p-Toluenesulfonic acid coated natural phosphate as an efficient catalyst for the synthesis of 2-substituted benzimidazole

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2-Substituted benzimidazoles are selectively synthesised in high yields *via* the condensation of *o*-phenylenediamine derivatives with aldehyde derivatives using catalytic amount of *p*-toluenesulfonic acid coated natural phosphate (NP/PTSA) under mild conditions. The use of NP/PTSA as a reusable catalyst makes this process simple, convenient, and environmentally friendly.

Keywords: benzimidazole, heterogeneous catalysis, natural phosphate, *p*-toluenesulfonic acid

Although some heterogeneous catalysts can be used in bulk or non-supported form, many involve materials that cannot be used directly without the aid of an additional material, termed a catalyst support.[1] Compared to conventional homogeneous acid catalysts, heterogeneous solid acids are more beneficial as they are adapted for large scale industrial processes.[2] Advantages of this approximation include simplicity in processing and handling, easy separation, high selectivity, reusability and environmentally safe disposal.[3,4]

The past decade has proved interesting in the field of the chemistry of benzimidazole.[5,6] It is one of the most promising moieties that are present in many clinically useful drugs. The antiviral activity of benzimidazole derivatives against human immunodeficiency retrovirus (HIV-1), hepatitis B virus (HBV), hepatitis C virus (HCV) as well as human respiratory syncytial virus (human RSV) has been evaluated.[7–10] Moreover, a huge market for commercially available benzimidazole-based drugs signifies the need to develop new and more environmentally friendly synthetic methods. The traditional synthesis of benzimidazoles requires the reaction between an *o*-phenylenediamine and a carboxylic acid or its derivatives (ortho-esters, nitriles, amidates) under severe dehydrating conditions.[3,4] Currently, a number of synthetic routes have been developed to bring out new reagents for the synthesis of benzimidazoles, for instance the reaction of *o*-phenylenediamine with aldehydes in the presence of acidic catalysts under various reaction conditions.[11–18] In recent years, different catalytic systems of various Lewis acids have been developed for the synthesis of benzimidazole, with different groups highlighting the advantages of their protocol over the other methods.[19] However, the main difficulties of these methods are the use of metals and expensive reagents, unsatisfactory yields and harsh reaction conditions.[20–25] Therefore, the search continues for a better catalyst for the synthesis of benzimidazoles, in terms of operational simplicity, economic viability and selectivity. In an effort to develop a new heterogeneous system, we have initiated a programme aimed at introducing natural phosphate (NP), as it is conveniently modified and can catalyse several organic transformations. Some examples include trans-esterification,[26] nucleoside derivatives,[27] Michael-addition,[28] Suziki reaction,[29,30] and *N*-alkylation of pyrimidines.[31]

In view of these observations, we report here the synthesis and characterisation of NP coated with *p*-toluenesulfonic acid (PTSA) and its application as a solid acid catalyst (NP/PTSA) in the synthesis of 2-substituted benzimidazoles from the reaction of aromatic aldehydes with *o*-phenylenedianmines.

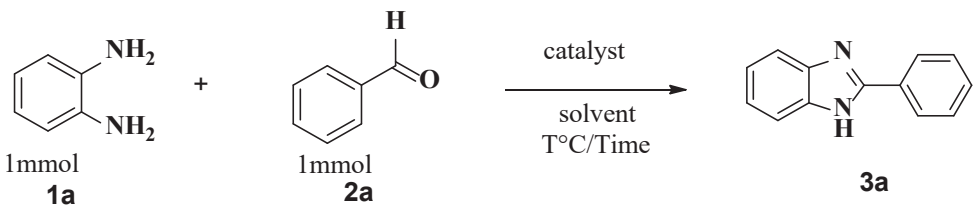
Results and discussion

With the aim of exploring the synthetic application and limitations of (NP/PTSA), we investigated its use as a catalyst in the synthesis of 2-substituted benzimidazoles *via* the condensation of different 1,2-phenylenediamines with aldehyde derivatives (Scheme 1). The use of NP/PTSA catalyst is crucial for the reaction evolution; otherwise, without catalyst or with NP alone, no product **3a** was detected even after 1 h of reaction time. Thereafter, the use of (NP/PTSA) as a catalyst was investigated. We performed a set of preliminary experiments to optimise the reaction conditions. The results are shown in Table 1.

Table 1 Effect of varying amounts of PTSA on the synthesis of 2-phenylbenzimidazole **3a**

Entry	PTSA (mmol)	NP/PTSA	Yield (%)[a,b]
1	1	PTSA	57
2	0.75	NPA3[c]	78
3	0.5	NPA2[d]	77
4	0.25	NPA1[e]	31
5	0	NP	0

[a]Isolated yield.
[b]The reaction was performed using CH_3CN as solvent at 80 °C for 1 h.
[c]473 mg (43.mg, 0.25 mmol of PTSA).
[d]516 mg (86 mg, 0.5 mmol of PTSA).
[e]560 mg (130 mg, 0.75 mmol of PTSA).



Scheme 1 Reaction for synthesis of 2-phenyl-1*H*-benzimidazole **3a**.

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Different ratios of the catalyst were examined to determine the catalytic amount of PTSA. The results indicate that NP/PTSA with 0.5 mmol of PTSA is a good catalyst for this reaction (Table 1, entry 3). However, the increase in yield is not dramatic, from 0.5 mmol of PTSA to 0.75 mmol (Table 1, entry 4).

The effect of different solvents such as CH_3OH, EtOH, H_2O, CH_3CN and dioxane has been also studied for the model synthesis (Table 2). All solvents tested led to the desired product **3a** with low to moderate yields. The water, as green solvent, led to only a 58% yield after 2 h, despite the increase in temperature to 100 °C (Table 2, entry 2). The best result was obtained using acetonitrile as solvent, yielding 77% of the corresponding product (Table 2, entry 3).

Furthermore, different acid catalysts were also investigated. We tested NP/H_2SO_4, NP/H_3PO_4, NP/$HClO_4$ and NP/$ZnCl_2$ to evaluate their catalytic activity in comparison with NP/PTSA and PTSA alone. The results shown in Table 4 clearly indicate the promoting effect of acid catalysis. It appears that NP/PTSA is the most active catalyst (Table 3, entry 3). As a result, the optimised reaction conditions were observed when the reaction was conducted with NP/PTSA (5/1) in 5 mL of CH_3CN at 80 °C for 1 h.

With the optimised conditions in hand, we next explored the scope and generality of the procedure using a variety of aldehydes (aliphatic, aromatic and unsaturated) with different 1,2-phenylenediamines in the presence of catalytic amount of NP/PTSA at 80 °C and CH_3CN as solvent. The corresponding 2-phenylbenzimidazole derivatives (Scheme 2) were obtained in good to excellent yields (Table 4). As shown in Table 4, the reaction of various aryl amines and aldehydes carrying either electron-donating or electron-withdrawing substituents were successfully reacted to produce their corresponding 2-phenylbenzimidazole derivative in good yields. This result shows that the substituent groups did not play any significant role in the reactivity of the substrate. On the other hand, comparing to previous work, Table 4 shows that 2-phenylbenzimidazole derivatives are obtained in short time with good to excellent yields in moderate conditions, using a cheap, and reusable catalyst.

In this procedure, the products were easily isolated by simple filtration and column chromatography. All known products were characterised by comparison of the melting points and the analytical data (^1H and ^{13}C NMR spectroscopy) with those reported for authentic samples.

The proposed mechanism for NP/PTSA catalysed synthesis of 2-substituted benzimidazoles may be visualised to occur *via* a sequence of reactions as depicted in Scheme 3. The synthesis involves the activation of the aldehydic carbonyl oxygen by the acid part of PTSA supported on NP through intermolecular hydrogen bonding, and protonation of the benzylidene-*o*-phenelenediamine (A) and ring closure leading to a five-membered ring in a concerted manner (B) followed by rearrangement and proton transfer to give PTSA.[39,40]

The recycling procedure is as follows: at the end of the reaction the catalyst was filtered, washed with CH_2Cl_2 and acetone; dried at 100 °C for 1 h; and subsequently reused. The recycled catalyst was used under the same conditions for four cycles in an attempt to evaluate its chemical stability. After two runs the catalytic activity of the catalyst was almost the same as those of the freshly used catalyst. In the third run, we noticed a small decrease in yield (Table 5).

Table 2 Effect of solvent, time and temperature on the yield of **3a**

Entry	Solvent	Temperature (°C)	Time (h)	Yield (%)[a,b]
1	CH_3OH	65	1.5	52
2	EtOH	80	1.5	70
3	H_2O	100	2	58
4	CH_3CN	80	1	77
5	Dioxane	80	2	37

[a]Isolated yield.

[b]The reaction was performed using 5 mL of solvent with NP/PTSA (0.5 mmol of PTSA) as catalyst.

Table 3 Comparison between NP/PTSA and several heterogeneous catalysts in the synthesis of **3a**

Entry	Catalyst	Yield (%)[a,b]
1	NP	0
2	PTSA	57
3	NP/PTSA	77
4	NP/H_2SO_4	58
5	NP/H_3PO_4	37
6	NP/$HClO_4$	23
7	NP/$ZnCl_2$	58

[a]Isolated yield.

[b]The reaction was performed using CH_3CN as solvent at 80 °C for 1 h with 516 mg of catalyst.

Table 4 Synthesis of 2-phenylbenzimidazole derivatives catalysed by NP/PTSA

Entry	Product	Yield (%)[a,b]	Yield (%) [time]	Reference
1	**3a**: R^1= R^2=H, R^3= C_6H_5	77	67 [4 h]	32
2	**3b**: R^1= R^2= H, R^3= C_3H_7	76	52 [12 h]	33
3	**3c**: R^1= R^2=H, R^3=C_3H_4O	62	55 [24 h]	34
4	**3d**: R^1= R^2= H, R^3=C_8H_7	82	82 [24 h]	35
5	**3e**: R^1= R^2= H, R^3=$C_6H_4NO_2$	73	71 [20 h]	32
6	**3f**: R^1= R^2= H, R^3= C_6H_4Cl	81	75 [12 h]	33
7	**3g**: R^1= R^2= CH_3, R^3= C_6H_5	69	90 [12 h]	36
8	**3h**: R^1= R^2= H, R^3=$C_6H_3Cl_2$	70	86 [3.5 h]	37
9	**3i**: R^1= R^2= H, R^3=C_6H_4F	73	55 [24 h]	34
10	**3j**: R^1= R^2= H, R^3=C_6H_4Br	71	60 [24 h]	38

[a]Isolated yield.

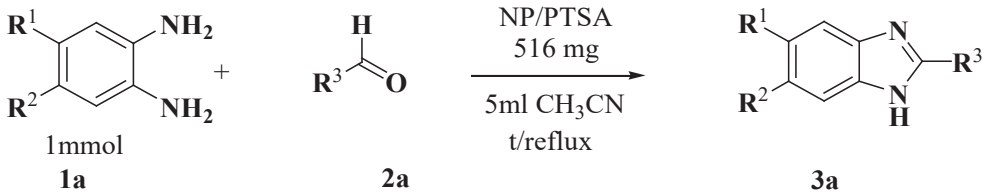
[b]The reaction was performed using CH_3CN (5 mL) as solvent at 80 °C for 1 h with 516 mg of catalyst.

Table 5 Recycling and reusing of the catalyst

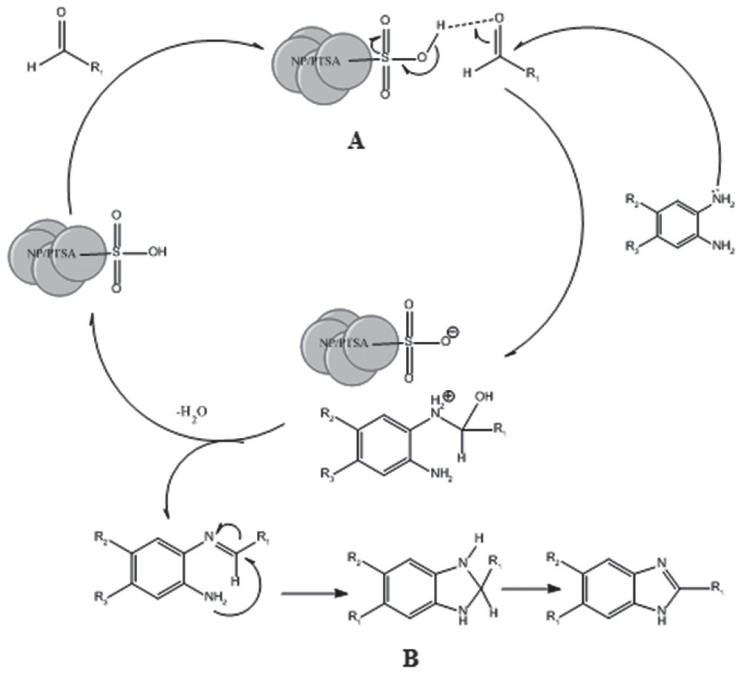
Entry	Runs	Yield (%)[a,b]
1	Fresh	77
2	First	77
3	Second	62
4	Third	60

[a]Isolated yield.

[b]The reaction was performed using CH_3CN (5 mL) as solvent at 80 °C for 1 h with NP/PTSA (516 mg; 0.5 mmol PTSA) as catalyst.



Scheme 2 Synthesis of 2-phenylbenzimidazole derivatives catalysed by NP/PTSA.



Scheme 3 The proposed mechanism for NP/PTSA catalysed 2-substituted benzimidazole synthesis.

Conclusion

In summary, NP coated with PTSA exhibited remarkable reactivity as a heterogeneous organocatalyst. The yields of obtained products are very good for a range of substrates showing that this coated material is highly active and versatile. The catalyst was recovered for successive condensation showing an appreciable catalytic activity. The yields of corresponding 2-phenylbenzimidazole were still reasonably good after the fourth run. The easy work-up procedure and very good yields make this method a valid contribution to existing methodologies.

Experimental

All the reagents and solvents for synthesis and analysis were commercially available and used directly. The stretching vibration frequency of the catalyst was recorded by FTIR spectroscopy in the range of 400–4000 cm^{-1} using a Bruker vertex 70 DTGS spectrometer. Spectrometer XRD measurements were performed on a XPERT-MPD Philips diractometer using CuKα radiation as the X-ray source in the range of 20–80°. Morphology of the microstructures were carried out on a VEGA3 TESCAN microscope equipped with an energy dispersive X-ray spectrometer (EDAX TEAM). BET specific surface areas and average pore diameter of the prepared catalyst were measured by N_2 adsorption–desorption technique using a Micromeritics analyser (P/N 05098-2.0 Rev A). Liquid chromatography was performed on silica gel (Merck 60, 220–440 mesh; eluents: hexane–AcOEt). ^{1}H and ^{13}C NMR spectra were recorded at 300 MHz a Brucker Avance spectrometer using $CDCl_3$ as the solvent, TMS as the internal standard and coupling constant (*J*) in Hz.

Synthesis of the catalyst and structural characteristics

NP was obtained in the Khouribga region (Morocco). Prior to use, NP requires initial treatment such as crushing and washing. To be used appropriately in heterogeneous synthesis, the NP is treated according to techniques of attrition, sifting, calcinations, and washing. A portion of 100–400 mm grain size was isolated, washed with water, calcined at 900 °C for 2 h, washed again, calcined at 900 °C for 30 min, and ground (63–125 mm) to give the NP catalyst.[41]

The structure of calcined phosphate NP is similar to that of fluorapatite $Ca_{10}(PO_4)_6F_2$, as shown by the X-ray diffraction pattern and IR spectroscopy (see ESI). The chemical composition was determined to be Ca (54.12%), P (34.24%), F (3.37%), Si (2.42%), S (2.21%), C (1.13%), Na (0.92%), Mg (0.68%), Al (0.46%), Fe (0.36%), K (0.04%), and other metals less than 6 ppm. The specific surface area of NP was determined by the BET method from the adsorption–desorption isotherm of nitrogen at its liquid temperature (77 K). The total pore volume was calculated by the BJH method at P/P0 ¼ 0.98. The NP shows a very low surface area (1–2 $m^2\ g^{-1}$) together with a low total pore volume (VT ¼ 0.007 $cm^3\ g^{-1}$).[41]

Synthesis of NP/PTSA

PTSA (200 mg) was dissolved in 5 mL of H_2O then 1000 mg of NP was added and put into a 50 mL volumetric flask. The suspended NP was stirred at room temperature for 1 h. The water was removed by rotary evaporation and the remaining solid was dried in an oven at 110 °C for 1 h. The obtained material was analysed by X-ray diffraction pattern, IR spectroscopy and scanning electron micrograph (see ESI).

Synthesis of 2-phenylbenzimidazole using NP/PTSA in acetonitrile; general procedure

A mixture of *o*-phenylenediamine (1 mmol), benzaldehyde (1 mmol) and catalyst NP/PTSA (0.5 mmol PTSA) (516 mg) in acetonitrile (5 mL) was refluxed under stirring for 1 h. The mixture was filtered off and the solvent was evaporated. The crude product was purified by column chromatography over silica gel by using hexane/ethyl acetate (4/1) as eluent to give the desired product. All compounds gave spectroscopic data in accordance with their proposed structures and those reported for authentic samples (see ESI).[32–37]

Spectroscopic data of 2-substituted benzimidazoles

*2-Phenyl-1*H*-benzo[*d*]imidazole* (**3a**): Yield 77%; m.p. 288–290 °C (lit[42] 291–293 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 11.88 (s, 1H), 8.209−8.186 (m, 2H), 7.677 (d, *J* = 7.3 Hz, 1H), 7.578−7.483 (m, 4H), 7.245−7.189 (m, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 151.7, 140.3, 135.5, 130.6, 130.3, 129.4, 123.0, 119.3 ppm.

*2-Isopropyl-1*H*-benzo[*d*]imidazole* (**3b**): Yield 76%; m.p. 231–233 °C (lit.[33] 232–234 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.20 (s, 1H), 7.45–7.41 (m, 2H), 7.14–7.10 (m, 2H), 3.15–3.13 (m, 1H), 1.31 (d, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 150.2, 141.2, 122.3, 118.0, 28.8, 21.5 ppm.

*2-(Furan-2-yl)-1*H*-benzo[*d*]imidazole* (**3c**): Yield 62%; m.p. 294–296°C (lit.[43] 296 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.78 (s,

1H), 7.96–7.95 (m, 1H), 7.55 (s, 2H), 7.25–7.21 (m, 3H), 6.72–6.70 (m, 1H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 145.8, 144.9, 143.6, 138.3, 122.6, 116.3, 112.7, 111.4 ppm.

*2-Styryl-1*H*-benzo[*d*]imidazole* (**3d**): Yield 82%; m.p. 200–202 °C (lit.[43] 201–203 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.50 (s, 1H), 7.60 (t, 3H, *J* = 8.5 Hz), 7.49 (s, 2H), 7.41 (t, 2H, *J* = 7.53 Hz), 7.35 (t, 1H, *J* = 7.28 Hz), 7.20–7.14 (m, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 140, 138, 136, 132, 128, 126, 124, 122, 113 ppm.

*2-(3-Nitrophenyl)-1*H*-benzo[*d*]imidazole* (**3e**): Yield 73%; m.p. 204–206 °C (lit.[44] 203–205 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.27 (s, 1H), 8.97 (s, 1H), 8.50 (d, *J* = 7.6 Hz, 1H), 8.30 (d, *J* = 7.9 Hz, 1H), 7.82 (t, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 7.3 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.26 (t, *J* = 6.7 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 150, 147.3, 144.8, 135, 133.1, 131.6, 130.7, 126.0, 123.0, 122.4, 120.8, 118.0, 112.5 ppm.

*2-(4-Cholorophenyl)-1*H*-benzo[*d*]imidazole* (**3f**): Yield 81%; m.p. 286–288 °C (lit.[45] 290–292 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.26 (s, 1H), 8.22 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.54–7.48 (m, 2H), 7.25–7.19 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 151.3, 143.6, 133.6, 129.2, 129.1, 128.4, 123.2, 120.1, 114.7 ppm.

*5,6-Dimethyl-2-phenyl-1*H*-benzo[*d*]imidazole* (**3g**): Yield 69%; m.p. 233–235 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.83 (s, 1H), 8.18–8.16 (m, 2H), 7.54–7.32 (m, 5H), 2.35 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 154.6, 142.5, 133.1, 131.7, 130.9, 129.5, 126.9, 116.7, 19.5 ppm.

*2-(2,4-Dichlorophenyl)-1*H*-benzo[*d*]imidazole* (**3h**): Yield 70%; m.p. 219–221 °C (lit.[46] 220–223 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.52 (s, 1H), 8.12 (d, *J* = 8.8, 2H), 7.83 (s, 1H), 7.50–7.48 (m, 2H), 7.20–7.18 (m, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 150.1, 139.7, 135.4, 133.8, 132.7, 130.6, 130.1, 128.2, 122.8, 115.5 ppm.

*2-(4-Fluorophenyl)-1*H*-benzo[*d*]diazole* (**3i**): Yield 73%; m.p. 247–249 °C (lit.[43] 248 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.10 (s, 1H), 7.74–7.65 (m, 2H), 7.53–7.48 (m, 2H), 7.39–7.26 (m, 2H), 7.23–7.11 (m, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 162.1, 151.2, 139.6, 134.1, 131.2, 128.1, 122.6, 116.0 ppm.

*2-(4-Boromophenyl)-1*H*-benzo[*d*]imidazole* (**3j**): Yield 71%; m.p. 251–253 °C (lit.[47] 253–255 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.14 (s, 1H), 8.30 (d, *J* = 8.1 Hz, 2H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.77–7.52 (m, 2H), 7.50 (m, 2H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 153.4, 142.1, 137.2, 131.4, 128.5, 125, 121.7, 113.5 ppm.

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Electronic Supplementary Information

The ESI, FTIR and IR spectra, X-ray diffractions and scanning electron microscopy images, is available through:

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