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RESEARCH PAPER

Kaolin-SO_3H Nanoparticles: A New Efficient and Reusable Catalyst for Synthesis of 2-Substituted Benzimidazoles at Room Temperature

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ABSTRACT

Kaolinite clay found its application in medicine, in toothpaste, in cosmetic and as a food additive. Recently, a specially formulated spray is used in fruit and vegetable production to repel the insects and prevent sunburn. Kaolin-SO_3H nanoparticles were prepared via reaction of kaolin and chlorosulfonic acid and characterized by FT-IR, XRD, FESEM, TEM, XRF, EDS, BET and TGA. 2-Substituted benzimidazoles have been used as selective neuro-peptides YY, receptor antagonists, antitumor, antivirus, antimicrobial, antioxidant, antiparasitic, antihelmintics, antiproliferative, anti-HIV, anticonvulsant, anti-inflammatory, antihypertensive, antineoplastic, analgesicand antitrichinellosis, topoisomerase IV inhibitors, potent inhibitors of TiE-2 and VEGFER-2 tyrosine kinase receptor, and 5-HT3 antagonists. 2-Substituted benzimidazoles are prepared via condensation of *o*-phenylenediamines and aldehydes. In this article, we have used Kaolin-SO_3H nanoparticles for the synthesis of 2-substituted benzimidazoles under mild reaction conditions. The structure of products were identified by FT-IR, ^{1}H-NMR and ^{13}C-NMR. This method has the advantages of high yields, short reaction times and easy work-up.

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INTRODUCTION

Benzimidazole nucleus is a bicyclic compound which is structurally similar to purine bases. This structure has been found in many natural compounds such as vitamin B_{12} and its derivatives [1]. These structures are one of the most biologically active classes of compounds, possessing a wide range of activities. They have been used as selective neuro-peptides YY [2], receptor antagonists [3], antitumor [4], antivirus [5],antimicrobial [6], antioxidant [7], antiparasitic [8], antihelmintics [9], antiproliferative [10], anti-HIV [11], anticonvulsant [12], anti-inflammatory [10], antihypertensive [13], antineoplastic [1], analgesic and antitrichinellosis [1], topoisomerase IV inhibitors [14], potent inhibitors of TiE-2 and VEGFER-2 tyrosine kinase receptor [15], and 5-HT3 antagonists [16]. Due to the importance of these compounds in industries, various methods have been reported in the literature for the synthesis of benzimidazoles [17-25].

Kaolinite (hydrated aluminum silicate) with chemical composition $Al_2Si_2O_5(OH)_4$ is one of the most common minerals [26]. Large volumes of kaolinite clays are used for the production of cement [27] and ceramics [28]. The greatest demand for kaolinit is in the paper industry to produce a high-quality paper [29]. It is also

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used as filler for paint rubber and plastics [21]. Kaolinite clay found its application in medicine, in toothpaste, in cosmetic and as a food additive [29]. Recently, a specially formulated spray is used in fruit and vegetable production to repel the insects and prevent sunburn [30]. Usually, suitable kaolin contains 70-73% of SiO_2, 18-20% of Al_2O_3, 0.4-1% of Fe_2O_3, and 0-0.8% of TiO_2 and no MnO.

Kaolin-SO_3H nanoparticles as a green heterogeneous catalyst was prepared by the reaction of kaolin nanoparticles with chlorosulfonic acid. It could be an efficient solid acid catalyst for promotion of many organic reactions.

In continuation of our efforts in using solid acids in organic synthesis [31-35], here, we wish to report the synthesis of 2-substituted benzimidazoles from aldehydes and o-phenylenediamines using kaolin-SO_3H nanoparticles as a mild heterogeneous catalyst. This procedure was done at room temperature and in the presence of O_2 of air as oxidant.

MATERIALS AND METHODS

All Chemicals and solvents such as ortho-phenylenediamines, aldehyde derivatives, chlorosulfonic acid, kaolin nanoparticles and ethanol were purchased from Fluka, Merck and Aldrich chemical companies and were used without any further purification. All of the products are known compounds which were characterized by comparison of their spectral (FTIR, ^1H and ^{13}C NMR) and physical data with authentic samples. FTIR spectra were determined on a Nicolet Magna series FT-IR 550 spectrometer using KBr pellets. Thin layer chromatography (TLC) on commercial aluminium-backed plates of silicagel 60 F_{254} was used to monitor the progress of the reactions. Melting points were obtained with a micro melting point apparatus (Electrothermal, Mk3). ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 Avance spectrometer in $CDCl_3$ as solvent and chemical shift are expressed in δ ppm relative to tetramethylsilane. The XRD patterns were collected on a Philips Xpert MPD diffractometer equipped with a Cu Kα anode (λ=1.54 A˚) in the 2θ range from 10 to 80˚. Elemental composition was investigated by XRF BRUKER S4 EXPLORER. Average size of kaolin-SO_3H nanoparticles was analyzed by FESEM and TEM using a Mira 3-XMU and Philips CM120 with a LaB6 cathode and accelerating voltage of 120 kV, respectively. Brunauer–Emmett–Teller (BET) surface area analysis of catalyst was done with Micromeritics, Tristar II 3020 analyzer. Quantitative elemental information (EDS) of kaolin -SO_3H nanoparticles was measured by EDS instrument, Phenom pro X.

Preparation of Kaolin-SO_3H nanoparticles

In a ventilated cabinet, a 100 mL suction flask containing 5 g of commercial kaolin nanoparticles was equipped with a dropping funnel containing 10 mL of chlorosulfonic acid and gas inlet tube for conducting obtained HCl gas over a water vessel. Then, 25 mL of chloroform was added to the suction flask and chlorosulfonic acid was added drop-wise to the mixture with vigorously mixing at room temperature. After the addition of chlorosulfonic acid was completed, a white solid was obtained. The solid was filtered and washed with chloroform and dried at room temperature. The kaolin-SO_3H nanopaticles was obtained with 98 % yield and characterized by FT-IR, XRD, SEM, TEM, XRF, TGA, EDS and BET techniques.

Preparation of 2-substituted benzimidazoles

A mixture of aromatic aldehyde (1 mmol), ortho-phenylenediamine (1 mmol) and Kaolin-SO_3H nanoparticles (0.025 g) was stirred in a tube for 10-55 minutes at room temperature in 10 ml ethanol as solvent. After completion of the reaction, the reaction mixture was washed with hot ethanol. Products were separated from the catalyst by filtration and after evaporation of the solvent, the pure products were obtained.

Spectroscopic data

2-Phenyl-1*H*-benzimidazole (1): white solid. Mp / °C: 285-288 (Lit. 289-291 [36]). ῡ (KBr) / cm^{-1}: 3421 (N-H), 3050 (=C-H), 1630-1461 (C=C and C=N), 755 (=C-H), 755 and 698 (=C-H). ^1H NMR (DMSO-d_6) / ppm: δ_H = 8.14 (d, 2H, J=7.6 Hz), 7.74 (m, 2H), 7.64 (m, 3H), 7.39 (m, 2H). ^{13}C NMR (DMSO-d_6) / ppm: δ_C = 149.41, 147.82, 133.13, 131.41, 131.34, 124.76, 124.71, 122.98.

2-(4-Methylphenyl)-1*H*-benzimidazole (2): White solid. Mp / °C: 261-262 (Lit. 262-264 [37]). ῡ (KBr) / cm^{-1}: 3414 (N-H), 3057 (=C-H), 2937 (-C-H), 1632-1464 (C=C and C=N), 1394 (CH_3), 824 (=C-H), 752 (=C-H). ^1H NMR (DMSO-d_6)/ppm: δ_H = 8.07 (d, 2H, J = 7.2Hz), 7.69 (m, 2H), 7.44 (d, 2H, J = 7.2Hz), 7.35 (m, 2H). ^{13}C NMR (DMSO-d_6)/ppm: δ_C = 150.7, 142.3, 135.9, 130.4, 127.6, 124.4, 124.2, 114.9, 21.6.

2-(4-Methoxyphenyl)-1*H*-benzimidazole (3):

Purple solid. Mp / °C: 224-227 (Lit. 224-226 [37]). ῡ (KBr) / cm^{-1}: 3420 (N-H), 3050 (=C-H), 2929 (-C-H), 1610-1462 (C=C and C=N), 1394 (CH_3), 1029 and 1266 (Ar-C-OCH_3), 837 (=C-H), 749 (=C-H bending). ^{1}H NMR (DMSO-d_6) / ppm: δ_H = 8.13 (d, 2H, J = 8.4Hz), 7.67 (m, 2H), 7.35 (m, 2H), 7.25 (d, 2H, J_{HH} = 8.4Hz), 3.86 (s, 3H). ^{13}C NMR (DMSO-d_6) / ppm: δ_C= 140.93, 136.29, 133.84, 131.47, 130.81, 129.35, 129.19, 128.39, 128.25, 127.76, 127.12, 61.07.

2-(4-Chlorophenyl)-1*H*-benzimidazole (4): White solid. Mp / °C: 292-293 (Lit. 288-291 [37]). ῡ (KBr) / cm^{-1}: 3418 (N-H), 3058 (=C-H), 1634-1460 (C=C and C=N), 836 (=C-H), 748 (=C-H). ^{1}H NMR (DMSO-d_6) / ppm: δ_H = 8.25 (d, 2H, J = 7.6Hz), 7.61 (m, 4H), 7.22 (m, 2H). ^{13}C NMR (DMSO-d_6) / ppm: δ_C = 132.55, 131.68, 130.62, 127.91, 123.21, 122.15, 119.55, 112.16.

2-(4-N, N-Dimethylaminophenyl)-1*H*-benzimidazole (5): White solid. Mp / °C: 294-295 (Lit. 292-294 [38]). ῡ (KBr) / cm^{-1}: 3428 (N-H), 3031 (=C-H), 2859 (-C-H), 1604-1446 (C=C and C=N), 1376 (CH_3), 1123 (C-N), 824 (=C-H), 767 (=C-H). ^{1}H NMR (DMSO-d_6) / ppm: δ_H = 8.15 (d, 2H, J = 8.8Hz), 7.70 (m, 2H), 7.70 (m, 2H), 6.91 (d, 2H, J = 8.8Hz), 3.05 (s, 6H). ^{13}C NMR (DMSO-d_6)/ppm: δ_C = 146.15, 138.19, 135.95, 133.51, 130.01, 129.68, 128.82, 128.21, 128.02, 127.53, 125.68, 21.35.

2-(4-Hydroxyphenyl)-1*H*-benzimidazole (6): Red solid. Mp / °C: 256-258 (Lit. 256 [39]). ῡ (KBr) / cm^{-1}: 3412 (N-H and OH), 3060 (=C-H), 1609-1462 (C=C and C=N), 1266 (Ar-O), 838 (=C-H), 750 (=C-H). ^{1}H NMR (DMSO-d_6) / ppm: δ_H = 10.37 (s, 1H, OH), 8.02 (d, 2H, J = 6.8Hz), 7.65 (m, 2H), 7.42 (m, 2H), 6.98 (d, 2H, J = 6.8Hz). ^{13}C NMR (DMSO-d_6)/ ppm: δ_C = 160.36, 151.62, 137.92, 129.11, 123.01, 122.71, 119.60, 116.35, 115.67, 114.86.

2-(4-Isopropylphenyl)-1*H*-benzimidazole (7): White solid. Mp / °C: 248-250 (Lit. 249-250 [38]). ῡ (KBr) /cm^{-1}: 3434 (N-H), 3035 (=C-H), 2962 (-C-H), 1641-1400 (C=C and C=N), 1394 (CH_3), 840 (=C-H), 767 (=C-H). ^{1}H NMR (DMSO-d_6)/ppm: δ_H = 8.12 (d, 2H, J = 7.6Hz), 7.74 (m, 2H), 7.54 (d, 2H, J = 7.6Hz), 7.42 (m, 2H), 2.99 (d, 1H, J = 6.0Hz), 1.24 (d, 6H, J = 6.0Hz). ^{13}C NMR (DMSO-d_6) / ppm: δ_C = 149.07, 146.13, 129.00, 128.87, 128.49, 128.29, 127.87, 127.00, 126.62, 126.22, 125.36, 33.79, 23.33.

2-(4-Nitrophenyl)-1*H*-benzimidazole (8): White solid. Mp / °C: 306-308 (Lit. 308-310 [37]). ῡ (KBr) / cm^{-1}: 3430 (N-H), 3058 (=C-H), 1605-1456 (C=C and C=N), 1522 and 1348 (ArN=O), 1110 (C-N), 858 (=C-H), 749 (=C-H). ^{1}H NMR (DMSO-d_6) / ppm: δ_H = 8.47 (d, 2H, J = 7.2Hz), 8.41 (d, 2H, J = 7.2Hz), 7.74 (m, 2H), 7.38 (m, 2H). ^{13}C NMR (DMSO-d_6)/ ppm: δ_C = 148.07, 147.87. 147. 50, 139.80, 139.06, 124.31, 121.88, 116.30.

2-(3-Nitrophenyl)-1*H*-benzimidazole (9): Yellow solid. Mp / °C: 202-204 (Lit. 202-204 [37]). ῡ (KBr) / cm^{-1}: 3428 (N-H), 3068 (=C-H), 1630-1455 (C=C and C=N), 1532 and 1350 (ArN=O), 1112 (C-N), 876, 812 and 706 (=C-H), 746 (=C-H). ^{1}H NMR (DMSO-d_6) / ppm: δ_H = 9.03 (s, 1H), 8.58 (d, 1H, J = 8.8Hz), 8.41 (d, 1H, J = 8.8Hz), 7.92 (t, 1H, J = 8.8Hz), 7.75 (m, 2H), 7.40 (m, 2H). ^{13}C NMR (DMSO-d_6) / ppm: δ_C= 148.71, 148.41, 136.15, 133.55, 131.47, 128.80, 126.15, 124.95, 122.21, 115.39.

2-(2-Nitrophenyl)-1*H*-benzimidazole (10): Orang solid. Mp / °C: 255-257 (Lit. 256-258 [40]). ῡ (KBr) / cm^{-1}: 3418 (N-H), 3062 (=C-H), 1587-1416 (C=C and C=N), 1524 and 1348 (ArN=O), 1147 (C-N), 766 (=C-H). ^{1}H NMR (DMSO-d_6)/ppm: δ_H= 13.05 (s, 1H), 8.17 (d, 1H, J = 7.2Hz), 7.85 (d, 1H, J= 7.2Hz), 7.84 (t, 1H, J= 7.2Hz), 7.72 (t, 1H, J = 7.6Hz), 7.63 (m, 1H), 7.58 (m, 1H), 7.22 (m, 2H). ^{13}C NMR (DMSO-d_6)/ppm: δ_C= 151.71, 144.26, 130.64, 130.31, 129.42, 126.91, 122.93, 122.20, 119.33, 111.17.

2-(3-Pyridyl)-1*H*-benzimidazole (11): Brown solid. Mp / °C: 245-247 (Lit. 246-258 [41]). ῡ (KBr) / cm^{-1}: 3418 (N-H), 3025 (=C-H), 1632-1457 (C=C and C=N), 753 (=C-H). ^{1}H NMR (DMSO-d_6) / ppm: δ_H = 9.35 (s, 1H), 8.47 (d, 2H, J = 7.2Hz), 8.77 (d, 1H, J= 5.0Hz), 8.55 (d, 1H, J= 8.0Hz), 7.72 (m, 3H), 7.38 (m, 2H). ^{13}C NMR (DMSO-d_6)/ppm: δ_C = 153.32, 146.52, 143.51, 128.83, 127.86, 124.93, 124.59, 121.20, 113.48.

2-(4-Pyridyl)-1*H*-benzimidazole (12): Brown solid. Mp / °C: 273-275 [4]. ῡ (KBr)/cm^{-1}: 3428 (N-H), 3025 (=C-H), 1632-1476 (C=C and C=N), 729 (=C-H). ^{1}H NMR (DMSO-d_6)/ppm: δ_H = 8.87 (d, 2H, J = 5.0Hz), 8.31 (d, 2H, J = 5.0Hz), 7.72 (m, 2H), 7.32 (m, 2H). ^{13}C NMR (DMSO-d_6)/ppm: δ_C = 149.43, 148.22, 136.45, 127.81, 124.73, 123.47, 123.46.

2-(2,4-Dichlorophenyl)-1*H*-benzimidazole (13): White solid. Mp / °C: 265-266 (Lit. 266-268 [37]). ῡ (KBr) / cm^{-1}: 3424 (N-H), 3103 (=C-H), 1625-1426 (C=C and C=N), 740 (=C-H). ^{1}H NMR (DMSO-d_6)/ ppm: δ_H = 7.97 (m, 2H), 7.8-7.68 (m, 3H), 7.44 (m, 2H). ^{13}C NMR (DMSO-d_6)/ppm: δ_C = 141.23, 136.17, 132.37, 131.33, 130.91, 129.26, 128.79, 128.70, 128.25, 128.16, 127.82, 127.64, 127.06.

2-(4-Carboxyphenyl)-1*H*-benzimidazole (14): White solid. Mp / °C: 215-217 (Lit. 215 [42]). ῡ (KBr) / cm^{-1}: 3418 (N-H), 2400-3600 O-H acid),

1738 C=O), 1610-1445 (C=C and C=N), 835 (=C-H), 768 (=C-H). ^{1}H NMR (DMSO-d_6)/ppm: δ_H= 8.29 (d, 2H, J = 8.8Hz), 8.16 (d, 2H, J= 8.8Hz), 7.73 (m, 2H), 7.37 (m, 2H). ^{13}C NMR (DMSO-d_6) / ppm: δ_C = 169.75, 160.10, 146.02, 133.25, 129.35, 129.17, 128.29, 127.85, 126.96, 126.74, 123.51, 114.01.

2-(3,4-Dimethoxyphenyl)-1*H*-benzimidazole (15): White solid. Mp / °C: 227-229 (Lit. 228-230 [37]). ῡ (KBr) / cm^{-1}: 3422 (N-H), 3050 (=C-H), 2941 (-C-H), 1632-1465 (C=C and C=N), 1392 (CH_3 bending), 1108 and 1273 (Ar-C-OCH_3), 752 (=C-H). ^{1}H NMR (DMSO-d_6)/ppm: δ_H = 7.80 (m, 2H), 7.71 (m, 2H), 7.04 (m, 2H), 7.23 (d, 2H, J = 8.4Hz), 3.86 (s, 3H). ^{13}C NMR (DMSO-d_6)/ppm: δ_C = 146.08, 138.28, 130.70, 129.69, 129.49, 129.22, 129.06, 128.87, 128.15, 126.93, 126.59, 126.21, 122.84, 61.07, 56.33.

2-(4-Nitrophenyl)-1H-4-methyl-benzimidazole (16): White solid.mp / °C: 199-201 [43]. ῡ (KBr) / cm^{-1}: 3420 (N-H), 3061 (=C-H), 1600-1400 (C=C and C=N), 1348 (CH_3), 1524 and 1348 (ArN=O), 1110 (C-N), 844 (=C-H). ^{1}H NMR (DMSO-d_6)/ppm: δ_H = 8.15 (m, 2H), 8.72 (m, 2H), 7.60 (dd, 1H, dd, J = 8.4 Hz and 4.0 Hz), 7.49 (d, 1H, J = 4.0 Hz), 7.21 (dd, 1H, J = 8.4 Hz and 4.0 Hz), 7.19 (d, 1H, J = 8.4 Hz), 2.49 (s, 3H). ^{13}C NMR (DMSO-d_6) / ppm: δ_C= 158.01, 146.43, 133.76, 129.00, 128.87, 128.57, 128.28. 127.87, 126.92, 126.71, 126.23, 122.43, 115.47,22.43.

2-(4-Methyl phenyl)-1H-4-methyl-benzimidazole (17): Green solid.mp / °C: 175-177 (Lit. 177 [36]). ῡ (KBr) / cm^{-1}: 3425 (N-H), 3108 (=C-H), 2924 (-C-H), 1633-1446 (C=C and C=N), 1345 (CH_3), 858 (=C-H). ^{1}H NMR (DMSO-d_6)/ppm: δ_H= 8.43 (d, 2H, J= 8.8 Hz), 8.37 (d, 2H, J= 8.8 Hz), 7.60 (d, 1H, J = 8.4 Hz), 7.49 (s, 1H), 7.19 (d, 1H, J= 8.4 Hz), 2.48 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (DMSO-d_6) / ppm: δ_C= 158.00, 146.39, 133.75, 128.88, 128.65, 128.29, 127.84, 126.93, 126.91, 126.71, 126.23, 122.42, 115.47, 25.32, 21.76.

RESULTS AND DISCUSSION

Characterization of kaolin-SO_3H nanoparticles

In order to identify the molecular structure of kaolin-SO_3H nanoparticles, FT-IR analysis of the kaolin nanoparticles and kaolin-SO_3H nanoparticles were compared (Fig. 1). In FT-IR spectrum of kaolin, many bands at 3686 and 3620, 1114, 990, 909, 791 and 752 cm^{-1} were existed. However in the kaolin-SO_3H nanoparticles, in addition to the above mentioned bands, a band at 1160 cm^{-1} and a very broad band at 2700-3400 cm^{-1} were appeared. The broad band at 1160 cm^{-1}and a very broad band at 2700-3400 cm^{-1} verify the O=S=O and –SO-H vibrations on kaolin-SO_3H, respectively. In the 990 cm^{-1} and 640 cm^{-1} region,

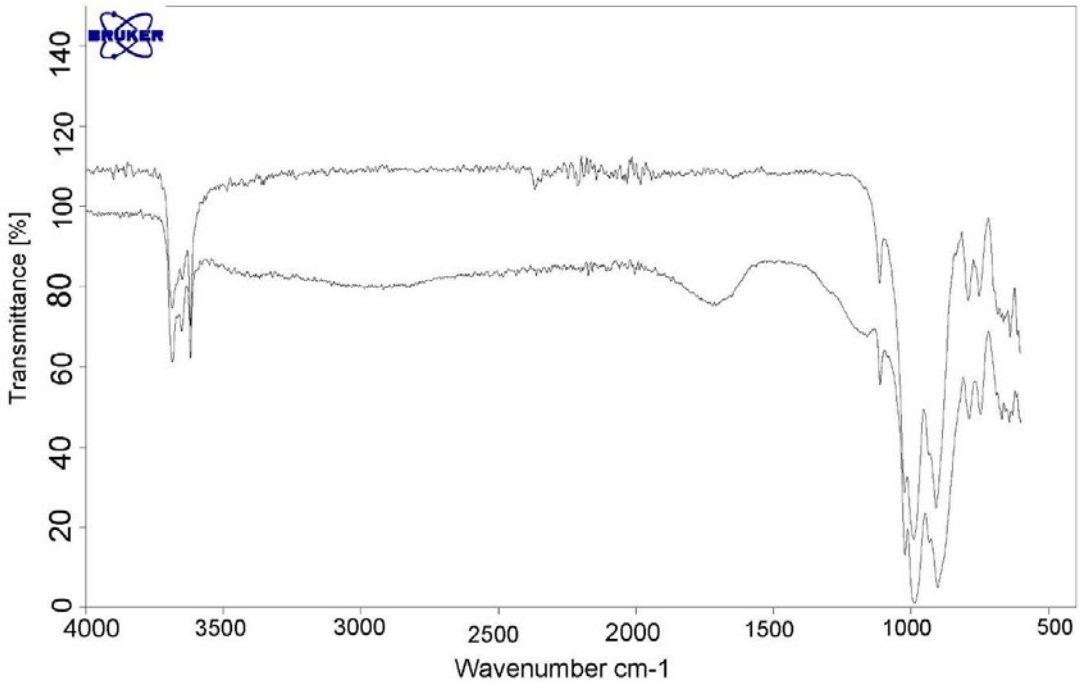


Fig.1. FT-IR (ATR) spectrum of (a) kaolin nanopaticles and (b) kaolin–SO_3H nanopaticles

main functional groups were Si-O and Al-OH.

Fig. 2 shows the XRD powder diffraction pattern of kaolin-SO_3H nanoparticles. As shown in this figure, incorporation of -SO_3H leads to some changes in the diffractogram of kaolin nanoparticles. In the diffractogram of kaolin nanoparticles in 2θ from 62 to 74, nine peaks but in kaolin-SO_3H nano particles, only three peaks (at 70.60, 72.67 and 74.08) are existed. In kaolin-SO_3H nanoparticles, three peaks in 2 θ from 20 to 25 were disappeared. Other peaks in kaolin and kaolin-SO_3H nanoparticles diffractograms are in the same position. The sharpness of peaks in the kaolin-SO_3H nanoparticles diffractogram shows crystalline form for this catalyst

Field emission scanning electron microscopy (FESEM) and transition electron microscope (TEM) images of the kaolin-SO_3H nanoparticles are displayed in Fig. 3. These images clearly showed the amorphous surface morphology of the kaolin-SO_3H nano particles with an average size distribution of 15 nm.

TG-DTG curves of starting kaolinite display a strong peak at 517 °C, which is due to dehydroxylation of kaolinite within the 450-600 °C temperature range resulting in a weight loss of 15.34 % and formation of meta-kaolinite. The peak on the TG-DTG curve at approximately 980 °C is an evidence of the breakdown of the meta kaolinite structure and the formation of mullite· Thermal gravimetric analysis (TG-DTG) pattern of kaolin-SO_3H nano particles was detected from 25 to 750 °C (Fig. 4). The catalyst is stable up to 100 °C and only 5 % of its weight was reduced in 120 °C. One endothermic processes were accrued between in 130 °C due to decomposition of –SO_3H group and

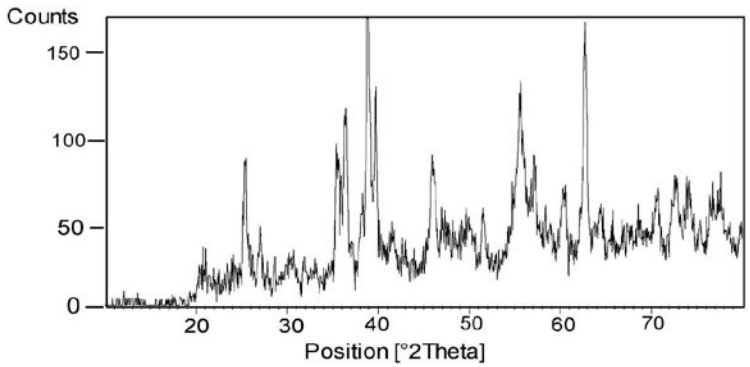


Fig. 2. X-ray diffraction (XRD) pattern of kaolin-SO_3H nanoparticles

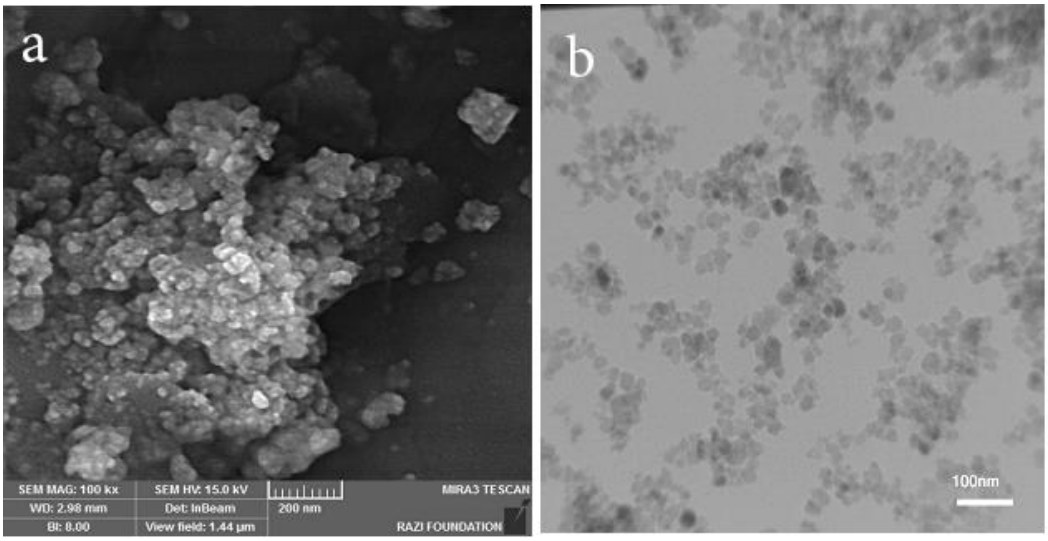


Fig. 3. (a) FESEM and (b) TEM photographs of kaolin-SO_3H nanoparticles

elimination of SO_2 and H_2O from catalyst. Another endothermic processes in 530 °C caused mass changed equal to 5 % due to dehydroxylation of kaolinite.

The results of X-ray fluorescence of kaolin-SO_3H nanoparticles are shown the presence of 15.9 % of SO_3 in its composition (Table 1).

The percentage of each element in nanocatalyst was approved by EDS analysis data (Fig. 5).

The percentage of S, O, Si and Al in kaolin-SO_3H nanoparticles is shown in Table 2.

The specific surface area of catalyst was measured by Brunauer–Emmett–Teller (BET) theory. The single point surface area at P/Po = 0.983 is 7.59 m^2/g, while the mean pore diameter is 20.601 nm and the total pore volume is 3.909 $cm^3\ g^{-1}$. The N_2 adsorption isotherm of catalyst is depicted in Fig. 6.

The acidity of the catalyst was compared with kaolin. The pH of 0.05 g of commercial kaolin or

Fig.4.Thermal gravimetric analysis (TGA-DTG) pattern of kaolin-SO_3H nanoparticles

Table 1. The results of X-ray fluorescence of kaolin-SO_3H nanoparticles

element	SiO_2	Al_2O_3	SO_3	CO_2
Percent %	43	30.5	15.9	8.2

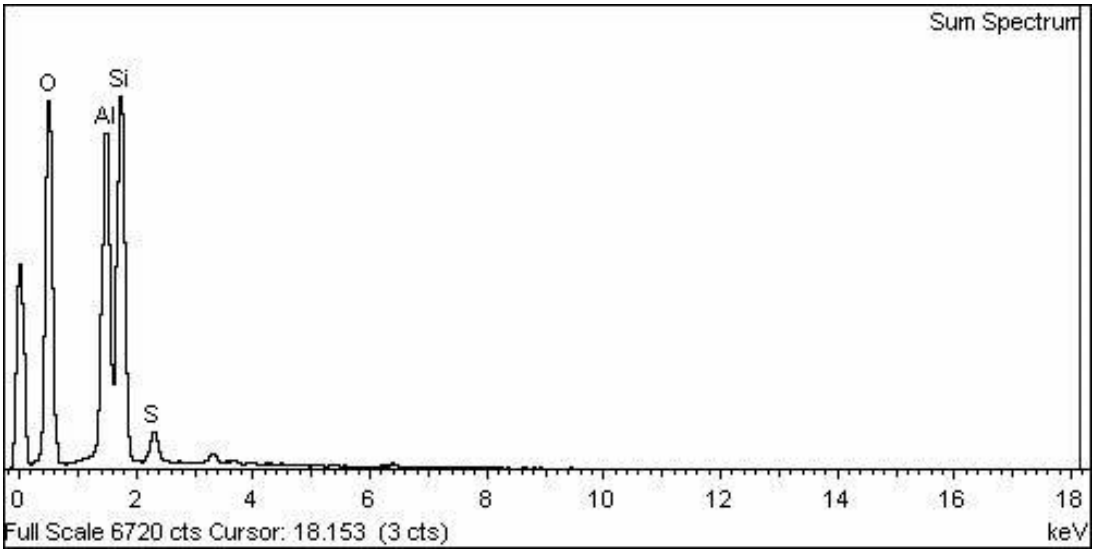


Fig. 5. EDS spectra of kaolin-SO_3H nanoparticles

Table 2. The EDS analysis of kaolin-SO_3H nanoparticles

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
O K	249.75	1.1405	61.06	0.28	73.17
Al K	49.20	0.8817	15.56	0.17	11.06
Si K	58.99	0.7736	21.26	0.21	14.51
S K	5.70	0.7514	2.12	0.09	1.27
Totals			100.00		

kaolin-SO_3H in 5 mL of distilled water is 6 and 3.4, respectively. The acidic capacity of catalyst was determined via titration of 0.05 g of it with 12.16 mL of 0.009 N of NaOH and was 2.268 meq/g H^+.

Preparation of 2-substituted benzimidazoles in the presence of kaolin-SO_3H nanoparticles

Kaolin-SO_3H nanoparticles as a new efficient heterogeneous catalyst, was used for the synthesis of 2-substituted benzimidazoles via reaction of

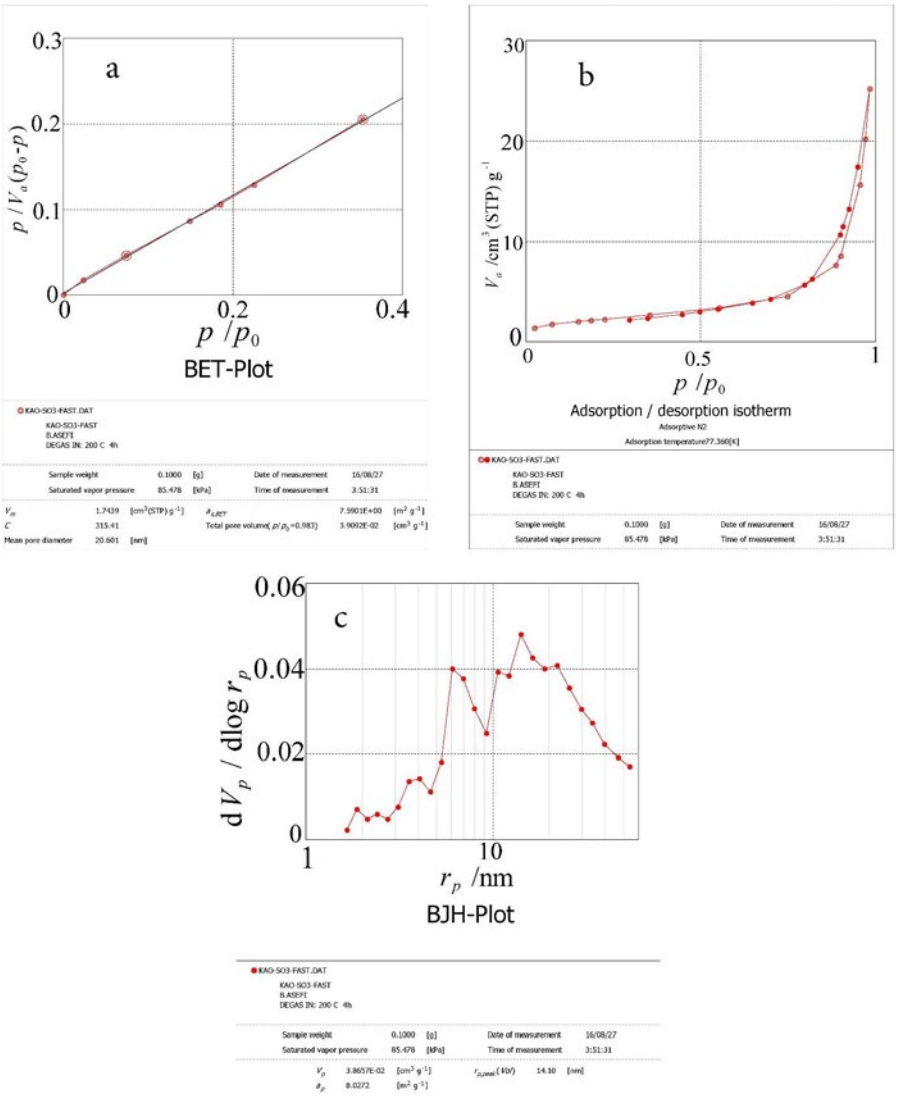
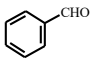
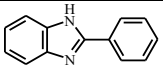
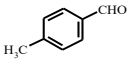
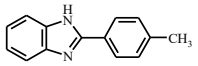
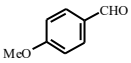
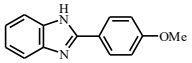
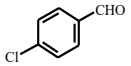
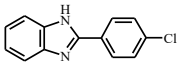
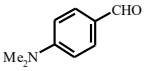
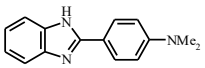
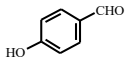
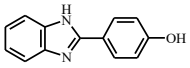
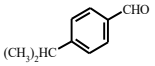
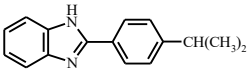
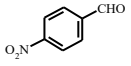
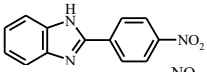
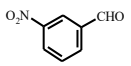
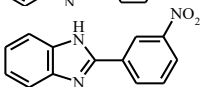
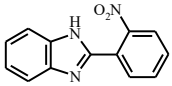
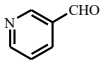
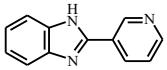
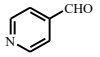
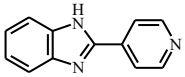
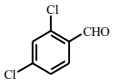
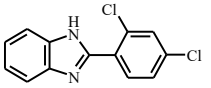
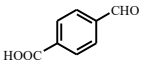
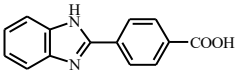
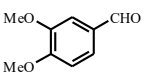
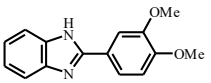
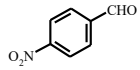
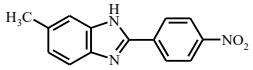
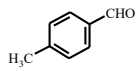
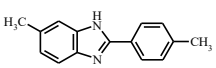


Fig. 6. (a) BET (Brunauer–Emmett–Teller), (b) adsorption/desorption isotherm and (c) BJH (Barrett-Joyner-Halenda) plots of kaolin-SO_3H nanoparticles

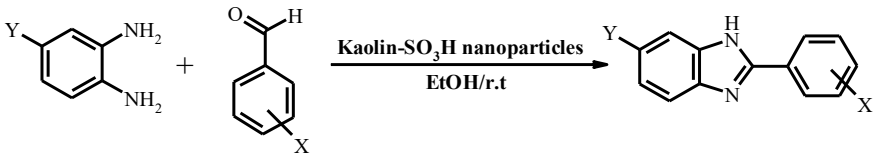
ortho-phenylendiamines and various aldehydes (Fig. 7, Table 3).

A suggested mechanism for synthesis of 2-substituted benzimidazole is shown in Fig. 8. In this mechanism, at first the solid acid catalyst protonates the carbonyl group of aldehyde which

Table 3. Synthesis of 2-substituted benzimidazoles in the presence of kaolin-SO_3H nanoparticles at room temperature[a]

Entry	Aldehyde	Product	Time (min)	Yeild (%)	M.P (°C)		Ref.
					Found	Reported	
1[a]			10	99	285-288	289-291	[36]
2[a]			20	95	261-262	262-264	[37]
3[a]			10	97	224-227	224-226	[37]
4[a]			15	94	292-293	288-291	[37]
5[a]			10	89	294-295	292-294	[38]
6[a]			10	98	256-258	256	[39]
7[a]			15	88	248-250	249-250	[38]
8[a]			15	86	306-308	308-310	[37]
9[a]			10	84	202-204	202-204	[37]
10[a]			10	80	255-257	256-258	[40]
11[a]			40	65	245-247	246-248	[41]
12[a]			40	70	273-275	-	[4]
13[a]			20	84	265-266	266-268	[37]
14[a]			30	90	215-217	215	[42]
15[a]			30	67	227-229	228-230	[37]
16[b]			55	87	199-201	-	[43]
17[b]			55	85	175-177	177	[36]

[a]*o*-Phenylendiamine (1 mmol), aldehyde (1 mmol), Kaolin-SO_3H nanoparticles (0.025 g).
[b]4-Methyl-1,2-phenylendiamine (1 mmol), aldehyde (1 mmol), Kaolin-SO_3H nanoparticles (0.025 g).



Y = H, CH_3, NO_2
X = different groups

Fig. 7. Synthesis of 2-substituted benzimidazole derivatives in the presence of kaolin-SO_3H nanoparticles

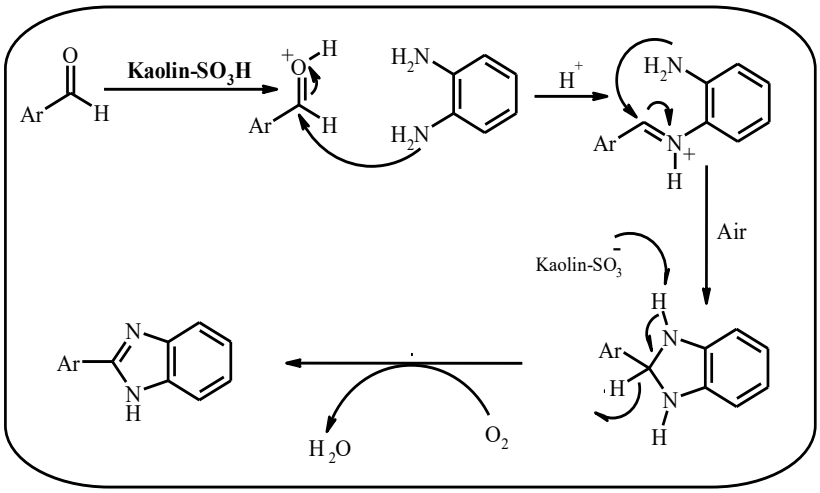


Fig. 8. Suggested mechanisms for synthesis of 2-substituted benzimidazoles in the presence of Kaolin-SO_3H nanoparticles

then condense with one of the NH_2 groups of ortho-phenylen diamine to produce corresponding schiff base. After this, the second NH_2 group of ortho-phenylenediamine condense with this intermediate via an intramolecular ring closure produces five membered ring which formed 1,3-benzodiazolidine. In the presence of O_2 of air as oxidant, 2-substituted benzimidazole is formed by removal of H^+.

CONCLUSION

In this paper, Kaolin-SO_3H nanoparticles were prepared and characterized with FT-IR, XRD, FESEM, TEM, XRF, EDS, BET and TGA. We have been able to introduce a new efficient and environmentally friendly pathway for one pot synthesis of 2-substituted benzimidazoles via condensation of ortho-phenylendiamine and aldehyde using Kaolin-SO_3H nanoparticles as a recyclable solid acid catalyst. This simple procedure is solvent- free and its easy and clean work up, high yields and heterogeneous conditions make this attractive for large–scale environment-friendly operations.

ACKNOWLEDGMENTS

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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