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New trends in the design of supported catalysts on mesoporous silicas and their applications in fine chemicals

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Abstract

Different strategies leading to the preparation of acid and base catalysts derived from ordered mesoporous silicas are reviewed. These include aluminum incorporation into the silicate network, entrapping of heteropolyacids, deposition of oxide precursors and direct or post-synthesis of anchoring of organic moieties. Their use in a variety of reactions related to fine chemicals synthesis is critically discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: MCM-41; Acid catalyst; Base catalysts; Hybrid materials; Fine chemicals

1. Introduction

Since the disclosure by Mobil group in 1992 of MCM-41s featuring hexagonal pore-ordered system [1], further research has been focused on the preparation of various micelle-templated silicas (MTS) such as MCM-48 [2], SBA-3 [3], SBA-15 [4] or MSU [5]. These materials exhibit different topologies depending on the nature of templating surfactants, the composition, the pH and the temperature of the synthesis mixture. The mechanism of the formation of the hexagonal phase has been extensively investigated and reviewed [6–12]. The formation of MCM-41s was studied by monitoring the strong interaction between charged surfactant heads and solid walls by EPR and UV–VIS fluorescence spectroscopy [13]. In the core of the micelles, the anisotropic organization would correspond to a tilting of the surfactant chains. Moreover, new insights about the nature of MCM-41 surface were obtained by this approach, regarding the distribution of hydrophobic and hydrophilic patches, near the corners and on the flat side surfaces of the hexagonal pores, respectively [14]. Calcination of the hybrid mesophases generally affords stable mesoporous materials with extremely high surface area, often exceeding $1000\,m^2\,g^{-1}$, mesopore volume larger than $0.7\,ml\,g^{-1}$ and narrow pore size distribution. The pore size can be tuned in the range 20–100 Å, by selecting the length of the alkyl chain of the surfactant [2], by adding expander organic molecules [2,15] or by post synthesis treatments [16–20]. Hence, the development of tailored surface and pore size MTS opened up opportunities for applications in various fields such as catalysis, selective adsorption of organics and metals. Because aluminum can be incorporated in MCM-41 by direct synthesis [21,22], these materials were immediately thought to represent an extension of zeolites to carry out acid catalytic conversion of large molecules [23–29]. The nature of the acid sites has been extensively studied by combination of different characterization techniques such as microcalorimetry of ammonia adsorption, thermal desorption of ammonia, FT-IR

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spectroscopy of various probes and ^{27}Al MASNMR [30–39].

The aluminum atoms have mainly tetrahedral configuration in the as-synthesized samples. Upon calcination, uncoordinated states, e.g. trigonal Al are formed, which behave as strong Lewis acid sites. These sites are converted into two possible Brönsted sites Si(OH) Al and SiAl(OH)Si by hydration [34]. It was speculated that the local structure of the Brönsted sites would strongly depend on the nature and the number of neighboring coordinatively unsaturated aluminum species. Some discrepancy between the results reported in literature also appear on account of the presence or not of positively charged non-framework cationic Al species with a low degree of condensation which could neutralize stronger acid sites [37]. In many case, the acidic properties in Al–MCM-41 are fundamentally different from those found in zeolites [40]. The acidity of Al–MCM-41 is reported to be lower compared to usual zeolites and resembles that of amorphous aluminosilicates [35].

Actually, the nature of the acid sites mainly depends on the source of aluminum [36], the pH adjustment during the synthesis [41,42], the mode of template extraction and calcination [43]. Hence, the different correlations between the physicochemical characteristics and the catalytic activities of Al–MCM-41, which were reported in the literature, should be considered with care. It is known indeed that the activity of zeolites and aluminosilicates depends strongly on the activation procedure and results on the same reaction may be significantly different depending on authors. However, the general trend for acid-catalyzed reactions is that Al–MCM-41 behave like classical amorphous aluminosilicates with as main characteristic a high tendency for coking or fouling.

On the other hand, it has been also established that the hydrothermal stability of MCM-41 is lower than that of zeolites. MCM-41 type materials suffer textural alteration upon prolonged exposure to water or water vapor [44–49]. The wetting instability was of course more significant in basic aqueous solutions. However, Si–MCM-41 synthesized with pH adjustment and salt addition was stable upon wetting with acidic aqueous solution. This particular behavior must be related to the thickness of the pore walls, which is pH dependent [50], and possibly to the presence of defects associated with incompletely polymerized silica–alumina walls. Interestingly, the stability of MCM-41s to moisture as to compression is enhanced when these materials were chemically post-modified by trimethylsilylation [48,51–54]. Another possible way to stabilize MTS lies in the crystallization of the walls to zeolitic structures or in the assembly of such materials from colloidal zeolite crystals [55,56].

In order to overcome the hydrothermal stability limitation, MCM-41 has been used for the preparation of bi-functional catalysts [57]. In addition, as the activation of olefins requires weaker acidities, reactions involving oligomerization, disproportionation or oligomerisation-craking of olefins have been successfully carried out on Al–MCM-41 catalysts [11,58,59]. Hence, the major advantage of mesoporous materials for acid-catalyzed reactions in petrochemicals stands on the unrestricted diffusion of reactants and products, minimizing unwanted consecutive reactions and catalysts decay by large size adsorbed molecules. These features are also of particular interest in fine chemical synthesis for reactions involving molecules that are too large to access the smaller pores of conventional molecular sieves and for the preparation of bulky organics, specially when performed in the liquid phase where diffusional problems can be enhanced [60–65] as shown in part 2.

In the last several years, many efforts have been also devoted to the use of ordered mesoporous materials as a support for immobilizing acid and/or base sites in order to overcome the low acid strength and stability of Al containing MCM-41s and to broaden the catalytic applications of the MTS materials as heterogeneous base catalysts. This strategy was attempted by following two strategies for anchoring active functions: i) immobilization of mineral acid or base compounds on the oxide framework by impregnation; ii) attachment organic acid or base moieties by covalent grafting onto the mesoporous surface. In parts 3 and 4 of this paper, we discuss on the different modes of preparation and on some applications of these new materials.

2. Typical applications of Al–MCM-41

Friedel–Crafts alkylation and acylation were successfully carried out on aluminosilicate MCM-41. The shape selectivity of the Al–MCM-41 was demonstrated during the alkylation of 2,3-di-*tert*-butylphenol

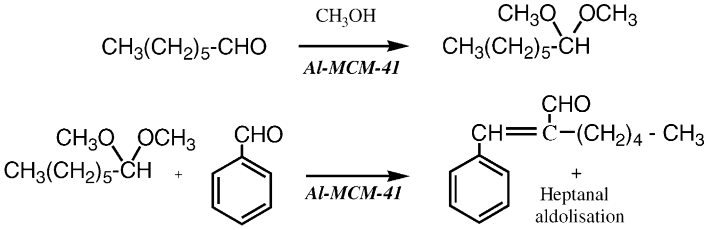

Fig. 1. One-pot synthesis of jasminaldehyde.

with cinnamyl alcohol [60]. However, this catalyst was enable to achieve high acylation at the 6-position of 2-methoxynaphthalene with acetic anhydride in view to produce a Naproxen precursor. Actually, this acid-catalyzed reaction selectively led to 1-acetoxy-2-methoxy-naphthalene [62]. Al–MCM-41 was also very efficient to achieve diacetalization of aldehyde with trimethylorthoformiate, which requires low acid strength, particularly, when bulky reactants and products are involved such as during the preparation diacetal from diphenylaldehyde [63]. A very nice development of this reaction was reported by Corma and co-workers, which concerns the preparation of a traditional perfumery material, the jasminaldehyde in a one pot process [64]. This synthesis involves three consecutive reactions: first acetalization of heptanal with methanol followed by hydrolysis of the acetal and finishing with aldol condensation. The key of the high selectivity in jasminaldehyde lies in the control of a low concentration of heptanal delivered by slow hydrolysis of acetal, which prevents the undesirable self condensation of heptanal (Fig. 1).

Dimitriu et al. reported about the synthesis of isoprene by Prins condensation of isobutene with formaldehyde over H–boralite (H–B) MCM-41 [65]. Even though, the conversion was lower than on H–B, the selectivity in isoprene was kept at the highest level (100%) imparted by the weak Brönsted acid strength of the catalytic sites which selectively protonated formaldehyde versus olefin. Hence, the route leading to by-product and possible intermediate 4,4-dimethyl-1,3-dioxane was suppressed.

Among other reactions which can be catalyzed by weak acid sites, Beckman rearrangement of bulky oximes leading to the corresponding lactames has been reported on Al–MCM-41, which illustrates the benefit of the mesoporous material with respect to zeolites [11].

Following these pioneering works, strong increase in application of Al–MCM-41 was expected for acid-catalyzed preparation of fine chemicals. However, most of the recent applications of MTS materials dealt with conventional acid-catalyzed reactions such as alkylation [28,41,66] or acylation [42], which serve as model reactions for catalytic characterization in order to improve the catalyst design. It seems now that the high expectations in the development of acid catalysis with the use of H–MTS in place of dealuminated zeolites, amorphous aluminosilicates or commercially available acid treated clays such as K10 [67], must be dampened for chemical production in industry [68].

3. Immobilisation of mineral acid and base compounds

Acidic or basic sites can be immobilized on the pore walls of MTS structure by impregnation or incorporation of purely acid or base inorganic functional groups.

3.1. Keggin-type heteropoly acid (HPA) supported on MCM-41

Izumi and co-workers reported the first example of heterogenization of HPA on silica gel [69,70]. The silica-included heteropoly compounds were prepared by a sol–gel technique through hydrolysis of ethyl orthosilicate in the presence $H_3PW_{12}O_{40}$ (PW) dispersed or dissolved in ethanol. These stable and easily handled acid catalysts were more active in the liquid phase ester hydrolysis than the homogeneous acid. The silica composite showed no migration of the active sites probably because the silica

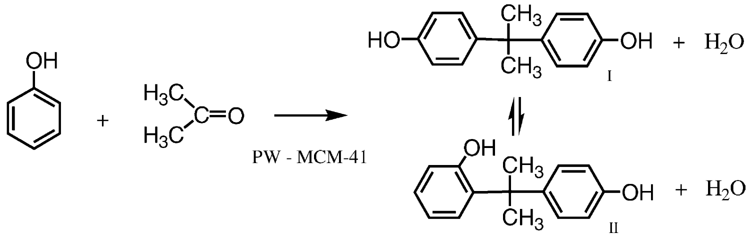

Fig. 2. Acid-catalyzed condensation of phenol and acetone over HPA/MCM-41.

network appeared to be narrow enough to prevent HPA from migration outside the silica network. On the other hand, Kozhevnikov et al. and van Bekkum co-workers have prepared PW and $H_4SiW_{12}O_{40}$/MCM-41 systems by impregnation of the HPA in MCM-41 channels [71,72,76]. The finely dispersed HPA on MCM-41 provided high catalytic activity in the liquid phase alkylation of 4-*tert*-butylphenol by isobutene and styrene [71,72] and alkylation of butene by isobutane [73,74]. The higher selectivity in monoalkylated compound versus dialkylated one was though to result from shape-selectivity [71].

Nevertheless, these catalysts have a tendency to lose HPA molecules by elution [75] and to form large HPA clusters on the external surface of the supporting materials during liquid phase esterification reaction [76]. The agglomeration of PW would result from severe distorsion of the MCM-41 wall at higher loadings [77]. When the HPA modified MCM-41 samples were treated with cesium or ammonium carbonates to obtain HPA salts inside the MCM-41 channels, the heteropoly anions were more strongly bonded to the support.

When these modified materials were used to catalyze the condensation reaction between phenol and acetone, highest selectivity in *p,p′*-bis phenol A isomer (I) versus *o,p′*-bis phenol A isomer (II) was obtained as the reaction occurs inside the pores (Fig. 2) [78].

3.2. Cesium oxide and binary cesium–lanthanium oxide supported on MCM-41

Cesium oxide particles have been occluded in the microporosity of Cs exchanged X and Y zeolites by wet impregnation of cesium acetate and subsequent calcination [79–84]. These modified zeolites were active as base catalysts e.g. for Knoevenagel condensation reaction or tranesterification or Michaël addition. However, catalysis is limited to relatively small molecules.

Following the same methodology van Bekkum et al. prepared exchanged and over exchanged cesium Al–MCM-41 in order to carry out the aldol condensation reaction of molecules as large as α-tetralone or isophorone with benzaldehyde. In the case of the aldol condensation of hydroxyacetophenone, the successive intramolecular Michaël addition led to flavanone (Fig. 3) which is one of the biologically active natural products and key intermediate in the synthesis of more complex flavanoids desired for their medicinal properties such as high antioxidant capacity, antivirus and anticarcicogenic activities

This catalyst was also able to catalyze the Michael addition of chalcone and neopenthyl glycol acrylate with diethyl malonate [85,86]. However as demonstrated recently by Noda Pérez et al., the impregnation of MCM-41 with cesium acetate followed by

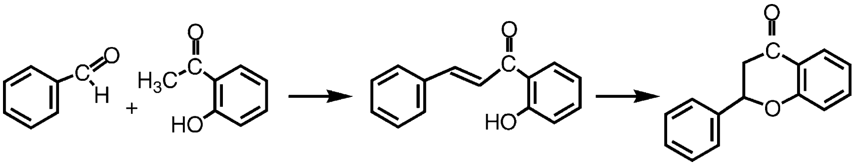

Fig. 3. Formation of flavanone from condensation of benzaldehyde and *o*-hydroxy-acetophenone.

calcination caused a severe damage to the structure, Al-containing MCM-41 being much less resistant than purely siliceous one to basic media [87]. In order to overcome this limitation, van Bekkum et al. achieved MCM-41 loading with binary oxide $CsLaO_x$, which revealed higher stability. These mixed oxides are probably anchored on the pore walls of the support via La–O bonds. In this system, the cesium oxide species would be located in the top layer of the binary submonolayer-shape clusters on the MCM-41 surface. These systems provided mild basic catalysts. Interestingly, their use is described for the Knoevenagel condensation and also for Michael addition without deactivation after several uses [88].

4. Hybrid mesoporous MTS containing organic base or acid moieties

4.1. Organically modified mesoporous silicas

Recently, modification of the MCM-41 surface with covalently bonded organic species, especially functional organosilanes, has attracted much attention in order to design hybrid materials (HMS) with engineered properties for advanced applications e.g. in catalysis [11,12,89–92], and selective adsorption of organics [54] and metals [92].

At the same time, the grafting of alkylsilane on the MCM-41 surface has provided an opportunity to obtain hydrophobic materials with tailored pore size and high surface area [93,94]. On the other hand, the functionalisation of various silica with covalently bonded organosilanes by different procedures has been studied in the past for various applications [95–98]. The synthesis of organically modified mesoporous siliceous materials has been performed via three different routes: i) silylation, ii) coating of the nanostructured silica surface with alkyl trialkoxysilane, iii) monophasic sol–gel assembly of alkyl trialkoxysilane and silica precursor $(RO)_4Si$ in presence of surfactants as templating agents.

4.1.1. Silylation of MTS surface

Firstly, the wall surface of pre-formed MTS has been functionalized by the covalent linkage of organic moieties carried out by silylation of the surface with alkyltrialkoxysilane in anhydrous conditions in apolar solvent (biphasic conditions) (Fig. 4) [99].

We have studied the mechanism of the silylation of MCM-41 surface to better understand the mode of alkylsilane chains anchorage which governs the local environment of the grafted chains. The water–surface interaction on MTS and on crystalline and amorphous silicas has been investigated by means of microcalorimetry and infrared spectroscopy [100].

MTS surfaces exhibit two distinct portions, showing hydrophobic and hydrophilic character, respectively, and are characterized by low amounts of water adsorbed (typical of hydrophobic silica) but with high adsorption heats (typical of hydrophilic silica).

Hydrophilic zones are best represented by flat surfaces covered by adjacent silanol groups, resulting from a peculiar orientation of the silicates condensed during the synthesis. Cooperative adsorption of water molecules by two adjacent silanol groups accounts for the high adsorption heats. Hydrophobic patches correspond to dehydroxylated portions featuring isolated silanol and siloxane bridges generated during the calcination of the surfactant. Moreover, the density of silanol groups on the surface of MTS was in the range of 1.5–2.5 OH per nm^2 compared to a value of 5–6 for amorphous silicas.

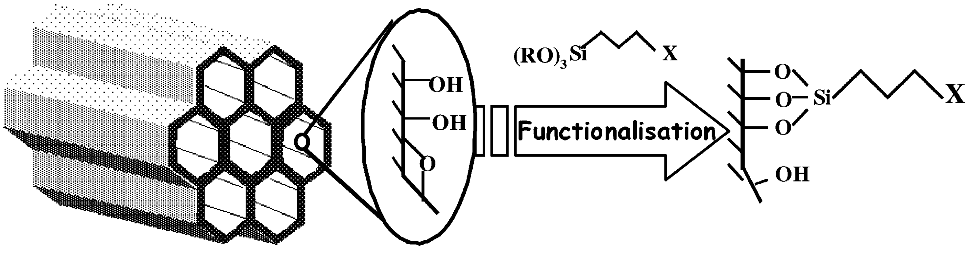

Fig. 4. Functionalization of MCM-41 surface.

The silylation of the surface of MTS by Tris-(ethoxy)alkylsilane with alkyl chain bearing or not either amine function or halogen atom, takes place in anhydrous non-polar solvent essentially on the hydrophobic patches of the surface on siloxane bridges and leaves unmodified the hydrophilic zones as demonstrated by microcalorimetry studies and IR spectroscopy [101]. On the other hand, ^{28}Si and ^{13}C MAS NMR shows that the organosilane chain is anchored to the surface at a coverage up to 0.6 chains per nm^2 through nucleophilic displacement at the silicon atom by the alkylsiloxane group of the silylating agent [102]. This situation has a main implication with regard to the properties of the final catalysts since the persistence of interacting silanols with strong hydrophilic character in the vicinity of the active centers may influence reactivity, by promoting other mechanism or secondary reactions.

4.1.2. Coating of MTS surface

Functionalization of various silica with covalently bonded organosilanes by different methods has been extensively studied in the past for analytical and preparative chromatographic applications [103–113]. However, the knowledge of the mechanism of the different grafting types are still a subject of debate [107,109,111].

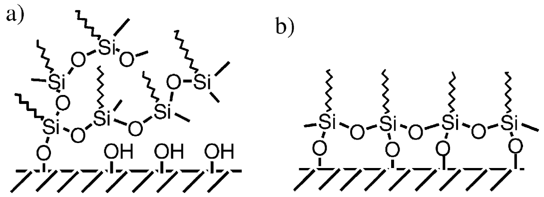

Fig. 5. (a) Vertical sol–gel surface polymerisation; (b) horizontal sol–gel grafting of MCM-41 surface.

In pioneering works on the functionalization of silica surface, Fritz and King activated the surface by acid treatment followed by reaction with alkyltrialkoxysilane in order to improve the coverage of the silica surface [114]. In some cases, water was added to the reaction mixture [105,115]. Nevertheless this conventional surface sol–gel process generally provides island-type grafting on silica gel by vertical-type polymerization induced by the presence of excess free water (Fig. 5a). In order to have the adequate amount of water associated to MTS surface for siloxane hydrolysis and to build a monolayer [112], Liu and co-workers have adjusted the amount of adsorbed water by azeotropic distillation prior to the addition of Tris-(methoxy)mercaptopropylsilane in excess relative to the ideal monolayer surface coverage (Figs. 5b and 6) [116].

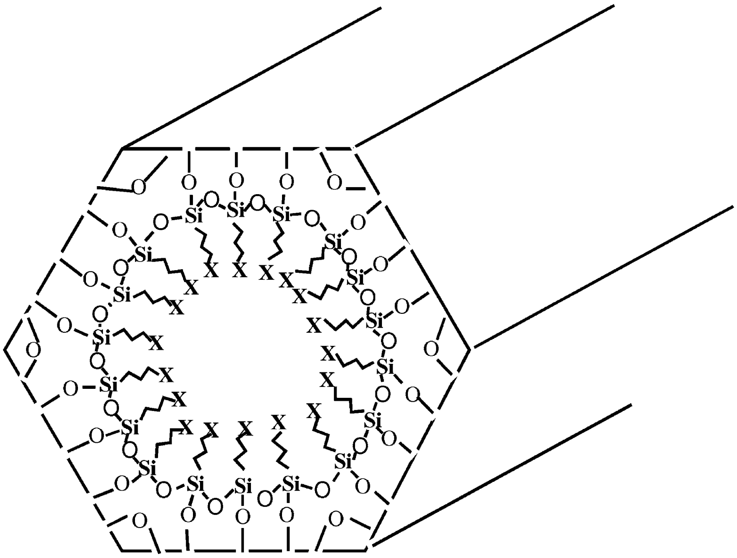

Fig. 6. Ideal monolayer surface polymerization.

According to the authors, the grafted materials contained nearly 5.6 mmol of thiol alkylsilane per gram of silica.

However, the preservation of the texture of the MCM-41 during the azeotropic distillation in presence of water is questionable. Actually, this process led to a loss of mesoporous volume upon silica reorganization [49]. Recently, we have investigated the coating of silica and MCM-41 surface in order to improve the surface coverage while preserving the texture. MTS sample dehydrated at 180 °C under vacuum was contacted with anhydrous solution of trialkoxyalkyl silane agent in order to insure uniform physisorption of the silane on the surface. Horizontal surface sol–gel (Fig. 5b) was obtained by addition of a controlled amount of water and acid catalyst able to perform fast alkoxide hydrolysis relative to the condensation rate. The efficiency of this process was excellent as shown by the performance of the resulting materials towards water intrusion or by their inertness towards solvolysis reactive reagents [117,118].

4.1.3. Monophasic preparation of mesoporous hybrid materials

Incorporation of organic functionalities has been achieved by co-condensation of organically functionalized silica precursors leading to HMS i.e. $RSi(OR')_3$ silica and a series of hydrolysis and self-assembly condensations in the presence of surfactants (monophasic conditions). Macquarrie first reported, the preparation of hybrid organic–mineral mesoporous materials with alkyl groups bearing amine function in the presence of non ionic templates [119]. The synthesis of nanostructured silicate (HMS) in the presence of neutral surfactants had been already performed by Pinnavaia and co-worker in order to easily remove the templating agent by solvent washing in place of calcination [120]. Hence, the anchored 3-aminopropyl chain [119] and the 3-mercaptopropyl chain [121] remain intact during removal of surfactants. This methodology was also applied by Mann and co-workers and Stein and co-workers, to prepare hybrid organic–mineral MCM-41 type materials bearing aromatic [122] and thiol function [123], respectively, using long chain quaternary tetralkyl ammonium hydroxyde. Removal of the ionic template by solvent extration is, however, known to be not complete.

4.2. Acid containing MCM-41

Stein and co-workers reported the preparation of a hybrid MCM-41 containing sulfonic groups by oxidation of mesoporous hybrid silicates coated with groups obtained by a direct surfactant based synthesis [123]. This hybrid material was active in the alkylation of 2–3 hydrogenopyran into 2-ethyl pyran. The authors pointed out that all the sulfur groups were not active because some of them were not oxidized. Interestingly, Jacobs and co-workers [124] have compared three differently prepared sulfonic acid containing ordered mesoporous materials via the 3-mercaptopropyl containing MTS synthesized by the three routes (i), (ii), and (iii) already mentionned. These acid supported materials were found to be excellent catalysts for the esterification of glycerol with fatty acids even though the selectivity in monoglycerides was relatively modest and decreased with increasing conversion due to the formation of diester by successive esterification (Fig. 7).

Recently Perez-Pariente and co-workers also investigated the esterification of glycerol with hybrid MCM-41 containing sulfonic groups [125] prepared through direct surfactant-based synthesis of anchored thiol precursor. Their objective was to carry out a better control of the texture of the material and the 3-mercaptopropyl chain packing in order to increase the selectivity. A mixture of surfactants was used as templating agent: a longer chain surfactant (C16) as the main structure directing agent which interacted with the silicate wall and a shorter one (C12 or C10) interacting with the thiol groups (Fig. 8) [126].

The authors reported high selectivity (~80% selectivity at 65% conversion) during the glycerol esterification, which was attributed to better ordered channels

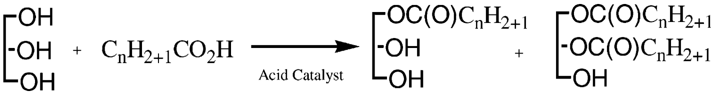

Fig. 7. Glycerol esterification with fatty acid.

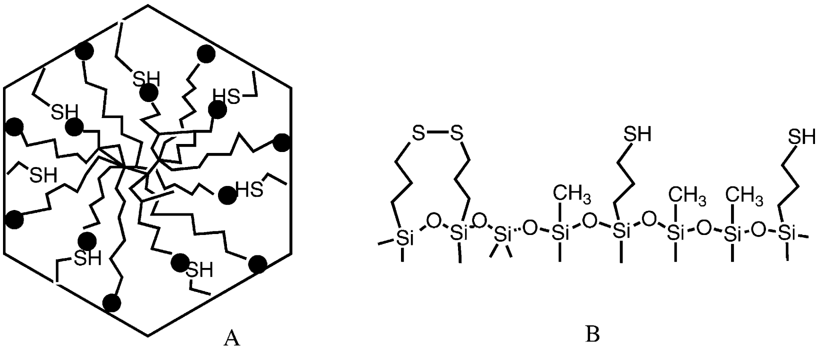

Fig. 8. Improvement of the chain packing (A) using mixed surfactant and dilution (B) according to [127].

and a more efficient packing inducing shape selectivity preventing secondary esterification leading to bulkier molecules. They pointed also the presence of disulfide, as noted already by Jacobs and co-workers, and Stein and co-workers. In order to avoid the easy thiol oxidation by air leading to the undesirable formation of disulfide, which cannot be converted into sulfonic acid, 3-mercaptopropyl chains were diluted with methyl or ethyl chains. Although, this objective was not reached (Fig. 8A), as-synthesized materials revealed better catalytic performance which was explained by easier product desorption due to higher lipophilic properties of the surface. [127].

4.3. Organic bases attached to mesoporous silica surface

Primary, secondary and tertiary amines [128–130] diamines [132], ammonium hydroxide [133], guanidines [134–139], have been grafted on MTS surface through direct or post silylation (Fig. 9).

Hybrid organic/mineral solid base catalysts bearing primary and tertiary amino functions have been used as catalysts in the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate (Fig. 10) at 375 K in the presence of DMSO as solvent.

Both catalysts exhibited a selectivity of approximately 100% in ethyl *trans*-α-cyanocinnamate and could be recycled several times, after filtration and washing, without decrease in their catalytic performance [129].

The activity was found directly proportional to the amount of base grafted indicating constant turn over numbers under a wide range of surface coverage. TONs were significantly higher in the case of the primary amine grafted solid than in the case of the tertiary one. This resulted from the transient formation of imine groups with enhanced catalytic activity (Fig. 11).

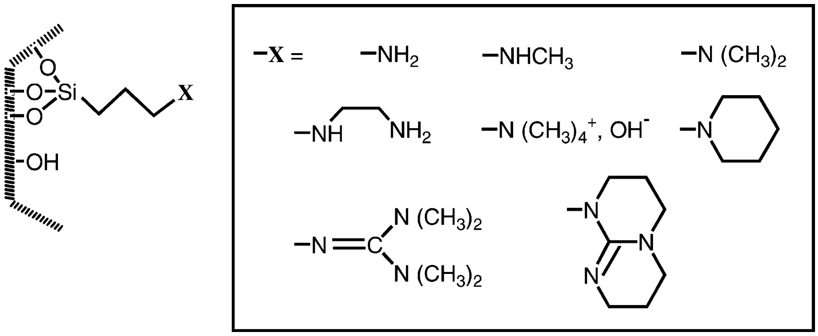

Fig. 9. Organic bases anchored on the MTS surface.

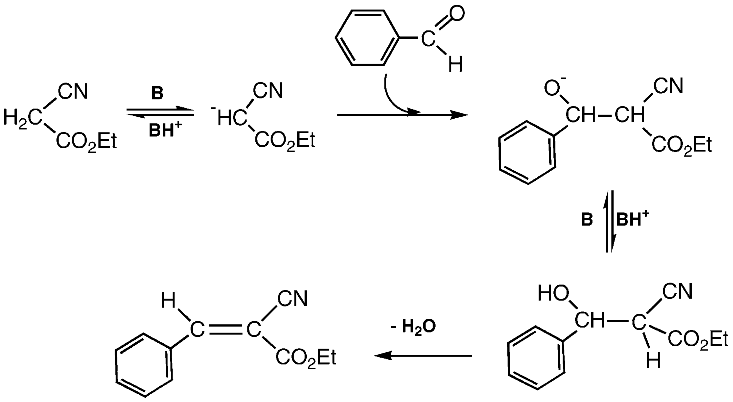

Fig. 10. Classical catalytic scheme for Knoevenagel condensation.

The reaction pathway proposed involves a concerted mechanism—which is probably favored under heterogeneous conditions—and is consistent with an enhanced base strength of the transiently formed imine groups. It also suggests that only one site is involved in each catalytic cycle.

When the amine group was previously converted into imine by reaction of benzaldehyde in toluene under azeotropic distillation, the isolated material exhibited higher an initial activity than the parent grafted amine under the same conditions. A same type of mechanism which encompasses an imine intermediate in the catalytic cycle has been also proposed by Sartori and co-workers for the nitroaldol condensation of benzaldehyde and nitromethane using primary amine tethered to amorphous silica or MCM-41-type materials [130]. Recent results suggest that the silanol groups of uncovered silica surface play a role in the imine formation [131].

Amine containing MTS has been also used for the synthesis of monoglycerides via a reaction route involving epoxide ring-opening of glycidol with fatty acids (Fig. 12).

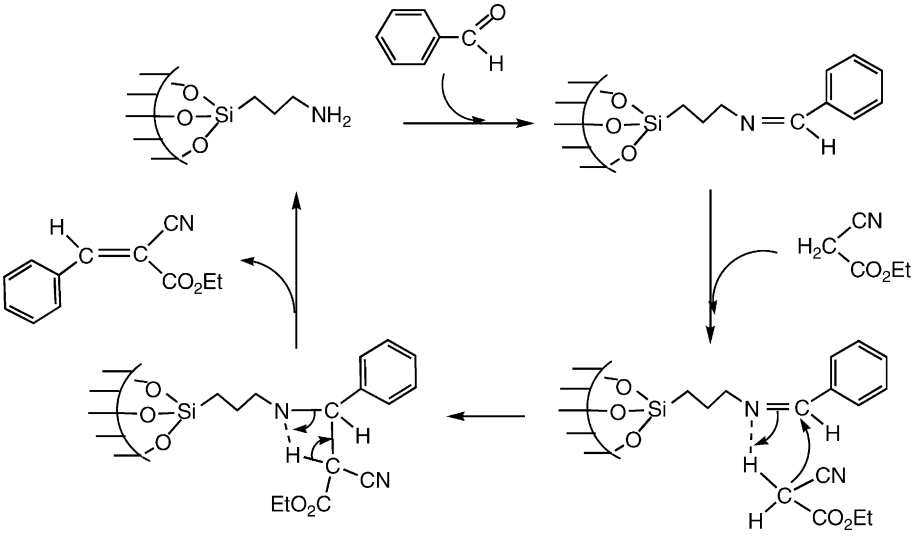

Fig. 11. Catalytic cycle during Knoevenagel condensation using MTS-grafted primary amine from [129].

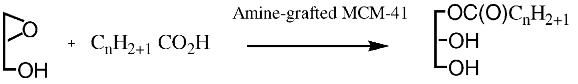

Fig. 12. Monoglyceride synthesis by fatty acid addition to glycidol.

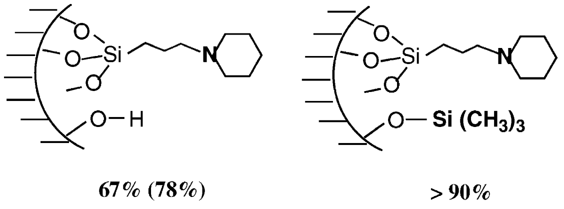

Fig. 13. Yields in α-monoglyceride after 24 h reaction using both catalysts at 293 K. Value in brackets corresponds to second run.

Selective synthesis of α-monoglycerides constitutes a major challenge for agrochemicals and pharmaceuticals production. The reaction of glycidol with lauric acid ($n = 10$) was performed at 293 K using toluene as solvent. Despite very high selectivities in α-monoglyceride, low yields were obtained on the fresh catalyst due to extensive consumption of glycidol by polymerization of the residual silanol groups. Re-use of the catalyst, after washing with toluene, ethanol and diethyl ether, led to enhanced yields (Fig. 13) on account of the passivation of the acidic surface sites by strongly adsorbed polymer. The initial performance of the catalysts could be significantly improved after silylation of the surface by CVD using hexamethyldisilazane (HMDS) as reagent [102].

Yields up to 90% in isolated pure α-monoglyceride could be then reached and the catalysts proved to be very stable after several recycles [128]. Such catalytic reaction induced by amine has been never described in the literature even though in homogeneous conditions.

Diamines grafted on MCM-41 revealed higher base catalytic activity because they were able to catalyze condensation between benzaldehyde and ethyl malonate which is usually less active than ethyl cyanoacetate. The catalytic activity was also high with less reactive carbonyl derivatives such as cyclic or aliphatic ketones. Moreover, aldolisation between acetone and aromatic aldehyde was also possible [132].

Quaternary ammonium hydroxides anchored on MCM-41 provide a stronger base catalyst than amine analogs [133] and was able to catalyze the same reaction than previously reported on the successive intermolecular Michaël leading to flavanone [85]. Moreover, this catalyst induced the successive intramolecular olefinic attack of phenolic group from the Knoevenagel condensation product of salicylaldehyde and diethyl glutaconate (Fig. 14). This fast cyclisation leads to chromene derivative (A) from which successive conversion induced by proton abstraction from the alpha position of the ester function gives coumarin derivatives (B) [133]. The ratio of chromene/coumarin produced should be influenced by the base strength of the catalyst. Hence, the possible control of the selective formation of one of them would be very useful, because of their growing interest for the preparation of pharmaceuticals.

Guanidines are stronger organic bases which were already immobilized on polymers in order to develop supported catalysis in organic synthesis [140,141]. The anchored guanidine on MTS provide useful catalysts for demanding reactions such as Michaël reactions [134] or transesterification reaction [136]. Hence, during the reaction between cyclopentenone and ethyl cyanoacetate, the strong basic sites selectively catalyze 1–4 addition versus undesirable

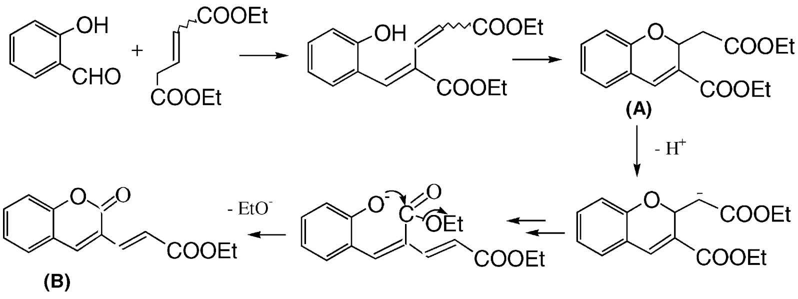

Fig. 14. Formation of chromene (A) and coumarin (B) derivatives.

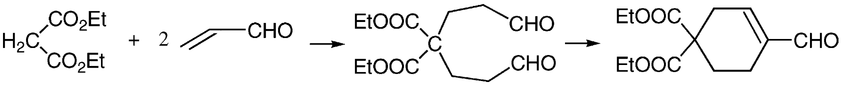

Fig. 15. Michaël reaction and successive aldolisation.

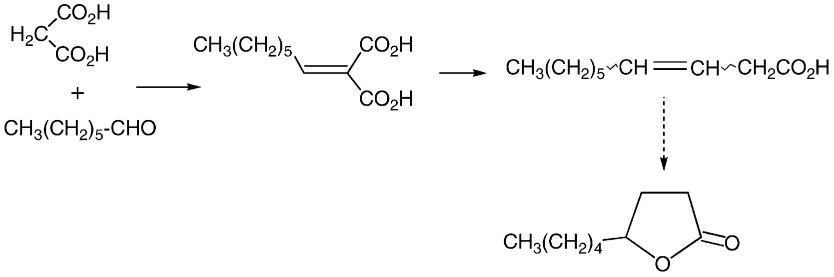

Fig. 16. Preparation of 3-nonanoic acid by base-catalyzed condensation.

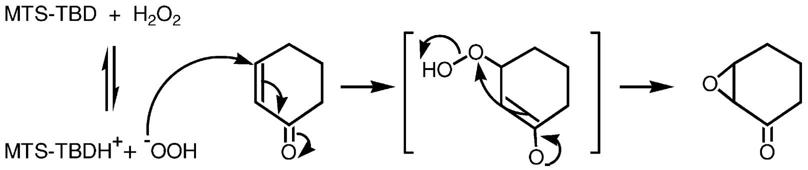

Fig. 17. Epoxidation of 2-cyclohexenone.

secondary reactions (dimerisations and rearrangements). Another interesting application guanidine containing MTS reported by Jacobs and co-workers deals with the double Michaël addition of acrolein on diethylmalonate followed by aldol condensation leading to a ring formation (Fig. 15) [134].

The Linstead variation of the Knoevenagel condensation catalyzed by a series of supported guanidines prepared via different routes, was also investigated by us in collaboration with Macquarrie's group, and revealed excellent results. This condensation reaction can be used for the synthesis of the precursor of coconut oil lactone, a fragrance component (Fig. 16) [139].

The base-catalyzed epoxidation of electron-deficient alkenes was also described [134,139] and proceeded with excellent conversions and selectivities, when the surface was passivated by silylation. Their high efficiency in the epoxidation of alcen-2-one would result from their ability to deprotonate H_2O_2 leading to an ion-pair (HOO^-, MTS–$TBDH^+$) and from their lipophilic character which favors the adsorption of olefin, which then reacts via 1–4 addition (Fig. 17).

It is noteworthy that chiral organic bases such as pyrolidines and cinchonines or cinchonidines were recently grafted on MCM-41 suport in order to catalyze enantioselective Michaël type addition between thiol and 5-methoxy-2(5H)-furanone [142]. Although, enantiomeric excess was only modest (maximum ee 35%), this attempt is very promising.

Other basic catalysis performed with in situ-prepared HMS have been also successfully developed by Macquarrie and co-workers [143,144].

5. Outlooks and conclusions

This brief review provides only a partial view of research underway in the field of acid and base catalysis. Other promising routes in acid catalysis can be mentionned such as MCM-41/Nafion composite prepared from a sol–gel preparation of nanostructured silica in the presence of cethyltrimethylammonium and Nafion gel in monophasic conditions. This novel material was applied in the dimerization of α-methylstyrene to produce selectively the corresponding acyclic dimer [145]. Other very interesting approaches are the attachment of Nafion monomer on MCM-41 as on silica surface [146], and immobilization of ionic liquids on MCM-41 [147]. Moreover, preparation of HPW/HMS type materials according to sol–gel procedure in presence of surfactants will deserve attention.

In the case of base catalysis, the stabilization of MCM-41 by hydrophobization could provide access to more base resistant materials. Other strategies would include use of other supports such as TiO_2 or ZrO_2.

The main advantages of these new hybrid mesoporous materials lie in their extremely high surface areas and free accessibility of their pore systems. The design of anchored catalytic sites possessing chirality and higher acid or base strength is in progress and will extend their application in fine chemical synthesis. However, the challenging task which needs to be addressed is the improvement of the chemical stability and the price of MTS versus silica gel in order to allow regeneration and reuse without loss of activity.

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