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Base-functionalized MCM-41 as catalysts for the synthesis of monoglycerides

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Abstract

The mesoporous molecular sieves of the M41S family have little intrinsic catalytic activity. However, it is possible to functionalize the material by grafting organic side chains on the walls. These organic–inorganic hybrid materials maintain the advantages of the inorganic support, notably a high surface area and structural stability at elevated temperature and pressure. Catalysts based on MCM-41 functionalized with either hindered amine bases or free primary amino groups have been evaluated for the facile synthesis of monoglycerides from fatty acids and glycidol. Yields as high as 95% in 8 h have been achieved. The catalysts can be reused several times with little loss of activity. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Organic–inorganic hybrid catalyst; MCM-41; Mesoporous materials; Monoglyceride synthesis; Hindered amine bases

1. Introduction

Monoglycerides are important food additives, which find uses as emulsifiers and antimicrobial agents. As emulsifiers, monoglycerides are far superior to diglycerides while the presence of triglycerides is undesirable. The commercial process for the production of monogylcerides uses the transesterification of fats and oils at high temperature in the presence of a strong base [1], preferably KOH or $Ca(OH)_2$. This process is energy intensive, and the product is only of limited purity. The resulting mixture of mono- and diglycerides has to be separated by vacuum distillation to yield a product, distilled monoglyceride, with about 90% monoglyceride content. Alternative methods are the enzymatic alcoholysis of a triglyceride [2] or the enzymatic synthesis from glycerol and a fatty acid [3]. The drawbacks of the enzymatic processes are a low space velocity and a relatively complex work-up of the reaction mixture. However, recent advances in enzyme immobilization have improved the viability of these processes [4,5].

The use of heterogeneous catalysts offers well-known advantages in process design, especially with respect to the separation of products from the catalyst, and recycling or retaining of the catalyst in the reactor. Corma et al. [6] evaluated solid base catalysts, e.g., Cs-exchanged MCM-41, MgO, and calcined hydrotalcites with different Al/Mg ratios for the glycerolysis of fats and oils. They obtained the best

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results with MgO where the conversion of the triglyceride reached 97% after 5 h reaction at 513°C and monoglyceride selectivities up to 75% were achieved. However, a large molar excess of glycerol (molar ratio glycerol to triglyceride 12:1) was used which resulted in a complex work-up procedure, whereby the reaction mixture is first dissolved in propan-2-ol, followed by extraction of the fatty esters with hexane.

Monoglycerides with a much higher purity can be obtained by the ring-opening glycolization between a fatty acid and glycidol [7]. This reaction takes place smoothly and with high regioselectivity in the presence of stoichiometric amounts of titanium tetrapropylate, $Ti(OPr)_4$ [8]. However, the large amount of titanium salts formed makes work-up difficult and restricts this method to the laboratory. Cauvel et al. [9] and Brunel et al. [10] described a novel heterogeneous catalyst for the ring opening reaction, which is based on the mesoporous molecular sieve, MCM-41. They prepared an organic–inorganic hybrid catalyst by grafting an organic side chain of three carbon atoms length on the silica surface, as described in Ref. [11]. This side chain was functionalized with a primary or tertiary amine as the active group. They compared the activity of a primary amino group (*n*-propylamine) with a tertiary aminde(piperidine). It was found that the tertiary amine is more active than the primary amine.

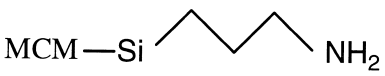
In related work, Iijima et al. [12] and Tamura et al. [13] proposed polymer-bound strong organic bases as reagents for the synthesis of phospholipids. Schuchard et al. [14] investigated the transesterification of edible oils with methanol, homogeneously catalyzed by organic guanidine bases [14], and with bases immobilized on chloromethylated styrene/divinylbenzene resins [15]. They reported reduced catalytic activity when the guanidinium cation had lower base strength due to steric, substitutional and symmetry effects. Triazabicyclo[4,4,0]dec-5-ene (TBD), is an extremely strong organic base and it was found to be particularly active, both in the free form, and immobilized on an organic resin. Subba Rao et al. [16] were the first to prepare a catalyst based on TBD immobilized on MCM-41. They reported high activity for base-catalyzed reactions such as Michael addition and Knoevenagel condensation. In this study, we prepared several catalysts by grafting organic bases onto MCM-41 and compare their activity for the reaction between glycidol and a fatty acid (lauric acid). In addition, the kinetics for the formation of the monogylceride is also investigated.

2. Experimental

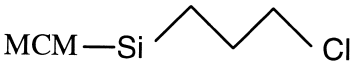
MCM-41 was prepared by a modification of the original disclosure [17]. *N*-Cetyl-*N*,*N*,*N*-trimethylammonium bromide ($C_{16}H_{33}N(CH_3)_3^+Br^-$; CTMA-Br) (Merck) was partially converted to CTMA-OH by batchwise ion exchange, and added to tetraethoxysilane ($Si(OC_2H_5)_4$; TEOS) and water to give a gel of composition Si:CTMA:H_2O of 1:1.06:45. The gel was stirred at 70°C for 3 h before it was transferred to a Teflon-lined stainless steel autoclave. The hydrothermal synthesis was carried out at 120°C for 48 h. The resulting material was recovered by filtration, washed, dried and calcined to 550°C for 10 h in order to remove the template CTMA molecules. The mesoporous nature of the calcined material was confirmed by powder X-ray analysis (Siemens D5005) and nitrogen adsorption measurements. The X-ray diffractogram shows three sharp reflexes at $2\theta \sim 1.9°$, 3.3° and 3.8°, which can be indexed as the (100), (110) and (200) reflexes for a hexagonal lattice. The nitrogen adsorption isotherm displays a sharp step at $P/P_0 = 0.35$ indicating pores with a very narrow pore size distribution around ~ 40 Å diameter. These features together with a very high surface area of $> 1000\ m^2/g$ confirmed the high quality of the material.

The organic bases used in this study are given in Table 1. Aminopropylsilyl-functional-

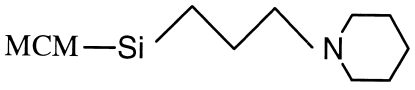
Table 1
Organic bases grafted on MCM-41 support



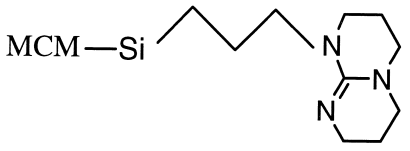
Amino-propylsilyl/MCM-41
(NH_2/MCM-41)



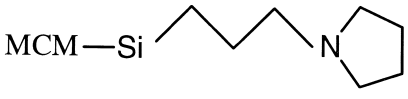
Chloro-propylsilyl/MCM-41
(Cl/MCM-41)



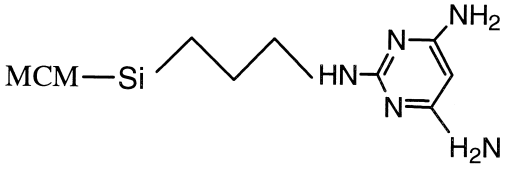
Piperidine-propylsilyl/MCM-41
(Pip/MCM-41)



Triazabicyclo[4,4,0]dec-5-ene-propylsilyl/MCM-41
(TBD/MCM-41)



Pyrolidine-propylsilyl/MCM-41
(Pyr/MCM-41)



Pyrimidine-propylsilyl/MCM-41
(PM/MCM-41)

ized MCM-41 was prepared as follows: 3 g of MCM-41 material was heated for 4 h at 350°C in vacuo to remove all adsorbed moisture but not the surface OH-groups. The material was left to cool in vacuo, and then transferred under argon into a dry 250 ml round bottom flask. It was suspended in 50 ml dry toluene, and 3 g of 3-aminopropyltriethoxysilane (Fluka) were added. The mixture was stirred and heated to reflux. After about 1.5 h, the ethanol was removed by azeotropic distillation together with some toluene (boiling point 106°C). The reaction was continued for another 30 min, before the material was removed by filtration. The catalyst was extensively extracted with methylene chloride (CH_2Cl_2) in a Soxhlet extractor over a period of 8 h and dried at room temperature.

Functionalizing with 3-chloropropyltriethoxysilane followed the same method. The chloropropylsilyl-compound obtained in this step was then reacted with free secondary amine bases (piperidine, pyrolidine, TBD and 2,4,6-triaminopyrimidine) to give the other basic catalysts shown in Table 1. For the reaction, the organic base was heated in toluene together

with the chloro-functionalized MCM-41. After 6 h under reflux, the solid was filtered off, and unreacted base was removed by extraction with methylene chloride. The amount of organic material grafted on the support was determined from the weight loss by thermogravimetric analysis in air and in nitrogen (DuPont SDT 2960). The sample was heated at 20°C/min to 100°C, which temperature was maintained for 30 min before ramping up to 600°C. This ensures thorough drying of the sample, so that the resulting weight loss at higher temperatures can be attributed wholly to loss of the grafted material. To check the completeness of the reaction between chloropropylsilyl/MCM-41 and the organic bases, the amount of chlorine in the re-

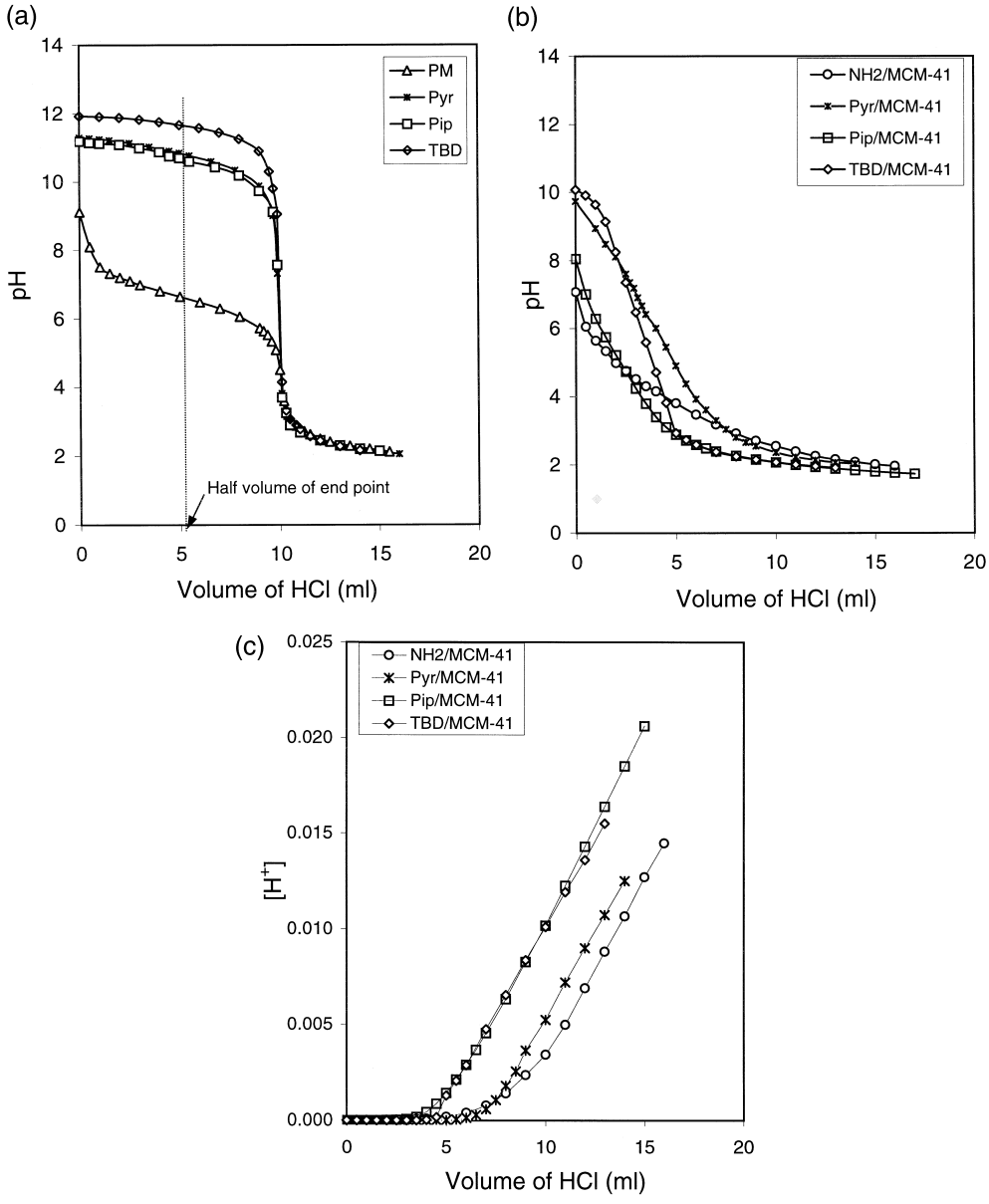


Fig. 1. Potentiometric titration curves of (a) free bases and (b) grafted catalysts. (c) Linear plot of $[H^+]$ versus volume of 0.1 M HCl added to 1 g of grafted catalyst to determine the base content.

sulting Pip/MCM-41, Pyr/MCM-41 and TBD/MCM-41 was determined. The material was digested in boiling HNO_3, followed by titration with $AgNO_3$. The concentration of base and the base strength in aqueous suspension was determined by potentiometric titration with 0.1 M HCl, and compared with that of the free bases. Elemental analysis of the silicon, carbon and nitrogen content in the samples was also carried out.

The activity of the catalysts was assessed from the reaction between glycidol (oxirane-2-methanol) and lauric acid (dodecanoic acid). One gram of the activated catalyst was transferred into a 100 ml round bottom flask and under argon, 2 g (10 mmol) of lauric acid, 0.74 g (10 mmol) of glycidol and 25 ml of toluene were added. The mixture was heated with stirring to 110°C. Samples were withdrawn initially every 2 h and later at longer intervals, and the reaction mixture was analyzed by gas chromatography (Supelco Petrocol™ $20'' \times 1/8''$; ramp to 350°C; FID). The products were identified by their retention times after initial GC-MS analysis. Glycidol cannot be quantified by this method because its signal overlaps with the solvent peak. The other compounds detected are the unreacted lauric acid, mono-, di- and triglycerides.

3. Results and discussion

3.1. Basicity of the catalysts

The potentiometric titration curves for the free bases and the grafted bases are shown in Fig. 1. The free bases show typical titration curves with a pronounced step at the equivalence point. The pK_A values read from the curves at the half-titration point agree well with data found in the literature [18], except for TBD, where in the aprotic solvent CH_3CN, a pK_A of 25 has been reported [19], whereas the potentiometric titration in water gives a value of 11.8. However, the titration curves of the grafted materials show a continuous drop in pH with the added volume of HCl. The sites on the grafted material have generally a lower basicity than the free base, and they also show a wide distribution in the base strength. The base content of the grafted catalysts can be obtained by plotting $[H^+]$ as a function of added acid on a linear scale. This curve shows a distinct change in the slope at the equivalence point.

In thermogravimetric analysis, all the samples showed an initial weight loss below 100°C due to the removal of physically adsorbed water. Above this temperature, the MCM-41 suffered very little weight loss (Fig. 2). In contrast, the grafted samples showed a rather pronounced loss in weight above 300°C to ~600°C. This can be attributed to the decomposition of the organic base. Hence, the amount of base grafted on the MCM-41 can be determined from the weight loss in this temperature range. All the grafted samples showed a bigger weight loss when the decomposition was performed in nitrogen than in air. For example, for Pip/MCM-

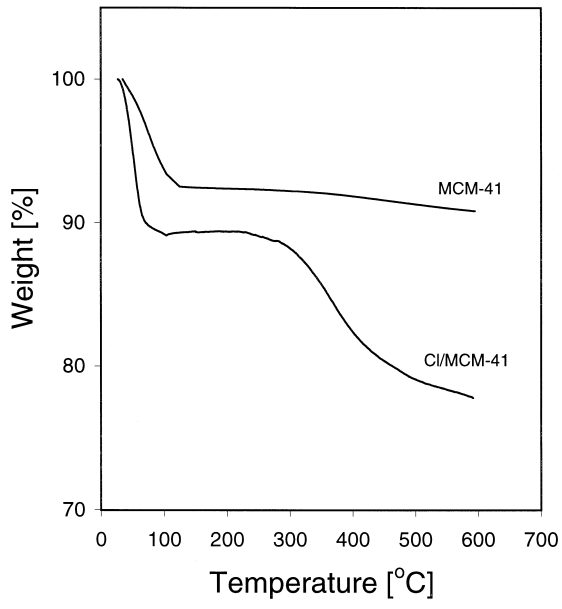


Fig. 2. Weight loss of MCM-41 and grafted catalyst Cl/MCM-41 during thermogravimetric analysis in air.

Table 2
Concentration of organic base (determined from weight loss in TGA and by potentiometric titration) and chloride in the grafted samples (n.a.: not applicable)

Catalyst	Base concentration [mol/g]		Chloride [mmol/g]
	TGA	Potentiometric	
NH_2/MCM-41	0.79	0.81	n.a.
Cl/MCM-41	0.76	–	0.83
Pip/MCM-41	0.77	0.49	0.29
Pyr/MCM-41	0.79	0.70	0.45
TBD/MCM-41	0.69	0.48	0.20

41, the weight loss in air was 9.45% of the dried sample while in nitrogen, the loss was 10.7%. This corresponds to a weight loss in air of 16 atomic units per mole of grafted side chains less than in nitrogen. Hence, we assume that the decomposition of the surface-bound organosilicon compound Si–R in air leads to a new Si–OH group, whereas in nitrogen, the Si–C bond is thermally cleaved, and a Si–H group remains at the surface. The values of the base content obtained from the weight loss above 300°C in TGA agree well with the values for free base, as determined by potentiometric titration, and the chloride content (Table 2). The presence of chloride in Pip/MCM-41, Pyr/MCM-41 and TBD/MCM-41 shows that some of the HCl released during the grafting reaction is readsorbed onto the basic sites of the sample. It therefore neutralizes part of the basic sites. Only for Pyr/MCM-41, a higher chloride content of 0.45 g/mol was detected. This seems to be related to the poor activity of this catalyst (see below).

3.2. Monoglyceride formation

The yield of the monolauryl glyceride for the different solid base catalysts with reaction time is shown in Table 3. Except for the first run with TBD, where the yield reaches a maximum after 2 h and decreases thereafter, all the other catalysts show a continuous increase in yield and conversion with time. With TBD, the conversion of the lauric acid reached 100%, but the monolauryl glyceride yield decreased due to the formation of di- and triglycerides. With this very strong base, the reaction reaches an equilibrium composition. In addition, glycidol is consumed in a side reaction, forming polymeric products. Another side reaction is the glycidation of surface silanol groups. Cauvel et al. [9] suggested to remove such OH-groups by silylation with hexamethyldisilazane ($(CH_3)_3$–Si–NH–Si$(CH_3)_3$). However, the authors observed that the effect of silylation was the same as that of the reaction with glycidol during the initial phase of reaction. Therefore, we did not use an additional silylation step but rather evaluated the performance of the catalyst during several catalytic cycles. The glycidation reaction with surface OH-groups removes glycidol and thus explains the lower monoglyceride yield in the first run seen with all the catalysts. In addition, primary amines are prone to *N*-alkylation. This reaction too reduces the amount of glycidol available for the formation of monoglyceride. Therefore, a very low yield in monoglycerides is obtained with the aminopropyl-catalyst (NH_2/MCM-41) in the first run, 32.7%. The second run had an increased yield of 80.9% after 24 h of reaction. The bulkier 3-aminopyrimidine group of the PM/MCM-41 catalyst cannot be alkylated so easily because it is confined to the pore space. As a result, the

Table 3
%Yield of monoglyceride over different solid bases as a function of reaction time

Catalyst	Run	Time (h)					
		2	4	6	18	21	24
NH_2/MCM	1st	17.1	24.9	30.8	31.9	32.6	32.7
	2nd	16.2	23.1	36.2	68.5	74.6	80.9
	3rd	14.9	22.8	38.0	71.2	77.9	84.2
	4th	14.1	24.4	40.0	66.5	71.3	75.7
Pip/MCM	1st	42.5	68.9	73.1	80.2	81.2	81.3
	2nd	36.0	65.0	79.1	84.5	85.5	86.2
TBD/MCM	1st	68.2	62.5	59.8	56.4	53.3	43.8
	2nd	58.3	79.7	84.1	95.0	95.0	95.0
PM/MCM-41	1st	31.1	38.8	46.7	55.9	60.6	62.4
	2nd	32.0	39.5	48.9	69.4	74.5	79.3

final yield is only slightly lower in the first run than in the second run (62.4% versus 79.3%). The used catalysts show an almost unchanged initial activity as indicated by the value for the monoglyceride yield after 2 h, and a very improved yield after 24 h of reaction, up to between 80 and 95% as compared to 30–50% for the fresh catalysts. The selectivity towards monoglyceride is now almost 100% over the entire reaction time.

Initially, used catalysts were recovered and regenerated by extensive extraction with toluene and methylene chloride, followed by vacuum activation at 150°C. Since this procedure is time consuming and labor intensive, we attempted to reuse the catalyst directly. It is found that the activity of the ''as-is'' catalysts is as good or better as that of the ''regenerated'' catalysts. We have re-used the catalysts for up to four cycles, and found that the activity is essentially constant within the statistical fluctuations due to thermal side reactions of glycidol.

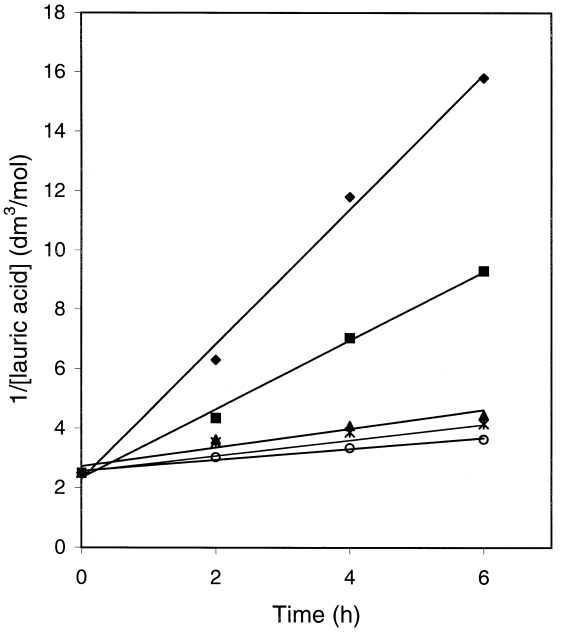


Fig. 3. Data analysis for second order kinetics. ◆ TBD/MCM-41, ■ Pip/MCM-41, ▲ PM/MCM-41, ○ NH_2/MCM-41, ☆ Pyr/MCM-41.

Table 4
pK_A of the free organic bases and rate constants for monoglyceride formation over the corresponding grafted catalysts

Compound	pK_A	Rate constant [$dm^3\ mol^{-1}\ s^{-1}$]
1,5,7-triazabicyclo-[4,4,0]dec-5-ene	25 [16], 11.8[a]	6.14×10^{-4}
Piperidine	11.123 [19]	3.14×10^{-4}
Pyrolidine	11.27 [19]	0.768×10^{-4}
2,4,6-triaminopyrimidine	6.42[a]	0.736×10^{-4}
Propylamine	10.60 [19]	0.528×10^{-4}

[a]Own measurements in water as solvent, this paper.

3.3. Reaction order and reaction rate

To compare the activities of the different catalysts, the kinetics of the reaction was studied. Except for TBD/MCM-41, the result of the first run was used for comparison as the rate of reaction was similar to that of subsequent runs. In the reaction catalysed by TBD/MCM-41, the second run had substantially higher yield than the first run, and data from the second run were used for evaluation of the kinetics. It is found that the reaction obeys second-order kinetics, being first-order in lauric acid and glycidol concentration. Since both reagents were used in stoichiometric concentration, a plot of 1/[concentration] against reaction time should result in a straight line. The data for the first 6 h of reaction do indeed fall on straight lines (Fig. 3), indicating that the reaction is pseudo-second-order. The reaction order in catalyst concentration was also determined, and it is found that the reaction rate is directly proportional to the amount of catalyst present. The initial rate constant for the reaction over the used TBD/MCM-41 catalyst is the highest followed by Pip/MCM-41, Pyr/MCM-41, PM/MCM-41 and NH_2/MCM-41 (Table 4). The activity correlates approximately with the base strength of the organic bases except for Pyr/MCM-41. The low activity of Pyr/MCM-41 may be due to the high chloride content found on this catalyst. The presence of hydrogen chloride results in the blocking of active sites.

4. Conclusion

Solid basic catalysts have considerable advantages, especially in reactions in non-aqueous solvents. The organic–inorganic hybrid catalysts, based on MCM-41 with a hindered amine base immobilized by a short but flexible spacer, show good activity and can be easily regenerated. The mesoporous nature of the support leads to a very high surface area and a loading of base in the order of 0.8 mmol/g. Because of the large diameter of the pores, all the catalytic sites inside the catalyst are easily accessible for reacting molecules. Turnover numbers of > 30 have been reached and the catalyst maintains its full activity. The catalyst can be used in organic solvents without swelling or dissolution.

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