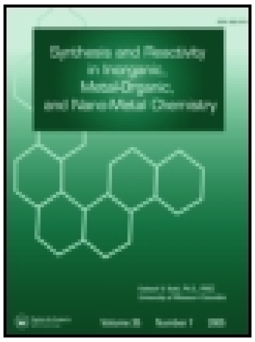

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Nano-Ni(II)/Y zeolite catalyzed synthesis of 2-aryl- and 2-alkyl benzimidazoles under solvent-free conditions

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Abstract

Synthesis of some benzimidazole derivatives via condensation reaction of *o*-phenylenediamine derivatives with aromatic aldehydes or orthoesters under solvent-free conditions over nano-Ni(II)/Y zeolite as a heterogeneous catalyst was reported. Some advantages of this green method are easy purification, environmental friendly conditions, low catalyst loadings and non-toxic nature.

Keywords

Nano-Ni(II)/Y zeolite, *o*-phenylenediamine, benzimidazole, orthoesters, catalyst

Introduction

Benzimidazole and its derivatives have found applications in design and discovery of new biological and pharmaceutical compounds including antifungal,[1] anticancer,[2] antitumor[3], antibacterial,[4] antimicrobial,[5] antihelmintic,[6] antihypertensive[7] and antiviral.[8] Also, they have been used as intermediates in organic and inorganic synthesis.[9]

The most general methods for preparation of benzimidazoles is the condensation reaction of carboxylic acids[10] and its derivatives such as acid chlorides,[11] nitriles,[12] orthoesters,[13] amides,[14] esters[15] and recently aldehydes[16] with *o*-phenylenediamine in the presence of different catalysts. The most of these methods, which used for preparation of 2-aryl- and not for 2-alkyl benzimidazoles, are faced with problems like requiring force reaction conditions, use of volatile or toxic organic solvents and use of special reagent or catalyst.

Recently, special attentions have been focused on using zeolite as a solid acid catalyst in industrial and organic synthesis due to their thermal stability, insolubility in organic solvents and low cost. It is worth mentioning that the acidic sites of zeolite can catalyze organic reactions like condensation of diamines and aldehydes.

In view of this report and also as a continuation of our works on the synthesis of benzimidazoles,[17-20] we wish to report the synthesis of these materials in the presence of nano-Ni(II)/Y zeolite as an efficient nano-catalyst via condensation reaction of orthoesters /aryl-aldehydes with *o*-phenylenediamines.

Experimental

Materials and physical measurements:

All chemicals purchased from the Merck or Aldrich Company and used without further purification. Melting points were measured in open capillary tubes and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained in DMSO-d_6 using Brucker spectrophotometer (300 MHz and 400 MHz). Chemical shifts (ppm) were referenced to the internal standards tetramethylsilane (TMS). The IR spectral data were obtained using a Galaxy FTIR 5000 spectrometer with KBr sample disk. The progress of reactions was monitored by thin-layer chromatography (TLC) on silica gel F254 aluminium sheets (Merck). The scanning electron microscopy (SEM) was done by *Hitachi S 4160* apparatus.

Preparation of nano-Ni(II)/Y zeolite catalyst

Zeolite NaY was prepared and activated according to the literature.[21] In a typical process, zeolite (2 g) and $NiCl_2.6H_2O$ (2 mmol) were mechanically mixed, ground and heated using a microwave oven for 10-20 min with 900 Watt power. The temperature in the solid state ion-exchange was estimated around 700 °C. The XRD pattern showed no metal salt remained and the solid state ion-exchange was completed.[22] The prepared Ni(II)/Y zeolite was sonicated for 10 min in aceton solvent at room temperature to obtain nano-sized catalyst.

Synthesis of 2-aryl benzimidazoles 3a-j

A mixture of *o*-phenylenediamine (1 mmol), aldehyde (1 mmol) and nano-Ni(II)/Y zeolite catalyst (0.02 g) was heated at 100°C for a desired time (Table 2) to give 2-aryl benzimidazole derivatives. The progress of the reaction was investigated by tin-layer chromatography (TLC, eluent: n-hexane/ethyl acetate 2:1). After completion of the reaction, hot ethanol was added (5-10 ml) and the catalyst was separated by filtration. Then, ethanol evaporated and the resulted precipitate was recrystallized from ethanol/water (1:2) to afford pure product.

Selected data:

2-Phenyl-1*H*-benzimidazole (3a): White solid; IR (KBr, cm^{-1}): 3435, 3113, 3063, 2943, 2868, 2791, 2542, 1770, 1682, 1587, 1485, 1410, 1363, 1302, 1273, 1246, 1201, 1134, 1003, 958, 887, 769, 746, 634 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) = 11.67 (br s, 1H), 7.73--8.67 (m, 9H); Anal. Calcd. for $C_{13}H_{10}N_2$: C, 80.39; H, 5.19; N, 14.42%. Found: C, 80.50; H, 5.38; N, 14.56%.

2-(4-Chlorophenyl)-1*H*-benzimidazole (3b): Light yellow solid; IR (KBr, cm^{-1}):3418, 3051, 2930, 2849, 1614, 1541, 1491, 1429, 1321, 1273, 1224, 1172, 1091, 1012, 962, 829, 744, 615 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) = 13.00 (br s, 1H), 8.19 (d, J = 8.70 Hz, 2H), 7.63 (d, J = 8.70 Hz, 2H), 7.49-7.24 (m, 2H), 7.26-7.19 (m, 2H); Anal. Calcd. for $C_{13}H_9ClN_2$: C, 68.28; H, 3.97; N, 12.25%. Found: C, 68.51; H, 4.16; N, 12.43%.

2-(2-Nitrophenyl)-1*H*-benzimidazole (3e): Yellow solid; IR (KBr, cm^{-1}): 3387, 3080, 2968, 2862, 1574, 1527, 1446, 1415, 1379, 1348, 1278, 1224, 1078, 1010, 972, 854, 796, 721, 648 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) = 13.09 (bs r, 1H), 7.84--8.56 (m, 8H); Anal. Calcd. for $C_{13}H_9N_3O_2$: C, 65.27; H, 3.79; N, 17.56%. Found: C, 65.11; H, 3.84; N, 17.67%.

2-(4-Nitrophenyl)-1*H*-benzimidazole (3f): Yellow solid; IR (KBr, cm^{-1}): 3418, 3020, 2918, 2789, 1604, 1514, 1435, 1340, 1292, 1226, 1101, 968, 854, 746, 711 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) = 13.34 (br s, 1H), 7.42 (s, 1H), 7.39-8.24 (m, 7H); Anal. Calcd. for $C_{13}H_9N_3O_2$: C, 65.27; H, 3.79; N, 17.56%. Found: C, 65.32; H, 3.74; N, 17.61%.

2-(4-Methylphenyl)-1*H*-benzimidazole (3h): Light yellow solid; IR (KBr, cm^{-1}): 3346, 3084, 2949, 2918, 1622, 1541, 1450, 1276, 972, 808, 704; ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) = 12.83 (br s, 1H), 8.06 (d, J = 8.40 Hz, 2H), 7.64-7.49 (m, 2H), 7.33 (d, J = 8.40 Hz, 2H), 7.19-7.18 (m, 2H), 2.37 (s, 3H); Anal. Calcd. for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45%. Found: C, 81.04; H, 6.11; N, 13.15%.

2-Methyl-1*H*-Benzimidazole (6b): pale cream brown solid; IR (KBr, cm^{-1}): 3443, 3097, 3063, 2993, 2914, 2791, 2679, 1622, 1556, 1450, 1417, 1386, 1271, 1219, 1028, 835, 734, 673, 617; ^1H NMR (DMSO-d_6): δ (ppm) = 12.23 (brs, 1H), 7.13-7.09 (m, 2H),7.48-7.44 (m, 2H), 2.49 (s, 3H);. Anal. Calcd. for $C_8H_8N_2$: C, 72.70; H, 6.10; N, 21.20%. Found: C, 72.30; H, 5.79; N, 20.90%.

2,5-Dimethyl-1*H*-Benzimidazole (6d): Dark brown solid; IR (KBr, cm^{-1}): 3300, 3013, 2914, 2858, 1629, 1552, 1452, 1400, 1280, 1222, 1030, 858, 804, 667, 601; ^1H NMR (DMSO-d_6, 400 MHz): δ (ppm) = 12.02 (br s,1H), 7.28(d, J = 8.00 Hz, 1H), 7.23 (s, 1H), 6.92 (dd, J_1 = 8.00 Hz, J_2 = 1.20 Hz, 1H), 2.45 (s, 3H), 2.38 (s, 3H); Anal. Calcd. for $C_9H_{10}N_2$: C, 73.94; H, 6.89; N, 19.16%. Found: C, 73.59; H, 6.54; N, 18.83%.

5-Nitro-1*H*-Benzimidazole (6e): Light yellow solid; IR (KBr, cm^{-1}): 3466, 3342, 3101, 2922, 2866, 2739, 1790, 1655, 1591, 1465, 1408, 1302, 1242, 1182, 1105, 1066, 1022, 952, 898, 794, 740, 626; ^1H NMR (DMSO-d_6, 400 MHz): δ (ppm) = 13.02 (br s, 1H), 8.56 (s, 1H), 8.52 (d, J = 2.00 Hz, 1H), 8.13 (dd, J_1 = 8.80 Hz, J_2 = 2.40 Hz, 1H), 7.78 (d, J = 8.80 Hz, 1H); Anal. Calcd. for $C_7H_5N_3O_2$: C, 51.54; H, 3.09; N, 25.76%. Found: C, 51.84; H, 3.41; N, 25.46%.

2-Methyl-5-nitro-1*H*-Benzimidazole (6f): Dark yellow solid; IR (KBr, cm^{-1}): 3485, 3317, 3107, 2978, 2922, 2850, 2798, 2710, 2677, 1676, 1631, 1593, 1512, 1473, 1444, 1417, 1383, 1338, 1313, 1267, 1219, 1124, 1064, 1026, 977, 879, 823, 738, 629;; ^1H NMR (DMSO-d_6, 400 MHz): δ (ppm) = 12.85 (br s, 1H), 8.38 (d, J = 2.00 Hz, 1H), 8.08 (dd, J_1 = 8.80 Hz, J_2 = 2.40 Hz, 1H), 7.66 (d, J = 8.80 Hz, 1H), 2.59 (s,3H); Anal. Calcd. for $C_8H_7N3O_2$: C, 54.24; H, 3.98; N, 23.72%. Found: C, 54.01; H, 4.21; N, 23.59%.

Results and Discussion

The scanning electron microscopy (SEM) image of the nano-Ni(II)/Y particles, which was prepared in solid state with microwave irradiation, is shown in Figure 1. The size of particles was mainly 80-100 nm.

Figure 1.

The FT-IR of the Ni(II)/Y zeolite nano-particles is presented in Figure 2. The intense band at ca.1060 cm^{-1} is corresponded to the asymmetric stretching of Al--O--Si chain of zeolite. The symmetric stretching and bending frequency bands of Al--O--Si framework of zeolite are observed at ca.790 and 451 cm^{-1}, respectively. Transition metal /complexes encapsulated in the nano cages of zeolite did not show any significant shift for functional groups stretching bond of zeolite. However, a new band appeared at 845 cm^{-1} is related to Ni--O--T(T = Si or Al).[23,24] For comparison the XRD pattern of zeolite Y and nano sized Ni(II)/Y zeolite particles is shown in Figures 3a and 3b, respectively. The results show that the structure of zeolite does not collapse and six characteristic peaks appear at 2Ө of 30.1, 35.5, 43.1, 53.4, 57.0 and 62.6, which are marked by their indices ((220), (311), (400), (422), (511) and (440)) as shown in Figure 3b.[25,26]

To optimize the reaction conditions, the reaction of *o*-phenylenediamine (1 mmol) and benzaldehyde (1 mmol) was carried out using different amounts of nano-Ni(II)/Y zeolite catalyst, different solvents and also under solvent-free conditions as a model reaction. A summary of obtained results is provided in Table 1. At room temperature, the reaction rate was found to be slow and was increased with increase in temperature. The best result was obtained when the reaction was carried out in the presence of 0.02 g of nano-Ni(II)/Y zeolite under solvent-free conditions at 100 °C (Table 1, entry 12). The catalyst and other reaction conditions are safe in comparison to already reported results.[27]

Encouraged by these results, we used this catalyst for synthesis of other benzimidazole derivatives under solvent-free conditions using different aromatic aldehydes. Both electron-rich and electron-deficient aldehydes worked well and leading to good yields of products **3a-j** (Scheme 1). The results are given in Table 2.

However, the aliphatic aldehydes such as formaldehyde or acetaldehyde were also examined under the same conditions, but the corresponding products were isolated in trace amounts. Then, we attended to synthesis some 2-alkyl benzimidazoles **6a-h** by reaction of *o*-phenylenediamine derivatives with orthoesters in the presence of nano-Ni(II)/Y particles at 60 °C under the same conditions (Scheme 2, Table 3). The possible mechanism for this reaction is shown in Scheme 3.

FT-IR, ^{1}H and ^{13}C NMR spectra data of 2-aryl and 2-alkyl benzimidazoles are similar and in consistent with the expected structures. The ^{1}H NMR spectra of benzimidazoles are simple and consist of a multiplet and a broad singlet at downfield shift due to the resonance of aromatic protons and the NH group, respectively. Also, the ^{1}H NMR spectra of 2-alkyl benzimidazoles show an additional signal at highfiled shift due to resonance of alkyl protons. The structure of compounds was also supported by IR spectra, which included absorption bands at the regions 3259-3485 cm^{-1} characteristic for the NH groups.

Conclusion

In conclusion, we have developed an efficient synthetic procedure for preparation of some benzimidazole derivatives in the presence of nano-Ni(II)/Y zeolite catalyst. The short reaction time, high yield of products, the absence of volatile organic solvents and non-toxic catalyst are some advantages of this green method.

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Table 1. The optimization of reaction conditions for synthesis of 2-aryl benzimidazole in the presence of nano-Ni(II)/Y zeolite as a catalyst

Entry	Catalyst amount (g)	Temperature (°C)	Solvent	Time (min)	Yield (%)[a]
1	0.01	25	EtOH	15	trace
2	0.01	50	EtOH	15	40
3	0.01	60	EtOH	15	83
4	0.02	60	EtOH	10	89
5	0.03	60	EtOH	10	90
6	0.02	50	EtOH	10	70
7	0.02	60	CH_3CN	38	84
8	0.02	60	DMF	42	81
9	0.02	60	DMSO	53	83
10	0.02	60	$CHCl_3$	68	69
11	0.02	80	solvent-free	10	89
12	0.02	100	solvent-free	6	92
13	0.02	120	solvent-free	4	90

[a] Isolated yields

Table 2. Synthesis of 2-aryl benzimidazole derivatives using nano-Ni(II)/Y catalyst at 100°C under solvent-free conditions

Product 3	R	Time (min)	Yield[a] (%)	Melting point (°C)	
				Found	Reported
a	H	6	92	289-291	[28]289-291
b	4-Cl	4	95	290-292	[29]288-290
c	2,4-Cl	20	91	219-221	[30]218-219
d	2,6-Cl	6	95	273-275	[31]274-276
e	2-NO_2	7	90	209-211	[32] 212-214
f	4-NO_2	5	92	308-310	[29]310-312
g	4-OCH_3	15	86	218-221	[33] 222-224
h	4-CH_3	6	89	267-269	[34]266-269
i	4-$N(C_2H_5)_2$-2-OH	30	87	190-192	[35]192
j	4-$N(CH_3)_2$	15	92	228-229	[36] 232

[a]Isolated yeilds

Table 3. Synthesis of 2-alkyl benzimidazoles using Ni(II)/Y zeolite catalyst at 60°C under solvent-free conditions.

Product 6	**R**	**R'**	**R''**	**Time (min)**	**Yield[f] (%)**	**Melting point (°C)**	
						Found	**Reported**
a	H	H	C_2H_5	60	92	170-172	[37]170-172
b	H	CH_3	C_2H_5	47	98	172-174	[38]176-177
c	CH_3	H	C_2H_5	80	83	112-114	[38]114-115
d	CH_3	CH_3	C_2H_5	46	99	198-200	[39]201-202
e	NO_2	H	C_2H_5	118	81	200-202	[38]201-202
f	NO_2	CH_3	C_2H_5	87	87	215-218	[40] 219-220
g	Cl	H	C_2H_5	122	79	113-115	[41] 117-118
h	Cl	CH_3	C_2H_5	85	80	190-192	[42] 195-198

[f] Isolated yeilds

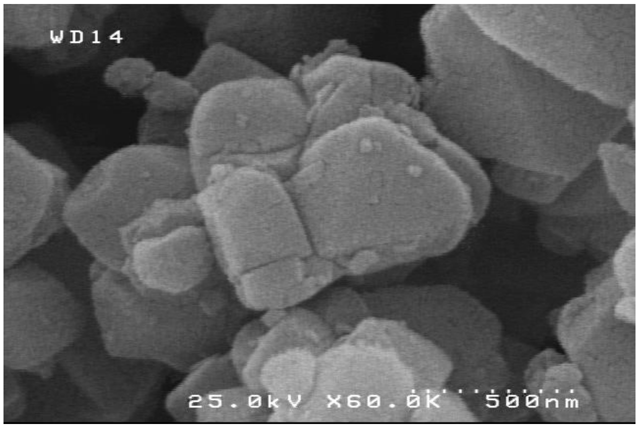


Figure 1. The SEM image of nano-Ni(II)/Y zeolite particles

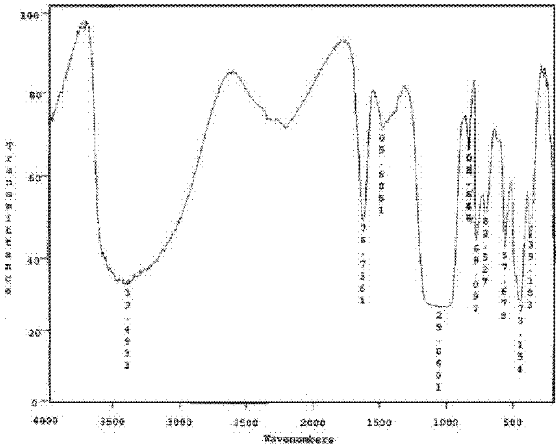


Figure 2. The FT-IR of the nano-Ni(II)/Y zeolite particles

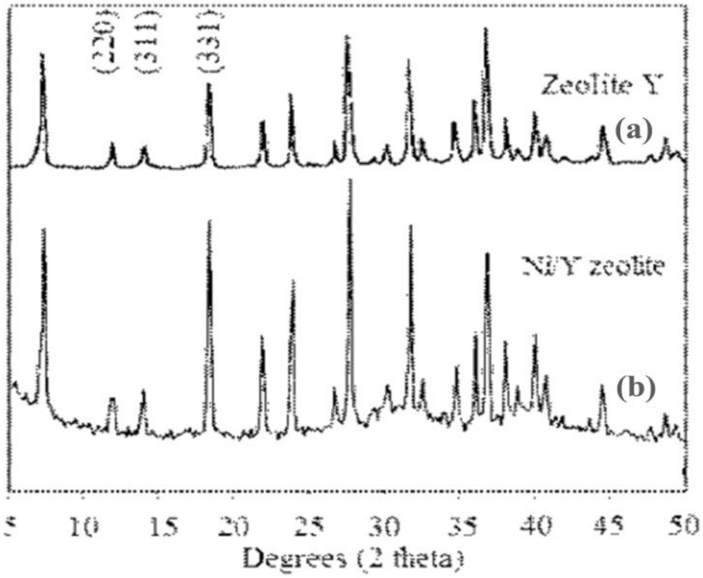
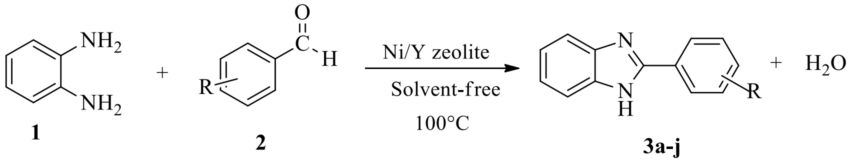
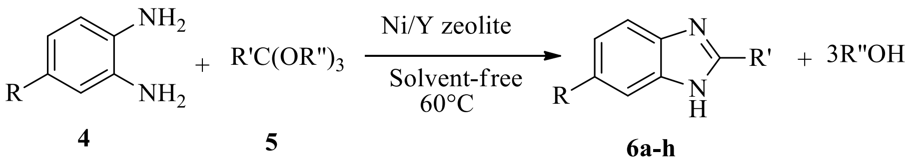


Figure 3. The comparison of the XRD of zeolite Y and Ni/Y zeolite



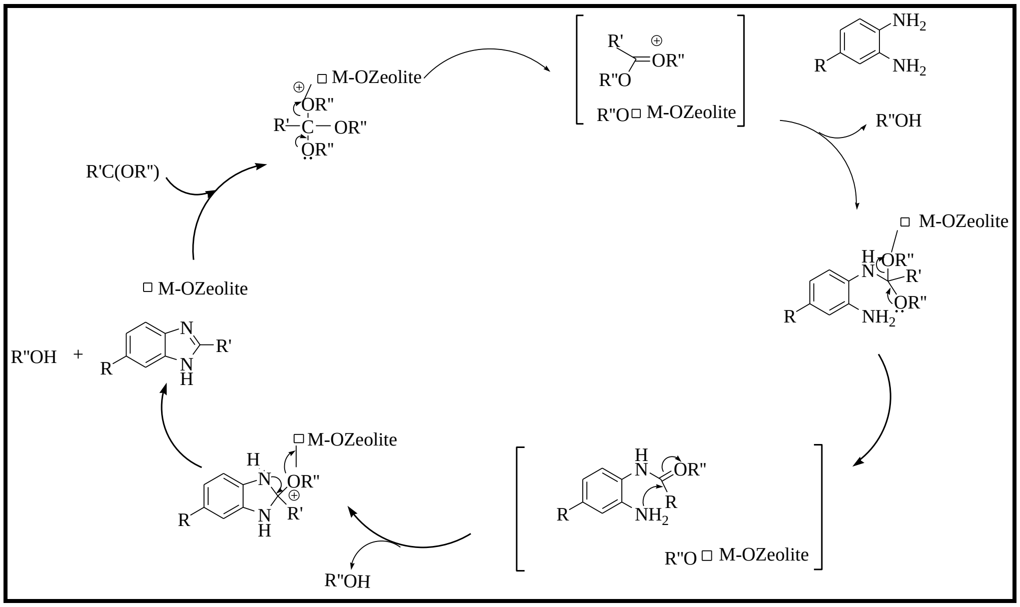
Scheme 1.

Scheme 1. The synthetic pathway for synthesis of 2-aryl benzimidazoles



Scheme 2

Scheme 2. The synthetic pathway for synthesis of 2-alkyl benzimidazoles



Scheme 3. The proposed mechanism for synthesis of 2-alkyl benzimidazoles in the presence of nano-Ni(II)/Y particles