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A mild and efficient method for the chemoselective trimethylsilylation of alcohols and phenols and deprotection of silyl ethers using sulfonic acid-functionalized ordered nanoporous Na^+-montmorillonite

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ABSTRACT

Sulfonic acid-functionalized ordered nanoporous Na^+-montmorillonite (SANM), is easily prepared by the reaction of Na^+-montmorillonite with chlorosulfonic acid. This reagent acts as a highly efficient and reusable catalyst for the chemoselective trimethylsilylation of alcohols and phenols and deprotection of silyl ethers under mild and completely heterogeneous reaction conditions.

1. Introduction

Protection of the hydroxyl group of alcohols and phenols during a multi-step synthesis is an important process, which is under considerable attention of organic chemists (Fieser and Fieser, 1999). The conversion of hydroxyl groups to their corresponding trimethylsilyl ethers is one of the popular methods used for this purpose. Among the different reagents which are available for the silylation of alcohols (Nishiguchi et al., 2000; Verboom et al., 1981), hexamethyldisilazane, as a cheap and commercially available reagent, (Cossy and Pale, 1987; Torkelson and Ainsworth, 1976), is selected as one of the best candidates. Even though the handling of this reagent does not need special precautions and work-up of the reaction mixture is not time consuming, the low silylating power of HMDS is the main drawback for its application (Bruynes and Jurrients, 1982). A variety of catalysts have been reported for the activation of HMDS (Curini et al., 1999; Firouzabadi et al., 2008; Firouzabadi et al., 2009; Ghorbani-Vaghei et al., 2006; Khazaei et al., 2007a,b; Narsaiah, 2007; Rajagopal et al., 2009; Shirini and Mollarazi, 2007; Shirini et al., 2005; Shirini et al., 2006; Shirini et al., 2008; Tillu et al., 2004; Zareyee and Karimi, 2007; Zhang et al., 1998). Although these methods provide an improvement, in most cases long reaction times, low selectivity, forceful conditions or tedious work-up are needed. In addition, some of the reagents are expensive and toxic or have to be prepared in a time consuming procedure, and most of them are not able to catalyze the reverse reaction.

Today, science and technology have paid attention toward environmental cost of heterogeneous solid acid catalysts for the synthesis of chemicals (Corma, 1995; Olah et al., 1986). This attention can be attributed to the simpler and easier procedures which are accompanied by the use of these types of reagents. In recent years, clays as nanostructured materials have been widely used in organic transformations as solid acid catalysts (Bergaya and Lagaly, 2001; Laszlo, 1987; Vaccari, 1998). The main reason is the large variety of clays and the ease with which these materials can be modified; also clays are cheap, noncorrosive and recyclable. Montmorillonite (MMT) is one of the most widely used clays. The montmorillonite minerals have very small micron sized particles and they are extremely fine-grained and thin-layered. The structure of montmorillonite has been well defined. The building blocks of montmorillonite layers contain silicon-oxygen tetrahedra ($Si_2O_5^{-2}$) and aluminum octahedra $[Al(OH_6)]^{-3}$. The repeat unit contains two tetrahedral and one octahedral layer. The MMT layers have permanent negative charges because of the isomorphous substitution of, for instance, Mg^{2+} for Al^{3+} or, rarely, Al^{3+} for Si^{4+}. These net negative charges are balanced by exchangeable cations such as sodium and potassium between the clay layers in the gallery spaces (Giannelis et al., 1999).The layers of MMT have thickness about 1 nm and length of 100 nm or a little more. Broken bonds on the edge are common phenomena for layered silicates and lead to the formation of hydroxyl groups (Shi et al., 1996; Yariv and Cross, 2002), which can be utilized for the chemical modifications. For the first time, in 1941, Berger found that the hydroxyl groups of montmorillonite can be methylated

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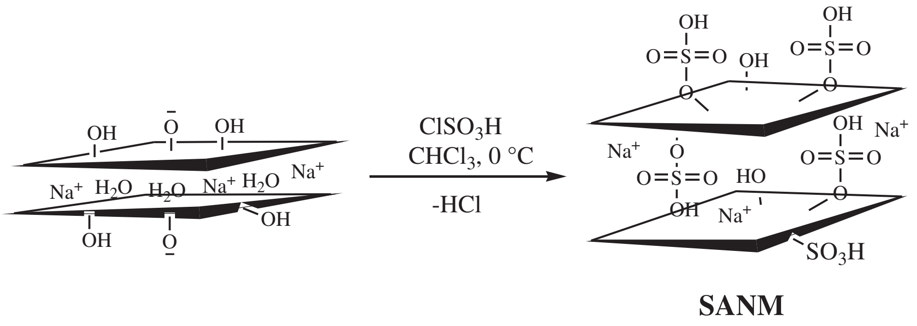

Fig. 1. Preparation of SANM.

with diazomethane (Berger, 1941). Then many scientists used this property for different modifications on the surface of montmorillonite (Deuel et al., 1950; Gieseking, 1949).

Taking cuse from these studies, we were interested to investigate the conversion of the hydroxyl groups of Na^+-montmorillonite to -OSO_3H functionalities. Our investigations clarified that Na^+-montmorillonite reacts with chlorosulfonic acid to yield sulfonic acid-functionalized ordered nanoporous Na^+-montmorillonite (SANM, I) during an easy and clean reaction. The method needs no special work-up procedures, because HCl gas is evolved from the reaction vessel immediately (Fig. 1).

On the basis of the structure of SANM, we hoped that this reagent would be a superior proton source to all of the reported acidic solid supports or acidic resins such as polystyrene sulfonic acid and Nafion-H (Olah et al., 1987) for running reactions under heterogeneous conditions. Therefore, we were interested in using SANM for promoting trimethylsilylation of alcohols and phenols with HMDS (Fig. 2).

2. Experimental

2.1. Materials

Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies. All yields refer to the isolated products. Products were characterized by their physical constants, comparison with authentic samples. The purity determination of the substrate and reaction monitoring were accompanied by TLC on silica-gel polygram SILG/UV 254 plates.

2.2. Instrumentation

Thermogravimetric analyses (TGA) were conducted by using a TGA PYRIS 1 thermoanalyzer instrument. Samples were heated 25 to 600 °C at ramp 10 °C/min under N_2 atm. Wide-angle X-ray diffraction (XRD) measurements were performed at room temperature on a Siemens D-500 X-ray diffractometer (Germany), using Ni-filtered Co-Kα radiation (λ = 0.15418 nm). The IR spectra were recorded by Shimadzu Corporation 200-91-527 instrument. The pristine clay and its sulfonated derivative were dried at 100 °C in the oven before recording the spectrum.

2.3. Catalyst preparation

A 500 mL suction flask charged with 2.5 g Na^+-montmorillonite (Southern Clay Products) and 10 mL $CHCl_3$, was equipped with a constant pressure dropping funnel containing chlorosulfonic acid (0.50 g, 9 mmol) and a gas inlet tube for conducting HCl gas over an adsorbing solution i.e. water. Chlorosulfonic acid was added dropwise over a period of 30 min while the reaction mixture was stirred slowly in an ice bath (0 °C). After addition was completed, the mixture was stirred for additional 30 min to remove all HCl. Then, the mixture was filtered and the solid residue washed with methanol (20 mL) and dried at room temperature to obtain SANM as white powder (2.58 g). The number of H^+ sites of Na^+-MMT-SO_3H was determined by pH analysis (0.88 mmol. g^{-1}) (Zareyee and Karimi, 2007).

$$ROH \underset{\text{SANM (20 mg), MeOH, r. t.}}{\overset{\text{HMDS (0.75 mmol), SANM (20 mg), CH3CN, r. t.}}{\rightleftharpoons}} ROSiMe_3$$

Fig. 2. Trimethylsilylation of alcohols and phenols catalyzed by SANM.

2.4. Catalyst characterizations

2.4.1. Thermal analysis

Thermogravimetric analysis (TGA) was performed for characterization of SANM in comparison with sodium montmorillonite. Fig. 3 provides the TGA curve of pristine clay (Na^+-MMT) and catalyst. The TGA curve of Na^+-MMT display a weight loss below 100 °C which is corresponding to the loss of the physically adsorbed water, also there is a slight weight loss (ca. 8 wt.%) in the range of 100–600 °C, possibly corresponding to the loss of the bonded H_2O within the gallery.

For SANM there is a small mass loss (ca. 1 wt.%) in the range of 25–240 °C, attributed to the loss of the bonded H_2O within the gallery similar to Na^+-MMT. However a greater mass loss that started from 240 °C happened, which can be attributed to the decomposition of –SO_3H group anchored to the clay surface. These show that Na^+-MMT-SO_3H has a greater thermal stability (until 240 °C) than Na^+-MMT.

2.4.2. Powder X-ray diffraction

In the reaction between sodium montmorillonite and chlorosulfonic acid, the expansion of the montmorillonite layers was demonstrated by X-ray diffraction. The XRD patterns of the montmorillonite before and after sulfonation are shown in Fig. 4. The basal spacing for the Na^+-

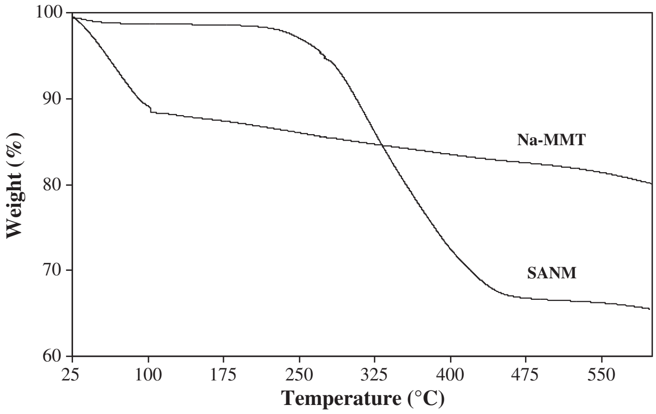

Fig. 3. TGA curves of Na + − MMT and SANM.