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3D-printing of hierarchical porous ZSM-5: the importance of the binder system

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Abstract

Intelligent catalyst design can help to further improve the stability, selectivity and activity of existing adsorbents and catalysts. The use of 3D-printing for manufacturing of structured supports is a useful tool for the rapid prototyping of different compositions and different architectures of structured adsorbents and catalysts. Despite their proven advantages in use as adsorbents and catalytic supports with respect to heat and mass transfer and pressure drop, coated structured supports still encompass some such as loading of catalyst. To overcome these drawbacks, in this work, 3D-printed monoliths were manufactured directly using ZSM-5 as active material to build up the structured adsorbent or catalyst. As sufficient mechanical strength of such structures is crucial for the use in industry, this was one of the main focus points in this work. A combined binary binder system is shown to be advantageous for the adjustment of the mechanical properties of the self-supporting structured material. Furthermore, the chemical properties can be adjusted according to the binder used.

Keywords: ZSM-5, structured catalyst, shaping, 3-D printing, mechanical strength

Introduction

The use of zeolites for catalytic, adsorption and ion exchange applications is well-known [1–3]. Although many types of zeolites have been described in literature, only a few are used for large scale applications [4]. The main problems for industrial applications of new types of zeolites are the cost of the silica source and the scale-up of the synthesis. Therefore, a lot of efforts in research are done to modify these few types of large scale zeolites to improve their sorption behavior, selectivity, stability and activity. Over the past decade, the introduction of meso- and macropores in catalysts has received increasing attention [5,6]. On one hand, the introduction of mesopores in the microporous zeolite material has been studied, using various techniques such as post-synthetic

delamination, demetallation, and the incorporation of soft or hard templates [7,8]. On the other hand, structured macroporous catalysts have been investigated, combining an inert structured support material with a thin active zeolite coating. A wide range of support materials have been proposed in literature such as Al_2O_3 [9], glass [10], stainless steel [11–13], alumina ceramic foam [14], cordierite honeycomb [15–17], or SiC [18–20]. Conventionally two types of coating methods are applied: wash coating [13,21] and hydrothermal coating [9–12,14–16,18]. The use of macroporous structured catalysts has a number of advantages over a packed bed of pellets, including lower pressure drop, higher mass transfer and evenly distributed flows. Major drawbacks of conventional structured systems are the low loading of zeolite per reactor volume and coating adhesion problems [22]. In order to increase the loading of zeolite onto the surface of the inert support, the thickness of the coated layer can be increased, however this will lead to higher pressure drop and lower mass and heat transfer. Increasing the loading even further will eventually lead to blockage of the macropores. Furthermore, the uniformity and adhesion of the coating can become an issue at these high loadings of zeolite on the support.

In order to avoid this kind of trade-off, the active component can be incorporated in the monolith structure, so called 'bulk' or 'self-supporting monolithic catalysts'. Another advantage of these structures is that less process steps are required during the manufacturing, in comparison with the coated catalytic structures that often need multiple coating steps to achieve sufficient loading of the catalyst. By using self-supporting monolithic catalysts, a high amount of catalyst can be uniformly introduced in the reactor [23]. Various methods are available for the synthesis of monolithic structures (e.g. extrusion [24], inverse replication[25,26], dry gel conversion [12] and 3D printing [27–30]). However, not all can be applied for the synthesis of bulk zeolite structures, as the final material needs to have high porosity for the accessibility of the pores and active sites. Extrusion is the most commonly used method to shape catalytic monoliths. However, other methods such as the template method for the formation of foams can also be applied [25]. Recently, 3D-printing of functional materials including zeolites for different applications such as catalysis [13,31–34] or sorption [35–37] has been growing rapidly.

The extrusion of zeolite monoliths has already been described in scientific and patent literature [24,38]. However, the impact of different binders on the extrusion behavior for 3D printing of zeolites and the effect on the mechanical and physico-chemical properties is not fully understood. In order to manufacture self-supporting zeolite structures, the rheology of the slurry is crucial to achieve good flow behavior during extrusion and avoid the collapse of the structure during

deposition of subsequent layers. Furthermore, careful adjustment of drying and calcination procedures is important to achieve defect-free structures. As binders can both influence the porosity and mechanical strength as well as the acidity of the zeolite, the formulation of the extrusion paste is crucial in order to achieve the desired properties. As these self-supporting structures do not have any support for mechanical strength achieving high porosity in combination with high mechanical compression strength is a key challenge in manufacturing [39]. The mechanical properties of the final material need to be high enough for shipping and handling of the catalyst without effect on the structure. Moreover, the zeolite particles should be bound sufficiently well to avoid any attrition of the structures in high flow applications.

In this work, a 3D-printing method [13,27,40–43] is utilized to rapidly scan different compositions of zeolite paste to elucidate the importance of the binder system. The detailed description of the technique is given elsewhere [43,44]. This rapid prototyping method allows testing of different zeolite-binder compositions as well as scanning different architectures of the monoliths, creating extra degrees of freedom. In this work, it is shown that the process parameters need to be optimized according to the composition of the 3D-printed slurry, as different binders have an impact on the rheology and drying behavior of the zeolite monoliths. Additionally, the effect of binder type(s) on the mechanical and physico-chemical properties of the final self-supporting structured zeolite will be discussed. Finally, the benefits of binary binder systems are investigated showing possibilities for synergic effects.

Experimental

Manufacturing of zeolite structures

Zeolite ZSM-5 powder with a Si/Al ratio of 25 was provided by Süd-chemie (particle size distribution 0.5 - 22 μm , d_{50} 8 μm). The zeolite powder was used as received. As permanent binders, bentonite (VWR), colloidal silica (Ludox HS-40, Sigma Aldrich) and aluminophosphate solution (Litopix P-1, Zschimmer und Schwartz) were used. The bentonite was milled in water using 15 mm zirconia balls at 250 rpm for 45 minutes in order to achieve the right particle size distribution ($d_{50} < 10 \mu\text{m}$), before use. After mixing of the binder(s) (35 w%) with water, zeolite (65 w%) was added to the suspension and mixed using a planetary centrifugal mixer for 2 minutes at 1900 rpm. Methylcellulose (Acros Organics) was used as temporary organic binder to modify the rheology of the extrusion paste (0.5 % of weight zeolite/binder mixture with silica binder; 1 % for aluminophosphate binder). Depending on the type of binder(s) used, the water content varied

between 37 and 65 % of the solid weight content in order to achieve good flow behavior of the paste. As the slurry temperature increased due to vigorously mixing, the viscous paste was cooled to room temperature before extrusion to prevent water evaporation and changes in paste composition.

The printing step, developed for printing of bone scaffolds, involves the extrusion of the paste through a nozzle, while the nozzle moves in X, Y and Z direction and is described in more detail in earlier work [13]. As the speed of the nozzle is determined by the CNC machine, the speed of extrusion is adjusted according to the diameter of the nozzle. By continuous extrusion and programmed movement of the CNC machine, the structure was built up layer-by-layer. The paste was extruded through a single nozzle as a continuous filament using a constant displacement of the plunger in the paste reservoir in order to achieve a homogeneous volumetric flow rate (Figure 1). In this work a zeolite with binder(s) combination was extruded material was extrusion. In order to avoid drying during the printing the temperature was kept at 20 °C and the relative humidity (RH) was 80 % during manufacturing. The structures were synthesized with an open porosity between the fibers of 68 %, not taking into account the internal porosity of the solid material. After 3D-printing, the samples were dried with a methodology adjusted to the binder type as determined by studying the impact of the drying process (see discussion and table 1 below). Subsequently, the dried structures were calcined at 550 °C for three hours using a heating rate of 1 °C/min under ambient atmosphere.

Characterization

Rheological measurements were applied to determine the viscosity of the extrusion paste as a function of the shear rate (HAAKE MARS Rheometer, Thermo Scientific). Shear rates between 0.01 and 10 s⁻¹ were applied at a constant temperature of 25 °C. The particle size distribution of the zeolite and bentonite powders was determined using laser diffraction (Mastersizer X, Malvern Instruments) with a beam length of 10 mm.

Hg-porosimetry (Pascal Mercury Porosimeters, Thermo Scientific) was used to analyze the macropores (pore sizes between 0.01 and 10 μm) inside the fibers of the 3D-printed structures. The apparent specific surface area of the different catalysts was measured by N₂ sorption at -196 °C using the BET method (Autosorb-1, Quantachrome). Prior to N₂ sorption measurements, the samples were degassed for sixteen hours at 200 °C in order to remove all adsorbed water from the zeolite. The t-plot method using the De Boer thickness equation was used to derive micropore and

external surface area. The micropore surface area was calculated by subtracting the external surface from the BET surface. The volume of the pores < 50 nm was measured at P/P_0 of 0.95.

X-ray diffraction (XRD; X'pert PRO, Philips) was applied to examine the phase and crystallinity of the self-supporting zeolites structures using a Cu-K α X-ray source ($\lambda = 0.154056$ nm).

Thermogravimetric analysis (TGA) and differential scanning calorimetry signals were recorded on different samples (STA 449C Jupiter, Netzsch). The samples were measured in air and heated from room temperature to 1000 °C with a heating rate of 10 °C/min.

The surface and cross-sections of the self-supporting zeolites were studied using a cold field emission scanning electron microscope (FEG-SEM) type JSM6340F (JEOL, Tokyo, Japan) at an acceleration voltage of 5 keV. To avoid charging under the electron beam during SEM, all samples were coated with a thin Pt(80)/Pd(20) (surfaces) or Au (cross-sections) layer (~1.5 nm), using a Cressington 208 HR (UK) and a Balzers Union SCD 040 (Balzers, Liechtenstein) high resolution sputter-coater, respectively.

The mechanical strength of the manufactured structures was determined by crushing samples of 1 cm height, length and width. A 100 kN measuring cell was used to detect the force needed to collapse the structures (model 5582, INSTRON, USA). For every sample, the average of eight crush tests was calculated.

Two-Cycle NH₃-Temperature Programmed Desorption (NH₃-TPD) was performed on the pure zeolite powder and the self-supporting zeolites structures to measure the number and strength of the acid sites. The total acid site concentration is first determined on the basis of the volumetric single-site chemisorption of ammonia at 100 °C (TCA), immediately followed by a dynamic temperature-programmed desorption measurement from 100 to 750 °C (TPD) [45]. Both the degassing and the measurement procedures are performed on a Quantachrome Autosorb-iQ-C equipped with a thermal conductivity detector (TCD). Prior to the measurements, the samples are degassed under high-vacuum conditions at 200 °C for 16 h. After the determination of the dry sample weight, the samples are degassed again by flowing with helium at 200 °C in order to remove any eventual adsorbed water molecules. Subsequently, a leak test is performed to confirm the complete degassing, and the temperature is lowered to 100 °C. Once the temperature is stabilized, the two-cycle (TCA) adsorption isotherms are recorded. A first adsorption isotherm with

ammonia is determined, followed by a degassing period of 45 min at 150°C using a high-vacuum system. Afterward, the second adsorption isotherm is recorded at the same temperature.

The first isotherm includes both chemisorbed and physisorbed ammonia, and the second isotherm consists only of physisorbed ammonia because the in-between degassing action removes only physisorbed species. Therefore, the difference between the two isotherms will give rise to the total amount of chemisorbed ammonia and thus the total number of acid sites. Using the weight and specific surface area (N₂-sorption at -196 °C) of the sample the acid site concentration per gram and per m² can be calculated. The TCA procedure is followed by a flowing period with helium of 1 h at 100 °C in order to remove the physisorbed ammonia. The removal of physisorbed ammonia is monitored by the TC detector, and in all cases the TCD signal had decreased to the baseline at the start of the TPD measurement. Subsequently, TPD is performed through the controlled heating of the sample under a flow of helium from 100 to 750 °C at a heating rate of 10 °C min⁻¹, which is analyzed with the TCD. The obtained TPD spectra have been deconvoluted, and the deconvoluted results have been divided into two groups: the relative contribution of the peak areas in the 100–200 °C region as a measure of the relative contribution of weak acid sites and the relative contribution of the peak areas in the 200–550 °C region as a measure of the relative contribution of strong acid sites. The relative contributions obtained by the TPD measurement are applied to the total acid site concentration obtained by TCA to obtain the numerical values. The peak areas in the 550–750 °C region are not taken into account because these results are possibly correlated to the release of water molecules as a result of dehydroxylation effects rather than to the release of chemisorbed ammonia. The final calcination of the structures had a maximum temperature of 550 °C, and thus upon exposure to higher temperatures we cannot exclude occurring condensation reactions.

Shrinkage upon drying and calcination was calculated by measuring the length and width of the 3D-printed structure with a vernier caliper (± 0.01 mm) after drying and calcination. By dividing these dimensions by the programmed lengths in the printing process, the shrinkage was obtained.

Results and discussion

Extrusion

Influence of the binder

The key elements in building up the structure layer-by-layer are the volumetric flow of the extrudate and the speed of nozzle movement. The extrusion behavior of the paste mainly depends on the rheology and particle size of the powders. A shear thinning effect of the extrudate is required for good flow behavior during extrusion. Also, sufficiently high viscosity is necessary to avoid collapse of the structure during and after extrusion. Therefore, addition of an inorganic binder (35 wt% inorganic binder/65 wt% zeolite) to the extrusion paste is necessary as it has an important impact on the rheology and thus flow behavior of the paste. Moreover, this inorganic binder will have an impact on the drying and calcination behavior, the mechanical strength and physico-chemical properties of the final material. Rheology measurements (Figure 2) demonstrated that the sample containing bentonite as inorganic binder showed good extrusion behavior compared to the sample with aluminophosphate binder; the shear-thinning effect of the paste results in a good flowing paste at higher shear rates and a high viscosity at low shear rates. Bentonite acts as a plasticizer of the paste and is commonly used for extrusion [46]. Moreover, the particle size of the bentonite and ZSM-5 zeolite has been found to be crucial for good extrusion through the thin nozzle. For the extrusion process, the particles should be at least an order of magnitude smaller than the width of the nozzle. The particle size measurements of the purchased zeolite confirm that the zeolites with a size of 0.5 to 22 μm will not cause the blockage of the nozzle of 900 μm . As the particle size of the bentonite binder was found to be higher, an extra milling step was needed in order to achieve good flow properties and avoid plugging of the nozzle. For the other inorganic binders, an extra milling step was not necessary as the particle size of these binders was sufficiently small (Ludox HS-40 $d_{50} = 12 \text{ nm}$, Litopix is a solution). Moreover, their particle size is at least an order of magnitude smaller than the one of the zeolite, which provides good binding properties of the particles and good mechanical strength as reported in literature [24]. Another variable that influences the viscosity is the water content. As the bentonite binder is known for its high water sorption capacity, 25 % more water was added in order to achieve an ideal paste composition.

As the pastes with silica and aluminophosphate binders show very limited shear-thinning effect, organic methylcellulose (MC) was added as a binder to modify the rheology of the pastes (Figure 2). The ideal concentrations of organic binder varied depending on the type of inorganic binder. A methylcellulose concentration of 0.5 wt% for the silica binder and 1 wt% for the aluminophosphate binder resulted in paste with an optimal extrusion behavior.

In order to investigate the effect of combinations of different binders on the extrusion behavior and physico-chemical properties, binary binder pastes were prepared. The binary binder extrusion pastes contain a combination of two inorganic binders in a 50/50 weight ratio. The total zeolite/binder ratio was kept at 65/35 on weight basis. No organic binders were needed when bentonite was used in the binary paste composition with either silica or aluminophosphate. The lower concentration of bentonite was still enough to act as plasticizer and achieve the desired shear thinning effect. The flow properties of the bentonite were determined during rheology measurements of these samples (Figure 3). However, a milling step of the bentonite powder was still needed to achieve good printing behavior and avoid nozzle blockage. The binary binder system containing the aluminophosphate binder in combination with the colloidal silica binder, still needed the addition of an organic methylcellulose (0.5 wt%) binder in order to be able to extrude the paste.

Optimization of 3D-printing process and post-process

In case of the 0.9 mm nozzle, the volumetric flow rate was kept constant at 600 $\mu\text{l}/\text{min}$ for all samples. Furthermore, for the extrusion of zeolite type materials, the temperature and humidity are important in order to control the drying of the structure during/after the printing process. The drying of the structure seemed to be crucial to achieve a defect-free self-supporting zeolite structure. Three different drying methods were evaluated (Figure 4): drying during printing using heating lamps, freeze drying after printing and slow drying in a controlled atmosphere. These experiments showed that the best drying method depended on the nature of the binder used. In case of bentonite binder, the shrinkage during drying (11 %) resulted in ruptures in the structures due to the large amount of water that desorbs from the bentonite. Fast drying of these structures (drying lamps) resulted in large defects and a convex upper plane of the structure, due to rapid shrinkage. Freeze drying led to small cracks and a concave upper plane of the structure (Figure 4). However, the slow controlled drying at 80 % RH and 20 °C resulted in a defect-free structure. These conditions were further applied, also during the printing process, to avoid fast uncontrolled drying.

In contrast, the structures containing the other types of binders (no bentonite in the composition) needed rapid drying during the 3D-printing in order to avoid collapse of the different layers. A possible reason for this is non-ideal rheological properties of these types of binder systems. The viscosity of the paste is too low after extrusion and the structure partially collapses (Figure 5B). Using the heating lamps (50 °C at 5 cm distance from the sample), the extruded paste rapidly loses water, leading to an increase of the viscosity and rendering the architecture of the structure more

stable. As these samples showed less shrinkage upon drying (Table 1), the rapid drying of these samples did not result in any cracks. The lower shrinkage can be a result of the difference in water contents as well as the different nature of the binder and thus different condensation kinetics during the drying and firing procedure. The freeze drying method was not tested for these samples as they needed the rapid drying during manufacturing to avoid collapse.

Table 1: Shrinkage upon drying of the self-supporting zeolite structures made with different binder(s) (65 wt% zeolite, 35 wt% binder(s); binary binders system 50/50 ratio binders).

| <i>Binder(s)</i> | <i>Shrinkage upon drying (%)</i> | <i>Issues processing and post-processing</i> | <i>Drying method</i> | <i>Shrinkage upon Calcination (%)</i> |
|--|----------------------------------|--|-----------------------|---------------------------------------|
| Bentonite | 11.1 | Cracks during drying | Controlled atmosphere | 1.1 |
| Silica | 0 | Collapse during printing | Lamps | 1.7 |
| Aluminophosphate | 1.1 | Collapse during printing | Lamps | 0.7 |
| Bentonite/ Aluminophosphate | 6.2 | Cracks during drying | Controlled atmosphere | 0.7 |
| Bentonite/ Silica | 3.6 | Cracks during drying | Controlled atmosphere | 1.0 |
| Silica/ Aluminophosphate | 0.4 | Collapse during printing | Lamps | 1.2 |

The binary binders systems showed intermediate behavior correlated to the type of single binders used. The bentonite-silica and bentonite-aluminophosphate structures showed a behavior more similar to the bentonite bound structure. Clear differences in shrinkage can be observed (Table 1), that could be a result of higher water content and the plate structure of bentonite. The high volumetric shrinkage behavior was already discussed in literature [47,48]. Moreover, recent studies have shown that the attraction of bentonite plates can change at lower pH so the acidic aluminophosphate can alter the shrinking behavior of bentonite. Structures with silica as permanent binder also exhibit low shrinkage upon drying, due to the lower water content in this sample. For the paste compositions with bentonite, the slow drying in a controlled atmosphere was needed to achieve a defect-free structure. Rapid drying created a tension between the dryer outer part of the structure, showing volumetric shrinkage, and the wetter inner part. This tension results in cracks. Parallel with the structures containing single binders (silica or aluminophosphate), the silica/aluminophosphate binary binder sample needed rapid drying during the printing process in order to avoid collapse of the structure.

Physico-chemical properties

Single binder systems

During calcination, the dried structures first lose the remaining physically adsorbed surface water that is evacuated from the samples at around 100 °C. At higher temperatures (150-400 °C), the chemically bound water is removed and the organic binder is burned out. What happens with the binder during calcination strongly depends on the nature of the binder used. The TGA-DSC data reveal what happens during calcination of the binder. The spectra show that bentonite loses its adsorbed water below 150 °C and shows weight loss from 450 to 650 °C due to dehydroxylation (Figure 6). The broader peak at 7.5° in XRD indicates the presence of bentonite next to the zeolite pattern (Figure 7). The colloidal silica binder with its small particle size undergoes condensation at elevated temperatures by adhesive forces and crosslinking of terminal hydroxyl groups between its neighboring particles. This process results in a meso/macroporous network of more or less strongly bound particles that provide mechanical strength to the structure. The data from TGA measurements of the pure binders, confirm that the colloidal silica condenses over the temperature range from 150 to 600 °C (Figure 8). Around 100 °C the adsorbed water is released from the silica, while at the higher temperatures the weight loss continues at a slower rate due to condensation and loss of surface hydroxyl groups. The silica phase was not detected by XRD, indicating that the amount of amorphous material content in the 3D structure was larger compared to the bentonite and aluminophosphate binder samples. The DSC data of the pure silica binder (Figure 8) show that there is a phase shift without loss of mass at 924 °C. At this point the crystallization of the silica seems to occur, but since the XRD measurements were done with the material calcined at 550 °C, no crystalline silica was detected. The aluminophosphate binder demonstrates different calcining properties as the solution of aluminophosphate hydrate is transformed to crystalline tridymite phase (Figure 9). The phase transformation and viscous sintering proceed at a temperature between 100 and 550 °C according to the TGA and DSC measurements and literature [49]. On the XRD pattern the tridymite peaks were not clearly visible. After loss of adsorbed water below 100 °C, the binder becomes more viscous and loses ionic water around 150 and 250 °C. Furthermore, a loss of weight and a small peak of the DSC signal around 500 °C reveal that the crystallization process occurs at this temperature. Freiding et al. already showed that the dense AlPO_4 -tridymite matrix does not show any porosity or specific surface area [49].

In Table 2, the physical properties of the calcined structures with single binders are shown. Nitrogen sorption measurements clearly show that the nature of the binder has an influence on the specific surface area and pore volume of the final structure. The micropore surface area of the bentonite and silica bound samples is not significantly different compared to 65 % of the ZSM-5

zeolite surface area (weight load of zeolite in the structure). The network of zeolite and binder was visually identified on cross-section SEM images of the zeolite structures (supplementary information). However, the aluminophosphate bound sample shows a decrease in micropore area due to the intrusion of the binder into the pores of the zeolite or encapsulation of zeolite particles by the dense aluminophosphate matrix formed during sintering [49]. Hg-porosimetry showed that the binder and zeolite form a macroporous network with pores ranging up to 2 μm (Figure 10, left). The bentonite binder shows the highest internal macroporosity of the fibers, slightly higher than the aluminophosphate bound structure, while the sample with silica binder has significantly lower macropore volume (Table 2). The first-order derivative of the Hg-porosimetry (Figure 10, right) curve also shows a very narrow pore size distribution of the aluminophosphate/ZSM-5 material, with pores between 0.5 and 2 μm . The other samples have a wider spread on the pore size distribution, however the largest part of the pore volume is also around 1 μm (Figure 10). On the other hand, the internal micro- and mesopore volume measured with N_2 -sorption (pores < 50 nm) of the fibers decreased in a following sequence: silica > bentonite >> aluminophosphate. These results seem to suggest that the pore size distribution is dependent on the particle size of the binder for bentonite and silica binders. The smaller particle size of colloidal silica (12 nm), compared to the bentonite gives rise to smaller pores. In case of silica, there is also considerably more condensation behavior resulting in smaller mesopores and lower macroporosity. Secondly, bentonite with its broader particle size distribution also shows a broader pore size distribution. The fact that all samples have their largest part of macropore volume around 1 μm implies that this is dependent on the particle size of the zeolite. Because the aluminophosphate undergoes viscous sintering into a dense matrix, no pores are formed in the range below 50 nm and the pore size distribution seems to be solely dependent of the particle size of ZSM-5. Only the pore volume of the zeolite pores, which were not blocked, was measured with N_2 -sorption in the aluminophosphate sample. It was already described in literature that aluminophosphate binder results in a dense phase with narrow macropore size distribution with pore sizes depending on the grain size of the embedded particles [49].

Table 2: Physical properties of pure zeolite and different single binder structures (65/35 weight ratio zeolite/binder) after calcination.

| Structure | BET surface area (m^2/g) | Micropore surface area (m^2/g) | Pore volume < 50 nm (cm^3/g) | Macropore volume (cm^3/g) | Crush strength (MPa) |
|--------------|--|--|--|---|----------------------|
| Pure H-ZSM-5 | 428 | 379 | 0.159 | - | - |
| Bentonite | 292 | 250 | 0.185 | 0.432 | 0.22 ± 0.03 |
| Silica | 305 | 234 | 0.266 | 0.275 | 0.25 ± 0.11 |

| | | | | | |
|-------------------------|-----|-----|-------|-------|-------------|
| AlPO₄ | 124 | 118 | 0.061 | 0.407 | 0.54 ± 0.16 |
|-------------------------|-----|-----|-------|-------|-------------|

The results of the compression tests (Table 2) of the different structures with the same architecture demonstrated that the binder is crucial in providing the necessary mechanical strength for industrial use of these materials. The structure with an aluminophosphate binder has a significantly higher mechanical strength than the structures with the other binders. It was already suggested that the aluminophosphate forms a dense continuous matrix by viscous sintering [49] resulting in its superior mechanical strength but, on the other hand, in loss of microporosity. Even with 35 % binder concentration the samples with silica and bentonite do not achieve the desired mechanical properties.

As acidity is an important feature in zeolite catalysis, but also in applications as gas sensing [50] and adsorption, NH₃-TPD profiles have been taken of the obtained structures, evaluating the impact of the binder. The NH₃-TPD profiles indicate a difference in acid strength depending on the binder used in the formulation of the structure (Figure 11). However, since standard NH₃-TPD is not a quantitative measurement of number of acid sites, a 2-cycle NH₃-TPD measurement was performed [45]. By doing a 2-cycle adsorption experiment the number of physisorbed and chemisorbed NH₃ molecules can be determined. The number of acid sites, equals the number of chemisorbed NH₃-molecules. When the results of the 2-cycle experiment of the pure zeolite (Supplementary information) are compared to that of the structures with the different binders (Table 3), a decrease both in number of acid sites per surface and per weight can be observed for the structures with bentonite and silica binder structures. This decrease is larger for the silica than for the bentonite sample. The difference between the number of acid sites per gram and per Å² is due to the difference in surface area between the structures and the pure zeolite (Table 2). The decrease of acidity when using bentonite and silica binder can be correlated to the adsorption of cations from the binder on the acid sites of ZSM-5. Furthermore, the NH₃-TPD measurement shows that for bentonite the acid strength profile does not change dramatically compared to the pure zeolite. For silica binder, on the other hand, the acid strength declines, so fewer strong acid sites can be observed. The difference between the two binders could be contributed to different ions present in the binder. The sodium ions present in Ludox HS-40 silica binder seem to neutralize part of the acid sites present in the zeolite resulting in the lower acidity; these sodium ions preferentially bind on the strongest acid sites [51]. Nevertheless, other phenomena like migration of silica in the water based extrusion or differences induced by their divergent calcination behavior cannot be excluded.

For the structure with aluminophosphate the behavior is different. The number of acid sites per gram decreases but due to the large decrease in surface area the number of acid sites per surface increases compared to the pure zeolite. Moreover, the acidity of the zeolite shifts as can be clearly seen in the TPD. The strong acid sites are transformed to intermediate and low acid site strength. These results suggest that the excess of phosphate in the binder interacts with the framework aluminum from the zeolite. Although the mechanism of the interaction of phosphate ions with the acid sites of the zeolite is still under discussion, the decrease in acid strength is reported by different sources [49,52,53]. However, to the best of our knowledge, the increase in number of acid sites per surface of the zeolite has not been reported yet. This intriguing observation, goes beyond the scope of this paper but should be investigated in more detail in future work in order to reveal the mechanism of interaction between the aluminophosphate binder and the zeolite. The adjustment of the acidity might have important implications on selectivity and stability when these materials are used as catalyst.

Table 3: Results of 2-cycle NH₃-TPD on pure zeolite and different single binder structures (65/35 weight ratio zeolite/binder) after calcination.

| Structure | Number of acid sites (1/Å ²) | Number of acid sites (μmol/g) |
|-------------------|---|----------------------------------|
| Pure H-ZSM-5 | 1.17 | 834.0 |
| Bentonite | 0.74 | 361.0 |
| Silica | 0.64 | 322.5 |
| AlPO ₄ | 2.62 | 710.1 |

Binary binder systems

The XRD patterns of the samples prepared using two binders showed that the ZSM-5 structure has not been altered during the manufacturing process. As the concentration of each binder is lower in the binary binder systems, it was very difficult to extract the binder phases from the XRD-pattern. The binary binder samples were further analyzed using N₂-sorption, Hg-porosimetry and mechanical testing (Table 4, Figure 12). The Hg-porosimetry reveals that the samples containing bentonite have a large pore volume, similar to single bentonite binder sample. The size distribution of the pores of binary systems including bentonite are similar in size, although the bentonite/aluminophosphate binder system also has a contribution of larger pores. Interestingly, the relative distribution of the pore sizes is different: a higher amount of smaller pores exist in case of bentonite/silica and a higher amount of larger pores in case of bentonite/aluminophosphate. Also, in case of a system containing silica, the macropore volume stays high: both samples show similar pore sizes between 0.1 and 1 μm but with a difference in relative distribution. The aluminophosphate seems to limit porosity at the lower end of the pore size distribution observed

in mercury porosimetry, which to a lesser extent is also visible in the bentonite/aluminophosphate material. At even lower pore diameters below 50 nm (determined with nitrogen sorption), the bentonite/silica sample showed some porosity whereas the bentonite/aluminophosphate sample had almost no porosity. Possibly, smaller colloidal silica particles allow the formation of smaller pores and the aluminophosphate again forms a denser matrix with only larger pores. The silica/aluminophosphate containing sample showed the lowest macroporosity similar as observed with single silica binders. There is a larger contribution of smaller pore sizes in the pore size distribution of the structures compared with single silica and single aluminophosphate binder. The nitrogen sorption measurements are in agreement with those of the single binder structures. The structures with an aluminophosphate binder show a decrease in specific surface, however the decrease is less in case of structure containing also bentonite, than in case of the structure with only aluminophosphate. This might indicate a reaction between the bentonite and the aluminophosphate. In the silica/bentonite doped structure, the entire micropore surface of the zeolite is still accessible.

The results of crush tests indicate that the combining different binders can be beneficial for the mechanical strength of the final structure, even resulting in a synergic effect. It is suggested that the bentonite binder allows the extrusion of a defect-free structure with good interconnection of the different layers, while the other binders form a strong network between the zeolite and bentonite binder during sintering. The aluminophosphate binder in combination with the bentonite binder results in a structure with excellent mechanical properties: the binary material shows three times higher strength than the single aluminophosphate binder sample and over seven times higher strength than the single bentonite sample. This synergic effect is also applicable for the bentonite/silica sample as the binary binder structure has three times higher mechanical strength than the single binder silica and bentonite structures. The combination of the silica binder with the aluminophosphate binder did not result in superior mechanical strength compared to the single binder system. The use of binder combinations needed for sufficient mechanical strength could be key in the use of these materials in industrial applications.

Table 4: physical properties of pure zeolite and different binary binder structures (50/50 binders weight ratio; 65/35 zeolite/total binder weight ratio) after calcination.

| Structure | BET surface area (m ² /g) | Micropore surface area (m ² /g) | Pore volume < 50 nm (cm ³ /g) | Macropore volume (cm ³ /g) | Crush strength (MPa) |
|------------------------------|--------------------------------------|--|--|---------------------------------------|----------------------|
| H-ZSM-5 | 428 | 379 | 0.159 | - | - |
| Bentonite /AlPO ₄ | 219 | 140 | 0.111 | 0.553 | 1.54 ± 0.24 |

| | | | | | |
|---------------------------------|-----|-----|-------|-------|-------------|
| Bentonite /Silica | 301 | 242 | 0.282 | 0.425 | 0.66 ± 0.25 |
| Silica /AlPO₄ | 177 | 126 | 0.051 | 0.276 | 0.57 ± 0.17 |

The results of NH₃-TPD measurements of the binary binder structures are shown in Figure 13. For the combination of the silica and bentonite binder, the observations are similar as for the single bentonite and silica binder, although some intermediate acidity appears in the binary system. Both the number of acid sites as the strength of the acidity decrease, probably due to the ion exchange from the binder onto the acid sites of the zeolite. Remarkably, for the aluminophosphate samples the decrease in strong acidity in the bentonite/aluminophosphate sample is much less pronounced than in the silica/aluminophosphate material. Whereas the number of acid sites inclines more towards the behavior of single binder aluminophosphate (Table 5) in the sample with silica/aluminophosphate compared to the combination with bentonite. As the concentration of aluminophosphate is equal in both samples, it seems that, similar to the observations on retained surface area, the bentonite interacts with the excess of phosphate from the aluminophosphate solution, limiting its influence on acidity. In order to give more insight into the interaction of the aluminophosphate binder with bentonite, an XRD measurement of a bentonite/aluminophosphate mixture, calcined at 550°C for 3 hours, was compared to the XRD pattern of pure bentonite (Figure 14). Interestingly, only the crystal structure of aluminophosphate was detected on the pattern from the bentonite and aluminophosphate mixture. These observations seem to imply that the bentonite crystal structure is destroyed by the acidic aluminophosphate solution when both binders are combined. Earlier work of Bendou and Amrani (2014) confirms that the bentonite crystal structure can be changed to an amorphous phase by acid treatment [54]. The obtained results show that there is a clear interaction between different binders, but the impact on the acidity of the final material is not yet fully understood. Next to the acidity, the micropore volume is also much higher when aluminophosphate is mixed with bentonite as binder compared to of its mixture with silica. Moreover, the rheological properties of bentonite in the mixture with aluminophosphate and zeolite were at least partially maintained, and the macropore structure over 0.1 μm seemed to be similar to the other samples with bentonite. So it is not clear in which degree and at which point in the synthesis the bentonite structure is destroyed.

Table 5: Results of 2-cycle NH₃-TPD on pure zeolite and different single binder structures (65/35 weight ratio zeolite/binder) after calcination.

| Structure | Number of acid sites (1/A²) | Number of acid sites (μmol/g) |
|-------------------------|---|--|
| Pure H-ZSM-5 | 1.17 | 834.0 |
| Bentonite/Silica | 0.80 | 401.3 |

| | | |
|-----------------------------------|------|-------|
| Bentonite/AlPO₄ | 1.47 | 533.0 |
| Silica/AlPO₄ | 1.77 | 520.8 |

Conclusions

It was shown that the binder used in the formulation of 3D-printed structures has a major impact on the behavior during the printing process, during calcination as well as on the physico-chemical properties of the final structure. Combining different types of binders in one structure was needed to achieve the desired mechanical properties of the final component. The use of the bentonite binder resulted in good rheological properties of the extrusion paste. In combination with the smaller, network forming binders such as aluminophosphate or silica, diminished shrinkage behavior and superior synergic mechanical properties were obtained. The use of an aluminophosphate/bentonite combination as binder system for zeolites resulted in some interesting properties of the extrusion paste and final material. While the crystalline phase of the bentonite seemed to be affected by the acidic aluminophosphate, the paste still retained the flow properties of bentonite. Furthermore, clear differences in acidity were shown depending on the binder applied as well as on combinations of binders that do not always result in linear changes in acidity nor porosity. The combination of binders resulted in a final structure with excellent mechanical strength. More research will be needed in order to fully understand the interaction between the zeolite and binder and between the different binders and its effect on the physico-chemical properties of the final material such as mechanical strength, acidity, porosity and surface area. On the other hand, the manufacturing and drying method should be developed further in order to achieve scale-up of this technique for industrial application.

The results discussed in this work could also be used to improve mechanical properties or adjust acidity of materials manufactured with other types of 3D-printing or manufacturing techniques. The use of the 3D-printing technique for manufacturing of self-supporting catalysts and adsorbents can improve the effectiveness of the active component in the structure and can increase the loading of active material per reactor volume compared to coated structured supports (here already up to 65 wt% compared to a maximum of 33.5 wt% reported for coating [55]). Both the physico-chemical properties (tuned via smart binder combinations) and the architecture of the 3D-printed structures can be tuned according to the application while still having sufficient mechanical strength. This combination leads to an enormous freedom of design for a whole range of applications. In a next step these ZSM-5 3D-printed materials will be tested in a catalytic application to study the effect of binders and architecture.

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