

Acylation of 2-methoxynaphthalene with acetic anhydride over silica-embedded triflate catalysts

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Abstract

Silica sol–gel immobilized triflate compounds like $\text{La}(\text{OTf})_3$, *tert*-butyldimethylsilyl trifluoromethanesulfonate (BDMST) and triflic acid (HOTf) were tested in the acylation of 2-methoxynaphthalene with acetic anhydride, leading to 1-acetyl-2-methoxynaphthalene as the major product. The reaction only proceeded with good yields on BDMST and HOTf catalysts, while $\text{La}(\text{OTf})_3$ presented a low activity. For BDMST in solvent-free conditions, the resulting TOF was superior to that reported in literature for other heterogeneous catalysts and even for homogeneous triflates. The rates of reactions in various solvents strongly depend on the donor number of these solvents.

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1. Introduction

Aromatic ketones are very important intermediates in fine chemical synthesis of fragrances and pharmaceuticals [1]. Their synthesis usually involves an aromatic acylation step. The conventional synthetic procedure is the homogeneous Friedel–Crafts acylation with carboxylic acid derivatives using Lewis acid anhydrous metal halides like AlCl_3 , TiCl_4 , SnCl_4 , etc. In contrast to Friedel–Crafts alkylations the acylations require a more than stoichiometric amount of the Lewis acid, as the aromatic ketone products coordinate to the Lewis centers. Moreover, these metal chlorides are not reusable and they generate corrosive acid waste [2]. Switching to solid acid catalysts instead of environmentally hazardous compounds

may bring about many advantages such as elimination of corrosion, recyclable catalysts and higher selectivity.

The reaction studied in this paper is the liquid phase acylation of 2-methoxynaphthalene (2-MN). This reaction may lead to 2-acetyl-6-methoxynaphthalene (6-AMN), which is an intermediate in the synthesis of the anti-inflammatory compound Naproxen [3]; on the other hand, the 1-acetyl-2-methoxynaphthalene (1-AMN) product can be an interesting intermediate as well, e.g. in phenylation reactions [4]. As solid catalysts for this reaction acid clays [5], Al-MCM-41 [6], heteropolyacids [7], arenesulfonic acid/SBA-15 [8] and zeolites [9–15] have been employed. In previous studies with these solid catalysts, several drawbacks have been encountered, such as low catalyst stability, high reaction temperatures and the use of environmentally unfriendly solvents such as chlorinated solvents. Moreover, in these reactions, zeolites are subject to coke formation [16,17].

Therefore, new solid strong acid catalysts for acylations are of current interest. Metal triflates and other triflate compounds possess strong Lewis acidity and, in contrast to metal halides, they exhibit a high tolerance towards water. Several papers already reported on the use of triflates and their derivatives in

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homogeneous acylation reactions. Trifluoromethanesulfonic acid was found to be active in acylation of aromatics with β -lactams [18] while rare-earth metal triflates showed good results using acetic anhydride as acylating agent [19].

Here, we report on the methoxynaphthalene acetylation using various triflate catalysts immobilized in a silica matrix via a sol–gel procedure, viz. La(OTf)₃, *tert*-butyldimethylsilyl trifluoromethanesulfonate (BDMST), and triflic acid (HOTf).

2. Experimental

2.1. Catalyst preparation

Silica-immobilized La(OTf)₃, BDMST and HOTf were prepared according to previously described procedures [20–22]. The catalyst series denoted with 1 (i.e. La-1, and BDMST-1, see Table 1) corresponded to catalysts prepared by incorporation of the above triflates in the silica after the formation of the sol, while that denoted with 2 (i.e. La-2, and BDMST-2, see Table 1) to catalysts in which (CH₃)₃C₁₆H₃₃NBr was added to the suspension prior to the triflate. Immobilization of HOTf was performed via adsorption on a silica with covalently attached-(CH₂)₃-NH₂ groups [22]. As for La- and BDMST-catalysts, series (1) corresponded to a catalyst prepared without template, and (2) to a catalyst in which silica was prepared in the presence of (CH₃)₃C₁₆H₃₃NBr. Sol–gel prepared triflates contained 15 wt.% active species, while those resulting from HOTf adsorption contain 22 wt.% of HOTf.

2.2. Reaction procedures

The catalytic experiments were carried out in a range of temperatures between 25 and 120 °C. At low temperatures the reactions were carried out in a 10 ml glass reactor heated on an oil bath under vigorous stirring. For experiments at high temperature a 10 ml stainless steel autoclave was used, equipped with a thermometer, a manometer and a magnetic stirrer. The reactions were carried out both in the presence and absence of solvents. Typical reactions used 5 mmol 2-methoxynaphthalene (2-MN), 30 mg catalyst, and/or 1 ml solvent. Only solvent free conditions or non-hazardous solvents like 1,4-dioxane, ethanol, isopropanol or THF were employed. Acetic anhydride (AA) was used as acylating agent.

At the end of the reaction, the catalyst was separated by simple filtration and the products were analyzed by GC (HP GC 5890-II, with a 50 m WCOT Fused Silica CP-Wax 58 (FFAP)

CB column). GC conditions were as follows: heating at 10 °C min⁻¹ till 190 °C, with a 2 min isothermal plateau at 100 °C, and a 50 min plateau at 190 °C. Products were identified by electron impact ionization GC–MS (Hewlett-Packard MS-5988) and by ¹H and ¹³C NMR with a Varian Gemini 300BB instrument, operating at 400 MHz for ¹H and 100 MHz for ¹³C. The selectivity was calculated as the molar ratio of the product of interest versus all products formed. TOF was calculated as the number of moles of product formed per mole of triflate and time.

NMR data obtained for 1-acetyl-2-methoxynaphthalene (1-AMN): ¹H NMR (CDCl₃, 400 MHz): δ 2.65 (s, 3H), 3.99 (s, 3H), 7.29 (d, J = 9.1 Hz, 1H), 7.35 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.49 (ddd, J = 8.1, 6.9, 1.5 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 9.1 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 32.5, 56.3, 112.7, 123.4, 124.0, 125.2, 127.9, 128.1, 128.9, 130.5, 131.4, 153.8, 204.9.

To check for leaching, the reaction products were chemically analyzed by ICP-AES, looking for F and S in case of the BDMST- and HOTf-catalysts, and for La in La-catalysts.

2.3. Characterization of catalysts

The FTIR spectra were collected on a Biorad FT-IR FTS 135 spectrometer. The measurements were performed before and after exposing the sample to the adsorbate of interest. Before the measurements the tested catalysts were separated by centrifugation, washed with toluene to eliminate the weakly chemisorbed species, and dried under vacuum at 110 °C. The acidity of the catalysts was determined by microcalorimetry of ammonia adsorption. Microcalorimetric studies were performed in a heat flow calorimeter (C80 from Setaram) linked to a conventional volumetric apparatus and equipped with a Barocel capacitance manometer for pressure measurements. Ammonia used for the measurements (Air liquide, >99.9%) was purified by successive freeze–pump–thaw cycles.

3. Results and discussion

As mentioned above the catalysts were prepared by sol–gel incorporation of La(OTf)₃ and BDMST in a silica matrix using a described procedure [20–22]. In principle, this corresponds to a sol–gel procedure in which the triflate derivative is introduced after the sol formation. Immobilization of HOTf was performed via adsorption on a silica with covalently attached-(CH₂)₃-NH₂ groups; the interaction between a weak base (\equiv Si-(CH₂)₃-NH₂) and a superacid (HOTf; H_0 = -14.1) results in residual Brønsted acidity [22]. Textural characteristics of these catalysts are given in Table 1. Previous spectroscopic and calorimetric studies on immobilized La(OTf)₃ and BDMST have indicated that these samples behave like strong Lewis acids catalysts, at least if the sol–gel procedure is performed without any surfactant [21,22]. The Lewis acid centers are the La³⁺ ion, for La-1, and the Si atom in the entrapped organo Si compound, for BDMST-1.

Table 2 compiles the conversion and product distribution data over the immobilized triflate catalysts under the various

Table 1
Surface area and pore diameter of the investigated catalysts (characterized by N₂ adsorption–desorption measurements at 77 K)

Catalyst	Surface area (m ² /g)	Pore diameter (nm)
BDMST-1	572	1.8
La-1	468	1.8
HOTf-1	325	2.1
BDMST-2	483	2.8
La-2	357	2.8
HOTf-2	307	2.6

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