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BEA coating of structured supports—performance in acylation

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Abstract

The development of a dip-coating method is described for the preparation of an active catalytic coating on a structured packing for the acylation of aromatics. The preparation was optimized by investigating various parameters in the dip-coating of both monolithic and wire gauze packings, such as the amount of zeolite, the amount of binder, the presence of a surfactant, the cell density of the monolith, and the packing material.

BEA coatings strongly bound on ceramic monoliths and metallic wire gauze packings were prepared by dipping the structured packings in a BEA-containing, water-based slurry. The activity and selectivity of the slurry catalyst in the acylation of anisole with octanoic acid were well preserved by the coating procedure, while the structures can also easily be regenerated by calcination in air.

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1. Introduction

In conventional (slurry) reactors the required separation of the fine particulate catalyst from the product mixture is a time- and energy-consuming process. By replacing the slurry system by a structured reactor configuration, filtration is no longer necessary. Examples of structured reactor internals are a monolith (*Fig. 1a*) and a wire gauze packing (*Fig. 1b*) on which the catalyst can be applied as a thin layer on the support.

A monolithic support consists of a macroporous material, often cordierite, which is structured in straight parallel channels. Currently, the most well known application of the monolith is in the automotive industry as an exhaust gas converter. In the monolith, higher

activities and selectivities can be achieved compared to a conventional packed bed because of the low internal diffusion resistance (due to the thin catalytic layer). For example, in the hydrogenation of α -methylstyrene (a very fast, often mass-transfer limited reaction), the monolithic reactor showed a higher productivity compared to a trickle-bed catalyst system [1]. In that study an activity of $22 \text{ mol}/\text{m}^3_{\text{reactor}} \text{ s}$ was found for the monolithic system compared to an activity of $5 \text{ mol}/\text{m}^3_{\text{reactor}} \text{ s}$ for the trickle-bed reactor at a similar geometrical surface area, even with a 10 times lower amount of catalyst. The higher activity of the monolith is attributed to a higher mass-transfer rate. From a model study [2] in which a three-phase hydrogenation was studied, based on a consecutive, three-phase hydrogenation and Langmuir–Hinshelwood–Hougen–Watson type of kinetics, the performance of a monolithic reactor gave a much higher selectivity towards the desired intermediate product than a trickle-bed reactor. The results of this modeling work were supported by the

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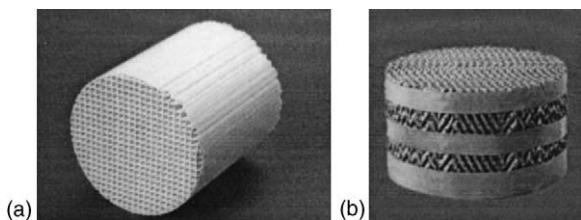


Fig. 1. Examples of a structured reactor packing. (a) Monolithic packing; (b) wire gauze packing (Sulzer DX).

study of the selective hydrogenation of benzaldehyde towards benzyl alcohol [1]. This product can be further hydrogenated towards the undesired toluene. The experiments performed in a monolith resulted in a selectivity of 96% towards the benzyl alcohol compared to 73% in the trickle-bed configuration at a conversion level of 50%. The higher selectivity of the monolithic configuration is attributed to both the shorter diffusion distance in the catalyst coating layer on the monolithic walls and the narrow residence-time distribution in the monolithic reactor.

Another example of a structured packing is a wire gauze packing. These packings, mostly consisting of a metal (stainless steel) are often used in practice for optimal (radial) mixing of reactants and they are very suitable for performing reactive distillation operations. Although a higher pressure drop is found when compared to a monolithic structure, an advantage of this material is the radial mixing.

In this paper, the development of a dip-coating method is described for the application of an active catalytic coating on a structured packing for the acylation of aromatics. The preparation method was optimized by investigating various parameters in the dip-coating of both monolithic and wire gauze packings. The activity of the catalytic coatings was investigated in the solid acid catalyzed acylation of anisole with octanoic acid as a model reaction (Fig. 2).

The acid catalyzed acylation of aromatics is the main route for the formation of aromatic ketones, important intermediates in the pharmaceutical, fra-

grance, flavor, and agrochemical industry. Due to the large disadvantages of the conventional catalysts, such as AlCl_3 , replacement by solid acid catalysts is very attractive to eliminate corrosion and environmental problems [3]. One of the solid acid catalysts that gives very high activities and selectivities is BEA zeolite [4–8]. Other examples of zeolites include faujasites and MFI zeolite [9].

Two main applications of zeolite coatings are the use of membranes for gas separations and the integration of separation and catalysis. Also the development of a catalytic membrane reactor, in which both applications are combined, is studied extensively [10]. Applying the zeolite crystals by a dip-coating technique results in a coating consisting of randomly oriented zeolite crystal layers useful for adsorption and catalysis purposes [11]. The support is immersed in a suspension of the zeolite crystals in a solvent containing a binder and other additives followed by evaporation of the solvent by drying and calcination. Because various zeolites are commercially available, this seems to be a relatively simple coating method, as synthesis issues concerning the zeolite itself do not need to be considered. A binder, e.g. colloidal silica [12], is added to the suspension for better adherence of the zeolite crystals onto the support. Without this binder the deposited crystals will only bind to the surface by ‘van der Waals’ forces.

Growing the zeolites directly on the surface of the carrier, is another coating method [10]. Numerous patents have been published describing the growth of a zeolite on a substrate. In literature mainly the preparation of directly grown MFI zeolite coatings on catalytic supports is reported (for example [13–17]). Examples are the synthesis of MFI-type zeolite coatings on cordierite monolithic supports [18] on stainless-steel supports [19] and the preparation of a thin layer of zeolite on a substrate by dipping this substrate in the synthesis mixture prior to synthesis [20,21]. The advantage of a directly grown zeolite layer compared to the dip-coated support, is that a complete coverage of an oriented zeolite crystal layer can be achieved. This

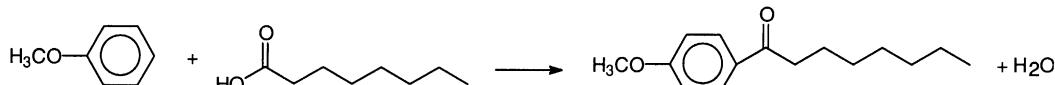


Fig. 2. The acylation of anisole with octanoic acid.

can be very relevant in, for example, membrane applications.

On the other hand, in the dip-coating technique, the loading of the zeolite is satisfactory and easily controllable [14]. Furthermore, it is not necessary to develop a special zeolite synthesis formulation for coating applications, so an already optimized zeolite can be applied.

For application in catalytic processes, mainly MFI zeolites are grown onto the support [15,16,18]. The catalytic applications in which a MFI zeolite is directly grown on a monolithic support can be found in the conversion of methanol and *n*-hexane to gasoline-range hydrocarbons. Catalyst loadings up to 31% were obtained [16]. Other applications are the development of a MFI and mordenite coated stainless-steel metal gauze support as a NO reduction catalyst for exhaust gas treatment [22] and a MFI zeolite disc for the alkylation of toluene with methanol [18]. Apart from catalytic applications, the major emphasis of research in the area of zeolite coating synthesis is on membrane applications. In the separation of gases zeolites have shown good performance [23].

2. Experimental

The macroporous ceramic monoliths consisted either of pure silica (SiO_2) or cordierite ($2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 2\text{MgO}$) and were kindly provided by Corning Inc. Dimensions: the length of all monolithic structures was 5 cm, the diameter of the cordierite and silica structures was 4.3 and 2.54 cm, respectively. Cell density varied from 31 and 93 cells/ cm^2 (200–600 cpsi). The metal gauze packings, Sulzer DX, with a specific surface area of $900 \text{ m}^2/\text{m}^3$ were kindly provided by Sulzer Chemtech Ltd. The BEA zeolite, with a Si/Al ratio of 37.5, was purchased from Zeolyst (CP 811E-75), the Na_2O content was 0.05 wt.% and the surface area $650 \text{ m}^2/\text{g}_{\text{zeolite}}$. The size of the zeolite crystals is in the range of 15–20 nm, as measured by TEM. The BEA crystals are found in clusters of 5–20 μm . The BEA extrudates were also obtained from Zeolyst (CP811E-75) and have the same Si/Al ratio of 37.5. These extrudates have an average length of 12 mm and average diameter of 1.65 mm. The characteristics of all the packings used in this study are listed in Table 1.

Dip-coating the monoliths with BEA zeolite was performed by preparing a mixture of BEA crystals, a solvent, a binder and optionally some extra components such as surfactants. Two solvents with a different surface tension were chosen; butyl acetate and demineralized water. Dip-solutions with various compositions were prepared. In the case of butyl acetate, the amount of BEA zeolite was varied between 5 and 15 wt.%, and in water this amount was varied between 5 and 25 wt.%. Colloidal silica (Ludox AS-40, a 40 wt.% suspension of colloidal silica in water) was added to the dip-mixture as a binder. The standard amount of Ludox added, was 1 wt.% of the total amount of solids for 20 wt.% BEA in solvent. To study the effect of the binder, dip-mixtures were prepared in water without binder and also with five times the standard amount of binder. Nitrocellulose, moistened with 35% ethanol, was added as a temporary binder to the mixtures prepared with butyl acetate for binding of the zeolite crystals before calcination. This amounts to 5 wt.% compared to the amount of BEA zeolite. To study the effect of nitrocellulose also a coating was made without this temporary binder. Teepol (4.3–4.7 g/l_{solvent}) was added as a surfactant to disperse the zeolite crystals in water. The effect of this surfactant was studied by varying the amount of Teepol. To obtain a homogeneously dispersed mixture, the slurry was well mixed with a high-shear mixer (UltraTurrax T25 from IKA Labortechnik) for approximately a minute at 13,000 rpm. Next, the monoliths were dipped into the mixture for 3 min (varying the time from 5 s to 5 min did not affect the loading). Excess liquid was removed gently with pressurized air. The BEA dip-coated monoliths were dried for one night at room temperature, while rotating in a horizontal position. Subsequently, the monoliths were dried in air by increasing the temperature by 1 K/min to 473 K and calcined at 673 K in air (heating rate 10 K/min) for 4 h. To activate the BEA zeolite coated monoliths, ion-exchange was performed in 1 M ammonium nitrate (NH_4NO_3) at 298 K for 15 h (overnight). After washing the zeolite coatings with demineralized water, a calcination was performed at 723 K (4 h), with a heating rate of 5 K/min to produce the protonated form. The adhesion of the BEA zeolite was tested by placing the coated monoliths in an ultrasonic water bath for 15 min. After this, the dried samples were weighed in order to determine any possible weight loss.

Table 1
Properties of various structured packings

| | Material | Channel diameter or crimp height (mm) | Void fraction | Corrugation angle (°) | Wall thickness or wire thickness (mm) | Wave-length of crimp (mm) | Geometric surface area (m ² /m ³) | Surface area, S _{BET} (m ² /g) | Pore volume, V _{pore} (ml/g) ^a |
|-------------------|-----------------|---------------------------------------|---------------|-----------------------|---------------------------------------|---------------------------|--|--|--|
| 200 cpsi monolith | Cordierite | 1.49 | 0.69 | — | 0.30 | — | 1850 | ≤4 | 0.20 |
| 400 cpsi monolith | Cordierite | 1.09 | 0.74 | — | 0.18 | — | 2710 | ≤4 | 0.20 |
| 600 cpsi monolith | Cordierite | 0.93 | 0.78 | — | 0.11 | — | 3450 | ≤4 | 0.20 |
| 400 cpsi monolith | Silica | 1.09 | 0.74 | — | 0.18 | — | 2710 | 89 | 0.18 |
| Sulzer DX | Stainless steel | 2.9 | 0.94 | 30 | 0.15 | 6.4 | 900 | 0.002 | 0 |
| BEA extrudates | Zeolite BEA | — | 0.41 | — | — | — | 1530 | 580 | 0.77 |
| BEA powder | Zeolite BEA | — | — | — | — | — | — | 644 | 1.3 |

^a As determined with Hg-porosimetry.

The zeolite coating on a metal gauze packing was prepared similarly. However, preliminary tests showed that the adhesion of zeolite was more difficult. This was solved by using an intermediate silica layer as a kind of primer. Before dip-coating the structure in the zeolite containing slurry, the metal packing was pre-coated with a silica layer according to the method of Mulder and coworkers [24,25]. This was done by dipping the packing into a 10 wt.% suspension of poly-dimethylsiloxane (Simson, “transparent”) in ethyl acetate which was stirred for 1 h to suspend the siloxane (not exposed to air). After drying in air at room temperature for 4 h, while rotating in a horizontal position, the structures were dried at 373 K for 5 h, after which the temperature was raised with 10 K/min to 823 K to calcine the coatings for 5 h.

The activity of the coated structures was measured batchwise in the acylation of the anisole with octanoic acid (Fig. 2). Anisole was used as a solvent to circumvent interactions introduced by an additional component. The activity measurements were performed with an octanoic acid concentration of 0.2 mol/l, the pressure was atmospheric, the reactor volume was 125 ml, and the internal diameter of the reactor was 45 mm. The reaction temperature was either 415 K or the boiling point of anisole, 428 K. The liquid reaction mixture was recirculated through the monolith using a nitrogen flow (Fig. 3). The reaction part was heated by an oil bath. On top of the cooling section a drying tube filled with silica gel was placed. Activity was defined as the initial apparent first-order rate constant k (h^{-1}) normalized for the catalyst concentration (g/l) [4].

Selectivities were calculated as the ratio of the acylated aromatic substrate *para*-octanoyl anisole and the converted octanoic acid.

3. Results and discussion

3.1. Preparation of the coating

The effect of the different parameters varied in the dip-mixtures of this preparation method will be discussed in the following sections.

3.1.1. Solvent effect

As solvents, butyl acetate and demineralized water were employed. The acetate was studied since its lower surface tension is expected to lead to a better dispersion of BEA in the dip-coating mixture. The solvent choice was found to have a large effect on the maximum BEA content of the dip-mixture; with the standard amount of 1 wt.% Ludox present, mixtures containing 15 wt.% in the case of butyl acetate and 25 wt.% in the case of water proved too viscous for use. The amount of BEA zeolite in the dip-mixtures was varied from 5 to 10 wt.% in butyl acetate and 5 to 20 wt.% in water. Apparently, the use of butyl acetate does not lead to higher catalyst loadings, since the viscosity of the BEA containing dip-mixtures has a stronger effect on the dip-coating than the surface tension of the solvents. Because relatively low loadings were obtained with butyl acetate as a solvent, all further work was dedicated to the water-based dip-coatings.

3.1.2. Catalyst loading

The measured loading of the monoliths that were dip-coated in a 20 wt.% BEA water-based dip-slurry, can be found in Fig. 4. It must be noted that measuring the loading by weighing the samples, implies that the amount of binder is included in the loading. The amount of binder, however, is relatively low compared to the amounts that are traditionally used [12]. The value of the loading increases with the solids content of the dip-mixture. The dip-mixtures prepared with water lead to high loadings of up to 9 wt.% after dip-coating the structures once and subsequent calcination. Due to the lower maximum amount of 10 wt.% of zeolite in butylacetate a lower loading of 2.3 wt.% (not

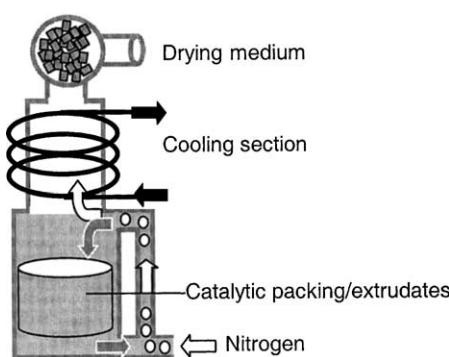


Fig. 3. A schematic representation of the set-up in which the activity measurements were performed.

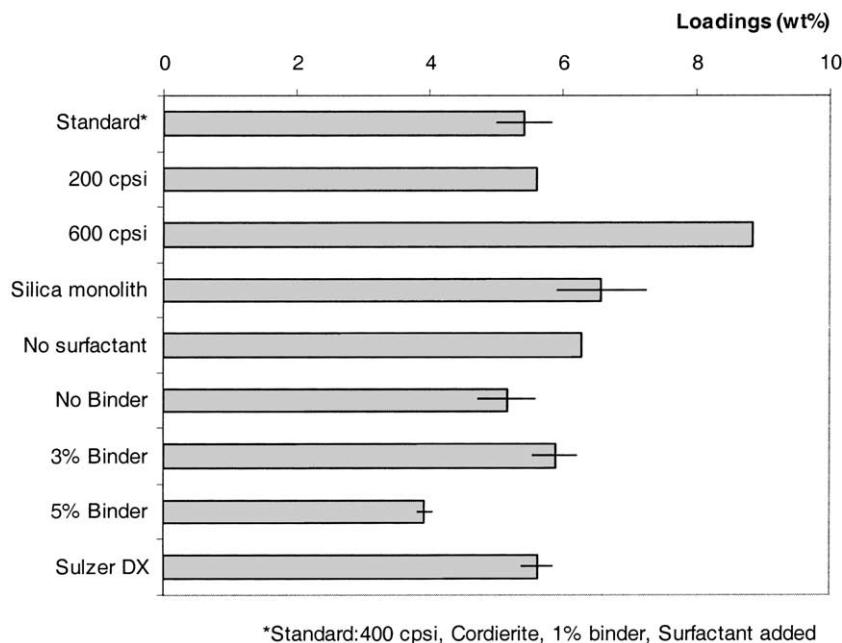


Fig. 4. The loadings of the various BEA dip-coated packings. Variation of dip-coat formulation. Error bars are indicated when duplicate experiments were carried out.

shown) is achieved. The dip-mixtures with 20 wt.% of BEA resulted in higher loadings (9 wt.%) compared to the 5 wt.% BEA (5 wt.%). The monolith with a cell density of 600 cpsi, prepared with a dip-mixture of the ‘standard’ 20 wt.% of BEA in water, resulted in a 40% higher loading compared to the monoliths with a cell density of 200 and 400 cpsi. The 600 cpsi monolith sample has a 20% lower density than the 200 and 400 cpsi monoliths, as the weight of the 600 cpsi sample was 27 g compared to 33 g for the 200 and 400 cpsi samples. As the absolute weight loading of the coated 600 cpsi sample is 30% higher than the 200 and 400 cpsi samples, this results in a higher relative loading (in %). Moreover, its higher geometric surface area ($3450 \text{ m}^2/\text{m}^3$) compared to the other values (2710 and $1850 \text{ m}^2/\text{m}^3$ for respectively the 400 and 200 cpsi monolith) leads to a higher catalyst loading assuming that the thickness of the washcoat layer was approximately the same for all structures.

The silica monolith (400 cpsi) prepared with a dip-mixture of 20 wt.% BEA in water shows a higher loading (average of 6.6 wt.%) than the standard cordierite monolith with a cell density of 400 cpsi

(average of 5.4 wt.%). This is ascribed to the higher surface area of the carrier (see Section 3.1.3) and a stronger bonding between the silica monolith and the zeolite coating.

3.1.3. Texture analysis—monoliths

Texture analysis was performed by subjecting the BEA-coated monoliths to mercury-porosimetry and nitrogen-physisorption. For the BEA-coated cordierite a BET surface area of $20\text{--}40 \text{ m}^2/\text{g}_{\text{total}}$ was found, so the surface area of the structure is increased by a factor of 6–10 because of the microporous structure of the BEA zeolite. Normalizing the BET surface area of the BEA coated monoliths ($20\text{--}40 \text{ m}^2/\text{g}_{\text{total}}$) for the amount of zeolite a range of $370\text{--}740 \text{ m}^2/\text{g}_{\text{zeolite}}$ is obtained which corresponds relatively well with the BET surface area of the BEA zeolite ($650 \text{ m}^2/\text{g}_{\text{zeolite}}$).

3.1.4. Wire gauze packings

Coating the stainless-steel wire gauze packing with a silica layer by the dip-coating technique as described in the Section 2, results in a surface area of $0.79 \text{ m}^2/\text{g}_{\text{total}}$ as determined with nitrogen adsorption.

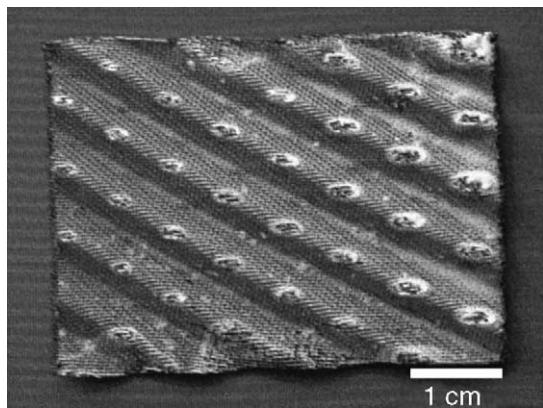


Fig. 5. A photograph of a BEA coated, silica pre-coated, wire gauze packing.

As the loading of the (microporous) silica layer was 0.68 wt.% the specific surface area of the silica can be calculated to be $116 \text{ m}^2/\text{g}_{\text{silica}}$ after calcination at 823 K. This value compares well with the surface areas obtained by Mulder [25], 135 m^2/g after calcination at 773 K and 90 m^2/g after calcination at 873 K. Coating the silica pre-coated wire gauze packing with BEA results in an average loading of 5.6 wt.% which does not differ much from the average BEA loadings

of the coated monoliths (6 ± 1.4 wt.%). In Fig. 5, a photograph can be found of a BEA coated/silica pre-coated wire gauze packing. In the corners of this type of structured packing much more dip-slurry resides after dip-coating which results in agglomerates of BEA crystals (shown in Fig. 5). These BEA accumulations can result lower activities (when normalized for the amount of catalyst) due to internal diffusion limitations in these thick layers. This aspect cannot occur in BEA coated monolithic structures, where the coating is much more evenly spread and therefore thinner. The surface area of this BEA coated wire gauze packing as determined with nitrogen adsorption is $25 \text{ m}^2/\text{g}$. Again, as with the BEA coated monoliths, when the BET surface area of the BEA coated wire gauze packing is normalized for the amount of BEA zeolite a value of $446 \text{ m}^2/\text{g}_{\text{zeolite}}$ is obtained which corresponds relatively well with the BET surface area of the BEA zeolite ($650 \text{ m}^2/\text{g}_{\text{zeolite}}$).

3.1.5. Morphology of BEA coatings

In Fig. 6, SEM micrographs are shown of a monolith coated in a dip-mixture of 20 wt.% BEA in water, with 1 wt.% of the solids as binder (Ludox), and Teepol as surfactant. Comparing the micrograph of a bare monolith with a BEA coated sample, the BEA

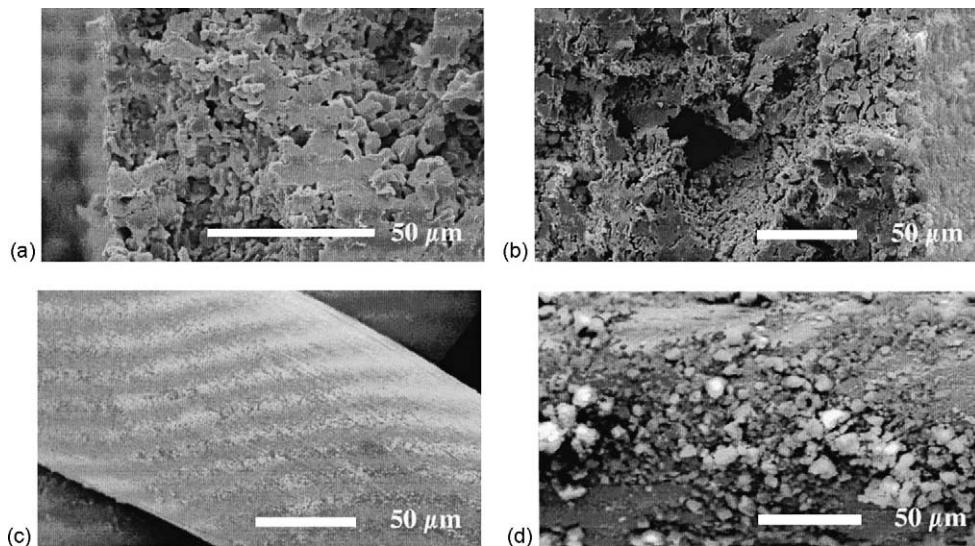


Fig. 6. SEM micrographs of bare and BEA-coated structured packings, prepared with a 20 wt.% BEA mixture in water. (a) Monolithic structure without any coating; (b) BEA coated monolithic structure—cross-section of the monolithic wall; (c) wire gauze without coating; (d) BEA coated wire gauze structure.

zeolitic layer is clearly visible from the cross-section of the monolith wall (**Fig. 6b**). The thickness of the layer, varying from 7 to 15 µm is of the same magnitude as the particle size of the BEA clusters (see **Section 2**). In **Fig. 6c and d**, SEM micrographs are shown of respectively a bare wire gauze and a BEA/silica coated sample (view from above). In this case also the BEA zeolite crystals are clearly visible when comparing to the bare sample.

3.1.6. Influence of the silica binder

Colloidal silica (Ludox AS-40, a 40 wt.% suspension of colloidal silica in water) was used as binder in the dip-mixtures. The influence of the binder was investigated by studying the viscosity of the water-based dip-slurry with various amounts of binder. The results are depicted in **Fig. 7**. By increasing the amount of binder from 0 to 13 wt.%, the apparent viscosity shows a strong decrease from 18,000 to 7 cP. Considering the loadings of the corresponding coatings (**Fig. 4**), coating the monolith with a mixture without binder does not seem to affect the catalyst loading much, but affects the strength of the carrier-catalyst bonding (see **Section 3.1.8**).

The loading of a monolithic coating prepared with 3 wt.% does not significantly differ much from the coating prepared without any binder, but increasing the amount of binder from 3 to 5 wt.% results in a drop of 35% of the catalyst loading. As the viscosity decreases (**Fig. 7**), removal of the liquid during the coating procedure goes easier resulting in a lower catalyst loading.

3.1.7. Influence of temporary binder and surfactant

In the case of butylacetate as a solvent, the influence of a ‘temporary’, i.e. decomposable, binder for the zeolite crystals was studied. Nitrocellulose, moistened with 35% ethanol, was added prior to calcination. This gave a loading of 2.3 wt.% (not shown), compared to the low loading of 0.6 wt.% without nitrocellulose (not shown), showing the effectiveness of the binding effect to the surface.

The influence of a surfactant to disperse the zeolite crystals in water was studied by adding Teepol to the water-based dip-mixtures. Adding the standard amount of 0.3 g (1.8 wt.% based on the BEA content) of Teepol gave a loading 5.4 ± 0.4 wt.%. Without the surfactant the catalytic coating shows a comparable loading of 6.3 wt.%. It seems that the addition of the surfactant does not affect the loading much.

3.1.8. Binding of the coating onto support

To investigate the adhesion of the zeolite crystals to the coated supports, the prepared coatings were subjected to an ultrasonic treatment and the weight loss was determined. The weight losses varied from 0.08 till 0.23 wt.% for the coated monoliths, compared with 0.11% of the uncoated monolith. This indicates the firm attachment of the zeolite coatings. The highest weight loss was found for the zeolite coating without the silica binder, indicating the function of the silica binder. If the coating prepared with 20 wt.% of BEA zeolite in water is considered, this means that 1 wt.% of binder (on the basis of the amount of BEA) suffices for a strong adhesion of a BEA zeolite coating on a

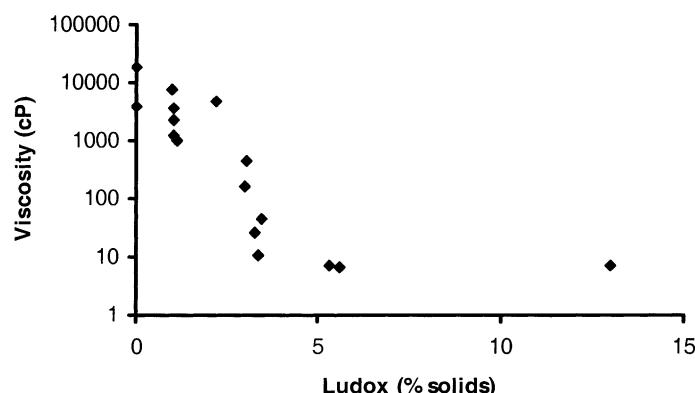


Fig. 7. The effect of the amount of binder on the apparent viscosity of the dip-slurry.

ceramic support. A low binder content can be favourable for the accessibility of the catalyst in the coating [12].

When applying ultrasonic treatment onto the BEA coated wire gauze packings, a substantial amount (50–80 wt.%) of BEA weight loss is found. The silica precoating, however, is firmly attached to the packing, as this material did not show any weight loss after ultrasonic treatment. During catalytic testing, however, no weight loss was observed, indicating that the binding strength is sufficient under reaction conditions.

3.2. Performance of the BEA coated structures

A typical result of the performance of a beta coated monolith is given in Fig. 8, in which the conversion of octanoic acid and the selectivity towards the desired aromatic ketone is plotted as a function of time. The activity of the prepared monoliths is expressed as the initial apparent first-order rate constant k (h^{-1}) normalized for the catalyst concentration (g/l). The results are shown in Fig. 9. All BEA coated monolithic structures were tested at a temperature of 415 K. To compare the activity with the activity of the zeolite as measured in slurry at reflux (428 K, i.e. boiling point

of anisole), some monoliths were also tested at this temperature of 428 K.

The BEA coated monolith prepared according to the standard method (a 400 cpsi cordierite monolith coated with a 20 wt.% BEA slurry in water, with 1% of the total solids of binder and a surfactant added) shows an activity which is 30% lower than the activity of the BEA particles in a slurry (0.05 l/(g h)), measured at 428 K. However, the remaining activity is quite satisfactory. The lower activity is attributed to the fact that the zeolite particles are only partly accessible since the particles are fixated on the support. Moreover, when considering the diffusion lengths in both the slurry system and the monolith system, diffusion limitations are expected to occur more easily in the case of the monolith than in the case of the slurry system as the layer thickness of the coated monolith is larger than the particle size of the beta catalyst in the slurry system.

The activity of the silica monolith measured at 428 K is close to the activity of the BEA particles at the same temperature (10% lower). Apparently, this high surface area, micropores-containing material apparently provides enough accessibility for the BEA particles resulting in a higher activity compared to the cordierite material. Also the material has a

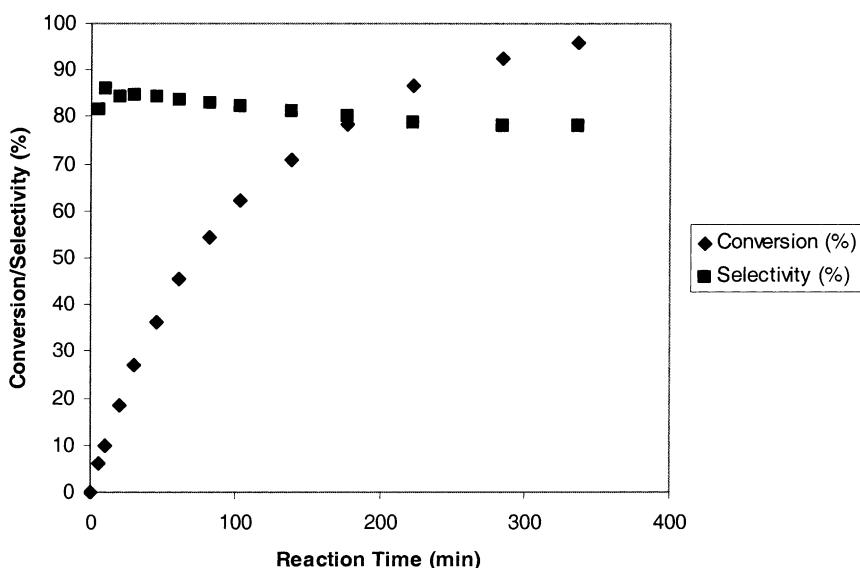


Fig. 8. A typical result of the performance of a beta coated cordierite monolith (400 cpsi) in the acylation of anisole with octanoic acid; (◆) Conversion (%) of octanoic acid as a function of time (428 K), (■) selectivity (%) towards *p*-octanoyl anisole as a function of time (428 K).

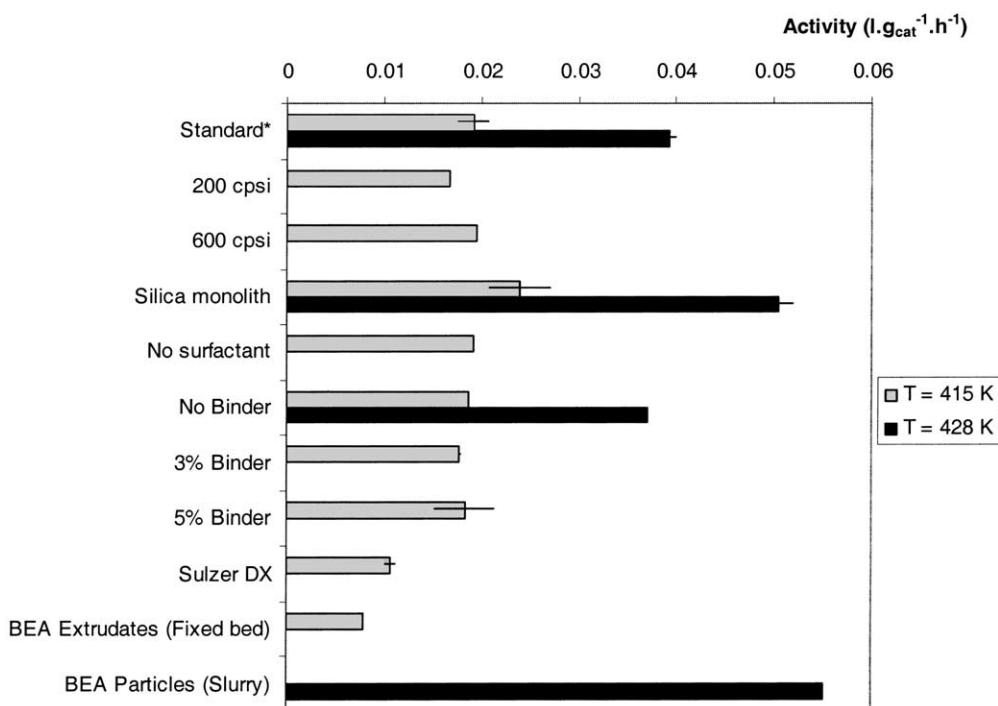


Fig. 9. Activity of the BEA coated monoliths in the acylation of anisole with octanoic acid, measured at two different reaction temperatures expressed as the first-order rate constant normalized for the amount of catalyst (g). Error bars are indicated when duplicate experiments were carried out.

higher purity than the cordierite which can result in a better performance. Also, at the lower reaction temperature of 415 K a higher activity is found for the silica monolith compared to the cordierite monolith.

3.2.1. Effect of cell density

The effect of cell density on the activity was studied for three cell densities—200, 400 and 600 cpsi. The activities are normalized per amount of BEA catalyst and do not differ much. A high cell density is more favorable because both the geometric surface area and the volume fraction of the catalyst are largest for the highest cell density when a constant coating thickness is considered. When increasing the coating thickness, the conversion becomes no longer limited by the amount of catalyst present in the reactor but by diffusion [26]. From these results, it is concluded that the performance of the BEA coated monoliths is not influenced by the geometric surface area of the carrier, indicating the absence of mass-transfer limitations.

3.2.2. Effect of additives—binder and surfactant

The effect of the binder was studied by preparing a coating without binder and by increasing the amount of binder with a factor of 3 and 5. In all cases a similar activity is found indicating that the amount of binder (upto 5% of the total amount of solids) does not effect the activity at the lower reaction temperature of 415 K. Apparently, in these cases the binder does not block the active sites of the zeolite either. As described earlier, the amount of binder effects the viscosity and thereby also the catalyst loading of the coated packing. In this way the amount of catalyst on the packing can be tuned without affecting the performance negatively in the acylation reaction.

Preparing a coating without a surfactant resulted in a similar activity at 415 K. Apparently the performance is also not influenced by this surfactant.

3.2.3. Effect of reactor configuration

The performance of the BEA coated cordierite monolith, prepared according to the standard method,

was compared to a wire gauze mesh coated packing (Sulzer DX) which was first pre-coated with a silica layer and then coated in the same way (standard method; see Fig. 9).

The activity of the wire gauze packing, normalized for the amount of BEA, is lower (44%) than the activity of the monolith packing, probably caused by the lower geometric surface area of the wire gauze packing ($900 \text{ m}^2/\text{m}^3$ compared to $2710 \text{ m}^2/\text{m}^3$ for a 400 cpsi monolith), and thereby being limited by diffusion of reactants in the coatlayer. Also the less homogeneous distribution of the zeolite over the packing (see Fig. 5) is likely to be a contributing factor for the lower activity.

The activity of the BEA extrudates was also tested in the fixed bed configuration under the same reaction conditions as the other packings that were tested at the lower reaction temperature of 415 K. In this configuration an activity of $0.00781 \text{ g}_{\text{cat}}^{-1}/\text{h}$ was obtained, which is 60% lower compared to the activity of the standard coated 400 cpsi cordierite monolith. As the tested extrudates were commercial samples, unfortunately the type and amount of binder are not known. However, it is very common to use alumina as a binder (which is inactive in this acylation reaction) in a relatively high amount (30–40%). So, as these activities are measured per gram of catalyst, the decrease in activity is mainly attributed to the loss in accessibility of the BEA particles after extrusion. Also mass-transfer limitations in the large zeolite particles could cause a lower activity in the acylation reaction.

3.2.4. Activity normalized for packing volume

The activities that were described earlier were all normalized for the amount of catalyst ($\text{l g}_{\text{cat}}^{-1}/\text{h}$). To investigate the effect of the catalytic activity of the packing on the size of the packing, the activities were also normalized for the volume of the packing ($\text{l m}_{\text{packing}}^{-3}/\text{h}$; see Fig. 10). This way of comparing activities is most important for a practical application, since these values determine the actual reactor size. When activities are compared in this way both activity and catalyst loading are important.

A monolithic structure of 600 cpsi has a higher activity than the standard 400 cpsi monolith, while the activity does not change when using a 200 cpsi monolith. The higher activity of the 600 cpsi monolith is attributed to a higher catalyst loading present in the

600 cpsi monolith when comparing to the 200 and 400 cpsi monoliths. After dipping the structure in de zeolite containing dip-solution, excess liquid is removed by pressurized air. Due to the smaller channels, the removal of the excess liquid will be more difficult which results into a higher loading.

The silica monolith shows a higher activity (40%) than the standard monolith, which can be attributed to the higher loading (20%) and also to the high surface area, the presence of micropores and the absence of contaminations in the carrier which can result in a more active coating (Fig. 9).

The activities of the monoliths prepared without any surfactant, any binder, with 3% of binder does not differ from the activity of the standard monolith. So, the active sites are not blocked by the binder. However, when applying 5% of Ludox as a binder, the activity decreases per monolith weight. This is caused by the lower loading (Fig. 4) as a result of the lower viscosity of the dip-slurry. By addition of binder, the viscosity of the dip-slurry drops (Fig. 7) resulting in a lower loading which in turn results in a lower activity. As the amount of loading is lower than in the case of the standard amount of binder, this decrease in activity is not caused by a blockage of the active sites.

The BEA coated wire gauze packings and the BEA extrudates both show a lower activity ($\text{in l m}_{\text{reactor}}^{-3}/\text{h}$) than the standard monolith, which can be explained by the lower geometric surface area for the wire gauze packing ($900 \text{ m}^2/\text{m}^3$ versus $9720 \text{ m}^2/\text{m}^3$ for a 400 cpsi monolith) and thereby the earlier occurrence of mass-transfer limitations in the larger extrudates or the local agglomerations on the wire mesh. The lower activity of the extrudates is attributed to the addition of binder; when extruding the BEA zeolite a substantial amount of binder (amount is unknown, presumably >10 wt.% [12]) is added, which results in a decreased accessibility of the active sites [12].

3.2.5. Stability of the BEA coated monoliths

To investigate the regenerability of BEA coated monoliths, the coatings prepared according to the standard method (20 wt.% mixture in water, including binder and surfactant) were washed with acetone after reaction, dried at 393 K (16 h), recalcined at 723 K for 4 h (heating rate 10 K/min). The activity of this regenerated BEA coating was measured in the acylation reaction (of anisole with octanoic acid). Between

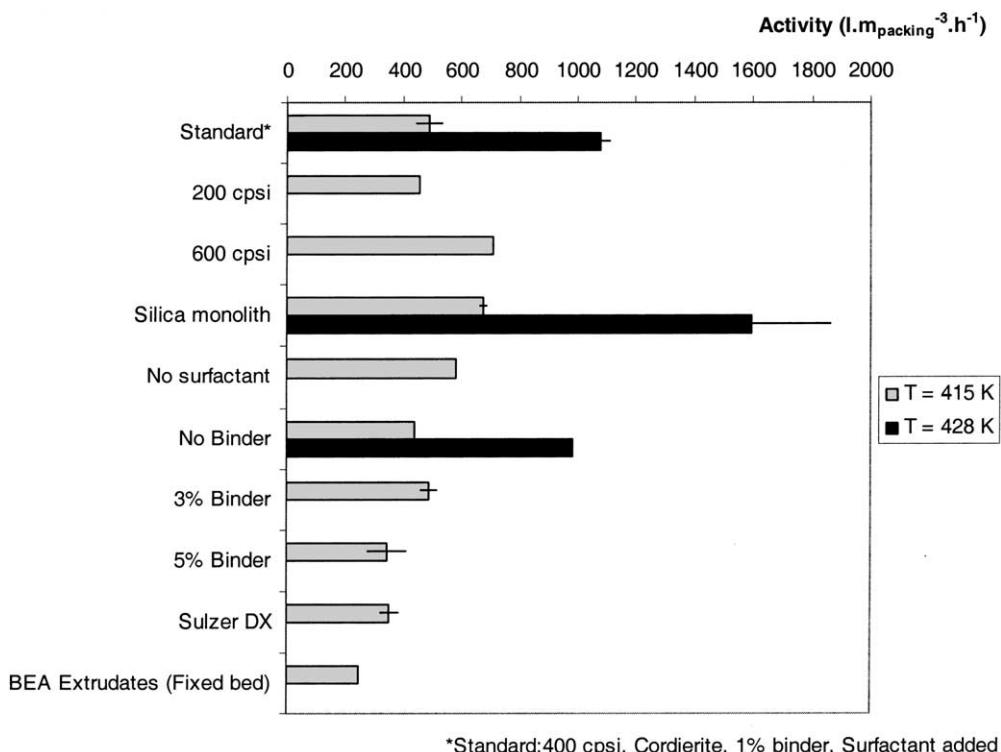


Fig. 10. Activity of the BEA coated monoliths in the acylation of anisole with octanoic acid, measured at two different reaction temperatures expressed as the first-order rate constant normalized for the packing volume (m^3). Error bars are indicated when duplicate experiments were carried out.

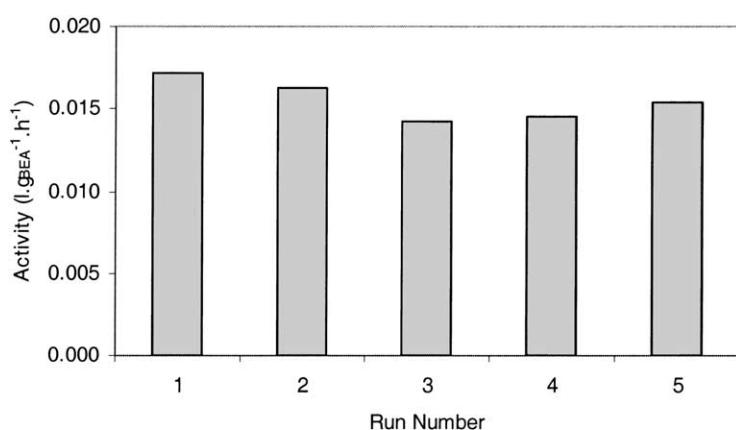


Fig. 11. Activity of a BEA coated cordierite monolith of 400 cpsi according to the standard preparation method after several runs in the acylation of anisole with octanoic acid.

run 4 and 5 the catalyst was also ion-exchanged with ammonium nitrate before the calcination step. See Fig. 11 for the results; even after five runs the activity does not decrease. Apparently, calcination after performing the reaction is an adequate step to maintain the activity leading to a high stability of the catalyst, and ion-exchanging the zeolite between two separate reaction cycles does not influence the activity.

3.2.6. Selectivity of the BEA coated monoliths

All monoliths give a similar selectivity of about 77–85% towards the main product, the para-substituted octanoyl anisole. So, compared to the selectivity of the original BEA as tested in slurry (84%), the selectivity is maintained.

4. Conclusions

A method was developed in which catalytic active and selective BEA coatings can be prepared onto ceramic monoliths and metallic wire gauze packings. High BEA-loadings (up to 9 wt.%) were obtained with the BEA dip-mixtures in water. The loadings are dependent on the cell density, the amount of binder and on the solids content of the dip-mixture, which in turn is dependent on the solvent choice. Addition of a surfactant does not effect the loading much. To coat the stainless-steel wire gauze packing the substrates have to be pre-coated with a silica layer (0.7 wt.%) after which a BEA zeolite layer (5.6 wt.%) is deposited. The coatings show strong bonding to the substrates, and they can easily be regenerated by calcination in air.

When normalizing the activity for the amount of catalyst (BEA), the silica monolith shows the highest activity, which is only 10% lower than the activity of the BEA particles in a slurry at 428 K (0.05 l/(g h)). When comparing this type of coated monolith with a coated cordierite monolith or a metal wire gauze packing, a lower activity is obtained (respectively 30 and 44% lower than the BEA particles in slurry). In the case of the metal structure, the activity decrease is attributed to diffusion limitation of reactants in the coat layer in this specific type of structured packing. BEA extrudates show an activity that is 60% lower than the BEA powder, caused by the loss in accessibility of the BEA particles after extrusion, and by mass-transfer limitations in the large zeolite particles.

When the activity of the coated structures is normalized for the total volume of the packing, both the BEA coated 600 cpsi cordierite monolith and the BEA coated silica monolith show the highest activity due to the high catalyst loadings obtained with these samples. These high loadings are caused by a high geometric surface area, and in the case of the silica monolith, also due to a strong bonding between the washcoat and the catalyst.

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