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Comparative behavior of silica-embedded *tert*-butyldimethylsilyltrifluoro-methanesulfonate and lanthanum triflate catalysts

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Abstract

A series of hybrid catalysts containing *tert*-butyldimethylsilyltrifluoro-methanesulfonate (BDMST) or lanthanum triflate (LaT), hexadecyltrimethylammonium bromide and silica were obtained by sol–gel immobilization. The catalysts were characterized by nitrogen adsorption–desorption isotherms at 77 K, TG-DTA, ^{1}H, ^{13}C, and ^{29}Si solid state MAS-NMR, XRD, TEM, scanning electron microscopy (SEM), XPS and, FT-IR after adsorption of NH_3. The catalytic tests were carried out in the reaction of the methyl ester of 1-cyclopentenylacetic acid in various solvents. The results revealed a completely different behavior of the hybrid catalysts compared with catalysts without surfactant or with free *tert*-butyldimethylsilyltrifluoro-methanesulfonate, or lanthanum triflate, or triflic acid, indicating a behavior for a typical heterogeneous catalyst. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metal triflates and other triflate derivatives as homogeneous catalysts for Lewis acid-catalyzed reactions have been reported a long time ago and they are widely utilized in organic synthesis [1]. These compounds possess strong Lewis acidity and, in contrast to metal halides, they exhibit a very high tolerance toward water. Therefore, from application point of view, their use may provide more environmentally friendly catalysts.

Lanthanide trifluoromethanesulfonates (triflates), in particular, have been found as very effective Lewis acid catalysts in a series of organic reactions like Diels–Alder [2], allylation [3], Friedel–Crafts [4], Mukaiyama aldol reaction [5], or direct acetylation of alcohols with acetic acid [6]. Many of these studies stressed the positive influence exerted by protonic media. Alkylsilyltrifluoromethane sulfonates were also very active catalysts in a series of reactions demanding Lewis acid sites [7,8].

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Since heterogeneous catalysis is more versatile for practical applications, several studies have been reported in the last years on the heterogenization of triflic acid [9] and various triflates by impregnation [10,11] or polymer incorporation [12,13], and on selective acid-catalyzed reactions using these materials. Silica-supported triflates or triflic acid are active and selective catalysts in the rearrangement of α-pinene oxide to campholenic aldehyde [11], polymerization and depolymerization of cyclic ethers [10], Friedel–Crafts reactions [12,13], alkylation of isobutane with *n*-butene [9], etc.

The aim of this paper is to present results concerning the immobilization of *tert*-butyldimethylsilyltrifluoromethanesulfonate (BDMST) and lanthanum triflate (LaT) in a silica matrix using a sol–gel procedure, and to discuss the comparative behavior of these catalysts in the reaction of the methyl ester of the 1-cyclopentenylacetic acid in various solvents. The target reaction was the alkylation of the cyclopentenyl cycle, but in fact we found a more complicated reaction sequence.

2. Experimental

Since BDMST is only soluble in carbon tetrachloride and triethylamine, the sol–gel synthesis was carried out in inert atmosphere (Ar), using an adapted route in which the silica sol was obtained by acid hydrolysis of a solution of tetraethoxyorthosilicate (TEOS). Water was then added to the acidic solution in a TEOS:H_2O molar ratio of 1:10 (samples A1 and A2) or 1:4 (sample A3), and the mixture was refluxed at 70 °C for 2 h. After cooling the silica sol solution at room temperature, the silyl triflate derivative was added under vigorous stirring as a 0.3 M solution in CCl_4 (samples A1 and A3) or as such (sample A2). The immobilization of LaT was made in the same way, except that the solvent was ethanol (samples B). Hexadecyltrimethylammonium bromide (as a surfactant) was then introduced and the gelation was carried out at 90 °C for 2 days in a teflon cylinder within an autoclave (samples A2, A3, B2, and B3), or at room temperature for 6 days (samples A1 and B1). The resulting gel was dried under vacuum, first at room temperature for 24 h and then at 100 °C for 6 h. Using this procedure, samples with 15 wt.% triflate were obtained.

The catalysts were characterized by nitrogen adsorption–desorption isotherms at 77 K, TG-DTA, ^{1}H, ^{13}C, and ^{29}Si solid state MAS-NMR, XRD, XPS, and FT-IR after adsorption of NH_3. TG-DTA curves were collected using a SETARAM 92 16.18 equipment. The sorption isotherms of N_2 at 77 K were obtained with a Micromeritics ASAP 2000 apparatus after outgassing the samples at 403 K for 12 h under vacuum. FT-IR spectra were recorded with a Bruker IFS88 instrument, equipped with KBr optics and a DTGS detector. The XPS spectra were obtained with a SSX probe FISONS spectrometer (SSX-100/206) with monochromated Al Kα radiation. The spectrometer energy scale was calibrated using the Au_{4f}7/2 peak (binding energy of 84.0 eV). For the calculation of the binding energies, the C_{1s} peak of the C-(C, H) component at 284.8 eV of adventitious carbon was used as an internal standard. The composite peaks were decomposed by a fitting routine included in the ESCA 8.3 D software. The surface composition of the investigated samples was determined using the same software. The F_{1s}, S_{2s}, Si_{2p}, La_{3d}, and O_{1s} peaks were investigated. The XRD patterns were recorded with a PW1050 diffractometer equipped with a secondary graphite monochromator and copper anticathode (λ of Cu Kα radiation = 1.54183 Å). Scanning electron microscopy (SEM) analysis was made using an ISI 60 apparatus combined with automatic PRODAS storage system. Solid state ^{13}C CP/MAS-NMR spectra were recorded on a Bruker MSL-300 spectrometer, equipped with a double-bearing probe. The triflate derivative rotor (7 mm i.d.) was charged with the samples and sealed by a Kel-F inset. The optimal contact time for ^{13}C cross-polarization was 2 to 3 ms. The spinning rate was between 2 and 4 kHz. The external standard for ^{13}C NMR was adamantine ($\delta(CH_2) = 38.40$, relative to tetramethylsilane).

The catalytic tests were carried out in the reaction of the methyl ester of the 1-cyclopentenylacetic acid in various solvents (cyclohexene, benzene, toluene, *ortho*- and *para*-xylene, 1-octene) using 40 mg of catalyst. The reactions were performed at temperatures between room temperature and 60 °C in a glass reactor under vigorous stirring (900 rpm), using 30 mg ester and an ester:solvent molar ratio of 1:60 for a reaction time of maximum 24 h.

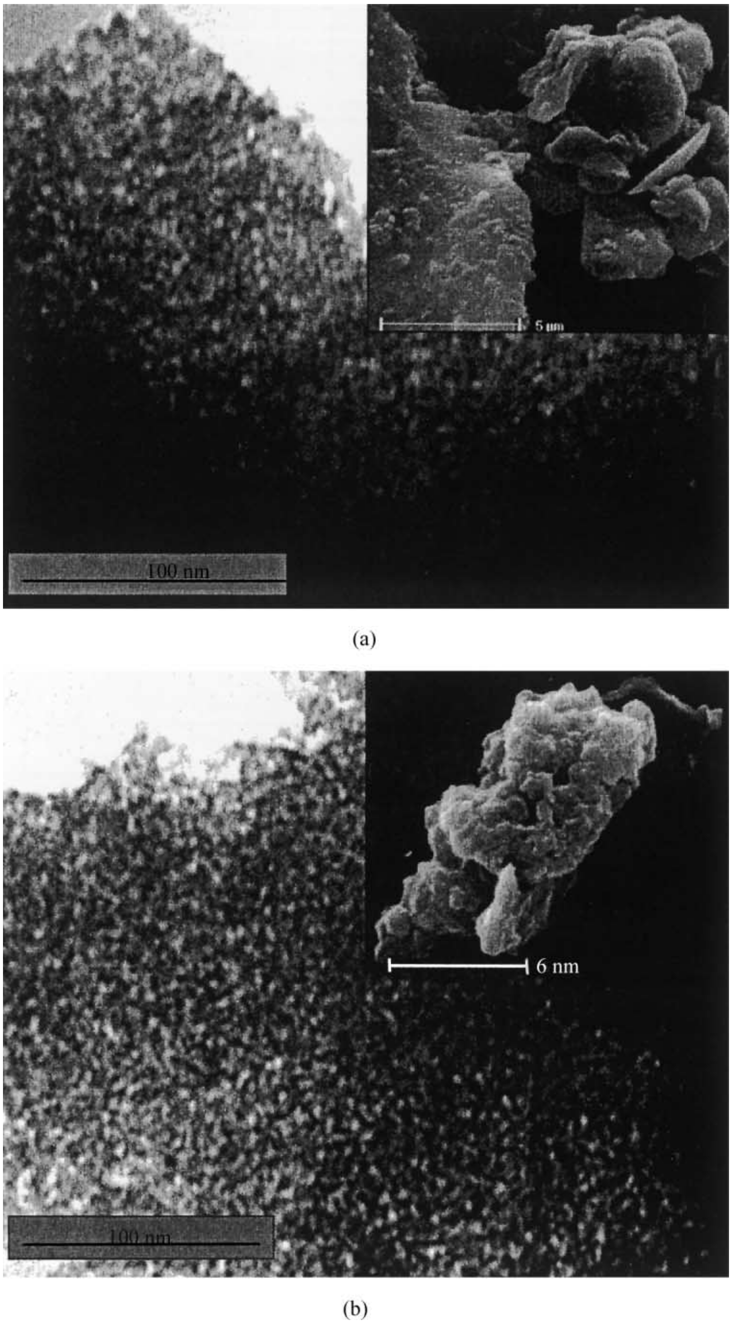


Fig. 1. TEM and SEM pictures: (a) A3; (b) B3.

3. Results

3.1. Texture and morphology analysis

According to the nitrogen adsorption–desorption isotherms, all the surfactant containing samples corresponded to mesoporous solids. The pore diameter was the same for all the catalysts (2.8 nm) but the surface area varied in the order A1 ($483\,m^2\,g^{-1}$) > A2 ($461\,m^2\,g^{-1}$)>A3 ($412\,m^2\,g^{-1}$) and, B1 ($421\,m^2\,g^{-1}$)> B2 ($357\,m^2\,g^{-1}$) > B3 ($312\,m^2\,g^{-1}$). The surface areas of the catalysts without surfactant followed the same order: A1 ($572\,m^2\,g^{-1}$)>A2 ($549\,m^2\,g^{-1}$)>A3 ($508\,m^2\,g^{-1}$) and, B1 ($468\,m^2\,g^{-1}$) > B2 ($427\,m^2\,g^{-1}$) > B3 ($403\,m^2\,g^{-1}$), exceeding the values of the samples with surfactant. The pore diameter determined for these samples was around 1.8 nm.

Fig. 1 shows TEM and SEM pictures of A3 and B3 catalysts. These micrographs are typical of the investigated catalysts. SEM corresponds to an irregular topography, typical of sol–gel-prepared samples. TEM indicated a porous texture which is in very good agreement with the data obtained from the nitrogen adsorption–desorption isotherms.

3.2. XRD

XRD patterns indicated amorphous materials which, according to the nitrogen adsorption–desorption isotherms, corresponded to mesoporous solids.

3.3. NH_3-FT-IR

Slight differences of the S–O bond population could also be appreciated from the FT-IR analysis. However, NH_3-FT-IR spectra indicated the presence of Lewis acid sites as inferred from a band at $1630\,cm^{-1}$, but also of Brønsted acid sites (bands located in the range $1460–1490\,cm^{-1}$, Fig. 2). These latter bands may indicate a partial hydrolysis of the S–O bond, leading to chemisorbed triflate.

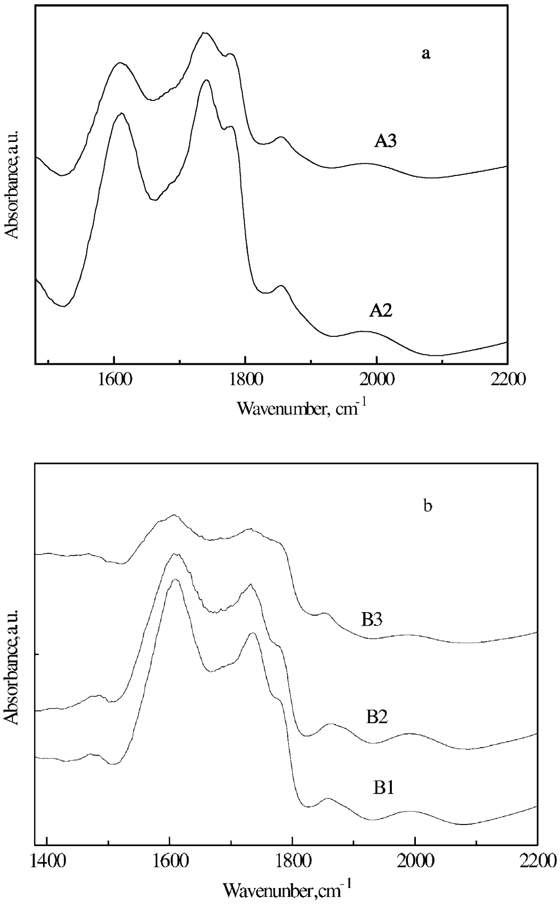


Fig. 2. NH_3-FT-IR spectra of the investigated catalysts after evacuation at 100 °C: (a) catalysts A; (b) catalysts B.

3.4. XPS

The binding energies of the F_{1s} (688.9 eV), S_{2p} (168.7 eV), Si_{2p} (103.4 eV), $La_{3d}/2$ (835.5 and 839.3 eV), and O_{1s} (532.6 eV) components were located at the same positions for all the investigated catalysts. XPS measurements showed that the triflate derivatives were not affected by sol–gel silica embedding. The XPS S:F atomic ratios were very close to 1:3, confirming the integrity of the triflate derivatives. XPS also gave information on the dispersion. The S:Si ratios were very close to the analytical ones, namely those corresponding to 15 wt.% triflate, indicating a good dispersion of the derivative in the silica matrix.

3.5. Catalytic data

The experiments performed without any catalyst showed no conversion of the methyl ester of the 1-cyclopentenylacetic acid (Table 1).

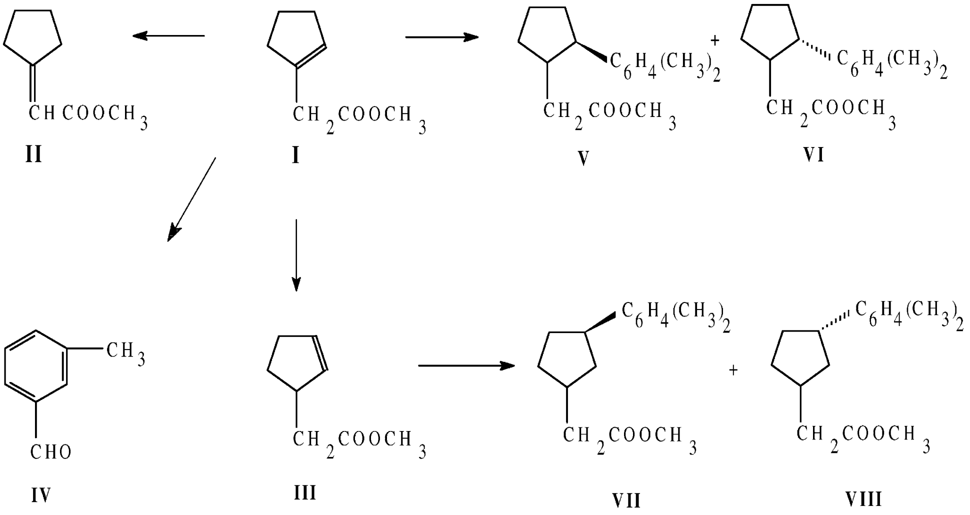
Table 1
Conversion of the methyl ester of 1-cyclopentenylacetic acid in the presence of free-precursor triflates, corresponding to 23 mmol triflic acid

Solvent	Temperature (°C)	Time (h)	Conversion of **I** (%)	Yield of 3-methyl-benzaldehyde (%)	Yield to **II** (%)	Yield of alkylated compounds (%)
BDMST	60	4	92.7	0	0	92.7
LaT	60	4	25.6	0	19.8	4.8
No catalyst	60	4	0	0	0	0

The catalytic tests carried out in homogeneous conditions (*p*-xylene as solvent) using pure BDMST or LaT led to the results presented in Table 1. For BDMST, these data correspond to a strong Lewis acid catalyst. Under the investigated conditions, almost all the ester was transformed in alkylated-like compounds using the solvent as alkylating agent. Similar results were obtained in benzene and toluene. Additional experiments using $AlCl_3$ as catalyst instead of embedded silyl triflate showed nearly the same results, confirming the very strong Lewis acid properties of BDMST. The reaction products in this case were the 2-cyclopentenylacetic ester (0.5% for $AlCl_3$ and 9% for triflate, **III**), *trans*-xylyl-2-cyclopentenylacetic (15.2% for $AlCl_3$ and 16.3% for triflate, **V**) and *cis*-xylyl-2-cyclopentenylacetic ester (0.5% for $AlCl_3$ and 9.0% for triflate, **VI**), and *cis*-xylyl-3-cyclopentenylacetic ester (63.8% for $AlCl_3$ and 68.4%for triflate, **VIII**, Scheme 1).

On LaT, the conversion to the ester was far from total and, the main reaction route corresponded to the exo-isomerization of the double bond. This behavior also suggests Lewis acid character but much weaker than those exhibited by BDMST.

The embedding of these Lewis acid molecules in the silica matrix led to a completely different reaction pathway. Figs. 3 and 4 indicate this behavior. On these catalysts, the main reaction product was 3-methylbenzaldehyde. The reaction of the methyl ester of the 1-cyclopentenylacetic acid was found to be dependent on the solvent nature. 3-Methylbenzaldehyde (**IV**) was obtained only in cyclohexene, *ortho*- and *para*-xylene (Figs. 3 and 4) while in the other solvents, the main reaction product was isomerization to exo-isomer **II** (see Scheme 1). The best yields of 3-methylbenzaldehyde were obtained in *para*-xylene. No alkylation product was identified for these catalysts in the presence of the indicated solvents.



Scheme 1. The reaction pathway in the reaction of the methylic ester of 1-cyclopentenylacetic acid.

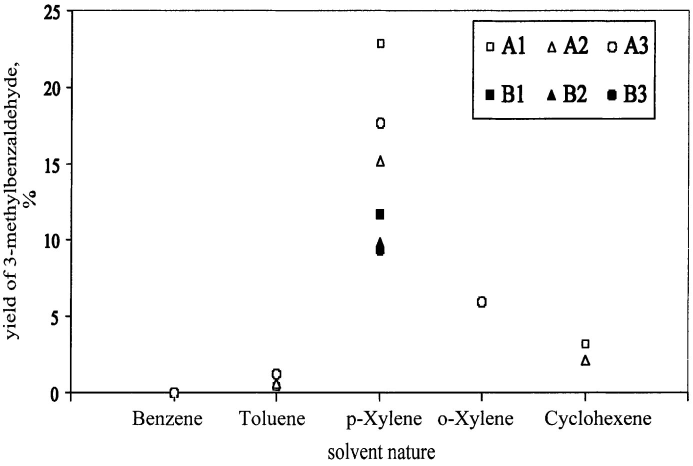


Fig. 3. Yield of 3-methylbenzaldehyde in the investigated solvents (40 mg catalysts; 60 °C; 30 mg ester; ester:solvent molar ratio of 1:60; 4 h; 900 rpm).

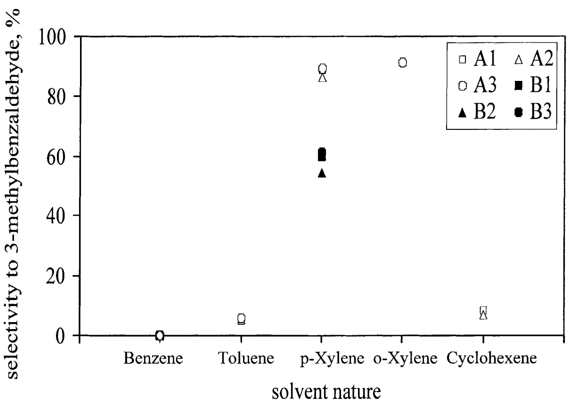


Fig. 4. Selectivity to 3-methylbenzaldehyde in the investigated solvents (40 mg catalysts; 60 °C; 30 mg ester; ester:solvent molar ratio of 1:60; 4 h; 900 rpm).

The analysis of the reaction products showed that the hydrogenated part of the solvent stoichiometrically corresponded to the amount released by cyclopentenyl derivative to pass to aromatic ring.

In order to better understand the catalyst contribution, separate tests were carried out using the catalysts without surfactant, and mixtures of surfactant and catalysts without surfactant. Table 2 compiles these data. The catalysts A without surfactant gave no conversion to 3-methylbenzaldehyde. The addition of the surfactant led to very small amounts of 3-methylbenzaldehyde but only for the catalysts A. The catalysts B gave no reaction even in the presence of surfactant.

Table 3 presents the conversion of the methyl ester of 1-cyclopentenylacetic acid in the presence of triflic acid under homogeneous conditions. The unusual formation of 3-methylbenzaldehyde in the presence of

Table 2
Conversion and selectivity to 3-methylbenzaldehyde

Catalyst	Solvent	Temperature (°C)	Time (h)	Conversion of **I** (%)	Yield of 3-methylbenzaldehyde (%)	Selectivity (%)
A3 without surfactant	*p*-Xylene	60	4	0	0	0
A3 without surfactant + surfactant	*p*-Xylene	60	4	2.5	0.5	20.0
B3 without surfactant	*p*-Xylene	60	4	0	0	0
B3 without surfactant + surfactant	*p*-Xylene	60	4	0	0	0

Table 3
Conversion of the methyl ester of 1-cyclopentenylacetic acid in the presence of 23 mmol triflic acid

Solvent	Temperature (°C)	Time (h)	Conversion of **I** (%)	Yield to 3-methylbenzaldehyde (%)	Yield of **II** (%)	Yield of alkylated compounds (%)
Benzene	60	4	49.6	0.3	45.7	3.3
p-Xylene	60	4	21.6	0.8	15.8	4.8
Cyclohexene	60	4	39.3	1.6	27.6	9.9

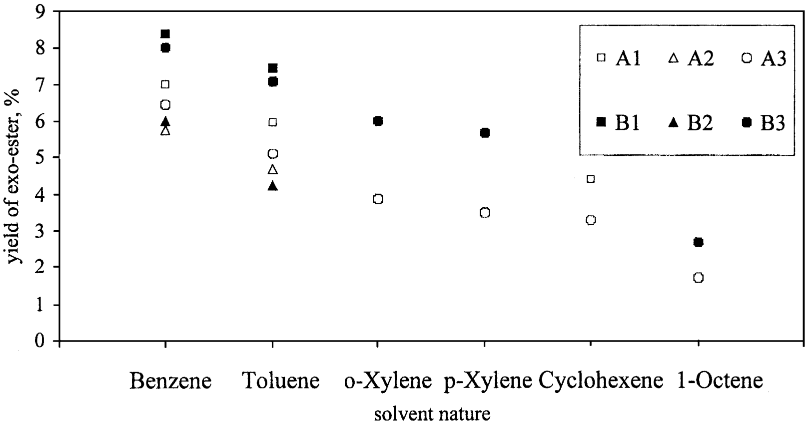


Fig. 5. Yield of exo-ester **II** in various solvents (40 mg catalysts; 60 °C; 30 mg ester; ester:solvent molar ratio of 1:60; 4 h; 900 rpm).

embedded triflate is thought to be the consequence of a partial hydrolysis of BDMST or LaT to triflic acid. These data show that the behavior of free triflic acid is more complex. It catalyses indeed the transformation of the methyl ester of 1-cyclopentenylacetic acid to 3-methylbenzaldehyde, but this occurs to a smaller extent than over the embedded catalysts. The main product was the exo-isomer (**II**) but alkylated compounds also formed in well detectable percentages. All the catalysts gave exo-isomerization of the double bond to **II** (Fig. 5).

4. Discussion

The immobilization of BDMST and LaT in a silica matrix using the sol–gel technique led to mesoporous materials with a monomodal pore size distribution. The characterization of these materials indicated that the triflate remained essentially unaffected during this process. XPS analysis showed a good dispersion of triflate as inferred from the comparison of the chemical and XPS S:Si ratios and, a good integrity, as shown from the analysis of the XPS S: F ratios. However, the FT-IR analysis suggested that in the case of BDMST, a small part of triflate was hydrolyzed, probably leading to a very small fraction of impregnated triflates. No similar evidence was found for LaT. The FT-IR analysis also indicated the existence of both Lewis and Brønsted acid sites. The surfactant also remained embedded in the silica matrix, more probably incorporated in the solid mesopores than in the silica network.

The catalytic tests carried out over these catalysts in the conversion of the methyl ester of 1-cyclopentenylacetic acid in various solvents led to a very surprising product, namely 3-methylbenzaldehyde. We merely expected as reaction product an alkylated one, as it typically results from this reaction in the presence of anhydrous $AlCl_3$ catalyst [14]. The results indicate that this reaction is sensitive to the solvent nature and is conditioned by the presence of the surfactant in the solid matrix. Based on the chemical analysis of the products, we suggest that the reaction occurred via a route in which the first step consists of a ring enlargement, typical of acid-catalyzed reaction. The second step involves a hydrogen transfer from the cyclohexane-enlarged cycle to the solvent, resulting in an intermediate which finally undergoes an oxygen elimination and a rearrangement to 3-methylbenzaldehyde. It is worth to note that in the absence of an adequate solvent, the reaction does not take place. The presence of the hydrogen acceptor molecule is therefore a key factor. Based on these data, one can say that the hydrogen accepting ability in this reaction varies in the order: p-xylene $>$ o-xylene $>$ cyclohexene $\gg$ toluene, benzene for both types of embedded triflate. The chromatographic analyses indicated in all the cases a stoichiometric reduction of the solvent.

The oxygen elimination is another key factor. The reduction of simple aryl triflates by trialkylammonium formate in the presence of Pd(0) as catalyst has already been reported [15,16]. Very recently, Kamochi and Kudo [17] reported another example in which triflate compounds were found to be effective reduction catalysts. These authors reported the reduction of carboxylic acids to the corresponding alcohols using samarium triflate. In the present case, neither the noble metal nor the rare earth element is necessary. During the reaction, aryl triflate may be formed by interaction with the silyl derivative or the cleavage of Si–O–S bonds. The participation of the tetra-alkyl ammonium salt in this process can be expected because of its mobility. The reaction may also involve some rearrangements [18] since a compound with $M/z = 152$ was identified by MS analysis of the sub-products.

The heterogeneous behavior of the catalysts was confirmed both by the profound dependence of activity on solvent and the analysis of the supernatant resulting after the catalyst separation and another 4 h reaction. Absence of further reaction is an evidence that this reaction is not influenced by the triflate leaching. In addition, the silyl triflate derivative being insoluble in the solvent used, the supernatant was always a clear solution. It should also be mentioned that catalytic tests done with emulsions of silyl triflate derivative showed that only the Friedel–Crafts alkylation occurred. Although small amounts of 3-methylbenzaldehyde were also observed using free triflic acid, the catalytic data show that it is not responsible for the results obtained with the embedded catalysts, but the silyl triflate derivative or lanthanum triflate in the silica matrix having the ammonium quaternary salt in close proximity. We speculate that the behavior of the hybrid catalysts is different from homogeneous ones, although various species exist as well as dispersed species as the characterization data showed, because of the formation of supermolecular ensembles. The formation of supermolecular ensembles does not induce changes of spectroscopic results, but it may modify the catalytic behavior, as observed using these catalysts. Such a supposition is sustained by the behavior of the catalysts without surfactants (see Table 2). The addition of the surfactant in the reaction medium led to small (catalysts A) or even no conversion (catalysts B), indicating that the formation of these ensembles requires a given environment.

Additional evidences about the behavior of this catalyst and the contribution of the surfactant to this reaction resulted from the catalytic tests carried out using catalysts without surfactant and mixtures of the catalyst without surfactant and surfactant solved in homogeneous solvent. On the catalysts without surfactant, no 3-methylbenzaldehyde was obtained. The only reaction product was exo-isomerization of the double bond in an extent less than 15%. The results also showed a contribution of the catalyst. Under the investigated conditions, the reactivity of catalysts A was superior to that of catalysts B.

5. Conclusions

The immobilization of *tert*-butyldimethylsilyltrifluoro-methanesulfonate or lanthanum triflate in a silica matrix containing hexadecyltrimethylammonium bromide as surfactant led to new hybrid catalysts. The characterization of these catalysts by nitrogen adsorption–desorption isotherms at 77 K, TG-DTA, ^{1}H, ^{13}C, and ^{29}Si solid state MAS-NMR, XRD, XPS, TEM and SEM, and FT-IR after adsorption of NH_3 revealed the formation of heterogeneous catalysts in which triflates existed as well dispersed species. The novelty of these catalysts was sustained by the catalytic tests carried out in the reaction of the methyl ester of 1-cyclopentenylacetic acid in various solvents. These tests showed a completely different behavior of the hybrid catalysts compared with catalysts without surfactant or with free *tert*-butyldimethylsilyltrifluoro-methanesulfonate, or lanthanum triflate, or triflic acid leading to 3-methylbenzaldehyde.

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