Supplementary information

Synthesis of Hierarchical ZSM-48 Nano-Zeolites

Amir Astafan[a,b,c], Mohammed Amine Benghalem[c], Laure Michelin[a,b], Severinne Rigolet[a,b], Joël Patarin[a,b], Ludovic Pinard[c,*] and T. Jean Daou[a,b**]

[a.] *Université de Haute Alsace (UHA), CNRS, Axe Matériaux à Porosité Contrôlée (MPC), Institut de Science des Matériaux de Mulhouse (IS2M), UMR 7361, 68093 Mulhouse, France*

[b.] *Université de Strasbourg, France*

[c.] *Institut de Chimie des Milieux et Matériaux de Poitiers, UMR 7285 CNRS, 86073 Poitiers Cedex 9 France*

[*] *Corresponding author: * ludovic.pinard@univ-poitiers.fr; ** jean.daou@uha.fr, Telephone number: * + 33 5 49 45 39 05, **+33 3 89 33 67 39, Fax number: **+33 3 89 33 68 85*

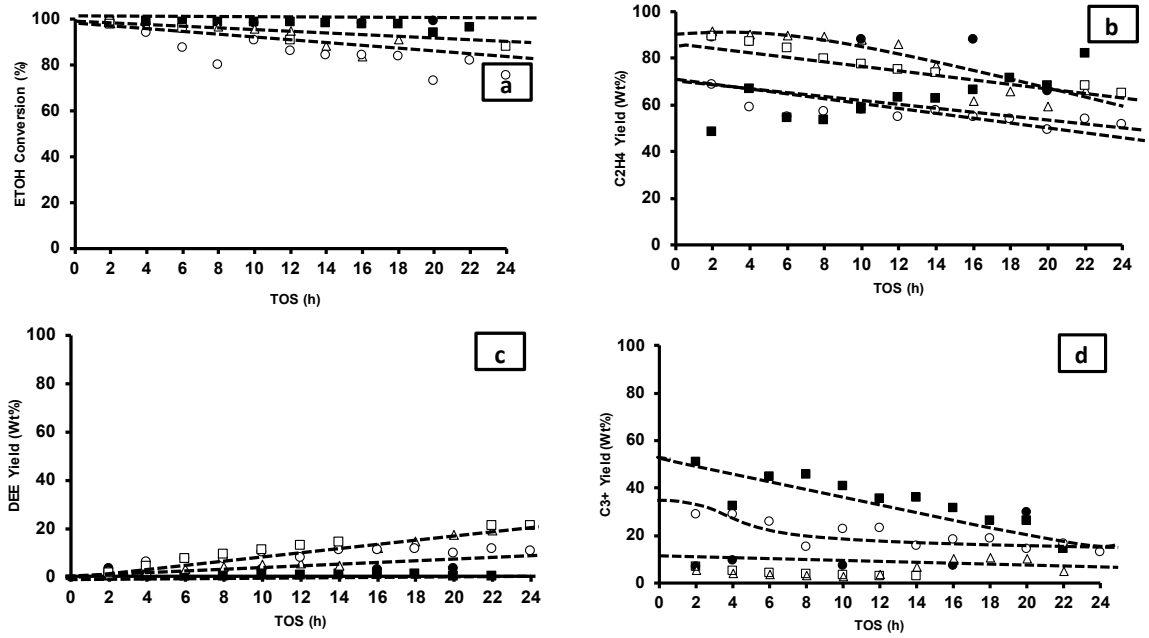

Fig.SI.1. : Ethanol conversion (a) and yield into ethylene(b), diethyl-ether (c) and hydrocarbons (C_3+) (d) as a function of time-on-stream, for the *MRE-type zeolites with different Si/Al molar ratio : $S_{0.016\text{-}7}$ (●), $S_{0.012\text{-}4}$ (■), $S_{0.01\text{-}4}$ (▵), $S_{0.012\text{-}7}$ (○) and $S_{0.01\text{-}7}$ (▫).

Note that the mass yield of a certain product (or products group) is given by the following equation:

$$Y_j = \frac{\sum_j a_j}{\sum_i a_i}$$

, Yi, product or group of product mass yield (wt. %), aj : product or group of products GC peak area, ai: all the GC peak areas

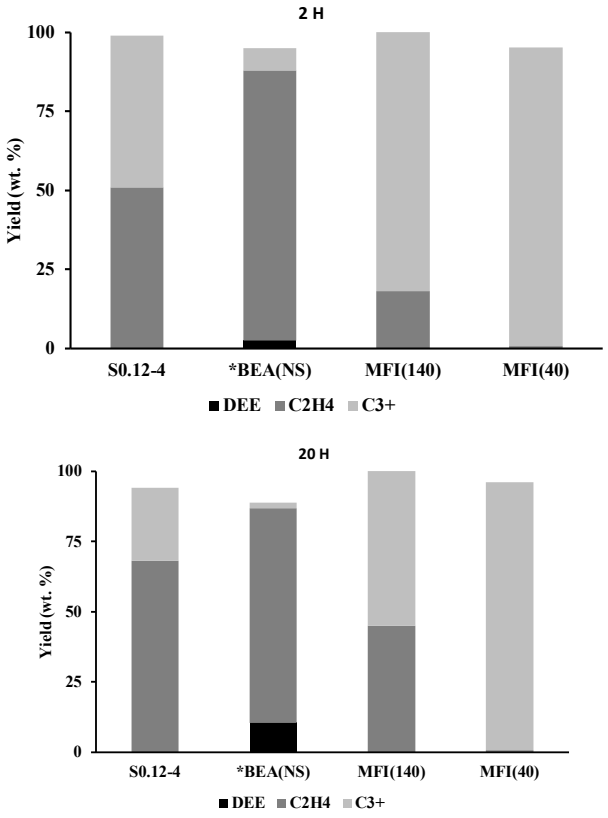

Fig. SI. 2 Ethanol transformation at 350 °C and 30 bar: Ethanol conversion (a), weight yields of C_2H_4 , DEE (diethyl ether) and C_{3+} hydrocarbons after 2 h and 20 h of reaction, for the *MRE-type zeolites $S_{0.012\text{-}4}$, *BEA-type nanosponges zeolites [1,2], MFI-type zeolite with 2 different frameworks Si/Al molar ratio (40 and 140) [3] catalysts.

Table SI.1. The structure directing agent used for the synthesis of *MRE-type zeolites, the textural properties of the calcined *MRE-type zeolite samples and their applications (a comparison between our results and some results found in the literature).

Samples & References	**Structure directing agent**	**S_{BET} [b] ($m^2.g^{-1}$)**	**V_{micro} [c] ($cm^3.g^{-1}$)**	**V_{meso} [d] ($cm^3.g^{-1}$)**	**d_{meso} (nm)**	**Application**
$S_{0.01-4}$ (our work)	$N_{4\text{-phe}}$ [e]	720	0.24	0.70	6	Ethanol transformation into hydrocarbons
$S_{0.012-4}$ (our work)		770	0.24	0.74	6	
$S_{0.01-7}$ (our work)		580	0.18	0.46	8	
$S_{0.012-7}$ (our work)		600	0.20	0.54	8	
$S_{0.016-7}$ (our work)		670	0.20	0.60	8	
Conventional ZSM-48 [4]	HMBr[f]	288	0.16	0.08	-	Non application mentioned
Hierarchical ZSM-48 (Nano-stick crystals) [4]	TPDAC[g] + HMBr[f]	373	0.14	0.21	2-4	
Hierarchical ZSM-48 (Nano-stick crystals) [4]		417	0.13	0.31	2-4	
Conventional ZSM-48 [5,6]	HMBr[f]	160	0.12	0	-	Isopropylation of benzene
Hierarchical ZSM-48 (Nanosponges) [5,6]	C_{18}-N_6-C_{18} [h]	380	0.08	0.27	4.7	
Conventional ZSM-48 [7]	HDA[i]	301	n.d.	n.d.	-	C_4-olefin

craking

[a] Deduced from XRD analysis
[b] Specific surface area measured by BET.
[c] micropore volume calculated by using *t*-plot method.
[d] Mesopore volume =V_{total}-V_{micro} (V_{total}: determined from the adsorbed volume at $p/p_0 = 0.90$).
[e] $N_{4\text{-phe}}$: $(C_{22}H_{45}N^+(CH_3)_2C_6H_{12}N^+(CH_3)_2CH_2pC_6H_4CH_2N^+(CH_3)_2C_6H_{12}N^+(CH_3)_2C_{22}H_{45}(Br^-)_2(Cl^-)_2)$
[f] HMBr : hexamethonium bromide
[g] TPDAC : [3-(trimethoxysilyl)propyl] dodecyldimethylammonium chloride
[h] C_{18}-N_6-C_{18} : $(C_{22}H_{45}N^+(CH_3)_2C_6H_{12}N^+(CH_3)_2CH_2C_6H_4CH_2N^+(CH_3)_2C_6H_{12}N^+(CH_3)_2CH_2C_6H_4CH_2N^+(CH_3)_2C_6H_{12}N^+(CH_3)_2C_{22}H_{45}(Br^-)_2(Cl^-)_4)$
[i] HDA: hexamethylenediamine
n.d.: not determined

Table SI. 2. Acidic properties of MFI and *BEA-type zeolite catalysts [1-3]

	MFI(40)	**MFI(140)**	***BEA(NS)**
$[PyH^+]$ ($\mu mol.g^{-1}$)	297	91	130
[PyL] ($\mu mol.g^{-1}$)	47	6	176

References:

1 A. Astafan, M.A. Benghalem, Y. Pouilloux, J. Patarin, N. Bats, C. Bouchy, T.J. Daou, L. Pinard, *J. Catal.,* 2016, **336**, 1-10.
2 A. Astafan, Y. Pouilloux, J. Patarin, N. Bats, C. Bouchy, T.J. Daou, L. Pinard, *New J. Chem.,* 2016, **40**, 4335-4343.
3 F.F. Madeira, K, Ben tayeb , L. Pinard, S. Maury, N. Cadran, Appl. Catal. A. Gen., **2012**, 443-444, 171-180.
4 X. Liu, X. Wang, Y. Wang, Y. Gong, T. Dou, *Advanced Materials Research*, 2012, **503-504**, 756-759.
5 W. Kim, J.C. Kim, J. Kim, Y. Seo, R. Ryoo, *ACS Catal.,* 2013, **3**, 192-195.
6 S. Lee, C. Jo, R. Ryoo, *J. Mater. Chem. A*, 2017, **5**, 11086-11093.
7 G. Zhao, J. Teng, Y. Zhang, Z. Xie, Y. Yue, Q. Chen, Y. Tang, Applied Catalysis A: General, 2006, 167-174.