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Nanoporous aluminosilicate catalyst with 3D cage-type porous structure as an efficient catalyst for the synthesis of benzimidazole derivatives

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ABSTRACT

Herein we demonstrate for the first time, the synthesis of benzimidazoles through the coupling of aldehydes with *o*-phenylenediamine by using highly acidic nanoporous aluminosilicate with 3D structure and cage-type pores as the catalyst. The catalyst resulted in excellent yields in short reaction times presumably due to its high acidity, large pore diameter, high surface area, and cage-type 3D porous structure.

1. Introduction

The benzimidazole derivatives are potent biologically active compounds and exhibit antiviral, antiulcer, antihypertension, and anticancer properties.[1] These compounds have been receiving a lot of attention in the recent years owing to their excellent biological activities. Generally, the synthesis of benzimidazoles involves the treatment of 1,2-phenylenediamine either with carboxylic acids under strongly acidic conditions or with aldehydes under oxidative conditions[2,3] using various oxidants such as 2,3-dichloro-5,6-dicyanobenzoquinone, molecular iodine, oxone, and $FeCl_3{\cdot}6H_2O$.[4,5] Subsequently, several reagents such as *p*-toluenesulfonic acid, borontrifluoride etherate, $In(OTf)_3$, $Yb(OTf)_3$, $Sc(OTf)_3$, $Bi(OTf)_3$, and ionic liquids have been employed as the catalysts for the synthesis of benzimidazoles.[6–10] Although the reaction was efficiently promoted by the above catalysts, they suffer from one or more disadvantages such as high cost, long reaction times, occurrence of several side reactions, drastic reaction conditions, difficulty in separation of the products from the reaction mixture, and strong oxidizing nature. In addition, these catalysts are highly corrosive and cannot be regenerated which make them less environmental friendly and not attractive for commercialization. Thus, it is highly imperative to find out stable, cheap, recyclable, and environmental friendly heterogeneous catalysts for the synthesis of benzimidazoles. Heterogeneous catalysts such as polymer-supported hypervalent iodine reagents and $KHSO_4/SiO_2$ have been used for the synthesis of benzimidazoles.[10] Unfortunately, these catalysts possess poor textural characteristics such as a low surface area and pore volume which limit the efficiency of the catalysts. Zeolites and nanoporous materials have been widely used as heterogeneous catalysts in several organic transformations owing to their excellent textural characteristics such as high surface area, uniform pores, large pore volume, and high thermal stability.[11,12] Unfortunately, organic reactions involving two or three bulky reactants cannot be carried out using zeolite catalysts as the size of their pore diameter is too small. On the other hand, the nanoporous materials can offer large pore diameter and high surface area, wherein the reactant molecules freely diffuse inside the channels and access the active sites. In addition, enhanced reaction rates, greater selectivity, easy handing of these materials, and simple workup are the added advantages of these materials. Among various heterogeneous solid acid porous catalysts, nanoporous catalysts with three-dimensional (3D) structures are more advantageous than the catalysts with one-dimensional (1D) nanoporous structures for various organic transformations. The 3D structure of the catalyst can provide more adsorption sites and allow easy diffusion of the reactants and products than 1D structure which supports the resistant to pore blocking and coke formation. Recently, we have reported the synthesis of AlKIT-5, which is highly

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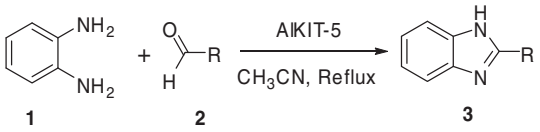
acidic and possesses 3D mesostructure with Fm3m symmetry, high surface area, large pore volume, cage type pores, and high acidity.[13] The catalytic activity of the AlKIT-5 catalysts has been studied for various organic transformations including the synthesis of triazolo indazolones, α-aminophosphonates, and dihydropyrimidinones. It has been found that the catalyst is extremely stable and showed superior activity in most of the organic transformations.[14–20] However, to the best of our knowledge, there has been no report available on the synthesis of benzimidazoles using AlKIT-5 catalysts in the open literature so far.

Herein we report for the first time a simple, convenient, and efficient method for the synthesis of benzimidazole and its derivatives by condensation of 1,2-phenylenediamine with aldehydes under acetonitrile reflux conditions using AlKIT-5 as the catalyst. Initially, we have attempted the condensation of 1,2-phenylenediamine (1.2 mmol) with benzaldehyde (1.0 mmol) using AlKIT-5 catalyst with different n_{Si}/n_{Al} ratios (Table 1 and Scheme 1). It was found that the amount of Al in the catalyst plays a significant role in controlling the activity of the catalyst. Among the catalysts studied, AlKIT-5(10) was found to be the best, giving a high yield. This was mainly due to the fact that AlKIT-5(10) has the highest Al content and the presence of each aluminum atom causes the appearance of an extra negative charge in the aluminosilicate framework of AlKIT-5 which must be compensated by proton in the form of bridged hydroxyls, resulting in Brönsted acid sites. This makes the AlKIT-5(10) more acidic than the other AlKIT-5 catalysts and is responsible for its high activity. It should also be mentioned that the specific surface area and specific pore volume of the AlKIT-5(10) are higher than those of AlKIT-5 materials with less Al content. These factors are highly critical for enhancing the adsorption and the transport of the reactant molecules on the surface and thereby increasing the catalytic activity. As the AlKIT-5(10) catalyst was found to be the most active, this catalyst was used for further studies.

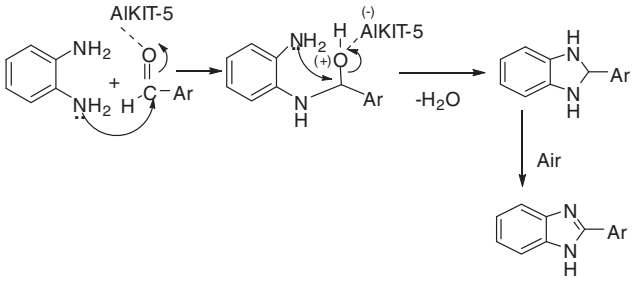
It is noteworthy that no product was observed at room temperature or under reflux conditions in the absence of a catalyst. However, when the reaction was carried out using AlKIT-5(10) catalyst under reflux conditions, the product **3a** with a yield of 95% was achieved within 4 h. The effect of the catalyst weight on the activity of the AlKIT-5(10) was also investigated (Table 1). It was observed that the yield of the final product increases with increasing the amount of the catalyst in the reaction mixture. The yield of the final product increases from 34% to 95% by increasing the catalyst weight from 50 to 150 mg.

Mechanistically, the reaction proceeds via the activation of aldehyde by AlKIT-5 followed by imine formation. The resulting imine further reacts with another amine group of 1,2-phenylenediamine resulting in the formation of dihydroimidazole which subsequently undergoes aromatization under the reaction conditions to give the benzimidazole as shown in Scheme 2.

Encouraged by these results, we examined several aromatic aldehydes under the optimized reaction conditions. This condensation proceeded smoothly in acetonitrile under reflux conditions and was completed within 5 h. Several aldehydes including aromatic, heteroaromatic, and aliphatic underwent smooth conversion to afford a wide range of benzimidazoles (Table 2). Aromatic aldehydes containing both electron-donating and electron-withdrawing groups worked well in this reaction. The catalyst was also found to be very active for the preparation of benzimidazoles from an acid-sensitive aldehyde such as furfural (**3l**) and a sterically hindered aldehyde, 2-naphthaldehyde (**3m**). Substituted aldehydes were used with similar success to provide the corresponding benzimidazoles in high yields. The products were formed in high yields (76–95%). The reaction was also carried out with substituted *o*-phenylenediamines using AlKIT-5(10) under reflux condition. The catalyst showed excellent activity and afforded the corresponding derivatives of benzimidazole in good yields. The structures of the products were determined from their spectral data (NMR, IR, and MS) and also by comparison with authentic samples.[5] Several examples illustrating this novel and general method for the synthesis of benzimidazoles are also summarized in Table 2.



Scheme 1. Synthesis of benzimidazoles using AlKIT-5 as catalyst.



Scheme 2. A plausible mechanism for the synthesis of benzimidazoles.

The effect of the solvents affecting the catalytic activity of the AlKIT-5(10) was also investigated under the optimized reaction conditions and the results are given in Table 3. Among various solvents like THF, acetonitrile, ethanol, and methanol used for this transformation, acetonitrile and methanol were found to be good solvents. Finally, recycling experiments were conducted to find out the stability of the catalyst after the reaction. The catalyst was separated by centrifuge and reused after activation at 500 °C for 3–4 h. The efficiency of the recovered catalyst was verified with entry 1. Using the fresh catalyst, the yield of product **3a** was 95%, while the recovered catalyst in the three subsequent runs gave the yield of 94%, 92%, and 90%, respectively.

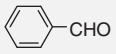
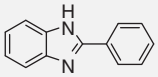
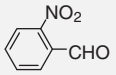
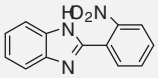
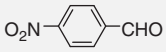
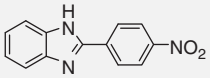
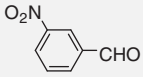
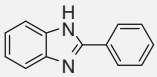
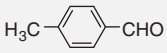
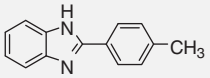
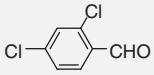
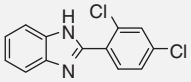
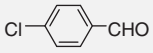
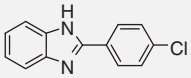
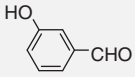
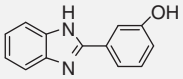
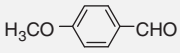
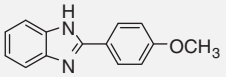
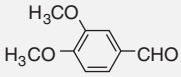
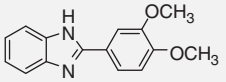
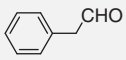
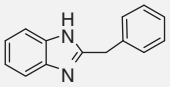
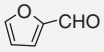
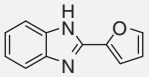
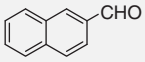
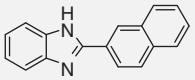
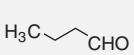
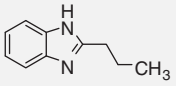
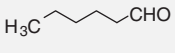
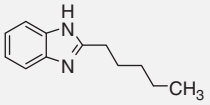
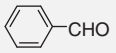
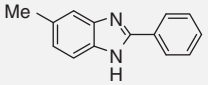
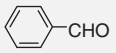
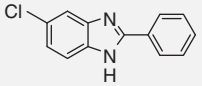
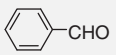
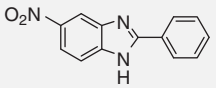
In conclusion, benzimidazole and its derivatives were synthesized by the coupling of aldehydes with *o*-phenylenediamine using AlKIT-5 catalyst with different Al contents. Benzimidazoles could successfully be synthesized using the AlKIT-5 catalyst with acid

Table 1
Effect of the textural parameters and the weight of the AlKIT-5 catalysts in the synthesis of benzimidazole **3a**

Catalyst	Weight (mg)	A_{BET} (m^2/g)	V_p (cm^3/g)	D_p BJH (nm)	Acidity (mmol/g)	Yield (%)
AlKIT-5(10)	50	989	0.68	6.0	0.50	34
AlKIT-5(10)	100	989	0.68	6.0	0.50	72
AlKIT-5(10)	150	989	0.68	6.0	0.50	95
AlKIT-5(28)	150	815	0.56	5.6	0.32	89
AlKIT-5(44)	150	713	0.45	5.2	0.14	78

Reaction conditions: substrates: 1,2-phenylenediamine, benzaldehyde, reaction time: 4 h, reaction temperature: reflux, solvent: acetonitrile, D_p: pore diameter, V_p: pore volume, A_{BET}: specific surface area.

Table 2
Synthesis of benzimidazole derivatives using AlKIT-5 catalyst

Entry	Aldehyde	Product[a] (3)		Time (h)	Yield[b] (%)
a			**3a**	4.0	95
b			**3b**	4.0	95
c			**3c**	4.0	92
d			**3d**	4.0	84
e			**3e**	4.0	92
f			**3f**	4.5	84
g			**3g**	4.5	90
h			**3h**	4.5	90
i			**3i**	4.5	88
j			**3j**	4.5	88
k			**3k**	4.5	88
l			**3l**	4.5	90
m			**3m**	4.5	82
n			**3n**	5.0	78
o			**3o**	5.0	76
p			**3p**	5.0	85
q			**3q**	6.0	80
r			**3r**	7.0	70

[a] All products were characterized by NMR, IR, and mass spectroscopy.
[b] Yield refers to pure products after purification. Reaction conditions: reaction temperature: reflux, solvent: acetonitrile, catalyst: AlKIT-5(10), catalyst weight: 150 mg.

sensitive, sterically hindered, and substituted aromatic and aliphatic aldehydes. The catalyst is highly active, stable, and could be reused several times without much loss of its activity. The heterogeneous nature, high surface area, large pore volume, and high acidity of the catalyst make the preparation of benzimidazoles simple, convenient, and practical. As this catalyst is highly active, this

Table 3
Effect of the various solvents on the activity of the AlKIT-5 catalyst in the synthesis of benzimidazoles

Name of the catalyst	Name of the solvent	Reaction time (h)	Yield (%)
AlKIT-5(10)	Acetonitrile	4	95
AlKIT-5(10)	Methanol	4	94
AlKIT-5(10)	Ethanol	4	89
AlKIT-5(10)	THF	4	80

Reaction conditions: substrate = 1,2-phenylenediamine (1.2 mmol), benzaldehyde (1.0 mmol), amount of the AlKIT-5 catalyst = 150 mg, reaction temperature = reflux temperature.

could also be used for several acid-catalyzed organic transformations and could replace the existing homogenous catalysts which are hazardous and currently being used in the industry.

2. Experimental section

All chemicals and solvents were obtained from Aldrich and used without further purification. Column chromatographic separations were carried out on silica gel 100–200 mesh size. The ^{1}H NMR spectra of samples were recorded on a JEOL 300-MHz NMR spectrometer using TMS as an internal standard in $CDCl_3$. Mass spectra were recorded on a MALDI-MS.

The AlKIT-5 materials with different n_{Si}/n_{Al} ratios were synthesized using polymeric Pluronic F127 as a template, and tetraethyl orthosilicate (TEOS) and aluminum isopropoxide as the sources of silicon and aluminum, respectively. In a typical synthesis, pluronic F127 (5 g) was dissolved in concd HCl (3 g, 35 wt %) and distilled water (240 g). To this mixture, TEOS (24 g) and the required amount of the aluminum source were added, and the resulting mixture was stirred for 24 h at 45 °C. Subsequently, the reaction mixture was heated for 24 h at 100 °C under static condition for hydrothermal treatment. After hydrothermal treatment, the final solid product was filtered off and then dried at 100 °C without washing. The white colored product was calcined at 540 °C for 10 h. The samples are denoted as AlKIT-5(x) where x denotes the n_{Si}/n_{Al} ratio in the final product.

2.1. General reaction procedure

To a mixture of an aldehyde (1.0 mmol) and 1,2-phenylenediamine (1.2 mmol) in acetonitrile (5 mL) under open air atmosphere, AlKIT-5 (150 mg) was added. The resulting mixture was stirred at reflux temperature for appropriate time (Table 2). After completion of the reaction, as monitored by TLC, the reaction mixture was diluted with ethyl acetate (20 mL) and the catalyst was separated by filtration. The organic layer was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography using ethyl acetate–*n*-hexane (1:9) as eluent to afford the pure benzimidazole. The spectral data are in full agreement with the data reported in the literature.[5,21,22] Spectral data for the selected products:

Compound **3a**: 2-phenyl-1*H*-benzimidazole (Table 2):[22a] **3a**: 2-phenyl-1*H*-benzimidazole (Table 2):[21a] Solid, mp 293 °C, IR (KBr): 3047, 2966, 1462, 1411, 1276, 970, 744, 703 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.89 (br s, 1H), 8.15–8.18 (m, 2H), 7.54 (d, 1H) 7.50–7.54 (m, 4H), 7.19–7.20 (d, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 151.8, 143.75, 134.96, 130.12, 129.7, 128.88, 126.39, 122.47, 121.62, 118.82, 111.26. HRMS (EI) m/z calcd for $C_{13}H_{10}N_2$ 194.0000, found 194.0004.

Compound **3f**: 2-(2,4-dichlorophenyl)-1*H*-benzimidazole (Table 2): solid, mp −218 to 220 °C, IR (KBr): ν 3192, 2984, 1622 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 12.41 (br s, 1H), 7.92 (d, J = 9.0 Hz, 2H), 7.82 (m, 1H), 7.64–7.58 (m, 3H), 7.25–7.22 (m, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 151.88, 148.80, 143.75, 135.10, 133.29, 129.91, 128.20, 127.78, 122.32, 121.62, 118.52, 111.40. HRMS (EI) m/z calcd for $C_{13}H_8N_2Cl_2$ 262.0065, found 262.0068.

Compound **3g**: 2-(4-chlorophenyl)-1*H*-benzimidazole (Table 2):[5] solid, mp 287–289 °C, IR (KBr): ν 3189, 2980, 1625 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 12.74 (br s, 1H), 8.17 (d, J = 9.0 Hz, 2H), 7.62 (m, 1H), 7.60–7.57 (m, 3H), 7.22–7.19 (m, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 151.80, 143.75, 134.50, 130.12, 129.10, 128.20, 126.20, 122.32, 121.62, 118.52, 111.10. HRMS (EI) m/z calcd for $C_{13}H_9N_2Cl$, 228.0454, found 228.0453.

Compound **3h**: 2-(3-hydroxy phenyl)-1*H*-benzimidazole (Table 2): solid, mp 280–282 °C, IR (KBr): ν 3185, 2989, 1620 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.77 (br s, 1H), 9.69 (br s, OH), 7.59–7.49 (m, 4H), 7.325 (s,1H), 7.17–7.20 (d, 2H), 6.88 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 157.71, 151.31, 143.71, 134.91, 131.38, 129.91, 122.37, 121.53, 118.76, 117.16, 116.89, 113.30, 111.21. HRMS (EI) m/z calcd for $C_{13}H_{10}N_2O$, 210.0793, found 210.0799.

Compound 3j: 2-(3,4-dimethoxy phenyl)-1*H*-benzimidazole (Table 2): solid, mp 180–182 °C, IR (KBr): ν 3192, 2985, 1629 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 12.79 (br s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.28–7.21 (m, 2H), 7.1–7.0 (d, 1H), 6.83–6.73 (m, 2H), 6.45–6.42 (d, J = 9.0 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 153.17, 150.06, 148.65, 135.97, 129.35, 122.31, 121.62, 121.58, 118.9, 111.97, 110.27, 55.8. HRMS (EI) m/z calcd for $C_{15}H_{14}N_2O_2$ 254.1055, found 254.1061.

Compound 3k: 2-benzyl-1*H*-benzimidazole (Table 2):[21b] solid, mp 184–186 °C; IR (KBr): 3047, 2966, 1625 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 12.22 (br s, 1H), 7.52 (d, J = 9.0 Hz, 1H), 7.37 (d, 1H), 7.31 (m, 4H), 7.22 (m, 1H), 7.10 (d, 2H), 4.14 (s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 153.44, 149.36, 143.33, 137.60, 128.69, 128.41, 126.44, 121.55, 120.87, 118.19, 110.85.

Compound **3m**: 2-(2-naphthyl)-1*H*-benzimidazole (Table 2): solid, mp 212–215 °C, IR (KBr): ν 3155, 2925, 2853, 1624 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.02 (br s, 1H), 8.72 (br s, 1H), 8.32 (dd, J = 8.0, 2.0 Hz, 1H), 8.08–7.96 (m, 3H), 7.68–7.57 (m, 4H), 7.24–7.21 (m, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 151.17, 133.38, 132.75, 128.45, 128.35, 127.71, 127.55, 127.01, 126.82, 125.73, 123.87.

Compound **3p**: 5-methyl-2-phenyl-benzimidazole (Table 2):[22a] solid, mp 243–245 °C. IR (KBr): ν 3262, 1745, 1586, 1445, 1261, 1115, 969, 746 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 12.72 (br s, 1H), 8.13 (d, J = 6.9 Hz, 2H), 7.45–7.55 (m, 5H), 7.00 (d, J = 7.0 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 151.3, 130.3 (3C), 129.7, 128.8, 128.9 (2C), 126.35 (2C), 126.25 (3C), 21.8.

Compound **3q**: 5-chloro-2-phenyl-benzimidazole (Table 2):[22b] solid, mp 212–214 °C. IR (KBr): 3580, 2918, 1580, 1430, 1270, 1108, 805, 693 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.1 (br s, 1H), 8.15 (d, J = 8.0 Hz, 2H), 7.68–7.58 (m, 1H), 7.57–7.47 (m, 4H), 7.23–7.22 (dd, J = 8.0, 1.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 153.0 (4C), 130.25, 129.6, 128.9 (2C), 126.5 (2C), 122.25 (3C). HRMS (EI) m/z calcd for $C_{13}H_9N_2Cl$ 228.0454, found 228.0458.

Compound **3r**: 5-nitro-2-phenyl-benzimidazole (Table 2): solid, mp 208–210 °C, IR (KBr): ν 3423, 3081, 1642, 1563, 1539, 1328, 758; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.50 (br s, 1H, NH), 8.46 (d, J = 1.8 Hz, 1H), 8.20–8.18 (m, 2H), 8.12 (dd, J = 7.8, 1.8 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.59–7.57 (m, 3H, ArH); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 155.8 (3C), 142.7, 131.0, 129.1, 129.0 (2C), 127.0 (2C), 118.0 (3C).

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