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Zhengxing Qin, Ludovic Pinard, Mohammed Amine Benghalem, T. Jean Daou, Georgian Melinte, et al.. Preparation of Single-Crystal “House-of-Cards”-like ZSM-5 and Their Performance in Ethanol-to-Hydrocarbon Conversion. *Chemistry of Materials*, 2019, 31 (13), pp.4639-4648. 10.1021/acs.chemmater.8b04970 . hal-03033911

HAL Id: hal-03033911

<https://normandie-univ.hal.science/hal-03033911>

Submitted on 1 Dec 2020

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1 Preparation of Single Crystals “House-of-Cards”-
2 like ZSM-5 and Their Performance in Ethanol-to-
3 Hydrocarbons Conversion

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1 **ABSTRACT**

2 The present study reports the unbiased chemical etching of micron-sized ZSM-5 crystals with an
3 NH_4F solution resulting in house-of-cards-like single crystals containing large rectangular
4 cavities surrounded by thin (15 – 30 nm), flat and highly crystalline walls. The formation of such
5 house-of-cards-like architecture is a result of the preferential extraction of mis-oriented
6 nanocrystalline domains followed by the uniform dissolution of the remaining part of the crystal.
7 The characteristic features of NH_4F -treated zeolites are the retention of framework composition
8 (Si/Al) and Brønsted acidity, high crystallinity, a moderate increase in external surface area and
9 increased accessibility to their active sites. Such a combination produces zeolitic catalysts with
10 superior performances (activity, stability and coke resistance) in the ethanol-to-hydrocarbons
11 conversion. The physicochemical properties of this newly engineered zeolite are compared with
12 a hierarchical zeolite obtained by caustic leaching and zeolite nano-sheets synthesized with a
13 bifunctional template, a di-quaternary ammonium-type surfactant.

14

1 **1. Introduction**

2 Zeolites revolutionized oil refining and petrochemistry due to their excellent chemical and
3 (hydro)thermal stability, unique microporous structures of molecular dimensions and tunable
4 acidity located in a shape-selective environment [1-3]. With an increasing demand for highly
5 active and stable catalysts for existing and emerging processes, recent work with zeolites focused
6 on morphology tailoring either during their synthesis (bottom-up approach) or by post-synthesis
7 modifications (top-down approach), the so-called zeolite crystal engineering [4-8].

8 Transport limitations in their micropore channels are probably the most serious drawback of
9 zeolite catalysts [9]. Decreasing zeolite crystal size is a straightforward approach to minimize
10 their impact. Advances in the understanding of zeolite nucleation/crystal growth allowed the
11 preparation of nanocrystals of many industrially important zeolites [10, 11]. However, the
12 number of zeolite crystals synthesized with nanosized dimensions is still limited. Zeolite
13 materials with nano-dimensions in a particular crystallographic direction were also prepared
14 [12]. These two-dimensional microporous materials, referred to as layered- or sheet-like zeolites,
15 offer the advantage of extended external surface areas and enhanced diffusion in a particular
16 crystallographic direction. They were prepared, for instance, by Corma and co-workers by
17 exfoliating layered MWW-type zeolite precursors [13]. The exfoliation approach is however
18 limited to a few zeolites since it works with layered precursors with weaker bonds in a particular
19 crystal direction. Ryoo *et al.* successfully synthesized a series of crystalline molecular sieves
20 (ZSM-5 and zeolite Beta) with tunable mesostructures and nanosheet or nanosponge
21 morphologies using amphiphilic organosilanes or multi-quaternary ammonium surfactants as
22 bifunctional templates [14-16]. A low-cost approach to zeolite nanosheets forming “house-of-
23 cards” structures was reported by Tsapatsis *et al.* [17]. They used a template promoting the

1 repetitive branching of orthogonally connected nanosheets. Such intergrowths generate structures
2 with a mesoporous network of 2-7 nm. The resulting polycrystalline hierarchical materials offer
3 the advantages of higher accessibility for bulky molecules, shorter diffusion pathlengths in the
4 microporosity and a larger external surface area. At present such advanced materials were only
5 obtained by a bottom-up approach. To the best of our knowledge, the preparation of house-of-
6 cards by a top-down approach has not yet been reported. A post-synthesis approach to house-of-
7 cards zeolites would provide significant advantages such as i) applicability to a large number of
8 zeolites; ii) easy transformation of single crystals in house-of-cards materials; iii) cost and
9 environmentally benign scaling-up to produce zeolites.

10 Extraction of framework cations by chemical etching has been used since the first commercial
11 applications of zeolites (*eg.* hydrocracking, fluid catalytic cracking [FCC], isomerization...) to
12 alleviate these ever-present mass transport limitations. For instance, high-temperature (> 600°C)
13 steaming extracts aluminum from zeolite frameworks and redistributes it in extra-framework
14 positions; while the overall Si/Al is unchanged, the framework Si/Al increases and
15 rearrangement of framework Si generates a secondary mesoporosity [18]. Recently, caustic
16 leaching [19-20] was extensively revisited, better understood and shown to generate secondary
17 mesopores in high silica zeolites [21]. Chemical etching is an efficient and straightforward
18 method to improve intra-crystalline transport and reduce diffusion barriers. However, the
19 preferential or biased extraction of a particular framework cation (Al or Si) leads to a dissolution
20 profile, strongly dependent on the zeolite composition and therefore difficult to control.
21 Recently, an unbiased chemical etching was developed using NH₄F solutions [22-26].
22 Concentrated ammonium fluoride solutions were shown to dissolve Si and Al from zeolite
23 frameworks at equal rates. While leaving the zeolite composition (Si/Al) unchanged, this

1 approach dissolves preferentially defects in zeolite crystals, such as interfaces between twin
2 crystals, grain boundaries, lattice defects... This unbiased fluoride extraction is HF-free;
3 moreover, the biased $(\text{NH}_4)_2\text{SiF}_6$ processing of zeolites is currently used in the commercial
4 production of modified (dealumination and subsequent healing by silication) FAU zeolites (LZ-
5 210 from UOP LLC. [27-28])

6 The objective of the present work is to develop a universal top-down approach to produce
7 single crystals house-of-cards-like zeolite catalysts. It is based on the recently discovered mosaic
8 structure of zeolite crystals, *i.e.*, the presence of rectangular nanocrystalline domains with well-
9 defined grain boundaries [24]. Such domains were observed in MFI [24], FER [29], FAU [30],
10 and appear to be ubiquitous. They are preferentially dissolved when an unbiased chemical
11 etching is applied to zeolite crystals, leaving behind rectangular cavities several tens of
12 nanometers wide. The remaining part of the crystals dissolves with a similar rate of dissolution
13 following the morphology of extracted nanocrystalline domains, which is employed in the
14 present study to form a house-of-cards-like material by post-synthesis etching. This is illustrated
15 by comparing the unbiased NH_4F etching of a parent (Z_P) ZSM-5 zeolite, Z_F , a Si biased caustic
16 leaching of the same parent, Z_B [31], and zeolite nano-sheets (Z_{NS}) prepared with a di-quaternary
17 ammonium-type surfactant acting as a bifunctional structure directing agent [32]. The Ethanol-
18 to-hydrocarbons (ETH) conversion was used as a model reaction to evaluate the catalytic
19 potential of these zeolites and relate it to their physicochemical properties.

20 **2. Results and discussion**

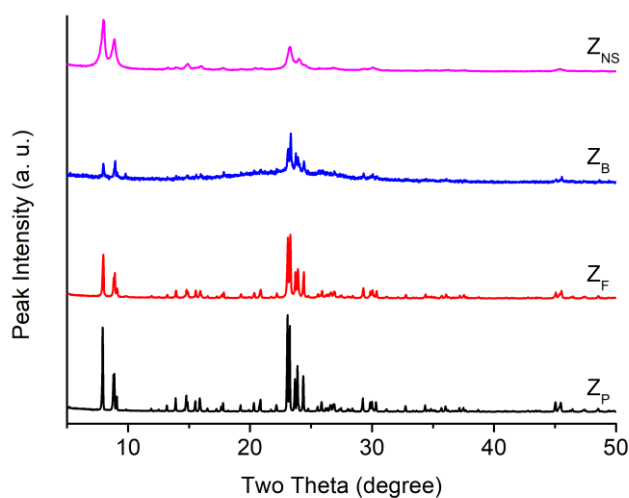
21 **2.1 Physicochemical characteristics of the zeolites**

22 **2.1.1 XRD**

1 The samples preparation is provided in the supporting information. The XRD patterns of Z_P
2 (commercially available zeolite ZSM-5, the parent), Z_B (a biased caustic etching of Z_P), Z_F (an
3 unbiased NH_4F etched derivative), and Z_{NS} (a bottom-up ZSM-5 nanosheets preparation) are
4 displayed in Figure 1. Z_P shows sharp and narrow peaks characteristic of a highly crystalline
5 micron-sized MFI-type material. The XRD peaks of Z_F are equally narrow and well-defined,
6 indicating that the NH_4F etching does not impact crystallinity. Z_B shows much lower peak
7 intensities than its parent. Some of the peaks are missing in the XRD pattern of Z_{NS} , as expected
8 for such type of material [32].

9

10



14

15 **Figure 1** The XRD patterns of the parent zeolite (Z_P), its NH_4F (Z_F) and caustic (Z_B) etched
16 derivatives, and a nano-sheet zeolite (Z_{NS}).

17 2.1.2 N_2 Physisorption

18 The physicochemical properties of all zeolites are summarized in Table 1. The parent micron-
19 sized (Z_P) crystals display a type I isotherm (Figure S1) characteristic of a purely microporous
20 zeolite [33]. Z_F and Z_B zeolites exhibit a second uptake and a hysteresis loop at high relative

1 pressure revealing the presence of mesopores. The micropore volume of Z_F is fully retained
2 compared to its parent and its external surface area is lower than its caustic leached counterpart,
3 Z_B ; Z_B has however lost some of its micropore volume, in agreement with the XRD data. The
4 zeolite nano-sheets, Z_{NS} , display a Type I isotherm at low p/p^0 combined with a type IV(a) at
5 high p/p^0 . The presence of a hysteresis loop in the relative pressure range $0.4 < p/p^0 < 1$ is typical
6 for such lamellar materials due to the stacking of nanosheets. Z_{NS} also exhibits a lower
7 micropore volume and larger external surface area. The mesopores distribution for all samples is
8 presented in Figure 2. No mesopores are observed in the parent micron-sized crystals, Z_P . Z_F
9 exhibits a large pore size distribution between *ca* 10 nm and more than 100 nm. The Z_B pore size
10 distribution is also large, but within the mesopore range, *i.e.*, 2 to 50 nm [33]. The pore size
11 distribution of Z_{NS} , with a maximum of around 6 nm, is much sharper compared with Z_B and Z_F .
12 All three hierarchical zeolites have a mesopore volume higher than $0.3 \text{ cm}^3 \text{ g}^{-1}$ (Table 1).
13 However, Z_F shows only a slight increase in external surface area compared to its parent.
14 Conversely, Z_B and Z_{NS} both develop external surfaces exceeding $200 \text{ m}^2 \text{ g}^{-1}$. We attribute these
15 differences to the types of pores formed by NH_4F and caustic leaching and the stacking of
16 nanosheets, respectively. The dissolution in fluoride medium results in the formation of large
17 meso- and macropores (Figure 2), which exhibit low specific surface area (Table 1). This can be
18 further interpreted based on a rough estimation of the relation between the surface (S), the pore
19 diameter (d) and the pore volume (V) using $d = 4V/S$. In contrast, both Z_B and Z_{NS} contain a
20 substantial amount of small mesopores with size below 10 nm (Figure 2). Accordingly, a
21 substantial increase in the external surface area is observed (Table 1).

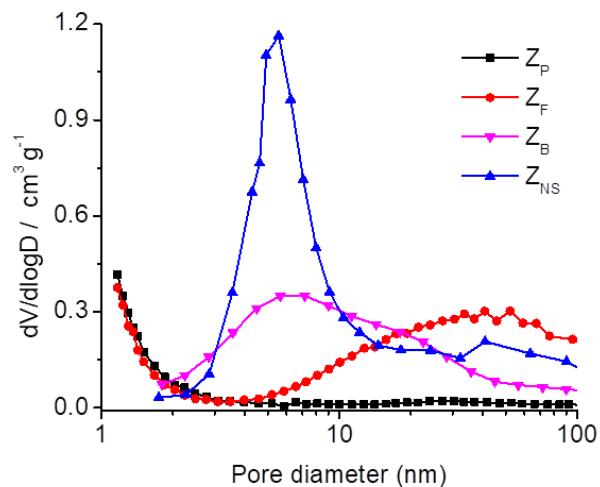
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1 **Table 1.** Physicochemical characteristics of the series of ZSM-5 samples.
 2

Samples	Si/Al ^a	S _{BET} ^b	S _{ext} ^c	V _{mic} ^c	V _{meso} ^d	B _{Py} ^e	L _{Py} ^e
		m ² g ⁻¹	m ² g ⁻¹	cm ³ g ⁻¹	cm ³ g ⁻¹	μmol g ⁻¹	μmol g ⁻¹
Z _P	21	377	9	0.18	0.02	617	91
Z _F	22	395	54	0.17	0.31	582	51
Z _B	9	494	206	0.13	0.36	495	282
Z _{NS}	37	504	266	0.11	0.40	162	98

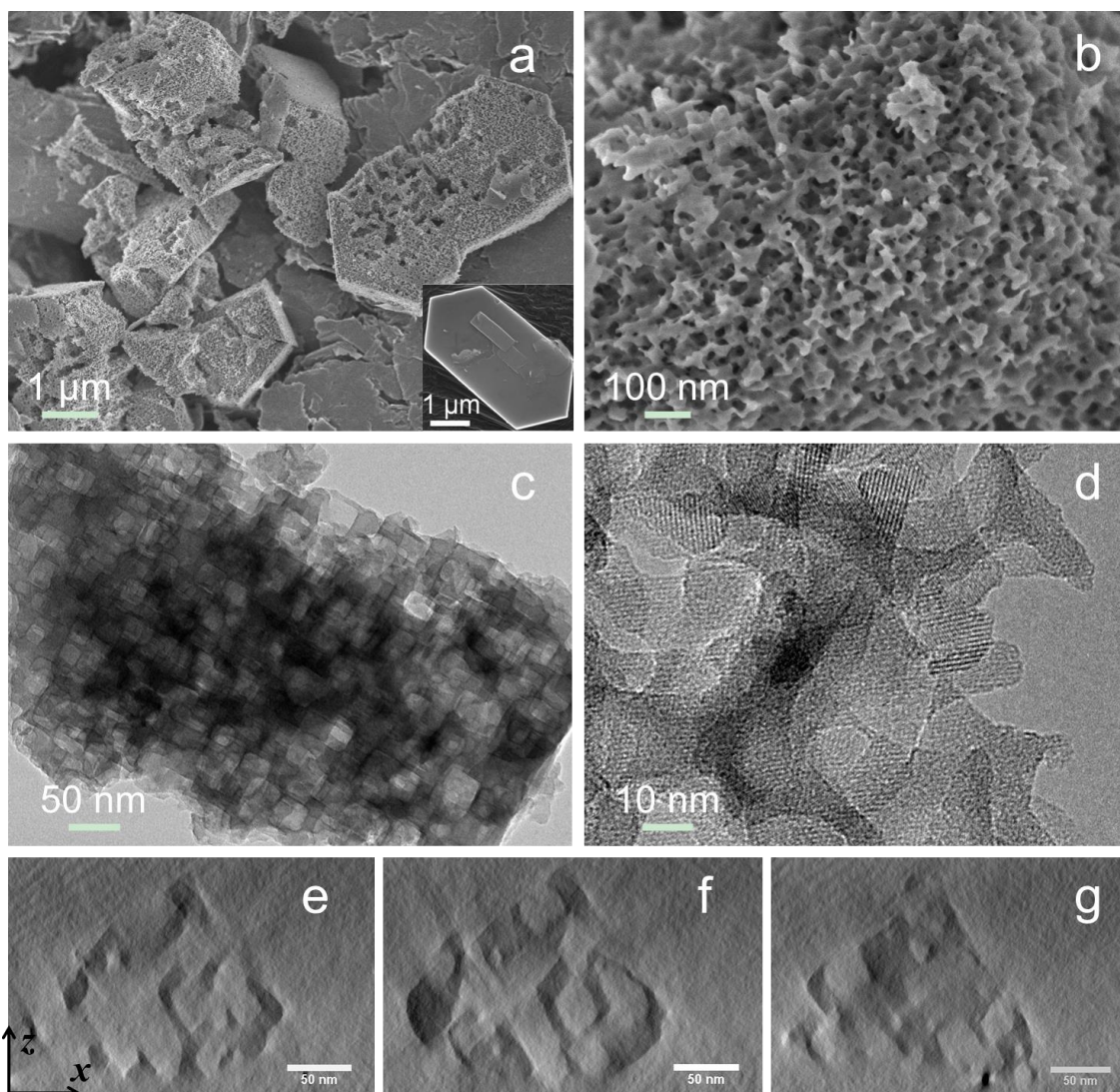
3 ^aICP. ^bBET surface area. ^c*t*-plot. ^dV_{meso} = V_{total} - V_{mic} (V_{total}: the volume absorbed at p/p⁰ =
 4 0.99). ^eThe Brønsted (B_{Py}) and Lewis (L_{Py}) acidity were determined by IR analysis of pyridine
 5 sorption.



6
 7 **Figure 2.** BJH pore size distribution of the parent zeolite (Z_P), its NH₄F (Z_F) and caustic (Z_B)
 8 etched derivatives and the nano-sheet zeolite (Z_{NS}).

9 **2.1.3 Morphological analysis**

1 The morphology and secondary porosity of the zeolites are described by combining scanning
2 (SEM) and transmission electron microscopy (TEM). NH_4F etching transforms the micron-sized
3 ZSM-5 crystals (Figure 3a, insert) into a foam-like material with thin crystalline walls (Figure
4 3a, b). The macro-morphological features of the crystals are retained. However, the crystalline
5 body is fully transformed into a mosaic of rectangular cavities, large enough to be observed with
6 a scanning electron microscope (Figure 3a, b). TEM provides further insights into the structure
7 and morphology of the NH_4F etched zeolite. Figure 3c shows a representative TEM image of
8 such an NH_4F etched ZSM-5 crystal. Figure 3e-g show slices through the electron tomography
9 reconstruction of a selected zeolite grain. The slices highlight the high porosity of chemically
10 treated zeolite but also the remained crystalline pore walls (Figure 3d) with a thickness ranging
11 from 10 to 30 nm. The tomography shows that the NH_4F etched zeolite contains two types of
12 secondary pores: i) large interconnected rectangular-shaped, ii) smaller ones probably formed
13 later on during the etching. 3D models indicate that even the vast majority of the smaller
14 mesopores are connected to the secondary porous network, indicating that pore connectivity
15 approaches 100 % and an overall meso-macroporosity of around 47%. This excellent
16 connectivity between the various pore networks is an important, albeit often overlooked, feature
17 in hierarchical zeolites [34]. The porosity could even be higher as some of the surface pores
18 (Figure S2) were excluded from the quantification. The 3D geometry of the porous network and
19 their walls resemble the “house-of-cards” architecture. A schematic presentation of the
20 remaining part of the crystals with the vast system of rectangular, interconnected cavities is
21 presented in Figure S3. It is remarkable that such a significant secondary porosity increase in Z_F
22 is achieved without loss of intrinsic microporosity and acidity (Table 1) as well as crystallinity
23 (Figure 1, Figure 3d).



1
 2 **Figure 3.** Low (a) and high (b) resolution SEM images of Z_F sample. Representative low (c) and
 3 high (d) resolution TEM images of Z_F . TEM tomography slices in zx direction (e, f, g).

4
 5 Zeolite dissolution process is strongly influenced by the zeolite framework composition and
 6 crystal zoning in the case of selective chemical extraction of a framework cation [35–37]. The
 7 NH_4F did not show any sensibility to the framework ratio, including in the case of very low silica

1 zeolites [25, 26]. Indeed the Z_F sample shows a Si/Al ratio very similar to its parent (**Table 1**).

2 For this reason, we consider that the exceptional resistance of the periferic parts of the crystals to

3 the NH₄F etching (Figure 3a, Figure S4, S5) is an important observation. In order to get a deeper

4 insight into this peculiar “selected-area” dissolution behavior, a comparative study was

5 conducted by combined use of high and low voltage SEM. The electron beam penetrates deep

6 into the sample at high accelerating voltage. Accordingly, the signal will carry information from

7 deeper layers of the sample. In contrast, low voltage high resolution SEM provides only the

8 surface information thanks to the much lower landing voltage [38]. Therefore, as the intensity of

9 the generated secondary electrons varies depending on the magnitude of the accelerating voltage,

10 variations in the roughness of specimen surface and the density of the substance can be detected.

11 As can be seen in Figure S6, the crystal surface of Z_P shows a uniform contrast under both high

12 and low voltage observation models. The 5 min NH₄F-treated sample also shows a uniform

13 contrast under the low voltage observation model (Figure S7a). In the case of the high voltage

14 model, however, obvious dark areas occur on the *b* crystal face of the NH₄F-treated sample

15 (Figure S7b). This contrast difference is not related to crystal surface etching (i.e. surface

16 roughness), since only a few seperated holes can be observed on the *b* crystal face (**Figure S8e**).

17 This crystal surface still shows a similar smouth morphology as the untreated sample, with the

18 growth steps clearly distinguishable (Figure S8b, e). In addition, the difference in surface

19 contrast is not an individual but a general phenomenon, as a similar inhomegeneous distribution

20 of the phase contrast was also observed in case of the 10 and 20 min NH₄F-treated samples

21 (Figure S9). The surface contrast is not so different in the case of the longer time (i.e. 30 and 60

22 min) treated samples (Figure S10). In the later case the original crystal surface are either deeply

1 etched, or detached as a result of the substantial dissolution of the inner part of zeolite crystals
2 (Figure S11).

3 Based on these intensive SEM observations, we attribute the difference in surface contrast to
4 the difference in density in different parts of zeolite crystals. Namely, the dissolution of zeolite
5 crystals in NH_4F solution is spatially inhomogeneous in the macro sense. In general, the inner
6 part of zeolite crystals are preferentially dissolved. The gravimetric measurement of the weight
7 loss of zeolite with the extension of NH_4F etching was also conducted (Figure S12). The
8 continuous decrease of the slope of the weight loss curve shows unambiguously that the
9 dissolution of the Z_P crystals is relatively faster at the initial stage and the dissolution rate slows
10 down with increasing etching time (Figure S12). We further attribute the faster dissolution of the
11 inner part to the fast growth rate at the early stage of crystal growth, and the slower dissolution
12 of the crystal periphery to the slow growth rate at the end of the crystallization process where a
13 few defects are formed. Thus the defect-poor parts of the crystals are resistant to the etching.
14 This result is additional evidence showing that the dissolution starts preferentially from
15 framework defects when unbiased etching solution is used.

16 The relation between the crystallographic structure of the zeolite crystals and the etching
17 direction shown in Figure S4 is confirmed by the high-resolution analysis of some similar grains.
18 Figure S13 shows a typical high-resolution TEM image and the corresponding FFT pattern
19 which illustrate that the preferentially etched facets are on $\{010\}$ face, as revealed also by the
20 low-magnification TEM images of the various analyzed zeolite crystals. It should be underlined
21 that the empty cages resulting from the crystal dissolution are oriented along the crystallographic
22 axes. This is a proof for the connection between the growing process and dissolution behaviour

1 of the crystals. The high-resolution image shown in Figure S14 also sustains this important
2 finding.

3 We attribute both the spatially inhomogeneous dissolution and the facet-dependent etching
4 behavior to the growth mechanism. The fluoride etching is sensitive solely to the zones of
5 structural stress and defect concentration (Figure S8d) which are more vulnerable to chemical
6 attack [24, 39, 40]. Thus the dissolution reflects the particularities of the growth process. Layer
7 type growth is characteristic of most of the zeolitic materials [41–44]. The detailed mechanism
8 of MFI growth was revealed recently by in situ AFM microscopy [43]. It was observed that the
9 MFI growth involves two simultaneous phenomenon - oriented attachment of nanoparticle and
10 mono- or low-weight silica species. The nanodomains integrated into the growing crystal contain
11 well defined grain boundaries and thus are rapidly dissolved by NH_4F etching (Figure S8c, f),
12 leaving behind rectangular cages [24]. These rectangular cages are surrounded by crystalline
13 material, which is a result of the uniform growth by means of low weight silica species. The rate
14 of dissolution of this more stable and uniform part of the crystal is lower (Figure S12). Judging
15 by the straight and flat crystalline walls surrounding the cages the dissolution can be described as
16 “layer-by-layer” process. The results of the present study show that the mechanism of dissolution
17 does not change with the time of treatment and thus a house-of-cards-like material can be
18 synthesized. A fundamental feature of this material is that each “house-of-cards” is a single
19 crystal thanks to the preferential removal of defect-rich zones (Figure 3c). Electron diffraction is
20 a very appropriate technique for the assessment of the crystallinity of various types of specimens
21 at the nanometer level. As shown in Figure S15, the ZSM-5 grains give rise to a unique set of
22 well-defined diffraction spots, allowing us to assign to these crystals a single crystalline
23 structure. In contrast to the interpenetrated “house-of-cards” with myriad intergrown plane

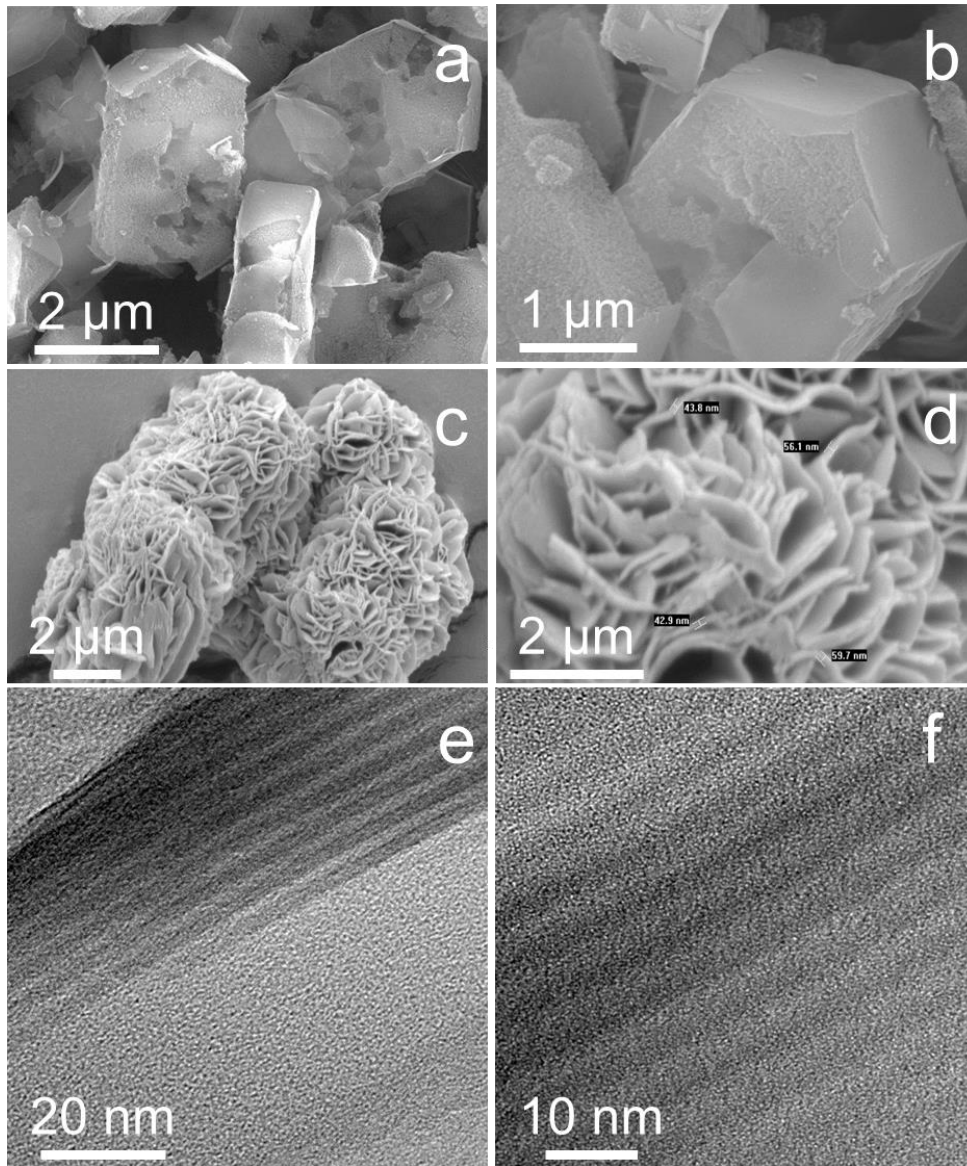
1 prepared by a bottom-up approach, the single crystal house-of-cards-like material reported here
2 offers highly crystalline with a few frameworks defects left.

3 In order to shed light in the dissolution process and the general applicability of the method, we
4 have employed a series of industrial ZSM-5 sample (see Supporting information). These samples
5 exhibit different morphology and particle size (Figure S16), Si/Al ratio (Table S1) and level of
6 aggregation. The samples were NH_4F etched under similar conditions as the time of treatment
7 was varied between 5 and 50 min. The product yield plotted against the etching time is presented
8 in Figure S12. As can be seen, the dissolution rate depends on the crystal size, the larger the
9 crystal size, the lower the dissolution rate is. We relate this result with the accomplishment of
10 the growth process. As discussed, the well shaped crystals with terminated crystal faces show
11 higher resistnace to the NH_4F etching. On the other side, all the trend lines show an initially
12 faster dissolution rate and then converge, with an apparently lower dissolution rate, to a similar
13 product yield value under the applied experimental conditions. This result shows that no matter
14 of basic zeolite crystal characteristics, the mechanism of dissolution is identical and the final
15 product is similar (Figure 3, Figure S17).

16 The silicon selective alkaline etching also leads to a hierarchical zeolite, Z_B (Figure 4a, b). It is
17 a highly porous material with large variation of mesopore size and pore distribution [31, 35].
18 Similarly to NH_4F etching, the crystal morphology is retained (Figure 4a). However, a closer
19 look reveals a grain-like morphology (Figure 4b), the result of preferential Si extraction and re-
20 deposition of most of the extracted Al on the etched surface. Such a biased Si etching changes
21 the zeolite framework composition and acidity (Table 1).

1 Z_{NS} displays a flower-like morphology composed of interpenetrating plate-like nanosheets
2 (Figure 4c, d). The overall thickness of the lamellar stacking of nanosheets is 20–60 nm (Figure
3 4e). TEM reveals that the stacking “plate” is composed of alternating 2 nm-thick aluminosilicate
4 nanosheets and 2.8 nm micellar layers (Figure 4f). This well-defined mesoporosity is inherently
5 related to the properties of the structure-directing agent used.

6



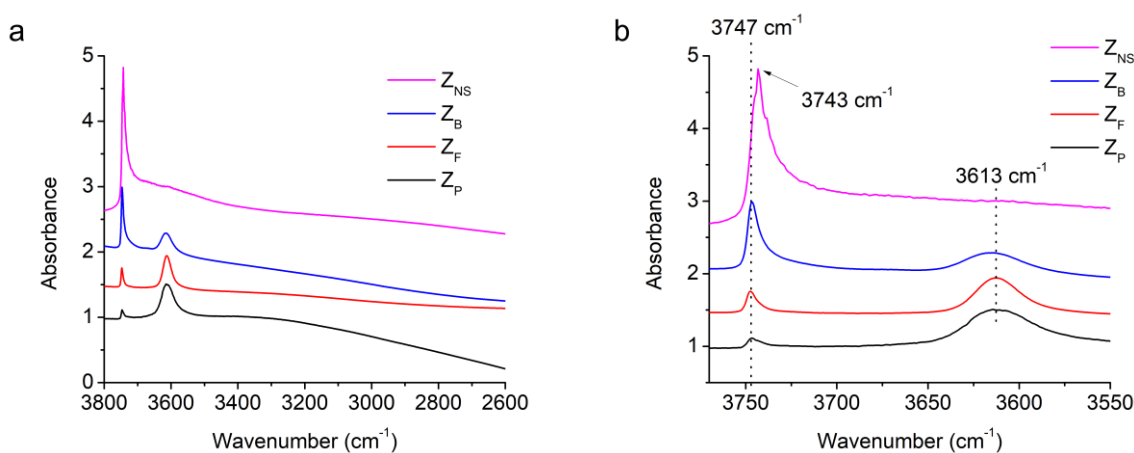
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Figure 4. Low (a) and high (b) magnification of SEM micrographs of caustic etched ZSM-5 crystals, Z_B . Low (c) and high (d) magnification images of ZSM-5 nanosheets (Z_{NS}) prepared by a bottom-up approach. TEM images representing the overall thickness of zeolite lamellas (e) and high-resolution micrograph of ZSM-5 nanosheets building the nanosheet sample (f).

2.1.4 IR spectroscopy

Chemical analysis of Z_P and Z_{NS} indicates Si/Al ratios of 21 and 37, respectively. A negligible change in the Si/Al ratio after NH_4F etching is observed, while caustic etching produces a material with a Si/Al ratio of 9 (Table 1). These results are expected for unbiased (NH_4F) and biased (NaOH) etchings, respectively [23]. IR spectroscopy of adsorbed pyridine highlights further these conclusions as Z_B has a lower concentration of Brønsted acid sites and a substantial increase of Lewis acid sites compared to its parent Z_P and its NH_4F etched derivative Z_F (Table 1). Z_F Brønsted acidity does not change significantly, as expected. Z_{NS} has a lower Brønsted acid sites concentration, due to a higher Si/Al ratio and the presence of numerous silanols, *vide-infra* [44]. The pristine surface of all samples can also be probed by FTIR spectroscopy, namely their $\nu_{(OH)}$ region where isolated silanols (3747 cm^{-1}) located on the external surface and bridged hydroxyls, *i.e.* Brønsted acid sites (3613 cm^{-1}) are clearly observed (Figure 5). Z_P shows such bands and a broad absorption extending from 3500 to 3000 cm^{-1} (Figure 5a), ascribed to H-bonded internal silanol nests [45]. The Z_F spectra does not show such a broad band, and the baseline is almost flat, indicating that a substantial part of the silanols is eliminated during NH_4F etching. Again, this is the result of a preferential dissolution of highly defective zones in the crystals, a typical characteristic of NH_4F etching [24, 40]. In Z_F , the intensity of the 3747 cm^{-1}

1 band increases compared to its parent Z_P , indicative of an increased external surface area (Table
2 1). For Z_B , the intensity of the 3747 cm^{-1} band further increases while 3613 cm^{-1} band decreases
3 noticeably. The IR spectra of Z_{NS} is dominated by external surface silanols at 3743 cm^{-1} (Figure
4 5a) while a very small amount of Brønsted acid sites is detected (Figure 5b).



5
6 **Figure 5.** IR spectra of Z_P , Z_F , Z_B , and Z_{NS} in the $2600\text{-}3800\text{ cm}^{-1}$ ν_{OH} region (a) and zoom on
7 the ν_{OH} ($3550\text{-}3770\text{ cm}^{-1}$) region (b).

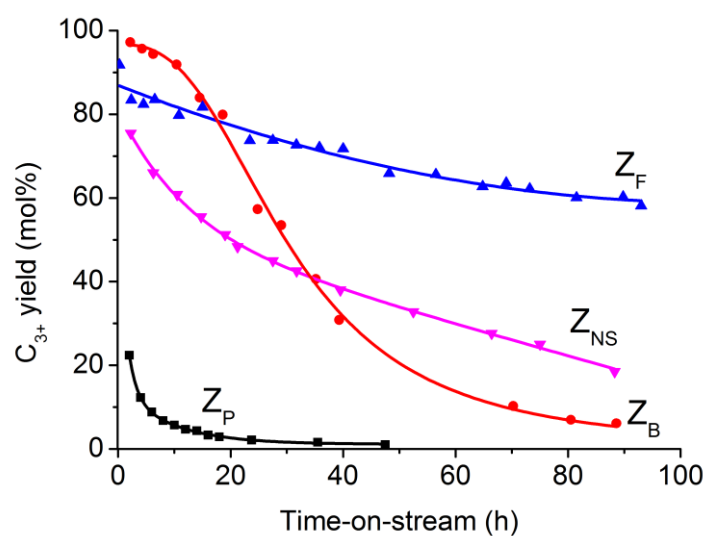
8 The above results indicate that a ZSM-5 house-of-cards-like architecture, Z_F , can be prepared
9 by a top-down unbiased NH_4F etching of ZSM-5. Single zeolite crystals are converted in a
10 mosaic of connected rectangular cavities separated by nanometer thick crystalline walls. Such
11 walls are thicker than the house-of-cards obtained by a bottom-up approach, Z_{NS} (Figure 3e-g
12 and Figure 4e, f). However, the aspect ratios between the wall thickness and mesopore space of
13 both Z_F and Z_{NS} are similar. As mentioned, the formation of rectangular cavities is a
14 consequence of the unbiased dissolution of highly defect zones and small crystalline domains
15 mostly presented in zeolite crystals. Thus, an essential advantage of the top-down approach is

1 that the “house” is a single crystal almost free of defect zones. A decrease of Lewis acid sites is
2 observed, again a consequence of the preferential dissolution of defective portions of the crystals
3 (Table 1) while the number of Brønsted acid sites is almost unchanged. The resulting house-of-
4 cards-like material comprises relatively large meso- and macro-pores with a flat surface. Another
5 essential feature of the house-of-cards-like material is the moderate increase in external surface
6 area and retention of micropore volume compared to the caustic leached ZSM-5. Nanosheet-like
7 ZSM-5 also shows relatively low micropore volume. Z_F differs substantially from the caustic
8 leached zeolite produced from the same parent (Z_B) and the nanosheet ZSM-5 (Z_{NS}). In contrast,
9 the preferential extraction of Si and redeposition of Al in the case of Z_B results in a considerable
10 increase of the external surface area at the expense of the micropore volume, dramatic changes in
11 the chemical composition and the acidic properties of the zeolite (Table 1). Nanosheet ZSM-5
12 also exhibits a huge external surface area and reduced micropore volume. It should be noted the
13 very low Brønsted acidity of this material (Table 1) and the vast presence of surface silanols in
14 this material (Figure 5). This series of catalysts with well distinct physicochemical properties
15 offers the possibility a structure-property relationship to be established.

16 **2.2 Ethanol-to-hydrocarbons (ETH) conversion on Z_B , Z_F , and Z_{NS} zeolite catalysts**

17 ETH, like the methanol-to-hydrocarbons (MTH) process, is a key step in the transformation of
18 biomass, coal, natural gas, heavy oils into olefins (major building blocks in petrochemistry) and
19 higher hydrocarbons (gasoline fuel) [46]. The performance of all these four zeolites is evaluated
20 in this reaction as already discussed previously [31]. Ethanol is converted into water and light
21 olefins as well as heavier hydrocarbons (3 to 18 carbon atoms). Small amounts of methane and
22 ethane are detected but no CO and CO₂. The yields are presented as molar % in the organic
23 fraction (Figures 6 and 7). While ethanol dehydration can take place on weak acid sites,

1 oligomerization, cyclization and hydrogen transfer reactions require strong acid sites as found in
2 zeolites. On all our catalysts, ethanol conversion is initially complete and decreases slowly with
3 time-on-stream (Figure S18a). Therefore, the catalyst deactivation is related to the time evolution
4 of the C_{3+} yield.



5
6 **Figure 6.** Molar yields of C_{3+} hydrocarbons as a function of time-on-stream during the
7 conversion of ethanol at 623 K and 3.0 MPa on Z_P , Z_F , Z_B , and Z_{NS} zeolite catalysts. The lines
8 are drawn simply to guide the eyes.

9 On the parent zeolite (Z_P), the initial yield of C_{3+} is only 35 % (extrapolated value at zero
10 conversion) and decreases rapidly becoming negligible after only 20 h (Figure 6). On Z_B , the
11 initial C_{3+} yield is slightly less than 100% (Figure 6), but the catalyst deactivates rapidly and
12 yields almost no C_{3+} after 90 h on stream. On Z_{NS} , the initial C_{3+} yield is lower than Z_B but quite
13 high considering its much lower Brønsted acid site concentration. However, its deactivation rate

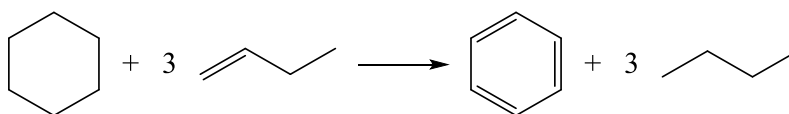
1 is much lower than Z_B : after 90 h on stream, the C_{3+} yield decreases to *ca.* 20 mol.% while it was
2 almost zero on Z_B . The direct synthesis of a hierarchical zeolite using a complex surfactant is an
3 efficient, albeit expensive, way of minimizing deactivation. Z_F , although not the catalyst with the
4 best initial C_{3+} yield retains it much longer as it deactivates much slower than Z_B and Z_{NS} (Figure
5 6); after 90 h of TOS, it still produces a substantial C_{3+} yield, *ca.* 60 mol.%.

6 The unbiased NH_4F etching of a micrometer-sized ZSM-5 zeolite leads to a diffusion path
7 length similar to that of nanosized one. Indeed, the stability of Z_F is similar, or even higher for
8 longer reaction time, to that on a commercial zeolite with a crystal size of 45 nm [31]. See also
9 Figure S19 in the present work. The superior stability of Z_F on a nanoscale zeolite can be related
10 to both a high intracrystalline mesoporous volume ($0.31 \text{ cm}^3 \cdot \text{g}^{-1}$) and quasi-perfect connectivity
11 with the microporous network, a consequence of single crystal nature of house-of-cards-like
12 material. As Z_F is devoid of defects, contrariwise on Z_{NS} , the immobilization and growth of coke
13 precursors are mitigated. Therefore the catalyst is more stable. On the other hand, as the caustic
14 leaching divides by only four the diffusion path length as shown by the desorption experiments
15 [47], the gain in stability is rather limited.

16 The molar yields of the paraffins (P), olefins (O), naphthenes (N), and aromatics (A), as well
17 as the paraffins to aromatics molar ratio (P/A), are reported as a function of the C_{3+} yield and
18 time-on-stream in Figure 7 and Figure S18b-f, respectively. As far as product distribution is
19 concerned Z_P , Z_{NS} and Z_F give the same product selectivity for the same C_{3+} yield, meaning that
20 the reactions involved are identical, even during the deactivation and regardless of the acid
21 properties of the three catalysts. It is worth to note that a difference exists only on Z_B with a yield
22 in O_{3+} . Yields in N and O_{3+} pass through a high yielding maximum in C_{3+} , while those in P and
23 A increase exponentially. Regardless of C_{3+} yield the paraffins to aromatics molar ratio (P/A) is

1 ca. 3 (Figure 7e), indicative of hydrogen transfer between naphthene and olefins (Scheme 1). The
2 initial low value of P/A ratio (open symbol in figure 7e) is due to coke formation.

3

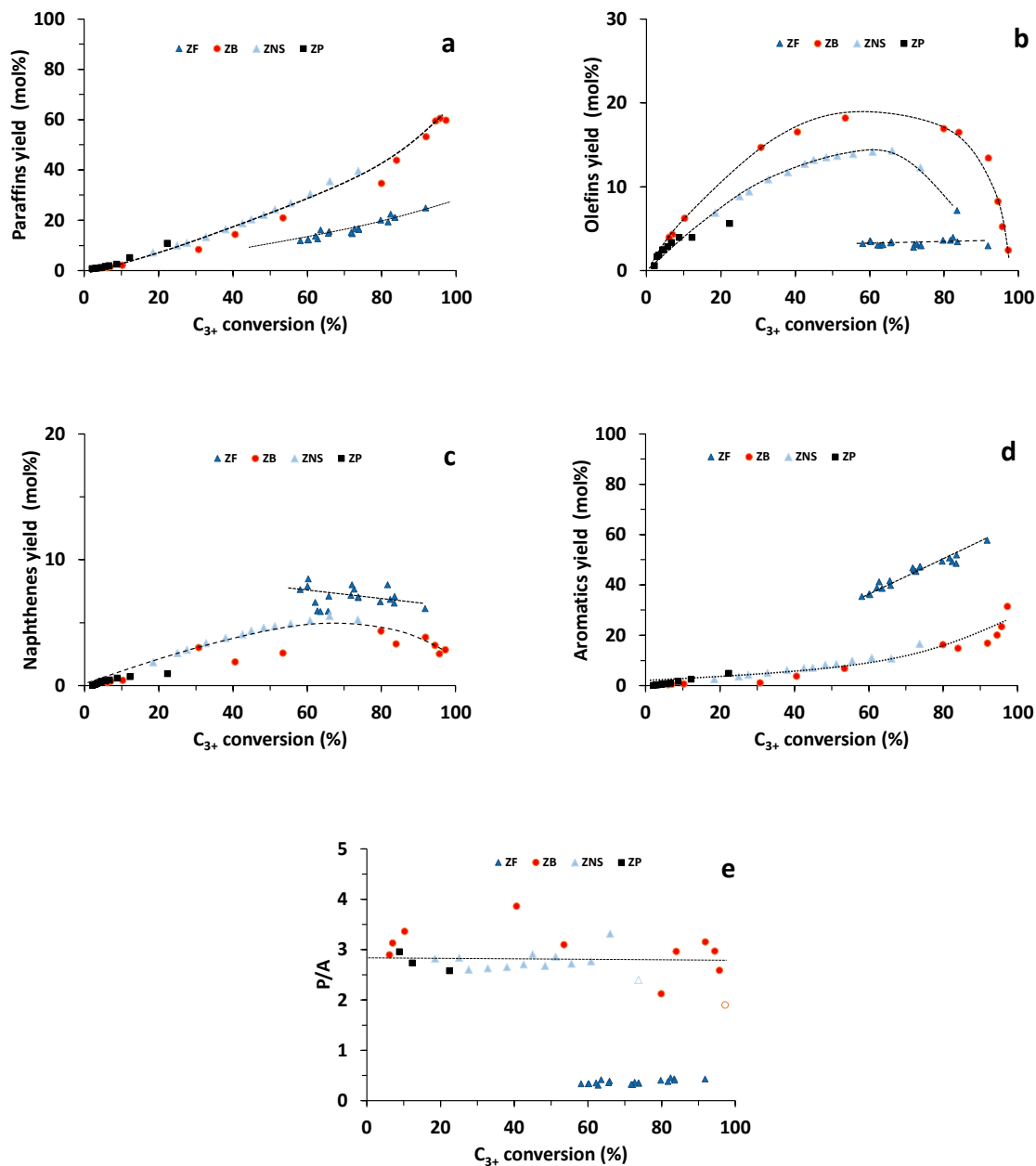


4

5 **Scheme 1.** The hydrogen transfer reaction between naphthene and olefins.

6 In sharp contrast, Z_F shows considerably higher aromatic and naphthene yields than Z_B and
7 Z_{NS} , while its paraffin yield is low (Figure 7a, c, d). Apparently, hydrogen transfer reactions are
8 substantially suppressed in this catalyst. Its P/A is lower than 0.5 (Figure 7e), implying that on
9 the NH_4F treated zeolite, aromatics are formed by a monomolecular protolytic dehydrogenation.
10 Lercher and coworkers [48] have shown that a high ratio of Brønsted acid sites to Lewis acid
11 sites (BAS/LAS) minimizes the alkenes concentration and causes high hydride transfer (HT)
12 activity. Yet on Z_F catalyst, HT is limited although the house-of-cards-like catalyst possesses the
13 highest BAS/LAS ratio. Lercher et al. [49] also demonstrated that the rate determining step for
14 dehydrogenation activity of alkane on H-ZSM-5 is represented by olefin desorption from the
15 catalyst surface which is promoted by a short diffusion path length. It is worth mentioning that
16 the products selectivity of Z_F is very close to nanometer-sized ZSM-5 zeolite (Figure S20),
17 confirming that the diffusion path length is limited to a few nanometers on both zeolites.

18



1

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3

4 **Figure 7.** Ethanol transformation at 623 K and 3.0 MPa on Z_P, Z_F, Z_B and Z_{NS} zeolite: (a) molar
 5 yields of paraffins (P), (b) olefins (O₃₊), (c) naphthenes (N), (d) aromatics (A), and (e) molar P/A
 6 ratio catalysts as a function of C₃₊ conversion. The lines are drawn simply to guide the eyes.

7 The coke content, the evolution of the number of acid sites (Brønsted and Lewis) and pore
 8 volumes accessible to nitrogen after more than 48 h of reaction are gathered in Table 2. The coke

1 content is around 13 wt % on Z_P after 48 h of reaction. NH₄F etching has no impact on the coke
 2 level, while on the alkaline leached Z_B catalyst, coke grows continuously to reach a level almost
 3 twice as high as its parent. On Z_{NS}, although its Brønsted acid site concentration is 4 times lower
 4 than on Z_P, coke content is quite similar. The residual acidity (Brønsted and Lewis), after
 5 deactivation, is very low for all samples. An important decrease of micropore volume occurs on
 6 all zeolites. On Z_{NS} which is the least acidic catalyst, the loss of microporosity is only 25%. The
 7 coked Z_F and Z_{NS} catalysts, despite a near total loss of acidity, keep converting ethanol to C₃₊
 8 hydrocarbons (~60 %, and ~20 %, respectively, (Figure 6)); ethanol transformation occurring
 9 probably by pore mouth catalysis on hybrid active sites (immobilized carbocations) by a carbon
 10 pool mechanism [31].

11 **Table 2:** Coke content, T₅₀ and T₉₀ (temperatures required to remove, by combustion, 50% and
 12 90% of coke respectively), pore volumes and acidity of Z_P, Z_F, Z_B and Z_{NS} zeolite spent
 13 catalysts.

Samples	Time	Coke	T ₅₀	T ₉₀	V _{mic} ^a	V _{meso} ^b	B _{Py} ^c	L _{Py} ^c
	h	wt%	°C	°C	cm ³ g ⁻¹	cm ³ g ⁻¹	μmol.g ⁻¹	μmol g ⁻¹
Z _P	48	12.9	615	705	0.01	0.02	4	5
Z _F	90	12.5	560	670	0.05	0.13	1	10
Z _B	110	20	580	680	0.03	0.36	2	14
Z _{NS}	90	10.5	560	665	0.08	0.17	0	14

14 ^at-plot. ^bV_{total} - V_{mic} (V_{total}: the volume absorbed at p/p⁰ = 0.99). ^cThe Brønsted acidity (B_{Py}) and
 15 Lewis acidity (L_{Py}) determined by pyridine sorption.

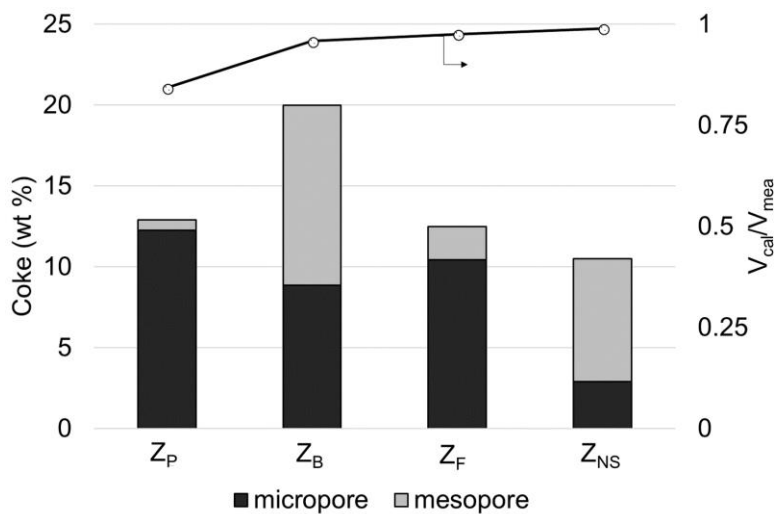
16 Differences in the activity and stability between Z_P, Z_B, Z_F, and Z_{NS} are related to changes in
 17 the carbon pool composition. The composition of the coke trapped in the zeolite micropores, *i.e.*,

1 internal coke, is determined by mineralizing the zeolite and subsequently analyzing the organic
2 phase after a liquid-liquid extraction with CH_2Cl_2 [50]. Coke molecules can be lumped in four
3 families according to their number of aromatic rings: alkylbenzenes (I), alkyl naphthalenes (II),
4 alkyl-phenanthrenes or -anthracenes (III) and alkylpyrenes (IV). The sizes of all compounds
5 trapped in the micropores vary between the dimensions of the pore openings (0.55 nm) and
6 channel intersections (~ 1 nm) of H-ZSM-5. The coke on Z_P and Z_B contain representatives of all
7 families. A simpler and lighter coke distribution is found on Z_F and Z_{NS} , where families I and III
8 dominate (Figure S21); such a coke composition is similar to that reported elsewhere on nano-
9 sized zeolite [31]. The average molar mass of coke trapped in the micropores, calculated from
10 these compositions, is 200 g mol^{-1} for Z_P and Z_B , and 180 g mol^{-1} for Z_F and Z_{NS} .

11 Taking this average molar mass of 200 g mol^{-1} for the coke molecules trapped inside the
12 micropores (*ca.* 13 wt % on the Z_P catalysts), its concentration is *ca.* 645 mol g^{-1} , corresponding
13 to the amount of Brønsted acid sites on the fresh zeolite. Coking is therefore mainly a site
14 poisoning effect, further confirmed by a complete disappearance of the bridged OH groups
15 (Figure S22). Assuming that on all hierarchical zeolites, one coke molecule poisons only one
16 protonic site, the coke trapped within the micropores and that located in the mesopores can be
17 estimated. The results are reported in the bar chart on Figure 8. The most significant
18 accumulations of coke on the mesopores are for the caustic leached micron-sized zeolite (Z_B) and
19 the nanosheet zeolite (Z_{NS}), reaching up to 55% and *ca.* 75% of the total coke, on the other hand,
20 it is limited to 16% on the catalyst free of defect (Z_F) and as expected, almost zero on the parent
21 zeolite. The accumulation of coke in mesopores is likely related to the quality of the crystals. The
22 increased number of silanols and Lewis acid sites on Z_B and Z_{NS} are prone to trap desorbed
23 products [51–53] as confirmed by the disappearance of silanol groups on spent catalysts (Figure

1 S22). Taking a coke density of 1.1 g cm^{-3} , the volume of coke in the micropores corresponds to
 2 the loss of micropore volume measured by nitrogen adsorption (Figure 8). These calculated
 3 values are very close to the experimental data, highlighting the relevance of this procedure to
 4 discriminate between internal and external coke contents.

5



6

7 **Figure 8.** Estimation of the coke distribution between micropores and mesopores on Z_P, Z_F, Z_B
 8 and Z_{NS} zeolite spent catalysts

9 In addition, the coke light-off performances of the spent catalysts are compared in Table 2
 10 where temperatures required to combust 50% (T₅₀) and 90% (T₉₀) of the coke are reported. T₅₀
 11 and T₉₀ are both lower on Z_B than on Z_P (-35 °C and -25 °C respectively) and much lower on
 12 Z_{NS} and Z_F (-55 °C). The differences are related to a higher accessibility (diffusion) of oxygen to
 13 the coke molecules trapped in the micropores. The house-of-cards-like zeolite, already the best

1 catalyst (cumulative performance due to its time stability) is as good as a nanosheet one for
2 regeneration.

3 The ETH reaction illustrates the superior stability and selectivity of Z_F , a house-of-cards-like
4 ZSM-5 catalyst, although other hierarchical zeolites, Z_B and Z_{NS} possess higher external surface
5 area and mesopore volume. The nano-sheet zeolite Z_{NS} with a higher Si/Al ratio of 37 and lower
6 acid site density displays a remarkably high initial C_3^+ yield and was once expected to be a
7 superior candidate for ETH reactions [54] but lacks stability as shown in this study. The Z_F
8 catalyst outperforms both Z_B and Z_{NS} in the present study, but the Z_{NS} hierarchization procedure
9 brings superior performances than a micron-sized zeolite, Z_P (Figure 6). Zeolite acidity and
10 mesoporosity cannot alone fully explain the differences in catalytic performances discussed
11 above. Based on our detailed comparison of the hierarchical zeolites, we propose that, in addition
12 to mesopore size, shape, uptake capacity and connectivity, the quality of the hierarchical zeolites
13 (micropore accessibility, absence of defects [silanol nests], Lewis acidity) also play important
14 roles in the ETH reaction. The higher catalytic performances of NH_4F leached zeolites could also
15 be related to their ability to dehydrogenate naphthenic compounds (Figure 7); this
16 monomolecular reaction requires less space than the bimolecular hydrogen transfer occurring on
17 the caustic leached zeolite and nano-sheet zeolite. The absence of defects combined with a small
18 diffusion pathlength inside the microporosity by retarding the transformation of the desired
19 active carbon pool to unwanted coke, slows catalyst deactivation. The presence of numerous
20 silanol groups, on the other hand, traps coke precursors on the surface, promoting a rapid catalyst
21 deactivation by a fast accumulation of aromatic compounds. Indeed, as coke formation is a
22 genuine shape selective reaction, the availability of more space favors the production of larger
23 molecules, coke, *i.e.* an inactive carbon pool. These results highlight that, in addition to the

1 loosely defined “mesopore quality” [21], the surface quality of the remaining microporous
2 crystal domains determines the catalytic performance of hierarchically structured zeolite crystals.

3 **Conclusion**

4 Single house-of-cards-like ZSM-5 crystals were prepared by a top-down approach using a
5 novel unbiased chemical etching with an NH_4F solution. Such an etching extracts Si and Al at
6 similar rates and preferentially removes less-stable defect zones in the crystals. The process is
7 therefore controlled by the number of intergrowths, the structural stress and the nanocrystalline
8 domains with well-defined grain boundaries, *i.e.* the history of the zeolite synthesis. Such a
9 unique dissolution behavior is inherently related to the growth process where simultaneous
10 monomer-by-monomer addition and oriented attachment take place [42]. The unbiased NH_4F
11 dissolution leads to the preferential extraction of misoriented and more vulnerable to chemical
12 attack nanocrystalline domain followed by progressive etching of the remaining part of the
13 crystals, which is more resistant due to the limited number of structural defects. This dissolution
14 proceeds by a layer-by-layer mechanism following the rectangular features of previously
15 extracted nanodomains, thus the well shaped cavities grown in size and connect each other
16 providing a house-of-cards-like morphology.

17 Such a hierarchical material is analogous to a collection of nanosized high quality crystals with
18 the same framework composition and Brønsted acidity of their parent. The high accessibility and
19 short diffusion pathlength offered by the house-of-cards-like morphology is therefore combined
20 with the intact native microporosity and acidity of their parent zeolite and does not require
21 expensive and one-off structure directing agents. The optimization of structural and chemical
22 parameters results in an excellent catalyst easier to regenerate, as demonstrated in the

1 challenging (deactivation prone) ethanol-to-hydrocarbon reaction. Indeed, regenerating
2 deactivated catalysts by controlled coke combustion often leads to, often overlooked, irreversible
3 changes due to the operating conditions (such an exothermic reaction produces steam near the
4 zeolite active sites and can lead to structural and chemical damages such as dealumination) of
5 this step. The performance of such single crystals house-of-cards-like catalysts is so far second to
6 none as it maintains its performance over longer periods of time and appears easier to regenerate,
7 which even outperforms the nanometer-sized zeolites (Figure S19). Noting that we have
8 previously concluded, based on the samples studied, that the reduction of crystal size is the most
9 efficient way to increase the performance of zeolites for applications such as alcohols to
10 hydrocarbons, and hence nano-zeolites are preferred [31].

11 This study highlights that hierarchical zeolitic catalysts with superior performances can be
12 designed not only by promoting high accessibility and short diffusion to and from their active
13 sites, but also by retaining the crystallinity and acidity of their parents while keeping a minimum
14 level of defects. Since the presence of crystalline domains with well-defined grain boundaries is
15 a ubiquitous in zeolite materials, the preparation of single crystal house-of cards can be extended
16 to other zeolite types. Further insights in the hierarchization process of zeolites, either bottom-up
17 or top-down (this work) hold much potential to design ever better zeolite catalysts for current
18 and forthcoming applications [55].

19

20 **Supporting Information.** Experimental details, the nitrogen physisorption isotherms, the
21 combined 3D models of zeolite body and pores, the additional SEM and TEM images and a
22 graphical representation of the house-of-cards-like architecture, the additional data of the

1 Ethanol-to-Hydrocarbons reaction, coke composition by GC analysis, and the IR spectra of the
2 coked zeolite samples.

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6 ACKNOWLEDGMENT

7 Zhengxing Qin acknowledges funding support from NSFC 21706285, China University of
8 Petroleum (East China) starting funding, and the Fundamental Research Funds for the Central
9 Universities (18CX02013A). ZQ, JPG and VV acknowledge funding from the French-Sino
10 International Laboratory (LIA) “Zeolites”.

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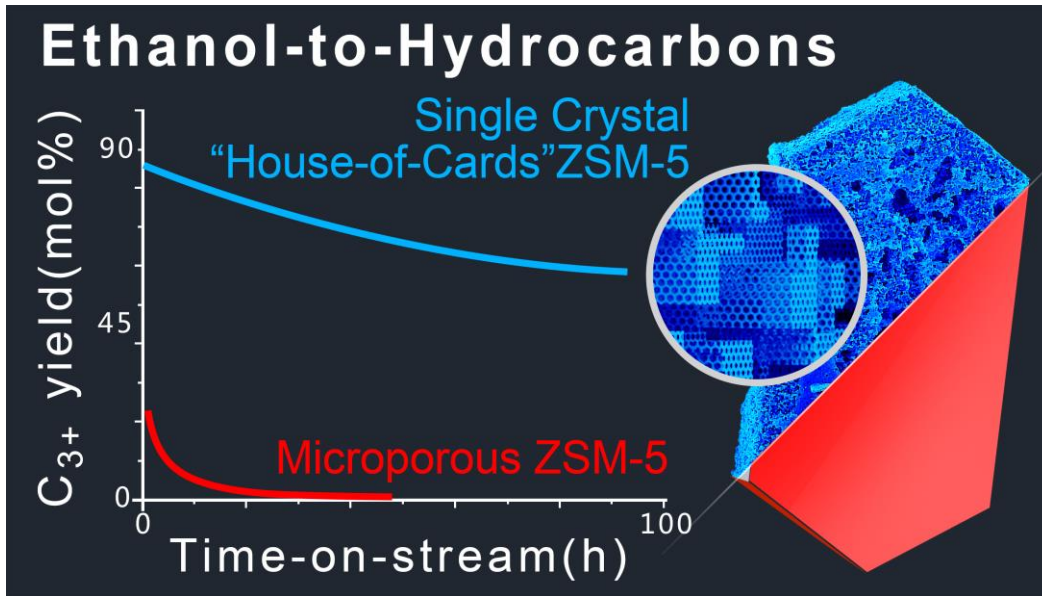
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SYNOPSIS (Word Style "SN_Synopsis_TOC").



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