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Imaging the effect of a hydrothermal treatment on the pore accessibility and acidity of large ZSM-5 zeolite crystals by selective staining

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Confocal fluorescence microscopy has been used in combination with bulky non-reactive dyes (i.e. proflavine, stilbene and Nile blue A) and two staining reactions (i.e. fluorescein synthesis and 4-fluorostyrene oligomerisation) to study the effect of steaming on pore accessibility and acidity of large ZSM-5 zeolite crystals. This approach enabled the 3-D visualization of cracks and mesopores connected to the outer zeolite surface as well as mesoporous "cavities" within steamed ZSM-5 zeolite crystals. It has been found that besides the generation of mesoporosity steaming makes the boundaries between the different crystal sub-units accessible for bulky molecules. Additionally, the fluorescein staining reaction reveals prominent formation of structural defects that are connected to the surface of the crystal via the microporous ZSM-5 system and which contain either Brønsted or Lewis acid sites. On the other hand, the 4-fluorostyrene staining reaction shows how mild steaming conditions increase the accessibility towards the Brønsted acid sites, while under severe steaming conditions the Brønsted acidity contained in the internal crystal sub-units is more accessible, although it is preferentially removed close to the surface of the lateral sub-units of ZSM-5 zeolite crystals.

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Introduction

Over the last few decades, large zeolite crystals have been used as model systems to gain insight into fundamental aspects of the underlying phenomena that govern the catalytic performance of their industrial counterparts. Despite the fact that these materials are rarely applied in industrial processes, their long range order and reduced amount of crystal sub-units enable a detailed study of their reactivity and diffusion properties. Recently, this approach has been used to disclose relevant information concerning (1) the influence of defects,^{1,2} (2) the presence of heterogeneities in the distribution of active sites,³ (3) the diffusion properties^{4–6} and (4) the influence that the catalyst porous network has on the alignment of host molecules.⁷ Additionally, the large size of these crystals minimizes the compromise between chemical information and spatial resolution, which is often faced by a wide variety of micro-spectroscopic techniques. This advantage has been exploited in combination with spectroscopic techniques possessing high chemical speciation capability^{8,9} and micrometre resolution^{10–15} to unravel differences in the catalytic behaviour at the level of a single zeolite crystal.

Given the prominent role that ZSM-5 zeolites play in the modern industry,^{16–18} several studies have been devoted to clarify the structure of large ZSM-5 zeolite crystals and its influence on the physicochemical alterations resulting from certain post-synthetic modifications.^{19–21} In this manner, it has been revealed that large ZSM-5 zeolite crystals are formed by the

Fig. 1 Schematic representation of the internal architecture and diffusion barriers in ZSM-5-P (a), ZSM-5-MT (b) and ZSM-5-ST (c). In all cases the lateral crystal sub-units (region II) expose the sinusoidal pores to the surface while the pyramidal crystal sub-units (region I) display the straight pores open to the surface along the [010] axis. The crystal regions depicted in green, red and blue represent the external and internal diffusion barriers present in large ZSM-5 zeolite crystals.

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assembly of a reduced number of intergrowth sub-units as illustrated in Fig. 1.^{19,22} In particular, two pyramidal sub-units are interconnected in the centre of the zeolite crystal, being surrounded by four lateral building blocks. The crystal sub-units, as is the case for the crystal domains characteristic of commercial ZSM-5 zeolites, are composed of a two dimensional pore system of sinusoidal ($5.6 \text{ \AA} \times 5.3 \text{ \AA}$) and straight pores ($5.5 \text{ \AA} \times 5.1 \text{ \AA}$) running perpendicular to each other.²³ In the pyramidal sub-units the straight pores are open to the surface along the [010] axis, whereas in the lateral sub-units they run parallel to the crystal surface. Recent studies have demonstrated that the intergrowth architecture of large ZSM-5 zeolite crystals accounts for their different response towards steaming.^{24,25} Briefly, these treatments, performed at high temperatures in the presence of steam, selectively extract aluminium from the zeolite framework inducing alterations in the pore accessibility and acidic properties.²⁶

In previous studies by our group it was found that the crystal regions exposing only sinusoidal pores opened to the surface were more susceptible to steaming than those regions partially exposing their straight channels.^{24,25} The different susceptibility upon steaming resulted in an internal architecture dependent distribution of mesopores within the steamed large ZSM-5 zeolite crystals. These findings are schematically illustrated in Fig. 1b and c, where the lateral sub-units, exposing the sinusoidal pores open to the surface, show a more pronounced generation of mesoporosity compared to their pyramidal counterparts. Moreover, the extent of these alterations was found to be fully dependent on the steaming temperature conditions. In this manner, mild steaming conditions induced alterations limited to the external regions of the zeolite crystals, while severe conditions resulted in the generation of a mesoporous network distributed within the whole crystal volume (Fig. 1b and c).

In the present work, the influence that the internal architecture of large ZSM-5 crystals has on the changes in pore accessibility and acidity during steaming has been investigated. This has been done using confocal fluorescence microscopy (CFM) in combination with bulky fluorescent dyes (*i.e.* proflavine, stilbene and Nile blue A) and two staining reactions (*i.e.* fluorescein synthesis and 4-fluorostyrene oligomerization). For this purpose, the results obtained from staining the as-prepared ZSM-5 material (sample name: ZSM-5-P) have been compared with those obtained from two samples steamed under different conditions, namely, a mildly treated sample (sample name: ZSM-5-MT) and a severely treated sample (sample name: ZSM-5-ST). It is noted that the set of samples used herein is the same as that investigated in earlier publications.^{24,25} In this way, the results of this study are complementary with those previously published, allowing us to draw a relation between the alterations observed in the topological and acidic properties of the steamed zeolite crystals.

Experimental section

Large ZSM-5 zeolite crystals with dimensions of $100 \times 20 \times 20 \text{ }\mu\text{m}^3$ and a Si/Al ratio of 17 were provided by ExxonMobil (Machelen, Belgium). The as-prepared ZSM-5 zeolite crystals were calcined, by first preheating them at $120 \text{ }^\circ\text{C}$ (30 min,

$2 \text{ }^\circ\text{C min}^{-1}$) and then increasing the temperature to $550 \text{ }^\circ\text{C}$ (360 min, $10 \text{ }^\circ\text{C min}^{-1}$). This was followed by a triple ion exchange with a 10 wt% ammonium nitrate (Acros Organic, 99+%) solution at $80 \text{ }^\circ\text{C}$. Subsequently, a second calcination was performed to obtain the ZSM-5-P sample. Before starting the hydrothermal treatment ZSM-5-P was preheated to $120 \text{ }^\circ\text{C}$ (30 min, $2 \text{ }^\circ\text{C min}^{-1}$) in a quartz tubular oven (Thermoline 79300). Afterwards, steaming was performed for 300 min at $500 \text{ }^\circ\text{C}$ (ZSM-5-MT) and $700 \text{ }^\circ\text{C}$ (ZSM-5-ST) *via* saturation of a nitrogen flow (180 ml min^{-1}) with water at $100 \text{ }^\circ\text{C}$. Subsequent to the hydrothermal treatment the zeolite crystals were calcined following the above-mentioned procedure.

Confocal fluorescence microscopy images of the different materials were acquired using a Nikon Eclipse LV150 microscope equipped with a $50 \times 0.55 \text{ NA}$ dry objective and a Nikon D-Eclipse C1 head containing a 488 nm, 561 nm and a 635 nm laser. Prior to staining the large ZSM-5 zeolite crystals with the fluorescent dyes, 5 mg of proflavine (Sigma Aldrich, pure) as well as $15 \text{ }\mu\text{l}$ of stilbene (Sigma Aldrich, 96%) and Nile blue A (Acros Organic, pure) were dissolved in 25 ml of ethanol. Subsequently, the ZSM-5 zeolite crystals were stained at room temperature and after drying for 5 min the visualization of proflavine, stilbene and Nile blue A was carried out by illuminating the large ZSM-5 zeolite crystals with a 488 nm (detection range 510–550 nm), a 561 nm (detection range 570–620 nm) and a 635 nm laser (detection range 662–737 nm), respectively. For *in situ* fluorescein synthesis, 1 ml of 2 M resorcinol (Sial, 99%) and 2 ml of 0.2 M phthalic anhydride (Acros Organic, 99%) solutions were mixed and adjusted to 10 ml with absolute ethanol (Antonides-Interchema, 99%) resulting in a 5 : 1 resorcinol-phthalic anhydride molar ratio. Subsequently, $25 \text{ }\mu\text{l}$ of the resulting solution were used to impregnate the zeolite samples. After a waiting time of 5 min, the samples were heated to $200 \text{ }^\circ\text{C}$ ($10 \text{ }^\circ\text{C min}^{-1}$) in an *in situ* cell (FTIR 600, Linkam) equipped with a temperature controller (Linkam TMS 94). Sample illumination was performed with the 488 nm laser, while the emission was detected by the photomultiplier tube in the 510–550 nm range. The Brønsted acid catalyzed oligomerization of 4-fluorostyrene (Acros Organic, 97%) was performed in the same *in situ* cell used for the synthesis of fluorescein. The zeolite crystals were placed on a glass plate and heated to $120 \text{ }^\circ\text{C}$ ($10 \text{ }^\circ\text{C min}^{-1}$) for 5 min, subsequently adding $15 \text{ }\mu\text{l}$ of the styrene derivative. After 5 min of reaction the generated carbocations were visualized using a 488 nm laser with a detection range of 510–550 nm.

Results and discussion

Probing pore accessibility with confocal fluorescence microscopy

In a first set of experiments, the three sets of large ZSM-5 zeolite crystals under study were stained with bulky fluorescent dyes in order to investigate the changes induced in the crystal accessibility by a mild and a severe hydrothermal treatment. The dyes selected were non-reactive bulky probe molecules, which are unable to completely enter the micropore system of ZSM-5, namely

Scheme 1 Bulky dye molecules used to investigate the changes taking place in the pore accessibility upon steaming: proflavine (a), stilbene (b) and nile blue A (c). (d) Schematic illustration of the crystal regions where the confocal fluorescence microscopy images were recorded and a microphotograph of the ZSM-5 crystals under investigation.

proflavine, stilbene and nile blue A. Scheme 1 shows the structure of these three non-reactive molecules. The use of these fluorescent dyes, in combination with confocal fluorescence microscopy (CFM), allows the visualization of cracks and mesopores connected to the outer surface²⁷ providing a reliable picture of the modifications taking place in the pore accessibility of the large ZSM-5 zeolite crystals under study.

The CFM results obtained after staining the ZSM-5-P crystals with proflavine are shown in Fig. 2. They show the restricted access of this dye towards the micropore system of ZSM-5-P. In contrast, ZSM-5-MT displayed strong fluorescence at the outer crystal surface as well as in the core of the crystal. The fluorescence signal shown by this sample was heterogeneously distributed within the different regions of the crystals, being more intense at the surface

and in the lateral sub-units as compared to its pyramidal counterparts. This heterogeneity in fluorescence is indicative of the different susceptibility of the distinct crystal regions to steaming and is in line with previous results obtained for the same set of large ZSM-5 zeolite crystals.²⁴

Alternatively, the CFM results obtained after staining the ZSM-5-ST sample with proflavine revealed increased pore accessibility in the lateral crystal sub-units as well as a partial opening of the crystal sub-unit boundaries. The latter observation is important as it discloses how particular regions of the zeolite crystals, acting as molecular diffusion barriers in ZSM-5-P,⁵ become accessible after steaming. Accordingly, the induced structural modifications facilitate the transport of molecules towards the internal zeolite regions, which were, prior to steaming, only accessible *via* the micropore system of ZSM-5.

To get further insight into changes taking place in the structural properties of large ZSM-5 zeolite crystals during mild and severe hydrothermal treatments the crystals were stained with stilbene. As shown in Fig. 3, results similar to those presented in Fig. 2 for proflavine were obtained for ZSM-5-P, indicative of a limited access to the microporous system of the non-steamed large ZSM-5 zeolite crystals. In the case of ZSM-5-MT, the fluorescence originating from the outer zeolite surface was more pronounced as compared to that from the lateral sub-units. In contrast, the more prominent generation of mesopores under severe steaming conditions induced a decrease in the spatial differences observed in the fluorescence intensity. In other words, the CFM data in Fig. 2 and 3 reveal that proflavine and stilbene are accessible to similar mesopore structures within ZSM-5-MT and ZSM-5-ST.

Fig. 2 Confocal fluorescence microscopy images obtained from the top and middle plane of ZSM-5-P, ZSM-5-MT and ZSM-5-ST after staining with proflavine. $\lambda_{\text{ex}} = 488$ nm, detection 510–550 nm. Images are presented as thermal maps, the warmer the colour, the higher the intensity of the fluorescence signal. All the intensities have been boosted with the same factor.

Fig. 3 Confocal fluorescence microscopy images obtained from the top and middle plane of ZSM-5-P, ZSM-5-MT and ZSM-5-ST after staining with stilbene. $\lambda_{\text{ex}} = 561$ nm, detection 570–620 nm. Images are presented as thermal maps, the warmer the colour, the higher the intensity of the fluorescence signal. All the intensities have been boosted with the same factor.

Fig. 4 Confocal fluorescence microscopy images obtained from the top and middle plane of ZSM-5-P, ZSM-5-MT and ZSM-5-ST after staining with nile blue A. $\lambda_{\text{ex}} = 635$ nm, detection 662–737 nm. Images are presented as thermal maps, the warmer the colour, the higher the intensity of the fluorescence signal. All the intensities have been boosted with the same factor.

To corroborate the above-mentioned findings the parent and two hydrothermally treated ZSM-5 zeolite crystals were stained with nile blue A, which is a more bulky dye molecule than proflavine and stilbene (Scheme 1). The obtained CFM results are summarized in Fig. 4. The data for ZSM-5-P showed a very weak overall fluorescence. In contrast, in the case of ZSM-5-MT the fluorescence originated from the outer surface and lateral crystal sub-units, which confirms the heterogeneity observed in the variations taking place within the different crystal sub-units during a hydrothermal treatment. In a similar manner, the fluorescence signal in ZSM-5-ST originated from the outer surface and lateral crystal sub-units. Nonetheless, in this case the highest fluorescence was observed in the regions in between the crystal sub-unit boundaries.

Complementary to the adsorption of the non-reactive bulky dye molecules, the synthesis of fluorescein (2-(6-hydroxy-3-oxo-(3H)-xanthen-9-yl) benzoic acid) from phthalic acid anhydride and resorcinol was performed for the three sets of large ZSM-5 zeolite crystals under investigation. The reaction as well as the molecular dimensions of fluorescein are shown in Scheme 2.²⁸ The advantage of using the *in situ* synthesis of fluorescein over the use of bulky fluorescent dye molecules, such as nile blue A, is related to the fact that the reactants are able to diffuse throughout the zeolite crystal, avoiding the steric restrictions imposed by the microporous network of ZSM-5. In other words, the *in situ* synthesis of fluorescein allows the visualization of “cavities”, which are mesoporous defects connected to the outer crystal surface *via* the micropore system. Moreover, as this reaction can be catalysed by both Lewis²⁸ and Brønsted^{29,30} acid sites, it also allows us to visualize “cavities” in regions that are seriously depleted in Brønsted acidity. Accordingly, the

Scheme 2 Staining reaction based on the *in situ* synthesis of fluorescein used to visualize mesoporous structural defects.

Fig. 5 Confocal fluorescence microscopy images obtained from the top and middle plane of ZSM-5-P, ZSM-5-MT and ZSM-5-ST during the *in situ* synthesis of fluorescein at 200 °C. $\lambda_{\text{ex}} = 488$ nm, detection 510–550 nm. Images are presented as thermal maps, the warmer the colour, the higher the intensity of the fluorescence signal. All the intensities have been boosted with the same factor.

in situ fluorescein synthesis provides valuable complementary knowledge to that obtained by staining the large ZSM-5 zeolite crystals with the non-reactive bulky dye molecules.

Fig. 5 summarizes the CFM results obtained from the *in situ* synthesis of fluorescein. It was found that the fluorescence originating from the outer surface of the parent and hydrothermally treated zeolite crystals is in line with the above-described observations making use of proflavin, stilbene and nile blue A. More specifically, the ZSM-5-P crystal showed a lack of fluorescence as compared to the hydrothermally treated samples. Furthermore, ZSM-5-MT exhibited a higher overall fluorescence than ZSM-5-ST in the top plane. The latter observation is indicative of a more affected outer crystal surface after applying mild hydrothermal treatments, which is in agreement with HRSEM studies previously performed on the three set of crystals under investigation.²⁵ Alternatively, the lack of

fluorescence signal collected from the central plane of ZSM-5-P points towards the absence of structural defects within this sample. In contrast, both ZSM-5-MT and ZSM-5-ST show fluorescence arising from the crystal's middle plane. In the case of ZSM-5-MT, fluorescence was mainly collected from the outer crystal surface and inner regions of the lateral crystal sub-units, confirming the different susceptibility of the crystal sub-units towards steaming. The difference with previous results, however, arises from the more homogeneous distribution observed in the fluorescence signal originating from the outer surface and inner core of the lateral crystal sub-units. This suggests that under mild steaming conditions a large number of "cavities" are generated in the lateral crystal sub-units. ZSM-5-ST, on the other hand, displayed the strongest fluorescence of the three ZSM-5 zeolite crystals under investigation. This is in line with previous results and supports the fact that a higher number of structural modifications take place with increasing steaming temperature. Furthermore, the fluorescence signal originating from the pyramidal crystal sub-units of ZSM-5-ST was very intense. This suggests that a significant amount of "cavities" are formed throughout the pyramidal crystal sub-units after a severe hydrothermal treatment.

Probing Brønsted acidity with confocal fluorescence microscopy

During the course of a hydrothermal treatment it is known that the generation of mesopores induces a reduction in the number of Brønsted acid sites, often involving an increase in the amount of Lewis acid sites.²⁶ To investigate the extent of this phenomenon in large ZSM-5 zeolite crystals the Brønsted acid catalyzed 4-fluorostyrene reaction was selected as the staining reaction and the process was followed by CFM. Scheme 3 summarizes the main species formed during the oligomerization of 4-fluorostyrene, which is initiated by the protonation of a 4-fluorostyrene monomer by a Brønsted acid site. Subsequent addition of another monomer gives rise to the formation of the cyclic dimeric 3-methyl-1,4-fluorophenylindanyl carbocation.^{31,32} This carbocation is fluorescent and CFM in combination with a 488 nm excitation laser enables its visualization in 3-D within the large ZSM-5 zeolite crystal.

The results obtained from these CFM experiments are summarized in Fig. 6, showing a homogeneous fluorescence

Scheme 3 Selective staining reaction used to visualize the Brønsted acidity. Styrene monomer (a), protonated styrene monomer (b) and 3-methyl-1,4-fluorophenylindanyl carbocation (c).

Fig. 6 Confocal fluorescence microscopy images obtained from the top and middle plane of ZSM-5-P, ZSM-5-MT and ZSM-5-ST during the oligomerization of 4-fluorostyrene at 120 °C. $\lambda_{\text{ex}} = 488$ nm, detection 510–550 nm. Images are presented as thermal maps, the warmer the colour the higher the intensity of the fluorescence signal. All the intensities have been boosted with the same factor.

throughout the ZSM-5-P crystal. This observation is indicative of a similar reactivity and hence a comparable distribution of Brønsted acid sites within ZSM-5-P. In a similar manner, the ZSM-5-MT sample presented a homogeneous distribution of the fluorescence signal within the different crystal regions, showing, however, an increase in the overall fluorescence intensity with respect to that of the ZSM-5-P sample. Given that steaming does not increase the number of Brønsted acid sites, this observation can be attributed to an increase in the accessibility towards these acid sites. Consequently, the structural modifications observed after a mild hydrothermal treatment enhance the accessibility towards the Brønsted acid sites without inducing a significant depletion and/or redistribution of this type of acidity.

In contrast to the above-mentioned observations, the fluorescence observed at the outer surface plane of ZSM-5-ST was lower than that of ZSM-5-P. We explain this observation by the loss of Brønsted acid sites under the severe steaming conditions applied. The results obtained from the middle plane of ZSM-5-ST, however, displayed a stronger fluorescence signal as compared to both ZSM-5-P and ZSM-5-MT. Following the same line of thought as for the ZSM-5-MT sample, this observation is a clear indication of an enhanced accessibility towards the Brønsted acid sites contained in the core of the zeolite crystal after severe steaming and is in agreement with the results presented in Fig. 2–4. Moreover, the fluorescence signal within the ZSM-5-ST crystal was heterogeneously distributed between the pyramidal and lateral crystal sub-units. In particular, the lateral sub-units showed lower fluorescence intensities, especially close to the surface as compared to their pyramidal counterparts. Accordingly, the CFM measurements suggest that

Fig. 7 Schematic illustration summarizing the main observations described in this study for ZSM-5-P (a), ZSM-5-MT (b) and ZSM-5-ST (c) zeolite crystals. The molecular diffusion barriers, depicted in green, red and blue in (a), are substantially modified with increasing steaming temperature. Additionally, steaming induces different modifications in the physicochemical properties of the distinct crystal sub-units. The lateral sub-units undergo significant structural modifications due to the mild and more severe hydrothermal treatment, whereas the pyramidal sub-units mainly alter their properties as a result of a severe hydrothermal treatment. These changes are translated in a relatively well preserved Brønsted acidity within the lateral sub-units of mildly steamed crystals and the preferential removal of Brønsted acidity in the same crystal regions after severe steaming.

despite the structural modifications taking place in the pyramidal sub-units under severe hydrothermal treatments,²⁴ a fraction of the Brønsted acidity is preserved. In contrast, the regions close to the surface in the lateral sub-units show an overall reduction in Brønsted acidity as compared to the rest of the large ZSM-5 zeolite crystal.

Conclusions

Confocal fluorescence microscopy has been used in combination with three bulky fluorescent dyes and two specific staining reactions yielding fluorescent molecules to investigate the role of the internal architecture of large ZSM-5 zeolite crystals in the physicochemical modifications induced by steaming. The use of bulky fluorescent dyes has disclosed a more significant variation in the structural properties of the lateral crystal sub-units upon steaming compared to that of the pyramidal sub-units. Simultaneously, it has been revealed that the crystal sub-unit boundaries, acting as molecular diffusion barriers, are accessible after steaming, facilitating the diffusion towards the internal crystal regions. The synthesis of fluorescein has been used to visualize the structural modifications that are connected to the surface *via* both a microporous and a mesoporous network. It was found that under mild conditions a considerable amount of “cavities” are generated in the lateral crystal sub-units, being extended to the pyramidal sub-units after steaming under harsher temperature conditions. The above-mentioned findings are schematically illustrated in Fig. 7.

Additionally, the Brønsted acid catalyzed oligomerization of 4-fluorostyrene is a valuable probe reaction to study the distribution and accessibility of the Brønsted acidity within the different parts of large ZSM-5 zeolite crystals. It has been shown how mild steaming conditions increase the accessibility

towards the Brønsted acid sites without causing a redistribution or depletion of this type of acidity. In contrast, under severe steaming conditions the Brønsted acidity contained in the internal crystal sub-units is more accessible, although it is preferentially removed close to the surface of the lateral sub-units of large ZSM-5 zeolite crystals.

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