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Mg/La MIXED OXIDE AS AN EFFICIENT HETEROGENEOUS BASIC CATALYST FOR SYNTHESIS OF 2-AMINOTHIOPHENES UNDER MICROWAVE IRRADIATION

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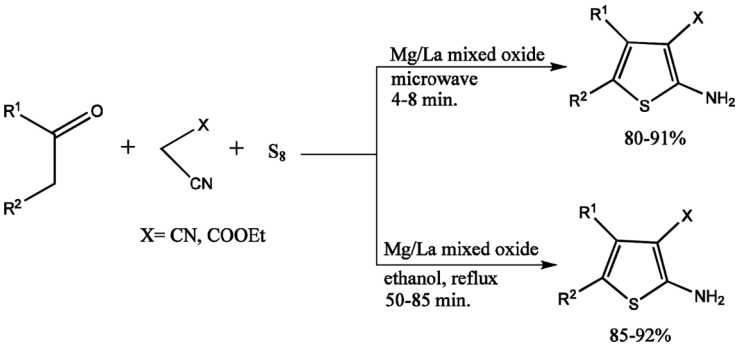
GRAPHICAL ABSTRACT



Abstract *Microwave-assisted synthesis of 2-aminothiophenes via a Gewald reaction using a heterogeneous strong basic Mg/La mixed oxide catalyst is described.*

Keywords 2-Aminothiophene; Gewald reaction; Mg/La mixed oxide catalysis; microwave-assisted synthesis

INTRODUCTION

The synthesis of substituted 2-aminothiophenes is attractive to chemical researchers as they are important intermediates in organic synthesis and frequently used as the scaffold motif of a variety of agrochemicals, dyes, and biologically active products.[1] Thus, because of their wide utility, researchers have synthesized the substituted 2-aminothiophenes via efficient and convenient methods. The one-pot

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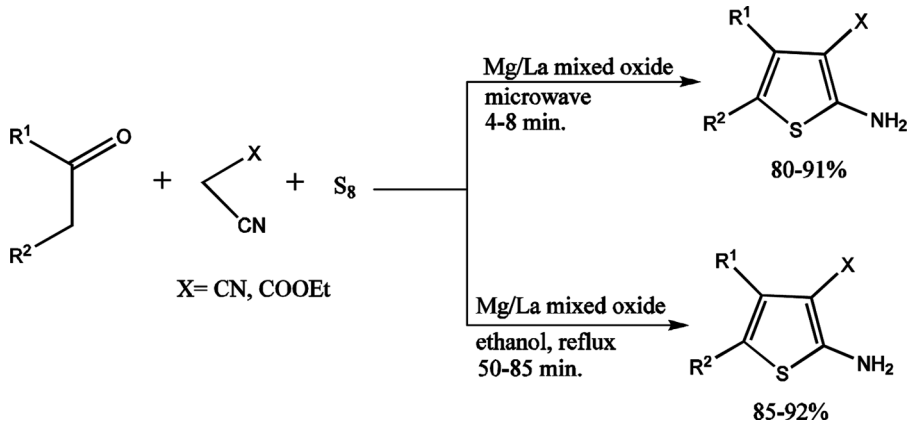
cyclocondensation of ketones having hydrogens at their α-position, a cyanomethylene containing an electron-withdrawing group such as cyanoacetate and elemental sulfur in the presence of organic base, for example, morpholine, diethylamine, etc, known as the Gewald reaction,[2] has been one of the most well-studied multicomponent reactions in recent years.[4]

To extend the scope of the reaction, many alterations have been made to the original Gewald's base-catalyzed, two-component combination of α-mercapto ketones with cyanoacetate[3] by varying the components[4] and the conditions.[5–7]

However, the major problem associated with these reactions in most of the published procedures is that high catalyst loading (normally 50–100 mol% or even more), and the usual long reaction time periods required for the reactions. Therefore, the development of a suitable method by the use of microwave irradiation in combination with the use of additional reagents and catalysts[6] for the efficient synthesis of 2-aminothiophenes in a one-pot reaction remains an attractive field to researchers. In the recent years, the synthesis of solid base catalysts derived from alkali earth metallic precursors has played an important role in the field of heterogeneous catalysis. These catalysts have several advantages over homogeneous organic basic catalysts, such as easy recovery of the catalyst, simple product isolation and reusability. Therefore, the solid base catalysts have been considered as potential alternatives to homogeneous organic basic catalysts.

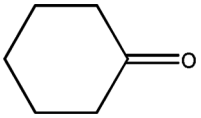
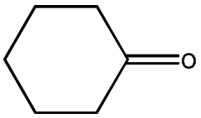
In this context, we have found that the Gewald reaction occurs efficiently in the presence of Mg/La mixed oxide as a heterogeneous solid base catalyst under microwave irradiation as well as conventional heating conditions by refluxing in ethanol Scheme 1.

The Mg/La mixed oxides are used as catalysts for various organic reactions. This catalyst has been used for various organic reactions such as Michael addition,[8a] Wadsworth–Emmons reaction,[8b] Heck reaction,[8d] Miyaura cross-coupling reaction[8e] and synthesis of polyfunctionalized pyrans[8f] and is suitable for classical conditions and microwave irradiation. To the best of our knowledge, there is no report in the literature on the use of Mg/La mixed oxide under solvent-free



Scheme 1. Synthesis of 2-aminothiophenes.

Table 1. Mg/La-catalyzed synthesis of 2-aminothiophenes

	Ketone			Reaction conditions		Mp (°C)	
Entry	R^1	R^2	X	Microwave[a] yield (%) (Reaction time, min)	Conventional[a] yield (%) (Reaction time, min)	Found	Reported
1	CH_3	CH_3	COOEt	90 (4.0)	91 (70)	90	91[3]
2	Ph	CH_3	COOEt	91 (6.5)	90 (60)	93	93[3]
3	Ph	H	COOEt	85 (6.0)	92 (55)	96	98[3]
4	CH_3	$COCH_3$	COOEt	80 (4.5)	85 (75)	161	161[3]
5			COOEt	89 (7.0)	86 (50)	115	115[6]
6	CH_3	CH_3	CN	91 (5.0)	90 (85)	142	141[3]
7			CN	85 (7.0)	90 (65)	147	147[6]
8	Ph	H	CN	88 (6.0)	88 (70)	142	142[6]
9	4-Br-Ph	H	CN	80 (8.0)	88 (80)	192	190[7]

[a]Isolated yields. All of the products are known and were identified by comparison of their physical and spectroscopic data (IR, NMR) with those of authentic samples.

conditions. The presence of La_2O_3 in proximity to MgO leads to enhanced basicity. In the present study, Mg/La mixed oxide was prepared by the co-precipitation method at pH = 10 described earlier.[9] The chemical analysis of the solid gave the composition: La_2O_3 29.5%, MgO 30.1%, K_2O 3.4%, H_2O 37%.

A variety of ketones were reacted with ethyl cyanoacetate (or malononitrile) and elemental sulfur in the presence of Mg/La mixed oxide as base catalyst. To the best of our knowledge, there is no report in the literature on the use of Mg/La mixed oxide in the synthesis of 2-aminothiophenes. This reaction was studied both under microwave irradiation as well as conventional heating conditions by refluxing in ethanol Table 1. In both the cases, the reaction proceeded well to produce 2-aminothiophene derivatives in good yields. All of the products are known and were identified by comparison of their physical and spectroscopic data (IR, NMR) with those of authentic samples.[3,6,7]

Table 2. Comparison results of Mg/La mixed oxide with general method of the Gewald reaction,[3] L-proline,[5] KF-alumina,[6] and ethylenediammonium diacetate[5] as catalysts in the reaction of cyclohexanone and ethylcyano acetate

Entry	Condition	Catalyst	Time (min)	Yield (%)
1	Ethanol, 78 °C	Diethylamine	240	82
2	Ethanol, 78 °C	KF-alumina	210	89
3	DMF, 60 °C	L-proline	1440	84
4	Ionic liquid, 50 °C	Ethylenediammonium diacetate	240	84
5	Ethanol, 78 °C	Mg/La mixed oxide	50	86

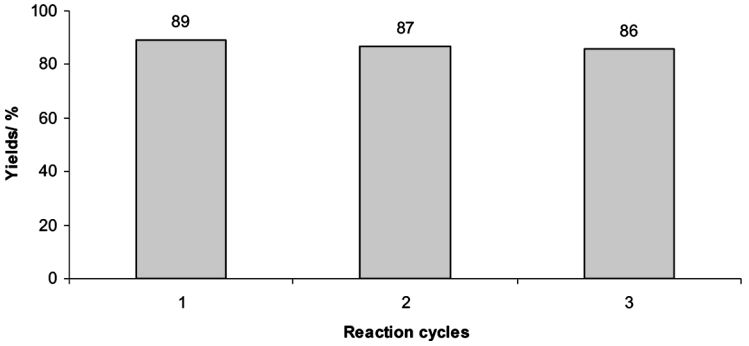


Figure 1. Recycling experiment of Mg/La mixed oxide basic catalyst.

To show merit of the present work in comparison with reported results in the literature, we compared results of Mg/La mixed oxide with general method of Gewald reaction[3], L-proline[5], ethylenediammonium diacetate (EDDA)[5] and KF-alumina[6] as catalysts in the reaction of cyclohexanone and ethyl cyanoacetate. As shown in Table 2, Mg/La mixed oxide can act as high efficiency catalyst with fast time and high yields of the obtained products.

Reusability of the catalyst was also investigated. For this purpose, the reaction of cyclohexanone and ethyl cyanoacetate was studied under the microwave irradiation condition. After the completion of the reaction, the catalyst was separated by simple filtration, washed with methanol, dried at 120 °C for 2 h and reused for the similar reaction. As it is shown in Fig. 1, the catalyst could be reused at least three times without significant loss of activity.

In summary, the current study is the first application of Mg/La mixed oxide as a base for the preparation of 2-aminothiophenes by microwave accelerated multi-component condensation, because substituted 2-aminothiophenes represents a category of an important precursors broadly employed in the synthesis of pharmaceuticals, dyes and potential building blocks in materials chemistry. This method offers an efficient and convenient modification to the Gewald reaction as it could be carried out with very short reaction times, easy work up under microwave irradiation. Alternatively, the current reaction also proceeds well under conventional heating by refluxing in ethanol.

EXPERIMENTAL

The melting points were recorded on an Electrothermal type 9100 melting point apparatus. The ^{1}H NMR (400 MHz) spectra were recorded on a Bruker AC 400 spectrometer. ^{13}C NMR spectra were determined using the Bruker AM-400 instrument operating at 100 MHz. IR spectra were determined as KBr pellets on a Shimadzu model 470 spectrophotometer. Elemental analyses were carried out on Carlo Erba CHNS-O 1108 apparatus and were in good accordance with theoretical data. The catalyst was analyzed by ICP-atomic spectroscopy after dissolution by acid attack.

Table 3. Spectral data of synthesized products

Compound	Spectral data
Ethyl 2-amino-4,5-dimethylthiophene-3-carboxylate (Table 1, entry 1)	^{1}H NMR ($CDCl_3$) δ 1.29 (t, 3H, $J = 7.2$ Hz), 2.20 (s, 3H), 2.36 (s, 3H), 4.30 (q, 2H, $J = 7.2$ Hz), 6.99 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 9.8, 10.4, 14.1, 60.9, 112.9, 132.4, 134.9, 148.8, 165.7; IR (KBr) 1647, 3299, 3405 cm^{-1}. Anal. calcd. for $C_9H_{13}NO_2S$: C, 54.25; H, 6.58; N, 7.03; S, 16.09. Found: C, 54.28; H, 6.60; N, 7.07; S, 16.07.
Ethyl 2-amino-5-methyl-4-phenylthiophene-3-carboxylate (Table 1, entry 2)	^{1}H NMR ($CDCl_3$) δ 1.31 (t, 3H, $J = 7.2$ Hz), 1.99 (s, 3H), 4.33 (q, 2H, J = 7.2 Hz), 6.83 (s, 2H), 7.41–7.52 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 12.3, 14.1, 60.2, 108.3, 127.5, 128.7, 129.2, 134.5, 136.1, 136.4, 159.9, 161.4; IR (KBr) 1677, 3334, 3441 cm^{-1}. Anal. calcd. for $C_{14}H_{15}NO_2S$: C, 64.34; H, 5.79; N, 5.36; S, 12.27. Found: C, 64.38; H, 5.81; N, 5.39; S, 12.29.
Ethyl 2-amino-4-phenylthiophene-3-carboxylate (Table 1, entry 3)	^{1}H NMR ($CDCl_3$) δ 1.28 (t, 3H, $J = 7.2$ Hz), 4.30 (q, 2H, $J = 7.2$ Hz), 6.39 (s, 1H), 6.91 (s, 2H), 7.40–7.53 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.4, 60.5, 105.1, 108.5, 127.7, 128.9, 129.6, 136.2, 143.6, 160.9, 164.8; IR (KBr) 1670, 3332, 3440 cm^{-1}. Anal. calcd. for $C_{13}H_{13}N\,O_2S$: C, 63.13; H, 5.30; N, 5.66; S, 12.97. Found: C, 63.10; H, 5.28; N, 5.63; S, 12.92.
Ethyl 5-acetyl-2-amino-4-methylthiophene-3-carboxylate (Table 1, entry 4)	^{1}H NMR ($CDCl_3$) δ 1.33 (t, 3H, $J = 7.2$ Hz), 2.50 (s, 3H), 2.82 (s, 3H), 4.35 (q, 2H, $J = 7.2$ Hz), 7.02 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 9.6, 14.5, 27.2, 60.6, 114.5, 142.8, 149.1, 161.4, 170.4, 191.1; IR (KBr) 1678, 3320, 3420 cm^{-1}. Anal. Calcd for $C_{10}H_{13}NO_3S$: C, 52.85; H, 5.77; N, 6.16; S, 14.11. Found: C, 52.81; H, 5.73; N, 6.11; S, 14.09.
Ethyl 2-amino-4,5,6,7-tetrahydrobenzo[b]-thiophene-3-carboxylate (Table 1, entry 5)	^{1}H NMR ($CDCl_3$) δ 1.33 (t, 3H, $J = 7.2$ Hz), 1.73–1.75 (m, 4H), 2.46–2.48 (m, 2H), 2.69–2.71 (m, 2H), 4.25 (q, 2H, $J = 7.2$ Hz), 6.01 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.5, 22.9, 23.3, 24.5, 27.0, 59.4, 105.5, 117.5, 132.4, 161.9, 166.6; IR (KBr) 1647, 3299, 3405 cm^{-1}. Anal. calcd. for $C_{11}H_{15}NO_2S$: C, 58.64; H, 6.71; N, 6.22; S, 14.23. Found: C, 58.68; H, 6.77; N, 6.28; S, 14.27.
2-Amino-4,5-dimethylthiophene-3-carbonitrile (Table 1, entry 6)	^{1}H NMR ($CDCl_3$) δ 2.20 (s, 3H), 2.35 (s, 3H), 6.87 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 9.5, 12.2, 83.3, 116.2, 117.1, 128.8, 149.7; IR (KBr) 2215, 3295, 3408 cm^{-1}. Anal. calcd. for $C_7H_8N_2S$: C, 55.23; H, 5.30; N, 18.40; S, 21.07. Found: C, 55.28; H, 5.36; N, 18.46; S, 21.09.
2-Amino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbonitrile (Table 1, entry 7)	^{1}H NMR ($CDCl_3$) δ 1.69 (m, 4H), 2.33–2.39 (m, 4H), 6.92 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 22.1, 23.4, 24.1, 24.5, 88.4, 115.5, 120.7, 132.4, 161.1; IR (KBr) 2196, 3328, 3445 cm^{-1}. Anal. calcd. for $C_9H_{10}N_2S$: C, 60.64; H, 5.65; N, 15.72; S, 17.99. Found: C, 60.69; H, 5.67; N, 15.75; S, 18.02.
2-Amino-4-phenylthiophene-3-carbonitrile (Table 1, entry 8)	^{1}H NMR ($CDCl_3$) δ 6.96 (s, 2H), 7.14 (s, 1H), 7.43–7.54 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 79.8, 115.4, 127.7, 129.4, 129.9, 136.4, 139.1, 154.2; IR (KBr)

(*Continued*)

Table 3. Continued

Compound	Spectral data
	2195, 3330, 3441 cm^{-1}. Anal. calcd. for $C_{11}H_8N_2S$: C, 65.97; H, 4.03; N, 13.99; S, 16.01. Found: C, 65.93; H, 4.01; N, 13.95; S, 15.98.
2-Amino-4-(4-bromophenyl)thiophene-3-carbonitrile (Table 1, entry 9)	^1H NMR ($CDCl_3$) δ 6.91 (s, 2H), 7.16 (s, 1H), 7.54 (d, 2H, $J = 7.2$ Hz), 7.68 (d, 2H, $J = 7.2$ Hz); ^{13}C NMR ($CDCl_3$) δ 79.6, 115.5, 121.7, 123.3, 129.2, 129.8, 135.3, 139.3, 153.6; IR (KBr) 2190, 3335, 3440 cm^{-1}. Anal. calcd. for $C_{11}H_7BrN_2S$: C, 47.33; H, 2.53; N, 10.04; S, 11.49. Found: C, 47.36; H, 2.57; N, 10.08; S, 11.53.

Ketone (1.0 mmol), nitrile (1.0 mmol), elemental sulfur (0.035 g, 1.1 mmol), Mg/La mixed oxide (1 mole %) and 2 ml of dry ethanol were mixed and placed in a 10 ml pressure tube. The mixture was subjected to microwave irradiation (MicroSynth, 160 W, 150 psi, 78 °C, 85 Hz) for the time indicated in Table 1 and then diluted with chloroform (5 ml) and filtered. The solid was rinsed with chloroform (2×3 ml) and the combined extracts were concentrated and purified by normal chromatography to afford the corresponding 2-aminothiophenes. The spectral data (IR and NMR) of all products matched in all respects with reported data. In the case of conventional heating, the reactants, as above in 20 ml ethanol, were heated at reflux (78 °C) for the time indicated in Table 1. When the reaction was complete (thin-layer chromatography; methanol/chloroform 1/9), solvent was removed by evaporation under reduced pressure and the reaction mixture was diluted with 10 ml of chloroform and filtered. After evaporation of the solvent, the mixture was purified by normal column chromatography to give the desired products. Spectral data of synthesized products are given in Table 3.

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