



# A recyclable magnetic nanoparticles supported antimony catalyst for the synthesis of *N*-substituted pyrroles in water



Fei-Ping Ma, Pei-He Li, Bao-Le Li, Li-Ping Mo, Ning Liu, Hui-Jun Kang, Ya-Nan Liu, Zhan-Hui Zhang\*

College of Chemistry & Material Science, Hebei Normal University, Shijiazhuang 050024, China

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## ABSTRACT

A new magnetic nanoparticle-supported antimony catalyst was prepared and evaluated as a recoverable catalyst for Clauson-Kaas reaction. The reaction proceeds efficiently in aqueous medium to give the corresponding *N*-substituted pyrroles in high yield. The immobilized catalyst could be easily recovered by magnetic separation and recycled for six times without significant loss of its catalytic activity.

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## 1. Introduction

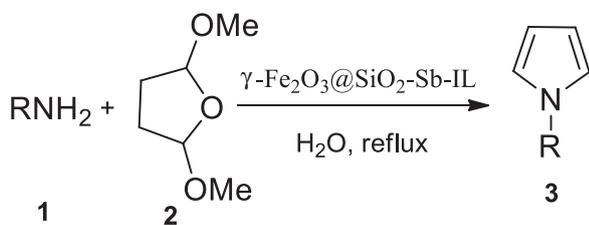
Organic reactions using heterogeneous catalysts are extremely important for the development of sustainable chemical processes. But the major limitation associated with heterogeneous catalysts is their lower activity. The best solution to this problem is to keep the size of the particles in the heterogeneous catalyst as small as possible. Nanoparticles (NPs) are referred to as quasi homogeneous support between conventional homogeneous and heterogeneous catalysts because of their high surface areas and improved dispersability in the reaction medium. However, for such suspensions of particles with less than 100 nm diameter, the conventional catalyst separation methods, such as filtration and centrifugation, become tedious and hamper the complete separation of the catalyst. To further address the issues of recyclability and reusability, magnetic nanoparticles (MNPs) have emerged as attractive catalyst support because of their unique separable features by magnetic forces [1]. Magnetic separation is a green process and it avoids use of extra chemicals and additional filtration or centrifugation step during the separation process. Moreover, they are accessible from inexpensive materials and can be easily tuned by structural appropriate surface modification [2–5]. Meanwhile, the concept

of supported ionic-liquid catalysis (SILC) has also recently been introduced, which combines the features of ionic liquids and heterogeneous systems [6]. These advantages prompted us to report our exploration of MNP-supported transition-metal-containing ionic liquid as an efficient and recoverable catalyst.

Pyrrole derivatives are one of the most important classes of nitrogen-containing heterocycles and have attracted attention, since they constitute the core unit of many natural products, synthetic materials and medicinal chemistry [7]. As a result, various strategies have been developed for the synthesis of diversely substituted pyrroles, which involve conjugate addition reactions [8], 1,3-dipolar cycloaddition reaction [9], reductive coupling [10], aza-Wittig reaction [11], classical Hantzsch procedure [12], annulations reactions [13], transition metal-mediated cyclization [14], multi-components reactions [15], and other operations [16–20]. Among them, Paal–Knorr reaction [21] and Clauson-Kaas reaction are the typical and commonly used protocols to produce *N*-substituted pyrroles. A number of catalysts have been introduced into the Clauson-Kaas reaction between primary amines and 2,5-dimethoxy-tetrahydrofuran, including glacial acetic acid [22], phosphorus pentoxide [23], montmorillonite K-10 [24], cerium (III) chloride [25], cupric chloride [26], iron(III) chloride [27], bismuth nitrate [28,29], scandium triflate [30], MgI<sub>2</sub> etherate [31], iodine [32], and nano-organocatalyst [33,34]. This reaction can be performed using microwave irradiation [35]. However, despite the potential utility of these catalysts, many of these methodologies are

\* Corresponding author. Fax: +86 31180787431.

E-mail address: [zhanhui@126.com](mailto:zhanhui@126.com) (Z.-H. Zhang).



Scheme 1. Synthesis of *N*-substituted pyrroles.

associated with several shortcomings such as low yields, prolonged reaction time, harsh reaction conditions, the requirement of excess of catalysts, use of expensive reagents and additional microwave oven. Additionally, in most of these methods, homogeneous catalysts were used and reusing them in consecutive reaction is difficult. Thus, the quest for a novel, efficient, and recyclable catalyst for Clauson-Kaas reaction remains a great challenge.

We were interested in developing magnetically separable heterogeneous catalysts, in particular, in an effort to achieve the high recyclability of heterogeneous catalysts. Previously, we reported that magnetic  $\text{Fe}_3\text{O}_4$  is highly efficient reusable catalyst for the synthesis of quinoxalines [36] and 2,3-dihydroquinazolin-4(1*H*)-ones [37]. We have developed an efficient method for one-pot reductive amination of carbonyl compounds using  $\text{NaBH}_4$  in the presence of a magnetically recoverable  $\gamma\text{-Fe}_2\text{O}_3\text{@HAP-SO}_3\text{H}$  [38]. Immobilization of TfOH [39] and dodecyl benzenesulfonic acid (DDBSA) [40] onto the silica-coated magnetic nanoparticles has also been successfully achieved. Considering the above subjects and along with our previous research programme on the development of efficient and environmental benign synthetic methodologies [41–45], herein, we report on the preparation of a new type of magnetic nanoparticle-supported antimony carbene complex ( $[\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-NHC-Sb(III)}]$ ) and its application towards a filtration-free, recyclable Clauson-Kaas reaction (Scheme 1).

## 2. Experimental

All solvents and chemicals were obtained commercially and were used as received. X-ray diffraction analysis was carried out using a PANalytical X'Pert Pro X-ray diffractometer. Surface morphology and particle size were studied using a Hitachi S-4800 SEM instrument. Transmission electron microscope (TEM) observation was performed using Hitachi H-7650 microscope at 80 KV. Elemental compositions were determined with a Hitachi S-4800 scanning electron microscope equipped with an INCA 350 energy dispersive spectrometer (SEM-EDS) presenting a 133 eV resolution at 5.9 keV. Melting points were determined using an X-4 apparatus and are uncorrected. IR spectra were recorded using a Bruker-TENSOR 27 spectrometer instrument. NMR spectra were taken with a Bruker DRX-500 spectrometer at 500 MHz ( $^1\text{H}$ ) and 125 MHz ( $^{13}\text{C}$ ) using  $\text{CDCl}_3$  as the solvent with TMS as internal standard. Elemental analyses were obtained on a Vario EL III CHNOS elemental analyzer. The ICP-MS analyses were carried out with an X Series 2 spectrometer.

### 2.1. Preparation of magnetic nanoparticles-supported antimony catalyst [ $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Sb-IL}$ ]

1-Methyl-3-(trimethoxysilylpropyl)-imidazolium chloride (**I**) was synthesized according to the procedure reported in the literature [46] as follows: *N*-Methylimidazole (50 mmol) and 3-chloropropyltrimethoxysilane (50 mmol) was mixed in a dry flask under nitrogen flow. The system was evacuated and refilled with nitrogen five times repeatedly and the mixture was refluxed for 3 days. After cooling to room temperature, the mixture was washed

with dehydrated ethyl acetate five times and dried by evacuation at room temperature for 48 h. 1-Methyl-3-(trimethoxysilylpropyl)-imidazolium chloride (**I**) was obtained as a transparent liquid.

Compound **I** (10 mmol) and anhydrous  $\text{SbCl}_3$  (10 mmol) were mixed in a round bottom flask and stirred at  $80^\circ\text{C}$  for 24 h under nitrogen atmosphere. Antimony-containing ionic liquid (**II**) was obtained as a pale yellow oil.

The solution of Sb(III)-IL (**II**) (0.8 mmol) in ethanol (20 ml) was added to a well stirred ethanol solution suspension (50 ml) of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2$  (1.0 g). The mixture was refluxed for 48 h under nitrogen. After cooling to room temperature, the catalyst was collected by a permanent magnet and rinsed with ethanol ( $3 \times 20$  ml), and then was dried at  $110^\circ\text{C}$  for 5 h to afford  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Sb-IL}$ . The loading amount of Sb metal was determined based on ICP-MS.

### 2.2. General procedure for synthesis of *N*-substituted pyrroles

To a solution of amine (1 mmol) in water (2 ml) was added tetrahydro-2,5-dimethoxyfuran (1.1 mmol) and  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Sb-IL}$  (0.08 g). The reaction mixture was stirred at  $100^\circ\text{C}$  for a certain period of time as required to complete the reaction. During that time, the reaction was monitored constantly by TLC. After completion of the reaction, the catalyst was removed by using a magnet and washed with ethyl acetate. The aqueous solution was extracted by ethyl acetate ( $3 \times 5$  ml). The combined organic phase was dehydrated with anhydrous sodium sulfate. After the evaporation of the solvent, the residue was purified by silica gel flash chromatography using petroleum ether/ethyl acetate as the eluent to afford the pure product.

### 2.3. Representative spectral and analytical data:

1-(4-Ethoxyphenyl)-1*H*-pyrrole (**3e**). IR (KBr): 3066, 1520, 1456, 1396, 1325, 1301, 1286, 1186, 1128, 1070, 1047, 1016, 920, 796,  $709\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 1.43 (t,  $J = 7.0$  Hz, 3H), 4.06 (q,  $J = 7.0$  Hz, 2H), 6.32 (t,  $J = 2.0$  Hz, 2H), 6.93 (d,  $J = 9.0$  Hz, 2H), 7.00 (t,  $J = 2.0$  Hz, 2H), 7.29 (d,  $J = 9.0$  Hz, 2H) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 14.9, 63.8, 109.8, 115.3, 119.7, 122.2, 134.4, 157.1 ppm; ESI-MS:  $m/z = 188$  ( $M + 1$ ) $^+$ ; Anal. Calcd. for  $\text{C}_{12}\text{H}_{13}\text{NO}$ : C, 76.98; H, 7.00; N, 7.48. Found: C, 77.16; H, 6.82; N, 7.65.

1-(3,4-Dimethylphenyl)-1*H*-pyrrole (**3h**). IR (KBr): 2933, 2918, 2734, 1608, 1517, 1479, 1458, 1448, 1334, 1228, 1124, 1072, 1033, 948,  $819\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 2.28 (s, 3H), 2.31 (s, 3H), 6.32 (t,  $J = 2.5$  Hz, 2H), 7.05 (t,  $J = 2.5$  Hz, 2H), 7.12 (dd,  $J = 9.0$ , 2.0 Hz, 1H), 7.16–7.18 (m, 2H) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 19.3, 20.1, 110.1, 118.1, 119.5, 122.1, 130.6, 134.1, 137.9, 138.9 ppm; ESI-MS:  $m/z = 172$  ( $M + 1$ ) $^+$ ; Anal. Calcd. for  $\text{C}_{12}\text{H}_{13}\text{N}$ : C, 84.17; H, 7.65; N, 8.18. Found: C, 83.98; H, 7.82; N, 7.98.

1-(2,4-Difluorophenyl)-1*H*-pyrrole (**3o**).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 6.35 (t,  $J = 2.0$  Hz, 2H), 6.92–7.00 (m, 4H), 7.33–7.38 (m, 1H) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 105.2 (d,  $J_{\text{FC}} = 24.3$  Hz), 105.4 (d,  $J_{\text{FC}} = 26.1$  Hz), 110.0, 111.7 (dd,  $J_{\text{FC}} = 22.4$ , 3.9 Hz), 121.5 (d,  $J_{\text{FC}} = 3.1$  Hz), 126.1 (d,  $J_{\text{FC}} = 9.7$  Hz), 155.3 (dd,  $J_{\text{FC}} = 250.9$ , 11.8 Hz), 160.7 (dd,  $J_{\text{FC}} = 247.3$ , 11.0 Hz) ppm; ESI-MS:  $m/z = 180$  ( $M + 1$ ) $^+$ ; Anal. Calcd. for  $\text{C}_{10}\text{H}_7\text{F}_2\text{N}$ : C, 67.04; H, 3.94; N, 7.82. Found: C, 67.21; H, 4.10; N, 7.68.

1-(3,4-Difluorophenyl)-1*H*-pyrrole (**3p**). IR (KBr): 3134, 3078, 1614, 1521, 1485, 1444, 1350, 1271, 1262, 1124, 1066, 1022, 954, 890,  $729\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 6.35 (t,  $J = 2.0$  Hz, 2H), 7.0 (t,  $J = 2.0$  Hz, 2H), 7.10–7.13 (m, 1H), 7.19–7.25 (m, 2H) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz) ( $\delta$ : 110.1 (d,  $J_{\text{FC}} = 20.3$  Hz), 111.1, 116.2 (dd,  $J_{\text{FC}} = 6.1$ , 3.6 Hz), 118.0 (d,  $J_{\text{FC}} = 18.0$  Hz), 119.5, 137.4 (dd,  $J_{\text{FC}} = 8.0$ , 3.0 Hz), 148.3 (dd,  $J_{\text{FC}} = 245.4$ , 12.6 Hz), 150.6 (dd,  $J_{\text{FC}} = 247.9$ , 13.5 Hz) ppm; ESI-MS:  $m/z = 180$  ( $M + 1$ ) $^+$ ; Anal. Calcd. for  $\text{C}_{10}\text{H}_7\text{F}_2\text{N}$ : C, 67.04; H, 3.94; N, 7.82. Found: C, 66.95; H, 4.12; N, 8.01.

1-(3-Chloro-4-methylphenyl)-1*H*-pyrrole (**3s**). IR (KBr): 1610, 1510, 1473, 1380, 1334, 1251, 1076, 1047, 1028, 937, 858, 819  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 2.38 (s, 3H), 6.34 (t,  $J=2.0$  Hz, 2H), 7.04 (t,  $J=2.0$  Hz, 2H), 7.19 (dd,  $J=8.5, 2.5$  Hz, 1H), 7.26 (d,  $J=8.5$  Hz, 1H), 7.40 (d,  $J=2.5$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 19.5, 110.8, 118.6, 119.3, 121.1, 131.7, 132.2, 135.1, 139.7 ppm; ESI-MS:  $m/z=192$  ( $M+1$ ) $^+$ ; Anal. Calcd. for  $\text{C}_{11}\text{H}_{10}\text{ClN}$ : C, 68.93; H, 5.26; N, 7.31. Found: C, 69.10; H, 5.08; N, 7.49.

1-(3-Chloro-4-fluorophenyl)-1*H*-pyrrole (**3t**). IR (KBr): 3132, 1598, 1514, 1419, 1269, 1245, 1076, 1055, 1022, 939, 860, 815, 727  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 6.35 (s, 2H), 7.01 (s, 2H), 7.20 (t,  $J=9.0$  Hz, 1H), 7.24–7.26 (m, 1H), 7.44 (dd,  $J=6.0, 2.5$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 111.0, 117.2 (d,  $^2J_{\text{FC}}=22.3$  Hz), 120.1 (d,  $^3J_{\text{FC}}=7.0$  Hz), 121.8 (d,  $^2J_{\text{FC}}=18.6$  Hz), 122.8, 137.6, 156.1 (d,  $^1J_{\text{FC}}=246.3$  Hz) ppm; ESI-MS:  $m/z=196$  ( $M+1$ ) $^+$ ; Anal. Calcd. for  $\text{C}_{10}\text{H}_7\text{ClFN}$ : C, 61.40; H, 3.61; N, 7.16. Found: C, 61.21; H, 3.80; N, 6.98.

1-(2,4,5-Trichlorophenyl)-1*H*-pyrrole (**3u**).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 6.36 (t,  $J=2.0$  Hz, 2H), 6.89 (t,  $J=2.0$  Hz, 2H), 7.46 (s, 1H), 7.63 (s, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 110.2, 121.9, 128.2, 128.8, 131.6, 131.7, 138.0 ppm; ESI-MS:  $m/z=246$  ( $M+1$ ) $^+$ ; Anal. Calcd. for  $\text{C}_{10}\text{H}_6\text{Cl}_3\text{N}$ : C, 48.72; H, 2.45; N, 5.68. Found: C, 48.90; H, 2.62; N, 5.50.

1-(4-Bromonaphthalen-1-yl)-1*H*-pyrrole (**3ag**). IR (KBr): 1591, 1521, 1473, 1357, 1267, 1155, 1078, 1028, 833, 724  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 6.41 (t,  $J=2.0$  Hz, 2H), 6.96 (t,  $J=2.0$  Hz, 2H), 7.31 (d,  $J=7.5$  Hz, 1H), 7.53 (t,  $J=8.0$  Hz, 1H), 7.63 (t,  $J=7.5$  Hz, 1H), 7.72 (d,  $J=8.5$  Hz, 1H), 7.80 (d,  $J=8.0$  Hz, 1H), 8.30 (d,  $J=8.5$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 109.5, 122.3, 123.3, 123.8, 123.9, 124.6, 127.6, 127.8, 128.1, 129.4, 131.1, 132.6, 133.2 ppm; ESI-MS:  $m/z=273$  ( $M+1$ ) $^+$ ; Anal. Calcd. for  $\text{C}_{14}\text{H}_{10}\text{BrN}$ : C, 61.79; H, 3.70; N, 5.15. Found: C, 61.60; H, 3.89; N, 4.98.

1-(9*H*-fluoren-2-yl)-1*H*-pyrrole (**3ah**). IR (KBr): 1618, 1500, 1473, 1400, 1334, 1305, 1230, 1112, 1064, 1001, 943, 823, 734, 723  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 3.96 (s, 2H), 6.37 (s, 2H), 7.14 (s, 2H), 7.31 (t,  $J=7.5$  Hz, 1H), 7.38–7.43 (m, 2H), 7.56 (d,  $J=8.0$  Hz, 1H), 7.57 (s, 1H), 7.77–7.81 (m, 2H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 37.1, 110.3, 117.5, 119.6, 119.8, 120.6, 125.1, 126.7, 127.0, 139.5, 139.7, 1141.0, 143.2, 144.8 ppm; ESI-MS:  $m/z=232$  ( $M+1$ ) $^+$ ; Anal. Calcd. for  $\text{C}_{17}\text{H}_{13}\text{N}$ : C, 88.28; H, 5.67; N, 6.06. Found: C, 88.10; H, 5.82; N, 5.89.

2-Methyl-6-(1*H*-pyrrol-1-yl)pyridine (**3aj**). IR (KBr): 3103, 2923, 1583, 1554, 1485, 1460, 1373, 1342, 1238, 1193, 1168, 1068, 943, 835, 785  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 2.55 (s, 3H), 6.35 (t,  $J=2.0$  Hz, 2H), 6.95 (d,  $J=8.0$  Hz, 1H), 7.10 (d,  $J=8.0$  Hz, 1H), 7.52 (t,  $J=2.0$  Hz, 2H), 7.61 (t,  $J=8.0$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,

125 MHz)  $\delta$ : 24.4, 108.2, 111.1, 111.6, 118.2, 119.6, 138.6, 150.8, 158.0 ppm; ESI-MS:  $m/z=159$  ( $M+1$ ) $^+$ ; Anal. Calcd. for  $\text{C}_{10}\text{H}_{10}\text{N}_2$ : C, 75.92; H, 6.37; N, 17.71. Found: C, 76.10; H, 6.55; N, 17.53.

6-Methyl-2-(1*H*-pyrrol-1-yl)benzo[d]thiazole (**3al**). IR (KBr): 3012, 1606, 1544, 1521, 1509, 1471, 1338, 1276, 1110, 1072, 1049, 999, 869, 817, 729  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 2.47 (s, 3H), 6.38 (s, 2H), 7.27 (d,  $J=8.5$  Hz, 1H), 7.44 (s, 2H), 7.58 (s, 1H), 7.75 (d,  $J=8.5$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 21.5, 112.5, 120.0, 121.2, 121.6, 128.1, 132.1, 134.6, 149.1, 158.7 ppm; ESI-MS:  $m/z=215$  ( $M+1$ ) $^+$ ; Anal. Calcd. for  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{S}$ : C, 67.26; H, 4.70; N, 13.07. Found: C, 67.08; H, 4.86; N, 12.90.

*N*-(1*H*-pyrrol-1-yl)benzamide (**3am**). IR (KBr): 3246, 1661, 1527, 1489, 1448, 1278, 1066, 970, 914, 711  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 6.23 ( $J=2.0$  Hz, 2H), 6.76 (t,  $J=2.0$  Hz, 2H), 7.50 (t,  $J=7.5$  Hz, 2H), 7.60 (t,  $J=7.5$  Hz, 1H), 7.86 (d,  $J=7.5$  Hz, 2H), 8.55 (br s, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 108.0, 121.8, 127.4, 128.9, 131.6, 132.7, 163.3 ppm; ESI-MS:  $m/z=187$  ( $M+1$ ) $^+$ ; Anal. Calcd. for  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$ : C, 70.95; H, 5.41; N, 15.04. Found: C, 71.12; H, 5.58; N, 15.20.

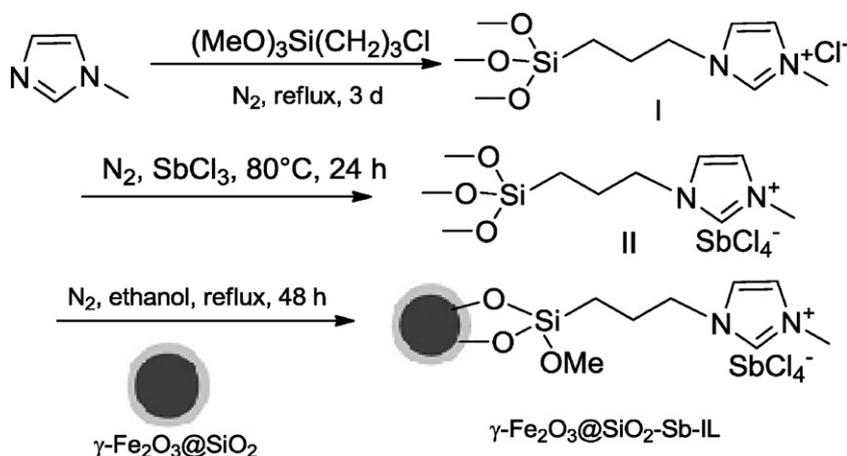
4-(1*H*-Pyrrol-1-yl)benzamide (**3an**). IR (KBr): 3142, 1645, 1613, 1577, 1525, 1475, 1425, 1394, 1327, 1199, 1120, 1064, 1014, 920, 846, 723  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 6.39 (t,  $J=2.0$  Hz, 2H), 7.16 (t,  $J=2.0$  Hz, 2H), 7.47 (d,  $J=8.5$  Hz, 2H), 7.89 (d,  $J=8.5$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 111.4, 119.1, 119.7, 130.0, 129.1, 143.4, 168.2 ppm; ESI-MS:  $m/z=187$  ( $M+1$ ) $^+$ ; Anal. Calcd. for  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$ : C, 70.95; H, 5.41; N, 15.04. Found: C, 71.12; H, 5.60; N, 14.86.

1,5-Di(1*H*-pyrrol-1-yl)naphthalene (**3ap**).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 6.43 (t,  $J=2.0$  Hz, 4H), 7.01 (t,  $J=2.0$  Hz, 4H), 7.50–7.51 (m, 4H), 7.75 (dd,  $J=8.5, 2.5$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$ : 109.4, 123.3, 123.4, 124.1, 126.3, 131.0, 138.5 ppm; ESI-MS:  $m/z=259$  ( $M+1$ ) $^+$ ; Anal. Calcd. for  $\text{C}_{18}\text{H}_{14}\text{N}_2$ : C, 83.69; H, 5.46; N, 10.84. Found: C, 83.50; H, 5.65; N, 10.66.

### 3. Results and discussion

#### 3.1. Preparation and characterization of magnetic nanoparticle-immobilized antimony-containing ionic liquid catalyst

Sb-containing immobilized ionic liquid on magnetic nanoparticle catalyst was readily prepared in a three-step as shown in Scheme 2. 1-Methyl-3-(trimethoxysilylpropyl)imidazolium chloride (**I**) was prepared by reaction of *N*-methylimidazole and 3-chloropropyltrimethoxysilane, followed by treatment with anhydrous  $\text{SbCl}_3$ . Immobilization of complex **II** in  $\gamma\text{-Fe}_2\text{O}_3@/\text{SiO}_2$



Scheme 2. Preparation of  $\gamma\text{-Fe}_2\text{O}_3@/\text{SiO}_2\text{-Sb-IL}$ .

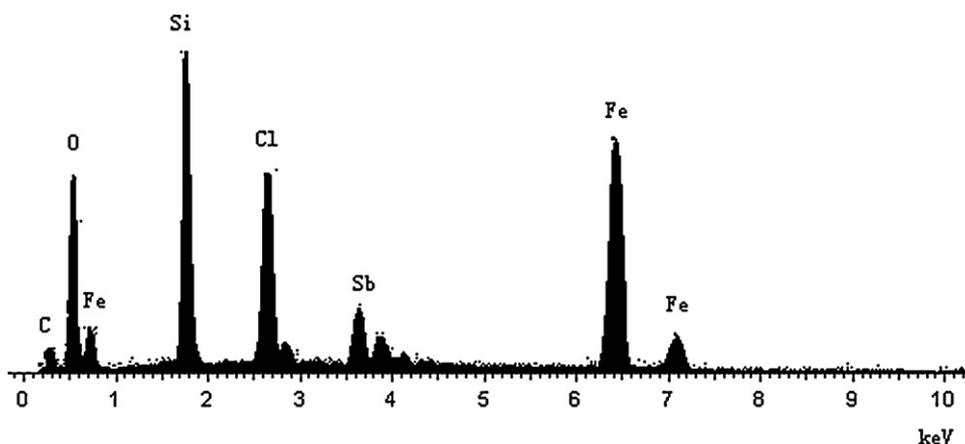


Fig. 1. EDS spectrum of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Sb-IL}$ .

was carried out in ethanol under reflux for 48 h. The antimony metal amount of the immobilized catalyst was found to be  $0.62 \text{ mmol g}^{-1}$  based on inductively coupled plasma mass spectrometry (ICP-MS) analysis. The energy dispersive spectrum (EDS) indicated the presence of Fe, Si, O, C, Cl and Sb (Fig. 1). Scanning electron microscopy (SEM) revealed that the catalyst presented the uniform particles with spherical morphology. Using the Debye–Scherrer equation, the average nanoparticle diameter was estimated to be 30 nm, which was in a good agreement with the results from SEM (Fig. 2). Transmission electron microscopy (TEM) further confirmed this catalyst was encapsulated by a thin silica layer (Fig. 3). FT-IR spectra of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Sb-IL}$  displayed peaks at 3144, 3097, 2963, 2935, 1563, 1460, 1098  $\text{cm}^{-1}$ , which clearly differs from that of the unfunctionalized silica-coated  $\gamma\text{-Fe}_2\text{O}_3$  [40] (Fig. 4). The magnetic core was analyzed by XRD and the observed diffraction pattern agree well with the JCPDS database for maghemite (Fig. 5).

### 3.2. Optimization of reaction conditions

The activity of the prepared catalyst was next tested in the model reaction of aniline and tetrahydro-2,5-dimethoxyfuran in water at reflux temperature. As shown in Table 1, the reaction occurred smoothly in the presence of 5 mol% of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Sb-IL}$ , affording a single product **3a** in 95% yield without any side-products (Table 1, entry 20). Some commercially available catalysts including trifluoroacetic acid, *p*-toluenesulfonic acid, silicotungstic acid, phosphotungstic acid, cerium ammonium nitrate,  $\text{NiCl}_2$ ,  $\text{ZnBr}_2$ ,

$\beta$ -cyclodextrin and  $\text{I}_2$  were also tested, in which the product was obtained in low yields (Table 1, entries 2–10). The reaction performed under similar conditions with other magnetic nanoparticles such as  $\text{Fe}_3\text{O}_4$ ,  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2$ ,  $\gamma\text{-Fe}_2\text{O}_3\text{@HAP-SO}_3\text{H}$ ,  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-SO}_3\text{H}$ , and  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-DDBSA}$ , resulted in low yields (entries 11–16). We also prepared magnetic nanoparticle-supported copper [ $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Cu-IL}$ ] and zinc [ $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Zn-IL}$ ], and found they did not give satisfactory results (entries 17 and 18). It is noteworthy that only a trace amount of the target product was formed when the reaction was performed in water in the absence of the catalyst (Table 1, entry 1).

The efficiency of the supported catalyst was found to be affected by the nature of the solvent and the quantity of the catalyst used in the reaction. As shown in Table 2, low yields of the target product **3a** were obtained when the mixture of aniline and tetrahydro-2,5-dimethoxyfuran was stirred under reflux temperature or  $100^\circ\text{C}$  in THF, MeCN, MeOH, EtOH, DMF, toluene, DMSO

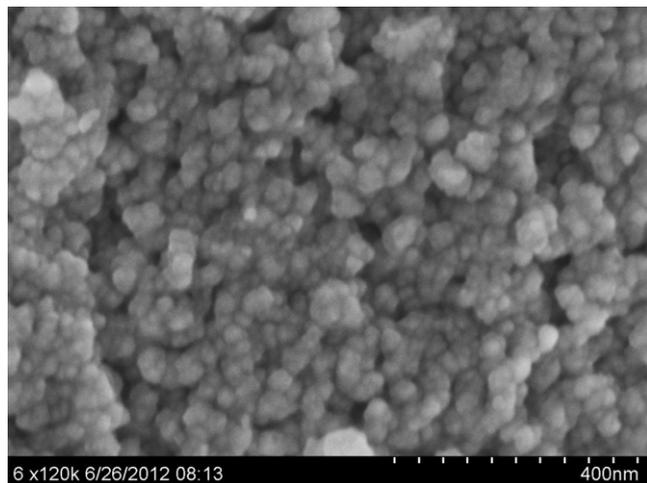


Fig. 2. SEM image of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Sb-IL}$ .

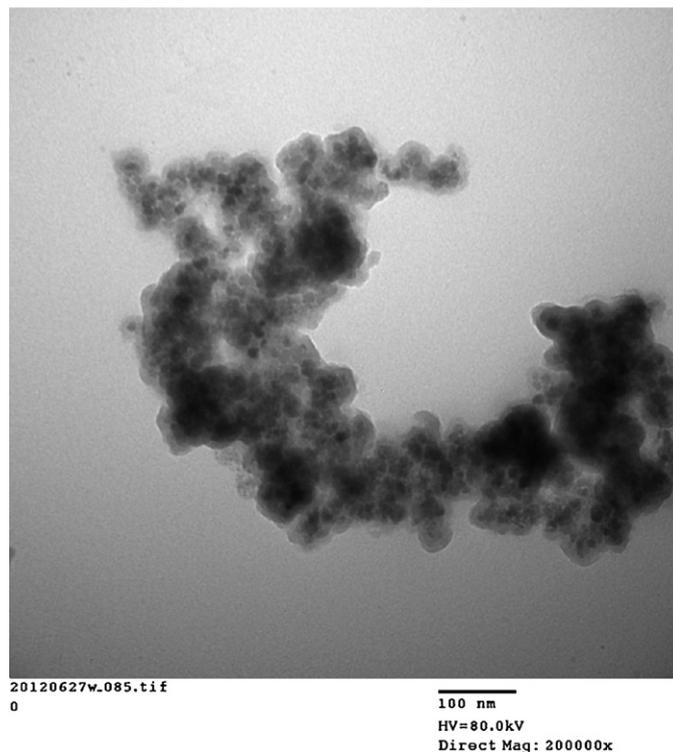


Fig. 3. TEM image of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Sb-IL}$ .

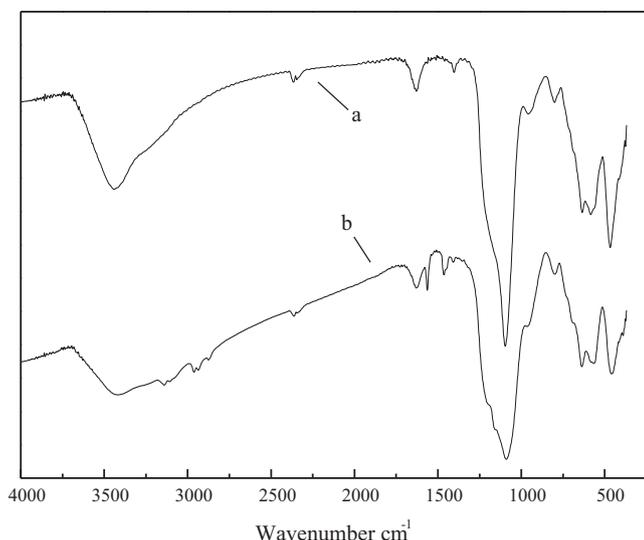


Fig. 4. IR spectra of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2$  (a) and  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Sb-IL}$  (b).

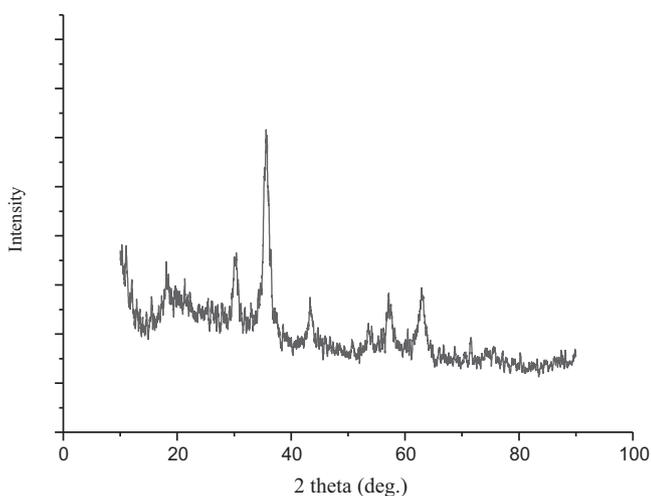


Fig. 5. XRD pattern of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Sb-IL}$ .

Table 1  
Influence of different catalysts on the reaction of aniline and tetrahydro-2,5-dimethoxyfuran.<sup>a</sup>

Entry	Catalyst (5 mol%)	Time (h)	Yield (%)
1	No	150	Trace
2	Trifluoroacetic acid	120	65
3	<i>p</i> -Toluenesulfonic acid	120	51
4	Silicotungstic acid	120	64
5	Phosphotungstic acid	120	61
6	Cerium ammonium nitrate	90	70
7	NiCl <sub>2</sub>	120	62
8	ZnBr <sub>2</sub>	80	48
9	$\beta$ -Cyclodextrin	120	35
10	I <sub>2</sub>	120	41
11	Nano Fe <sub>3</sub> O <sub>4</sub>	120	52
12	Nano $\gamma\text{-Fe}_2\text{O}_3$	120	51
13	Nano $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2$	120	53
14	Nano $\gamma\text{-Fe}_2\text{O}_3\text{@HAP-SO}_3\text{H}$	120	56
15	Nano $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-SO}_3\text{H}$	120	76
16	Nano $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-DDBSA}$	120	55
17	Nano $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Cu(II)-IL}$	120	75
18	Nano $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Zn(II)-IL}$	120	56
19	Nano $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Sb(III)-IL}$	40	95

<sup>a</sup> Experimental conditions: aniline (1 mmol), tetrahydro-2,5-dimethoxyfuran (1 mmol), H<sub>2</sub>O (5 ml).

Table 2  
Optimization of reaction conditions.<sup>a</sup>

Entry	Catalyst loading (mol%)	Solvent	Temperature (°C)	Time (min)	Yield (%)
1	No	No	100	240	21
2	5	No	100	100	75
3	5	THF	reflux	90	51
4	5	MeCN	reflux	100	65
5	5	MeOH	reflux	70	40
6	5	EtOH	reflux	90	75
7	5	DMF	reflux	40	92
8	5	Toluene	reflux	70	55
9	5	DMSO	100	40	92
10	5	PEG 400	100	80	62
11	3	H <sub>2</sub> O	reflux	50	87
12	5	H <sub>2</sub> O	reflux	30	95
13	10	H <sub>2</sub> O	reflux	30	95

<sup>a</sup> Experimental conditions: aniline (1 mmol), tetrahydro-2,5-dimethoxyfuran (1 mmol), solvent (5 ml).

and PEG 400 or neat conditions in the presence of 5 mol% of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Sb-IL}$ . The reaction using water, DMF and DMSO as the solvents gave the corresponding product **3a** in high yield. From the economical and environmental point of view, water was chosen as the reaction medium for further reaction. Furthermore, the relation between the yields of the model reaction and catalyst loading was also studied. The results showed that 5 mol% of catalyst was the best choice for the completing the reaction. Increasing the amount of catalyst to more than 5 mol% showed no substantial improvement in the yield, whereas the reaction took longer time and was not completed by decreasing the amount of catalyst to 3 mol%. It is worthy to mention that we examined the reaction in the absence of any catalyst under solvent-free conditions at 100 °C [47]. After 4 h, the desired product was obtained in 21% yield along with unreacted starting materials (Table 2, entry 1). This result suggests that a catalyst plays a critical role in this reaction. Again, in order to show the practical applicability of this process the model reaction was carried out in a scale of 50 mmol. As expected, the reaction proceeded well with 92% yield in 40 min.

### 3.3. Synthesis of *N*-substituted pyrroles

The successful results obtained for the catalytic Clauson-Kaas reaction presented above, the generality and scope of this protocol was further investigated. We performed the reaction with a variety of amines under the optimal conditions and the results are displayed in Table 3. The results obtained using the substituted anilines indicated that an electronic effect influenced this catalytic transformation. Anilines bearing an electron-donating group showed a slightly better result than those with electron-withdrawing substituent. The reaction was also sensitive to the steric environment of the anilines, and thus sterically congested substrate such as 2,6-diisopropylaniline required prolonged heating and afforded the desired product **3k** in a relatively lower yield (Table 3, entry 11). Moreover, naphthylamine and fluorenamine reacted smoothly with tetrahydro-2,5-dimethoxyfuran to afford the expected products in excellent yields (Table 3, entries 32–34). Additionally, heteroatomic amines, such as pyridin-2-amine, pyrimidin-2-amine, and benzo[*d*]thiazol-2-amine were also efficiently transformed, affording the potentially bio-important *N*-substituted pyrroles in good yields (Table 3, entries 35–38).

We also studied the condensation of aryl amides with tetrahydro-2,5-dimethoxyfuran. Unfortunately, aryl amides are inert in the presence of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-Sb-IL}$ . Therefore, the Clauson-Kass reaction of 4-aminobenzamide with tetrahydro-2,5-dimethoxyfuran exclusively gave the 4-(1*H*-pyrrol-1-yl)benzamide **3an** in high yield. Subjecting aromatic

**Table 3**  
Synthesis of *N*-substituted pyrroles **3**.

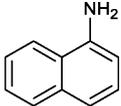
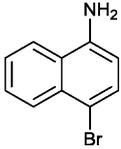
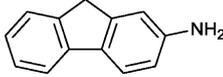
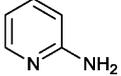
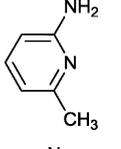
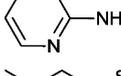
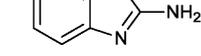
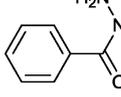
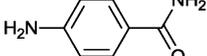
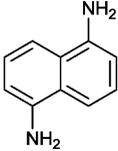
Entry	Amine	Product	Time (min)	Yield (%) <sup>a</sup>	m.p. (°C)
1	PhNH <sub>2</sub>	<b>3a</b>	40	95	60–61 (61–62) [26]
2	3-OHC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3b</b>	60	93	62–63 (63–64) [48]
3	2-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3c</b>	40	85	Oil [26]
4	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3d</b>	30	96	111–112 (112–113) [26]
5	4-OEtC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3e</b>	25	96	70–71
6	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3f</b>	40	89	Oil [31]
7	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3g</b>	30	94	82–83 (81–82) [26]
8	3,4-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	<b>3h</b>	65	96	50–51
9	2,5-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	<b>3i</b>	70	90	52–53 (50–51) [49]
10	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	<b>3j</b>	80	87	46–47 (45–46) [26]
11	2,6- <sup>i</sup> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	<b>3k</b>	100	75	76–77 (75–77) [26]
12	4- <sup>t</sup> BuC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3l</b>	90	92	70–72 (68–72) [50]
13	2-FC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3m</b>	90	81	Oil [51]
14	4-FC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3n</b>	80	82	51–52 (50.6–51.7) [31]
15	2,4-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	<b>3o</b>	80	85	Oil [31]
16	3,4-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	<b>3p</b>	70	90	62–63
17	3-ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3q</b>	60	86	51–52 (50–51) [26]
18	4-ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3r</b>	60	87	87–88 (88–89) [26]
19	3-Cl-4-MeC <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	<b>3s</b>	50	92	49–50
20	3-Cl-4-FC <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	<b>3t</b>	60	89	67–68
21	2,4,5-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> NH <sub>2</sub>	<b>3u</b>	90	88	95–97
22	2-BrC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3v</b>	90	82	Oil [26]
23	3-BrC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3w</b>	90	85	81–82 (81–83) [52]
24	4-BrC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3x</b>	60	88	93–94 (92) [25]
25	4-IC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3y</b>	60	89	129–131 (130–131) [30]
26	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3z</b>	80	80	Oil [26]
27	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3aa</b>	60	85	187–188 (187–188) [26]
28	4-AcC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3ab</b>	50	89	120–120 (119–121) [53]
29	3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3ac</b>	60	84	48–49 (49.7–50.0) [31]
30	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3ad</b>	60	83	112–113 (112–114) [54]
31	4-COOEtC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3ae</b>	55	90	76–77 (73) [53]
32		<b>3af</b>	60	93	Oil [26]
33		<b>3ag</b>	60	95	Oil
34		<b>3ah</b>	70	93	201–202
35		<b>3ai</b>	120	71	Oil [31]
36		<b>3aj</b>	120	70	Oil
37		<b>3ak</b>	80	85	83–84 (81–82) [30]
38		<b>3al</b>	90	80	129–130
39		<b>3am</b>	70	90	178–179
40		<b>3an</b>	50	92	256
41		<b>3ao</b>	100	94	80–82 (79–80) [26]

Table 3 (Continued)

Entry	Amine	Product	Time (min)	Yield (%) <sup>a</sup>	m.p. (°C)
42		<b>3ap</b>	100	55 <sup>b</sup>	205–206

<sup>a</sup> Isolated yield.

<sup>b</sup> 2 equivalents of tetrahydro-2,5-dimethoxyfuran was used and bis-pyrrole was obtained.

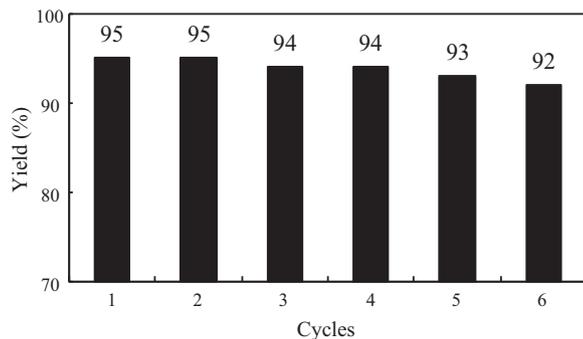


Fig. 6. Reusability of catalyst.

diamine to the optimized condition described above, the monopyrroles **3ao** were selectively formed in 94% yield. When naphthalene-1,5-diamine reacted with 2 equivalents of tetrahydro-2,5-dimethoxyfuran, the corresponding bis-pyrrole **3ap** was obtained. However, the reaction failed when more basic aliphatic amines such as cyclohexanamine and benzylamine were used under these conditions, resulting in the recovery of the starting materials.

#### 3.4. Recyclability of the catalyst

To verify whether or not the catalysis is truly heterogeneous or is due to some leached active species present in the liquid phase, the model reaction of aniline and tetrahydro-2,5-dimethoxyfuran was carried out under the optimized conditions, and the catalyst was separated by applying external magnetic field from the reaction mixture at 60% formation of **3a**. After removal of the catalyst, the solution was again stirred for 1 h, no further product formation was observed. Inductively coupled plasma mass spectrometry (ICP-MS) analysis showed that the amount of Sb leaching into the reaction mixture is very low (0.3 ppm). No quantifiable amount of leached Fe was detected in the filtrates. These studies demonstrated that only the Sb bound to support was active and the reaction proceeded on the heterogeneous surface. The recyclability of catalyst was examined using the model reaction under identical conditions. After the required time, the catalyst was recovered from the reaction mixture by magnetic separation, washed with ethyl acetate, and subsequently dried at 100 °C then reused. After six consecutive reuses, the catalyst exhibited almost identical catalytic activity (Fig. 6). Furthermore, the TEM images of the catalyst after six recycles did not show noticeable change in the shape and size of catalyst particles compared to fresh  $\gamma\text{-Fe}_2\text{O}_3/\text{SiO}_2\text{-Sb-IL}$ .

#### 4. Conclusion

In summary, we have proposed a facile approach to prepare magnetic nanoparticle-supported antimony catalyst ( $[\gamma\text{-Fe}_2\text{O}_3/\text{SiO}_2\text{-Sb-IL}]$ ), which exhibited excellent catalytic efficiency in Clauson-Kaas reaction of amines to 2,5-dimethoxy-tetrahydrofuran in aqueous medium. The catalyst is easily

prepared, stable to air and magnetically recoverable by simple magnetic decantation. The catalytic activity of the catalyst remains unaltered after six consecutive cycles. Work is in progress to develop novel magnetically separable heterogeneous catalysts and study their application in the fields of organic synthesis, industrial production, and green chemistry.

#### Acknowledgments

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