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An Efficient, Solvent Free One Pot Synthesis of Tetrasubstitued Imidazoles Catalyzed by Nanocrystalline γ-alumina

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ABSTRACT

γ-Alumina nanoparticles (γ-Al_2O_3 NPs) have been successfully synthesized by electrochemical reduction method. The aqueous solution of tetrapropylammonium bromide was used as an electrolyte cum stabilizer. To prevent spontaneous agglomeration and control nanoparticles size various parameter such as current density, distance between electrodes and concentrations of electrolyte are optimized. γ-Al_2O_3 NPs thus synthesized were characterized by sophisticated analytical techniques including X-ray diffraction, scanning electron microscopy, energy dispersive spectrophotometer and high- resolution transmission electron microscopy These synthesized γ-Al_2O_3 NPs were tested used as a catalyst for one pot synthesis of tetraaryl imidazole derivatives from the cyclodehydration and condensation of benzil, aromatic aldehyde, anilines and ammonium acetate under solvent free condition. This method has various advantages like convenient work-up procedure, environmentally benign and less reaction times along with excellent yields. Easy availability, several times recyclability, very simple isolation and eco-friendliness were some attractive features of the nanocrystalline γ-Al_2O_3 catalyst.

Keywords: Nanocrystalline γ-alumina; electrochemical reduction method; heterogeneous catalyst; tetraaryl imidazole; solvent free.

INTRODUCTION

Among heterocycles, imidazoles are an important class of compounds being an active component of not only many naturally occurring products like biologically important amino acids histidine, histamine; highly significant biomolecule, vitamin B_{12}, vitamin-H; bases in nucleic acid adenine, guanine; pilocarpine alkaloids and other alkaloids but also synthetic derivatives such as Losartan, Olmesartan, Eprosartan and Trifenagrel[1]. Imidazole and its analogues are centre of attraction for

researchers around the globe due to their diverse bioactivities. Imidazole derivatives were reported to be involved in the biosynthesis of interleukin-1 (IL-1)[2] and were also reported to function as cyclooxygenase-2 (COX-2) [3] B-Raf kinase[4], transforming growth factor β1 (TGF-β1) type 1 activin receptor-like kinase (ALK5)[5] and p38 MAP kinase[6] inhibitors. Appropriately substituted imidazoles were used as CB1 cannabinoid receptor antagonists[7], modulators of P-glycoprotein (P-gp) mediated multidrug resistance (MDR)[8] and glucagon receptors[9]. The imidazole core was reported to exhibit antiedema and anti-inflammatory[10, 11], analgesic[13], antifungal [12], antiviral[14], anthelmintic[15], antibacterial[16], antitumor[17], antitubercular[18], antibiotic, anti-ulcerative[19]. The potency and pertinence of imidazole pharmacophore is largely due to its hydrogen bond forming nature as well as its high affinity towards metals like Fe, Zn, and Mg in the protein active sites[20].

A numerous ways have been developed for the synthesis of polysubstituted imidazoles. Condensation involving cyclodehydration of different aldehyde/substituted aldehydes, anilines/substituted anilines with benzil is an important and mostly employed method for tetrasubstituted imidazole formation in organic synthesis. The various types of bulk catalysts, such as DABCO[21], $HClO_4$-SiO_2[22], molecular I_2[23], heteropoly acids[24], $InCl_3.3H_2O$[25], PEG-400[26], $ZrCl_4$ [27], $K_5CoW_{12}O_{40}.3H_2O$[28], silica gel or zeolite HY[29], $BF_3.SiO_2$[30], silica bonded propyl piperazine N-sulfamic acid (SBPPSA)[31] and silica gel / $NaHSO_4$ [32], were employed for synthetic purpose. All these catalyst / methods suffered from disadvantages like, moisture sensitive, expensive, toxic catalysts, volatile organic solvents, painstaking workup, high reaction time, higher quantities of catalysts, need of special apparatus and tedious procedures of recovery and reusability of the catalysts. Among various nano-catalysts, nanocrystalline metal oxides have found application in multi-component reactions. Some of the most frequently used metal oxides are: Fe_3O_4, ZnO, CuO, In_2O_3, TiO_2, MgO, Fe_2O_3, ZrO_2, CeO_2 and Al_2O_3. The multi-component reactions are very lethargic in absence of catalyst. Consequently the development of a mild, simple, more efficient, cheaper and green procedure for the synthesis of highly substituted imidazole is exceedingly desirable. Solvent free reactions are becoming more popular as they are safe, nontoxic and inexpensive. The recovery of the catalyst and separation of product is easier in case of solvent free reactions than conventional routes. Use of nanoparticles as catalysts in organic transformations is one of the emerging trends currently. Literature survey showed that nanocatalysts are associated with selectivity, reactivity and improved product yields[33-37].

In recent years, nano-catalysts have gained prominence efficiency, moisture insensitivity and greater selectivity due to their high surface area. Alumina is one of the inert biomaterial used in implants due to its biocompatible nature [38-41]. Aluminium oxide exists in number of metastable forms (γ, δ, θ, κ, ε, η, χ) and γ-Al_2O_3 has significant applications as a catalyst[42]. Electrochemical reduction method was firstly reported by Reetz et al[43] for the synthesis of transition metal nanoparticles.

In focus of this extensive literature survey, we have reported an efficient, solvent free synthesis of imidazoles. These multi-component reactions were carried without the assistance of any acid or base. We have synthesized γ-Al_2O_3 NPs by electrochemical reduction method and cyclodehydration-condensation reaction of aromatic aldehyde, anilines, ammonium acetate and benzil was successfully carried out in the presence of γ-Al_2O_3 NPs.

EXPERIMENTAL

Materials

All chemicals (upto 99% purity) were purchased from Loba chemie and Merck chemicals suppliers and liquid chemicals were purified. The purity of the chemicals was confirmed by FT-IR spectrum.Distilled water were used as a solvent.

Catalyst preparation

In the synthesis of catalyst used a sacrificial anode in the form of aluminium sheet (1 cm x 1 cm) and platinum sheet (1 cm x 1 cm) as inert cathode. These two electrodes were separated from each other by a distance 1 cm in electrolysis cell. The aqueous solution of tetrapropylammonium bromide (TPAB 0.01M) was the electrolyte cum stabilizer. Formation of aluminium hydroxide was observed by monitoring the turbidity in solution applying constant current density 10 mA/cm^2 for two h. As electrolysis process was not carried out in an inert atmosphere

and therefore due to presence of dissolved moisture, the aluminium hydroxide nanoparticles were formed instead of pure aluminium metal nanoparticles. These nanoparticles were white in color. The intermediate product collected simply by decantation, washed with distilled water 3-4 times to remove unreacted tetrapropylammonium bromide and dried under vacuum desiccators. This dried sample was calcined at 900°C to convert it γ-Al_2O_3 NPs and stored under ambient conditions.

Catalyst characterization

The synthesized nanoparticles were characterized by using XRD, SEM-EDS and HRTEM techniques. The crystallinity and crystal phase of the γ-Al_2O_3 NPs was recorded using Bruker D8 Advance X-ray diffractometer with Cu - $K_{\acute{a}}$ radiation (λ = 1.5406 Å). To study morphology of γ-Al_2O_3 NPs SEM analysis was carried out with JEOL-JED 2300 (LA) equipment. The elemental composition of the γ-alumina nanoparticles was examined using an energy dispersive spectrophotometer (EDS). The HRTEM was carried out with a FEI Model Tecnai F 30 equipment operated at 100-300kV.

General reaction procedure

Benzil (1 mmol), substituted anilines (1 mmol), benzaldehyde (1 mmol), ammonium acetate (2 mmol), and 35 mg of γ-Al_2O_3 NPs were mixed, stirred vigorously and heated on bare flame for 5-15 minutes. The progress of reaction was monitored by thin layer chromatography technique on aluminium TLC plate and visualization under ultraviolet (UV) light. Chloroform was added to the reaction mixture to dissolve the organic materials and γ-Al_2O_3 nanocatalyst was filtered for recylization purpose. Chloroform was removed to separate the products. It was then recrystallized to obtain the pure compound. The products (3a-3e) were confirmed by comparison with standard data using FTIR, ^{1}H NMR, ^{13}C NMR and melting points. The melting points of compounds were determined with the help of digital melting / boiling point apparatus (EQ 730, Equiptronics). Infrared Spectra were recorded on Schimadzu IR-Affinity-1 FTIR spectrophotometer in cm^{-1} (KBr). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 NMR spectrometer operated at 400 MHz and 100 MHz respectively with DMSO d_6 as solvent. In NMR & CMR spectrum, chemical shift (δ) values are recorded in ppm using internal standard tetramethylsilane as an internal standard.

RESULT AND DISCUSSION

XRD characterization

The crystallinity and crystal phase of nanoparticles were examined by the X-ray diffraction pattern and shown in Fig. 1. The grain or crystallinity size of nanoparticles is related to the diffraction peak broadening. Fig. 1 shows the XRD pattern of a synthesized sample after calcinations at 900°C for 2 h. There is a formation of single phase of well crystalline γ-Al_2O_3 with cubic structure (JCPDS 02-1420). No peaks from impurities were observed. The (440) peak has a stronger intensity than the other peaks, indicating that the (440) planes may be preferential growth direction. The X-ray line broadening was used to calculate average particle size using Debye-Scherrer's equation, $D = k\lambda / \beta\cos\theta$, where D is average particle size, k is shape constant, λ is wavelength, è is diffraction angle and β is full width half maxima. The average particle size was found to be 3.93 nm.

SEM-EDS analysis

The SEM micrograph Fig. 2(a) of γ-Al_2O_3 NPs showed well dispersed irregular spherical shape. The qualitative and quantitative analysis was carried out using EDS spectrum. Results of elemental composition of γ-Al_2O_3 NPs are shown in Fig. 2(b). The elemental 56.72 weight % of O (68.85 atomic %) and 43.28 weight % of Al (31.15 atomic %). EDS data exhibited peaks only for Al and O which support the formation of γ-Al_2O_3 NPs.

HRTEM analysis

HRTEM analysis was carried for evaluation of particle size, crystallinity and morphology of the sample. Fig. 3(a) showed that the particles were well dispersed. The HRTEM micrograph of the γ-Al_2O_3 NPs reveals the formation of ultra-fine nanoparticles Fig. 3(a) with the polycrystalline nature being confirmed by the ring pattern of the SAED (the insets Fig. (3a)). Lattice fringe image Fig. 3(b) exhibits the regular spacing of the lattice plane which is found to be 0.140 nm corresponding to the (440) lattice plane of the γ- phase of alumina. The atomic scale imaging Fig. 3(b) of the nanocrystallites were carried out from a small region as indicated by a circle in Fig. 3(a).

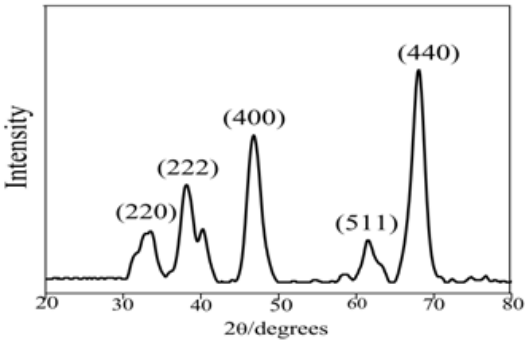


Fig. 1: XRD pattern of the γ-Al_2O_3 NPs

Catalytic activity

In present investigation, synthesis of 1,2,4,5-tetraaryl substituted imidazoles using benzil 1, substituted anilines 2, benzaldehyde 3, ammonium acetate 4 by applying γ-Al_2O_3 NPs as catalyst as shown in Scheme 1. All reaction was performed under dichloromethane, ethanol and solvent free condition. Physical data shown in Table 1.

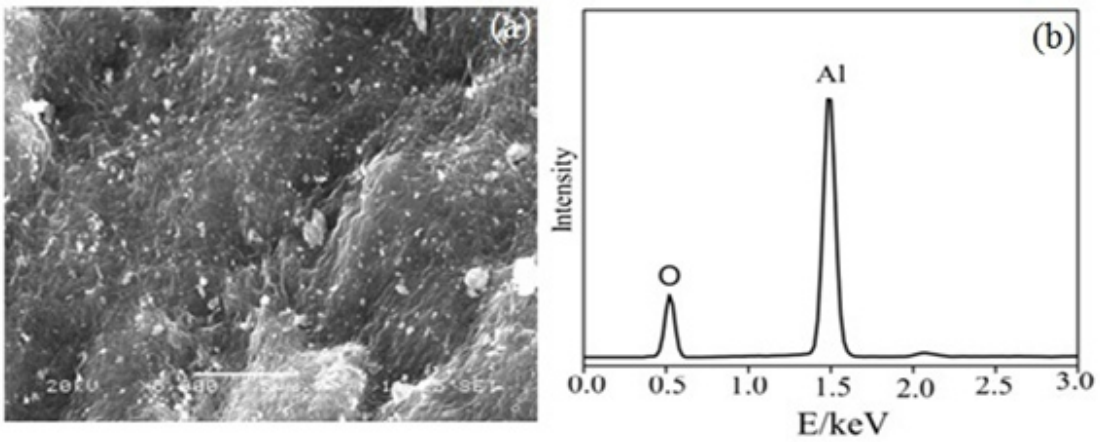


Fig. 2: (a) SEM and (b) EDS characterization of the γ-Al_2O_3 NPs

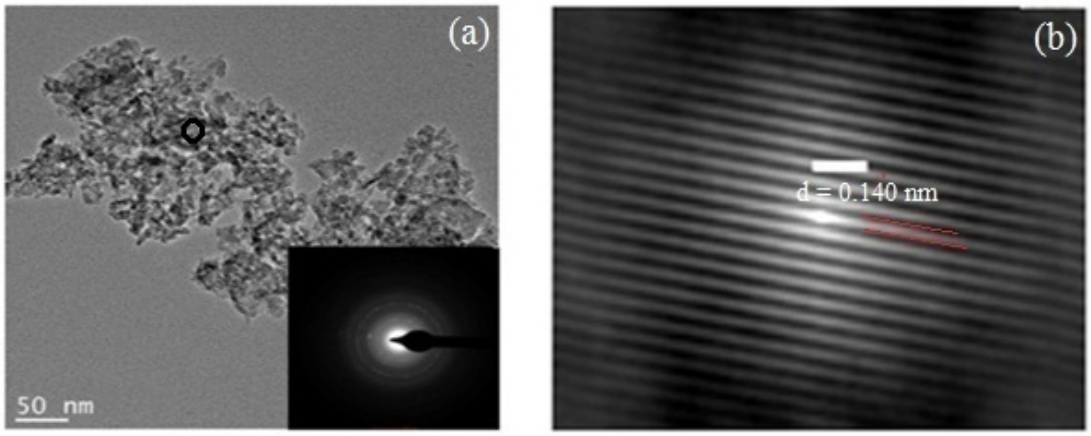


Fig. 3: HRTEM image of the γ-Al_2O_3 NPs (a) particles along with the SAED pattern (b) lattice scale fringes

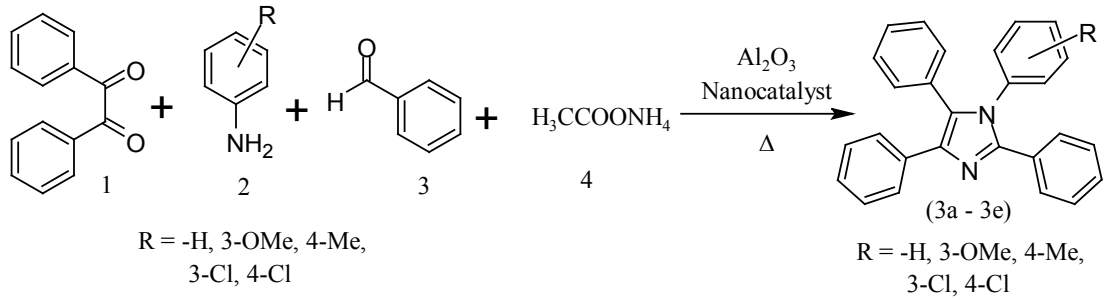
Spectral data of compounds

1,2,4,5-Tetraphenyl-1H-imidazole

Cream crystal. ^{1}H NMR (DMSO, ppm) δ = 7.94-7.96 (m, 2H, ArH), 7.46-7.51 (m, 4H, ArH), 7.37-7.39 (m, 2H, ArH), 7.32 (m, 3H, ArH), 7.24-7.28 (m, 4H, ArH), 7.16-7.22 (m, 5H, ArH); IR-(KBr) η = 3061 (Ar-H stretch), 1494,1600 (Aromatic C=C stretch) 1442 (C=N stretch), 1249 (Ar-N stretch)

1-(3-Chlorophenyl)-2,4,5-triphenyl-1H-imidazole

White powder. ^{1}H NMR (DMSO, ppm) δ = 7.46-7.51 (m, 3H, ArH), 7.39-7.42(m, 3H, ArH), 7.33-7.36 (m, 7H, ArH), 7.24-7.29 (m, 5H, ArH), 7.18 (m, 1H, ArH); IR-(KBr) η= 3050 (Ar-H stretch), 1492, 1598 (Aromatic C=C stretch), 1446, 1394 (C=N stretch), 1249, 1230, 1174 (Ar-N stretch)



Scheme 1: Synthesis of tetraaryl imidazole derivatives using γ-Al_2O_3 NPs

Table 1: Synthesis of 1,2,4,5-tetraaryl imidzole derivatives catalyzed by γ-Al_2O_3 NPs

Product[a]	-R	Using dichloromethane		Using ethanol		Solvent free		Melting point(°C)	
		Time (min)	Yield[b] (%)	Time (min)	Yield[b] (%)	Time (min)	Yield[b] (%)	Found	Reported
3a	-H	110	67	75	73	10	85	214-216	213-215 [44]
3b	3-OMe	100	70	85	76	08	89	218-220	New
3c	4-Me	100	80	95	84	06	94	184-186	183-185[45]
3d	3-Cl	130	72	110	80	08	92	208-210	205-207[46]
3e	4-Cl	120	77	100	82	07	92	230-232	New

[a] Reaction condition : Benzaldehyde (1 mmol), substituted anilines (1 mmol), ammonium acetate (2 mmol), benzil (1 mmol) and 35 mg of γ-Al_2O_3 NPs.

[b] Isolated yield

Table 2: Screening of catalyst for the synthesis of 3c

Entry	Catalyst amount (mg)	Time (min)	Yield (%)
1	10	50	40
2	20	30	60
3	30	10	80
4	35	06	94
5	50	07	95

1-(3-Methoxyphenyl)-2,4,5-triphenyl-1H-imidazole

Cream crystal. ^{1}H NMR (DMSO, ppm) δ = 7.41-7.50 (m, 4H, ArH), 7.27-7.31 (m, 7H, ArH),

Table 3: Studies of recyclability of γ-Al_2O_3 NPs in the synthesis of 3c

Run	Fresh	1	2	3	4
Yield (%)	94	91	89	88	84

7.16-7.26 (m, 5H, ArH), 6.75-6.89 (m, 3H, ArH), 3.61 (s, 3H, Ar-OCH_3); ^{13}C NMR (100 MHz, DMSO) δ = 55.05, 120.49, 126.18, 126.48(s), 127.83(s), 128.01, 128.04, 128.11, 128.17(vs), 128.53, 129.16, 129.57, 130.33, 130.78, 130.85(s), 132.40, 134.30, 137.06, 137.56, 145.87, 159.38; IR-(KBr) η = 2926 (Aliphatic C-H stretch) 3062 (Ar-H stretch), 1479,1498, 1583(Aromatic C=C stretch), 1444, 1392 (C=N stretch), 1180(Ar-N stretch)

1-(4-Chlorophenyl)-2,4,5-triphenyl-1H-imidazole

White powder. ^{1}H NMR (DMSO, ppm) δ = 7.48-7.50 (m, 2H, ArH), 7.35-7.40 (m, 4H, ArH), 7.30-7.33 (m, 6H, ArH), 7.21-7.26 (m, 6H, ArH), 7.17 (m, 1H, ArH); ^{13}C NMR (100 MHz, DMSO) δ = 126.28, 126.44(s), 127.85(s), 127.97(s), 128.18, 128.22(vs), 128.33, 128.99(s), 130.04(s), 130.07, 130.79, 130.90(s), 133.33, 134.13, 135.37, 137.17, 146.06; IR-(KBr) η =3039, 3055 (Ar-H stretch), 1492,1600 (Aromatic C=C stretch), 1444, 1396 (C=N stretch), 1182 (Ar-N stretch)

1-(4-Methylphenyl)-2,4,5-triphenyl-1H-imidazole

White powder. ^{1}H NMR (DMSO, ppm) δ = 7.44-7.59 (m, 7H, ArH), 7.34-7.40 (m, 6H, ArH), 7.28-7.33 (m, 4H, ArH), 7.15 (d, 2H, ArH), 2.25 (s, 3H, Ar-CH_3); ^{13}C NMR (100 MHz, DMSO) δ = 122.84, 123.41, 126.54, 126.85, 127.37, 127.72(s), 128.01, 128.42, 128.52(s), 128.60, 128.65, 128.83, 128.97, 129.25, 129.34, 129.58, 129.78, 129.83(s), 130.29, 131.02, 131.16, 131.53, 139.71, 143.82, 144.56, IR-(KBr) η = 3055 (Ar-H stretch), 2964 (Aliphatic C-H stretch), 1489, 1512, 1595 (Aromatic C=C stretch), 1442 (C=N stretch), 1219 (Ar-N stretch)

The optimization of reaction condition and amount of catalyst was carried out using benzil, 3-methoxy aniline, ammonium acetate and γ-Al_2O_3 NPs (3c) as shown in Table 2.

Considering the green chemistry aspect, efficient recovery and reprocess of the catalyst are highly enviable. As a result, the recovery and reusability of γ-Al_2O_3 NPs were investigated. After completion of the reaction, the reaction mixture was dissolved in chloroform and catalyst was separated by filtration catalyst. The catalyst was washed thoroughly with ethanol and distilled water followed by activating it at 260°C about 2 h for reusability. The reusability of the catalyst was checked for the synthesis of 1-(4-methylphenyl)-2,4,5-triphenyl-1H-imidazole (3c) and this was carried out four successive reactions giving 91, 89, 88, 84% yields of the product Table 3. The study exposed us even after four cycles, the catalyst was found to be efficient to carry out the reaction offering almost same catalytic activity.

In summary, γ-Al_2O_3 NPs are practical alternative to existing procedures for the synthesis of various derivatives of polysubstituted imidazole. The promising points of the present methodology were a simple, efficient and environmentally benign one pot procedure for the synthesis of 1,2,4,5-tetraaryl substituted imidazole by using catalytic amount of γ-Al_2O_3 NPs under thermal and solvent-free conditions. The method has salient features like mild reaction conditions, environmental compatibility, ease of isolation of product, easy separation of catalyst and easy availability of starting materials. By using above procedure good to excellent yields of products are obtained in minimum reaction time, which might be due to Lewis acid behavior of small particle size of γ-Al_2O_3 NPs (with large surface area). The enhancement of the yield reveals catalyst can be used as an attractive alternative for the synthesis of many similar compounds.

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