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Simultaneous application of ultrasonic irradiation and immobilized ionic liquid onto the SBA-15 nanoreactor (US/[MPIm]Cl@SBA-15): A robust, recyclable, and useful combined catalytic system for selective and waste-free Kabachnik Fields reaction

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ABSTRACT

Simultaneous application of the ultrasonic irradiation (US) and immobilized ionic liquid (IL@SBA-15) is used as an alternative to conventional catalysts in the Kabachnik–Fields reaction of an amine, aldehyde with phosphite leading to the formation of (α-aminoalkyl)phosphonate. The reaction time is reduced drastically and the reaction is progressed in an environmentally friendly way. The yields are around 93–96%.

1. Introduction

The application of ionic liquids (ILs) as catalyst for a wide variety of organic synthetic processes is an area of intense research in organic synthesis [1]. The design and development of new and novel ILs that are air and moisture stable have provided renewed vigor in ionic liquid chemistry, and the emerging use of these ILs will be considered first. Immobilization of the ILs provides vaporless, thermally stable, and 'green' auxiliary substances for chemical reactions [1,2]. Immobilization of the ILs into the mesoporous nanomaterials such as SBA-15 has gained increasing attention in replacement of the conventional mineral amorphous materials because of their high surface area, low densities, and high thermal and mechanical stability during reaction processes [3]. On the other hand, the employment of the ultrasound has been demonstrated for its potential applications in the fields of organic synthesis, green chemistry, and industry. Compared with traditional methods, this method is more convenient and easily controlled [4].

Base on importance of (α-aminoalkyl)phosphonate, synthesis of these units is excellent in using them as inhibitors and a wide range of antibacterial [5] or antifungal [6]. Several synthetic methods of α-aminophosphonate were reported in literature [7,8]. However, using immobilized ILs in ultrasonicated condition (US) is very helpful to a clean environment. As part of our ongoing program [9–13], we report herein our results for the application of the US/IL@SBA-15 catalytic system (Fig. 1) as rapid catalyst for the three-component chemoselective condensation of an amine, aldehyde and phosphite with excellent yields of α-aminophosphonates.

2. Experimental

2.1. Chemical and statues

All reagents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus. ^{1}H NMR spectra were measured on a Bruker AV-300 instrument (300 MHz) with $CDCl_3$ as solvent. A multi-wave ultrasonic generator (Sonicator_3000; Misonix Inc., Farmingdale, NY, USA), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating as continues irradiation with a maximum power output of 600 W, was used for the ultrasonic irradiation.

2.2. Synthesis of SBA-15 and IL-immobilized SBA-15

The synthesis of methyl propylimidazolium chloride immobilized to SBA-15 [MPIm]Cl@SBA-15 has been achieved using three main steps: the first step is for the preparation of the SBA-15 based on our previous

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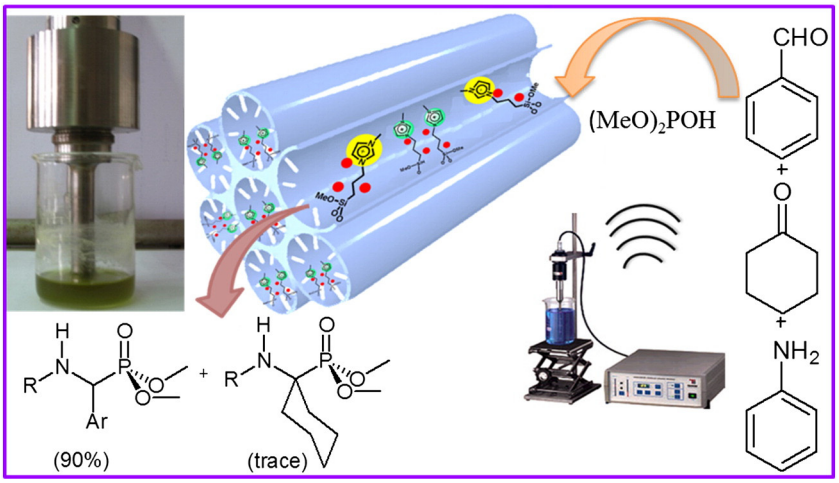

Fig. 1. The US/IL@SBA-15 system for Kabachnik–Fields reaction.

reports [12,13]. The second step is the preparation of the 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium chloride [TMSPIm]Cl and the third is immobilization of the [TMSPIm]Cl onto the SBA-15 (Fig. 2).

As shown in Fig. 2, the [MPIm]Cl@SBA-15 was synthesized as a IL immobilized nanoreactor. To accomplish this, 3-chloropropyltrimethoxysilane (CPTS, 1 mmol) was reacted with 1-methylimidazole (1.2 mmol) at 88 °C for 30 h in dry toluene. The resulting [TMSPIm]Cl was obtained as a brown-colored paste. After that, the [TMSPIm]Cl was reacted with the calcined SBA-15 (1 g) under reflux condition for 24 h. Finally, the solid product was filtered, and then dried under vacuum.

In the FT-IR spectrum, the band from 807 to ~1100 cm^{-1} belongs to the vibrations of (Si – O – Si) bond, and the small band at about ~980 cm^{-1} is assigned to functionalized (Si – OH) bond and the SiO-H groups are shown by the very broad IR absorption band in the 3000–3700 cm^{-1} region (Fig. 3a). The TEM and SEM images as channels and morphological view of the hybrid mesoporous material of the IL@SBA-15 are presented in Fig. 3c and d.

Thermal gravimetric analysis and differential thermal analysis (TGA/DTG) of the [MPIm]Cl@SBA-15 nanoreactor show a weight loss due to the desorption of water below 100 °C. This is finally followed by a set of weight losses centered at 400 °C corresponding

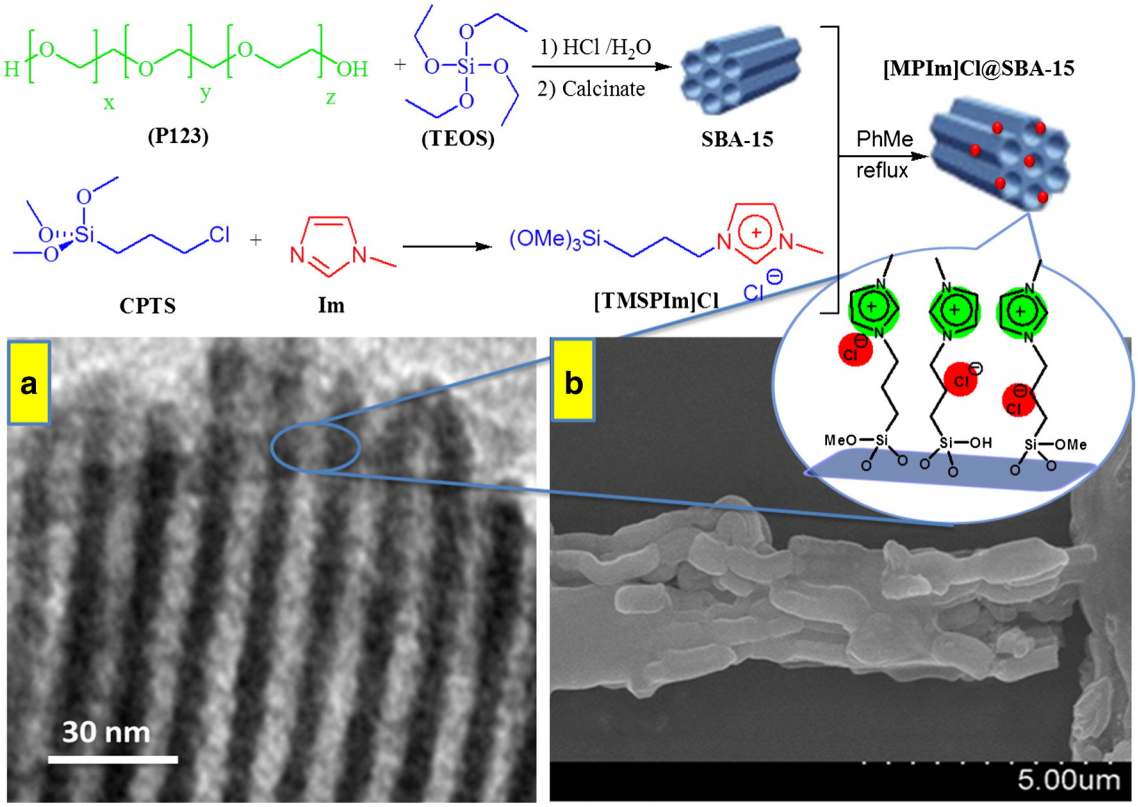

Fig. 2. Schematic representation of the synthetic procedure for the [MPIm]Cl@SBA-15 and its TEM (a) and SEM (b) images.