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# Mono-directional pressure induced downsizing of zeolite crystals increases their catalytic performances<sup>†</sup>

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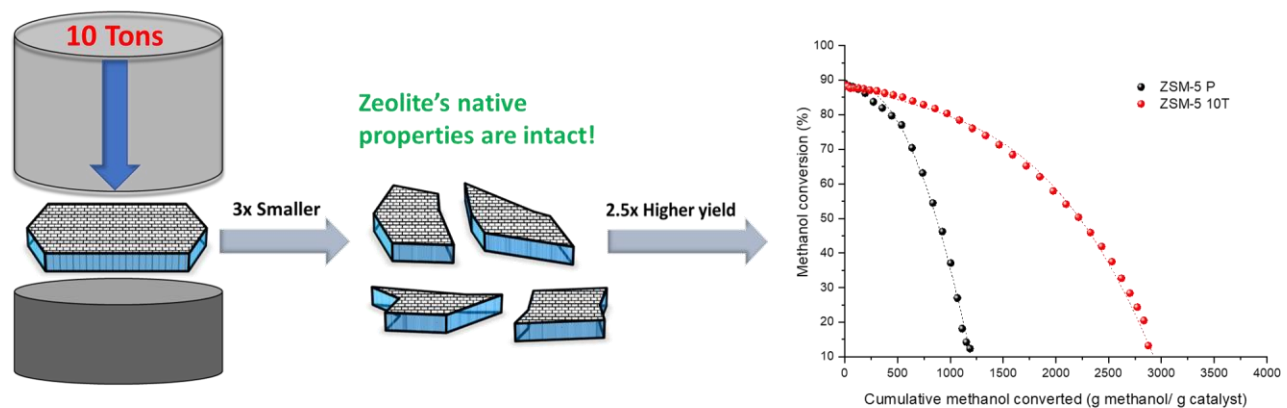
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<sup>†</sup>Electronic Supplementary Information (ESI) available.

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This study introduces a novel non-chemical method for increasing the catalytic activity of zeolites by applying constant mono-directional pressure to downsize crystals, resulting in reduced ZSM-5 crystal size while preserving other parent material properties and exhibiting enhanced catalytic activity in Methanol-to-Olefins, converting 2.5 times more methanol than its parent.



Caption

## Abstract

Zeolite crystals are often subjected to different post-synthetic chemical treatments prior to being used in catalytic or separation processes. We highlight a novel non-chemical post-synthetic approach to overcome diffusion limitations in zeolite catalysts and boost their catalytic activity by applying a constant pressure to downsize micron-sized zeolite crystals to sub-micron-sized particles. The method is highlighted by treating a ZSM-5 with hydraulic pressure. The physicochemical characterization of the resulting material shows a substantial reduction in the size of the crystals without altering their native properties (crystallinity, porosity, acidity). ZSM-5 crystals processed in such a way exhibit improved catalytic activity in the Methanol-to-Olefins (MTO) reaction, where the cumulative amount of methanol converted is two and a half times greater than their parent. This is ascribed to the enhanced molecular diffusion of the pressure-treated crystals, which is supported by breakthrough curve analysis.

# 1 Introduction

Zeolites are inorganic microporous materials with frameworks composed of cages and channels with different dimensions accessible through pore openings of angstrom-sized diameters<sup>1</sup>. The substitution of heteroatoms such as aluminum in their framework leads to forming Brønsted sites generating a solid acid catalyst. The synergy of microporosity and acidity produces superior heterogeneous catalysts for numerous industrial applications<sup>2-4</sup>, particularly in the petrochemical industry where the confined cages and channels are nanoreactors for hydrocarbon upgrading<sup>5,6</sup>. For instance, introducing zeolites into the fluid catalytic cracking (FCC) process in the early 60's dramatically revolutionized oil refining. Compared to other catalysts, such as amorphous silica-alumina and clays, zeolites display higher activity and selectivity towards the gasoline fraction<sup>7,8</sup>.

Despite their remarkable catalytic performance, zeolites can suffer from a short lifetime due to deactivation by the deposition of carbonaceous species, commonly referred to as coke. Its formation is mainly related to the strength and density of the acid sites and the length of the diffusion pathway of the products/reactants through the zeolite microporosity. The conversion of hydrocarbons on acidic zeolites involves intermediates (e.g. carbocations, neutral molecules). Diffusion limitations on intermediates will favor the production of heavier molecules trapped in the micropores and on the external crystal surfaces poisoning active sites and further restricting the diffusion of reactants and products<sup>9,10</sup>.

These challenges inspired the zeolite community to develop various procedures to overcome such diffusion limitations by shortening the reaction pathway to extend the catalyst's lifetime. In-depth reviews of the topic are widely available<sup>11-13</sup>. Synthesizing nano-sized zeolite crystals is the most intuitive approach to extending the zeolite lifetime. Smaller crystals result in shorter diffusion pathways for reactants and products, reducing mass transfer constraints within the micropores. For instance, we previously demonstrated<sup>14</sup> the superior catalytic performance of nanosized-Y zeolite (approximately 10 nm) compared to its commercial counterpart, LZY-62 (crystal size 1-2  $\mu\text{m}$ ), for the de-alkylation of 1,3,5-triisopropyl benzene (TiPBz). Although much progress has been achieved in understanding and controlling the synthesis of

nano-sized zeolites<sup>15</sup>, not all framework types have so far been obtained as nanocrystals.

Post-synthetic treatment of zeolites by chemical etching using steaming, alkaline (desilication), or acidic (dealumination) medium treatment can extend the catalyst's lifetime by shortening the diffusion pathways while generating mesoporosity<sup>16,17</sup>. However, their major drawback is that substantial modifications of other native zeolite properties (especially Si/Al ratio, by biased etching of either Si or Al), make it difficult to assign their improved catalytic performances to a single parameter. Recently, we developed a protocol that involves etching zeolite crystals in a bifluoride medium, leading to the unbiased chemical leaching of both Si and Al atoms from the zeolitic framework<sup>18</sup>. In this case, parent zeolites and their hierarchical derivatives have nearly the same chemical composition allowing an easier understanding of the improved performances.

Mechanical post-synthetic treatment of zeolites by ball milling is often used at laboratory and industrial scale as a green route to modify zeolite properties to enhance their performance. Several reports on the potential of ball milling to downsize crystal size and exfoliate layered zeolites to enhance diffusion properties and catalytic performance are available<sup>19-21</sup>. While zeolite downsizing is achieved, a significant disadvantage is extended amorphization of the treated zeolite leading to a considerable loss of Brønsted acid sites, formation of Lewis acid sites, and a modification of the zeolite crystal morphology.

In a recent study, we investigated the time-resolved dissolution of MFI zeolites in a fluoride medium ( $\text{NH}_4\text{F}$ ) to elucidate their crystallization mechanism<sup>22</sup>. We concluded that the dissolution of the crystals proceeds by an hourglass mechanism where the weakest bonds (under structural stress caused by defects) break first while more stable domains dissolve last. We postulated that applying a non-destructive mechanical force to the zeolite crystals could break them at the defect sites that dissolved first without damaging the more stable zones of the crystals. Such mechanical treatment should lead to the downsizing of zeolite crystals to enhance their diffusion properties and catalytic performances without losing their intrinsic properties, notably the microporosity and acidity. This hypothesis was validated, and a patent was filed earlier where hydraulic pressure was applied to different zeolites (ZSM-22 (TON), Zeolite-Y

(FAU), Mordenite (MOR), Zeolite-A (LTA), and Zeolite-L (LTL)) without modifying the original properties of these materials<sup>23</sup>.

Here we further focus on hydraulic pressure treatments (mono-directional and isostatic hydraulic pressure; in the latter, equal pressure is applied in all directions) of ZSM-5 crystals to increase their catalytic performances by enhancing reactants and products diffusion. The physicochemical properties of parent and hierarchical ZSM-5 derivatives (crystallinity, morphology, microporosity, and acid sites) are investigated, and their catalytic performances are evaluated in the conversion of methanol to olefins (MTO), a reaction where the zeolite catalysts suffer from significant deactivation due to coke deposition. In addition, CO<sub>2</sub> breakthrough curve analysis highlights mechanical treatment's effect on diffusion properties without any chemical transformation.

# Results and Discussion

## Physico-chemical characterization

Figure 1 shows the powder X-ray diffraction (PXRD) patterns of the  $\text{NH}_4$ -ZSM-5 before and after mono-directional hydraulic pressing under 10 tons, referred to as ZSM-5 P and ZSM-5 10T, respectively. The sharp intensity of the peaks and absence of a broad baseline corresponding to amorphization shows that crystallinity is retained in the treated sample. Amorphization is more pronounced when ZSM-5 is treated under isostatic pressure. Figure S1 illustrates the PXRD patterns of  $\text{NH}_4$ -ZSM-5 before and after various isostatic pressing conditions. As pressure increases, a substantial decrease in peak intensities relative to their parent is observed, with a slight broadening of the  $2\theta$  range between 20–25 °C baseline.

The nitrogen adsorption and desorption isotherms of the parent H-ZSM-5 and its 10 T mono-directional derivatives exhibit type I behavior characteristic of microporous materials (Figure S2); their textural properties are summarized in Table 1. The 10 T derivative shows lower nitrogen uptake than its parent, along with a slight decrease in micropore volume. This highlights some amorphization resulting from the pressure treatment, estimated to be 8 wt% based on the decrease of the micropore volume. The parent ZSM-5 shows a hysteresis loop corresponding to textural mesoporosity due to the packing of the crystals. The downsizing of the crystals leads to a slight increase in the textural mesoporosity shown by a higher nitrogen uptake at  $P/P_0 = 0.98$ . ZSM-5 treated with isostatic pressure also exhibits reversible type I isotherms for different applied pressures, albeit with a decrease in the uptake proportional to the value of the applied pressure. The textural characteristics of isostatically pressed ZSM-5 are listed in Table S1. A 9 T isostatic pressure amorphized the ZSM-5 by about 15 wt%, as shown by a decreased micropore volume and a substantial reduction in the BET specific surface area. Mono-directional pressure breaks the crystals along the defect zones with minimal collateral damage to more crystalline domains. On this basis, mono-directional hydraulic pressing under 10 T warrants further spectroscopic characterizations and catalytic testing.

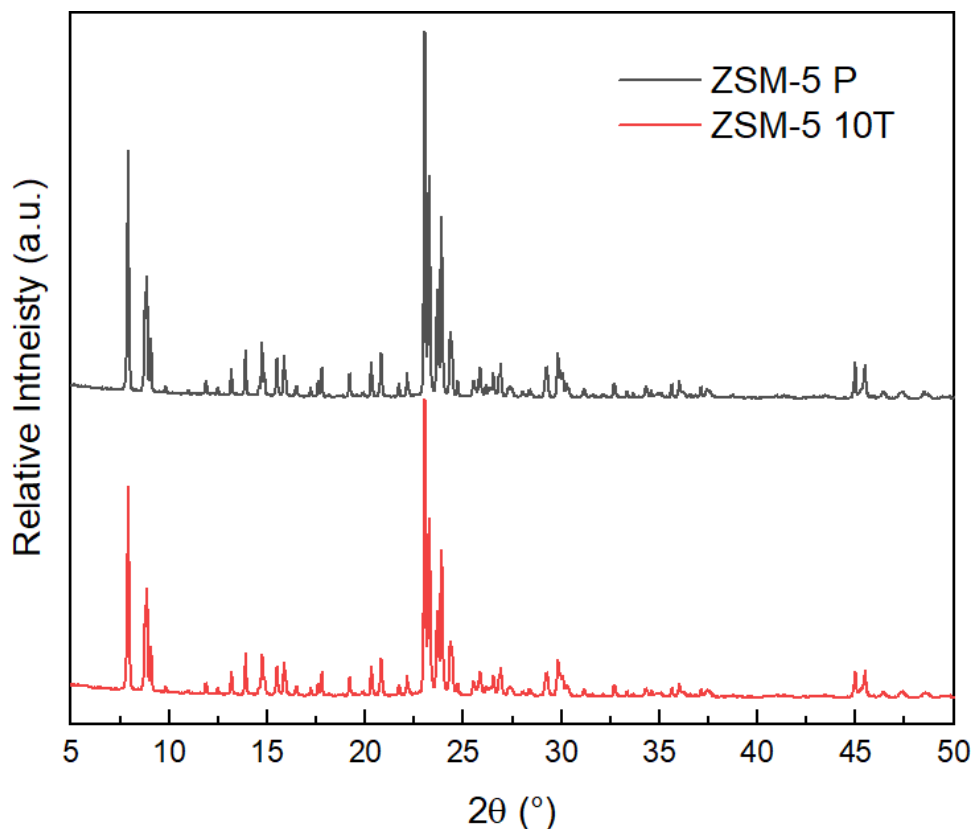


Figure 1: PXRD patterns of  $\text{NH}_4$ -ZSM-5 before and after mono-directional hydraulic press treatment.

Table 1: Textural and acidic properties of H-ZSM-5 before and after mechanical treatment by hydraulic pressure.

Samples	$S_{BET}$ [ $\text{m}^2 \text{g}^{-1}$ ][a]	$V_{micro}$ [ $\text{cm}^3 \text{g}^{-1}$ ][b]	$V_{meso}$ [ $\text{cm}^3 \text{g}^{-1}$ ][c]	Bronsted sites [ $\mu\text{mol g}^{-1}$ ][e]	Lewis sites [ $\mu\text{mol g}^{-1}$ ][e]
ZSM-5 P	416	0.12	0.1	$737 \pm 1$	$17.5 \pm 0.5$
ZSM-5 10T	416	0.12	0.1	$634 \pm 28$	$18 \pm 1$

[a] Apparent surface area calculated using the Roquerol BET criteria. [b] Micropore volume and external surface area are calculated by the t-plot method. [c] Mesopore volume calculated by  $V_{meso} = V_{total} - V_{micro}$ , where  $V_{total}$  is the total pore volume calculated at  $P/P_0 = 0.98$ . [e] Calculated using the molar extinction coefficients  $E_{Bronsted}$  at  $1550 \text{ cm}^{-1} = 1.35 \text{ cm} \mu\text{mol}^{-1}$  and  $E_{Lewis}$  at  $1450 \text{ cm}^{-1} = 1.8 \text{ cm} \mu\text{mol}^{-1}$  [24].



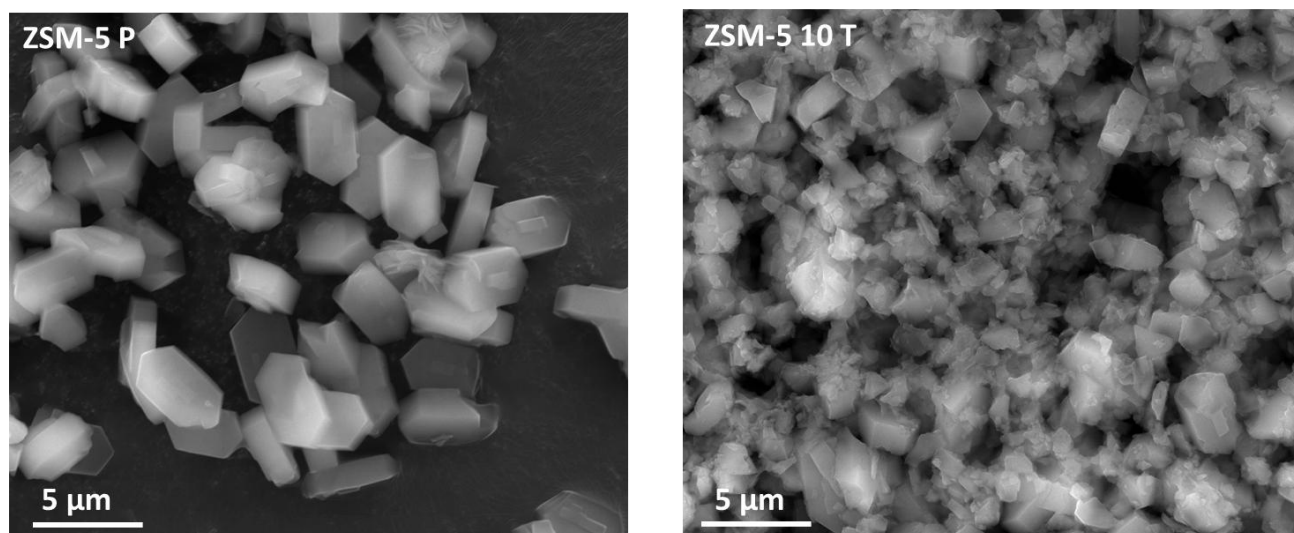


Figure 2: SEM images of the parent and mono-directional hydraulic press treated NH<sub>4</sub>-ZSM-5.

Scanning electron microscopy (SEM) highlights the impact of mono-directional hydraulic pressing on the NH<sub>4</sub>-ZSM-5 crystal size and morphology (Figure 2). The parent shows the classical coffin-shaped morphology of the MFI framework with an average crystal size of around 5  $\mu\text{m}$ . Upon treatment, the crystal size is reduced by nearly a factor of 3 to 1.7  $\mu\text{m}$ . A similar effect has been observed for the treatment of NH<sub>4</sub>-ZSM-5 by the isostatic hydraulic pressure at different values (see Figure S4).

The experimental and deconvoluted <sup>29</sup>Si MAS NMR spectra for the parent and mono-directional pressed material are presented in Figure S5. The parent spectrum agrees well with the published NMR spectra of ZSM-5 with Si/Al = 20<sup>25</sup>. The chemical shift at -106 ppm corresponds to tetrahedral silicon with a single aluminum in its second coordination sphere (Q<sup>4</sup> 1Al). The broad peak combining two chemical shifts at -112 ppm and -116 ppm is attributed to tetrahedral silicon species with all silicon species in their second coordination sphere (Q<sup>4</sup> 0Al). The <sup>29</sup>Si spectra of the mono-directional pressed derivative is similar. The <sup>27</sup>Al NMR spectra, Figure S6, indicate that this treatment does not affect the aluminum coordination in the ZSM-5 framework. Both samples exhibit similar peaks at  $\delta = 56$  ppm (tetrahedral) and  $\delta = 0$  ppm (octahedral)<sup>26</sup>. The relative intensities for the extra-framework aluminum peak are nearly identical, thus, no aluminum is leaving the framework.

In situ infrared spectroscopy demonstrates the impact of the pressure treatment on the hydroxyl

groups of H-ZSM-5. Figure S7A shows the hydroxyl group stretching vibration region after activation under vacuum. The bands observed at ca. 3700 and 3600  $\text{cm}^{-1}$  correspond to internal silanols and Brønsted hydroxyl groups, respectively. The amount of Brønsted and Lewis acid sites is quantified using pyridine as a probe molecule due to its small kinetic diameter (0.53 nm), allowing it to diffuse easily along the 10-membered ring channels. Figure S7B shows the stretching vibration bands of the C–C bond rings of pyridinium ions after desorption at 423 K. The band at 1545  $\text{cm}^{-1}$  corresponds to pyridinium ions bonded to Brønsted acid sites, while the band at 1450  $\text{cm}^{-1}$  is for pyridine adsorbed on Lewis acid sites. The results presented in Table 1 indicate the absence of new extra-framework Al as the Lewis acid site concentrations are similar. The decrease in the concentration of Brønsted acid sites agrees with the small observed amorphization deduced from a decrease in micropore volume.

## Catalytic tests

Zeolite catalysts utilized in the MTO reaction often experience severe deactivation caused by coke deposition. Consequently, we have chosen to examine the effects of monodirectional pressing on the catalytic performance of H-ZSM-5 to highlight its influence. Figure 3A shows the amount of methanol converted as a function of the time on stream for the parent and treated zeolite. During the initial 200 minutes of the reaction, both materials exhibit a constant methanol conversion of approximately 88%. After 200 minutes, both conversions decline linearly with respect to time. However, for the parent material, the conversion declines slightly earlier and more rapidly than on its more hierarchical derivative. After 500 minutes, H-ZSM-5P reaches its half-life at 54% conversion, while H-ZSM-5 10T is still at 71%. The cumulative amount of methanol converted after complete deactivation of the two catalysts is displayed in Figure 3B; the H-ZSM-5 10T is two and a half times higher than that of H-ZSM-5 P at 10% conversion, and the catalyst lifetime is three times higher.

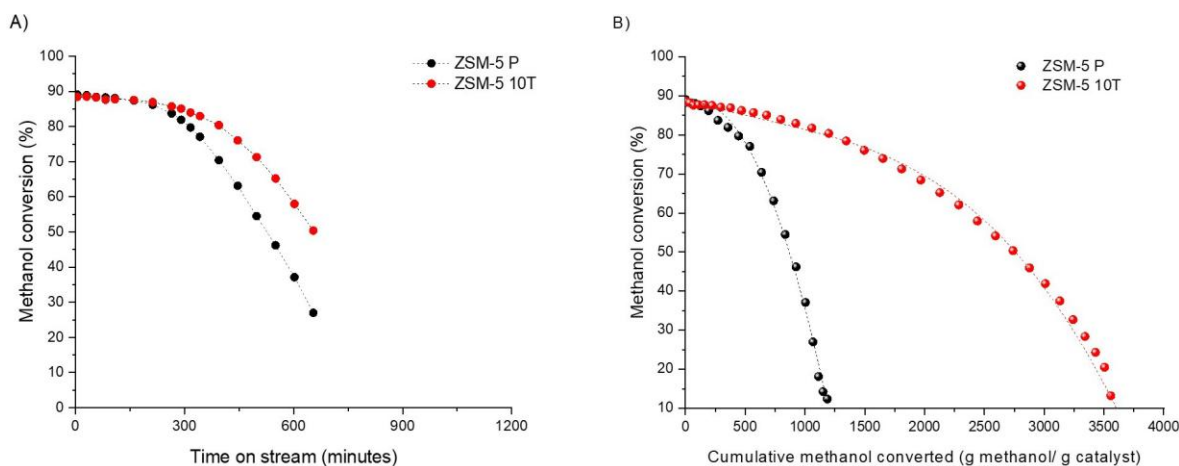


Figure 3: Percent of methanol converted versus: A) time on stream, and B) cumulative methanol converted. To evaluate the total methanol conversion, dimethyl-ether is considered as a product.

## CO<sub>2</sub> breakthrough

To further investigate the effect of downsizing by mono-directional hydraulic pressure on the diffusion properties without any chemical reaction, single-component CO<sub>2</sub> breakthrough curve analysis is performed on Na<sup>+</sup>-exchanged samples of the parent and treated zeolites. CO<sub>2</sub> was chosen as a model molecule due to its relatively small size compared to the pore apertures, and the Na-sodium form of zeolite was used to ensure sufficient interaction between the probe molecule and adsorbent. Adsorption isotherms of CO<sub>2</sub> are measured on both the parent and its derivative at 20 °C revealing similar type I adsorption profiles with near-identical adsorption capacities of 2.86 and 2.79 mmol/g at 0.95 bar (Figure S8)<sup>27,28</sup>.

CO<sub>2</sub> breakthrough curve analysis is performed using a binary mixture of He and CO<sub>2</sub> (95/5 vol%) at 1 bar at 20 °C, He is considered as a non-adsorbing gas (Figure 4). Both the parent and its derivative show relatively sharp CO<sub>2</sub> breakthrough curves and a differential loading of CO<sub>2</sub> of 1.54 and 1.46 mmol/g, respectively. During the adsorption step, the column experienced a minor temperature excursion of < 0.15 °C (Figure S9A). Close inspection of the breakthrough curves (Figure 4 inset) and calculation of the first derivative of the CO<sub>2</sub> breakthrough curve demonstrates that the treated sample exhibits a sharper breakthrough curve than its parent, indicative of more uniform and improved diffusion through the adsorbent bed. This result is

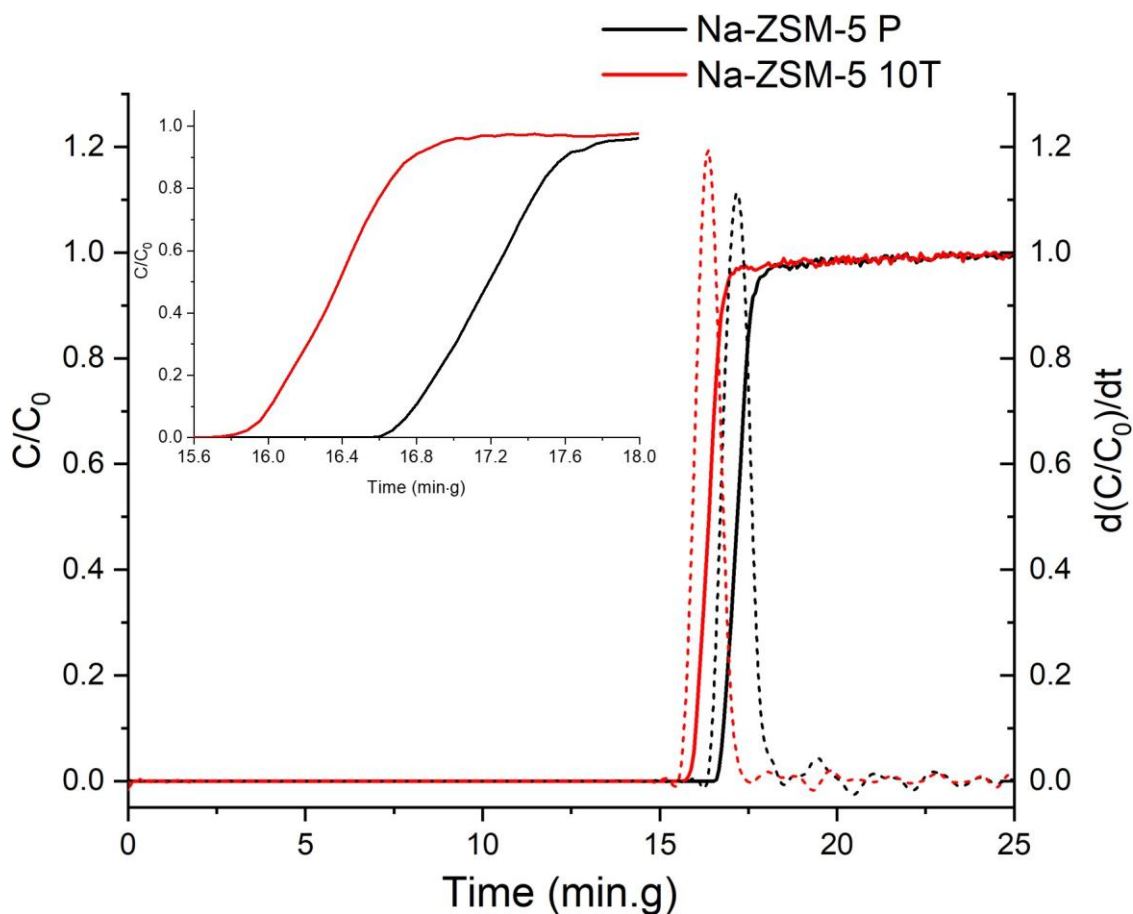


Figure 4: A) CO<sub>2</sub> breakthrough curves (solid lines) and first derivatives (dashed lines) at 20 °C of the Na-ZSM-5 parent and mono-directional pressed samples, obtained from dynamic adsorption experiments, He/CO<sub>2</sub>, 95/5. Inset of the breakthrough curves to highlight the difference in the slope of the curves.

consistent with the catalytic data, which shows that the enhanced lifetime of the treated ZSM-5 10T compared to the parent ZSM-5 P is due to enhanced diffusion kinetics of molecules along the ZSM-5 crystals; hence, the treated sample is more efficient than its parent.

## Discussion

Physicochemical characterizations and catalytic test provide strong evidence of the positive impact of mono-directional pressure treatment on zeolites. Such a mechanical treatment at 10 tons (4.87 MPa/mg of zeolite) is benign to the native properties of the parent zeolite, whereas

the structural damage from isostatic pressure under much milder conditions (0.086 MPa/mg) is dramatic. This can be attributed to mono-directional pressure applying mechanical force in a particular crystallographic direction, allowing it to attack the most fragile and defective sites of the crystals, ultimately leading to breakage. Conversely, even when a significantly lower pressure (0.086 MPa/mg) is applied to the crystals in all directions, the breaking is not crystallographically guided and, thus, no longer restricted to the weak points. The net result of iso-directional pressure damages a more substantial part of the crystal. This further explains why the mechanical treatment of zeolites by ball milling is significantly damaging. Ball milling is iso-directional under a more intense power and significant heat generation, thus severely destroying the zeolite's framework. Our findings suggest that mono-directional pressuring is an effective and controlled approach to downsizing zeolite crystals, a top-down approach applicable to any zeolite or related materials.

NMR and IR results are in good agreement. From the  $^{29}\text{Si}$  MAS NMR spectra, no changes occur to the Si environment except for a tiny band at  $-100.5$  ppm corresponding to a minor amount of silanols generated. The in situ infrared spectra of the hydroxyl group stretching vibration region further confirm the benign influence of the pressure treatment on the native properties of the zeolite since there was no change in the band corresponding to the internal silanols at around  $3700\text{ cm}^{-1}$ ; this preservation of the density of silanols results from a clean downsizing of the crystals by a factor of three, keeping the crystals still in the micron-size domain. Despite a minor amorphization (ca. 8%), both  $^{27}\text{Al}$  NMR and pyridine adsorption experiments show that the amounts of Lewis acid sites are similar. Therefore, aluminum species are stable under the applied pressure and will not move to extra-framework positions.

The methanol conversion as a function of time on stream shows that the treated zeolite has an improved lifetime compared to its parent. Our previous work<sup>29</sup> showed that smaller zeolite crystal size increases the catalyst lifetime by forming coke more on the external or mesoporous surface, reducing its toxicity and leaving more active sites accessible in the microporosity. A bonus of locating coke preferentially on the external/mesoporous zeolite surface is easier regeneration by its combustion as it is more accessible to the oxygen co-reactant. The enhanced

diffusion properties of the mono-directional pressure-treated zeolite are supported by CO<sub>2</sub> breakthrough curve analysis. The sharper CO<sub>2</sub> breakthrough curve of the treated sample is indicative of improved mass transfer kinetics relative to the untreated sample. This further supports the enhanced molecular traffic within the zeolite micropores and improved catalytic performance.

## Conclusion

We report here a novel mechanical post-synthetic treatment method to enhance the diffusion properties of zeolitic material, namely mono-directional hydraulic pressing. We demonstrate this concept on micron-sized ZSM-5 crystals. It successfully downsizes zeolite crystals by a factor of three without altering the native properties of the parent material. The zeolite treated by hydraulic pressure shows enhanced diffusion properties leading to an extended lifetime and higher conversion of methanol during the MTO reaction. Such behavior is typically a crystal-size effect on the secondary reaction, here, coking. The enhanced diffusion properties of the pressure-treated sample are supported by CO<sub>2</sub> breakthrough curve analysis showing a sharper breakthrough curve for the treated sample. Mono-directional hydraulic pressing is the first example of a cost-effective, chemical and heating-free post-synthetic treatment that meets the ongoing demand for more economical and ecological technologies to increase the performance of zeolitic materials. Mono-directional pressure-induced downsizing of zeolites is rapid and does not require sophisticated equipment.

## Acknowledgments

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## Conflict of Interest

The authors declare no conflict of interest.

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