

# First Acidic Macrocellular Aluminosilicate Monoliths "SiAl(HIPE)" and their Catalytic Properties

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## Electronic Supplementary Information (ESI)

## Full experimental details

### 2.1. Materials

#### *Preparation of Si(HIPE)<sup>1</sup>*

tetraethoxysilane ('TEOS', Aldrich, 98%) (5.02g) was added to a 30 wt. % aqueous solution of tetradecyltrimethylammonium Bromide ('TTAB', Fluka, 98%) (16 g). Then, a concentrated hydrochloric acid solution (37 wt. %) was added (6 g). The aqueous phase was stirred for approximately 5 min in order to perform TEOS hydrolysis. Then the emulsion was prepared manually in a mortar by including dodecane drop by drop (40g). The emulsion was transposed into a canister and left to age for one week at room temperature. The gel obtained was then washed, dried and calcined in the same way as the SiAl(HIPE).

#### *Preparation of SiAl(HIPE)*

Solution A: 5 g TEOS and 4.8g of TTAB were added to 35g of dodecane (Fluka, >98%). Solution B: 1.33g of an aqueous solution of tetrapropylammonium hydroxide ('TPAOH', 40% in water, Aldrich) and 0.43g aluminium isopropoxide ('Al(<sup>i</sup>OPr)<sub>3</sub>', ACROS Organics, 99.9%) were added in 15g of distilled water. Solution A was then added drop wise in solution B while stirring vigorously with a fork, until a stable emulsion is obtained. The latter is put to rest (ageing) for one week in ambient conditions (vial closed).

After ageing, it is put in an oven at 70°C for 2 hours. The self-standing gel is then washed three times with acetone/tetrahydrofuran mixtures (50:50 v/v) to remove the oil phase. It is then left to dry. The dried monolith is then calcined for 2h at 200°C (2°C/min) and then at 650°C for 6h (2°C/min). Their mechanical strength has not been determined experimentally but, to the skilled person, it appear to be in the same order or higher than that of Si(HIPE).

#### *Reference commercial aluminosilicate*

The reference commercial aluminosilicate is a commercially available powder available from Aldrich (Grade 135). This sample contains ca. 13 wt.% of Al<sub>2</sub>O<sub>3</sub> and has a specific surface area of 490 m<sup>2</sup> g<sup>-1</sup>. Full textural analysis is provided elsewhere.<sup>2</sup>

## 2.2. Characterization

Scanning electron microscopy (SEM) observations were performed with a Hitachi TM-1000 apparatus at 15 kV equipped with an energy dispersive X-ray spectroscopy (EDX) probe.

Specific surface areas and pore characteristics were obtained with a Micromeritics ASAP 2010 apparatus after degassing one night at 150°C under vacuum.

Intrusion/extrusion mercury measurements were performed using a Micromeritics Autopore IV porosimeters.

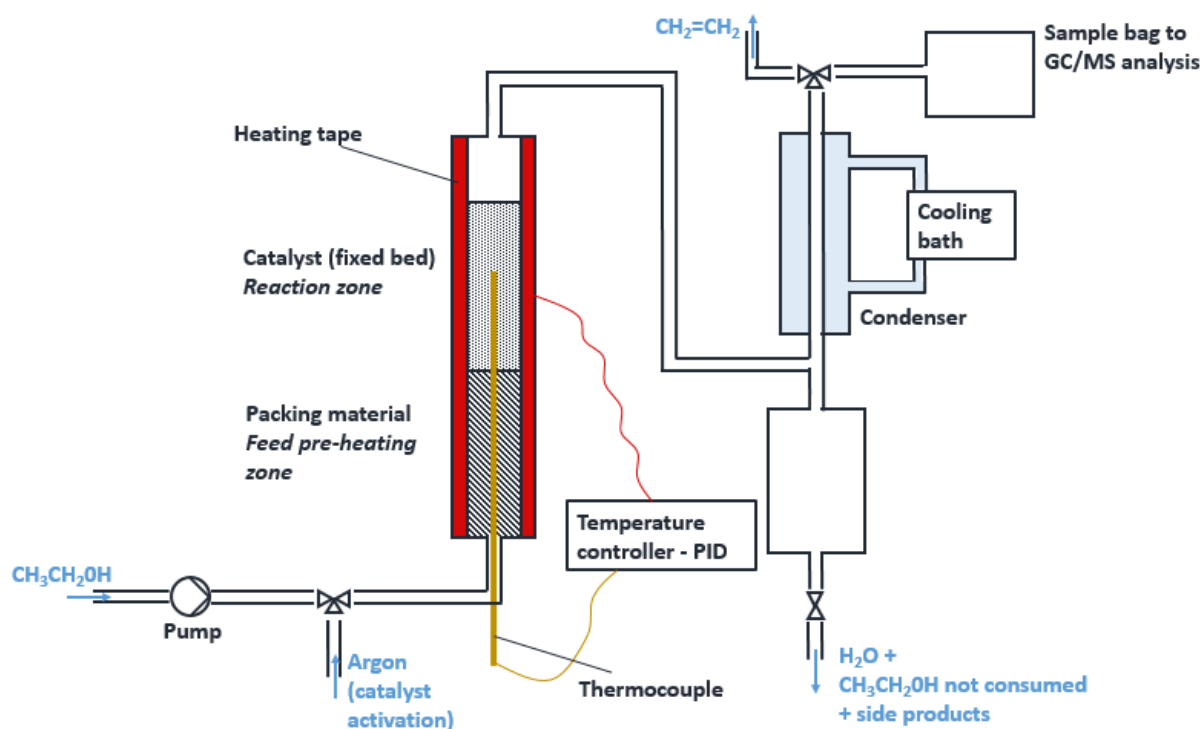
NH<sub>3</sub>-chemisorption was performed on a Micromeritics ASAP 2010C apparatus with the procedure described in details in reference.<sup>3</sup> Briefly, the total acidity is defined as the amount of NH<sub>3</sub> that remains chemisorbed upon evacuation down to  $6.6 \times 10^{-7}$  MPa at 50°C and the strong acidity is defined as the amount of NH<sub>3</sub> that remains chemisorbed upon evacuation down to  $6.6 \times 10^{-7}$  MPa at 150°C (medium acidity is obtained by difference).

For solid state NMR spectroscopy, <sup>29</sup>Si experiments were done on a 7 T Bruker Avance III spectrometer operating at 60 MHz with a 7 mm standard double resonance probe. Spinning rate of 5 kHz, 30 ° flip angle, 60 s recycling delay and 480 to 910 scans were recorded. <sup>27</sup>Al and <sup>1</sup>H experiments were done on a 16.4 T Bruker Avance III spectrometer operating at 182 and 700 MHz respectively. For <sup>27</sup>Al, a 1.3 mm rotor spinning at 40 kHz, in a standard double resonance probe, was used with 15 ° flip angle, 0.3 s recycling delay and 32k scans. For {<sup>27</sup>Al}-<sup>1</sup>H TRAPDOR experiments,<sup>4</sup> a 3.2 mm rotor was used in a trigamma probe. <sup>1</sup>H spectra were acquired with and without irradiation on <sup>27</sup>Al and echo time ranging from 0.9 to 9.1 ms. Sample was previously dehydrated in a vacuum manifold and rotor was filled in a glove box.

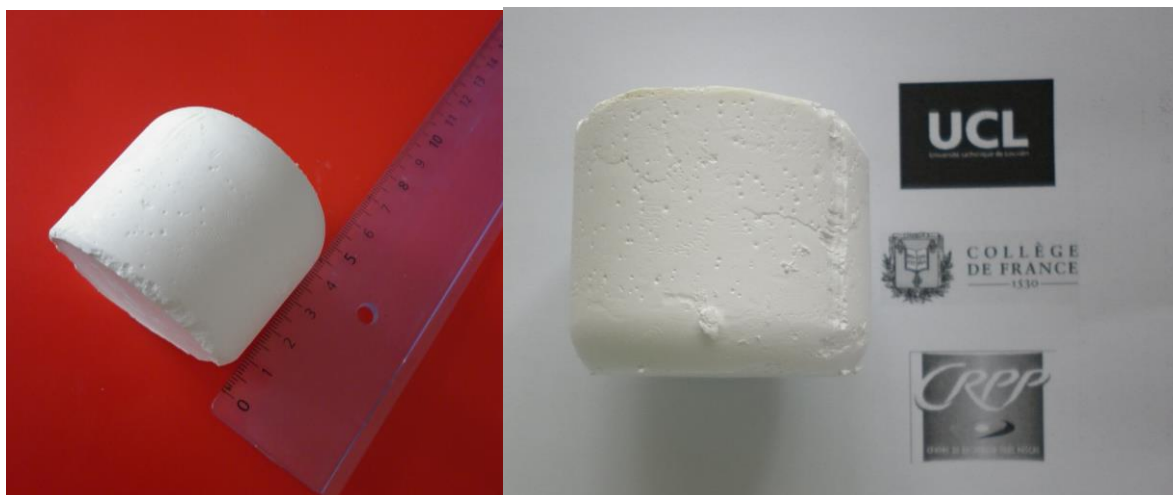
## 2.3. Bioethanol dehydration

The reference was pressed, crushed and sieved to get particles in the 1-2 mm range. The SiAl(HIPE) monolith was cut into particles of the same size. 1.2 g of catalyst was loaded in a tubular stainless steel reactor of 17 mm inner diameter. For the test with the reference, 45 g of inert glass beads have been added to account for the difference in density and to obtain an identical bed volume. The catalyst is first heated in argon above 100°C and then ethanol (first generation bioethanol from BioWanze; 99.7wt.% ethanol – 0.3wt.% water) is fed at the desired flow rate and evaporated in a preheating zone. The reactor is heated up to 400°C and

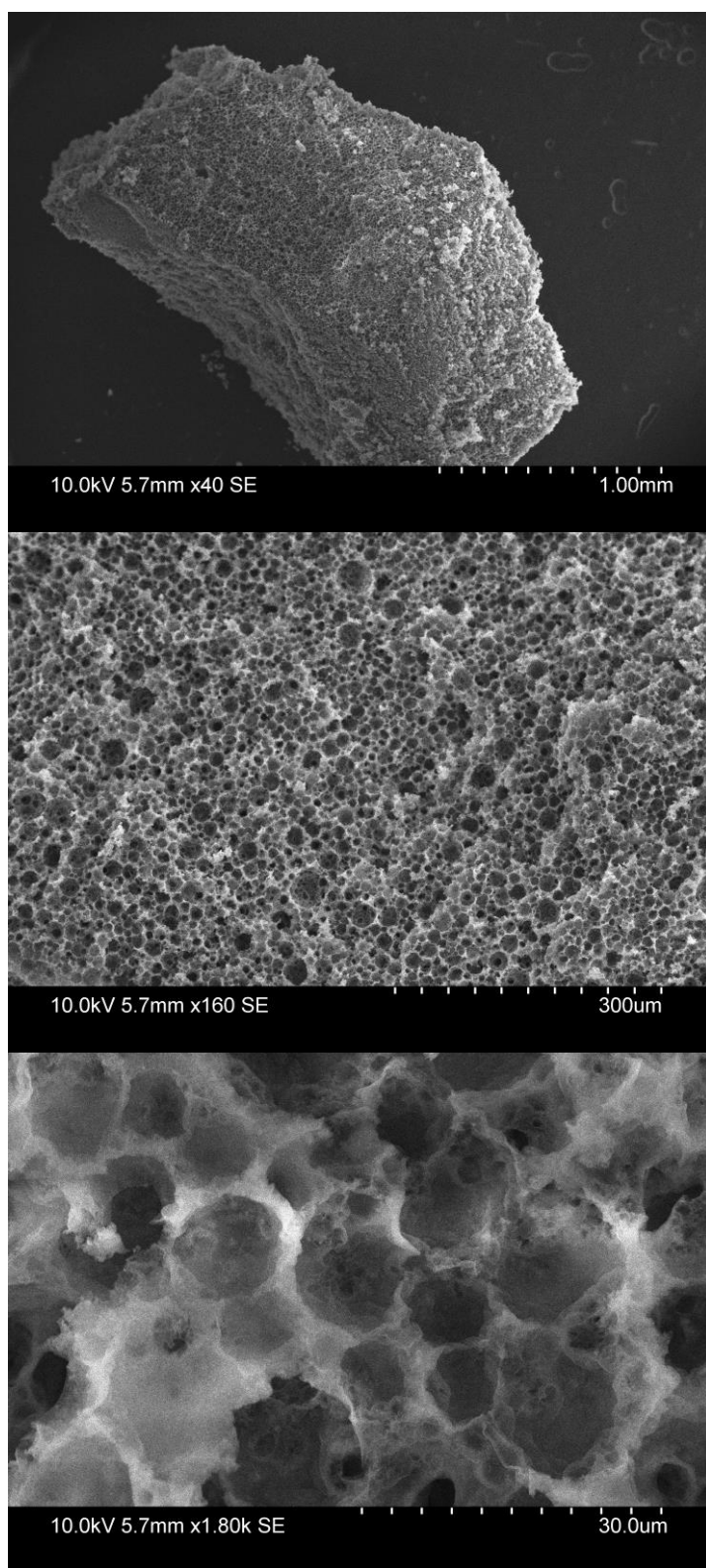
when the temperature is stable, sampling of gas and liquid (in a reservoir bag and in a cold trap respectively) is performed for 30 min. The products are analyzed by GC-MS.



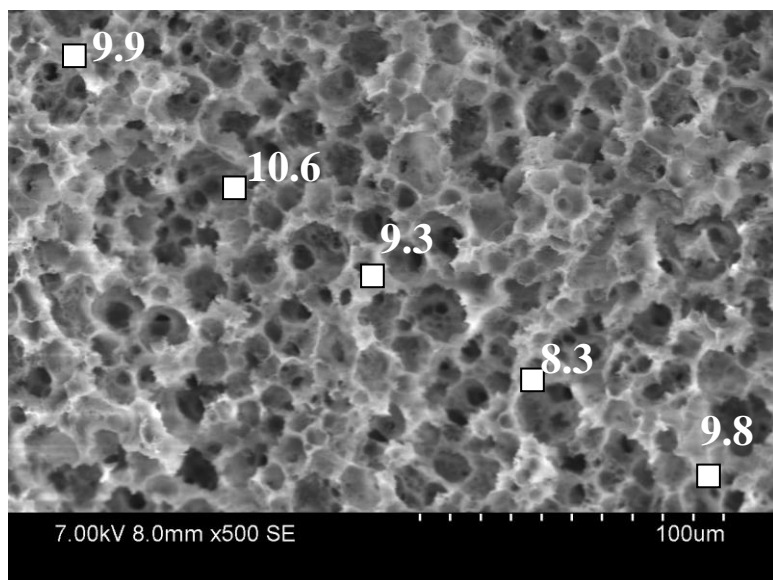
**Figure ESI-1:** Scheme of the experimental set-up for ethanol dehydration reaction.



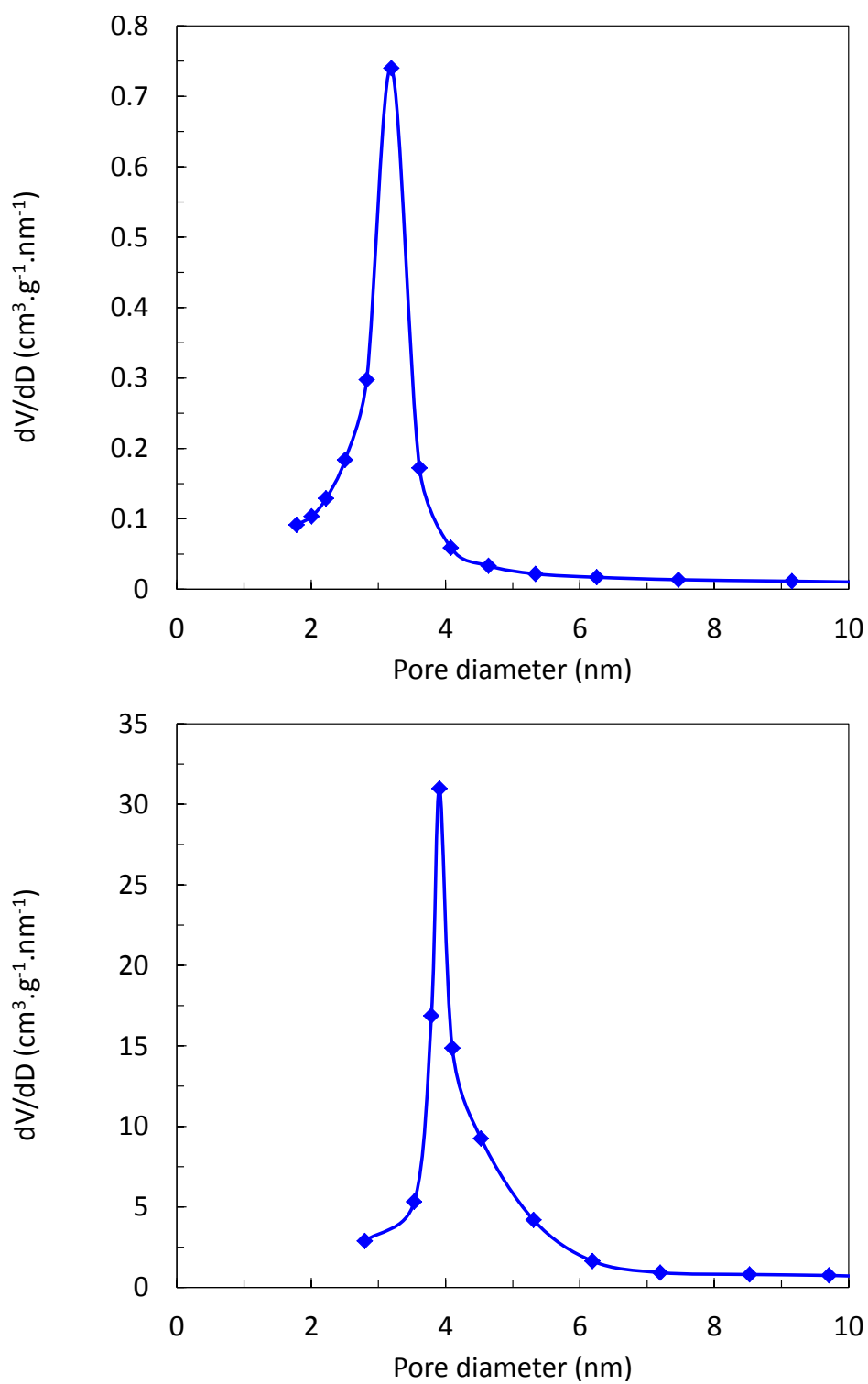
**Figure ESI-2.** Additional picture of SiAl(HIPE) monolith.



**Figure ESI-3.** Additional SEM micrographs of SiAl(HIPE)



**Figure ESI-4.** EDX composition mapping. Square represent the localized zone where the composition was measured and the atomic Si/Al are given for each zone analyzed.



**Figure ESI-5.** Pore size distribution obtained by the (top) BJH and (bottom) Broekhoff and De Boer methods.



**Table ESI-1.** Peaks used for quantifying TRAPDOR effect at 0.9 ms and 9.1 ms. Spectra were simulated using dmfit program.<sup>5</sup> A minimum number of peaks was used.

Peak	amplitude	position (ppm)	width (ppm)	gaussien / lorentzien	(S <sub>0</sub> -S)/S <sub>0</sub>	
					0.9 ms	9.1 ms
#1	40.74	5.02	5.77	1	0.26	0.93
#2	147.89	2.68	2.34	1	0.08	0.14
#3	503.86	1.93	0.61	1	0.06	0.12
#4	1458.67	1.81	0.23	1	-0.05	0.00

**Table ESI-2.** Conversion of ethanol, selectivities for various products, yield and productivity for ethene. Comparison of the reference commercial aluminosilicate and the SiAl(HIPE) catalyst for three different contact times. Reaction temperature is 400°C.

Catalyst	Flow [ml/h]	WHSV [h <sup>-1</sup> ]	Ethanol conversion	Selectivity				Y <sub>ethene</sub>	Productivity (g <sub>ethene</sub> ·g <sup>-1</sup> h <sup>-1</sup> )
				ethene	Diethyl ether	Acetaldehyde	Butene		
SiAl ref	18.0	11.8	0.92	0.98	0.010	0.001	0.013	0.90	8.9
SiAl(HIPE)	18.0	11.8	0.99	0.94	0.001	0.004	0.052	0.94	9.2
SiAl ref	26.7	17.6	0.85	0.97	0.021	0.001	0.010	0.82	12.0
SiAl(HIPE)	26.7	17.6	0.99	0.95	0.002	0.003	0.041	0.95	13.8
SiAl ref	36.2	23.8	0.77	0.94	0.040	0.001	0.017	0.72	14.3
SiAl(HIPE)	36.2	23.8	0.97	0.95	0.007	0.004	0.040	0.92	18.3

## References

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