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Alumina-grafted macro-/mesoporous silica monoliths as continuous flow microreactors for the Diels–Alder reaction

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ABSTRACT

Bimodal macro-/mesoporous silica monoliths (6 mm diameter, 1–4 cm length) were functionalized with aluminum oxide allowing the preparation of a new solid Lewis acid catalyst named Al-MonoSil. Al-MonoSil was used as catalytic microreactor for the in-flow implementation of the Diels–Alder reaction. Due to the interconnected and homogeneous system of macropores of 5 μm within the monolith, the Al-MonoSil shows high conversion and productivity in continuous flow without pressure drop. The external mass transfer limitations and the productivity were controlled by adjusting monolith length and flow rate. Al-MonoSil is a stable microreactor for long time productivity for Lewis acid–catalyzed reactions.

1. Introduction

Synthesis of fine chemicals or intermediates using continuous flow microreactors in the presence of a solid catalyst presents several key advantages in comparison with reactions carried out in batch reactors. Among them, miniaturization, safer process operation, better control of reaction parameters, easier product recovery, and improvement of productivity through intensification of transfer phenomena can be cited [1]. In that respect, many efforts are currently paid to design and engineer more efficient microsystems featuring internal structures with sizes ranging from a few micrometers to a few tens millimeters such as microstructured multichannel reactors [2–4] or macroporous monolithic bodies with multimodal porosity [5,6].

Compared with millimetric parallel multichannel reactors, macroporous monoliths are characterized by a higher surface-to-volume ratio (due to their lower macropore size at the micrometer scale) and a very efficient mixing of fluids or reactants (due to the interconnected nature of their macroporous network). Several strategies have been investigated to prepare monolithic microreactors for in-flow reactions [6,7]. The very first macroporous monolithic flow reactors were made of polymers [8–13]. These reactors have then been further improved by Jas and Kirschning [14] and Kirschning et al. [15] to obtain hybrid glass/polymer reactors that have been used for a great variety of organic transformations in flow [15]. To avoid swelling problems inherent to polymers, we introduced a new generation of structured catalytic reactors, under the name of MonoSil [7], which consists of silica materials with multimodal macro-/mesoporosity. MonoSils feature high chemical and mechanical stability, and their surface can be readily functionalized *via* the grafting of organic and inorganic moieties [6]. The present paper describes the preparation and evaluates the performance of this novel type of macroporous/mesoporous monolith catalyst [7]. In this work, the Diels–Alder cycloaddition between crotonaldehyde and cyclopentadiene has been chosen as model reaction to investigate in more detail the efficiency of MonoSil-structured reactors more particularly with regard to mass transfer limitations and productivity.

The Diels–Alder cycloaddition is a reaction of considerable interest for synthetic organic chemistry [16]. This reaction is mainly catalyzed by homogeneous Lewis acids [17–20], but it can also be activated by Brønsted acids [21]. Following the general trend of replacing homogeneous catalysts by their heterogeneous counterparts, a number of studies have been performed in the presence of acid solids. The first examples of Diels–Alder reactions catalyzed by zeolites showed interesting results, as the geometry of the zeolite cages strongly influences the regio- and stereoselectivity of the reaction [22]. However, the small pore openings of zeolites restrain the

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synthesis of bulky molecules. These drawbacks were overcome in part by using zeolites with a secondary mesopore system [23] or mesoporous materials with pores larger than 2 nm [24–27]. In a comparative study by Kugita et al. [28], mesoporous silica materials consisting of MCM-41 modified with aluminum oxide proved more active in the Diels–Alder reactions than other heterogeneous solid acids such as mesoporous SBA-15, microporous H-ZSM-5 and HY zeolites, amorphous silica–alumina, Amberlyst 15, active alumina, silica-gel and homogeneous acid catalysts such as *p*-toluene sulfonic acid and $AlCl_3$. It was therefore of interest to investigate the promise of an aluminum oxide–grafted MonoSil in this reaction.

2. Experimental

2.1. Synthesis of macro-/mesoporous silica monoliths

Distilled H_2O of 46.3 g and HNO_3 of 4.6 g (68%, Aldrich) were mixed for 15 min at 0 °C, and 4.79 g of polyethylene oxide 20,000 (PEO, Aldrich 99%) was added and stirred for 1 h. Then, 37.7 g tetraethoxysilane (TEOS, Aldrich 99%) was added, and the mixture was stirred for 1 h. The resulting solution was poured into PVC tubes of 10 cm length and 8 mm internal diameter and kept at 40 °C for 3 days. The monoliths were then washed in water and treated in an ammoniac solution (0.1 M) at 40 °C for 20 h. The monoliths, with a final diameter of 6 mm, were then dried at 40 °C for 24 h and calcined at 550 °C for 8 h. These silica monoliths are hereafter named as parent monoliths or MonoSil.

2.2. Synthesis of Al-MonoSil

For the alumina grafting, MonoSil (12 cm length, 6 mm diameter, 0.96 g, 0.016 mol silica) was deposited in a round bottom flask (250 mL) and activated for 2 h at 150 °C under reduced pressure. Then, aluminum *sec*-butoxide (29 g, 0.028 mol, Aldrich 99%) and triethylamine (1.38 g, 0.009 mol, Acros 98%) were added in a flask containing the parent monolith in anhydrous toluene (120 mL) at 85 °C and stirred gently for 8 h (molar composition: $SiO_2/(sec\text{-}BuO)_3Al/NEt_3$, 1/1.8/0.8). The resulting monolith was washed with toluene and then stirred gently for 1 day in ethanol (20 mL) and H_2O (0.2 mL). The Al-MonoSil was then dried at 40 °C for 1 day and then calcined at 550 °C for 8 h.

The monoliths were cut in elements of 1, 2, 3, and 4 cm length, corresponding to 0.076, 0.152, 0.228, and 0.304 g, respectively, cladded with a heat-shrinkable DERAY PTFE clad for 2 h at 280 °C, and ended by two glass tubes to insure the connections to the pump for flow continuous processes [6,7].

2.3. Diels–Alder reaction

The cladded Al-MonoSils were activated for 4 h at 150 °C under reduced pressure in a Schlenk tube prior to be inserted in the setup for the flow catalysis. Diels–Alder reactions were carried out using the cladded Al-MonoSil microreactors in the setup for flow catalysis [6,7]. A solution containing freshly distilled cyclopentadiene (264 mg, 4 mmol, Aldrich) and crotonaldehyde (224 mg, 4 mmol, Aldrich, predominantly trans, >99%) was prepared in anhydrous dichloromethane (20 mL, Aldrich). This solution is processed through the Al-MonoSil using an HPLC pump with flow rates adjusted between 0.01 and 0.4 mL min^{-1}. During reaction, the Al-MonoSil is kept at 37 °C in a thermostatic box, which assures constant temperature throughout the experiments.

The contact time ($\tau = V_T/F$) was expressed by the ratio between the total pore volume ($V_T = V_{macro} + V_{meso}$) and the flow rate ($F$). For a monolith of x cm length and a weight per cm of m (g cm^{-1}), the total pore volume is thus expressed as $V_T = xm(V_{meso} + V_{macro})$ and the contact time becomes

$$\tau = \frac{xm(V_{meso} + V_{macro})}{F}$$

The productivity (P, expressed in mmol of product formed per g of catalyst and per min) is calculated from the conversion ($Conv$) and initial concentration of reactant (C_0) by the formula:

$$P = C_0 Conv \frac{F}{mx} = C_0 Conv \frac{V_T}{\tau}$$

Diels–Alder reactions carried out in the batch mode reactor were performed in round bottom flasks (100 mL) under agitation at 1000 rpm with a magnetic stir bar (1 cm) under the same temperature (37 °C) controlled by an oil bath and reaction mixture composition (4 mmol cyclopentadiene and 4 mmol crotonaldehyde in 20 mL dichloromethane) as for flow catalysis using 76 mg of a crushed and sieved fraction (50–100 μm) of the Al-MonoSil.

Concentrations of reactants and products were determined by sampling to a GC periodically. To obtain pure products for NMR analysis, reaction mixtures were purified using flash column chromatography (ethylacetate/heptane ratio of 10:0.1). After evaporation of the solvents, a yellow oil (3-methyl-bicyclo[2.2.1]hept-5-ene-2-carbaldehyde) is obtained.

2.4. Characterization

The physico-chemical properties of the monoliths were characterized by nitrogen sorption, NH_3 and pyridine sorption, scanning electron microscopy (SEM), mercury intrusion, and ^{27}Al MAS NMR spectroscopy. The adsorption–desorption isotherms of nitrogen at 77 K were determined using a Micromeritics ASAP 2010 instrument. The amount and distribution of the acid sites of the materials was monitored by temperature-programmed desorption of NH_3 using a Micrometrics AutoChem II 2910. The type of acidity (Lewis and/or Brønsted) of the sample was tested by pyridine adsorption on self-supported pellets (15 mg, 1.3 cm^2) previously activated at 450 °C and then cooled down to 150 °C. Pyridine adsorption (15 mbar) was performed at 150 °C to avoid pyridine physisorption, and the excess of pyridine was evacuated under vacuum before recording FTIR spectra using a Vector 22 instrument. After pyridine adsorption, the sample was outgassed stepwise from 200 to 400 °C to characterize the strength of the acidity. The morphology of the monoliths was determined using Hitachi S-4500 I SEM. Mercury porosimetry experiments were carried out with Micromeritics Autopore 9220 equipment. The ^{27}Al MAS NMR spectra were recorded on a Varian VNMRS 400-MHz solid spectrometer with 7.5-mm rotors. A one pulse with proton decoupling was applied with a $\pi/12$ pulse and 60-s recycling delay and a rotation at 20 kHz.

3. Results and discussion

3.1. Characterization of the alumina-functionalized silica monolith (Al-MonoSil)

3.1.1. Porosity analysis of Al-MonoSil

Sorption measurements reveal that the functionalization of the silica monolith with aluminum oxide decreases the mesopore volume from V_{meso} = 1.12 to 0.89 mL g^{-1}, mesopore size from 10 to 9 nm, and also in parallel, the BET surface area decreases from 550 to 450 m^2 g^{-1} (Fig. 1A).

The SEM images show that the macroporous network of the original silica monolith has kept intact, presenting macropores of

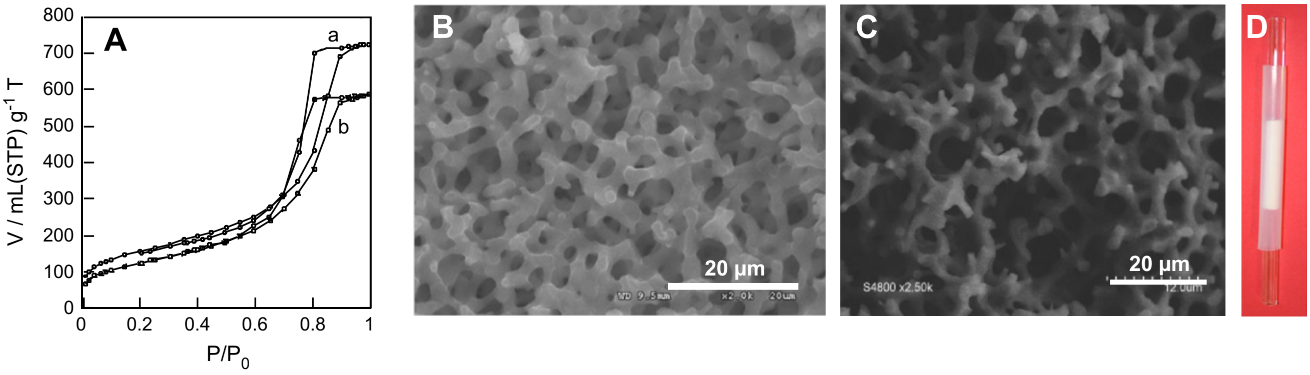


Fig. 1. Nitrogen sorption isotherms at 77 K of the parent silica macro-/mesoporous monolith, MonoSil (a) and the aluminum oxide–functionalized silica monolith (Al-MonoSil) (b) (A). SEM images of MonoSil (B) and Al-MonoSil (C), picture of cladded Al-MonoSil (D).

5 μm and a skeleton thickness of 3 μm (Fig. 1B and C). Mercury porosimetry analysis confirms the preservation of the macropore size and of the macropore volume (V_{macro}) equal to 1.22 mL g^{-1}.

3.1.2. Acidity analysis of Al-MonoSil

EDX analysis of a cross-section of the Al-MonoSil indicates an even distribution of aluminum throughout the sample with an average Si/Al ratio of 6.7 (Fig. 2a and b), corresponding to 0.12 g of Al_2O_3 per gram of silica monolith. This result is confirmed by elemental analysis.

The ^{27}Al MAS NMR spectrum (Fig. 2c) shows a typical profile of an amorphous alumina or a silico-alumina material, with an intense peak at 10 ppm followed by two peaks with lower intensity at 30 and 55 ppm characteristic of hexa-, penta-, and tetra-coordinated alumina species, respectively. The functionalization of silica monolith by alumina gives thus mainly Al_2O_3 hexa-coordinated species on the silica surface expecting to give rise to Lewis acidity and a smaller fraction of Si–O–Al tetra-coordinated aluminum usually responsible for Brønsted acidity.

The total acidity of the Al-MonoSil has been measured by ammonia TPD. An acid site density of 0.73 mmol g^{-1} with a broad distribution of strengths was observed. The maximal desorption temperature was at around 220 °C, which is typical for a moderate acid strength. Stronger acid sites were, however, present since complete desorption of ammonia molecules required a high desorption temperature (350–450 °C). Pyridine/FTIR spectroscopy allows to discriminate the contributions of Brønsted and Lewis sites to the global acidity. Fig. 3a shows the IR spectrum of the sample after desorption at 150 °C. The acid sites within Al-MonoSil are mostly of Lewis type characterized by the high intensity of the peak at 1453 cm^{-1}. A smaller contribution of Brønsted sites is deduced by the small signal at 1546 cm^{-1}. After desorption at 400 °C (Fig. 3c), a significant portion of base is still retained on the surface, confirming the TPD conclusion on the presence of strong acid (Lewis type) sites on Al-MonoSil.

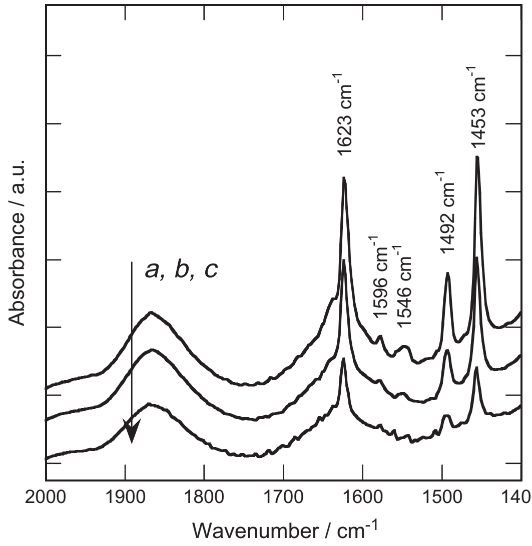


Fig. 3. Pyridine adsorption and FTIR spectra after desorption at 150 °C (a), 300 °C (b), and 400 °C (c).

3.2. Diels–Alder reaction with Al-MonoSil

The catalytic reaction performed with the Al-MonoSil is the Diels–Alder reaction between crotonaldehyde and cyclopentadiene

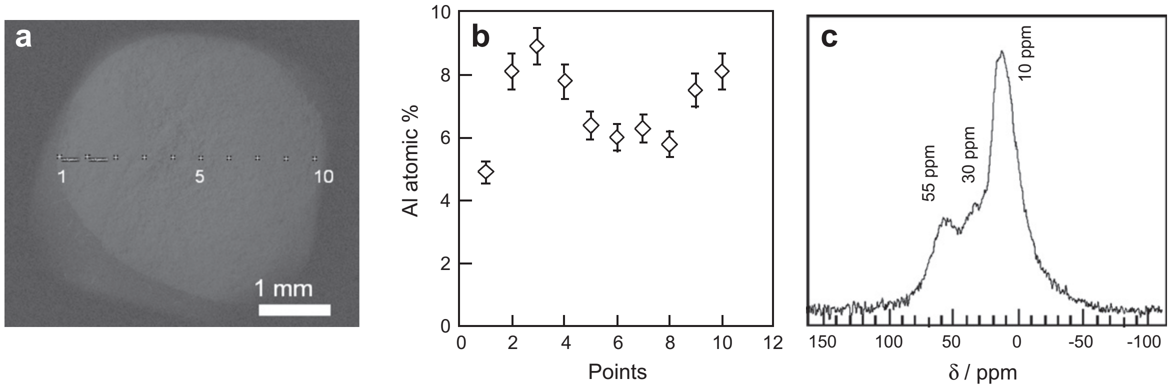


Fig. 2. EDX analysis on a cross-section of the Al-MonoSil (a). Atomic% of Al on the Al-MonoSil cross-section (b). ^{27}Al MAS NMR spectrum of the Al-MonoSil (c).

leading to the *exo* and *endo* stereoisomers presented in scheme 1. Blank reactions without catalysts and with native silica monolith have shown no conversion of both reactants. Therefore, the Diels–Alder reaction occurs only through the acid sites of Al_2O_3 grafted on the monolith.

3.2.1. Diels–Alder reaction with Al-MonoSil in an open batch reactor

Prior to investigate the Diels–Alder reaction in flow conditions, the reaction was performed in a batch reactor (flask) using a crushed and sieved fraction (50–100 μm) of the Al-MonoSil suspended in 20 mL of dichloromethane. From Fig. 4a, it can be seen that the conversion level reached with the Al-MonoSil reactor after 20 h of reaction is equal to 80%. Such an activity is similar to that reported by Kugita et al. [28] for the most active Al-MCM-41 material (Si/Al = 30) prepared by surface functionalization with aluminum oxide. In terms of activity, Al-MonoSil compares therefore favorably with more traditional solid acid catalysts.

3.2.2. Diels–Alder reaction with Al-MonoSil as microreactor in flow

3.2.2.1. External diffusion limitations study. The occurrence of external diffusion limitations on the monolithic flow reactor has been checked experimentally by performing a series of experiments at constant contact time (16 min) while increasing the flow proportionately to the catalyst volume. To this end, Al-MonoSil monoliths of 6 mm diameter (0.076 g cm^{-1}) were cut into pieces of different length, from 1 to 4 cm, cladded, and put in the setup for in-flow catalysis. The flow rates were adjusted from 0.01 to 0.04 mL min^{-1} for each microreactor in accordance with the increasing length of the monolith (Fig. 4b). The conversion of reactants achieved as a function of time over the four monolithic reactors is shown in Fig. 4b. All the systems showed an initial decrease in conversion during the first 24 h in flow, most probably related to the deactivation of the most acidic sites of the surface by a strong adsorption of the aldehyde reactant and products [29]. After this initial stabilization period, the conversion remained remarkably constant in all cases. Plots of conversion versus flow rate (Fig. 5) show that at flow rates equal to 0.01 and 0.02 mL min^{-1}, the reaction is limited by mass transfer, while above a flow rate of 0.03 mL min^{-1} a constant value of the conversion (*ca.* 80%) is obtained, indicating the absence of external diffusion limitations in the monolith. Under these conditions, Al-MonoSil catalyst was able to maintain a constant productivity of 0.021 mmol min^{-1} g^{-1} for more than 4 days.

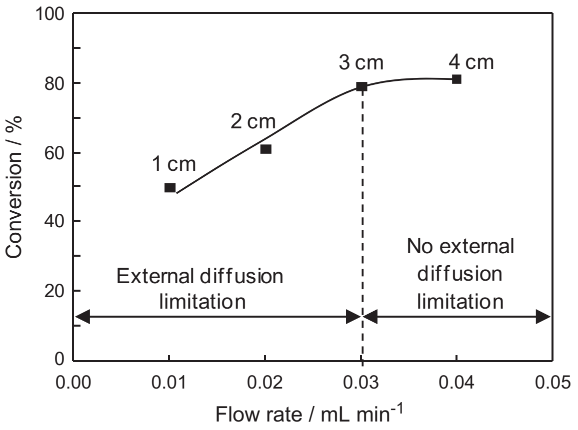
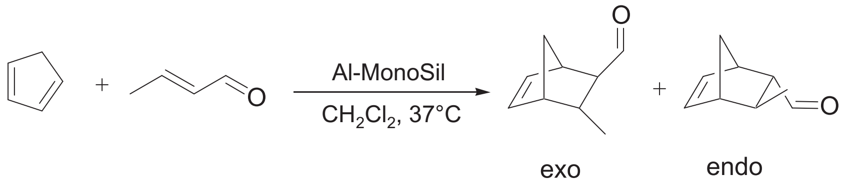


Fig. 5. Conversion as function of the flow rate at constant contact time of 16 min.

3.2.2.2. Productivity of the Al-MonoSil reactor. In order to determine the maximum productivity achievable with the 6-mm-diameter monoliths, the contact time was varied between 1.5 and 16 min by varying flow rates between 0.4 and 0.04 mL min^{-1} using a 4-cm-long monolith (Fig. 6). Maximum productivity (around 0.04 mmol min^{-1} g^{-1}) was achieved for contact times lower than 6 min and conversions in the range 15–55%. Optimal conditions, combining high conversion and productivity, can be set for a contact time of 9.4 min (flow rate 0.07 mL min^{-1}), where the conversion reached 72% and the productivity 0.033 mmol min^{-1} g^{-1}. Though productivities cannot be strictly compared for batch and in-flow reactors, the "equivalent productivity" at 72% conversion



Scheme 1. Diels–Alder reaction between cyclopentadiene and crotonaldehyde.

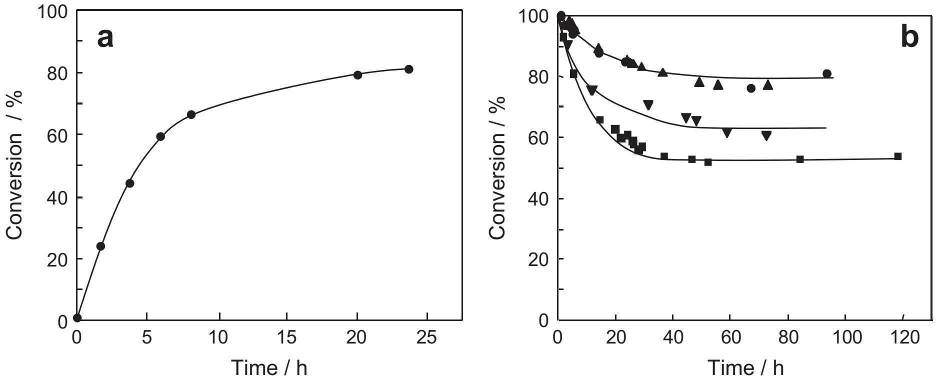


Fig. 4. Crotonaldehyde conversion as function of the reaction time for the batch reactor (a), and for the monolithic reactor in flow for Al-MonoSils of different lengths (■) 1, (▼) 2, (▲) 3, and (●) 4 cm at a constant contact time of 16 min (using corresponding flow rates of 0.01, 0.02, 0.03, and 0.04 mL min^{-1}, respectively) (b).

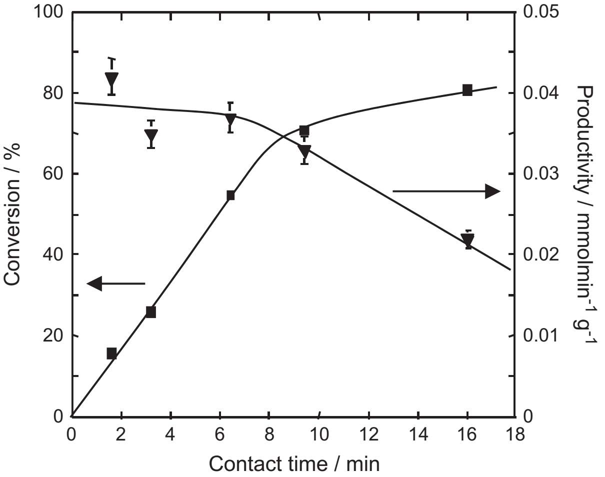


Fig. 6. Crotonaldehyde conversion and catalyst productivity as function of the contact time.

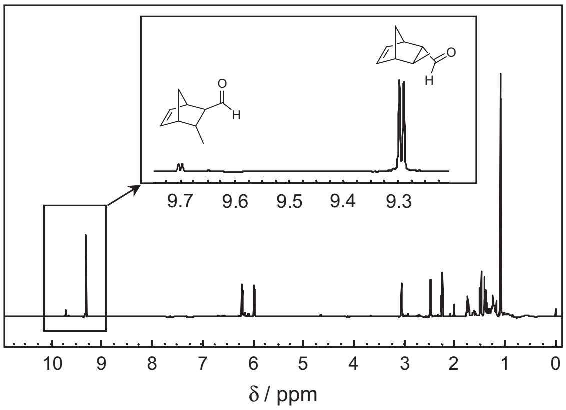


Fig. 7. ^{1}H NMR spectrum of the Diels–Alder products.

for the batch reactor is calculated to be 0.014 mmol min^{-1} g^{-1} after 11 h of reaction. This gross evaluation thus indicates a productivity two times lower for the batch reactor than that obtained using the flow microreactor.

For practical applications, space time yields can be calculated (STY, mass of product per unit of catalyst volume per unit of time) for the Al-MonoSil reactor (4 cm × 6 mm). The STY is expressed as

$$\mathrm{STY} = C_0 Conv \frac{F}{vx} M$$

where v is the volume occupied by the monolith per cm (0.28 mL cm^{-1}) and M the molar mass of the product. STY is therefore equal to 76 g h^{-1} L^{-1} or 13 kg of Diels–Alder product produced per week per liter of Al-MonoSil catalyst.

3.2.2.3. Recyclability of the Al-MonoSil catalyst. In order to assess the recyclability of the Al-MonoSil for the in-flow catalysis, the monolith was washed under flow with ethanol and was reactivated at 150 °C under reduced pressure. Similar conversion curves as a function of time as for the first cycle were observed, demonstrating that no polymerization of cyclopentadiene has occurred during the reaction due to the presence of the Brønsted sites and that the catalyst is stable under reaction conditions.

3.2.2.4. Stereoselectivity of the reaction. As shown in scheme 1 the Diels–Alder reaction between crotonaldehyde and cyclopentadiene gives rise to two stereoisomers, the *endo* and *exo* products. From the ^{1}H NMR spectra, the amount of *endo* and *exo* isomers (Fig. 7) can be calculated.

In comparison with spectra given in the literature for norbonene derivates [30,31], the two doublets for each carbonyl proton can be assigned to the *endo* and *exo* molecules with a higher chemical shift for the doublet of the *exo* product. Thus, it can be deduced that the obtained reaction products feature an *endo*/*exo* selectivity of 9/1. Constant values for the *endo*/*exo* selectivity were monitored over the entire reaction periods (from few minutes to 5 days), showing that the small amount of Brønsted sites (probably responsible for the initial 24-h deactivation) does not influence the *endo*/*exo* selectivity. Such high *endo*/*exo* stereoselectivities are typical for Diels–Alder reactions catalyzed by strong Lewis acid sites, [26,32] but are different from the one obtained with Al-MCM-41 by Kujita et al. [28] (stereoselectivity *endo*/*exo* = 1.06). In the case of the reaction with cyclopentadiene, it has been shown that the stereoselectivity is dependent mostly on the steric hindrance of the dienophile: *endo*/*exo* ratios of 24 and 1.2 were achieved with methylacrylate and methylmethacrylate, respectively [26]. Therefore as the same dienophile (crotonaldehyde) has been used in our study and in Kujita et al.'s study [28], some hindrance effect due to the catalyst itself could be at the origin of the difference as Al-MCM-41 features smaller pores (2.7 nm) in comparison with Al-MonoSil (9 nm). In order to check the effect of pore size and of confinement, Al_2O_3 was grafted following the same protocol on a non-porous fumed silica (Aerosil 200) and similar stereoselectivities (*endo*/*exo* = 9) as Al-MonoSil were observed for the reaction carried out in batch reactor. The range of application of the Al-MonoSil was assessed for another Diels–Alder reaction between cyclopentadiene and cinnamaldehyde, showing a higher steric hindrance, which should favor the *exo* stereoisomer formation. Similar pathways for the conversion as for the reaction between cyclopentadiene and crotonaldehyde were observed reaching steady-state conversions of 45% for a flow rate of 0.05 mL min^{-1} on a 2-cm Al-MonoSil. The observed *endo*/*exo* selectivity is lower (*endo*/*exo* = 4.5) than the reaction with crotonaldehyde as expected for bulkier dienophiles and, however, remains favorable for *endo* stereoisomer.

4. Conclusion

A method for the functionalization with aluminum oxide of bimodal macro-/mesoporous silica monoliths has been presented allowing the preparation of a new solid Lewis acid catalyst named Al-MonoSil. Due to the interconnected and homogeneous system of macropores of 5 μm within the monolith, the Al-MonoSil can be readily implemented as microreactor for in-flow reactions in liquid phase with low pressure drop (<0.5 bar). We have demonstrated that this material can be used advantageously as continuous flow reactor for the Diels–Alder reaction and that external mass transfer limitations and productivities can be controlled by adjusting monolith lengths and flow rates. A productivity of 13 kg of adduct per week and per liter of monolith can be achieved using the Al-MonoSil microreactor.

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References

[1] J.M. Commenge, L. Falk, J.P. Corriou, M. Matlosz, Chem. Eng. Technol. 28 (2005) 446.

[2] A. Cybulski, J.A. Moulijn, Catal. Rev. Sci. Eng. 36 (1994) 179.
[3] P. Avila, M. Montes, E. Miró, Chem. Eng. J. 109 (2005) 11.
[4] J.L. Williams, Catal. Today 69 (2001) 3.
[5] M.V. Twigg, J.T. Richardson, Ind. Eng. Chem. Res. 46 (2007) 4166.
[6] (a) A. Sachse, A. Galarneau, B. Coq, F. Fajula, New J. Chem. 35 (2011) 259;
(b) A. Sachse, A. Galarneau, F. Fajula, F. Di Renzo, F. Fajula, B. Coq, Micropor. Mesopor. Mater. 140 (2011) 58;;
(c) A. Sachse, A. Galarneau, F. Di Renzo, F. Fajula, F. Fajula, B. Coq, Chem. Mater. 22 (2010) 4123.
[7] A. El Kadib, R. Chimenton, A. Sachse, F. Fajula, A. Galarneau, B. Coq, Angew. Chem. Int. Ed. 48 (2009) 4967.
[8] F. Svec, J.M.J. Fréchet, Anal. Chem. 64 (1992) 820.
[9] C. Viklund, F. Svec, J.M.J. Fréchet, K. Irgum, Chem. Mater. 8 (1996) 744.
[10] E.C. Peters, F. Svec, J.M.J. Fréchet, Adv. Mater. 11 (1999) 1169.
[11] N. Hird, I. Hughes, D. Hunter, M.G.J.T. Morrison, D.C. Sherrington, L. Stevenson, Tetrahedron 55 (1999) 9575.
[12] J.A. Tripp, J.A. Stein, F. Svec, J.M.J. Fréchet, Org. Lett. 2 (2000) 195.
[13] J.A. Tripp, F. Svec, J.M.J. Fréchet, J. Comb. Chem. 3 (2001) 216.
[14] G. Jas, A. Kirschning, Chem. Eur. J. 9 (2003) 5708.
[15] A. Kirschning, C. Altwicker, G. Dräger, J. Harders, N. Hoffmann, U. Hoffmann, H. Schönfeld, W. Solodenko, U. Kunz, Angew. Chem. Int. Ed. 40 (2001) 3995.
[16] M.B. Smith, J. March, March's Advanced Organic Chemistry, fifth ed., Wiley, New York, 2001. p. 1062.
[17] K.N. Houk, R.W. Strozier, J. Am. Chem. Soc. 95 (1973) 4094.
[18] P.V. Alston, R.M. Ottenbrite, J. Org. Chem. 40 (1975) 1111.
[19] P. Yates, P. Eaton, J. Am. Chem. Soc. 82 (1960) 4436.
[20] H.B. Kagan, O. Riant, Chem. Rev. 92 (1992) 1007.
[21] J.M. Fraile, J.I. Garcia, D. Gracia, J.A. Mayoral, T. Tarnai, F. Figueras, J. Mol. Catal. A 121 (1997) 97.
[22] F. Fringuelli, A. Taticchi, The Diels-Alder Reaction, Wiley, Chichester, UK, 2002. p. 148.
[23] M.V. Gomez, A. Cantin, A. Corma, A. de la Hoz, J. Mol. Catal. A 240 (2005) 16.
[24] M. Onaka, R. Yamasaki, Chem. Lett. (1998) 259.
[25] M. Onaka, N. Hashimoto, R. Yamasaki, Y. Kitabata, Chem. Lett. (2002) 166.
[26] M. Onaka, N. Hashimoto, Y. Kitabata, R. Yamasaki, Appl. Catal. A 241 (2003) 307.
[27] J.P. Park, S.W. Kim, T. Hyeon, B.M. Kim, Tetrahedron Assym. 12 (2001) 1931.
[28] T. Kugita, S.K. Jana, T. Owada, N. Hashimoto, M. Onaka, S. Naba, Appl. Catal. A 245 (2003) 353.
[29] E.G. Derouane, J. Mol. Catal. A 134 (1998) 29.
[30] J.C. Davis, T.V. Van Auken, J. Am. Chem. Soc. 87 (1965) 3900.
[31] W. Heinen, L.N. Ballijns, W.J.A. Wittenburg, R. Winters, J. Lugtenburg, M. Van Duin, Polymer 40 (1999) 4353.
[32] K.N. Houk, R.W. Strozier, J. Am. Chem. Soc. 95 (1973) 4094.