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Heterogenised chiral amines as environmentally friendly base catalysts for enantioselective Michael addition

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Abstract

Heterogenised chiral amines on silica, MCM-41 and delaminated zeolite ITQ-2 have been prepared and fully characterised. These new catalysts have been tested in the Michael addition of ethyl 2-oxocycloalkanecarboxylates to acrolein. The heterogenised amines presented higher rates than referable homogeneous counterparts; moreover these catalysts were recovered quantitatively by simple filtration and reused in without loss of activity. MCM-heterogenised catalysts show slightly lower reaction rate but improved enantiomeric excess than silica-heterogenised materials, especially with bulky reagents. The use of a high specific surface support (ITQ-2) does not imply an improvement in the catalytic activity of the material.

Keywords: Enantioselective Michael addition; Heterogenised chiral base catalyst

1. Introduction

Nowadays, increasing demanding environmental legislation, public and corporate pressures have forced chemists to develop cleaner technologies. This fact will provide opportunities for new catalysts and new environmental friendly catalytic processes and the possibility for easy recovery and reuse of these materials, mainly in the case of the expensive or not-easily available reagents. The two preferential tendencies are polymer-supported catalysts and inorganic oxides heterogenised catalysts [1,2]; the last ones show several advantages, such as more mechanical stability, easier handling and a wider range of solvents that could be used. Furthermore, among the inorganic oxides, the zeolites that present regular crystalline structure with high specific surface and periodic regular cavities and pores of molecular dimensions are the support of election for tuning activities and selectivities. The support acts like many small molecular reactors and modifies the characteristics of free catalysts by increasing the steric constraints and enhancing the local concentrations of reagents near the surface where the reaction takes place. Recently, some groups have described the preparation of simple solid catalysts based on zeolite and their successful application as base catalysts in organic reactions [3–6].

In a previous work we found that some heterogenised chiral amines, based on cinchonine and cinchonidine, are active in Michael addition of nucleophiles to enones [7], although the enantioselectivity of the reaction were moderated. Taking this into account and trying to improve the enantioselectivity, in the present work we prepare new chiral amines, having a chiral environment instead of a chiral base centre.

We report a very feasible methodology to synthesise and heterogenise new amines, having a chiral environment, on inorganic supports such as silica, mesoporous MCM-41 and delaminated zeolite ITQ-2, and their use as ''green'' and reusable catalysts in the enantioselective Michael addition of ethyl 2-oxocycloalkanecarboxylate to acrolein.

2. Experimental

All solvents were carefully degassed before use. The silylating agents, $Cl(CH_2)_3Si(OEt)_3$ and $NH_2(CH_2)_3Si(OEt)_3$

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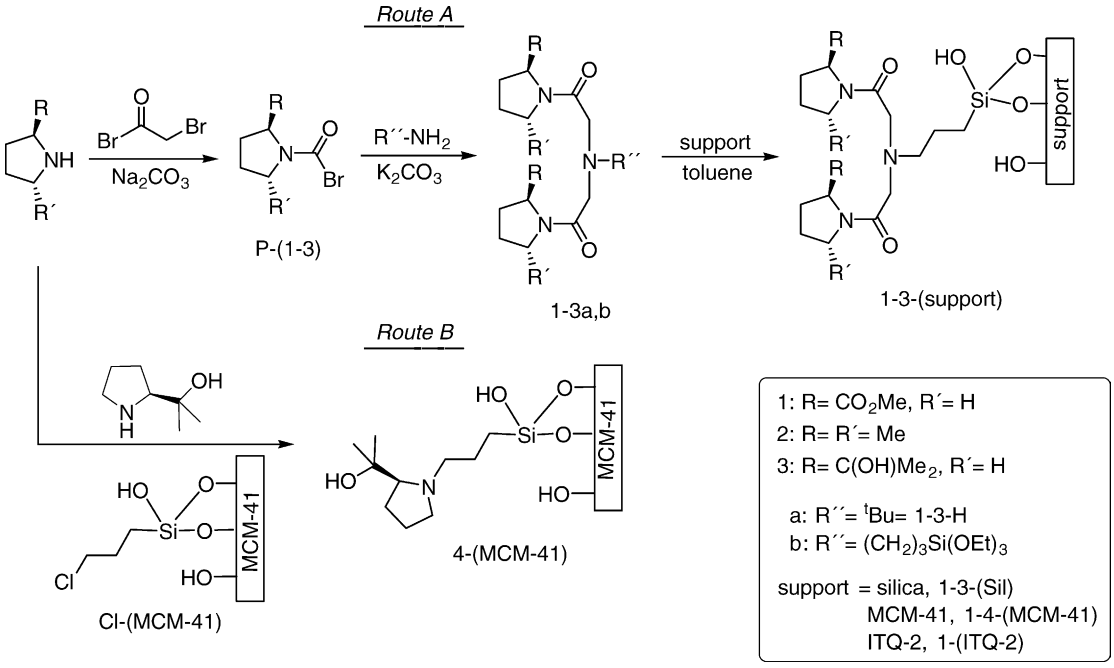


Scheme 1. Synthesis of homogeneous and heterogenised catalysts.

were obtained from Aldrich (96%) and were distilled before use. C, H and N analysis were carried out with a Heraeus and a Perkin-Elmer 240C apparatus, respectively. IR spectra were recorded with a Nicolet XR60 spectrophotometer (range 4000–200 cm^{-1}) in KBr pellets; ^{1}H and ^{13}C NMR spectra were taken on Varian XR300 and Bruker 200 spectrometers; signals were unequivocally assigned based on bidimensional experiments (HMQC, HSQC). Chemical shifts are given in ppm using tetramethylsilane as an internal standard. Optical rotation values were measured at the sodium-D line (589 nm) with a Perkin-Elmer 241 MC polarimeter. Gas chromatography analysis was performed using a Hewlett-Packard 5890 II with a flame ionisation detector. The inorganic supports for anchoring were silica gel (Merck silica, average pore diameter 40 Å), purely siliceous MCM-41 [8], and delaminated zeolite ITQ-2 [9].

2.1. Synthesis of homogenous catalysts

Catalysts **1**–**3a**,**b** were prepared in a two-step sequence (Scheme 1) starting from methyl (*S*)-pyrrolidine-2-carboxylate (for ligand **1a**,**b**), (*2R*,*5R*)-2,5-dimethylpyrrolidine [8] (for ligand 2**a**,**b**) or 2-[(*S*)-pyrrolidin-2-yl]-propan-2-ol (for ligand 3**a**,**b**).

2.1.1. Synthesis of bromoacetyl derivatives *P-(1–3)*

General procedure: To a mixture of the corresponding ligand {(*S*)-methyl pyrrolidine-2-carboxylate, (*2R*,*5R*)-2,5-dimethylpyrrolidine [10] or 2-[(*S*)-pyrrolidin-2-yl]-propan-2-ol} (0.025 mol) and Na_2CO_3 (0.040 mol) in CH_2Cl_2 (100 ml), cooled at −40 °C for 2 h, a solution of 2-bromoacetyl bromide (0.025 mol) in the same solvent (10 ml) was slowly added. Then, 2 h later, it was allowed to warm up to room temperature. After 16 h, the organic solvent was removed under vacuum. The residue was purified by chromatography on silica gel using mixtures of AcOEt/Hex as eluent. Chemical yields of these ligand precursors **P-**(**1**–**3**) are reported in Table 1.

2.1.2. Synthesis of ligands (*1–3a,b*)

I*General procedure*: *tert*-Butylamine or trietoxysilylpropylamine (1 mmol) was added to a mixture of corresponding bromoacetyl derivative **P-**(**1**–**3**) (2 mmol) and Na_2CO_3 (20 mmol) in acetonitrile (50 ml). After 15 h at 70 °C the reaction mixture was filtered and solvent evaporated under reduced pressure. The residue was purified by chromatography on silica gel using mixtures of AcOEt/Hex as eluent. Chemical yields of new ligands **1**–**3a**,**b** are reported in Table 1.

*2.1.2.1. bis-{2-[(R)-2-Methoxycarbonylpyrrolidin-1-yl]-2-oxoethyl}-tert-butylamine (**1a**).* ^{1}H NMR (ppm): 4.37–4.32

Table 1
Chemical yields of homogeneous and heterogenised base catalysts

Ligand precursor	Yield (%)	Homogenous catalyst	Yield (%)	Heterogenised catalyst	Yield (%)	Ligand content (mmol/g)[a]
P-1	67	**1a**	57	1-(Sil)	95	0.380
		1b	78	1-(MCM-41)	82	0.328
				1-(ITQ-2)	100	0.402
P-2	58	**2a**	46	2-(Sil)	91	0.364
		2b	50	2-(MCM-41)	95	0.378
P-3	32	**3a**	83	3-(Sil)	57	0.229
		3b	87	3-(MCM-41)	45	0.181
				4-(MCM-41)	17	0.514

[a]mmol of ligand per gram of support.

(m, 2H, CH cycl); 3.90–3.82, 3.58–3.48 (2 m, 4H, CH_2N cycl); 3.68 (s, 6H, Me); 3.57, 3.40 (AB, 4H, J = 12.7 Hz, CH_2CO); 2.18–2.07, 1.72–1.64 (2 m, 4H, $C\underline{H}_2CH$ cycl); 1.99–1.85 (m, 4H, $CH_2C\underline{H}_2CH_2$ cycl); 1.11 (s, 9H, ^{t}Bu).

^{13}C NMR (ppm): 172.92 (2C, CO); 170.63 (2C, $\underline{C}O_2Me$); 59.06 (2C, CH cycl); 58.51 (2C, CH_2N cycl); 55.19 (1C, C ^{t}Bu); 52.04 (1C, OCH_3); 46.49 (2C, $\underline{C}H_2CO$); 26.53 (2C, $\underline{C}H_2CH$ cycl); 26.99 (3C, CH_3 ^{t}Bu); 24.99 (2C, $CH_2\underline{C}H_2CH_2$ cycl).

*2.1.2.2. bis-{2-[(2R,5R)-2,5-Dimethylpyrrolidin-1-yl]-2-oxoethyl}-tert-butylamine (**2a**).* ^{1}H NMR (ppm): 4.26–4.05 (m, 4H, CH cycl); 3.62, 3.46 (AB, 4H, J = 13.5 Hz, CH_2CO); 2.17–1.96, 1.55–1.41 (2 m, 8H, CH_2 cycl); 1.14, 1.09, 0.98 (3 s, 12 H, Me); 1.12 (s, 9H, ^{t}Bu).

^{13}C NMR (ppm): 170.82 (2C, CO); 54.76 (1C, C ^{t}Bu); 53.16 (2C, $\underline{C}H_2CO$); 52.50, 51.50 (4C, CH cycl); 30.92, 27.40 (4C, CH_2 cycl); 28.67 (3C, CH_3 ^{t}Bu); 21.51, 18.85 (4C, Me).

*2.1.2.3. bis-{2-[(S)-2-(2-Hydroxypropan-2-yl)-pyrrolidin-1-yl]-2-oxoethyl}-tert-butylamine (**3a**).* ^{1}H NMR (ppm): 6.58 (s, 2H, OH); 4.14–3.97, 3.31–3.18 (2 m, 4H, CH_2N cycl); 3.93 (t, 2H, J = 7.7 Hz, CH cycl); 3.58, 3.38 (AB, 4H, J = 13.8 Hz, CH_2CO); 2.07–1.92, 1.60–1.46 (2 m, 4H, $C\underline{H}_2CH$ cycl); 1.89–1.73 (m, 4H, $CH_2C\underline{H}_2CH_2$ cycl); 1.12 (s, 6H, Me); 1.11 (s, 9H, ^{t}Bu); 0.97 (s, 6H, Me).

^{13}C NMR (ppm): 173.82 (2C, CO); 73.76 (2C, COH); 69.50 (2C, CH cycl); 55.88 (1C, C ^{t}Bu); 53.08 (2C, $\underline{C}H_2CO$); 48.49 (2C, CH_2N cycl); 28.82 (2C, $\underline{C}H_2CH$ cycl); 28.30 (2C, Me); 27.29 (3C, CH_3 ^{t}Bu); 24.83 (2C, $CH_2\underline{C}H_2CH_2$ cycl); 23.74 (2C, Me).

*2.1.2.4. bis-{2-[(R)-2-Methoxycarbonylpyrrolidin-1-yl]-2-oxoethyl}-3-(triethoxysilyl)propylamine (**1b**).* ^{1}H NMR (ppm): 4.50–4.48 (m, 2H, CH cycl); 3.78 (c, 6H, J = 7.1 Hz, $OC\underline{H}_2CH_3$); 3.62–3.51, 2.76–2.63 (2 m, 4H, CH_2N cycl); 3.52, 3.47 (AB, 4H, J = 15.5 Hz, CH_2CO); 2.22–2.09, 1.74–1.58 (2 m, 4H, $C\underline{H}_2CH$ cycl); 1.99–1.78 (m, 4H, $C\underline{H}_2CH_2$ cycl); 1.22 (t, 9H, J = 7.1 Hz, $OCH_2C\underline{H}_3$); 0.63–0.51 (m, 2H, CH_2Si).

^{13}C NMR (ppm): 172.75 (2C, CO); 169.63 (2C, $\underline{C}O_2Me$); 58.79 (2C, CH cycl); 58.32 (2C, $\underline{C}H_2N$ cycl); 56.04 (2C, $\underline{C}H_2CO$); 51.97 (1C, OC, OCH_3); 51.86 (1C, $N\underline{C}H_2CH_2$); 46.67 (3C, $O\underline{C}H_2CH_3$); 28.97 (2C, $\underline{C}H_2CH$ cycl); 25.02 (2C, $CH_2\underline{C}H_2CH_2$ cycl); 20.83 (1C, $NCH_2\underline{C}H_2$); 18.27 (3C, $OCH_2\underline{C}H_3$); 7.93 (1C, CH_2Si).

*2.1.2.5. bis-{2-[(2R,5R)-2,5-Dimethylpyrrolidin-1-yl]-2-oxoethyl}-3-(triethoxysilyl)propylamine (**2b**).* ^{1}H NMR (ppm): 4.28–4.05 (m, 4H, CH cycl); 3.77 (c, 6H, J = 7.1 Hz, $OC\underline{H}_2CH_3$); 3.65, 3.45 (AB, 4H, J = 13.5 Hz, CH_2CO); 2.78–2.69 (m, 2H, $NC\underline{H}_2CH_2$); 2.15–1.98, 1.53–1.40 (2 m, 8H, CH_2 cycl); 1.65–1.52 (m, 4H, $NCH_2C\underline{H}_2$); 1.18 (t, 9H, J = 7.1 Hz, $OCH_2C\underline{H}_3$); 1.14, 1.10, 1.08 (3 s, 12H, Me); 0.62–0.50 (m, 2H, CH_2Si).

^{13}C NMR (ppm): 170.62 (2C, CO); 53.04 (2C, $\underline{C}H_2CO$); 52.53, 51.51 (4C, CH cycl); 51.87 (1C, $N\underline{C}H_2CH_2$); 48.72 (3C, $O\underline{C}H_2CH_3$); 30.92, 27.52 (4C, CH_2 cycl); 21.32, 18.95 (4C, Me); 20.93 (1C, $NCH_2\underline{C}H_2$); 18.38 (3C, $OCH_2\underline{C}H_3$); 8.11 (1C, CH_2Si).

*2.1.2.6. bis-{2-[(S)-2-(2-Hydroxypropan-2-yl)-pyrrolidin-1-yl]-2-oxoethyl}-3-(triethoxysilyl)propylamine (**3b**).* ^{1}H NMR (ppm): 6.35 (s, 2H, OH); 4.05 (t, 2H, J = 7.5 Hz, CH cycl); 3.82–3.60, 2.76–2.68 (2 m, 4H, CH_2N cycl); 3.77 (c, 6H, J = 7.0 Hz, $OC\underline{H}_2CH_3$); 3.58, 3.49 (AB, 4H, J = 15.7 Hz, CH_2CO); 3.35–3.21 (m, 2H, $NC\underline{H}_2CH_2CH_2$); 2.08–1.93, 1.65–1.50 (2 m, 4H, $C\underline{H}_2CH$ cycl); 1.91–1.82, 1.77–1.68 (2 m, 4H, $CH_2C\underline{H}_2CH_2$ cycl); 1.18 (t, 9H, J = 7.0 Hz, $OCH_2C\underline{H}_3$); 1.14 (s, 6H, Me); 0.99 (s, 6H, Me); 0.60–0.52 (m, 2H, CH_2Si).

^{13}C NMR (ppm): 172.90 (2C, CO); 73.80 (2C, COH); 68.86 (2C, CH cycl): 58.67 (2C, CH_2N cycl); 57.08 (2C, $\underline{C}H_2CO$); 50.87 (1C, $N\underline{C}H_2CH_2$); 48.66 (3C, $O\underline{C}H_2CH_3$); 28.76 (2C, $\underline{C}H_2CH$ cycl); 28.28 (2C, Me); 24.94 (2C, $CH_2\underline{C}H_2CH_2$ cycl); 23.85 (2C, Me); 21.32 (1C, $NCH_2\underline{C}H_2$); 18.58 (3C, $OCH_2\underline{C}H_3$); 8.31 (1C, CH_2Si).

2.2. Heterogenisation of amines on silica, mesoporous MCM-41 and delaminated zeolite ITQ-2

Both used supports, silica and MCM-41, are short-range amorphous materials containing a large number of silanol groups available for grafting. In the case of MCM-41, however, the material presents a long-range ordering with hexagonal symmetry with regular monodirectional channels of 3.5 nm diameter. On the other hand, ITQ-2 delaminated zeolite presents short and long-range order, together with a very large-well structured external surface in where the silanol groups act as grafting centres. Indeed, there are ''cup-like'' apertures to the external surface with ~0.8 nm × 0.8 nm dimensions where the molecules could fit, as shown by quantum-mechanic calculations.

Heterogenised amines were synthesised following two different strategies (see Scheme 1):

Route A: A solution of the corresponding amine **1**–**3b** (0.4 mmol) in toluene (5 ml) was added to a suspension of the inorganic support (1 g) in the same solvent (50 ml). The slurry was heated at 60 °C for 12 h and the solid was filtered off and washed successively with toluene and ethyl ether, and was Soxhlet-extracted with diethyl ether-CH_2Cl_2 for 16–24 h to remove all organic material non-covalently bounded to the support. The solid was dried under vacuum to afford the heterogenised amines **1–3-(support)**. The content of ligand incorporated to the supports is reported in Table 1.

Route B: MCM-41 was first treated with a refluxing toluene solution (50 ml) of 3-chloropropyltrietoxysilane (3 mmol) followed by washing with in a Soxhlet apparatus for yielding covalently anchored 3-chloropropylsilane moiety **Cl-(MCM-41)**. The chlorinated zeolite (0.5 g) was treated with the dry DMF solution of 2-[(*S*)-

pyrrolidin-2-yl]-propan-2-ol (1 mmol). The mixture was stirred under reflux for 24 h, filtered and washed successively with DMF, water and ethanol. The crude solid was Soxhlet-extracted with acetone for 16 h, for removing any trace of free amine from the catalytic material [4-(MCM-41)], and dried under vaccum. The content of ligand incorporated to the MCM-41 calculated from elemental analysis is reported in Table 1.

2.3. Catalytic studies on Michael addition reactions

General procedure for the addition of ethyl 2-oxocycloalkanecarboxylates to acrolein: In a typical experiment ethyl 2-oxocyclopentanecarboxylate (**A**) or ethyl 2-oxocyclohexanecarboxylate (**B**) (1 mmol) and acrolein (2 mmol) were added to a suspension of the catalysts (0.1 mmol) in toluene (3 ml). The reaction was stirred at indicated temperature, samples were taken at regular times and, after filtration, they were analysed. Chemical yields and enantiomeric excess of Michael-adduct were measured by GC, using undecane as internal standard, with a chiral glass capillary column {15/85 mixture of methylsilicone (OV-1701) and methylsilicone-heptakis-[2,3-dipentyl-6-(*t*-butyldimethylsilyl)]-β-cyclodextrin as stationary phase} [17]. Results obtained with different catalysts and reactants are summarised in Figs. 1–4.

3. Results and discussion

A series of different homogeneous and heterogenised chiral amines, based on the pyrrolidine skeleton, was synthesised and screened as catalysts for the direct enantioselective Michael addition of ethyl 2-oxocycloalkanecarboxylates to acrolein under neat reaction conditions.

3.1. Synthesis of homogeneous catalysts

Homogeneous catalysts **1–3a**,**b** were prepared in a two-steps sequence as shown in Scheme 1 from methyl (*S*)-pyrrolidine-2-carboxylate, (*2R*,*5R*)-2,5-dimethylpyrrolidine [8] and 2-[(*S*)-pyrrolidin-2-yl]-propan-2-ol, which were previously synthesised in our laboratory using (*L*)-proline or pentane-2,4-dione as precursors. Reaction between these starting materials and acetyl bromide allowed synthesising the compounds **P-(1–3)** in good yields (∼65%). In a second step, free amine group from *t*-butylamine or trietoxysilylpropylamine promoted the nucleophilic displacement of bromine atom of the corresponding bromoacetyl derivatives [**P-(1–3)**] to yield the diastereoisomeric pure chiral amines **1–3a**,**b**.

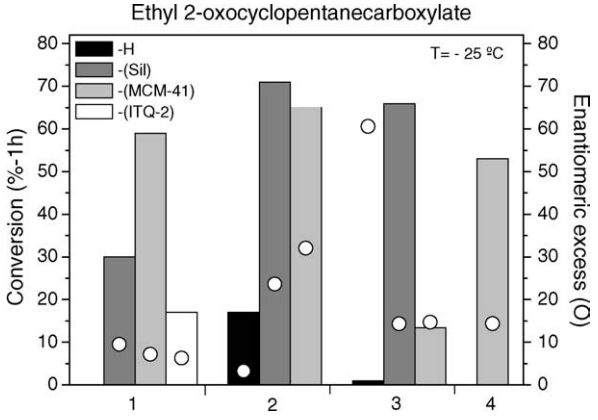


Fig. 1. Catalytic Michael addition of ethyl 2-oxocyclopentanecarboxylate to acrolein.

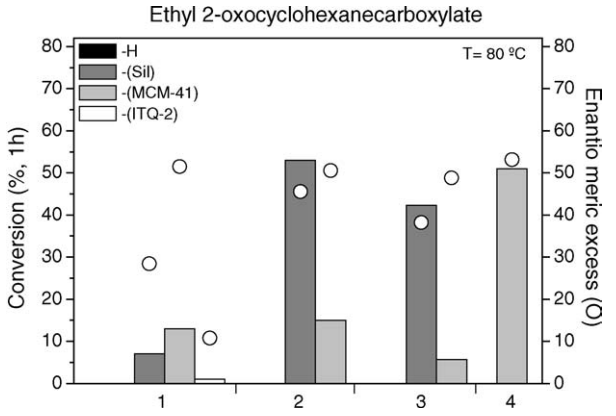


Fig. 2. Catalytic Michael addition of ethyl 2-oxocyclohexanecarboxylate to acrolein.

3.2. Synthesis of heterogenised catalysts

The heterogenised catalysts were prepared easily and with excellent yields following two different strategies, in a sequence such as shown in the Scheme 1. One strategy is basically based on synthesis and heterogenisation of a functionalised amine (**1–3b**), whereas the alternative way [synthesis of **4**-(**MCM-41**)] involves the previous functionalisation of support with a 3-chloropropyl group followed for the reaction with the corresponding ligand.

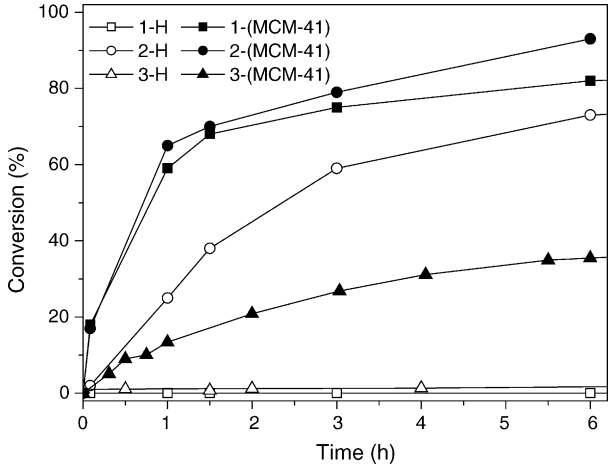


Fig. 3. Kinetic profile of ethyl 2-oxocyclopentanecarboxylate to acrolein with homogeneous and MCM-41-heterogenised catalysts.

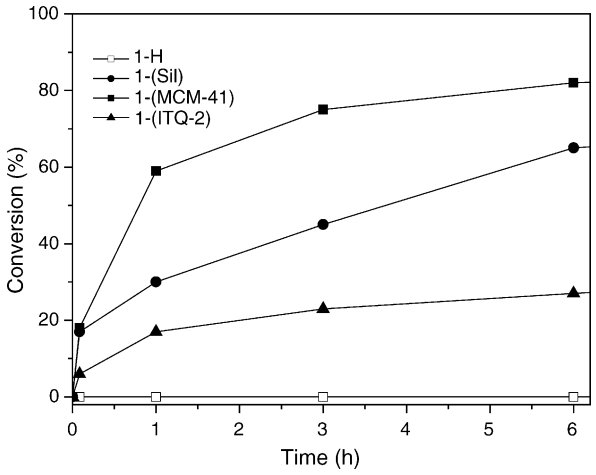


Fig. 4. Comparative kinetic profile for amine-1 and corresponding heterogenised catalysts.

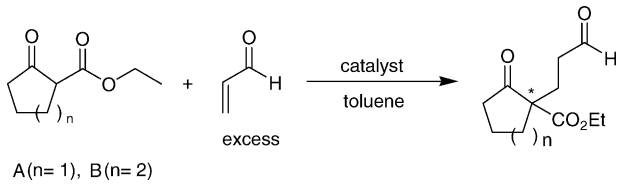
The homogeneous complexes that bearing a $Si(OEt)_3$ group (**1–3b**) were anchored to different inorganic support according to Scheme 1, route A. Preparation of these materials was carried out by controlled hydrolysis of Si–OEt bond at room temperature and reaction with the free silanols (Si–OH) on the surface of support, forming stable covalent bonds between siliceous atom and two or three oxygen atoms from the crystalline net. The loading of ligand in the heterogenised materials ranged from 0.2 to 0.5 mmol/g, dependently on the support. These values have been used for calculating the ratio catalyst/substrate in the reaction tests.

On the other hand, catalyst **4**-(**MCM-41**) was synthesised following the alternative route B (Scheme 1). Support was treated in a previous step with 3-chloropropyltrietoxysilane to include on the support several 3-chloropropyl group, as available centres for heterogenisation. The nucleophilic displacement of chlorine atom for amine group of ligand 2-[(*S*)-pyrrolidin-2-yl]-propan-2-ol yielded the heterogenised material **4**-(**MCM-41**), achieving higher contents of ligand incorporated to the matrix in comparison to its referable heterogenised route A-materials [**1–3**-(**MCM-41**)]. This fact could probably due to the smaller molecular size of the heterogenised ligand.

3.3. Catalytic studies on Michael addition reactions

The catalytic enantioselective conjugate additions are cornerstone reactions in organic chemistry [16]. This class of reactions has over the years been dominated by the application of chiral Lewis acids as catalysts and it is only recently that chiral organocatalysts [11] and chiral amines [12–14] have been applied as catalysts for this class of enantioselective transformations.

Although impressive results have been achieved in many asymmetric reactions, the number of reports on enantioselective Michael addition reactions, where excellent enantioselectivities (>90% ee) have been obtained, is limited [15].



Scheme 2. Catalytic Michael addition of ethyl 2-oxocycloalkanecarboxylate to acrolein.

Based on these facts and our own results obtained with cinchonine and cinchonidine derivatives heterogenised on MCM-41 [7] we selected the Michael addition of ethyl 2-oxocycloalkanecarboxylates to acrolein for testing our solid base catalysts (Scheme 2). The evolution of the reaction was monitored by g.l.c. using a chiral column based on alkylated β-cyclodextrin-methylsilicone developed in our laboratory which permits to estimate simultaneously conversion and enantiomeric excess.

The results obtained with homogeneous catalysts (**1–3**-H) and heterogenised ones [**1-4**-(**support**)] in Michael addition of ethyl 2-oxocyclopentanecarboxylate and ethyl 2-oxocyclohexanecarboxylate to acrolein are shown in Figs. 1–4.

All the chiral environment amines catalysed the Michael addition of the different ethyl 2-oxocycloalkanecarboxylates to acrolein, however, the catalytic and enantioselective properties differ significantly (Figs. 1 and 2). For an easy comparison, results of the Michael addition of 2-ethylpentanecarboxylate to acrolein, catalysed by homogeneous and MCM-41-heterogenised samples, are shown in Fig. 3. Although only MCM-41-heterogenised catalysts are shown in Fig. 3 the same behaviour is observed when other supports are used (Figs. 1 and 2). It can be noted that, in all cases, much higher conversions are obtained with heterogenised samples [**1-3**-(**MCM-41**)] comparing with their referable homogeneous (**1–3-H**). On the other hand, enantioselectivity was low to moderated (5–60%), depends on the support, and no variation was observed with conversion or along the reaction time. Thus, racemisation of the Michael adduct under test conditions have been discarded. It must be noted that enantioselectivity achieved with these new base catalysts, having a chiral environment, is higher than obtained previously with cinchonine and cinchonidine derivatives [7], where only a chiral base centre is present in the structure of catalyst, as we predicted.

The influence of the topology of support and volume size of reactants on the catalytic results obtained with the same chiral amine heterogenised on different supports are shown in Fig. 4. In this case, when chiral amine **1** as ligand, and in general for all heterogenised amines under study [**1–4**-(**support**)] (Figs. 1 and 2), those heterogenised on mesoporous MCM-41 induced higher enantioselectivity to the process, especially with bulky reagents [ethyl 2-oxocyclohexylcarboxylate (**B**) more significant than ethyl 2-oxocyclopentylcarboxylate (**A**)]. This fact is a consequence of the steric constraints derived from the tubular structure of the support (MCM-41), absents in the cases of

amorphous silica or delaminated ITQ-2. Additionally, the use of delaminated zeolite ITQ-2 does not improve the catalytic activity or enantioselectivity properties of this material and low conversion and enantiomeric excess were obtained.

In the case of the Michael-adduct formation catalysed by **4**-(**MCM-41**) similar results were obtained comparing with other amines heterogenised on MCM-41 [**1**–**3**-(**MCM-41**)], only a slightly improved conversion was observed.

Heterogenised catalysts have been recycled in several successive runs shown similar activity (conversion–time plot) and enantioselectivity. The potential leaching was studied as followed: in an standard reaction the organic phase was separated from the solid after the first hour, new reagents were added to the clear filtrate and monitored by GC, showing no reaction after 24 h, which exclude the presence of active species in solution, whilst the filtered solid in the same conditions catalyse Michael reaction.

4. Conclusions

A series of heterogenised amines on silica, MCM-41 and delaminated zeolite ITQ-2 and their homogeneous analogues have been prepared and unequivocally characterised. These new materials present a high activity in Michael addition of ethyl 2-oxocycloalkanecarboxylates to acrolein, being much higher in the case of heterogenised catalysts.

Moderated enantioselectivity have been found under tested conditions although it has been demonstrated that chiral environment amines induce higher enantioselectivity than amines with a unique chiral base centre. Additionally, the use of MCM-41 with a defined crystalline structure in form of channels instead of amorphous silica or delaminated zeolite ITQ-2 yields improved enantioselectivity.

New heterogenised base catalysts are a practical alternative to soluble analogues in view of the following advantages: high stability of catalysts, high activity under mild conditions, free election of solvent, easy separation of catalysts by simple filtration and reuse without lost of activity.

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