

Catalysis Science & Technology

Accepted Manuscript

View Article Online View Journal

This article can be cited before page numbers have been issued, to do this please use: F. Marques Mota, P. Chlubná-Eliášová, J. Jung and R. Ryoo, *Catal. Sci. Technol.*, 2016, DOI: 10.1039/C5CY02029H.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/catalysis

Published on 14 January 2016. Downloaded by University of York on 21/01/2016 14:44:57.

YAL SOCIETY CHEMISTRY

Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/



F. Marques Mota,^a P. Eliášová,^a J. Jung,^a and R. Ryoo^{* a,b}

The gas-phase hydroconversion of ethylbenzene was investigated in the presence of intimate mixtures of *MRE, MFI and MTW-type zeolite nanosponges and a hydrogenating component (Pt/Al_2O_3). The nanomorphic zeolites were prepared using multiammonium surfactants acting as dual-porogenic agents directing formation of micro- and mesopores simultaneously. The effects of the zeolite topology (pore size and dimensionality) and crystal thickness on the product selectivity of ultra-thin zeolite frameworks (<10 nm) were investigated. Enhanced catalytic activity confirmed the importance of improved molecular diffusion. These nanosponges were unique in producing more xylenes, suggesting lower confinement effects. The selectivity to *p*-xylene and the selectivity towards ethylbenzene hydroisomerization, dealkylation, disproportionation, transalkylation and hydrocracking was evaluated. Despite the similar <10 nm crystal thickness of all nanosponge zeolites, the presence of spacious channel interconnections in MFI improved the product selectivity compared to straight channels as of *MRE and MTW. Our findings clarify the relatively unexplored transformation of alkyl-aromatics over ultra-thin zeolite crystals, through five typical catalytic reactions of major industrial interest.

1. Introduction

Innovative use of existing benzene-toluene-xylene (BTX) resources has been greatly extended following the increased global demand for para-xylene.¹⁻³ Separation of p-xylene by adsorption and the conversion of the remaining C_8 aromatics have become important branches in the integrated aromatics complex. The C₈ aromatic cut from catalytically reformed naphthas and pyrolysis distillates contains not only xylenes but also ethylbenzene in a wide composition range. Although the latter has large scale application for the production of styrene monomer, it is rarely isolated as such from C_8 aromatic mixtures due to the difficulty and cost of the separation.⁴ Xylene hydroisomerization preferentially occurs over Brønsted acid sites traditionally provided by zeolites. Based on the balance between the supply of benzene and xylenes and their market demand, ethylbenzene may be dealkylated or alternatively hydroisomerized depending on the selected catalyst.³⁻⁷ Catalysts for the conversion of C₈ aromatics have ordinarily been classified by the manner of processing ethylbenzene associated with the xylene isomers.⁶ The ethylbenzene content in the C₈ aromatic fraction can range up to 50%, which further highlights the choice of the zeolite applied here.⁸ When the simultaneous hydroisomerization of hydrogenated into ethylcyclohexene isomers in the presence of a strong hydrogenating component (Pt/Al₂O₃), followed by isomerization into dimethylcyclohexenes and further dehydrogenation to xylenes.⁹ This process is nonetheless accompanied by numerous reactions, e.g., naphtha ring opening, followed or otherwise by hydrocracking, aromatization, and polymerization of aliphatic hydrocarbon chains, as well as dealkylation, disproportionation, and transalkylation reactions of alkyl-aromatics.¹⁰

xylenes and ethylbenzene is preferred, ethylbenzene is

With a focus on the acid component of the bifunctional catalyst, continuous research has described the impact of the zeolite topology on the catalytic performance.^{11,12} In particular, recent studies highlighted the dependence of the selectivity on the size, dimensionality, presence of large cavities, and even the shape and tortuosity of zeolitic pore systems.^{8,13} Whereas a 3-dimensional (3-D) 10-ring (10-R) MFI zeolite has found general application for the dealkylation of ethylbenzene, the zeolite of choice in the selective hydroisomerization of ethylbenzene is still under discussion. Optimized formulations of 1-D large-pore mordenite catalysts are generally used for ethylbenzene transformation towards the formation of xylenes.^{11,14-17} Yet, zeolites with narrow nonintersected 10-R channels have recently emerged as a new generation of more selective catalysts.^{8-10,12,13,18,19} Sensitivity to coke retention in the core of the zeolite crystals has been a crucial factor for choosing the catalyst when ethylbenzene is preferentially hydroisomerized. For the simultaneous hydroisomerization of xylenes and ethylbenzene, the zeolitebased catalyst is required to balance the desired shape-

^{a.} Center for Nanomaterials and Chemical Reactions, Institute of Basic Science (IBS), Daejeon 305-701, Korea.

^{b.} Department of Chemistry, KAIST, Daejeon 305-701, Korea. E-mail: ryongryoo@kaist.ac.kr

⁺Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

DOI: 10.1039/C5CY02029H

Journal Name

Published on 14 January 2016. Downloaded by University of York on 21/01/2016 14:44:57

selectivity, the tendency toward fast deactivation by coke formation, and the limited molecular transport.

In a wide range of catalytic applications, hierarchical zeolites are of primary interest as they may overcome main zeolite drawbacks associated with limited molecular diffusion, resulting in low catalyst effectiveness. Over the years, numerous approaches have been designed to tailor the synthesis of hierarchical zeolites exhibiting mesoporosity in addition to zeolitic-micropores, using both top-down and bottom-up approaches.²⁰⁻³² In particular, Ryoo and collaborators have synthesized MFI, *MRE, BEA, and MTW zeolites, and AEL, AFI and ATO-type aluminophosphates, in the form of nanosponges with improved molecular diffusion. These investigators designed special multiammonium surfactants, e.g., $C_{22}H_{45}N^{+}(CH_{3})_{2}C_{6}H_{12}N^{+}(CH_{3})_{2}C_{6}H_{13}$, for application as dual-porogenic agents.³³⁻³⁶ The microporous framework is directed by the ammonium groups while the long hydrocarbon chains can direct the formation of the mesostructure due to their self-assembly ability similar to mesoporous materials. The resulting nanosponge materials have nano-sized crystals and a narrow mesopore size distribution. Recent works demonstrated the major impact of the crystal thickness of these ultra-thin materials on the catalyst lifetime and catalytic activity in several catalytic reactions.^{33,37-44} Yet, the impact of the crystal thickness on the attained catalytic selectivity has been relatively unexplored so far. Our research aims to shed some light into this area.

In the present work, three zeolite nanosponge materials, namely *MRE, MFI, and MTW, and their corresponding bulk counterparts were evaluated in the hydroconversion of ethylbenzene to inspect the effect of acid site accessibility on the resulting activity and, in particular, on the catalytic selectivity. In each case, the nanosponge crystals exhibited dimensions below 10 nm. Whereas in previous reports the impact of the zeolite topology determines the reaction selectivity, the question of whether the unique molecular shape-selectivity of each zeolite is preserved with such thin materials remains unanswered. In this regard, we assessed the multitude of side reactions occurring during ethylbenzene transformation to evaluate the impact of crystal size on the product distribution. We intentionally varied the dimensionality and pore opening sizes of the chosen zeolite topologies, *MRE, MFI, MTW, to examine the roles these factors play in the studied catalytic reaction. Corresponding illustrations of their channel systems are presented in Fig. 1.⁴ *MRE possesses symmetrical, straight, 1-D 10-R channels with dimensions of 5.3×5.6 Å. MFI zeolite has a 3-D pore architecture with 10-R straight channels (5.1×5.5 Å) interconnected through 10-R sinusoidal channels (5.3×5.6 Å), thus generating 8.6 Å intersections. The MTW zeolite exhibits straight, 1-D, 12-R channels with openings 5.6×6.0 Å. The comparison of the catalytic performance of their nanosponge forms should extend our understanding of the impact of the framework topology on the obtained product spectrum in the case of zeolites as ultra-thin crystals. This effect is reflected in five typical catalytic reactions of major industrial interest hydroisomerization. dealkylation. disproportionation. transalkylation, and hydrocracking – in the transformation of alkyl-aromatic hydrocarbons, with ethylbenzene as a probe molecule.

2. Experimental

2.1. Synthesis of zeolites

Nanosponge zeolites were prepared in accordance with previously established protocols optimized for each zeolite structure.^{33,46} In order to differentiate between the acidity impact and the influence of the pore topology, each zeolite was synthesized with a similar framework Si/Al molar ratio close to 100. MTW and *MRE-type zeolites were synthesized using the same multiammonium surfactant SDA, $[C_{22}H_{45}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_2H_{45}](Br^-$

 46 (Cl⁻)₄. ⁴⁶ Tetraethylorthosilicate (TEOS, 95%, Junsei) and sodium aluminate (53 wt%, Sigma-Aldrich) were used as silica and alumina sources, respectively. For MFI-type zeolite, the SDA was [C₁₆H₃₃-N⁺(CH₃)₂-C₆H₁₂-N⁺(CH₃)₂-C₆H₁₃](Br⁻)₂.³³ Sodium silicate solution (Si/Na = 1.75, 15 wt% SiO₂) and sodium aluminate (53 wt%, Sigma-Aldrich) were in this case used as silica and alumina sources. The molar composition of the gel was 100 SiO₂: 0.5 Al₂O₃: x SDA: y Na₂O: z H₂O with (x, y, z) as (1.67, 13, 3000) for *MRE, (7.5, 27, 5000) for MFI, and (3.33, 13, 4500) for MTW. The nano-zeolites were obtained after 3, 3 and 10 days at 423 K. The nanosponge samples were denoted as nano-*MRE, nano-MTW, and nano-MFI. The corresponding bulk counterparts (bulk-*MRE, bulk-MTW, and bulk-MFI) were also synthesized for comparison purposes. Detailed synthesis procedures are given in the ESI⁺.

2.2. Preparation of bifunctional catalysts

The preparation of bifunctional catalysts involved the mechanical mixing of each solid acid with alumina impregnated with platinum (Pt/Al₂O₃). The indicated catalyst formulation was based on long-term literature results and well-established patent data available for the industrial process.^{10-13,15} The hydrogenating phase was prepared by ion exchange of γ -Al₂O₃ with a hexachloroplatinic acid solution in the presence of 0.2 M HCl following literature reports.^{11,12} The hydrogenating phase was then calcined under 2 dm³ g⁻¹ min⁻¹ of dry air flow at 773 K for 4 h (1 K min⁻¹). The Pt content was equal to 1.2 wt.% to assure an ideal bifunctional catalytic behavior. The Pt content, based upon literature results, was believed sufficient to balance the comparatively weak acid phase of the tested zeolites with high Si/Al ratios.¹³ High Pt dispersion was corroborated by collected scanning transmission electron microscopy (STEM) images. Metal particle domains ranged from 0.8 to 1.2 nm-diameter (Fig. S1, ESI[†]). The bifunctional catalysts were prepared by milling the zeolite samples with the prepared Pt/Al₂O₃ solid in 10:90 wt. proportion. The samples were pelletized, crushed, and sieved to consistently obtain a particle size of 0.200 to 0.355 mm.

2.3. Characterization techniques

Published on 14 January 2016. Downloaded by University of York on 21/01/2016 14:44:57

Powder X-ray diffraction patterns of all zeolites were recorded with a Rigaku Multiflex diffractometer using Cu K α radiation (40 kV, 30 mA). Scanning electron microscopy (SEM) images were obtained with a FEI VERIOS operating at 1 kV. Crystal thickness was evaluated through TEM photographs taken with a Philips F30 Tecnai at an accelerating voltage of 300 kV (Cs=0.6 mm, point resolution 0.17 nm). STEM micrographs of the hydrogenating phase were obtained using a spherical aberration-corrected Titan ETEM G2 60-300 system operated at 300 kV and equipped with a high angle annular dark field (HAADF) detector. Nitrogen adsorption-desorption isotherms were measured using an Tristar volumetric adsorption analyzer at 77 K, with the samples being outgassed for 4 h at 573 K under vacuum prior to measurement. The Brunauer-Emmett-Teller (BET) equation was used to estimate the surface area from the adsorption branch of isotherm in the 0.05-0.2 range of relative pressures. The total pore volume was equated to the amount of adsorbed N₂ at $P/P_0 = 0.98$. The content of Si, Al and Pt in the samples was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) carried out on an OPTIMA 4300 DV instrument (Perkin Elmer). ²⁷Al NMR spectra were acquired in a solid state with magic angle spinning (MAS) using a Bruker Avance 400WB spectrometer at room temperature.

2.4. Ethylbenzene hydroconversion

The gas-phase hydroconversion of ethylbenzene (Sigma-Aldrich, 99%) was conducted in a fixed bed stainless steel reactor at 10 bar and a H₂: ethylbenzene molar ratio of 4. The bifunctional catalyst (1.0 g) was loaded into the reactor and activated *in situ* at 753 K for 4 hours under H₂ flow (5 K min⁻¹, at 10 bar). The reaction was carried out at decreasing weight hourly space velocity (WHSV) values at a fixed reaction temperature (683 K). WHSV values were varied over the range of 2 to 45 g of ethylbenzene g⁻¹ h⁻¹, by adjusting the ethylbenzene flow. Reaction products were analyzed online by flame ionization detector (FID) gas-chromatography (GC, Agilent 7890A) using a CP-Chirasil-Dex CB capillary column (0.25 mm × 25 m).

3. Results and Discussion

3.1. Zeolites characterization

Zeolites under study were synthesized as traditional bulk crystals and as nanosponge materials. For this purpose we applied the method reported by Ryoo and coworkers using multivalent cation surfactants acting as a dual-porogenic agent.^{33,34} The prepared nanosponge zeolites with *MRE, MFI, and MTW topologies exhibited powder X-ray diffraction (XRD) patterns similar to those of the corresponding bulk counterparts (Fig. S2, ESI[†]). The overall decrease in the intensities and peak-broadening observed for the nanosponge samples corroborated the changes in their crystal size towards smaller dimensions and was in a good agreement with previous reports.^{33,46} The zeolite morphologies of both bulk (Fig. 2a-c) and nanosponge solids (Fig. 2d-f) were studied by

SEM microscopy. Bulk-MFI crystals (20-µm in length) were strikingly voluminous compared to the approximately 2-µm long and narrow MTW and *MRE bulk crystals. The individual nanocrystals of all nano-zeolites were arranged in an irregular manner resulting in the nanosponge-type morphology. Representative TEM images of the nanosponge samples evidenced the presence of ultra-thin nanocrystals in each case (Fig. 2g-i). The thickness of the nano-MFI crystals corresponded to a single-unit-cell-size, 2.5-nm along the b axis, with the zig-zag channels extended along the ac plane. Both nano-MTW and nano-*MRE are characterized by about 10 nm sized crystals with the pore openings on the bc and ac planes, respectively. The uniform thickness of the nanocrystals agreed with previous reports,^{33,46} evidencing a good reproducibility of the synthesis procedures applied. For the bulk samples, the measured N₂ sorption at 77 K revealed type I isotherms characteristic of microporous zeolites (Fig. S3, ESI⁺). The nanozeolites additionally exhibit a prominent hysteresis loop in the range $0.5 < p/p_0 < 0.9$ region. This result points to the presence of an intercrystalline mesoporous network in addition to framework micropores.⁴⁷ The nanosponge zeolites have higher total BET surface areas in comparison to the bulk ones (Table 1). Larger surface areas were attributed to the presence of mesopores. Relatively narrow mesopore size distributions in the range 2.5-6.0 nm correspond to the typical features of nanosponge zeolites.³⁵ Elemental analysis using ICP-AES confirmed that the silicon to aluminum atomic ratios were close to the nominal value (Table 1). According to ²⁷Al NMR the quasi-totality of the aluminum in all nanosponge zeolites had the tetrahedral coordination (Fig. S4, ESI⁺). This outcome highlights the noteworthy stability of these solid acids.

3.2. Catalytic testing

3.2.1. Catalytic activity Nanosponge *MRE, MFI, and MTW zeolites were evaluated in the gas-phase hydroconversion of ethylbenzene and compared with their corresponding bulk counterparts. The conversion increased stepwise with increasing contact time, taken as the reverse of the corresponding WHSV (Fig. 3). The catalytic activity was assessed at the end of the catalytic test at a lower WHSV value (15 h⁻¹). All bifunctional catalysts remained relatively insensitive to deactivation in the evaluated range. The catalyst stability was attributed to their low acidity (see Table 1), whereas reduced crystal thickness was believed to further play a crucial role in the prolongation of their lifetimes as reported previously.^{33,36,38,46}

To eclipse the potential impact of slightly varied Al content in each zeolite on its performance, the turn-over frequencies (TOF), defined as the number of moles of ethylbenzene converted *per* mole of Al *per* second, were determined at a WHSV value of 15 h^{-1} . At a fixed contact time, hierarchical nano-zeolites reveal higher TOF values compared to their purely microporous counterparts (see Table 1). Assuming relatively similar acid strength, these profiles affirmed the expected enhanced molecular diffusion in ultra-thin crystals (< 10 nm) compared to conventional micrometer-sized ones.

ARTICLE

Catalytic results confirmed that we generated nanosponge zeolites with easier access to the acid sites. Over the bulk zeolites, the TOF (at 15 h^{-1} WHSV) followed the order MFI (0.24) < *MRE (0.35) < MTW (0.50). In principle, a 3-D channel system enables a faster diffusion of organic molecules. Nevertheless, the involved molecules are believed to experience higher diffusion hindrance inside the 20-µm long bulk-MFI crystals compared to the only 2-µm long MTW and *MRE crystals (Fig. 2). The ethylbenzene hydroconversion may be significantly limited to the outer part of the MFI zeolite crystals. As only a smaller part of the protonic sites may participate in the reaction, it seems reasonable that bulk-MFI shows the lowest TOF value. On the other hand, the sequence in the nanosponge counterparts is quite different, *MRE (0.65) < MTW (0.76) < MFI (1.10). The MFI pair exhibited the most striking activity discrepancy. Furthermore, these results suggest that our nanosponge zeolites provide easier access to the acid sites.

3.2.2. Xylene isomers distribution Shape-selectivity of the micropore channels often plays a critical role in the selectivity toward *p*-xylene. The change in the *para*-selectivity in the xylene mixture was plotted against conversion (Fig. 4). For each catalyst, the *p*-selectivity shows the tendency to converge to the thermodynamic equilibrium value at higher conversion degrees. In the case of bulk-*MRE, the mixture of xylenes is remarkably richer in the *p*-isomer, attaining ca. 90%, at an early stage of the reaction. This isomer distribution highlights the shape-selective properties of the *MRE-type narrow channel system, in which the less bulky p-isomer (6.7 Å) is preferred over m- and o-xylene dimensions of 7.1 and 7.4 Å, respectively.^{48,49} The critical size of *p*-xylene further corroborates the occurrence of the catalytic reaction within the *MRE microporous network. Interestingly, this selectivity pattern was not observed with our nano-*MRE. The thickness of the nano-zeolite (about 10 nm) is likely unable to generate transition-state and diffusion shape-selectivity responsible for the hampered formation of both *m*- and *o*-isomers. Diffusion pathways of a certain length are needed to increase the paraselectivity, which may not be fulfilled in micro-mesoporous zeolites.^{3,50} The steric hindrance was also evidenced over bulk-MFI as conspicuously reported for the transformation of alkylaromatics, e.g., toluene disproportionation and alkylation, and corroborated by molecular dynamics simulations. 51,52,53 Despite similar a 10-R pore size, bulk-*MRE and bulk-MFI exhibited distinct para-selectivity at low conversion degrees, 90% and 70%, respectively. The lower propensity over bulk-MFI may be tentatively explained based on the findings of Llopis et al.⁵¹ The presence of cavities or interconnections is believed to allow consecutive reactions that lead to the thermodynamic equilibrium, and consequently lower pselectivity. Conversely, direct channels (*MRE) allow diffusion without trapping if their free diameter is large enough. Surprisingly, no noticeable changes in the xylene distribution were observed over bulk- and nano-MTW with 12-R channels. With both catalysts the para-selectivity is only ca. 30% at the initial reaction stages. Whereas MTW is a relatively narrow 12R zeolite, the slightly divergent diameters, as compared to both MFI and *MRE, appear to be sufficient to generate a notable difference in the xylene distribution over both solids.

Catalytic selectivity During the simultaneous 3.2.3. hydroisomerization of xylene and ethylbenzene, the latter can undergo other reactions along with the desired formation of xylenes. All reactions products were carefully identified by gas chromatography to gain advanced insight into the impact of decreased crystal thickness and pore topology on the shapeselective ability of the studied zeolites. Fig. 5 illustrates a simplified scheme of the ethylbenzene intramolecular hydroisomerization mechanism and considers the main side reactions based on the obtained catalytic results as follows: (1) the disproportionation of ethylbenzene into benzene and diethylbenzene; (2) transalkylation of ethylbenzene and xylenes, leading to ethyltoluene/toluene and to benzene/dimethylethylbenzene; (3) dealkylation followed by hydrogenation of ethylene; and (4) bifunctional hydrocracking into light C₃-C₈ hydrocarbons following an initial naphthene ring opening step. With every tested sample, at low contact times, only hydrogenation products could be observed. This result reflects the activity of the metallic phase, and corresponds to the catalytic behavior of an individually tested zeolite-free catalyst containing only Pt/Al₂O₃. Methane could not be observed, confirming the absence of monofunctional hydrogenolysis over platinum sites. The result further highlights the achieved balance between the acidic and metallic functions of these ideal bifunctional catalysts. The consecutive disproportionation of xylenes, the formation of C₅-C7 naphthenes and heavy aromatic products, or the transalkylation of ethylbenzene with other alkylbenzene species were confirmed to be minor in each case. Aromatization and oligomerization reactions were not taken into account assuming that all C2 resulted from dealkylation of ethylbenzene. The performance of the individual zeolitic topology is discussed below at the same conversion levels for each zeolite topology (Fig. 6).

*MRE topology This zeolite showed similar selectivity trends for both bulk and nano crystals in the scoped conversion range. In the hydroisomerization, higher selectivity towards the formation of xylenes (up to ca. 95%) was attained over nano-*MRE (Fig. 6). At an early stage of the reaction, the nanozeolite proved highly advantageous compared to the bulk-*MRE, enhancing the initial hydroisomerization reaction rate 2.6-fold (Fig. S5, ESI⁺). A higher number of exposed protonic sites, which was deduced from a 5-fold increase of the external surface area of nano-*MRE compared to bulk-*MRE (from 76 up to 354 m^2/g), is believed to be favorable for higher xylenes selectivity. Indeed, similar observations were reported for industrially applied EUO and other 10-R zeolites.^{12,13} In each case, the improved selectivity towards hydroisomerization was associated with the presence of highly accessible acid sites, which are most likely located close to the external surface, in the pore mouths and in the exposed side pockets. The *auasi*isolation of acid sites, the easy access by hydrogenated Published on 14 January 2016. Downloaded by University of York on 21/01/2016 14:44:57

Journal Name

cycloalkene intermediates, and short residence time in the micropore channels have been identified as potential key factors in this matter.⁹

While the concentration and accessibility of the acid sites define the conversion rates, the proximity of protonic acid sites often presents a determining effect on the reaction product distribution.¹¹ In particular, low diethylbenzene selectivity has been ascribed to the high Si/Al molar ratio. An increase in the distance between the protonic sites at lower Al content favors the selectivity towards the formation of isomers at the expense of acid-catalyzed reactions which demand more than one protonic acid site (e.g., disproportionation and transalkylation). The density of acid sites has been underlined as the crucial parameter directing the disproportionation rate, while the acidic strength has apparently no effect.⁵⁴ In a context of high acid sites accessibility, the choice of low Al content should hence be of primary interest to reduce xylene losses by diethylbenzene formation.

A lower propensity to dealkylation was also confirmed in the presence of nano-*MRE (<1%). Based on the current data, the 5-fold increase of the external surface area in nano-*MRE may serve as a tentative explanation. We may expect that Brønsted acid sites located on the exposed framework can be less strained from the perfect tetrahedral geometry and therefore can form weaker acid centers. In that case, the nano-*MRE would possess fewer strong acid sites compared to its bulk counterpart. Nevertheless, the dealkylation reaction is supported by strong acids centers that are necessary for the formation of a very unstable ethyl carbenium ion $CH_3-CH_2^{+,55}$

Multi-step reactions notably depend on the reaction temperature and contact time of the molecular species with the acid surface.⁵⁶ Herein, ethylbenzene underwent transalkylation and hydrocracking at a higher extent at higher conversion degrees. Multi-step reactions occurring in the 10-R channels of bulk-*MRE crystals suffered from higher diffusive restrictions in comparison with reactions proceeding in the 10nm-thick crystals of nano-*MRE. Among the side reactions studied here, the reduced crystal thickness had the most striking impact on hydrocracking. At ca. 50% conversion, the selectivity of light hydrocarbon by-products was decreased from 11% to 2% for bulk and nano-*MRE, respectively. Overall, the result was quite notable since over bulk-*MRE, the involved molecules are believed to experience diffusion hindrance inside the mere 2-µm long channels. The hydrocracking products were rich in paraffins with 3, 4 and 5 carbon atoms even at high degrees of conversion (Fig. S6, ESI⁺). The obtained distribution was symmetrically centered around half of the original molecule (8 carbon atoms), although it is visually disturbed by a higher ethane formation caused by ethylbenzene dealkylation. The result shows a similarity between the theoretical molar carbon number distribution of cracked products and the ideal hydroconversion of a considered *n*-paraffin.⁸ An ideal hydroconversion catalyst achieves the balance between a number and an activity or strength of a metal and acid sites in the absence of striking steric hindrances.⁵⁷⁻⁵⁹ The results thus corroborate the sufficient content of the metallic function and mutual distance between the two catalytic functions, which indicates that the Weisz's intimacy criterion is respected. The almost entire absence of aliphatic compounds with ≥ 6 carbons further supports the lack of oligomerization reactions.

MFI topology The MFI-type zeolites exhibited an obviously distinct catalytic behavior based on different crystal thickness (Fig. 6). Over the purely microporous bulk-MFI, a notable maximal selectivity (65%) towards dealkylation was observed at 42% conversion. The stoichiometry between benzene and ethane seemed, however, not to be respected as lower amounts of the C_2H_6 were consistently determined. This mismatch may indicate that ethylene undergoes rapid secondary transformations, e.g., aromatization, before the hydrogenation of the C₂ species over the platinum sites occurs.^{3,60} When high dealkylation rates are witnessed, transalkylation or disproportionation of alkylaromatics can further proceed not only via a bimolecular mechanism involving diphenylalkane intermediates but also through dealkylation-realkylation pathways, which include free olefins.^{56,61} This appears to be the case for bulk-MFI as indicated by the significant maintenance in the diethylbenzene selectivity, ca. 72% at 5% conversion. This particular selectivity towards dealkylation and disproportionation has been attributed to the presence of strong acid sites and confinement effects in the MFI-type architecture. Conversely, the presence of spacious intersections of the 3-D pore system (8.6 Å) connected to narrow 10-R channels is known to be disadvantageous for the hydroisomerization of ethylbenzene.¹³

At ca. 50% conversion, the maximal attained hydroisomerization selectivity was merely 17%. When compared with the bulk-*MRE with 82% selectivity at a similar conversion degree, the bulk-MFI was confirmed to be a poor hydroisomerization catalyst. This behavior reflects the outlined industrial acceptance of MFI-type zeolite when the isomerization of xylenes is preferentially accompanied by the transformation of ethylbenzene into valuable products by disproportionation (acid process) or dealkylation (bifunctional process).⁶² Herein, the selected operating conditions (high temperature) are believed to favor the dealkylation mechanism.⁵⁶ In agreement, single-event microkinetic methodology applied towards the transformation of ethylbenzene on a Pt/H-MFI zeolite catalyst confirmed that dealkylation was energetically most demanding (194 kJ mol⁻¹) compared to alkyl shift and transalkylation reactions (134 and 125 kJ mol⁻¹, respectively).⁶³

The ultra-thin crystals of nano-MFI led to an impressive boost in selectivity towards hydroisomerization with 71% selectivity at ca. 50% conversion (Fig. 6, Fig. S5, ESI[†]). Based on the previous studies, ca. 30% of the Brønsted acid sites are located at the external surface of the MFI nanosponge.^{39,44,52} The desired accommodation of the aromatic species at the channel intersections, where the strong protonic sites are located in bulk-MFI, was somehow lost. In addition, rapid molecular diffusion through the MFI nanostructure is believed to favor the reaction towards the formation of xylenes. In this Published on 14 January 2016. Downloaded by University of York on 21/01/2016 14:44:57

context, our MFI nanosponge represents a valuable hydroisomerization catalyst in the simultaneous transformation of ethylbenzene and xylenes with improved molecular transport compared with the purely microporous bulk-zeolite.

Fig. 6 confirms a continuous increase in the hydrocracking selectivity with conversion with both MFI-type zeolites. As molecular diffusion was highly affected in the case of bulk-MFI, it can only be expected that long contact times would lead to higher formation of light hydrocarbon by-products. Following the first naphthene ring opening step, the resultant long-chain alkyl species are assumed to rapidly undergo hydrocracking inside the MFI zeolite. In both cases the hydrocracked product spectrum clearly differs from the theoretical molar carbon number distribution for ideal hydroconversion catalysts (Fig. S6, ESI[†]). The impact of pore dimensionality on the product selectivity in the hydroconversion of paraffins with MFI-based catalysts has been comprehensively discussed in the literature.⁶⁴⁻⁶⁶ The large interconnections within the zeolite structure would allow the formation of bulky alkyl-branched species that are unable to diffuse out of narrow 10-R pores.

Under the selected conditions, nano-MFI and nano-*MRE showed strikingly different hydroisomerization selectivity over the evaluated conversion range. Conversely, nano-MFI revealed higher ethylbenzene disproportionation (12% vs. 1%), dealkylation (4% vs. 0.5%), and hydrocracking selectivity (14% vs. 2%) at the same conversion degree (ca. 50%) (Fig. 6). Hence intrinsic preferential reaction mechanisms in ultra-thin nanocrystals appear to still depend on the zeolite pore dimensionality even when very similar pore-sizes are considered (5.1×5.5 Å in MFI vs. 5.3×5.6 Å in *MRE). We believe that this divergence reflects the molecular confinement provided through a single layer of narrow 3-D interconnections in the MFI nanosponge (Fig. 2). The framework termination in the b crystallographic direction with narrow 10-membered rings has been thought essential for the shape-selectivity of ultra-thin MFI crystals applied in the hydroconversion of *n*-decane.⁶⁷ Our results seem to corroborate this assumption. The nano-MFI appears able to retain its shape-selectivity up to a certain extent in the hydroconversion of ethylbenzene. This result is of particular interest if the decrease of the crystal thickness is optimized to achieve higher catalytic stability and activity while simultaneously affording the desired selectivity in a wide multitude of reactions involving the hydroconversion of alkylaromatics.

MTW topology The trend in xylenes formation over both MTWtype zeolites was comparable (Fig. 6). Higher maximal hydroisomerization selectivity was attained over the nanosponge (91% over nano vs. 83% over bulk) enhancing the initial reaction rate 1.8-fold (Fig. S5, ESI[†]). Similarly to the aforementioned cases, the catalytic benefit of reducing the zeolite crystal thickness was evident also with the MTW topology. Experimental results demonstrated that a decrease of the crystal thickness in nano-MTW could suppress the occurrence of multi-step reactions. In particular, at 80% conversion bulk-MTW showed higher selectivity to transalkylation (5% vs. 3%) and hydrocracking (8% vs. 4%) compared to nano-MTW. The bulk-MTW catalyst displayed a product spectrum with substantial amounts of hydrocracking products reflecting a theoretical carbon number distribution for ideal hydroconversion catalysts (Fig. S6, ESI[†]).

The bulk-MTW zeolite exhibits a conspicuous selectivity toward disproportionation with diethylbenzene formation. This tendency (selectivity 25%) was better illustrated compared with the bulk-*MRE sample (with selectivity 8%) at the initial stages of the reaction. The pore size of both zeolites is believed to play a key role. The assumption is corroborated by the striking divergence of the attained para-selectivity of xylenes with 90% over bulk-*MRE and 30% over bulk-MTW at an early stage of the reaction (Fig. 4). During the transformation of the involved alkyl-aromatic species, the larger MTW channel system facilitated the formation and diffusion of the involved species in the monomolecular ethyltransfer reaction pathway. These 12-R pores may further accommodate the demanded bulky transition-state needed for the bimolecular disproportionation of ethylbenzene. The assumption has been widely explored in the presence of MORtype 1-D 12-R channels applied in the simultaneous xylene and ethylbenzene industrial hydroisomerization.11,15,16,54 Whereas transalkylation or disproportionation of alkyl-aromatics can proceed via a dealkylation/alkylation mechanism, as suggested with our bulk-MFI, bimolecular reactions are likely to occur inside larger channels.⁶⁸ The reaction was shown to proceed via a carbocation chain mechanism involving the benzylic carbocation and diarylmethane intermediates.⁵⁶ Lower Si/Al ratio suggesting higher acid density is, however, further believed to play a role in the increasing diethylbenzene formation. Conversely, our nano-MTW was able to restrain the formation of diethylbenzene with selectivity ca. 3% below 10% conversion. Nonetheless, disproportionation occured to a higher extent than over the 10-R nano-*MRE. In spite of the similar channel length provided by these <10 nm-thick nanocrystals. the catalytic behavior of ultra-thin aluminosilicates with similar acidity was still believed to be dependent on the varying zeolite pore aperture size. In this context, larger pore size though appears to have a minor impact in the attained hydrocracking and dealkylation selectivity when both 1-D channel nanosponge zeolites (MTW, *MRE) are compared. Furthermore, the similar profiles obtained with both zeolites suggest an impact of the pore size at a significantly lower extent compared to the effect of pore dimensionality observed with our MFI nanosponge. High selectivity towards hydroisomerization has been reported to be a particular feature of exposed protonic sites located in the pore-mouths and exposed side-pockets of tubular 10-R ${\sf zeolites.}^{12,13}$ Nonetheless, the present results proved that within highly accessible 1-D 12-R zeolites, a remarkable xylene selectivity (92%) can also be achieved as demonstrated with our nanosponge MTW.

Conclusions

Catalysis Science & Technology Accepted Manuscript

Journal Name

Herein, we synthesized a series of nanosponge zeolites with topologies *MRE, MFI, and MTW, and their bulk counterparts. The nanosponge-zeolites possess, in addition to their intrinsic microporous architecture, a significant volume of intercrystalline mesoporosity with a narrow size distribution. For the first time they were investigated in the gas-phase hydroconversion of ethylbenzene (EB) in the presence of a hydrogenating phase (Pt/Al₂O₃). Improved catalytic activity compared to bulk zeolites suggested an enhanced molecular transport within zeolitic crystals, which is a challenging industrial sidestep for the hydroconversion of alkyl-aromatic species. A lower confinement effect inside these nanosponge zeolites proved to be unique to increase the xylene formation. This effect was further reflected on the selectivity to pxylene and on the selectivity towards ethylbenzene dealkylation, disproportionation, transalkylation, and hydrocracking (see Fig. 7). In particular, when the MFI crystal thickness is decreased from 20 μ m to 2.5 nm, a remarkable performance is observed when the simultaneous hydroisomerization of xylenes and ethylbenzene is desired.

Assuming relatively similar acidity, we attributed the divergence in the product selectivity to the pore size and channel dimensionality of ultra-thin nanosponge zeolites. We observed a dramatic impact of the presence of spacious interconnections within narrow 10-R channels (MFI zeolite) on the resulting product selectivity compared to straight channels in *MRE and MTW. Conversely, this work emphasizes ultra-thin zeolites with tubular-like micropores, exhibiting outstanding maximal isomer product yields, as catalysts of choice when ethylbenzene is preferentially hydroisomerized.

Whereas EB has a crucial impact in the choice of the zeolite applied in the hydroconversion of the C₈ aromatic, this work additionally sheds light on the study of five catalytic reactions of major industrial interest in the transformation of alkylaromatic species over ultra-thin nanosponge zeolites. Accordingly, it serves as a new effort in understanding the shape-selectivity provided by <10 nm zeolite crystals, to further define and improve their potential utility in a wide number of applications.

Acknowledgements

This work was supported by IBS-R004-D1.

References

- 1 T.-C. Tsai, S.-B. Liu and I. Wang, *Appl. Catal. A Gen.*, 1999, **181**, 355.
- 2 J.J. Jeanneret, C.D. Low and V. Zukauskas, *Hydrocarb. Process*, 1994, **6**, 43.
- S. Al-Khattaf, S. a. Ali, A.M. Aitani, N. Žilková, D. Kubička and J. Čejka, *Catal. Rev. Sci. Technol.*, 2014, 56, 333.
- 4 W. Vermeiren and J.-P. Gilson, *Top. Catal.*, 2009, **52**, 1131.
- 5 J.S. Buchanan, X. Feng, G.D. Mohr and D.L. Stern, European Patent 1,620,374 B1, 2011.
- 6 S.B. Sharma, S.V. Gurevich, B.D. Riley and G.A. Rosinski, U.S. Patent 6,143,941, 2000.
- 7 T.-C. Tsai, I. Wang, C.-K. Huang and S.-D. Liu, *Appl. Catal. A Gen.*, 2007, **321**, 125.

- E. Guillon, S. Lacombe, T. Sozinho, P. Magnoux, S. Gnep, P. Moreau and M. Guisnet, *Oil Gas Sci. Technol.*, 2009, 64, 731.
 M. Guisnet, *Catal. Today*, 2013, 218, 123.
- 10 E. Guillon and L. Brandhorst, U.S. Patent 2014/0135550 A1, 2014.
- 11 L.D. Fernandes, J.L.F. Monteiro, E.F. Sousa-Aguiar, A. Martinez and A. Corma, *J. Catal.*, 1998, **177**, 363.
- 12 F. Moreau, P. Moreau, N.S. Gnep, P. Magnoux, S. Lacombe and M. Guisnet, *Microporous Mesoporous Mater.*, 2006, **90**, 327.
- 13 P. Moreau, N.S. Gnep, P. Magnoux, E. Guillon, S. Lacombe and M. Guisnet, *Stud. Surf. Sci. Catal.*, 2008, **174**, 1179.
- 14 Y.S. Hsu, T.Y. Lee and H.C. Hu, *Ind. Eng. Chem. Res.*, 1988, **27**, 942.
- 15 C. Travers, F. Raatz, C. Marcilly, F. Ramôa Ribeiro and M.F. Gomes Ribeiro, European Patent 0,363,253, 1989.
- 16 F. Moreau, N.S. Gnep, S. Lacombe, E. Merlen and M. Guisnet, Ind. Eng. Chem. Res., 2002, 41, 1469.
- 17 H.H. John, H.D. Neubauer and P. Birke, *Catal. Today*, 1999, **49**, 211.
- 18 W. Souverijns, L. Rombouts, J.A. Martens and P.A. Jacobs, *Microporous Mater.*, 1995, **4**, 123.
- 19 J.L. Casci, B.M. Lowe and T.V. Whittam, U.S. Patent 4,537,754, 1985.
- 20 R. Ryoo, K. Cho and F. Marques Mota, "Mesostructured zeolites", in *Sustainable Chemistry: Synthesis, Characterization and Catalytic Applications*, ed. F.-S. Xiao and X. Meng, Springer, 2015, ch. 4, p. 101.
- 21 C.J.H. Jacobsen, C. Madsen, J. Houzvicka, I. Schmidt and A. Carlsson, J. Am. Chem. Soc., 2000, **122**, 7116.
- 22 M. Choi, H.S. Cho, R. Srivastava, C. Venkatesan, D.-H. Choi and R. Ryoo, *Nat. Mater.*, 2006, **5**, 718.
- 23 D. Verboekend and J. Pérez-Ramírez, *Catal. Sci. Technol.*, 2011, **1**, 879.
- 24 M. Milina, S. Mitchell, P. Crivelli, D. Cooke and J. Pérez-Ramírez, Nat. Commun., 2014, 5:3922, DOI: 10.1038/ncomms4922.
- 25 M.S. Holm, E. Taarning, K. Egeblad and C.H. Christensen, *Catal. Today*, 2011, **168**, 3.
- 26 A. Corma, V. Fornes, S.B. Pergher, T.L.M. Maesen and J.G. Buglass, Nature, 1998, **396**, 353.
- 27 I. Ogino, M.M. Nigra, S. Hwang, J. Ha, T. Rea, S.I. Zones and A. Katz, J. Am. Chem. Soc., 2011, **133**, 3288.
- 28 P. Eliášová, M. Opanasenko, P.S. Wheatley, M. Shamzhy, M. Mazur, P. Nachtigall, W.J. Roth, R.E. Morris and J. Čejka, *Chem. Soc. Rev.*, 2015, **44** (20), 7177.
- 29 W.J. Roth, P. Nachtigall, R.E. Morris, P.S. Wheatley, V.R. Seymour, S.E. Ashbrook, P. Chlubná, L. Grajciar, M. Položij, A. Zukal, O. Shvets and J. Čejka, *Nat. Chem.*, 2013, 5, 628.
- 30 W.J. Roth, P. Nachtigall, R.E. Morris and J. Čejka, *Chem. Rev.*, 2014, **114**, 4807.
- 31 M. V. Opanasenko, E. Montanari, M. V. Shamzhy, ChemPlusChem, 2015, **80**, 599.
- 32 M. Opanasenko, W.O.N. Parker, M. Shamzhy, E. Montanari, M. Bellettato, M. Mazur, R. Millini and J. Čejka, J. Am. Chem. Soc., 2014, 136, 2511.
- 33 M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki and R. Ryoo, *Nature*, 2009, **461**, 246.
- 34 K. Na, C. Jo, J. Kim, K. Cho, J. Jung, Y. Seo, R.J. Messinger, B.F. Chmelka and R. Ryoo, *Science*, 2011, **333**, 328.
- 35 C. Jo, K. Cho, J. Kim and R. Ryoo, *Chem. Commun.*, 2014, **50**, 4175.
- 36 Y. Seo, S. Lee, C. Jo and R. Ryoo, J. Am. Chem. Soc., 2013, 135, 8806.
- 37 K. Na, C. Jo, J. Kim, W.-S. Ahn and R. Ryoo, ACS Catal., 2011, 1, 901.
- 38 J. Kim, W. Park and R. Ryoo, ACS Catal., 2011, 1, 337.
- 39 Y. Seo, K. Cho, Y. Jung and R. Ryoo, ACS Catal., 2013, 3, 713.

DOI: 10.1039/C5CY02029H

Journal Name

Published on 14 January 2016. Downloaded by University of York on 21/01/2016 14:44:57

- 40 M. V. Opanasenko, M. V. Shamzhy, C. Jo, R. Ryoo and J. Čejka, *ChemCatChem*, 2014, **6**, 1919.
- 41 J. Jung, C. Jo, F. Marques Mota, J. Cho and R. Ryoo, *Appl. Catal. A Gen.*, 2015, **492**, 68.
- 42 K.V. Agrawal, X. Zhang, L.F. Francis and M. Tsapatsis, Procedia Eng., 2012, 44, 198.
- 43 J.-C. Kim, S. Lee, K. Cho, K. Na, C. Lee and R. Ryoo, *ACS Catal.*, 2014, **4**, 3919.
- 44 J.-C. Kim, R. Ryoo, M. V. Opanasenko, M. V. Shamzhy and J. Čejka, ACS Catal., 2015, 5, 2596.
- 45 International Zeolite Association Home Page, 2014.
- 46 W. Kim, J. Kim, J. Kim, Y. Seo and R. Ryoo, ACS Catal., 2013, 3, 192.
- 47 A. Zukal and M. Kubů, Dalt. Trans., 2014, 43, 10558.
- 48 J.A. Martens, E. Sastre, A. Corma and P.A. Jacobs, Appl. Cotal., 1988, 45, 85.
- 49 J. Dewing, J. Mol. Catal., 1984, 27, 25.
- 50 Z. Musilová, N. Žilková, S.-E. Park and J. Čejka, Top. Catal., 2010, 53, 1457.
- 51 F. Llopis, G. Sastre and A. Corma, J. Catal., 2004, 227, 227.
- 52 C. Jo, R. Ryoo, N. Žilková, D. Vitvarová and J. Čejka, *Catal. Sci. Technol.*, 2013, **3**, 2119.
- 53 L. Zhang, J. Gao, J. Hu, W. Li and J. Wang, *Catal. Letters*, 2009, **130**, 355.
- 54 F. Moreau, S. Bernard, N.S. Gnep, S. Lacombe, E. Merlen and M. Guisnet, J. Catal., 2001, 202, 402.
- 55 H.G. Karge and J. Ladebeck, Stud. Surf. Sci. Catal., 1980, 5, 151.
- 56 H.G. Karge, J. Ladebeck, Z. Sarbakt and K. Hatada, *Zeolites*, 1982, **2**, 94.
- 57 C. Bouchy, G. Hastoy, E. Guillon and J.A. Martens, Oil Gas Sci. Technol. - Rev. l'IFP, 2009, **64**, 91.
- 58 J.W. Thybaut, C.S.L. Narasimhan, J.F. Denayer, G. V. Baron, P.A. Jacobs, J.A. Martens and G.B. Marin, *Ind. Eng. Chem. Res.*, 2005, 44, 5159.
- 59 P. Mériaudeau, V.A. Tuan, V.T. Nghiem, G. Sapaly and C. Naccache, J. Catal., 1999, **185**, 435.
- 60 V.S. Nayak and V.R. Choudhary, Appl. Catal., 1984, 9, 251.
- 61 J.M. Silva, M.F. Ribeiro, F. Ramôa Ribeiro, E. Benazzi and M. Guisnet, Appl. Catal. A Gen., 1995, 125, 1.
- 62 F.G. Dwyer, N.Y. Chen and W.E. Garwood, "Shape Selective Catalysis in Industrial Applications", in *Chemical Industries*, Marcel Dekker, 1989, vol. 6.
- 63 K. Toch, J.W. Thybaut, B.D. Vandegehuchte, C.S.L. Narasimhan, L. Domokos and G.B. Marin, *Appl. Catal. A Gen.*, 2012, **425**, 130.
- 64 J.A. Martens and P.A. Jacobs, Zeolites, 1986, 6, 334.
- 65 J. Weitkamp, P.A. Jacobs and J.A. Martens, *Appl. Catal.*, 1983, **8**, 123.
- 66 J.A. Martens, R. Parton, L. Uytterhoeven, P.A. Jacobs and G.F. Froment, *Appl. Catal.*, 1991, **76**, 95.
- 67 E. Verheyen, C. Jo, M. Kurttepeli, G. Vanbutsele, E. Gobechiya, T.I. Korányi, S. Bals, G. Van Tendeloo, R. Ryoo, C.E.A. Kirschhock and J.A. Martens, J. Catal., 2013, **300**, 70.
- 68 J. Huang, Y. Jiang, V.R.R. Marthala and M. Hunger, J. Am. Chem. Soc., 2008, 130, 12642.

Tables

Table 1 Physicochemical properties of bulk and nanosponge zeolites and corresponding TOF for the hydroisomerization of ethylbenzene

| Sample | Surface area (m² g⁻¹) | | V_{total} | (c;/ʌl)* | Turn-over frequency, |
|-----------|-----------------------|----------|------------------------------------|----------|---|
| | BET | External | (cm ³ g ⁻¹) | (31/AI) | TOF (s ⁻¹) at WHSV value 15 h ⁻¹ |
| bulk-*MRE | 173 | 76 | 0.129 | 99 | 0.35 |
| nano-*MRE | 468 | 354 | 0.785 | 100 | 0.65 |
| bulk-MFI | 307 | 21 | 0.141 | 82 | 0.24 |
| nano-MFI | 614 | 383 | 0.630 | 90 | 1.10 |
| bulk-MTW | 224 | 48 | 0.116 | 75 | 0.50 |
| nano-MTW | 441 | 276 | 0.420 | 103 | 0.76 |

*determined by ICP

Figures



Fig. 1. Representative illustrations of the porous channel system of *MRE, MFI, and MTW zeolites.



Fig. 2. SEM images of (a) *MRE, (b) MFI, and (c) MTW conventional zeolite samples and of corresponding nanosponge counterparts (d, e and f). TEM images of (g) nano-*MRE, (h) nano-MFI and (i) nano-MTW.

Published on 14 January 2016. Downloaded by University of York on 21/01/2016 14:44:57.



Fig. 3. Ethylbenzene conversion against contact time taken as the reverse of WHSV over the bulk (\blacklozenge) and nanosponge samples (\diamondsuit) with *MRE, MFI, and MTW-type zeolites. (\blacklozenge , \bigcirc) Corresponding back-points at the end of the catalytic test at a WHSV=15 h⁻¹.



Fig. 4. *p*-Xylene content (mol %) against conversion over the bulk (\blacklozenge) and nanosponge samples (\diamondsuit) with *MRE, MFI, and MTW-type zeolites.



Fig. 5. Illustration of a simplified reaction scheme of ethylbenzene hydroisomerization and the main side reactions considered in this contribution: **1** ethylbenzene disproportionation, **2** ethylbenzene transalkylation with xylene, **3** ethylbenzene dealkylation and **3** hydrocracking following naphthene ring opening.

Catalysis Science & Technology

View Article Online DOI: 10.1039/C5CY02029H

Page 12 of 13



Fig. 6. Comparison of the selectivity towards hydroisomerization, dealkylation, disproportionation, transalkylation and hydrocracking against conversion over the bulk (\blacklozenge) and nanosponge samples (\diamondsuit) with (a) *MRE, (b) MFI and (c) MTW-type zeolites.



Published on 14 January 2016. Downloaded by University of York on 21/01/2016 14:44:57.

Fig. 7. Comparison of the selectivity towards hydroisomerization, dealkylation, disproportionation, transalkylation and hydrocracking at ca. 50% conversion over *MRE, MFI and MTW-type bulk and nanosponge zeolites.



55x30mm (300 x 300 DPI)