-
036 search topic that seems attractive.
037