"SiAl(HIPE)": An acidic macro-mesocellular aluminosilicate foam monolith showing high ethanol dehydration activity

Damien P. Debecker,[a,*] Cédric Boissière[b], Guillaume Laurent[b], Stéphanie Huet[c], Philippe Eliaers[d], Clément Sanchez[b], Rénal Backov[c]

[a] *Institute of Condensed Matter and Nanoscience - Université catholique de Louvain., 1348 Louvain-La-Neuve, Belgium.*

[b] *UPMC, Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris, 75231 Paris, France.*

[c] *Centre de Recherche Paul Pascal, Université de Bordeaux 1, 33600 Pessac, France*

[d] *Centre de Ressources Technologiques en Chimie (Certech), 7180 Seneffe, Belgium.*

**Corresponding author: damien.debecker@uclouvain.be*

1. Introduction

Amorphous aluminosilicates are of utmost importance as catalysts and catalyst supports.[1] Zeolites and their mesoporous counterparts – for which both textural and acidic properties can be somewhat tuned – have played a major role in the progress of industrial chemistry in the last decades. Nevertheless, powdery catalytic materials have to be (i) shaped as extrudates, pellets or monoliths, or (ii) impregnated onto structured supports before being used in industrial flow processes and this still remains an important challenge.[2] The one-step preparation of structured materials with desired properties is hence highly needed. Coupling sol-gel chemistry with an emulsion technique ('High Internal Phase Emulsion' method, "HIPE"), macroscopic silica blocs of defined shape can be obtained, featuring high surface area and good mechanical strength.[3] Such materials can be casted directly in tubular reactors and be employed as catalyst supports for flow reactions.[4] The incorporation of alumina centers in tetrahedral coordination in such material is desired (high acidity) but not straightforward as the classical synthesis conditions usually generate aluminum oxide chunks in octahedral environment. Here we report on a new alkaline version of the 'HIPE' method.

2. Experimental

Solution A: TEOS (5g) and TTAB (4.8g) were added to 35g of dodecane. Solution B: an aqueous solution of tetrapropylammonium hydroxide (1.33g; 40%) and Al(^{i}OPr)$_3$ (0.43g) were added in 15g of water. Solution A was added drop wise in solution B while stirring vigorously with a fork, until a stable emulsion was obtained. The latter was put to rest for one week in ambient conditions and then put in an oven at 70°C for 2 hours. The gel was washed 3 times with acetone/THF mixtures to remove the oil phase. It was then left to dry and then calcined for 2h at 200°C (2°C/min) and at 650°C for 6h (2°C/min). The resulting "SiAl(HIPE)" was are characterized by an array of techniques and tested in the dehydration of ethanol at 400°C.

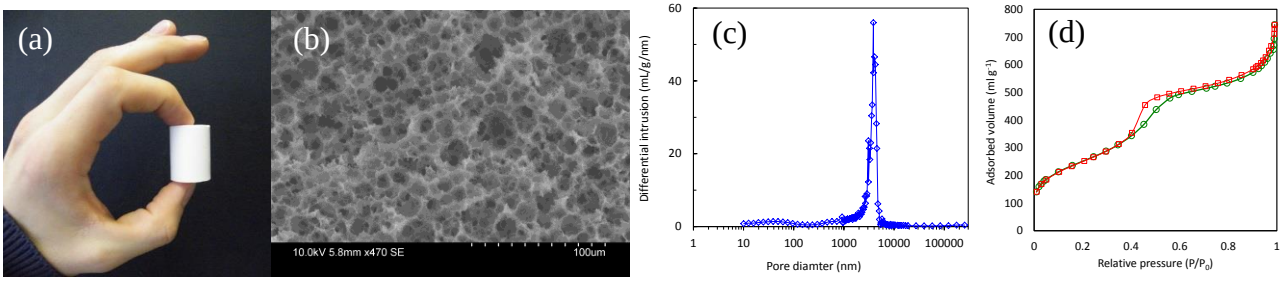

Figure 1. (a) photograph, (b) SEM micrograph, (c) macropore analysis by Hg intrusion porosimetry and (d) N_2-sorption isotherms.

3. Results and discussion

SiAl(HIPE) was prepared in the form of cm-scale self-standing monoliths (Fig. 1a). SEM reveals their macrocellular structure (Fig. 1b). Interconnected macro-cells have a diameter in the 5-45 µm range. The Si/Al atomic ratio (12 in nominal) was checked by EDX and was shown to be homogeneous throughout the

sample. Macroporosity is confirmed by Hg-porosimetry (Fig. 1c). Macrocells are interconnected by rather monodisperse pore openings around 4 µm in size. Intrusion volume is 10.2 $cm^3.g^{-1}$ and porosity reaches 89%. Bulk density is 0.087 $g.cm^{-3}$. N_2-physisorpiton measurements (Fig. 1d) demonstrate that the SiAl(HIPE) walls are mesoporous (pore size ~3.6 nm; no microporosity). BET surface area reaches 900 $m^2.g^{-1}$.

Acidity was measured by NH_3 chemisorption and compared to both a popular commercial aluminosilicate support (Aldrich, Grade 135, 475 $m^2.g^{-1}$, 12 wt.% Al_2O_3) and to Si(HIPE) (Fig. 2a). SiAl(HIPE) was the most acidic (and exhibited more abundant strong acid sites per surface unit; not shown here).

^{29}Si MAS NMR spectrum (not shown here) showed a broad peak strongly shifted to the left, typical for true aluminosilicates mixed oxide.[5] This shows that Si and Al precursors have reacted together to form Si-O-Al bonds. ^{27}Al MAS-NMR (Fig. 2b) showed a remarkably large proportion of framework Al atoms in tetrahedral coordination, characteristic of pre-zeolitic materials prepared in basic media.[6] Consistently, NMR (TRAPDOR experiment) also allowed confirming the presence of Si-(OH)-Al hydrogen-bonded species (strong Brönsted acidity). The successful incorporation of aluminum centers within the silica network is explained by the progressive dodecane/water interfacial hydrolysis of TEOS and deprotonation of silicic acid that locally induces a pH drop, allowing the progressive polycondensation of aluminum hydroxide with silicate species. Both TEOS and TTAB diffusions within dodecane phase, and aluminate diffusion within aqueous phase being slow, a progressive self-assembly of positively charged TTAB structuring agent and negatively charged aluminosilicate oligomers has time to take place, creating the mesostructured (SiAl)HIPE.

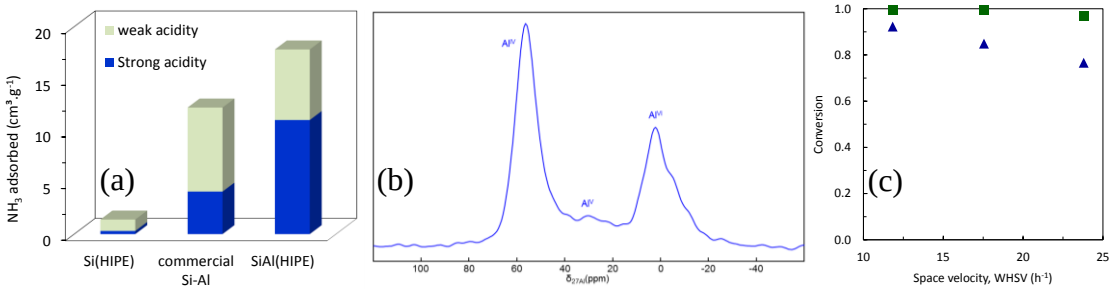

Figure 2. (a) Acidity probed by NH_3-chemisorption, (b) 27Al-MAS-NMR of SiAl(HIPE), (c) ethanol dehydration at 400°C.

SiAl(HIPE) is clearly more active than the commercial silica-alumina in the dehydration of ethanol (Fig. 3c). Ethene selectivity is ~95% and the production rate reaches 13.3 $g_{ethene}.g_{cat}^{-1}.h^{-1}$. Consistently with the presence of strong acid sites, diethyl ether selectivity is relatively low (incomplete dehydration of ethanol) but 1-butene selectivity (consecutive dimerization of ethene) is relatively high for SiAl(HIPE).

4. Conclusions

The new alkaline sol-gel route presented here allows preparing meso-macrocellular self-standing aluminosilicate monoliths that are easy to cast and manipulate and that exhibit open and interconnected macroporosity, high surface area and strong acidic properties. Strong acidity is brought about by the formation of a true mixed oxide. Effectiveness of these catalysts is demonstrated here in the case of bioethanol dehydration, and good performance can be expected in other processes like cracking, isomerization, alkylation reactions, etc.

References

1. A. Corma, Chem. Rev. 95 (1995) 559-614.
2. S. Mitchell, N.-L. Michels, K. Kunze and J. Pérez-Ramírez, Nature Chem. 4 (2012) 825-831.
3. F. Carn, A. Colin, M.-F. Achard, H. Deleuze, E. Sellier, M. Birot and R. Backov, J. Mater. Chem. 14 (2004) 1370-1376.
4. N. Brun, A. Babeau-Garcia, M.F. Achard, C. Sanchez, F. Durand, G. Laurent, M. Birot, H. Deleuze and R. Backov, Energy Environ. Sci. 4 (2011) 2840-2844.
5. G.J. Kennedy, J.W. Wiench and M. Pruski, Solid State Nucl. Magn. Reson. 33 (2008) 76-81.
6. S. Pega, C. Boissière, D. Grosso, T. Azaïs, A. Chaumonnot and C. Sanchez, Angew. Chem. 121 (2009) 2822-2825.