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ORIGINAL PAPER

Micron-particulate crystalline hexagonal aluminium nitride: a novel, efficient and versatile heterogeneous catalyst for the synthesis of some heterocyclic compounds

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Abstract The present work reports the application of micron-particulate crystalline hexagonal aluminium nitride/aluminium as a novel, mild acidic and reusable solid heterogeneous catalyst in organic synthesis. The catalyst was synthesized by thermal plasma technique and characterized using X-ray diffractometer and scanning electron microscopy. It catalyzes efficiently many organic transformations such as the synthesis of heterocyclic compounds 2,4,5-triaryl-substituted imidazoles and 2-aryl benzimidazoles.

Keywords Aluminium nitride · Heterogeneous catalyst · 2,4,5-Triaryl imidazoles · 2-Aryl benzimidazoles

Introduction

Heterogeneous solid acid catalysts constitute an important role in organic synthesis. The use of conventional Lewis acids is limited on account of their handling risks, disposal problem, inability for recycle, toxicity and corrosiveness. It is essential to minimize the use of environmentally harmful acids and replace them by some novel regenerable solid acid catalysts. Heterogeneous catalysts provide several advantages over the homogeneous catalysts such as recycling ability, easy isolation of the product, high selectivity etc. The nano world helps to minimize such difficulties. Recently, several nano particulate catalysts are being extensively studied for their catalytic applications in numerous organic transformations.

Classically aluminium nitride (AlN) is wide band gap (6.2 eV) semiconductor material having many attractive properties [1–7] such as high thermal conductivity, low electrical conductivity, high dielectric constant, high hardness, high mechanical strength, low thermal expansion coefficient, high temperature stability, high piezoelectric coefficient, high corrosion resistance, non-toxicity [8] and transparency to UV light. These interesting properties make it useful as a potential material in optoelectronic devices [9], high power microwave devices, UV detector [10], biomedical research and water and air purification.

To the best of our knowledge and as per literature survey, AlN is not utilized as a catalyst in organic synthesis besides its applications in the field of nanotechnology and electronic devices.

So, apart from its utilities in semiconductor, electronic and optical devices, in the present paper, we wish to disclose for the first time the application of AlN as an efficient, reusable and versatile heterogeneous catalyst in organic synthesis for carrying out several organic transformations. The increased efficiency of AlN, grown in the present method is supported on the basis of high crystallinity arising from high temperature processes in the thermal plasma reactor [11].

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Experimental

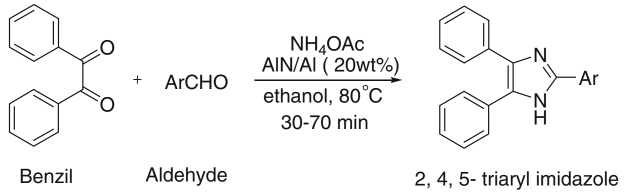
Chemicals and apparatus

The chemicals used are commercially available (SD fine or Sigma Aldrich) and were used without further purification. The reactions were carried out in liquid phase by refluxing the reactants under stirring condition for appropriate reaction time. After completion of reaction as monitored by TLC, the catalyst was separated by filtration, washed with proper solvent and dried to recycle for several times. The products were recovered from the filtrate after concentration on rotary evaporator followed by purification using simple silica gel chromatography. The isolated products were characterized by NMR (400 MHz varian spectrophotometer), IR (Brucker spectrophotometer), ESMS (Shimadzu) and comparison of their melting points reported in the literature. The catalyst was found to promote the following synthetic reactions:

Synthesis of 2,4,5-triaryl-substituted imidazoles

2,4,5-Triaryl and 1,2,4,5-tetraaryl substituted imidazoles constitute a class of biologically potent molecules due to their pharmacological properties [12]. Besides a wide range of their activities (analgesic, fungicidal, herbicidal, anti-inflammatory etc.), 2,4,5-triaryl-substituted imidazole ring skeletons are also used in photography and photosensitive compounds. 2,4,5-Triaryl-substituted imidazoles are synthesized from the benzoin or benzil, ammonium acetate, aromatic aldehydes in the presence of various catalysts such as $InCl_3 \cdot 3H_2O$ [13], $ZrCl_4$ [14], $NiCl_2 \cdot 6H_2O$ [15], p-TSA [16], $Ce_1Mg \times Zr_{1-x}O_2$ [17], L-proline [18], potassium dihydrogen phosphate [19], microwave irradiation [20–22], molecular iodine [23] etc. Many of the previously employed catalysts suffer from several disadvantages such as non-recyclable nature, strong Lewis acids which may create environmental hazards, longer reactions time etc. The mild Lewis acidity associated with the aluminium nitride encouraged us to use it as a catalyst to carry out certain organic transformations. Herein, we wish to report the synthesis of 2,4,5-triaryl-substituted imidazoles using AlN as a novel catalyst (although it is known in nanotechnology for electronic and optical devices, it is till never used in organic synthesis for catalytic applications) (Scheme 1).

In a typical model condensation reaction, a mixture of benzil (1 mmol), aromatic aldehydes (1 mmol) and ammonium acetate (2.5 mmol) with a catalytic amount of the microcrystalline AlN catalyst was refluxed under stirring in ethanol for appropriate reaction time as specified in Table 1. After completion of reaction as monitored by TLC, the reaction mass was diluted with hot ethanol, filtered off to separate the catalyst and the filtrate was concentrated to get crude product which was further purified by crystallization from ethanol. All the aldehydes reacted smoothly to afford high purity products. The advantages associated with this protocol are high yield, short reaction time, mild conditions, ease of product isolation and potential for recycling of the catalytic system.



Scheme 1 Synthesis of 2,4,5-triaryl-substituted imidazoles using AlN/Al catalyst

The spectral data some principal compounds:

4-(4,5-Diphenyl-1H-imidazol-2-yl) phenol (1a) M.P. 267–268 °C; IR (cm^{-1}) 1,213, 1,662, 2,998, 3,592; H^1NMR (DMSO-d_6, 400 MHz) 6.80–6.84 (d, $J = 8$ Hz, 2H), 7.20–7.70 (m, 10 H), 7.95–7.99 (d, $J = 8$, 2H), 9.68 (s, 1H, OH), 12.40 (br, s, 1H). ESMS: 313.39 (M + 1).

2-(4-Chlorophenyl)-4,5-diphenyl-1H-imidazole (2a) M.P. 257–259 °C; IR (cm^{-1}) 3,470, 3,059, 1,602; H^1 (DMSO-d_6, 400 MHz) 7.20–7.40 (m, 10H, Ar–H), 7.55 (d, 2H, $J = 10$ Hz), 12.78 (br, s, NH), ESMS: 331.25 (M + 1).

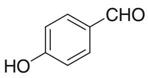
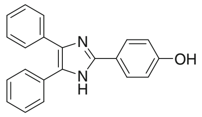
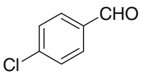
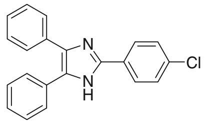
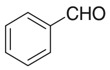
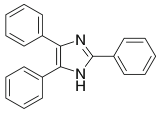
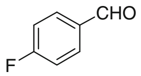
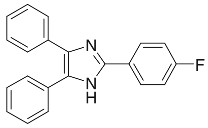
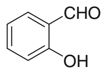
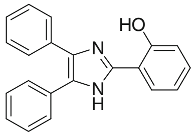
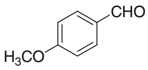
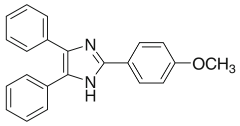
2,4,5-Triphenyl-1H-imidazole (3a) M.P. 273–275 °C, IR (cm^{-1}) 3,450, 3,057, 1,601; H^1 (DMSO-d_6, 400 MHz) 7.20–7.80 (m, 15H, Ar–H), 12.79 (br, s, NH), ESMS: 297.30 (M + 1).

Synthesis of 2-aryl benzimidazoles

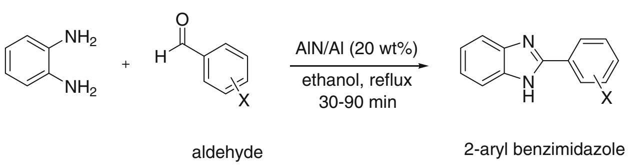
Substituted benzimidazoles heterocyclic moiety containing compounds are of pharmacological and biological interest as some of them are HIV-1 RT inhibitors [24], dipeptidyl peptidase IV inhibitors [25], antimalarial, cytotoxic and antitubercular agents [26] and also inhibitors of MDA-MB-231 human breast cancer cell proliferation [27]. Benzimidazoles are normally synthesized by the condensation reaction of orthophenylene diamine with aldehydes or by the reductive cyclization of ortho nitro anilines. Various reagents/catalysts reported for this transformation include CAN [28], CuI/L-proline [29], copper (II) oxide nanoparticles [30], hypervalent reagents like $PhI(OAc)_2$ [31], NaH [32], iron(II) bromide [33], p-TSA [34], polymer support/MW [35], $NaHSO_3$/MW [36], and TBAF/ultrasound irradiation [37].

In our present study, we have demonstrated microcrystalline AlN/Al synthesized by the high temperature plasma route as a new catalyst for the synthesis of benzimidazoles

Table 1 Microcrystalline AlN catalyzed synthesis of 2,4,5-triaryl substituted imidazoles

Sr. no.	Aldehyde	Product	Time (min)	Yield (%)	M.P. (°C) [References]
1		 **1a**	60	92	267–268 [18]
2		 **2a**	45	94	257–259 [18]
3		 **3a**	45	86	273–275 [16]
4		 **4a**	50	89	189–190 [18]
5		 **5a**	75	90	181–183 [16]
6		 **6a**	30	92	228–230 [16]

(Scheme 2). The reaction was performed by simply refluxing an equimolar mixture of orthophenylene diamine (OPD), aromatic aldehydes and a catalytic amount (20 wt%) of micron-particulate AlN particles for appropriate reaction time as specified in Table 2. After completion of reaction as monitored by TLC (30–50 % EA: petroleum ether), the catalyst was separated as described in the previous section. Almost all the aldehydes reacted cleanly to afford high yield with excellent purity of the benzimidazoles.



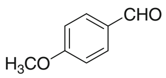
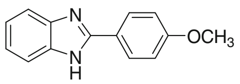
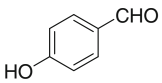
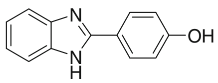
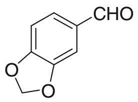
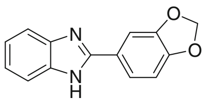
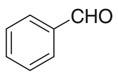
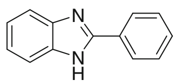
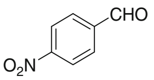
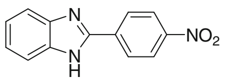
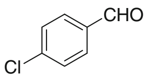
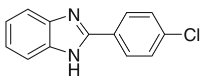
Scheme 2 AlN/Al catalyzed synthesis of 2-arylbenzimidazoles

The spectral data some principal compounds:

2-(4-Methoxyphenyl) benzimidazole (7a) M.P. 182–184 °C; IR (cm^{-1}) 3,320, 2,963, 1,610, 1,479, 1,295; H^1 (DMSO-d_6, 400 MHz) 3.85 (s, 3H), 6.9 (d, 2H), 7.08–7.25 (m, 4H), 7.72 (d, 2H), 12.76 (brs, NH); ESMS: 225 (M + 1).

2-(4-Hydroxyphenyl) benzimidazole (8a) M.P. 169–171 °C; IR (cm^{-1}) 3,270, 3,052, 1,597, 1,470; H^1 NMR (DMSO-d_6, 400 MHz) 4.4 (s, 1H, OH), 6.6–6.75

Table 2 Micro crystalline AlN catalyzed synthesis of 2-arylbenzimidazole

Sr. no.	Aldehyde	Product	Time (min)	Yield (%)	M.P. (°C) [References]
1		 **7a**	50	89	223–224 [37]
2		 **8a**	45	90	169–171 [28]
3		 **9a**	35	92	234–236 [28]
4		 **10a**	50	89	289–290 [36]
5		 **11a**	90	87	253–255 [28]
6		 **12a**	30	93	291–293 [36]

(d, 2H), 6.8–6.95 (m, 4H), 7.3 (d, 2H), 9.9 (1H, s, NH); ESMS: 211 (M + 1).

2-(3,4-Methylenedioxyphenyl) benzimidazole (9a) M.P. 234–236 °C; IR (cm^{-1}) 2,905, 1,610, 1,466, 1,282; H^{1} (DMSO-d$_6$, 400 MHz) 5.96 (s, 2H), 6.45 (d, 1H), 6.6 (s, 1H), 6.8 (d, 1H), 7.1–7.8 (m, 4H), 12.75 (br, 1H, NH); ESMS: 211 (M + 1).

Catalyst preparation

The catalyst was synthesized by known method in a DC-transferred arc plasma reactor (DCTATPR). The reactor consists of a double-walled, water-cooled stainless steel cylindrical chamber with a hemispherical top flange. The vertical movable plasma torch was mounted on the top flange and aluminium block was placed on the graphite anode. The plasma forming gas was N_2, the flow of which was maintained at 5 lpm. The reactor chamber was pre-evacuated to a pressure of 0.01 mbar and the pressure in the reactor was maintained at a level close to atmospheric pressure, by purging nitrogen into the chamber with a controlled flow rate. The operating parameters of the reactor are given in Table 3.

The aluminium anode was melted by the plasma impingement and at sufficient high temperature, nitrogen from the plasma started reacting with aluminium. The growth of the anode block was seen to occur. The crystallites of aluminium nitride as well as those of aluminium were identified by their appearance (luster and color). Morphology of the crystallites was studied with the help of scanning electron microscopy (SEM), whereas the crystalline structure was ascertained from the X-ray diffraction (XRD) analysis.

The ingot was then purified by treating it with HCl and crushed into the powder. Aluminium was dissolved off and the crystals of hexagonal AlN (h-AlN) were obtained for the further catalytic application.

Catalyst characterization

X-ray diffraction studies

The as-grown product and post-process samples were characterized at room temperature by powder XRD analysis. Plots in Fig. 1a and b correspond to the standard line pattern for h-AlN and cubic Al (c-Al) as referred to JCPDS

Table 3 Typical operating condition for synthesis of AlN/Al crystals

Sr. no.	Operating parameter	Range of values
1	Plasma current	70, 100 A
2	Torch voltage	50–60 V
3	Flow rate of plasma forming gas (N_2)	5 lpm
4	Flow rate of ambient gas (N_2)	15 lpm
5	Operating pressure	710 mbar
6	Arc length	70–80 mm
7	Size of aluminium anode	Disc with diameter 50 mm and 12 mm thick

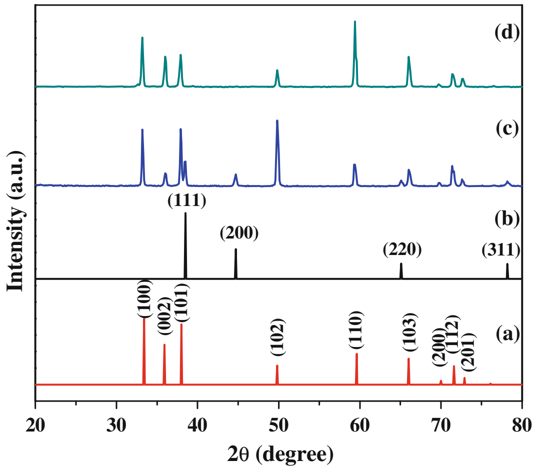


Fig. 1 XRD pattern of **a** standard hexagonal AlN (JCPDS #79-2479), **b** standard cubic Al (JCPDS #85-1327), **c** as grown crystals and **d** HCl-etched powder sample

data's from #79-2497 and # 85-1327, respectively. The indices of h-AlN and c-Al are marked in line pattern. Figure 1c refers to the XRD pattern recorded for the as-synthesized crystalline ingot. From XRD pattern, it is seen that it consists of both h-AlN and c-Al phases. Calculated lattice parameters for h-AlN: $a = 3.11$ A, $c = 4.97$ A, c/a ratio $= 1.60$ and for c-Al: $a = 2.4$ A are consistent with wurtzite AlN and c-Al structure [2, 7, 12–15]. Volume fraction of Al content in the samples was calculated by comparing the observed intensity of AlN (100), AlN (101), Al (111) and Al (200) lines. Average volume fraction of c-Al and h-AlN phase is found to be 30 and 70 %, respectively. Figure 1c shows the XRD pattern of HCl-treated powder sample. The sample is seen to consist of pure h-AlN phase and is free of c-Al traces.

Scanning electron microscopy

Figure 2a shows the SEM micrograph of the as-synthesized crystalline sample obtained from the ingot. Hexagonally facetted crystalline structure having dimensions of approximately 100–150 µm in size are observed. These pallets most probably belong to crystalline AlN as already been confirmed from the XRD analysis; however, there seems to be added traces of aluminium as found in XRD pattern in Fig. 1c. In order to remove the traces of Al, the ingot was post-processed (etched) with HCl. Figure 2b shows the SEM micrograph of the post-processed sample. Black holes are formed as a result of etching, and provide improved reaction sites for catalytic applications.

Results and discussion

The transformations described herein are normally reported in strong acidic (both conventional and Lewis) conditions, using various ionic liquids, microwave or ultrasound promoted synthesis. Strong acids are not beneficial as far as environmental safety is concerned. Also the microwave or ultrasound promoted synthesis requires the additional use of microwave oven or sonicator. As a part of our attempts to develop versatile and efficient methods for the synthesis of heterocyclic compounds, we have successfully synthesized 2,4,5-triaryl-substituted imidazoles and benzimidazoles using microcrystalline AlN as a novel, heterogeneous, reusable and efficient catalyst. The yield of products using this practical approach for the synthesis of various pharmacologically important heterocyclic molecules is comparable with the previous reported methods.

Although the laboratory synthesis of catalyst seems to be difficult, there are certain advantages associated with the catalyst. This catalyst is mild Lewis acidic in nature. An important advantage of the catalyst is that it is heterogeneous owing to which it facilitates the separation process from the reaction mass after completion of the reaction simply by diluting with organic solvent (ethanol in this case) and filtering. The catalyst after drying offers good reusability results without any loss of its catalytic activity. It is stable in hydrogen and carbon dioxide atmospheres up to 980 °C. Furthermore, melting point of the catalyst being high (2,200 °C), its effective catalytic activity can be studied up to high temperature; maintaining its heterogeneous nature. It provides a new route for the synthesis of 2,4,5-triaryl imidazoles and 2-aryl benzimidazoles. On the basis of above stated facts, the catalyst is found to be

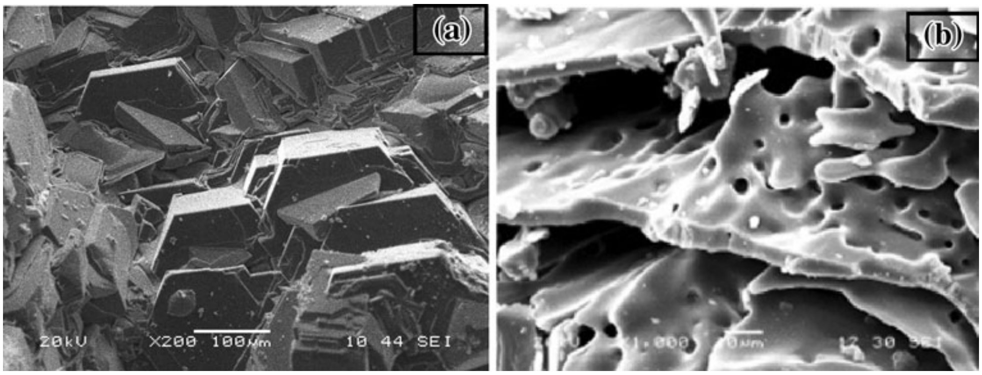


Fig. 2 **a** SEM micrograph of grown crystallites, **b** SEM micrograph of etched powder sample

Table 4 A comparative study of the effect of catalyst (AlN) on the synthesis of 2,4,5-triaryl-substituted imidazoles

Sr. no.	Catalyst	Conditions	Yield (%)	References
1.	L-Proline	EtOH/reflux, 2–5 h	75–94	[18]
2.	$InCl_3 \cdot 3H_2O$	MeOH/r.t., 8.3–9.4 h	54–82	[13]
3.	p-TSA	TBAI, 140 °C, 1–4 h	75–95	[16]
4.	AcOH	180 °C, MW, 5 min	87–97	[20]
5.	$Ce_1Mg \times Zr_{1-x}O_2$	$EtOH:H_2O$, 70 °C, 35–50 min	80–94	[17]
6.	Silica gel	MW, 8 min	58–92	[21]
7.	AlN	EtOH/reflux, 30–70 min	86–94	Present work

superior and hence can be further used for the synthesis of various heterocyclic compounds. A comparative study of the catalytic effect of our catalyst with the literature reported protocols for the synthesis of 2,4,5-triaryl imidazoles is summarized in Table 4. The reduced time and enhanced yield of the corresponding products can be accounted on the basis of small particle size.

Conclusion

In conclusion, micron particulate crystalline AlN is used as a mild heterogeneous and convenient catalyst for the synthesis of a variety of pharmacologically and biologically potent heterocyclic scaffolds. The present synthetic methodology is a simple, efficient and involves easy catalyst separation than those achieved by the traditional methods. The advantages of this catalyst include easy handling, excellent yields and high purity of the products. We strongly believe that the material AlN will really emerge as a novel and efficient catalyst in organic synthesis in addition to its applications in nanotechnology as in case of semiconductors, optical and electronic devices.

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