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SHORT COMMUNICATION

## Synthesis of Benzimidazole Using Reusable Nanocatalyst Zirconia and Sulfated Zirconia

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### ABSTRACT

Benzimidazole derivatives have been synthesized by solid Nanocatalysts Zirconia and Sulfated Zirconia with Green reusability method. Synthesis of benzimidazole was carried out by conventional as well as microwave method. Synthesis carried out by reacting o-phenylenediamine and few aldehydes in the presence of catalytic amount of Nanoparticles. Particles used were sized in between 53-100 nm. Nanoparticles and synthesized benzimidazole derivatives were characterized by DLS, powder XRD, SEM-EDX and Mass, CHNS, FT-IR, NMR analysis respectively.

**Keywords:** Nanocatalyst, Sulfated Zirconia, Benzimidazole, Reusable

### 1. INTRODUCTION

Nanoparticles as catalyst have large surface area compared to macro particles<sup>[1]</sup>. Only molecules on the surfaces are in direct contact with the reactant molecules<sup>[2]</sup>. The macro particles have large number of internal molecules and are not capable to attain direct contact with the reactant molecules<sup>[3,4]</sup>. Larger the surface area of Nanoparticles, more efficiently the

number of moles of reactants get reacted, which yields more number of moles of product. While light weight nanoparticles are very smaller in size, so they can float and/or reach to the each part of the vessel<sup>[5]</sup>. This makes the reaction mixture homogeneous. However, insolubility in reaction solvents renders them easily separable from the reaction mixture, which resembles a heterogeneous catalyst<sup>[6]</sup>. Hence, the rate of reaction enhances effectively and Dual natured Nanoparticles with larger surface area, smaller size and light in weight make them beneficiary as catalyst<sup>[7,8]</sup>. Metal and their oxide dominate the vast panorama of heterogeneous catalyst. Zirconia Nanoparticle are widely used for organic synthesis for various Coumarin derivatives<sup>[9]</sup>. Benzimidazole derivatives<sup>[10-12]</sup>, Pyrrole derivatives<sup>[13,14]</sup>, Benzodiazepine derivatives<sup>[15,16]</sup>, and Dihydropyrimidine derivatives with Biginelli reaction<sup>[17,18]</sup>, Hantzsch reaction, Cyclodehydration<sup>[19]</sup>, Aldol synthesis<sup>[20]</sup>, Friedel-Crafts acylation<sup>[21]</sup>, Prins condensation reaction<sup>[22]</sup>. In this current work, we have synthesized Nano zirconium dioxide ( $ZrO_2$ ) and sulfated zirconia ( $SO_4^{2-} ZrO_2$ ) (SZ). Both nanoparticles were studied for its catalytic activity to synthesis benzimidazole derivatives. We found that Nano  $ZrO_2$  and Nano SZ both are reusable till 3-4 times with increase in product. In particular, characterization we found that, in DLS, Nano  $ZrO_2$  and Nano SZ were nearly similar in size and were about 100 nm. From Powder XRD, we found that, geometrical structure of Nano  $ZrO_2$  and Nano SZ was monoclinic and tetragonal respectively.

## 2. RESULT / EXPERIMENTAL

Thin-layer chromatography was accomplished on 0.2 mm pre-coated plates of silica gel G60 F254 (Merck). IR spectra were recorded on a FTIR-8400 spectrophotometer using DRS prob.  $^1H$  (400 MHz) and  $^{13}C$  (100 MHz) NMR spectra were recorded on a Bruker ADVANCE II spectrometer in DMSO- $d_6$ . Chemical shifts are expressed in  $\delta$  ppm downfield from TMS as an internal standard. Solvents were evaporated with a BUCHI rotary evaporator. Melting points were measured in open capillaries and are uncorrected. X-Ray diffraction (XRD) measurements were performed on the XPERT-MPD by an X-Ray diffractometer using Cu  $K\alpha$  radiation source ( $\lambda = 1.5418$ ) at power 200 kW. XRD Crystallite Size calculation was done using Scherrer equation from powder XRD data. Particle size measurements were carried out on DLS Nanotrak of Microtrac Europe GmbH. Domestic microwave was used at 400w. Preparation of Zirconia and Sulfated Zirconia were adapted<sup>[23,24]</sup> and modified.

### 2. 1. Preparation of zirconia catalyst

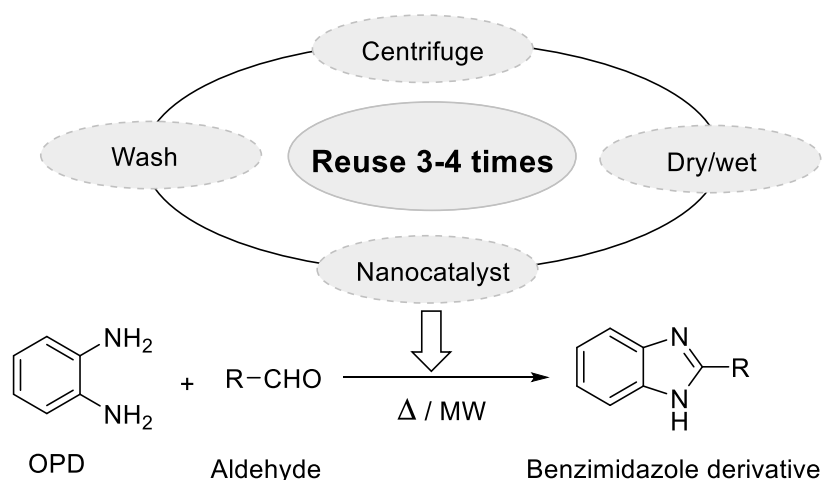
Hydrated Zirconium oxychloride was dissolved in water then added ammonium hydroxide till solution become basic. The precipitate obtained was filtered. Zirconium-hydroxide gel was dried in oven then formed solid was crushed. The fine powder was calcinated at 600 °C for 4 hours. The particle obtained were stored in cold and anhydrous environment.

### 2. 2. Preparation of Sulfated-Zirconia

Previously prepared Zirconium hydroxide was acidified with 0.1M sulfuric acid then stirred for 24 hour then centrifuged and dried in oven then formed solid was crushed. The fine powder was calcinated at 600 °C for 4 hour. The particle obtained were stored in cold and anhydrous environment.

### 2. 3. General procedure for synthesis of Benzimidazoles

A mixture of o-phenylenediamine (0.1 mole), different benzaldehyde (0.1 mole), methanol (25 ml) was taken in round bottom flask. Sulfated zirconia or zirconia in catalytic amount (0.02 gm) added and refluxed reaction mixture in oil bath. All reactions were monitored by TLC (in-Chloroform:Metahnol = 9.5:0.5). After completion of reaction the nanoparticles were recovered by adding dichloromethane (10 ml) and then centrifuged in high RPM until nanoparticles were settled in bottom. Washed nanoparticles 2-3 times with dichloromethane and nanoparticles were reused in reaction after wet/dried at 600 °C. Similarly reactions were carried out in microwave



**Scheme 1.** Synthetic scheme.

**Table 1.** Physical Data of Synthesized Benzimidazole derivatives

Sr. No.	Aldehyde	Product	Melting point °C	RF value	ZrO <sub>2</sub>				Sulfated ZrO <sub>2</sub>			
					Yield <sup>1</sup> %		Time (In min)		Yield <sup>1</sup> %		Time (In min)	
					Δ	MW	Δ	MW	Δ	MW	Δ	MW
1	4-Hydroxy Benzaldehyde	PBF-1	110-114	0.17	76	82	40	10	85	86	40	10
2	4-Chloro Benzaldehyde	PBF-2	240	0.57	68	70	45	10	72	76	45	10
3	4-Methoxy Benzaldehyde	PBF-3	146-150	0.65	64	68	45	10	72	80	45	12
4	2,6-Dichloro Benzaldehyde	PBF-4	108-110	0.62	68	70	45	10	64	70	45	12
5	4-N,N'-Dimethylaminebenz aldehyde	PBF-5	238	0.66	72	76	45	10	80	86	40	10

6	2-Nitro benzaldehyde	PBF-6	234-238	0.72	76	82	45	10	85	94	45	10
7	2-Hydroxy benzaldehyde	PBF-7	206-210	0.31	80	86	40	10	88	90	40	10
8	4-Floro benzaldehyde	PBF-8	212-216	0.67	70	74	45	15	76	70	45	10
9	5-Bromo 2-Hydroxy benzaldehyde	PBF-9	178-180	0.62	68	72	45	15	74	80	40	10
10	Formaldehyde	PBF-10	170-174	0.66	70	76	40	10	88	90	40	10

<sup>1</sup>\* yield % isolated by crystallization in dichloromethane.

<sup>2</sup>(Chloroform:Metahnol = 9.5:0.5)

## 2. 4. Spectral data of the synthesized compounds

### PBF-1

Elemental Analytical Calculation for C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>O (210 g/mol): C, 74.27%; H, 4.79%; N, 13.33%; Found: C, 74.29%; H, 4.80%; N, 13.34%; IR (KBr, cm<sup>-1</sup>): ν(Ar-CH str) 3022; ν(Ar-CH ben) 1606; ν(Ar-C=C) 1506; ν(NH str) 2750; ν(NH ring str) 1448; ν(NH ring ben) 839; ν(OH str) 3304; ν(OH ben) 1246; <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>): δppm 4.03 (s, 1H, OH); 6.921-6.929 (dd, 2H, Ar-H); 7.244-7.262 (m, 2H, Ar-H); 7.474-7.478 (d, 2H, Ar-H); 7.530 (s, 1H, NH); 7.571-7.580 (m, 3H, Ar-H); <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>): δppm 115.12, 116.23, 118.49, 120.95, 123.33, 123.62, 126.96, 137.50, 137.69, 150.30, 160.73 (Ar-C);

### PBF-2

Elemental Analytical Calculation for C<sub>13</sub>H<sub>9</sub>ClN<sub>2</sub> (228 g/mol): C, 68.28%; H, 3.97%; N, 12.25%; Found: C, 68.26 %; H, 3.96%; N, 12.24%; IR (KBr, cm<sup>-1</sup>): ν(Ar-CH str) 3061; ν(Ar-CH ben) 1606; ν(Ar-C=C) 1595; ν(NH str) 2785; ν(NH ring str) 1492; ν(NH ring ben) 829; ν(C-Cl) 740; <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>): δppm 7.241-7.301 (m, 2H, Ar-H); 7.425-7.470 (d, 2H, Ar-H); 7.529 (s, 1H, NH); 7.551-7.597 (d, 2H, Ar-H); 7.599-7.643 (d, 2H, Ar-H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>): δppm 115.12, 118.49, 123.33, 123.62, 128.15, 129.55, 134.50, 134.54, 137.50, 137.69, 150.30 (Ar-C);

### PBF-3

Elemental Analytical Calculation for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O (224 g/mol): C, 74.98%; H, 5.39%; N, 12.49%; Found: C, 74.96%; H, 5.38 %; N, 12.48 %; IR (KBr, cm<sup>-1</sup>): ν(Ar-CH str) 3057; ν(Ar-CH ben) 1608; ν(Ar-C=C) 1508; ν(NH str) 2835; ν(NH ring str) 1384; ν(NH ring ben) 1028; ν(CH<sub>3</sub> str) 2835; ν(OCH<sub>3</sub> ben) 1467; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δppm 3.750 (s, 3H, CH<sub>3</sub>); 5.298 (s, 1H, NH); 6.760-6.861 (d, 1H, Ar-H); 6.937-7.069 (dd, 2H, Ar-H); 7.131-7.210 (m, 2H, Ar-H); 7.536-7.557 (d, 1H, Ar-H); 7.745-7.764 (d, 1H, Ar-H); 7.963-7.984 (d, 1H, Ar-H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δppm 55.38 (O-CH<sub>3</sub>); 119.65, 122.35, 122.58, 122.78, 127.22, 128.45, 128.49, 130.70, 154.15, 160.90, 161.07 (Ar-C);

### PBF-4

Elemental Analytical Calculation for C<sub>13</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>2</sub> (263 g/mol): C, 59.34%; H, 3.06%; N, 10.65%; Found: C, 59.36%; H, 3.07; N, 10.66%; IR (KBr, cm<sup>-1</sup>): ν(Ar-CH str) 3066; ν(Ar-CH ben) 1616; ν(Ar-C=C) 1589; ν(NH str) 3022; ν(NH ring str) 1431; ν(NH ring ben) 773; ν(C-CL) 738; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δppm 6.699-6.726 (m, 2H, Ar-H); 7.060-7.157 (m, 2H, Ar-H); 7.197-7.223 (t, 1H, Ar-H); 7.238-7.276 (d, 2H, Ar-H); 7.231 (s, 1H, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>):

$\delta$ ppm 118.34, 120.30, 128.18, 128.67, 130.47, 131.47 (Ar-C); 132.31, 135.26 (Ar-C-Cl); 136.17, 153.12 (Ar-C);

#### **PBF-5**

Elemental Analytical Calculation for  $C_{15}H_{15}N_3$  (237 g/mol): C, 75.92%; H, 6.37%; N, 17.71%; Found: C, 75.94%; H, 6.38%; N, 17.72%; IR (KBr,  $cm^{-1}$ ):  $\nu$ (Ar-CH str) 3018;  $\nu$ (Ar-CH ben) 1599;  $\nu$ (Ar-C=C) 1492;  $\nu$ (NH str) 2897;  $\nu$ (NH ring str) 1531;  $\nu$ (NH ring ben) 812;  $\nu$ (N-(Me)<sub>2</sub> str) 3464;  $\nu$ (N-(Me)<sub>2</sub> ben) 1367; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$ ppm 2.937 (s, 6H, N(Me)<sub>2</sub>); 6.581-6.675 (m, 4H, Ar-H); 6.912-6.943 (d, 2H, Ar-H); 7.685-7.707 (d, 2H, Ar-H); 8.302 (s, 1H, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ ppm 40.24 (CH<sub>3</sub>); 116.75, 117.25, 118.52, 120.26, 122.11, 126.49, 127.79, 134.78, 152.38, 141.86 (CH<sub>3</sub>);

#### **PBF-6**

Elemental Analytical Calculation for  $C_{13}H_9N_3O_2$  (239 g/mol): C, 65.27%; H, 3.79%; N, 17.56%; Found: C, 65.25 %; H, 3.78 %; N, 17.55%; IR (KBr,  $cm^{-1}$ ):  $\nu$ (Ar-CH str) 3086;  $\nu$ (Ar-CH ben) 1527;  $\nu$ (Ar-C=C) 1444;  $\nu$ (NH str) 2748;  $\nu$ (NH ring str) 1417;  $\nu$ (NH ring ben) 970;  $\nu$ (NO<sub>2</sub> str) 1350; <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>):  $\delta$ ppm 4.060 (s, 1H, OH); 7.221-7.305 (m, 3H, Ar-H); 7.543-7.773 (m, 2H, Ar-H); 7.790-7.825 (d, 1H, Ar-H); 7.860 (d, 1H, Ar-H); 7.532 (s, 1H, NH); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$ ppm 106.43, 115.12, 118.49, 119.15, 121.38, 123.33, 123.62, 127.74, 137.50, 137.69, 147.26, 151.41, 162.10(Ar-C);

#### **PBF-7**

Elemental Analytical Calculation for  $C_{13}H_{10}N_2O$  (210 g/mol): C, 74.27%; H, 4.79%; N, 13.33%; Found: C, 74.29%; H, 4.80 %; N, 13.34%; IR (KBr,  $cm^{-1}$ ):  $\nu$ (Ar-CH str) 3055;  $\nu$ (Ar-CH ben) 1597;  $\nu$ (Ar-C=C) 1492;  $\nu$ (NH str) 2700;  $\nu$ (NH ring str) 1456;  $\nu$ (NH ring ben) 839;  $\nu$ (OH str) 3331;  $\nu$ (OH ben) 11271; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$ ppm 6.386-6.409 (m, 1H, Ar-H); 6.409-6.433 (m, 1H, Ar-H); 7.012-7.076 (m, 2H, Ar-H); 7.118-7.121 (m, 2H, Ar-H); 7.239-7.243 (m, 1H, Ar-H); 7.304-7.372 (s, 1H, NH); 7.748-8.101 (m, 1H, Ar-H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ ppm 118.17, 122.03, 122.53, 122.61 (Ar-C); 127.41 (Ar-C-OH); 130.23, 132.03, 133.17 (Ar-C);

#### **PBF-8**

Elemental Analytical Calculation for  $C_{13}H_9FN_2$  (212 g/mol): C, 73.57%; H, 4.27%; N, 13.20%; Found: C, 73.55 %; H, 4.26%; N, 13.19 %; S, IR (KBr,  $cm^{-1}$ ):  $\nu$ (Ar-CH str) 3055;  $\nu$ (Ar-CH ben) 1599;  $\nu$ (Ar-C=C) 1498;  $\nu$ (NH str) 2712;  $\nu$ (NH ring str) 1440;  $\nu$ (NH ring ben) 837;  $\nu$ (C-F str) 1111; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$ ppm 7.228-7.257 (m, 2H, Ar-H); 7.256-7.264 (m, 2H, Ar-H); 7.338-7.360 (m, 2H, Ar-H); 7.486-7.535 (m, 2H, Ar-H); 7.751-7.759 (s, 1H, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ ppm 119.28, 122.17, 126.78, 131.40, 135.75, 140.34 (Ar-C);

#### **PBF-9**

Elemental Analytical Calculation for  $C_{13}H_9BrN_2O$  (289 g/mol): C, 54.00%; H, 3.14%; N, 9.69%; S, Found: C, 54.02%; H, 3.15%; N, 9.70%; IR (KBr,  $cm^{-1}$ ):  $\nu$ (Ar-CH str) 3066;  $\nu$ (Ar-CH ben) 1600;  $\nu$ (Ar-C=C) 1485;  $\nu$ (NH str) 2715;  $\nu$ (NH ring str) 1352;  $\nu$ (NH ring ben) 871;  $\nu$ (OH str) 3363;  $\nu$ (OH ben) 1224;  $\nu$ (Ar C-Br str) 582; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$ ppm 6.641 (s, 1H, Ar-H); 6.708-6.748 (t, 1H, Ar-H); 6.837-6.859 (d, 1H, Ar-H); 6.944-6.966 (m, 1H, Ar-H); 7.032-7.073 (m, 1H, Ar-H); 7.182 (s, 1H, NH); 7.354-7.382 (m, 1H, Ar-H); 7.437-7.443 (d, 1H, Ar-H); 13.004 (s, 1H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ ppm 116.16, 118.97(Ar-C); 119.13 (Ar-C-Br); 120.93, 134.19, 134.68, 135.61, 159.74, 166.48 (Ar-C);

**PBF-10**

Elemental Analytical Calculation for  $C_7H_6N_2$  (118 g/mol): C, 71.17%; H, 5.12%; N, 23.71%; Found: C, 71.15 %; H, 5.11%; N, 23.70%; IR (KBr,  $cm^{-1}$ ):  $\nu$ (Ar-CH str) 3009;  $\nu$ (Ar-CH ben) 1730;  $\nu$ (Ar-C=C) 1423;  $\nu$ (NH str);  $\nu$ (NH ring str) 1653;  $\nu$ (NH ring ben) 1033;  $^1H$ -NMR (DMSO- $d_6$ ):  $\delta$ ppm 7.210-7.243 (m, 2H, Ar-H); 7.530-7.533 (dd, 2H, Ar-H); 7.765 (s, 1H, Ar-H); 8.08 (s, 1H, NH);  $^{13}C$  NMR (DMSO- $d_6$ ):  $\delta$ ppm 114.01, 117.85, 121.71, 122.45, 137.02, 139.25, 144.34 (Ar-C).

**3. RESULT AND DISCUSSION**

Synthesized Nano particles were synthesized by solution gel method which is beneficiary in terms of bulk synthesis of Nano particles. This method was better because it is easy to handle and give a high yield. The shape of Nano zirconium dioxide particles found from powder XRD were monoclinic and of Nano sulfated zirconia (SZ) particles were tetragonal in shape.

The surface area and physical properties of solid Nano zirconium dioxide powder and Nano super acid sulfated zirconia particles were characterized by different spectroscopic method for example DLS and Powder-XRD. In particular, characterization we found that, in DLS, the size of nano zirconium dioxide was near about 100 nm, and the similar size of Nano sulfated zirconia was also found near 100 nm. Powder XRD study suggested average bulk size of crystalline particles and also confirms the geometrical structure pattern of Nano zirconium dioxide and sulfated zirconia. From Powder XRD we found that the average bulk size of Nano zirconium dioxide was ranging between the 53-59 nm and geometrical structure was monoclinic. While, the average bulk size of Nano SZ was ranging between the 53-59 nm and geometrical structure was tetragonal. From references, without any catalyst general reaction time for the synthesis of Benzimidazole was around 24 hour, but when we add little amount of  $ZrO_2$  powder reaction time was decreased to 90-100 minutes with increase in yield. While, Nano SZ shown very much better results and shown much decrease in time till 40-60 minutes and yield was high. The use of Nano particles of  $ZrO_2$  and SZ have minimized the reaction rate drastically and increase the practical yield. As well, Nanoparticles were easy to recover and reusable up till 3-4 time.

**3. 1. The statistics of Nano SZ and  $ZrO_2$  reusability****Table 2.** Reusability of Nano  $ZrO_2$  and Nano SZ.

Sr. No.	Nanocatalyst	Average Product	
		With Nano $ZrO_2$	With Nano SZ
1	1 <sup>st</sup> Run	80%	85%
2	2 <sup>nd</sup> Run	75%	80%
3	3 <sup>rd</sup> Run	70%	76%
4	4 <sup>th</sup> Run	65%	72%

After completion of reaction, rest of solution were treated with dimethyl chloride to dissolve organic part, then centrifuged the solution to recover the Nano particles and separated by decantation of solution. Particles were washed twice by cold dimethyl chloride and centrifuged before its further use. Each time after re-run, it's been noted that decrease in product is seen and based on average benzimidazole product found were generalized in percentile and shown in Table 2. In general, Nano SZ shows better reusability compared to Nano ZrO<sub>2</sub> in both microwave and conventional condition.

#### **4. CONCLUSIONS**

We were able to synthesize ZrO<sub>2</sub> and Sulfated ZrO<sub>2</sub> (SZ) Nanoparticles by Sol-Gel method. The nanoparticles were characterized by IR, Powder XRD and DLS. The sizes of Nanoparticles were found in the range of ~50 nm. The prepared Nanoparticles shows higher catalytic activity compared to other methods described. Synthesis of benzimidazole derivatives were characterized by Mass, FT-IR and NMR. However, using this SZ Nanoparticles shows greater reusability up till 3-4 times, hence SZ nanoparticles were beneficiary as catalyst.

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