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Guanidines encapsulated in zeolite Y and anchored to MCM-41: synthesis and catalytic activity

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Abstract

The preparation and characterisation of guanidines encapsulated in zeolite Y and anchored to MCM-41 are described. The catalytic activity of the immobilised and free guanidines were tested in the aldol reaction of benzaldehyde with acetone. In homogeneous phase, the guanidines give in 90–94% yield the condensation product alone. When anchored to MCM-41, the total yields range from 31% to 89% and the addition product is also formed depending on the solvent used. However, for the guanidine encapsulated in zeolite Y, the rate is strongly reduced and the addition product is preferentially formed in only 48% yield after 6 days. The reduced activity of this catalyst is explained by diffusional restrictions of the reactants and products inside the microporous system.

Keywords: Guanidine; MCM-41; Zeolite Y; Aldol reaction; Encapsulation; Anchoring

1. Introduction

Guanidines are strong bases that find applications in a large number of organic reactions widely employed in organic synthesis, including carbon–carbon bond formation [1] and transesterification of vegetable oils [2]. Coupled with the increasing emphasis on the development of environment-friendly catalysts, the heterogenisation of these bases is a desirable goal. There are many examples of highly dispersed or porous basic catalysts in the literature, which include those prepared by exchange or impregnation of alkaline metals into the framework of zeolites or mesoporous molecular sieves [3], by impregnation of lanthanide amides [4] and of other basic oxides [5]. Recently, it has been shown that Mg–Al hydrotalcite materials give good results for aldol and Knoevenagel condensations [6], cyanoethylation of alcohols [7] and for the epoxidation of olefins with H_2O_2 in the presence of nitriles [8]. In particular, alkyl substituted guanidines heterogenised on organic polymers [9] show only a slightly lower activity than their homogeneous analogous in the transesterification of soybean

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oil with methanol, but are found to leach during the reaction. In addition, guanidines can also be immobilized in zeolite Y by encapsulation [10] or by anchoring onto the surface of MCM-41 [11,12].

This work describes the heterogenisation of 1,2,3-tricyclohexylguanidine (TCG) and 1,3-dicyclohexyl-2-*sec*-butilguanidine (DCSG) in hydrophobic zeolite Y and mesoporous silica MCM-41 and compares the catalytic activity of these materials, with that of their homogeneous counterparts, in the aldol reaction of benzaldehyde with acetone.

2. Experimental

2.1. Guanidines

1,2,3-tricyclohexylguanidine (TCG) and 1,3-dicyclohexyl-2-*sec*-butyl-guanidine (DCSG) were prepared from 1.03 g (5 mmol) of 1,3-dicyclohexylcarbodiimide (Aldrich, 99%) and 1.0 g (10 mmol) of cyclohexylamine (Aldrich, 99%) or 0.73 g (10 mmol) of *sec*-butylamine (Aldrich, 99%), respectively, as described in the literature [13]. TCG: mp: 94–95°C; yield: 1.40 g (68%); IR (KBr, cm^{-1}): 3250 (ν N–H) and 1615 (ν C=N); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.0–1.9 (32 H, m) and 3.1–3.3 (3 H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.2, 25.9, 34.2 and 52.5. DCSG: bp: 150°C/3 mbar; yield: 1.18 g (85%); IR (neat, cm^{-1}): 1643 (ν C=N); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.9 (3 H, t), 1.0–1.9 (27 H, m) and 3.1–3.3 (3 H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.5, 20.8, 24.8, 25.2, 30.4, 51.0, 52.5 and 153.4.

2.2. Heterogenisation of TCG on siliceous MCM-41

Siliceous MCM-41 was synthesised as described in the literature [14]. A reaction gel with a molar composition 1 SiO_2:0.18 CTMABr:0.26 TMAOH:27 H_2O was prepared by suspending 2.6 g of Aerosil 200 (Degussa) in a solution of 28 mmol of TMAOH (Aldrich, 97%) in 12.6 ml of water and subsequent addition of a suspension of 10 mmol of CTMABr (Aldrich) in 100 ml of water. The final mixture was transferred into an autoclave and heated at 140°C for 16 h. The resulting solid was filtered, washed with water and dried until constant weight in an oven at 120°C. The occluded templates were removed by calcination at 540°C for 1 h under a stream of dry nitrogen (100 ml/min) and for 6 h under a stream of dry air (100 ml/min). The material was characterized by XRD (Cu Kα, 30 kV, 20 mA) $2\theta = 2.4$, 4.2, 4.8 and 6.1° and ^{29}Si CP MAS NMR (59 MHz) $\delta -90$, -100 and -109.

For the organofunctionalisation, the calcined MCM-41 (3 g) was dried under vacuum at 150°C for 12 h and subsequently suspended in 30 ml of dry toluene. 3-Glycidyloxypropyltrimethoxysilane (1.0 ml, 4.5 mmol, Fluka) was added to the stirred suspension at room temperature and the mixture refluxed under vigorous stirring and a nitrogen atmosphere for 24 h. The resulting material {GLY}-MCM-41 was filtered off, washed with 200 ml of toluene and methanol and dried under vacuum at 80°C. {GLY}-MCM-41 (0.3 g) was suspended in 2.0 ml of dry toluene under a nitrogen atmosphere, 0.2 g of TCG (0.65 mmol) were added and the mixture heated at 70°C for 36 h. The resulting material {TCG}-MCM-41 was filtered off, submitted to extensive Soxhlet extraction with dichloromethane and dried at 100°C for 12 h. {GLY}-MCM-41: ^{13}C CP MAS NMR (75 MHz) δ 8.6, 22.9, 44.7, 51.4, 71.4 and 73.0; ^{29}Si CP MAS NMR (59 MHz) $\delta -55$, -65, -100 and -109. {TCG}-MCM-41: microanalysis: C 16.8%, H 2.57%, N 2.35% which corresponds to 0.56 mmol of TCG/g of MCM-41; IR (KBr, cm^{-1}): 1618 (ν C=N); ^{13}C CP MAS NMR (75 MHz) δ 9.1, 23.4, 33.3, 43.6, 51.0 and 73.4; ^{29}Si CP MAS NMR (59 MHz) $\delta -57$, -65, -100 and -109.

2.3. Encapsulation of TCG and DCSG in Wessalith®

A 10 ml Schlenk flask was charged with 2.2 ml of *tert*-butanol (Merck), 0.14 g (0.7 mmol) of 1,3-dicyclohexylcarbodiimide (Aldrich, 99%) and 1.0 g of Wessalith® (zeolite DAY, Si/Al > 100, Degussa) previously dried at 100°C for 24 h. The mixture was left under a nitrogen atmosphere at 25°C for 24 h. The flask was then equipped with a reflux condenser, 0.14 g (1.4 mmol) of cyclohexylamine (Aldrich, 99%) or 0.10 g (1.4 mmol) of *sec*-butylamine (Aldrich, 99%) were added and the suspension refluxed for 24 h. After the reaction, 5.0 ml of *tert*-butanol were added and the reaction mixture filtered. The solid was neutralised with a suspension of lithium carbonate in dry methanol at 25°C, washed three times with 20 ml of chloroform and dried at 50°C under reduced pressure. {TCG}-Y: microanalysis: C 13.2%, H 2.0%, N 2.4% which corresponds to 0.58 mmol of TCG/g of Wessalith®; IR (KBr, cm^{-1}): 1627 (ν C=N) and 3330 (ν N–H); ^{13}C CP MAS NMR (75 MHz) δ 24, 26, 31 and 51; ^{29}Si CP MAS NMR (59 MHz) $\delta -107$ and -100; XRD (Cu Kα, 30 kV, 20 mA) $2\theta = 6.1$, 7.6, 10.1, 11.9, 15.4, 15.7, 17.2 and 18.8°. {DCSG}-Y: microanalysis: C 11.2%, H 1.8%, N 2.3% which corresponds to 0.55 mmol of DCSG/g of Wessalith®; IR (KBr, cm^{-1}): 1626 (ν C=N); ^{13}C CP MAS NMR (75 MHz) δ 9, 25, 29, 34, 50, 57 and 157; ^{29}Si CP MAS NMR (59 MHz) $\delta -107$ and -100 (Cu Kα, 30 kV, 20 mA) $2\theta = 6.1$, 7.3, 10.1, 11.9, 15.7, 16.9 and 18.8°.

2.4. Characterisation of the heterogeneous catalysts

The catalysts were characterised by X-ray diffraction (XRD) using Cu Kα radiation (30 kV, 20 mA) in a Shimadzu XD-3A diffractometer, from 2 to 10° (2θ) for MCM-41 and from 5 to 50° (2θ) for Wessalith®, with a scanning rate of 2°/min. Infrared spectra were obtained on a Perkin Elmer 1600 FTIR M-80 Specord spectrometer from KBr waffers (16 scans). C/H/N analysis were performed with a Perkin Elmer 2401 analyser. The mass spectra were obtained by electron impact at 70 eV and 1.10^{-5} bar, using a Shimadzu QP-5000 spectrometer, coupled to a direct inlet for solids Shimadzu DI-50. The temperature was maintained for 2 min at 60°C, then heated with 15°C/min to 250°C where it was maintained for 8 min. The solid state ^{13}C and ^{29}Si CP MAS NMR spectra were recorded on a Bruker AC 300/P spectrometer at 75 and 59 MHz, respectively, using zirconium oxide rotors and a rotation frequency of 4000 Hz. The ^{13}C spectra were recorded with an acquisition time of 0.18 μs, contact time of 1 ms and accumulation of 25,600 scans with 3 s between each scan. The ^{29}Si spectra were recorded with an acquisition time of 0.11 μs, contact time of 3 ms and accumulation of 2630 scans with 3 s between each scan.

2.5. Catalytic reactions

The homogeneously catalysed reactions were accomplished in a 10 ml Schlenk flask, charged with 0.35 g (3.3 mmol) of freshly distilled benzaldehyde (Aldrich, 99.5%), 0.56 g (9.6 mmol) of acetone (Merck), 0.7 ml of methanol (Merck) and 0.33 mmol of TCG or DCSG. The reaction mixtures were magnetically stirred at 25°C for 24 h. In the heterogeneously catalysed reactions, approximately 10% of the reactants used in the homogeneous reactions, and 0.1 g of the heterogeneous catalysts (10 mol%) were employed. The reaction mixtures were stirred under an Ar atmosphere at 25°C for 24 h or 6 days. In the kinetic experiments, samples were taken in the indicated time intervals. The products were analysed with an HP 5890 series II gas chromatograph equipped with a 25 m × 0.22 mm × 0.33 μm CBP1 column, coupled to a flame ionisation detector, interfaced to an HP Vectra VL Pentium workstation, using cyclooctane as internal standard. The temperature was maintained for 7 min at

80°C, then heated with 10°C/min to 160°C where it was maintained for 4 min. The products were quantified using calibration curves and identified in an HP 5890 series II gas chromatograph equipped with a 25 m × 0.22 mm × 0.33 μm CBP1 column, coupled to an HP 5970B mass detector operating at 70 eV, by comparison with a Wiley/NBS Database and NIST62 libraries.

3. Results and discussion

The anchoring of TCG was accomplished as shown in Fig. 1. The surface of MCM-41 is organofunctionalised by reaction of the silanol groups with 3-glycidyloxypropyltrimethoxysilane and TCG is covalently bonded after its nucleophilic attack on the oxirane ring. The use of 3-glycidyloxypropyltrimethoxysilane instead of organosilanes that have an halide as the reactive group [12] prevents the undesirable formation of inorganic acids in the following reaction with the guanidine, which can also be carried out under milder conditions. On the other hand, the immobilisation reaction of TCG requires harder conditions than those used for TBD in an analogous procedure [11], as the driving force of this reaction depends on the nucleophilicity of the base.

The X-ray diffractograms of the organofunctionalised and TCG-containing MCM-41 compared to that of as-synthesised MCM-41 shows the preservation of the hexagonal mesoporous arrangement during the experiments. The ^{13}C CP MAS NMR spectrum shows peaks in close agreement with the peaks of free 3-glycidyloxypropyltrimethoxysilane. The signal in δ 44.3 shows that the oxirane ring is still intact and the signal of the $SiCH_2$ resonance is shifted from δ 5.2 to 8.6 as a result of the surface bonding. After immobilisation of TCG, the spectrum shows the opening of the epoxide, besides the peaks of the guanidine. IR spectrum confirms the identity of TCG, by the characteristic band of the C=N double bond at 1618 cm^{-1}. C/H/N microanalysis gives a content of TCG of 0.56 mmol/g of MCM-41, which is higher than the 0.35 mmol of TBD per g of MCM-41 obtained by Subba Rao et al. [11]. The ^{29}Si CP MAS NMR spectrum of siliceous MCM-41 shows peaks around $\delta -90$, -100 and -109 that are attributed to $(SiO)_2Si(OH)_2$, $(SiO)_3Si(OH)$ and $(SiO)_4Si$ groups, respectively. The high intensity of the peak at $\delta -100$ shows the large number of OH groups present at the surface of the MCM-41 framework. The successful organofuctionalisation of MCM-41 with the silanising agent is demonstrated by the absence of the peak at $\delta -90$ and the decreased intensity of the peak at $\delta -100$ relative to the peak at $\delta -109$. The additional peaks at $\delta -55$ and -65 can be attributed to $(SiO)_2Si(OH)(GLY)$ and $(SiO)_3Si(GLY)$ groups, respectively. The ^{29}Si CP MAS NMR spectrum of {TCG}-MCM-41 shows peaks at $\delta -57$ and -65, together with the peaks at $\delta -100$ and -109, which have approximately the same intensity, demonstrating that part of the $(SiO)_3Si(GLY)$ groups have been transformed to $(SiO)_2Si(OH)(GLY)$ groups after the reaction with TCG.

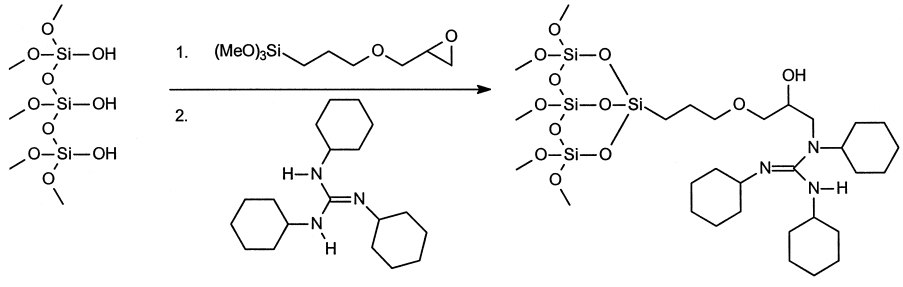


Fig. 1. Anchoring of TCG in MCM-41.

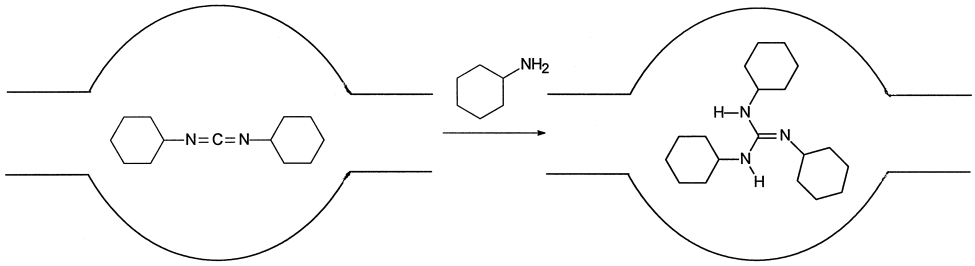


Fig. 2. Encapsulation of TCG in Wessalith®.

The encapsulated guanidines TCG and DCSG were prepared by reacting 1,3-dicyclohexylcarbodiimide with cyclohexylamine or *sec*-butylamine, respectively, inside the supercages of Wessalith®, as shown in Fig. 2 for TCG. The X-ray diffractogram of TCG-containing Wessalith® shows three additional small peaks at $2\theta = 7.6$, 15.4 and 17.2°, whose intensities increase with increasing amounts of TCG. These peaks are also observed for free TCG at $2\theta = 8.5$, 15.4 and 18.1. On the other hand, as the intensity ratio of the other peaks is the same for Wessalith® and TCG-containing Wessalith®, and the SEM micrographs and ^{29}Si CP MAS NMR show no changes after encapsulation, it is confirmed that the structure of Wessalith® is not affected by the reaction. The DCSG-containing Wessalith® shows two additional peaks at $2\theta = 7.3$ and 16.9° (very close to those observed for TCG), which may be attributed to DCSG. The ^{13}C CP MAS NMR spectra of the encapsulated TCG and DCSG show signals in agreement to those of free guanidines. The IR spectra of the encapsulated TCG and DCSG show shifts of ν C=N double bond from 1615 to 1627 cm^{-1} and from 1643 to 1626 cm^{-1}, respectively. Encapsulation of TCG and DCSG was proven by pyrolysis coupled to mass spectrometry. While TCG or DCSG impregnated on Wessalith® gives a mass spectrum similar to that of the free compounds at 60°C, encapsulated TCG or DCSG gives only a minor peak ($< 5\%$) for cyclohexylamine at the same temperature. The encapsulated guanidines decompose at 150°C giving a mass spectrum equivalent to that reported for hexamethylene-1,6-diisocyanate (NIST62 library, SI of 90%). This result clearly shows that TCG and DCSG are not impregnated onto the external surface of Wessalith® and can only leave the supercages after decomposition into smaller molecules. Furthermore, the encapsulated guanidines cannot be removed by extensive Soxhlet extraction with dry chloroform.

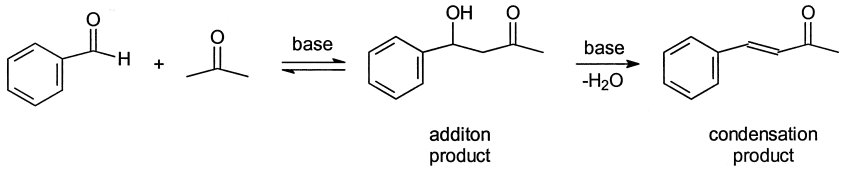
The catalytic activities of the guanidines anchored on MCM-41 and encapsulated in Wessalith® were compared to those of their homogeneous counterparts in the versatile aldol reaction, which has

Table 1
Yields obtained in the homogeneously catalysed aldol reaction

Catalyst	Solvent	Products (%)	
		Condensation	Addition
KOH	methanol	95	0
TCG	methanol	94	0
TCG	*i*-propanol	94	0
TCG	*tert*-butanol	90	0
DCSG	methanol	90	0

Reaction conditions: 3.3 mmol of benzaldehyde, 9.6 mmol of acetone, 0.33 mmol of catalyst, 0.7 ml of solvent, 24 h, 25°C.
TCG = 1,2,3-tricyclohexylguanidine.
DCSG = 1,3-dicyclohexyl-2-*sec*-butyl-guanidine.

been shown to be catalysed by other strong bases [15–17]. The results for the homogeneously catalysed aldol reaction of benzaldehyde with acetone (see Reaction 1) are shown in Table 1. The bases employed have a pK_a high enough to quantitatively condense benzaldehyde with acetone giving, after 24 h, yields of up to 95% for the condensation product, without the formation of the addition product. The slight differences found in their activities (Fig. 3) are within the experimental error of the chromatographic analysis. The differences in the pK_as of the alcohols used as solvents do not significantly influence the activities of TCG in homogeneous phase. On the other hand, the activity of TCG is strongly reduced (less than 49%) when the reaction is carried out in ethyl acetate, diethyl ether or an excess of acetone, indicating the need for highly polar solvents for this reaction.



The results obtained for the TCG-containing MCM-41 catalysed aldol reaction are given in Table 2. The yield obtained in methanol is very close to that observed for free TCG, showing that the porous system does not compromise the reaction, as shown in Fig. 3. The slight difference is probably due to the hydrophilicity of the MCM-41 surface, that reduces the concentration of the hydrophobic reactants inside its porous system. This becomes more evident when the more hydrophobic solvents *i*-propanol and *tert*-butanol are used, as the conversions are reduced and the addition product is also formed. The activity of TCG may also be reduced due to interactions with the acidic silanol groups on

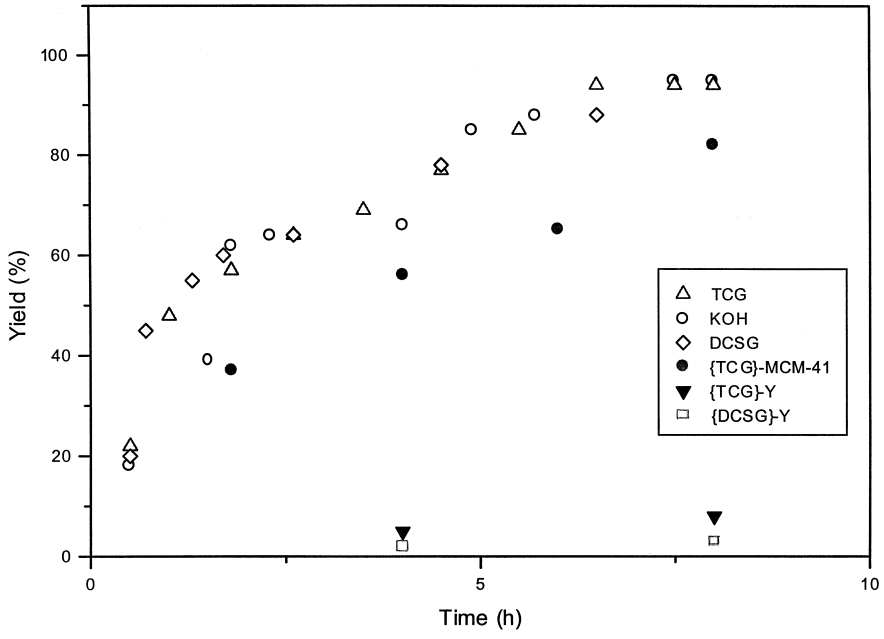


Fig. 3. Yield of total products as a function of time. Conditions for the homogeneous systems: 3.3 mmol of benzaldehyde, 9.6 mmol of acetone, 0.33 mmol of catalyst, 0.7 ml of methanol, 25°C. Conditions for the heterogeneous systems: 100 mg of catalyst, 0.37 mmol of benzaldehyde, 1.4 mmol of acetone, 0.7 ml of methanol, 25°C.

Table 2
Yields obtained in the aldol reaction catalysed by 1,2,3-tricyclohexylguanidine (TCG) anchored on MCM-41

Solvent	Products (%)	
	Condensation	Addition
methanol	89	0
i-propanol	40	22
tert-butanol	20	11

Reaction conditions: 100 mg of catalyst, 0.37 mmol of benzaldehyde, 1.4 mmol of acetone, 0.7 ml of solvent, 24 h, 25°C.

the surface of MCM-41 [12], which seem to be dependent on the solvent used. This becomes more evident in the kinetic experiments (Fig. 4) as, contrary to the homogeneous system, the addition product is formed also in methanol at the beginning of the reaction. At longer reaction times, the addition product is dehydrated, forming only the condensation product, after 24 h. The initial formation of the addition product can be attributed to the reduced basicity of TCG heterogenised on MCM-41. Microanalysis shows that 8–10% of TCG is leaching during the reaction. The leached guanidine is probably responsible for the dehydration of the addition product, but cannot explain its formation as the yield is only 15% after 24 h if 1 mol% of TCG in homogeneous phase is used. When TCG-containing MCM-41 is recycled, a strong loss of activity to 24% is observed. This cannot be only attributed to the leaching of TCG from the catalyst, but is also due to a partial protonation, probably caused by silanol groups of the support.

The yields obtained in the aldol reaction catalysed by TCG and DCSG encapsulated in Wessalith® are given in Table 3. Considering that the reaction time is 6 days, the product yields are low. Fig. 3 shows that the products are slowly formed when compared to other catalysts. The kinetic experiments

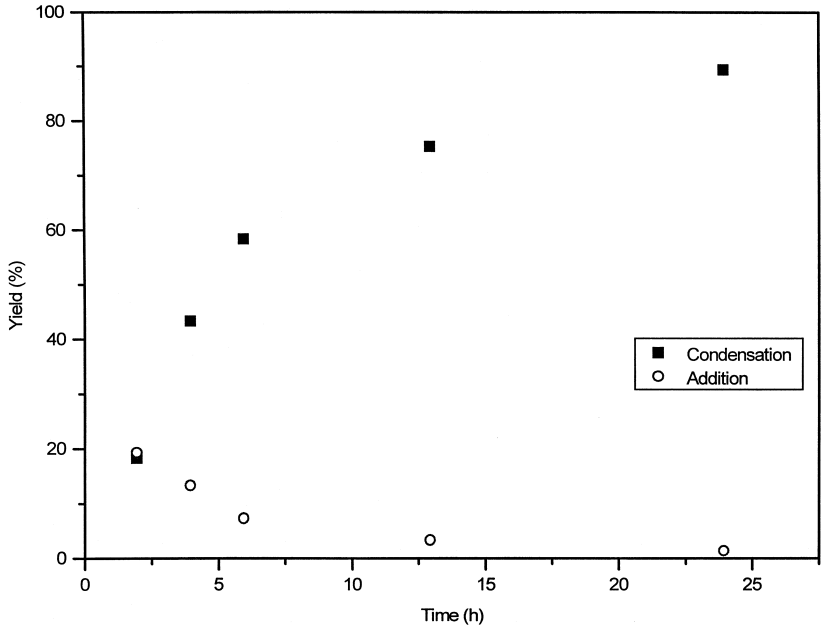


Fig. 4. Yields of the condensation and addition product as a function of time in the reaction catalysed by {TCG}-MCM-41. Conditions: 100 mg of catalyst, 0.37 mmol of benzaldehyde, 1.4 mmol of acetone, 0.7 ml of methanol, 25°C.

Table 3
Yields obtained in the aldol reaction catalysed by guanidines encapsulated in Wessalith®

Catalyst	Solvent	Products (%)	
		Condensation	Addition
{TCG}-Y	methanol	8	48
{TCG}-Y	*i*-propanol	3	6
{TCG}-Y	*tert*-butanol	2	4
{DCSG}-Y	methanol	6	21

Reaction conditions: 100 mg of catalyst, 0.37 mmol of benzaldehyde, 1.4 mmol of acetone, 0.7 ml of solvent, 6 day, 25°C.
{TCG}-Y = 1,2,3-tricyclohexylguanidine encapsulated in Wessalith®.
{DCSG}-Y = 1,3-dicyclohexyl-2-*sec*-butyl-guanidine encapsulated in Wessalith®.

(Fig. 5) show the rather rapid formation of the addition product, which after 1 day, increases only slightly together with the condensation product. The lower activity can be attributed to diffusional restrictions as the formation of the condensation product requires a larger kinetic diameter. This is more evident when *i*-propanol and *tert*-butanol are used as solvent, as the solvated reactants have an even larger kinetic diameter. Furthermore, for TCG encapsulated in Wessalith® only a small dehydration of the addition product is found, thus confirming that TCG does not leach. However, we believe that the smaller pores of Wessalith® make the diffusion of the reactants to the guanidines and the products from it more difficult, thus explaining the low activity of the catalyst.

Blank experiments using the molecular sieves only gave no reaction products. Impregnated TCG leaches totally from the solids and gives similar results to those obtained in the homogeneous phase.

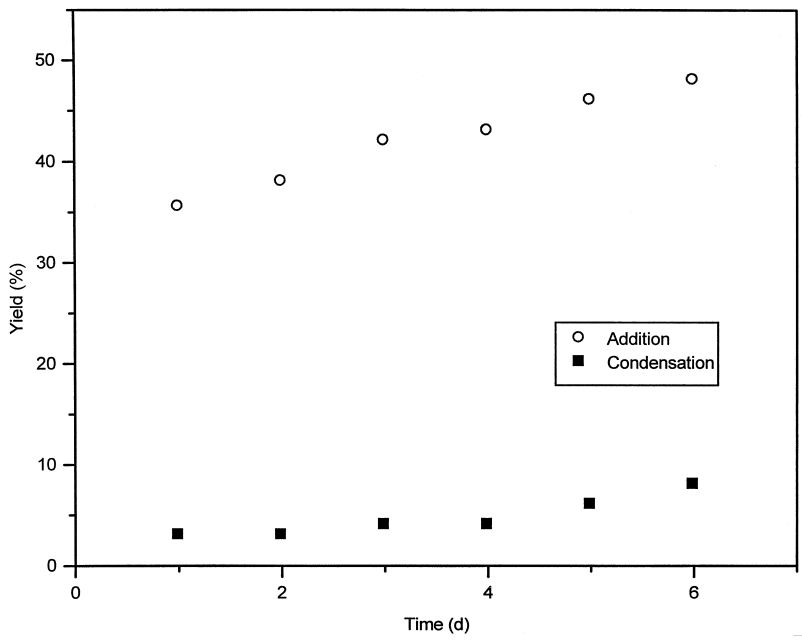


Fig. 5. Yields of the condensation and addition product as a function of time in the reaction catalysed by {TCG}-Y. Conditions: 100 mg of catalyst, 0.37 mmol of benzaldehyde, 1.4 mmol of acetone, 0.7 ml of methanol, 25°C.

4. Conclusions

Guanidines show high activities in methanol after immobilisation on the mesoporous support, but both activity and selectivity become dependent on the solvent used. However, the deactivation of this catalytic system is a challenge that has to be overcome, in order to achieve a novel strong heterogeneous basic catalyst that will certainly find applications in industrial processes. Guanidines encapsulated in Wessalith® are not effective catalysts for organic synthesis, as the smaller pores make the diffusion of reactants and products more difficult. On the other hand, the preferential formation of the addition product may be interesting for synthetic purposes.

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