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FTIR study on deactivation of sulfonyl chloride functionalized ionic materials as dual catalysts and media for Beckmann rearrangement of cyclohexanone oxime

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Abstract

Several novel sulfonyl chloride functionalized ionic materials were used as media and catalysts for Beckmann rearrangement of cyclohexanone oxime and satisfactory results were achieved under mild conditions. The effects of all parameters were discussed. Moreover, the deactivation of ionic liquid catalytic system during the recycle was investigated by using FTIR spectroscopy and mass balance calculation. The trapping of acidic ionic material with basic product is proved to be mainly responsible for the difficulties encountered in the reuse of this type of material. A possible mechanism was conjectured.

Keywords: Beckmann rearrangement; Cyclohexanone oxime; Caprolactam; Sulfonyl chloride functionalized ionic materials; IR investigation

1. Introduction

The rearrangement of a ketoxime to the corresponding amide is a powerful method in organic synthesis and is known as the Beckmann rearrangement [1]. This reaction, however, generally requires a large amount of a strong Brønsted acid such as sulfuric acid and forms ammonium sulfate as a byproduct [2]. So more and more attentions have been paid to improve this important process for a long time. In the vapor-phase process, a few examples of the Beckmann rearrangement catalyzed by solid acid such as modified molecular sieves were reported and good results were achieved [3–5]. The vapor-phase reaction, however, suffers from its intrinsic features such as the requirement of high temperature and rapid deactivation of catalyst due to the coke formation [6,7]. Without using other media and catalysts, Beckmann rearrangement were carried out in supercritical water with fast reaction time and excellent selectivity [8–10]. But it is too rigorous to fulfill in industrial application. Liquid-phase catalytic rearrangement in organic solvents, on the contrary, can partially overcome the above-mentioned problems, in which solvent plays an important role [11]. A relatively large amount of organic solvent, however, was generally needed [12–14], which would also cause environmental problems because of the volatility and toxicity. Some of them involved the use of noble metal compound and/or organic strong acid as catalysts [15,16].

Recently, ionic liquids have gained recognition as environmentally benign alternatives to more volatile organic solvents and functional materials in many fields because of their interesting properties such as wide liquid range, negligible vapor pressure, high thermal stability and good solvating ability for a wide range of substrates and catalysts [17–22]. Beckmann rearrangement was also found to be efficiently progressed with satisfactory conversions and selectivities using ionic liquids as reaction media in the presence of phosphorus compounds [23,24], but they produced irritant gas of HCl and needed longer reaction time. Subsequently Sun et al. [25] and Yokoyama et al. [26] reported that functionalized ionic

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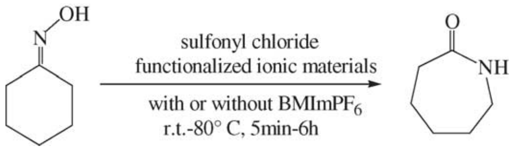

Scheme 1. Beckmann rearrangement of cyclohexanone oxime over SCFIMs.

liquid containing chlorosulfonyl group could promote this reaction. However, the efficiency of these catalytic systems is still far from satisfactory, particularly for the reuse of ionic liquids. Additionally the reason of deactivation and the reaction mechanism have not yet been discussed in detail.

As an extension of our recent investigation on the clean Beckmann rearrangement of cyclohexanone oxime (CHO) in room temperature ionic liquids, we report herein the catalytic Beckmann rearrangement of CHO over sulfonyl chloride functionalized ionic materials (SCFIMs) under mild conditions and satisfactory conversions and excellent selectivities were obtained. (Scheme 1). Mass balance calculation and IR spectroscopy were then used to investigate the cause of deactivation of SCFIMs during the process. Furthermore, a possible mechanism of Beckmann rearrangement of CHO over SCFIMs was also conjectured.

2. Experimental

All solvents and chemicals used were commercially available and used without further purification unless otherwise stated. Cyclohexanone oxime, trifluoromethanesulfonic acid (99% of purity with water content <0.1%), 1,4-butane sultone (99% of purity) were purchased from Fluka chemical corporation; benzene was dried for 3 days over 5 Å molecular sieve prior to use; others were all purchased from Beijing Chemical Reagent Corporation Ltd.

2.1. Instrumental analysis and measurements

The C and H elemental analysis were performed on a Yanaco CHN FOER MT-3 element analyzer. IR spectra were recorded on a Nicolet NEXUS 670 FTIR spectrometer using liquid film or KBr tablet. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were obtained as solutions in deuterium-substituted reagent. Chemical shifts were reported in parts per million (ppm, δ).

2.2. Synthesis and characterization of SCFIMs

The SCFIMs were prepared by three-step reactions through 1-methylimidazole, pyridine and triphenylphosphine quaternized first with 1,4-butane sultone to form zwitterions, as described in previous literatures [27,28], which then reacted with an acid to yield acidic ionic compounds. The resulting products readily underwent reaction with thionyl chloride to form the target ionic materials (Scheme 2). Here we take the synthesis of 1-(4-chlorosulfonylbutyl)-3-methylimidazolium trifluoromethanesulfonate (**1a**) as an example and describe as follows.

1-(Butyl-4-sulfonate)-3-methylimidazolium zwitterion and 1-(4-sulfonyl butyl)-3- methylimidazolium trifluoromethanesulfonate were prepared according to the procedures we have described formerly [29,30]. Then thionyl chloride was added with an excess of 5 mol times and refluxed for 24 h. The unreacted thionyl chloride was removed by evaporation. The brown viscous liquid was formed with yield of 97% and in high purity. ^{1}H NMR (400 MHz, d$_6$-DMSO):δ9.21 (s, 1H), 7.79 (t, $J = 2.0$, 1H), 7.73 (t, $J = 1.8$, 1H), 4.21 (t, $J = 6.8$, 2H), 3.88 (t, $J = 7.0$, 3H), 2.68 (t, $J = 7.6$, 2H), 1.91 (quint, $J = 8.0$, 2H), 1.59 (q, $J = 7.6$, 2H). ^{13}C NMR (100 MHz, d$_6$-DMSO):δ136.81, 123.78, 122.47, 121.08 (q, $J_{\text{C–F}} = 320.0$, CF$_3$), 50.59, 48.63, 35.92, 28.61, 21.53. IR (cm^{-1}): 3156, 3116, 1369, 1165, 593. $C_9H_{14}F_3O_5N_2S_2Cl$ (386.58): calcd: C 27.96, H 3.62. Found: C 27.81, H 3.72.

The spectral data of other SCFIMs are listed herein.

2.2.1. 1-(4-Chlorosulfonylbutyl)-3-methylimidazolium trifluoroacetate (*1b*)

An orange liquid with yield of 95%. ^{1}H NMR (400 MHz, d$_6$-DMSO): δ9.43(s, 1H), 7.88(t, $J = 2.0$, 1H), 7.81(t, $J = 1.8$, 1H), 4.30(t, $J = 7.2$, 2H), 3.93(s, 3H), 3.69(t, $J = 6.4$, 2H), 1.97(quint, $J = 7.2$, 2H), 1.72(q, $J = 6.4$, 2H). ^{13}C NMR (100 MHz, d$_6$-DMSO): δ137.04, 123.98, 122.62, 50.79, 48.82, 36.19, 28.86, 27.37, 21.71.

2.2.2. 1-(4-Chlorosulfonylbutyl)-3-methylimidazolium p-toluenesulfonate (*1c*)

A dark brown viscous liquid with yield of 92%. ^{1}H NMR (400 MHz, d$_6$-DMSO): δ9.51(s, 1H), 7.89(t, $J = 1.6$, 1H), 7.79(t, $J = 1.6$, 1H), 4.24(t, $J = 6.8$, 2H), 3.84(s, 3H), 3.64(t, $J = 6.8$, 2H), 1.87(quint, $J = 7.2$, 2H), 1.65(q, $J = 6.8$, 2H). ^{13}C NMR(100 MHz, d$_6$-DMSO): δ136.86, 128.35, 123.68, 122.28, 47.92, 44.71, 35.80, 28.63, 27.02.

2.2.3. 1-(4-Chlorosulfonylbutyl)pyridinium trifluoromethanesulfonate (*2a*)

A dark brown semisolid with yield of 96%. ^{1}H NMR (400 MHz, d$_6$-DMSO): δ9.07(s, 2H), 8.53(s, 1H), 8.09(s, 2H), 4.60(s, 2H), 2.65(s, 2H), 1.97(s, 2H), 1.56(s, 2H). ^{13}C NMR(100 MHz, d$_6$-DMSO): δ146.10, 145.31, 128.68, 125.64(q, $J_{\text{C–F}} = 320.0$, CF$_3$), 60.89, 50.86, 30.26, 21.74.

2.2.4. 1-(4-Chlorosulfonylbutyl)pyridinium trifluoroacetate (*2b*)

A brown semi-solid with yield of 95%. ^{1}H NMR (400 MHz, d$_6$-DMSO): δ9.32(d, $J = 3.6$, 2H), 8.62(t, $J = 7.6$, 1H), 8.18(t, $J = 6.8$, 2H), 4.76(t, $J = 7.2$, 2H), 3.65(t, $J = 6.8$, 2H), 2.01(quint, $J = 7.2$, 2H), 1.69(quint, $J = 6.8$, 2H). ^{13}C-NMR(100 MHz, d$_6$-DMSO): δ145.64, 144.97, 128.18, 59.64, 44.67, 28.46.