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Silica Supported PPA : An Efficient and Recyclable Catalyst for Benzimidazoles Synthesis at Room Temperature

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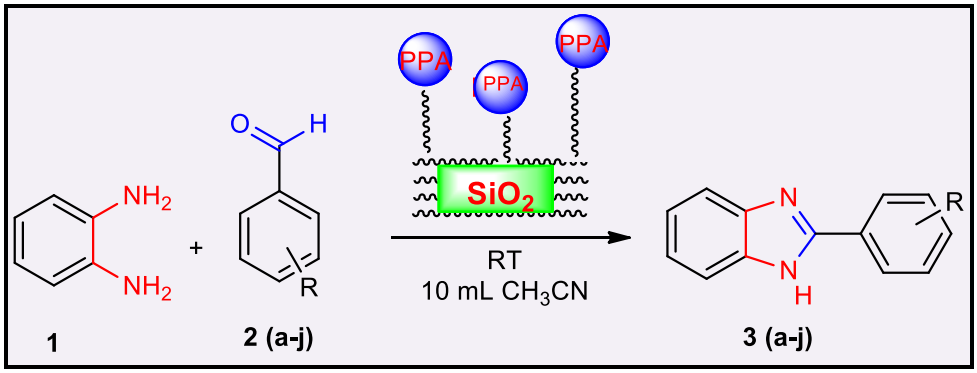
ABSTRACT

Benzimidazolesare well known heterocyclic moiety in the field of pharmacological and organic synthesis. We have designed the efficient protocol for 2-phenyl benzimidazolesynthesis. A simple, highly efficient and environmental being procedure for the condensation of *o*-phenylenediamine with aromatic aldehydes in the existence of catalytic amount of SiO_2-PPA have been designed. Prepared SiO_2-PPA catalyst has remarkably efficient up to fifth cycles, reported excellent to good yield of target molecule. The mild reaction conditions, the high yield of the products and recyclability of catalyst are the attractions of reported methodology. Such advantages make it ecofriendly and proficient route for synthesis of benzimidazoles under prescribed reaction conditions.

Keywords: Diamine, Benzimidazoles, SiO_2-PPA catalyst, Room Temperature, Recyclability etc.

Graphical Abstract



I. INTRODUCTION

Recently, (SiO_2- PPA) has been used as an efficient heterogeneous catalyst for many organic transformations. PPA/SiO_2 has some advantages including its low cost, ease of preparation, and ease of handling [1]. In addition, the catalyst can be easily separated from the reaction mixtures by simple filtration and is reusable.

Previously [2], the conversion of carbonyl compounds into oxathioacetals or dithioacetals using PPA/SiO_2 and a convenient method for the synthesis of isoxazole derivatives using PPA/SiO_2 as a reusable catalyst have been reported [3]. In the last several years the development of non-toxic, low cost, eco-friendly, recyclable catalyst systems which give high productivity under mild reaction conditions has received much attention in organic synthesis [4]. Solid supported catalysts [5,6] have gained much prominence due to their inherent economic and environmental benefits, ease of handling, easy catalyst separation and regeneration, thermal stability and long catalytic life [7]. Since the activity and selectivity of a reagent dispersed on the surface of the support is improved, as the effective surface area of reagent can be increased manifold, they are expected to perform better than the individual reagents [8]. Low toxicity, moisture, air tolerance and low price are other common features that make the use of solid supported reagents attractive alternative to the conventional catalysts.

As we know, N-heterocyclic compounds are the most abundant and integral scaffolds that occur ubiquitously in a large number of bioactive natural products, drug intermediates, pharmaceuticals, and agrochemicals. Benzimidazoles are a privileged class of compounds among the N-heterocycles with a diverse spectrum of biological activities and therapeutic potentialities including anti-ulcers, anti-hypertensives, anti-virals, anti-fungals, anti-cancers, anti-histaminics also it exhibits medicinal properties such as serotoninergic 5-HT_3 and 5-HT_4 receptors in the CNS [9, 10]. In addition, the unique benzimidazole moiety is "Master key" in anti-inflammatory, anti-analgesic, antioxidant, anti-diabetic, selective neuro peptide YY1 receptor antagonists, anti-malarial, anti-tubercular, etc., drugs [11-15]. Moreover, benzimidazoles are very important intermediates in dyes and polymer synthesis and widespread applications in fluorescence, chemo sensing, crystal engineering, and corrosion science [16]. Furthermore, with their biological consequence, benzimidazoles form unvarying complexes with diverse metals in transition group [17]. Metal chelations of 2-substituted imidazole and benzimidazole based structures with various ligands have been published with mono, bi and tri dentate co-ordination structures [18]. Some of the commercially important benzimidazole product structures, which are industrially very important, are illustrated in **Fig.1.**

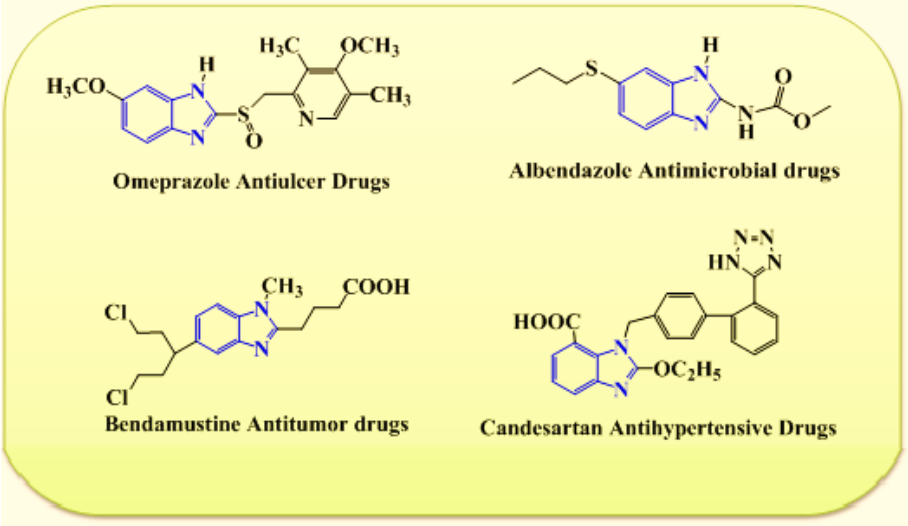


Fig. 1. Examples of important commercial drugs containing benzimidazole structural moiety.

Recently, benzimidazole derivatives have also been prepared from the oxidative condensation of 1,2-arylenediamines with aldehydes using different oxidative and catalytic reagents such as sulphur, $Sc(OTf)_3$ or $Yb(OTf)_3$[19], Silica-Sulphuric acid [20-21], NH_4Br [22], Lewis acids like pyridinium-p-toluene sulfonate, ionic liquids [23] like polyaniline-sulfate and zeolite. $SiO_2/ZnCl_2$ [24], nitrobenzene (high boiling oxidant/solvent) [25], silphox [$POCl_3$_n(SiO_2) n] [26], $Fe_3O_4@SiO_2@(NH_4)_6–Mo_7O_{24}$ magnetic core-shell nano composite, boron tri-fluoride etherate ($BF_3.OEt_2$), Cu-nano particles/SiO_2, LiBr, GO-HSO_4 [27-30], PPA [31],fluorinated phosphoric Acid [32], methane sulfonic acid [33]these catalysts were utilized in the same procedure.

However, many of these protocols have not been entirely satisfactory because of some drawbacks such as low yields, long reaction time, strong acidic conditions, tedious workup procedures, requirement of excess amounts of catalyst and use of toxic reagents, catalysts or solvent, cumbersome experimental processes, and use of moisture-sensitive and costly catalysts. The development of simple, efficient, high yield green synthetic approach for the synthesis of biological active compounds is one of the major challenges in organic synthesis. Therefore, it is necessary to find a new catalyst or path for this important synthesis reaction. In addition, to overcome from all these disadvantages here we report a practical, inexpensive and green method for the synthesis of benzimidazole derivatives with reusable catalyst.

Herein, we present an efficient, simple, and economical cheap method for the preparation of benzimidazole derivatives catalyzed by Heterogeneous SiO_2@PPA catalyst. Present method obtained selective, efficient, and high yield of respective product in short reaction period. Furthermore, we have also studied the influence of concentration of catalyst, effect of solvent as well as temperature on benzimidazole yield. Various substituted benzimidazole derivatives were prepared by using o-phenylenediamine and various substituted aldehydes in the presence of SiO_2@PPA in ethanol at room temperature. We found that, the present protocol has easy and simple workup procedure with the separation of products and catalyst from reaction mixture, which shows one of the efficient alternative protocol for the benzimidazole derivative preparation.

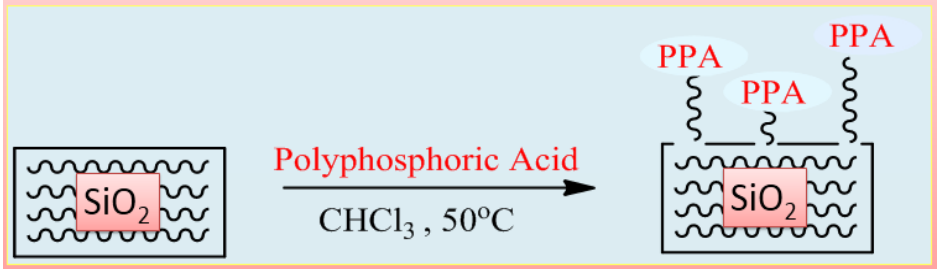
II. EXPERIMENTAL

2.1 General

All the chemicals used for synthesis were of LR (laboratory reagent) grade. Silica used for catalyst synthesis is of 70– 230 mesh size. TLC (thin layer chromatography) was performed on microscopic glass slides coated with silica gel-G using, petroleum ether:ethyl acetate (8:2) as a solvent system and the spot were visualized by exposure to iodine vapours. The XRD pattern acquired on a multi -purpose x-ray diffractometer at a scan rate of 0.17-2qs^{-1}. All the melting points of prepared compounds were determined in open capillary tubes and are uncorrected. The FT-IR spectra were recorded on a Perkin-Elmer spectrophotometer using KBr pellets. ^{1}HMR spectra were recorded on Varian Gemini (200 MHz) spectrometer using DMSO-d_6 as solvent and TMS as internal standard.^{13}C-NMR spectra were recorded on 50 MHz in DMSO-d_6 solvent, in δ ppm. All chemical shifts values are reported in δ scale downfield from TMS. Homogeneity of the compound was checked by TLC on silica gel plates.

2.2 General procedure for the synthesis of PPA/SiO2catalyst

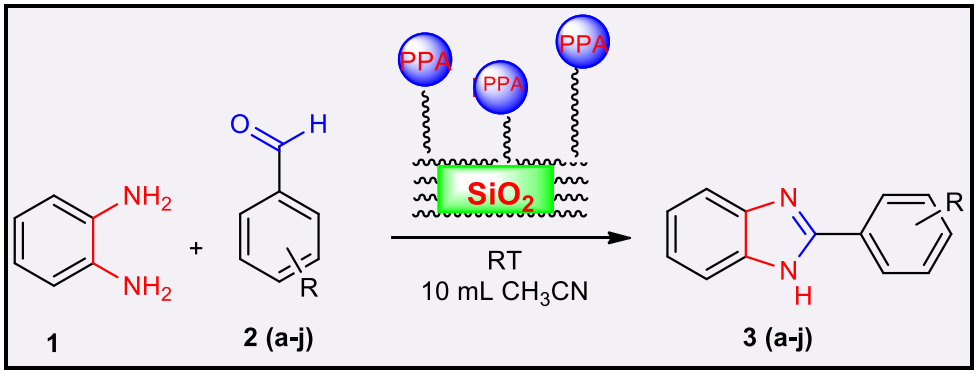
PPA (4.0 gm) was charged in the round-bottom flask, and CHCl3 (100 mL) was added. After the mixture was stirred at 50 °C for 1 h, followed by SiO2 (16.0 gm, 70– 230 mesh) was added to the solution, and the mixture was stirred for another 1 h. $CHCl_3$ was removed by evaporation, and the resulting solid was dried in vacuum at room temperature for 3 h. Used PPA/SiO_2 was regenerated as follows: PPA/SiO_2 was recovered by filtration from the reaction mixture, and then it was put in the 50 mL round-bottom flask and dried in vacuum at 100 °C for 2 hr.



Scheme 1: Preparation of SiO_2 supported PPA catalyst.

2.3 General procedure for the synthesis of benzimidazole derivatives

To a mixture of o-phenylenediamine (0.01 mol.) and aromatic aldehydes (0.01 mol.), ethanol (10 mL) were added in 50 mL round bottom flask. To this solution, added a known amount of catalyst SiO_2@PPA(0.5 gm). Resulting reaction mixture was stirred at room temperature.The progress of reaction was traced by TLC. After completion of the reaction vessels poor in 50 mL H_2O and extracted with ethyl acetate (10 mL X 3), catalyst was filter out and separated from the above solution. The collected organic layer was concentrated and the crude product was obtained and it was purified by recrystallization.purebenzimidazole products and further characterized by ^1H and ^{13}C NMR spectroscopy.



Scheme 2: Synthesis of benzimidazole derivatives using SiO_2@PPA catalyst.

2.4 Spectral study of specified synthesized products 3 (a-j)

2.4.1 2-Phenyl- 1H-benzimidazole (3a):1 H-NMR spectrum (200MHz, DMSO-d6, in δ ppm): 12.86 (s, 1H, NH), 8.12 (m, 2H), 7.50-7.62 (m,5H), 7.18 (m, 2H); 13 C-NMR (50 MHz, DMSO-d6, in δ ppm): 114.7, 118.9, 121.4, 123.4, 126.4, 129.0, 129.8, 130.1, 136.4, 145.5, 153.0. FT-IR (KBr) in cm^{-1}: 3048, 1460, 1418, 1280,972, 745; Analy. Calcd. for $C_{13}H_{10}N_2$: C 80.39, H 5.19, N 14.42; Observed: C 80.42 H 5.18 N 14.40.

2.4.2 2-(4- Methoxyphenyl)-1H- benzimidazole (3b): 1 H NMR (in δ ppm): 12.52 (s, 1 H, NH), 8.19 (dd, 2 H, J = 8.0 Hz), 7.66 (d, 1 H), 7.45 (d, 1 H), 7.24–7.10 (m, 2 H), 7.13 (d, 2 H, J = 8.0Hz,), 3.86 (s, 3 H). 13 C NMR (in δ ppm): 158.38, 152.86, 139.88, 129.22, 124.67, 124.19, 122.20, 120.46, 114.30, 113.16, 58.31; IR (in cm -1): 3450, 2242, 2120, 1655, 1045; Analy. Calcd.for $C_{14}H_{12}N_2O$: C 74.98, H 5.39, N 12.49, O 7.13; Observed: C 75.02, H 5.37, N 12.50, O 7.11.

2.4.3 2- [4- (2-propyl) phenyl]- 1H-benzimidazole (3d): 1 H NMR (in δ ppm): = 12.86 (br. s, 1 H, NH), 8.15 (d, 2 H, J =8 Hz),7.72 (d, 1 H),7.58 (d,1H) 7.36 (d, 2 H, J = 8 Hz), 7.22–7.15 (m, 2H), 2.95 (m, 1 H), 1.26 (d, 6H). 13 C NMR (in δ ppm): 151.33, 149.40, 143.85, 136.16, 128.77, 126.94, 126.43, 122.23, 120.65, 116.56, 112.20, 40.20, 24.00; IR (in cm –1): 3456, 2350, 2127, 1665, 1073; Analy. Calcd. for $C_{16}H_{16}N_2$: C 81.32, H 6.82, N 11.85; Observed: C 81.32, H 6.80, N 11.87.

2.4.4 2-(3- Nitrophenyl)-1H- benzimidazole (3g): 1 H-NMR (in δ ppm): 13.2 (s, 1H, NH), 8.86(s, 1H), 8.46 (d,1H, J=6 Hz), 8.24 (d, 1H, J=7 Hz), 7.89 (m, 1H, J=7 & 6 Hz), 7.53 (m, 2H), 7.24(m, 2H); 13 C-NMR (in δppm): 115.3, 123.1, 123.6, 124.4, 126.2, 127.4, 128.1, 133.4, 134.6,135.2, 143.8, 149.7, 150.2; IR (KBr in cm -1): 3060, 1524, 1450, 1357, 973, 746; Analy.Calcd. for $C_{13}H_9N_3O_2$: C 65.27, H 3.79, N 17.56, O 13.38; Observed: C 65.32, H 3.77, N 17.55, O 13.36.

2.4.5 2-(4- Chlorophenyl)-1H- benzimidazole (3i): 1 H-NMR (in δ ppm): 12.9 (s, 1H, NH), 8.25(d, 2H, J=8.5 Hz), 7.6 (d, 2H, J=8.5 Hz), 7.45 (m, 2H), 7.20 (m, 2H). 13 C-NMR (in δ ppm): 116.4,124.1, 126.3, 128.9, 128.2, 129.7, 130.4, 134.3, 145.9, 152.6; IR (KBr in cm-1): 3041, 1450,1402, 1280, 965, 750; Analy. Calcd. for $C_{13}H_9ClN_2$: C 68.28, H 3.97, Cl 15.50, N 12.25; Observed: C 68.25, H 3.96, Cl 15.55, N 12.24.

2.4.6 2-(4- Bromophenyl)-1H- benzimidazole (3k): 1 H NMR (in δ ppm): 12.65 (s, 1H, NH), 8.20(d, 2H J = 8.5 Hz), 7.66 (d, 2 H J = 8.5 Hz), 7.66–7.48 (m, 2 H), 7.23–7.12 (m, 2H). 13 C NMR (inδ ppm): 155.14, 142.06, 133.85, 131.74, 130.47, 124.56, 123.37, 115.22; IR (in cm –1):3325, 2167, 2119, 1650, 1035, 827; Analy. Calcd. for C 13 H 9 Br N 2: C 57.17, H 3.32, Br 29.26, N 10.26; Observed: C 57.20, H 3.32, Br 29.24, N 10.25.

III. RESULTS AND DISCUSSION

We have worked on design an efficient protocol for the synthesis of benzimidazoles, various Lewis acid, heterogeneous, recyclable catalysts have been utilized for synthesis of benzimidazole preparation by the cyclization reaction of diamine and aldehydes. In the present work, we explored the potential of silica supported PPA as a catalyst for the synthesis of benzimidazoles. SiO_2@PPA showed remarkable efficiency at room temperature under optimized conditions. We have prepared ten derivatives of benzimidazoles from various substituted aldehydes and diamine in the presence of catalytic amount of SiO_2@PPA in 10 mL ethanol at room temperature.

Reaction parameters were finalized after optimization of amount of catalyst, effect of solvent and temperature, for this we flameout the model reaction as diamine (0.01 mol) and benzaldehyde (0.01 mol) were stirred in 10 mL solvent. The effect of different solvents have been studied under the same reaction conditions, as shown in table. The yield of the product varied with the nature of the solvents, better conversion and easy isolation

of product wasfound with acetonitrile. Acetonitrile dissolves a wide range of ionic and non-polar compounds. In a similar manner, the reaction with O- phenylenediamine and aldehydewas carried out without any solvents. The observation shown that the reaction was not brought into completion, even after starting for a period 12hrs at room temperature, and the reaction mixture showed a number of spot in thin layer chromatography (TLC).

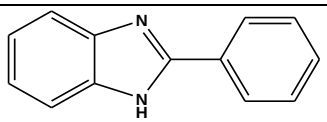
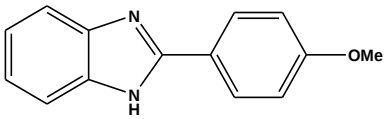
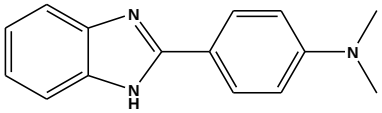
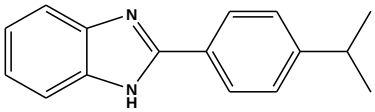
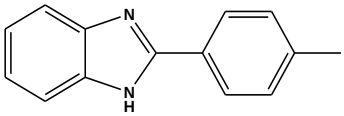
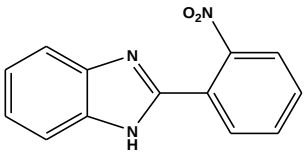
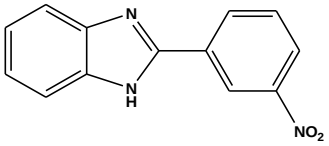
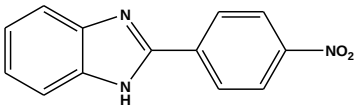
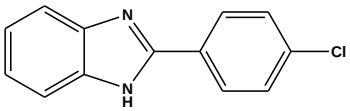
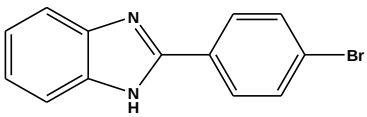
After the screening of solvents, we have finalized acetonitrile as solvent; we have screened same reaction under varying temperature. After the study, we have concluded as the studied reaction gave excellent output at room temperature for given transformation in presence of SiO_2-PPA, stirred in 10 mL acetonitrile. Additionally, the effect of amount of catalyst on present reaction also studied and we have found (0.5 gm) of SiO_2-PPA catalyst showed remarkable efficiency for the studied transformation. After the screening of all parameters, we have outline optimized conditions as o-phenylenediamine (0.01 mol.) and aromatic aldehydes (0.01 mol.), ethanol (10 mL) stirred at room temperature in presence of 0.5 gm of SiO_2-PPA catalyst.

Table 1: Influence of various reaction parameters on reaction out comes.

Sr. No.	Catalyst SiO_2 PPA (in gm)	Solvent	Temp. (in C°)	Reaction Time(in hr)	Yield (In %)
1	0.5	Solvent free	R.T	12	30
2	0.5	ETOH	R.T	12	56
3	0.5	DMF	RT	14	62
4	0.5	CH_3-CN	RT	6	92
5	0.5	Toluene	RT	16	50
6	0.5	CH_3-CN	40	6	80
7	0.5	CH_3-CN	60	6	72
8	0.5	CH_3-CN	Reflux	6	45
9	0.7	CH_3-CN	RT	6	92
10	0.4	CH_3-CN	RT	6	85

With this optimized reaction condition, we have proceeded to investigate the scope and generality of this protocol using collection of various substituted aromatic aldehydes and diamine in ethanol as solvent. Consequently, a diversity of commercially accessible different structurally substituted aldehydes were treated in the optimized reaction conditions to obtained benzimidazole derivatives and obtained results are summarized in Table 2. As shown in Table 2, all substituted aldehydes participated well in this cyclization reaction and afforded the desired products of benzimidazole in good to efficient yields using catalytic amount of SiO_2-PPA and all the functionality of reactants were preserved throughout the transformation.

Table 2: Synthesis of benzimidazole compounds 3(a-j) from diamine and aldehydes under optimized conditions [a]

Entry	Product	Time (h)	M.P.(°C)	Yield (%) [b]
1		6.00	291	92
2		4.10	232	94
3		3.40	238	90
4		3.50	243	93
5		2.50	224	92
6		4.40	255	82
7		5.30	145	85
8		4.10	316	92
9		3.40	293	90
10		4.10	258	88

Reaction conditions: diamine (0.01 mol), aldehyde (0.01mol), 10 mL CH_3CN, 0.5 gm SiO_2@PPA, stirred at room temperature.Reaction time is monitored by TLC. **(b)** Isolated yield.

IV. RECYCLABILITY OF SiO2-PPA

We have also studied the reusability of reported catalyst to the course of benzimidazole from substituted aldehyde and O-phenylenediamine in 10 mL acetonitrile solvent. Result showed that prepared catalyst were give remarkable yield of target molecule up to 5th cycle (shown in figure 2). It was easily separated from reaction vessels and reuse after just washing with water, heated at 100 °C for 2 hr.

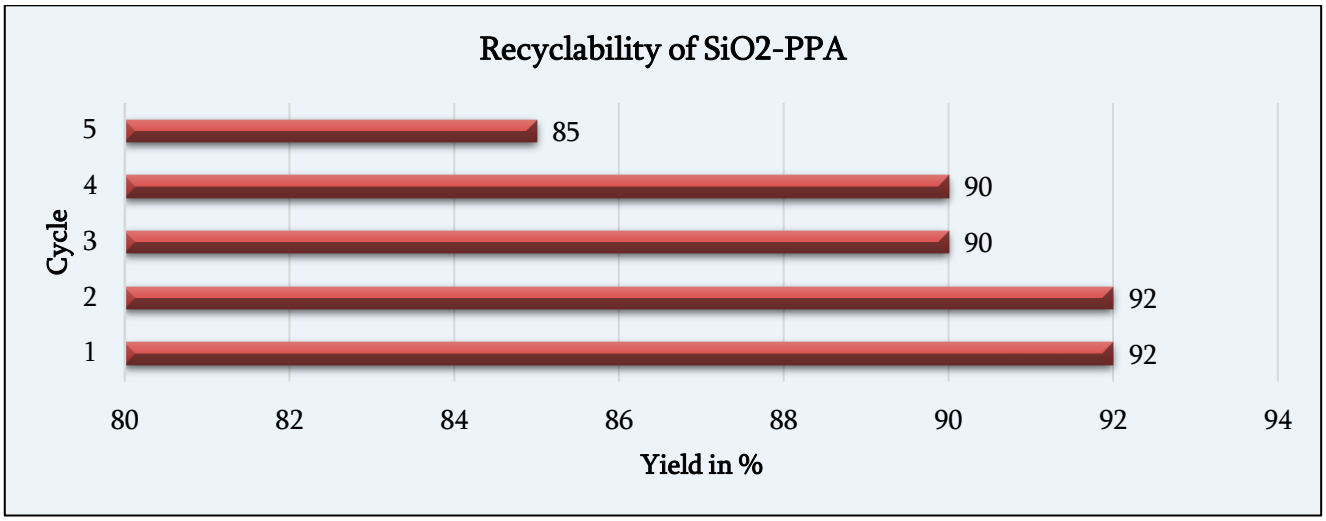


Fig. 2: Study of recyclability of SiO_2-PPA catalyst for synthesis of benzimidazoles.

V. CONCLUSIONS

In conclusion, we have developed a simple and efficient method for the synthesis of benzimidazole derivatives using silica supported poly phosphoric acid catalyst under mild reaction conditions with competitive and high yield. The advantages of the present technique are the operational simplicity, high efficiency, no side products formation, easy of workup procedure, less reaction time, thus suitable for large-scale production of benzimidazole derivatives. Reported catalyst was easily synthesised from available starting material and has stress-free workup process with outstanding productivity up to five cycles.

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