

# Nanosized sulfated zirconia as solid acid catalyst for the synthesis of 2-substituted benzimidazoles

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The condensation reaction of o-phenylenediamine and arylaldehydes was investigated in the presence of nanosized sulfated zirconia (SO<sub>4</sub><sup>2-</sup>-ZrO<sub>2</sub>) as the solid acid catalyst. Nanosized SO<sub>4</sub><sup>2-</sup>-ZrO<sub>2</sub> was prepared and characterized by the XRD, FT-IR, and SEM techniques. The results confirm good stabilization of the tetragonal phase of zirconia in the presence of sulfate. Reusability experiments showed partial deactivation of the catalyst after each run; good reusability can be achieved after calcinations of the recovered catalyst before its reuse.

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## Introduction

Benzimidazoles and their derivatives have received considerable attention due to their broad spectrum of biological and pharmaceutical activities. These compounds have found applications in diverse therapeutic areas as antitumour (Denny et al., 1990), antiparasitic (Valdez et al., 2002), antimicrobial (Fonseca et al., 2001), antiviral (Song et al., 2005), and antifungal (Katritzky et al., 1998) agents. Moreover, these compounds are important intermediates in many organic reactions (Hasegawa et al., 1999) and can also act as ligands of transition metals for modeling biological systems (Fekner et al., 2004).

There are two general methods for the synthesis of benzimidazoles including the condensation of *o*-phenylenediamines with carboxylic acids (Dudd et al., 2003), nitriles (Hein et al., 1957), acid halides (Nadaf et al., 2004), and orthoesters (Mohammadpoor-Baltork et al., 2007; Karami et al., 2012) in the presence of strong acids as the catalyst, and the condensation of *o*-phenylenediamines and aldehydes (Abdollahi-Alibeik & Moosavifard, 2010) in the presence of various acid catalysts at elevated temperatures. The latter method involves two steps that include the formation of a Schiffs base and then oxidative cyclocondensation.

Recently, a variety of catalysts have been used in the condensation reaction of *o*-phenylenediamines and aldehydes including: FeCl<sub>3</sub>-dopped polyaniline (Abdollahi-Alibeik & Moosavifard, 2010), FeCl<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> (Chen & Dong, 2012), molecular iodine (Ponnala & Prasad Sahu, 2006), L-proline (Varala et al., 2007), Zn<sup>2+</sup>-K10-clay (Dhakshinamoorthy et al., 2011), polyaniline sulfate (Srinivas et al., 2007), MnAl<sub>2</sub>O<sub>3</sub> (Rekha et al., 2012), and sodium hydrogen sulfite (Lopez et al., 2009).

Although these methods are suitable under certain synthesis conditions, sometimes, some drawbacks such as long reaction times, low yields of the products, the use of an excess amount of the catalyst and co-occurrence of several side reactions occur. Therefore, development of new catalytic systems for this transformation, which are superior to the existing catalysts regarding toxicity, handling, and reusability, is required.

In recent years, the interest in the replacement of traditional environmental hazardous and homo-

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Fig. 1. 2-Arylbenzimidazoles preparation by the condensation reaction of arylaldehydes with *o*-phenylenediamine.

geneous catalysts by heterogeneous solid acid catalysts in organic transformations has been growing. This is mainly due to the advantages of solid acids such as the ease of handling, non-toxicity, non-corrosiveness, simple work-up, and reusability of the catalysts (Abdollahi-Alibeik & Heidari-Torkabad, 2012; Adam et al., 2012; Wolfson et al., 2009).

Further to our recent studies on the synthesis of heterocyclic compounds (Abdollahi-Alibeik & Heidari-Torkabad, 2012; Abdollahi-Alibeik & 2008; Abdollahi-Alibeik & Pouriayevali, 2011, 2012; Abdollahi-Alibeik & Zaghaghi, 2009), in this paper, we wish to report on the application of sulfated zirconia,  $SO_4^{2-}$ -ZrO<sub>2</sub> (SZ), nanoparticles as a solid acid catalyst in the condensation reaction of arylaldehydes with *o*-phenylenediamine in order to synthesize 2-arylbenzimidazoles (Fig. 1).

#### Experimental

All chemicals were commercial products (Merck, Germany). All reactions were monitored by TLC and all yields refer to isolated products. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in DMSO- $d_6$  on a Bruker (DRX-500 AVANCE) 500 MHz spectrometer (Bruker, Germany) and are reported in ppm related to TMS. Infrared spectra of the catalysts and reaction products were recorded on a Bruker FT-IR Equinax-55 spectrophotometer (Bruker, Germany) in KBr with the absorption in cm<sup>-1</sup>. XRD patterns were recorded on a Bruker CuK<sub> $\alpha$ </sub> radiation. Morphology of nanoparticles was studied using a Philips XL30 scanning electron microscope (Philips, The Netherlands).

#### Preparation of sulfated zirconia (SZ)

 $ZrCl_4$  (1.4 g) was dissolved in deionized water (50 mL) and to this clear solution, dilute aqueous ammonia (NH<sub>4</sub>OH, 5 mass %) was added drop-wise under vigorous stirring until the pH of the solution reached 9.5. The obtained  $Zr(OH)_4$  gel was stirred for 24 h, centrifuged, washed with distilled water to remove chloride ions and dried at 120 °C for 12 h. The uncalcined hydroxide gel ( $Zr(OH)_4$ ) was sulfated by stirring in concentrated H<sub>2</sub>SO<sub>4</sub> (1 M, 15 mL g<sup>-1</sup>) for 24 h. The solid was separated by centrifugation and washed with water, dried at 120 °C for 4 h and calcined at 600  $^{\circ}\mathrm{C}$  for 4 h to obtain sulfated zirconia nanoparticles.

# Typical procedure for 2-arylbenzimidazoles synthesis

o-phenylenediamine А mixture containing (1 mmol), ethanol (3 mL), and sulfated zirconia (100 mg) was put in a 10 mL round bottom flask. To this suspension, a solution containing aldehyde (1 mmol) in ethanol (2 mL) was added drop-wise and the suspension was stirred at 50 °C for an appropriate period of time. After the reaction completion (monitored by TLC, eluent: EtOAC : hexane,  $\varphi_{\rm r} = 1 : 1$ ), EtOH (5 mL) was added and the solid catalyst was separated by centrifugation. To the obtained solution, water (9 mL) was added and the precipitated product was filtered. Crude products of high purity were obtained. Further purification was achieved by recrystallization from an EtOH-H<sub>2</sub>O solution ( $\varphi_r = 3:1$ ).

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2-(3-Chlorophenyl)benzimidazole, (*IIIc*): M.p. 230–232 °C (Chen & Dong, 2012); 232–233 °C; IR (KBr)  $\tilde{\nu}$ /cm<sup>-1</sup>: 1442 (C=C aromatic), 1572; <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ),  $\delta$ : 7.20–7.27 (dd, 2 H, J = 14.89Hz, J = 8.32 Hz), 7.55–7.61 (m, 3 H), 7.70 (t, 1 H, J =7.71 Hz), 8.16 (dd, 1 H, J = 7.32 Hz, J = 1.30 Hz), 8.23 (t, 1 H, J = 1.58 Hz), 13.03 (s, 1 H, NH); <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ),  $\delta$ : 112.4, 119.9, 122.8, 123.8, 125.9, 126.9, 130.4, 131.8, 133.1, 134.6, 135.9, 144.5, 150.6.

2-(2-Furyl)benzimidazole (*IIIk*): M.p.: 300 °C (Du & Wang, 2007); 288 °C; IR (KBr)  $\tilde{\nu}/\text{cm}^{-1}$ : 1620 (C—N), 3400 (NH); <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ),  $\delta$ : 6.72–6.73 (m, 1 H), 7.18–7.22 (m, 3 H), 7.56 (d, 2 H, J = 3 Hz), 7.94 (d, 1 H, J = 1 Hz), 12.97 (s, 1 H); <sup>13</sup>C NMR (125.7 MHz, <sup>1</sup>H-decoupled),  $\delta$ : 111.35, 113.15, 123.03, 144.53, 145.45, 146.48.

#### **Results and discussion**

#### Catalyst preparation

The preparation of sulfated zirconia can proceed by the two-step sol-gel process. In general, this process involves the formation of a sol by the hydrolysis of zirconium alkoxide as a zirconia precursor and a threedimensional network gel of zirconium hydroxide after the condensation in the first step. This is followed by the sulfation with sulfuric acid or ammonium sulfate for the preparation of sulfated zirconia in the second step (Reddy & Patil, 2009).

In the present study,  $ZrCl_4$  was used as the precursor of zirconia. The hydrolysis of  $ZrCl_4$  was carried out in aqueous media with pH adjusted up to 9.5 by



Fig. 2. SEM Image of ZrO<sub>2</sub>.



Fig. 3. FT-IR spectra of  $ZrO_2$  (a) and  $SO_4^{2-}$ -ZrO<sub>2</sub> (b).

additions of an ammonia solution. Sulfated zirconia was prepared by sulfation of dried  $Zr(OH)_4$  using 1 M  $H_2SO_4$  (15 mL g<sup>-1</sup>) and calcination of the dried solid at 600 °C for 4 h.



Fig. 4. XRD patterns of  $SO_4^{2-}$ -ZrO<sub>2</sub> calcined at 600 °C (a) and ZrO<sub>2</sub> cacined at 600 °C (b).

#### Catalyst characterization

Particle morphology of the prepared SZ was studied by scanning electron microscopy (Fig. 2). The SEM image shows agglomerated  $ZrO_2$  nanoparticles with the size up to 100 nm.

The presence of sulfate in the structure of the catalyst was confirmed by FT-IR spectroscopy. FT-IR spectra of  $ZrO_2$  and SZ are shown in Fig. 3, where line a, the FT-IR spectrum of SZ, exhibited characteristic peaks of sulfate at 1244 cm<sup>-1</sup>, 1136 cm<sup>-1</sup>, 1082 cm<sup>-1</sup>, and 1043 cm<sup>-1</sup>, which are attributed to asymmetric and symmetric stretching frequencies of partially ionized double bond SO and single bond SO, due to the presence of an inorganic chelating bidentate sulfate group in the  $ZrO_2$  structure (Tyagi et al., 2007).

It is well known from literature that the tetragonal phase of zirconia is more active in the catalytic process (Yamaguchi, 1994). The powder X-ray diffraction technique was used to describe the crystalline phase and the effect of sulfate on the phase change of zirconia (Fig. 4). XRD pattern of ZrO<sub>2</sub> exhibited characteristic peaks of both tetragonal and monoclinic phases (Fig. 4, line a) while that of SZ showed only characteristic peaks of the tetragonal phase at  $2\theta = 30^{\circ}, 35^{\circ},$  $50^{\circ}, 60^{\circ}$ . This indicates that sulfate affects the phase modification and stabilizes zirconia in the tetragonal phase. This result is in agreement with literature (Negrón et al., 2005).

Entry	Catalyst amount	Solvent	Temperature	Time	Yield	
	mg		°C	min	%	
1	100	EtOH	r.t.	45	10	
2	100	EtOH	reflux	30	65	
3	100	EtOH	50	45	77	
4	25	EtOH	50	70	42	
5	50	EtOH	50	60	65	
6	75	EtOH	50	50	70	
7	150	EtOH	50	30	79	
8	100	$CH_3CN$	50	45	65	
9	100	$CHCl_3$	50	45	35	
10	100	$CH_2Cl_2$	50	45	60	
11	100	-	50	45	10	

Table 1. Optimization of the catalytic amount of  $SO_4^{2-}$ -ZrO<sub>2</sub> in the synthesis of benzimidazole

#### Catalyst activity

To investigate the performance of  $SO_4^{2-}-ZrO_2$  in the synthesis of benzimidazoles, the reaction of benzaldehyde with *o*-phenylenediamine was selected as the model reaction. The effect of different amounts of catalysts and different reaction temperatures on the reactivity of  $SO_4^{2-}-ZrO_2$  was investigated and the results are shown in Table 1 (entries 1–7). To investigate the effect of the solvent on the catalytic reaction, the model reaction was carried out in the presence of 100 mg of SZ in various solvents and under solventfree conditions (Table 1). The results show that EtOH is the best solvent in terms of time and yield of the product (Table 1, entries 3, 8–11), it is also suitable in regard to environmental considerations, and thus it was selected as the solvent for the reaction.

As can be seen from Table 1 (entry 3), the best reaction conditions were provided by the model with the molar ratio of aldehyde : diamine of 1 : 1 in the presence of 100 mg of  $SO_4^{2-}$ -ZrO<sub>2</sub> in EtOH as the solvent at 50 °C.

Considering the optimization results, the reaction of 1 mmol of benzaldehyde and 1 mmol of o-phenylenediamine in the presence of 100 mg of  $SO_4^{2-}$ -ZrO<sub>2</sub> in EtOH at 50 °C was carried out and 2-phenylbenzimidazole was obtained in a 77 % yield (Table 2, entry *a*). In order to investigate the scope and generality of this method, the reaction of various types of arylaldehydes with both electron-donating and electron-withdrawing substituents were carried out at the same reaction conditions and the corresponding 2-arylbenzimidazoles were obtained in 68– 93 % yields. This method was also successfully used for the synthesis of heteroaryl benzimidazoles and bisbenzimidazoles using the heteroaryl aldehydes and bisaldehyde as starting materials.

Work-up of the reaction is very easy. After the completion of the reaction (monitored by TLC, eluent; hexane : EtOAc,  $\varphi_{\rm r} = 2 : 1$ ), the catalyst was separated by centrifugation and the solid was washed by EtOH. The solution was poured onto crushed ice and the product precipitated after a few minutes. Crude products with high purity were obtained by filtration of the mixture.

To study the reusability of the catalyst, the recovered catalyst after used in the reaction of benzaldehyde and o-phenylenediamine was reused in the same reaction. The recovered catalyst for the model reaction was washed with EtOH and dried in an oven at  $120 \,^{\circ}$ C for 2 h. The results show that the catalyst activity decreased after the first and the second runs (Table 3, runs 2 and 3). These results suggest that the deactivation is caused by a blockage of active sites of the catalyst. The catalyst recovered after the third run was calcined at 600  $^{\circ}$ C for 2 h and reused in the fourth run. The results show that the catalyst activity increased to nearly the same value as that of the fresh catalyst (Table 3, run 4). This result is consistent with a previous report (Negrón et al., 2005).

It is noticeable that experiments on the reusability of SZ prepared using different methodologies showed the same results as those for SZ employed in this work. The yield differences between the first, second, and third run in the reusability experiment are higher than those reported in some other studies on the SZ reusability in various reactions such as esterification of acetic acid (Yu et al., 2012), synthesis of 7-isopropyl-1,1-dimethyltetralin by the rearrangement of (+)-longifolene (Tyagi et al., 2009) and Mannich-type reactions between ketene silvl acetals and aldimines (Du & Wang, 2007). However, different results on the decrease in the catalytic activity after the reuse may be due to the different reaction media and conditions. Although an exact reusability study was employed for the model reaction, SZ in the other reactions including different aldehydes showed a decrease in its activity after the first run. This decrease in the activity is different for various aldehydes.

Entre	Aldebude (I)	Densimidarala (III)	Time	Yield
Entry	Aldenyde (1)	benzimidazoie (III)	min	%
a	CHO		45	77
b	CHO		50	76
С	CI		55	74
d	CI CHO		50	73
e	CHO	$H_{N} \to H_{HO}$	150	74
f	носно	С N N OH	120	76
$g^a$	O <sub>2</sub> N CHO	$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\$	60	97
$h^a$	O <sub>2</sub> N CHO	$N$ $N$ $NO_2$	180	93
i	H <sub>3</sub> C	$H \rightarrow CH_3$	40	79
j	H3CO CHO	$\underset{N}{\overset{H}{\longrightarrow}} OCH_{3}$	50	70
k	CHO CHO		60	69
l	CHO CHO	N N N N N N N N N N N N N N N N N N N	120	68
m	OHC	$ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	70	84

Table 2. Synthesis of benzimida zoles by the reaction o-phenylenediamine and benzal dehyde in the presence of the catalytic amount of  $SO_4^{2-}$ -ZrO<sub>2</sub>

a) Reactions were performed under reflux condition.

### Conclusions

In conclusion, a mild, convenient and efficient

method for the synthesis of 2-substituted benzimidazoles by the reaction of aldehydes with ophenylenediamine using the catalytic amount of

Dun	Time	Yield	
Itun	min	%	
1	45	77	
2	60	69	
3	70	67	
$4^a$	55	72	

**Table 3.** Reusability of  $SO_4^{2-}$ -ZrO<sub>2</sub> in the reaction of *o*-phenylenediamine and benzaldehyde

a) Catalyst was calcined at 600 °C for 2 h before use.

 $SO_4^{2-}$ -ZrO<sub>2</sub> in EtOH as the solvent was introduced. The mild reaction conditions, simple experimental procedure, the ease of the catalyst recovery, as well as the reusability of the catalyst are some of the advantages of this method.

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