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Immobilized Proton Sponge on Inorganic Carriers

The Synergic Effect of the Support on Catalytic Activity

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1,8-bis(dimethylaminonaphthalene) (DMAN), a proton sponge, was grafted onto amorphous and pure-silica MCM-41. The results show that DMAN supported on MCM-41 is an excellent base catalyst for the Knoevenagel condensation between benzaldehyde and different active methylene compounds as well as for the Claisen–Schmidt condensation of benzaldehyde and 2′-hydroxyacetophenone to chalcones and flavanones. The influence of the solvent and the polarity of the support on the activity of the catalysts was studied. It was found that the activity of the supported catalyst is directly related to the polarity of the inorganic support. Moreover, the support can also preactivate the reagents by interaction of the carbonyl groups with the weakly acidic silanol groups of the MCM-41. This preactivation step enables DMAN, anchored onto MCM-41, to abstract protons with a higher pK_a than that of the DMAN. Finally, the study of the deactivation and recycling of the DMAN anchored onto MCM-41 catalysts showed that it is a stable material with respect to deactivation and leaching and results in comparable rates in successive batch reactions.

Key Words: **immobilized proton sponge; base catalyst; MCM-41; Knoevenagel condensation; Claisen–Schmidt condensation.**

INTRODUCTION

The development of green chemistry for the production of fine chemicals is an area of growing interest. In the case of base catalysis, the replacement of liquid by solid bases has the advantage of decreasing corrosion and environmental problems, while allowing the separation and recovery of the catalyst. Mesoporous molecular sieves provide an excellent inorganic support, with the aim of designing catalysts with isolated and uniform basic sites, for anchoring organic moieties containing basic sites. To this end, solid Lewis bases were generated by grafting simple amines onto micelle-templated silicas supports (1–8); chiral amines, cinchonine and cinchonidine (9); β-aminoalcohols (10); 1,5,7-triazabicyclo[4.4.0]dec-5-ene (11, 12); and quaternary organic ammonium hydroxides (13, 14). The modified mesoporous materials are found to be excellent catalysts for Knoevenagel (4–8, 13, 14) and aldol codensation (8, 11, 14), Michaël addition (11, 13, 14), alkylation (10), transesterification (12), and α,β-unsaturated ketone epoxidation (11) reactions.

Diamines with neighboring atoms and aromatic frames such as for naphthalene, fluorene, and phenanthrene exhibit unusually high basicity constants and are referred to as proton sponges, the archetype of which is 1,8-bis(dimethylamino)naphthalene (DMAN) with p$K_a = 12.1$. Despite the interest in proton sponges as potential base catalysts and the fact that they are widely used for proton abstraction (15), reports dealing with their application as catalysts for the preparation of fine chemicals were published only recently. Thus, we were able to study the behavior of DMAN as a homogeneous catalyst for a series of Knoevenagel condensation reactions to form carbon–carbon bonds (16).

To benefit from the catalytic properties of this organic base and to obtain a solid recyclable catalyst, we present the heterogenization of DMAN on an amorphous silica as well as on pure-silica MCM-41 material. To do so, the aromatic rings were functionalized and grafted through the silanol groups of the molecular sieve. This procedure obtained stable basic catalysts which show good activity for the Knoevenagel condensation of benzaldehyde with active methylene compounds and Claisen–Schmidt synthesis of chalcones and flavanones.

EXPERIMENTAL

Catalyst Preparation

The general procedure for preparing the catalysts is presented in Scheme 1. More specifically, in a first step, 4-nitro-1,8-bis(dimethylamino)naphthalene (17) was prepared as follows. A mixture of HNO_3 (0.64 ml, 0.01 mol;

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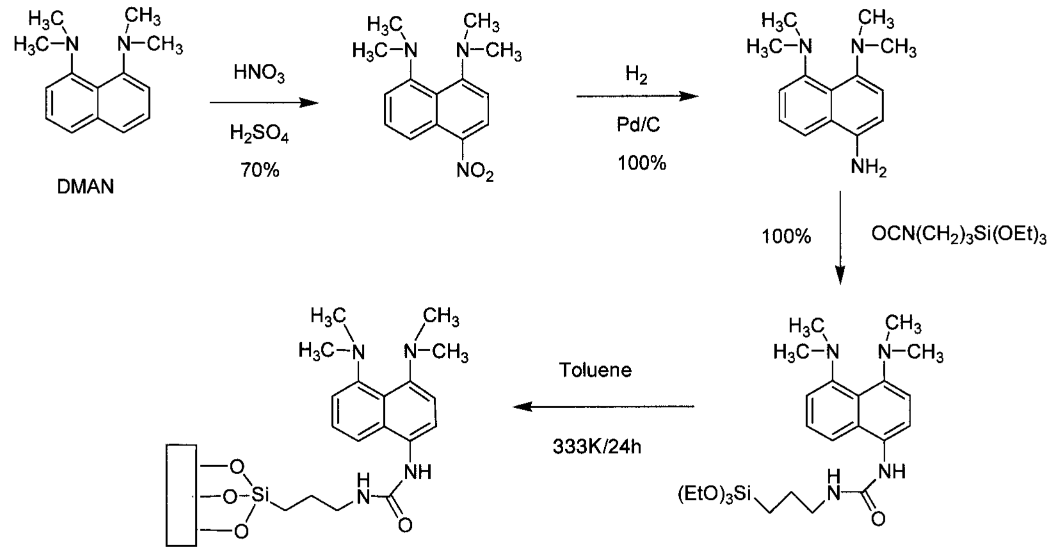


SCHEME 1

$d = 1.41$ g cm^{-3}) and concentrated H_2SO_4 (2 ml), precooled at 253 K was added dropwise to a stirred solution of DMAN (2.14 g, 0.01 mol) for 2 min. After an additional 5 min at that temperature, the reaction mixture was poured onto crushed ice ($\approx$200 ml), neutralized with aqueous ammonium hydroxide ($\approx$60 ml), and extracted with chloroform (5 × 25 ml). The combined organic extracts were dried over magnesium sulfate and concentrated in vaccum. The residue was chromatographed on silica gel using ethyl acetate–hexane (1 : 2) as the eluent to obtain 1.8 g (70%, m.p. 134–135°C).

The nitro group was reduced to the corresponding amino group according to the following procedure. Ten wt% Pd on a carbon catalyst (100 mg) was added to a solution of 4-nitro-1,8-bis(dimethylamino)naphthalene (260 mg, 1 mmol) in ethanol (75 ml), and H_2 (1 bar) was introduced into the autoclave; after stirring for 2 h at room temperature, the reaction was monitored by TLC using ethyl acetate–hexane (1 : 2). When the reaction was finished, the mixture was filtered through a short pad of celite and concentrated to dryness under reduced pressure. The 4-amino-1,8-bis(dimethylamino)naphthalene (18) was quickly dissolved in dry methylene chloride (4 ml), and 3-isocyanatepropyltriethoxysilane (1 mmol) was added under inert atmosphere while stirring. After 2 h of reaction, 4-[(triethoxysilyl)propylaminocarbonylamino]-1,8-bis(dimethylamino)naphthalene was quantitatively obtained. The structure of the silylated derivative was established by means of NMR spectroscopic techniques, including two-dimensional correlated NMR spectroscopy (COSY 45) for assignment of the ^{1}H and ^{13}C signals. ^{1}H-NMR (Cl_3CD): 7.52 (d, JH-3-H-2 = 8.27 Hz, 1H, H-3 arom.); 7.28 (dd, JH-6-H-5 = 7.89, JH-6-H-7 = 7.74 Hz; 1H, H-6 arom.); 7.21 (d, 1H, H-5 arom.); 6.88 (d, 1H, H-7 arom.); 6.78 (d, 1H, H-2 arom.); 6.11 (s, 1H, Ar NH); 4.64 (t, $J =$ 5.80 Hz, NH–CH_2); 3.66 (q, $J = 7.05$ Hz, 6H, OCH_2); 3.14–3.07 (m, 2H, CH_2N); 2.74, 2.73 (s+s, 6H+6H, NCH_3); 1.19–1.12 (m, 2H, CH_2); 1.08 (t, 9H, CH_3–C); 0.45 (m, 2H, CH_2–Si) ppm.

Heterogenization of the Functionalized Proton Sponge on Silica and MCM-41

General method. A solution of 4-[(triethoxysilyl) propylaminocarbonylamino]-1,8-bis(dimethylamino)naphthalene in methylene chloride (4 ml, 1 mmol) was added to a well-stirred toluene suspension (40 ml) of 1 g of either amorphous silica (silica gel Merck, 230–240 mesh, 550 m^2 g^{-1}) or pure-silica MCM-41 prepared according to the literature (19), which was previously dried *in situ* at 413 K and 0.1 Torr for 3 h. The mixture was stirred at 333 K for 24 h. The solid was filtered and soxhlet-extracted with methylene chloride–ethyl ether (1 : 1) for 16 to 24 h to remove the remaining unsupported naphthalene derivative. The SiO_2 and MCM-41 containing the grafted DMAN were dried in vacuum, analyzed, and are referred to as PS-Silica and PS-MCM-41 respectively.

Surface loading, determined by elemental analyses based on N wt%, using a CHNS analyser (Fisons EA 1108), was 0.20 and 0.31 mmol g^{-1} for PS-MCM-41 and PS-Silica, respectively.

Infrared measurements were performed on an FTIR Nicolet 710 spectrophotometer using sealed cells with CaF_2 windows. Wafers (10 mg) of solid catalyst were pressed (1 Tm cm^{-2}) and outgassed under vacuum (10^{-2} Pa) for 1 h at 473 K.

Thermogravimetric analyses of the catalysts were obtained in a Netszch microbalance under an air stream using kaolin as the inert standard.

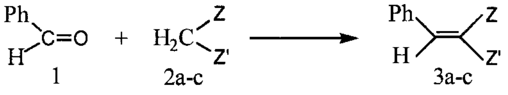
Catalytic Activity: General Reaction Procedures

The Knoevenagel condensation. A mixture of benzaldehyde (8 mmol) and an active methylene compound (7 mmol) was heated and stirred at the desired reaction temperature in a batch reactor with or without solvent under N_2 atmosphere. When the reaction temperature was stable, the catalyst (0.5 to 1 mmol% of anchored DMAN with respect to the active methylene compound) was added and the reaction started. Samples were taken periodically, and the evolution of the reaction was followed by GLC on a 25-m capillary column coated with 5% cross-linked phenylmethylsilicone.

The Claisen–Schmidt condensation. A mixture of benzaldehyde (12 mmol) and 2′-hydroxyacetophenone (10 mmol) was stirred and heated at 403 K without solvent in a batch reactor under N_2 atmosphere. When the temperature was stable, the PS-MCM-41 catalyst (2 mmol% of anchored DMAN with respect to the 2′-hydroxyacetophenone) was added and the reaction started. Samples were taken periodically, and the evolution of the reaction was followed by GLC on a 25-m capillary column coated with 5% cross-linked phenylmethylsilicone.

RESULTS AND DISCUSSION

The efficiency of the grafted proton sponge as a base catalyst was tested with the Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate (Scheme 2) in the absence of a solvent at room temperature, using a 0.5% molar ratio of immobilized proton sponge on MCM-41 (PS-MCM-41) with respect to the ethyl cyanoacetate. After 7 h of reaction time, the conversion of ethyl cyanoacetate was 78% with 100% selectivity to the condensation product (**3a**)(*trans*-α-ethyl-2-cyanocinnamate). However, under these reaction conditions the product remains strongly adsorbed on the catalyst, which is deduced from the small increase in conversion observed after a 2-h reaction time (Fig. 1). Nevertheless, when the reaction temperature was increased to 313 K under the same reaction conditions, 99% product yield was obtained after a 7-h reaction time (Fig. 1). These results show that this organic–inorganic composite catalyst performs the Knoevenagel condensation between **2a** and benzaldehyde with excellent activity and selectivity at relatively low reaction temperatures.



	a	b	c
Z	CN	$COCH_3$	CO_2Et
Z'	CO_2Et	CO_2Et	CO_2Et

SCHEME 2

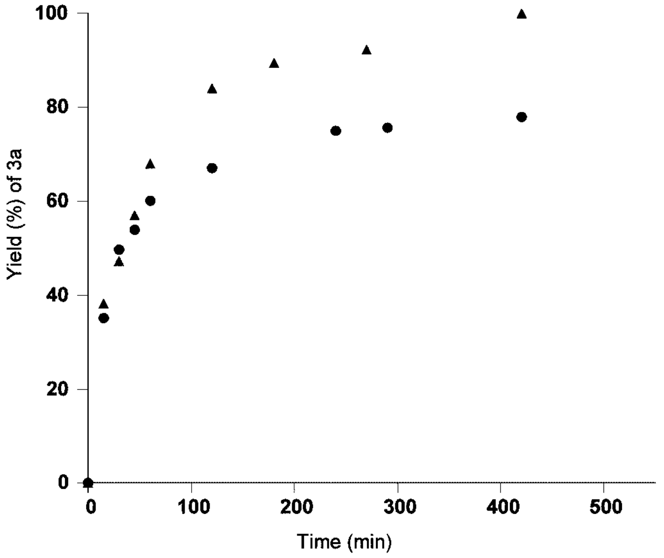


FIG. 1. Knoevenagel condensation of benzaldeyde with ethyl cyanoacetate (**2a**) using PS-MCM-41 catalyst (0.5% molar ratio of immobilized DMAN with respect to **2a**): ●, at room temperature; ▲, at 313 K.

We previously found (16) that, when using DMAN as a base catalyst in homogeneous phase for the condensation of benzaldehyde and ethyl cyanoacetate, the polarity of the solvent has a strong effect on the reaction rate, increasing the reaction rate with the solvent polarity (Fig. 2). Furthermore, with nonpolar solvents the reaction rate decreased dramatically. This behavior was attributed to the influence of the solvent on the reaction mechanism and not

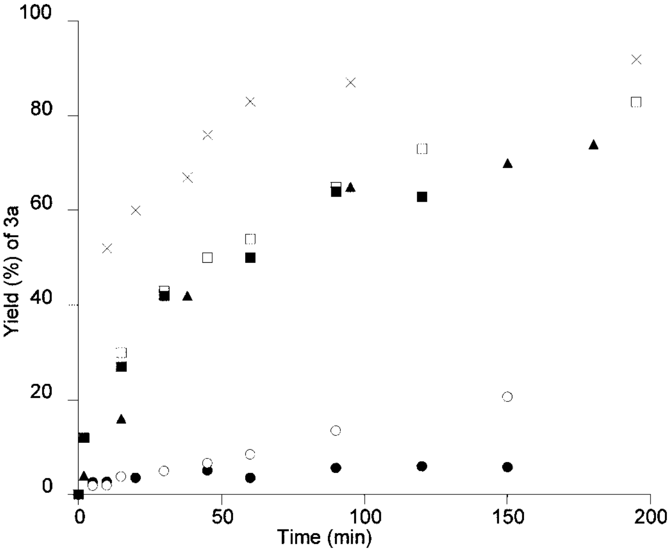


FIG. 2. Knoevenagel condensation of benzaldeyde with ethyl cyanoacetate (**2a**) using DMAN (2% molar ratio with respect to **2a**) as homogeneous catalyst at room temperature and using different solvents: ●, toluene; ○, chlorobenzene; ▲, acetonitrile; ■, dimethylformamide; □, dimethyl sulfoxide; ×, ethanol.

to a change in the capacity of the catalyst for proton transfer. Thus, when polar reagents are involved, the transition-state complex is better solvated by polar solvents, decreasing the activation free enthalpy and enhancing the reaction rate (20, 21).

To study the influence of the solvent on the initial rate of the condensation between benzaldehyde and **2a**, the reaction was carried out using solvents with different polarities in the presence of PS-MCM-41 as a catalyst at 313 K, and using a 0.5% molar ratio of immobilized proton sponge with respect to the ethyl cyanoacetate (**2a**).

As can be seen in Fig. 3, a polar protic solvent such as ethanol was the most effective for the formation of the product **3a**, in good agreement with previous observations in the homogeneous phase (16). However, with the exception of the behavior observed with ethanol, the other tested solvents (Fig. 3) showed that a change in solvent polarity had only a moderate effect on the reaction rate. The most polar aprotic solvent (CH_3CN) did not have the expected positive impact on the reaction rate (Fig. 3). These results are in clear contrast with those obtained when working with the homogeneous phase, where a dramatic decrease in the reaction rate was observed with nonpolar solvents (see Fig. 2). Thus, we assumed that since the presence of the solid support is the only difference between the homogeneous and the heterogeneous DMAN, this should be a determinant for the different catalytic behavior with respect to the solvent polarity. Thus, in a first approximation we assumed that the relatively weak dependence of the reaction rate on the polarity of the solvent when the DMAN is supported on MCM-41 must be related to the surface polarity of the support. Indeed, in heterogeneous catalysis, the reaction occurs on the surface; when polar reagents are involved (as in Knoevenagel condensations) the implicated transition-state complex should be stabilized by polar surfaces, which lead to an increase in the reaction rate.

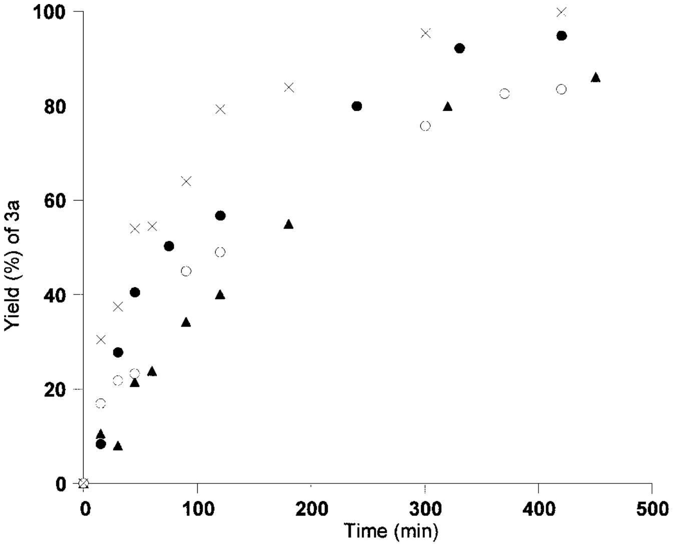


FIG. 3. Knoevenagel condensation of benzaldeyde with ethyl cyanoacetate (**2a**) using PS-MCM-41 catalyst (0.5% molar ratio of immobilized DMAN with respect to **2a**) at 313 K using different solvents: ●, toluene; ○, chlorobenzene; ▲, acetonitrile; ×, ethanol.

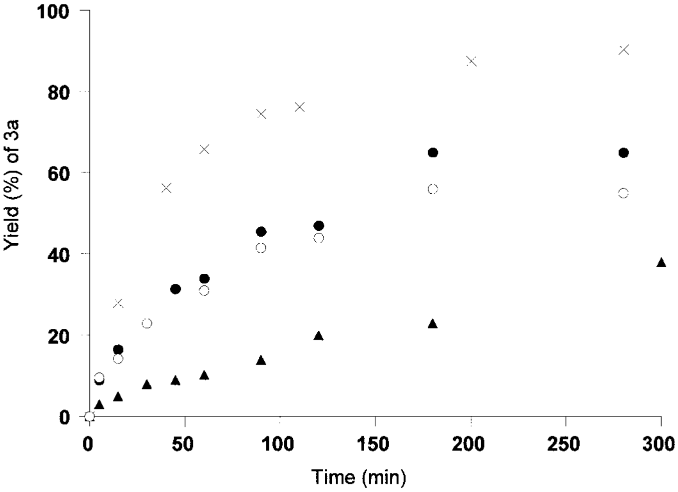


FIG. 4. Knoevenagel condensation of benzaldeyde with ethyl cyanoacetate (**2a**) using PS-Silica catalyst (0.5% molar ratio of immobilized DMAN with respect to **2a**), at 313 K using different solvents: ●, toluene; ○, chlorobenzene; ▲, acetonitrile; ×, ethanol.

To check the influence of the polarity of the support, derivatized DMAN was anchored onto silica according to the same procedure used for MCM-41, and the condensation of benzaldehyde and **2a** was carried out under the same reaction conditions. When the effect of solvent was studied, a different behavior was observed for the reaction catalyzed by PS-Silica and PS-MCM-41 (Fig. 4). Whereas the activity of PS-MCM-41 is hardly dependent on the nature of the solvent (see Fig. 3), reactions catalyzed by the amorphous silica-based catalyst show strong dependency on the solvent. The reasons for the different behavior of the two solid catalysts are found in the different polarity of the catalyst surface. Results published by Macquarrie and Jackson (22) showed that surface polarity of aminopropyl-functionalized MCM, measured using adsorption of Reichardts dye (23), is higher than the corresponding silica-derived materials. Therefore, it might be that in our case the trend is the same. In fact, however, the PS-silica material was more hydrophobic than PS-MCM-41, which is deduced by the small amount of adsorbed water (Table 1) and that most of the silanol groups of the silica were used to graft the organic base. Indeed, the amount of free silanol groups at 3745 cm^{-1} is lower on the PS-silica material than on PS-MCM-41 (Fig. 5). Therefore, it is assumed that in the course of the reaction, the polar surface of the support stabilizes the transition state. In the case of the more polar surface (PS-MCM-41), reactants are preferentially adsorbed onto the catalyst, and even a polar solvent such as CH_3CN only moderately affects

TABLE 1

Main Characteristics of the Catalysts

Catalyst	Surface loading[a] mmol g^{-1}	Water adsorption[b] (%)
PS-MCM41	0.20	4.9
PS-Silica	0.31	2.4

[a] Determined by elemental analyses based on N wt%.
[b] From TG measurements.

the reaction rate. However, with the less polar surface of PS-Silica, reactant molecules are preferentially solvated by polar solvents interfering with the catalytic process.

To evaluate the intrinsic activity of both MCM-41 and the silica-derivatized catalyst, and to compare the findings with the activity of the parent homogeneous DMAN, we calculated turnover frequencies of the catalysts for reactions carried out at room temperature in the absence of a solvent. The turnover frequencies (TOF; expressed as initial reaction rate per mmol of base moieties per min) were PS-MCM-41 (TOF = 85), DMAN (TOF = 65), and PS-Silica (TOF = 38). Therefore, it seems that the polarity of the support may play a role similar to that of the polar solvent in the homogeneous phase, thus increasing the rate of the reaction. As stated earlier, the solvent, and therefore the support effect, can be related to the stabilization of the charged transition state, leading to the reaction product.

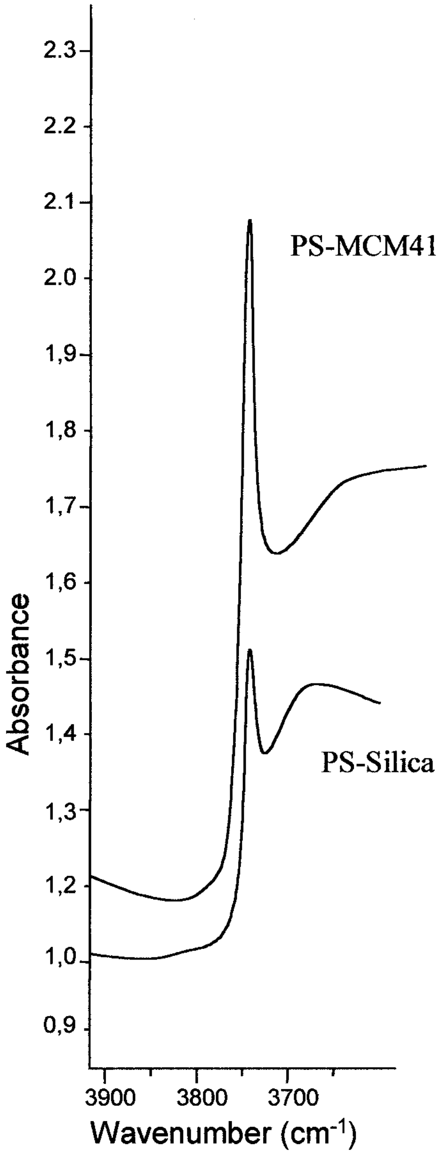


FIG. 5. IR spectra of the PS-MCM-41 and PS-Silica samples.

Preactivation of Reactants by Adsorption on the Support

There is another factor besides surface polarity that can contribute to the high catalytic activity of the DMAN grafted onto MCM-41. This could be the participation of the weakly acidic silanol groups of the support surface in the reaction mechanism. Bearing this hypothesis in mind, a concerted acid–base mechanism may operate, in which the weakly acidic silanol groups interact with the carbonyl group of the benzaldehyde resulting in polarization of the group and an increase in the positive charge of the corresponding carbon atom. If this occurs, then the attack of the carbanion formed on the basic sites (DMAN) should be favored; this would explain the higher activity of the PS-MCM-41 sample catalysts, which contain more silanol groups. Angeletti *et al.* (24) and Lakshmi Kantam and Sreekanth (25) proposed a concerted mechanism for condensation reactions catalyzed by both amino-functionalized silica and mesoporous material, in which silanol groups of the support promote the nucleophilic addition on the carbonyl compound by means of a hydrogen bond. Moreover, these silanols would allow the regeneration of the catalytic sites by proton abstraction.

To examine this possibility, benzaldehyde was adsorbed on both silica and MCM-41-grafted DMAN in a vacuum IR cell. As shown in Fig. 6, the two samples give a band at ~1690 cm^{-1}, corresponding to the physically adsorbed benzaldehyde, while a second band appears at ~1654 cm^{-1} and must be assigned to the carbonyl groups interacting with the weakly acid silanol centers. This indicates that a certain polarization of the carbonyl group of benzaldehyde took place, and this is responsible for preactivation of the benzaldehyde reactant molecule. The concentration of preactivated molecules of benzaldehyde is higher on the MCM-41 than on the silica composite (Fig. 6) as a consequence of the larger number of silanol groups on the surface of the former (Fig. 5). This could lead to an increase in reaction rate observed with the PS-MCM-41 catalyst with respect to the PS-Silica and even more so with respect to DMAN in the homogeneous phase especially in the presence of nonpolar solvents.

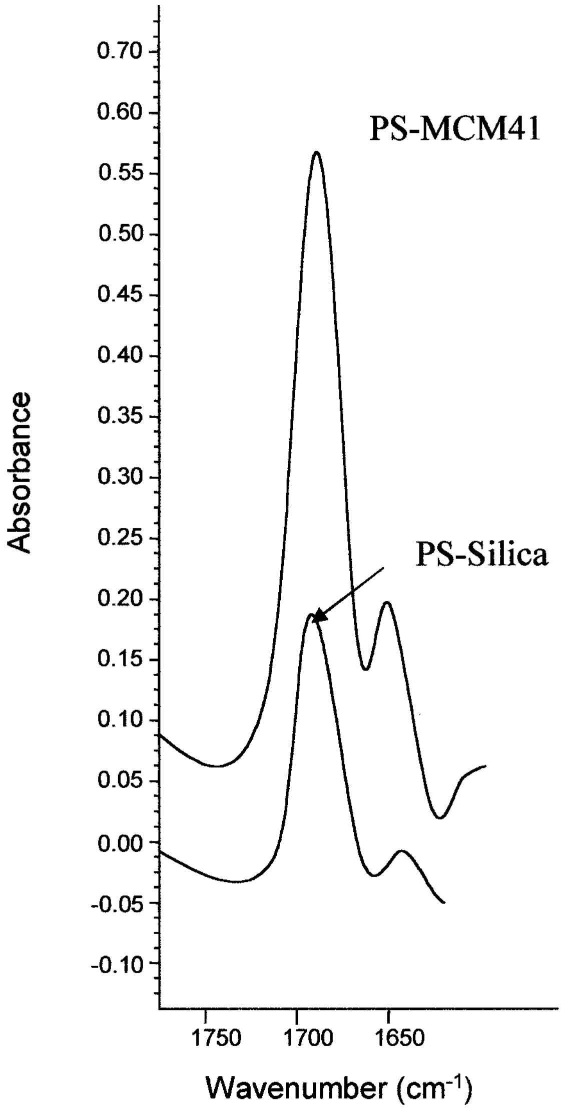
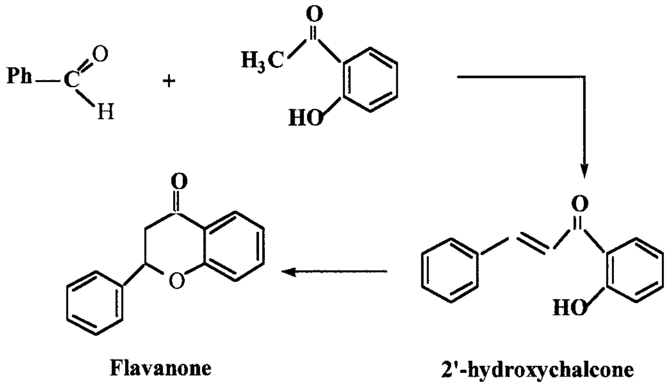


FIG. 6. IR spectra of the benzaldehyde adsorbed on PS-MCM-41 and PS-Silica samples.

The foregoing hypothesis is supported by the results obtained when PS-MCM-41 was used as a catalyst and when these results are compared with those obtained with the parent DMAN in the homogeneous phase for the Knoevenagel condensation of active methylene compounds requiring increasing basicity for proton abstraction, i.e., ethyl acetoacetate (**2b**) ($pK_a = 10.7$), ethyl malonate (**2c**) ($pK_a = 13.3$) and 2′-hydroxy acetophenone (Scheme 3) ($pK_a = 15.8$). Thus, when the reaction between benzaldehyde and **2b** was carried out in EtOH at 353 K under the conditions described earlier, a yield of 20% condensation product was reached after 3 h on PS-MCM-41 (Table 2, entry 1), whereas the reaction did not take place in the homogeneous phase, even with an amount of catalyst four times larger (16).

Moreover, when a more demanding reactant (diethylmalonate, **2c**) was used and the Knoevenagel reaction was carried out at 383 K, without a solvent in the presence of PS-MCM-41 as the catalyst (1% mmol/mmol), 70% yield of the Knoevenagel adduct was produced with a selectivity of 90% (Table 2, entry 2), while almost no conversion was observed with DMAN in the homogeneous phase and DMAN supported on amorphous silica.



SCHEME 3

Claisen–Schmidt Condensation

PS-MCM-41 catalyst was tested for the Claisen–Schmidt condensation between benzaldehyde and 2′-hydroxyacetophenone (Scheme 3). This condensation led to 2′-hydroxychalcone which can cycle through an intramolecular Michael addition to yield the corresponding flavanone. When the reaction was carried out at 403 K without solvent, but with PS-MCM-41 as the catalyst, a conversion of 40% with a selectivity of 80% for flavanone was obtained after an 8-h reaction time.

The fact that the pK_a of both ethyl malonate (13.3) and 2′-hydroxyacetophenone (15.8) is higher than that of the proton sponge (12.1) suggests that factors other than the basic strength of the amine are also responsible for the catalytic activity. As discussed earlier, we propose a mechanism where a weak Brønsted acid site (SiOH group) will interact with the carbonyl group of the benzaldehyde, diethyl malonate, or acetophenone, polarizing the carbon–oxygen bond and increasing the density of the positive charge on

TABLE 2

Results of the Knoevenagel Condensation Using PS-MCM-41 as a Catalyst

Entry	Z-CH_2-Z′	Catalyst (% mol)	Solvent	Temperature (K)	Yields[a] (%)
1	**2b**	0.5	EtOH	353	20 (100)
2	**2c**	1	—	383	70 (90)[b]

[a] 3-h reaction time. Selectivity to the condensation product in parentheses.

[b] Decarboxylation of the Knoevenagel adduct is also detected.

the carbon supporting the carbonyl group. In the case of benzaldehyde, this polarization leads to a quicker attack of the carbon by *carbanion*-type species. At the same time, in the case of the diethyl malonate or acetophenone, the increase in the positive charge on the carbon of the carbonyl group enhances the acidity of the hydrogens in the α-position of the carbonyl group, allowing easier abstraction by the catalyst. Calculations of the density of the positive charge on the hydrogen atoms attached to the methylenic group of a protonated diethyl malonate species give a value of 0.356, clearly superior to that of the neutral species (0.302). This increase in the acidity of the protonated diethyl malonate could explain why the basic sites existing on PS-MCM-41 abstract the proton and generate carbanion-type species with molecules such as diethylmalonate and 2′-hydroxyacetophenone which then react with the activated benzaldehyde.

Catalyst Deactivation and Recycling

To determine whether leaching and/or deactivation of the catalyst occurs, PS-MCM-41 was reused several times for the Knoevenagel reaction of benzaldehyde with ethyl cyanoacetate (**2a**). The reactions were carried out in ethanol solvent at 313 K using a 1.1% molar ratio of PS-MCM-41 catalyst. When the reaction was complete, the solid was filtered and thoroughly washed with CH_2Cl_2 and reused in a second and third cycle. As shown in Fig. 7, a small decrease in activity was observed after the first recycling, and no further loss was observed when the small amount of catalyst lost during the process was considered.

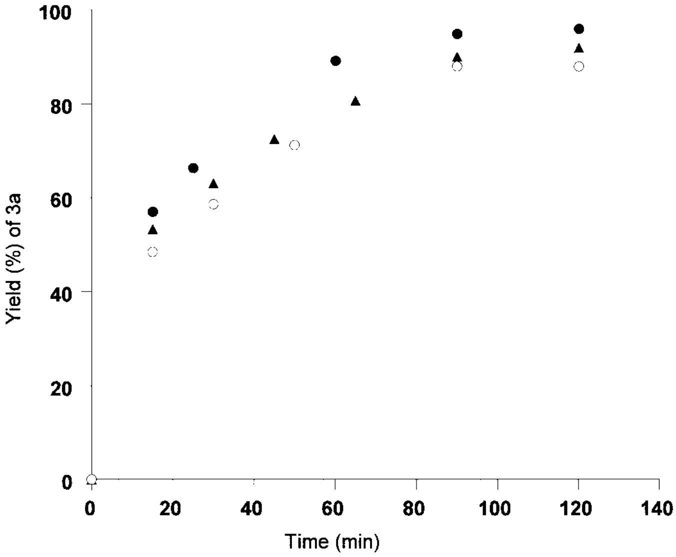


FIG. 7. Knoevenagel condensation of benzaldeyde with ethyl cyanoacetate (**2a**) using PS-MCM-41 catalyst (1.1% molar ratio of immobilized DMAN with respect to **2a**) at 313 K in ethanol as solvent: ●, first cycle; ▲, second cycle; ○, third cycle.

CONCLUSIONS

A proton sponge (DMAN) was functionalized and grafted onto amorphous silica and onto pure-silica MCM-41. It was shown that, in the homogeneous phase, DMAN requires the presence of polar solvents to reach high reaction rates. However, supported DMAN gives better intrinsic activity in the absence of a solvent and when polar solvents are not used. The activity of the supported catalysts is directly related to the polarity of the support, which is higher in the case of MCM-41. In this sense the support acts as a polar solvent that can stabilize the transition-state charged complex. The support can also preactivate the reagents by interaction of the carbonyl groups with the weakly acidic silanol groups. This preactivation step allows PS-MCM-41 catalyst to abstract protons with a higher pK_a than that of the DMAN. Our results demonstrate that the activity of homogeneous proton-sponge catalysts could be strongly improved by grafting them onto MCM-41. The resulting organic–inorganic catalysts are stable against deactivation and leaching.

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