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Cu-bentonite as an efficient and recyclable material catalyst for the synthesis of benzimidazoles, benzoxazoles and benzothiazoles

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- ✓ Benzoxazoles,
- ✓ Benzothiazoles.

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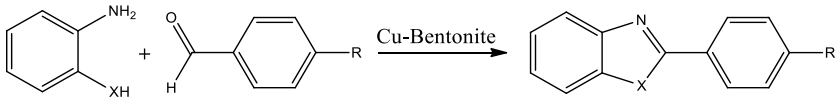
Abstract

A new natural clay-based support, doped with a Lewis acid (Cu-bentonite), was used in heterogeneous catalysis for the efficient synthesis of benzimidazoles, benzoxazoles and benzothiazoles. The salient features of the present method are the mild conditions required, short reaction times, high yields, and recyclability of the catalyst. The method has the advantage of being very stable, non-corrosive, with a low toxicity and high selectivity.

1. Introduction

Benzimidazoles, benzoxazoles and benzothiazoles are attractive targets for synthesis since they often exhibit diverse and important pharmacological activities such as antiviral [1], antimicrobial [2], antifungal [3], antiparkinson [4], anticancer [5] and antibacterial [6] properties. They are also used as ligands for asymmetrictransformations [7] and exhibit nonlinear optical [8] and luminescent [9] /fluorescent [10] properties. Benzimidazole derivatives show significant activity against several viruses such as HIV [11], herpes (HSV-1) [12], HCV [13], and influenza [14], and are potential antitumor [15] and antimicrobial agents [16]. They also act as topoisomerase inhibitors [17], selective neuropeptide YY1 receptor antagonists [18], angiotensin II inhibitors [19], and smooth muscle cell proliferation inhibitors [20] and play an important role in organic synthesis [21]. A number of methods have been reported for the synthesis of these heterocycles (benzimidazoles [22–24], benzoxazoles [25–27] and benzothiazoles [28–30]). The synthesis of these compounds has also been developed on heterogeneous catalysis, using supports such as ABMs doped with Lewis acids [31], Calcined Limpet Shell doped with $ZnCl_2$ (CLS/$ZnCl_2$)[32], Ghassoulite clay doped with Al (Al_{13}-PILC) [33], calcined eggshell meal [34], Calcined mussel shells doped with metal halides [35],Bentonite clay [36] and CuO nano-particles supported on silica in methanol [37].

In this work, we used a doping process of the Bentonite by the copper Oxide (Cu-bentonite) for the elaboration of a natural support based on clay. This solid was used in heterogeneous catalysis and has the advantage of being very stable and less toxic [38], non-corrosive, with a high selectivity, mild reactionconditions and easy work-up [39]. This new method could be an alternative to conventional conditions, leading to better yields and the desired products with good purity. In this work we describe the use of Cu-bentonite in the reaction of *o*-phenylenediamine, *o*-aminophenol and *o*-aminothiophenol with different aldehydes for the synthesis of benzimidazoles, benzoxazoles and benzothiazoles (Scheme 1).



1 X= NH
2 X= O
3 X= S

4
R= H, NO_2, Cl, F, OCH_3, CH_3

5a-f X= NH
6a-f X= O
7a-e X= S

Scheme 1:*Synthesis of benzimidazoles**5a-f**,benzoxazoles**6a-f** and benzothiazoles**7a-e**catalyzed by Cu-bentonite*

2. Material and Methods

2.1. Preparation of the Cu-bentonite catalyst

All chemicals were obtained from commercial suppliers and were used without further purification. In a typical procedure, the material was prepared in two steps: first, a quantity of clay (A) was added to ultrapure water at room temperature and stirred for 30 min at 300 tr/min. Second, a copper hydroxide solution (B) was prepared by adding the sodium hydroxide to the copper chloride with an OH/Cu ratio kept at 2. The solution (B) was added to suspension (A) slowly; the mixture was stirred at room temperature for 15 hours, centrifuged at 3000 tr/min for 10min then washed several times with distilled water to remove the chlorides. The recovered product was oven-dried at 110°C for 24 hours. The solid was finally calcined at 425°C.

2.2. Characterization

The materials were characterized by powder X-ray diffraction (XRD) using a Phillips Xpert-pro diffractometer Bruker D8 advanced. Copper Kα radiation (λ=1.5406) was produced at 50 KV and 20 mA. Diffractograms were recorded from 5 to 85° (2θ) with a step size of 0.02º and a count time of 5s per step. IR spectra were recorded on a Bruker Vertex-70 FT-IR spectrophotometer. The chemical composition was analysed by ICP-MES (ICP MES VARIAN.2011) and scanning electron microscopy (SEM) was used to study the surface morphology. Nuclear magnetic resonance (NMR) spectra were performed on a Bruker Advance DPX250 apparatus (250.13 MHz for ^{1}H and 62.9 MHz for ^{13}C) or a Bruker Advance 400 (400.13 MHz for ^{1}H and 101 MHz for ^{13}C), using DMSO as solvent to characterize organic products, and melting points were determined using a SUNON (50Hz) apparatus.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Analysis by ICP (% of oxides)

The analysis of these results shows that the predominant constituents of the raw bentonite and Cu-bentonite are silica, alumina and iron oxide (Table 1). Characterization by ICP of Cu-bentonite compared with raw bentonite showed an increase in copper oxide from 0% to 23.71%, and a decrease in Ca^{2+}, K^{+}, Mg^{2+}, Na^{+} Fe^{2+} and Al^{3+}. This is explained by the good cation exchange between the solute and the solution.

Table 1: Chemical composition of raw bentonite and Cu-bentonite.

Clay (%)	CuO	CaO	K_2O	MgO	Na_2O	P_2O_5	SO_3	Al_2O_3	Fe_2O_3	MnO_2	SiO_2
Raw bent	0.00	0,01	0,25	0,06	2.1	0,15	0,03	13.30	7.90	0,22	69,4
Cu-bent	23.71	0.005	0.08	0.01	1.45	0.2	0.09	7.13	4.13	0.1	62.9

3.1.2. FT-IR spectroscopy

FT-IR spectra of raw bentonite and Cu-bentonite are illustrated in Figure 1. The three bands at 3620, 3404 and 1635 cm^{-1} were assigned to stretching vibrations of water-adsorbed molecules and the exchangeable cations. Furthermore, the water molecules exhibited fundamental vibrational modes, namely symmetric stretching and H-O-H bending. The typical bands for the silicate components of the clay appear between 1200 and 400 cm^{-1}. The band at 1039 cm^{-1} is due to in-plane band stretching of Si–O bonds. The bands at 472 and 535 cm^{-1} can be assigned to Si–O–Mg and Si–O–Al species, respectively [40, 41].

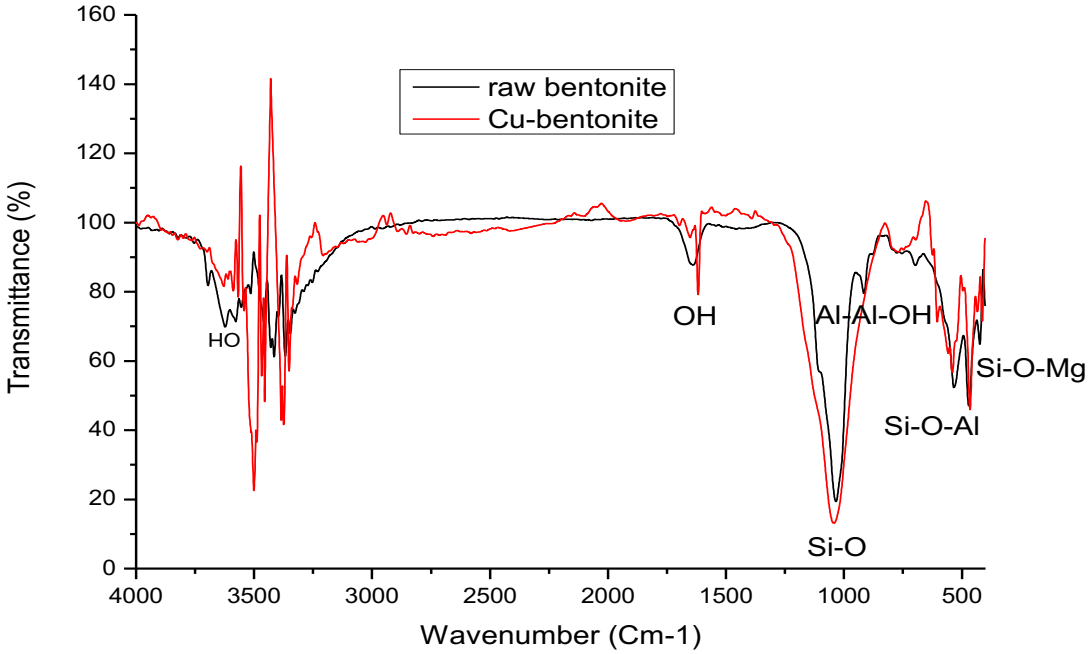


Figure 1: *FT-IR spectra of raw bentonite and Cu-bentonite*

On the FTIR spectrum of the Cu-doped bentonite a small change can be observed at the peaks attached to the water molecule adsorbed in the interlayer space. In view of this change, it can be concluded that doping occurred in the interlayer space.

3.1.3. Analysis by SEM and EDX

The SEM micrographs of raw bentonite and Cu-bentonite indicate that the surface texture of raw bentonite was not smooth but granule-like with an anomalous character (Figure 2 (a)). The Cu-bentonite image shows a clear change in the morphology of bentonite because we observe a smaller black vacuum formation (Figure 3 (a)). This feature can be ascribed to an increase in the interlayer spacing brought about by the addition of CuO, as also indicated by the IR characterization (Figure 1).

The results of the EDX analysis of raw bentonite and Cu-bentonite indicate that Si and Al are the main constituents of the material with an increase in copper in Cu-bentonite (Figure 2 (b) and Figure 3 (b)). This is related to the doping effect as also shown by the ICP characterization (Table 1).

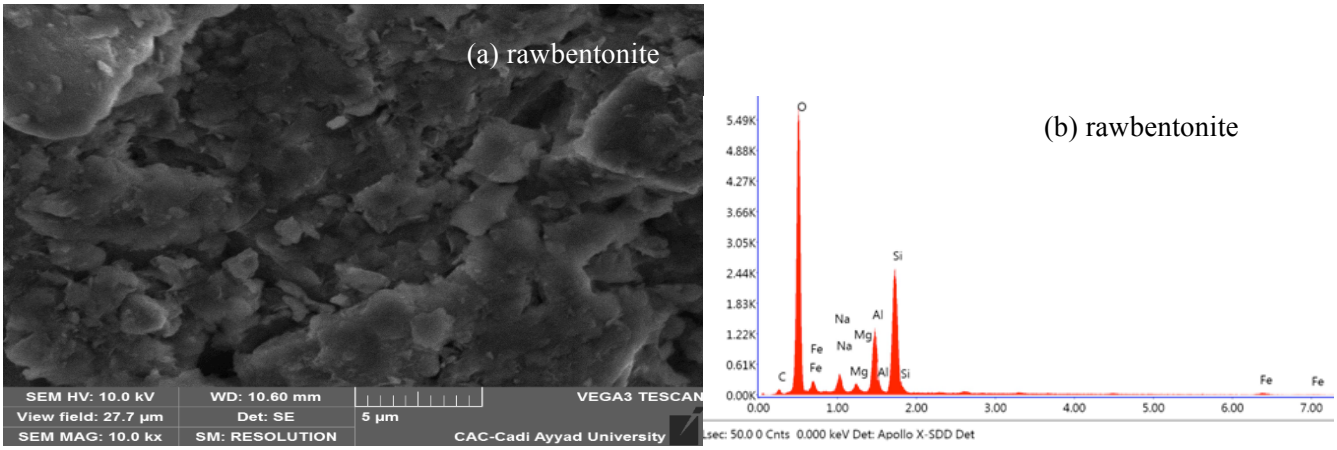


Figure 2: *SEM images and EDX spectra for the raw bentonite*

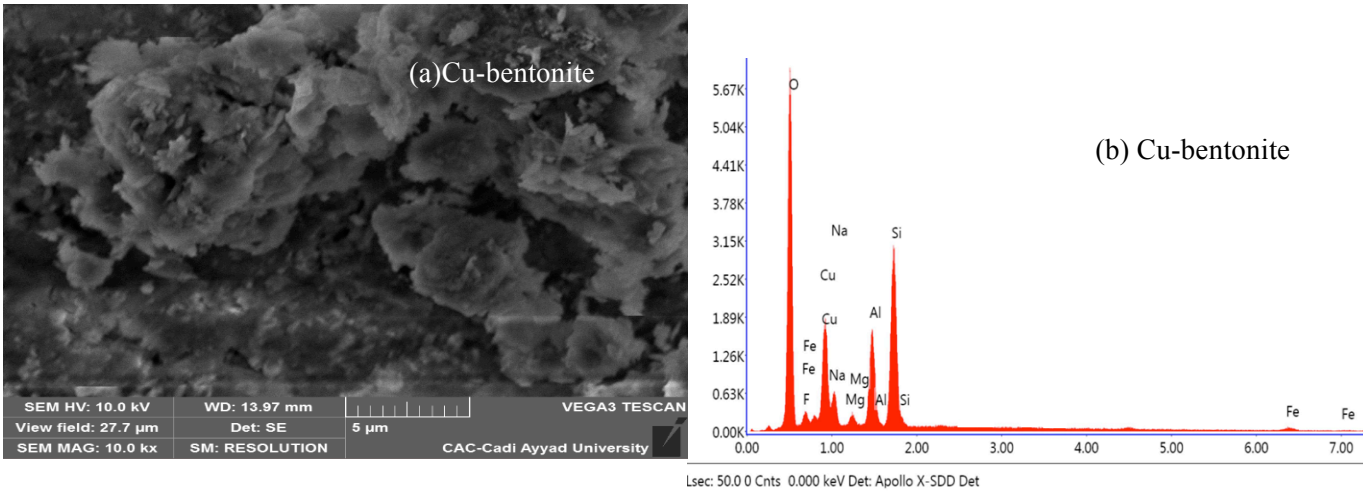


Figure 3: *SEM images and EDX spectra for the Cu-bentonite*

3.1.4. Analysis by XRD of the raw bentonite

Figure 4 shows that the d_{001} spacing of clay is 12-13Å (2θ: 7.2215), which could be attributed to the presence of water molecules and some cations such as Na^+ in the interlayer spaces. Quartz reflections corresponding to 2θ: 25.3630, 28.4096, 35.0494, 36.7825, 39.6180, 50.8999, 60.1141 and anatase reflections to 2θ: 21.0692, 53.8457, 68.3468 and Mica at 2θ: 20.0045, 36.7825, 61.9570, are the major impurities. The clay mineral can be identified by the peaks appearing in 2θ at 7.2215, 20.0045, 28.4096, 35.0494, 53.8457 and 61.9570 which match the structure of beidellite. Beidellite and bentonite belong to the same category of clays, i.e. Smectites (2/1 sheet type). These clays are differentiated by small changes in the structure caused by the isomorphic substitution of Al^{3+} by Mg^{2+} in bentonite.

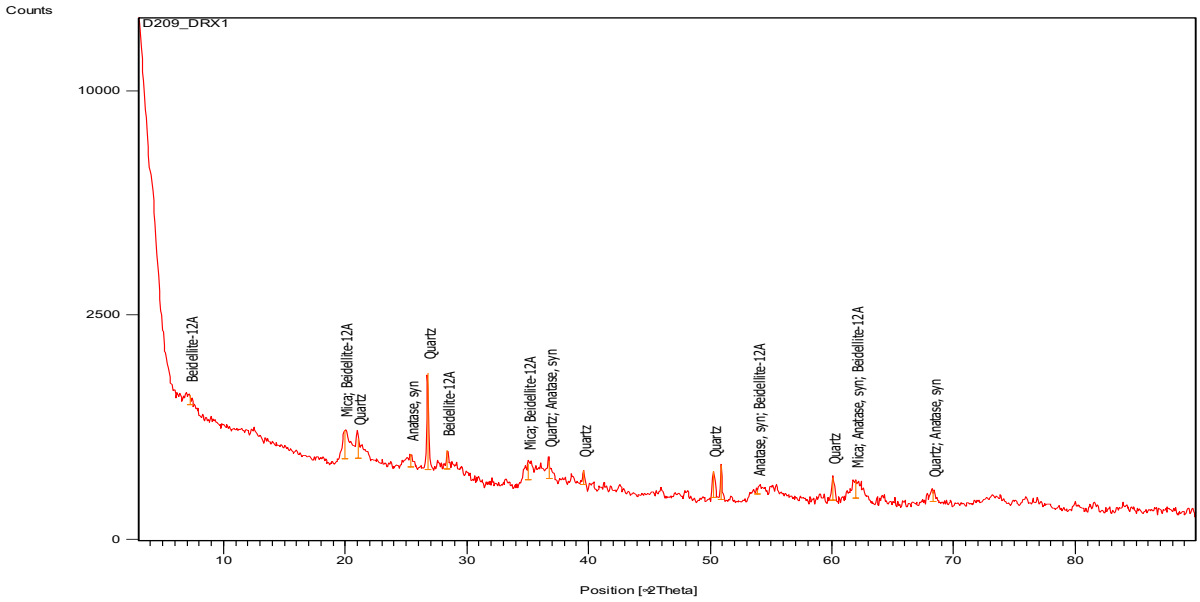
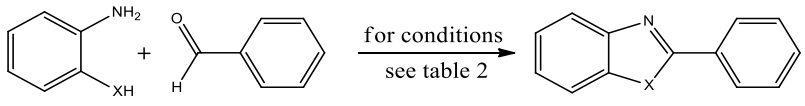


Figure 4: *XRD patterns of the raw bentonite*

3.2. Reaction procedure

In a round-bottom flask a mixture of *o*-phenylenediamine**1**, *o*-aminophenol **2** or *o*-aminothiophenol**3** (1 mmol) with different aromatic aldehydes **4a-f** (1,1 mmol), and a pinch of catalyst (50 mg) in 3 mL DMF were stirred for 1.5 hours and heated at 160°C in an oil-bath for an appropriate time which was monitored by TLC (n-Hexane/EtOAc: 8/2). After completion of the reaction, the separated catalyst was filtered and washed with methanol, concentrated under reduced pressure and chromatographed on a silica gel column to afford a pure product.

Table 2: Optimization for the synthesis of benzimidazoles**5a**, benzoxazoles**6a**, and benzothiazoles**7a**



1 X= NH
2 X= O
3 X= S

4a

5a X= NH
6a X= O
7a X= S

Entry	Reagent	Solvent	T (°C)	Catalyst	Time (h)	Yield [b] (%)
1	1	DMF	160	No a	18	25
2	1	DMF	160	raw bentonite	2	51
3	**1**	**DMF**	**160**	**Cu-bentonite**	**2**	**88**
4	1	Toluene	110	Cu-bentonite	2	76
5	1	Dioxane	110	Cu-bentonite	2	55
6	1	Ethyl acetate	60	Cu-bentonite	2	52
7	1	Ethanol	79	Cu-bentonite	2	49
8	1	Methanol	65	Cu-bentonite	2	43
9	1	Water	100	Cu-bentonite	2	56
10	1	THF	66	Cu-bentonite	2	51
11	1	DMF/water	100	Cu-bentonite	2	61
12	1	CH3CN	82	Cu-bentonite	2	63
13	**2**	**DMF**	**160**	**Cu-bentonite**	**2**	**91**
14	**3**	**DMF**	**160**	**Cu-bentonite**	**2**	**91**

[a] No: absence of catalyst for 18h
[b] Yields in pure isolated products.

The reaction was first optimized using *o*-phenylenediamine **1** (1eq) with benzaldehyde **4a** (1.1eq) in the presence and absence of catalyst (Table 2). The Cu-doped bentonite has a high catalytic capacity as compared with raw bentonite in the synthesis of benzimidazoles in DMF solvent. In the absence of catalyst, the yield ofbenzimidazoles is very low, only 25%.

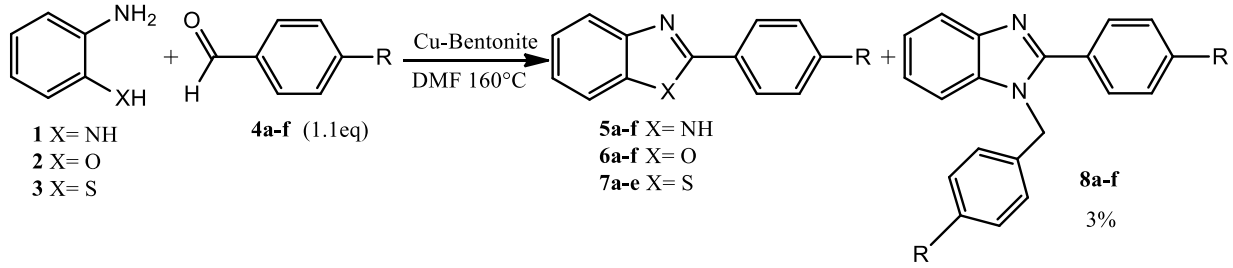
In the second experiment, we investigated the effect of various solvents in the condensation reaction of *o*-phenylenediamine **1** (1eq), with benzaldehyde **4a** (1,1eq) in the presence of Cu-bentonite as catalyst in different solvents (Table 2), with stirring and refluxing for 2 hours. The results indicated that the solvents had a significant effect on the product yield.The use of ethanol, methanol and THF as solvents gave poor yields (Table 2, Entries 7, 8 and 10). Solvents such as toluene, dioxane, ethyl acetate, water and CH_3CN gave moderate yields (Table 2, Entries 4, 5, 6, 9 and 12).The best conversion was observed when the reaction was performed in DMF (Table 2, Entry 3). Based on these results, DMF was therefore selected as the best solvent for the synthesis of benzimidazoles, benzoxazoles and benzothiazoles (Table 2, Entries 3, 13 and 14).

To test the generality of this reaction, a series of aromatic aldehydes **4a-f** (1.1eq) was used in the presence of amino derivatives **1-3** (1eq) and 50 mg of Cu-bentonite at 160°C in DMF for the time indicated in Table 3 so as to build a small library of fused heterocycles of type **5-7**. Progress of the reaction was monitored by TLC (n-Hexane/EtOAc: 8/2). After completion of the reaction, the separated catalyst was filtered and washed with methanol, concentrated under reduced pressure and chromatographed on a silica gel column in order to afford a pure product. The characterization of the productswas confirmed by ^1H NMR, ^{13}C NMR and melting points.These products were also confirmed by comparison with available literature data [31, 42].

In the synthesis of benzimidazoles, benzoxazoles and benzothiazoles, excellent yields were obtained with aromatic aldehydes using bentonite doped by copper as catalyst. The nature of the substituents on the benzene ring of aromatic aldehydes showed some effect on the yield of the corresponding products. Electron-withdrawing substituents such as $–NO_2$, –F and –Cl gave better results (Table 3, Entries 4-6, 10-12 and 16-17) than electron-donating substituents such as $–OCH_3$ and $–CH_3$ (Table 3, Entries 2-3, 8-9 and 14-15). This variation in product yields with the nature of substituents may be due to resonating, inductive and steric effects.

In the synthesis of the benzimidazoles there was also a by-product **8a-f** with a yield of 3%. This may be due to the excess of the aromatic aldehydes (1.1eq) which can react with the benzimidazoles via the nitrogen atom (NH).

Table 3: Synthesis of benzimidazoles**5**, benzoxazoles **6**, and benzothiazoles**7** under Cu- bentonite catalysis



1 X= NH
2 X= O
3 X= S

4a-f (1.1eq)

5a-f X= NH
6a-f X= O
7a-e X= S

8a-f
3%

Entry	Product	X	R	Time (h)	Yield [a] (%)	MP °C (lit.) [Ref.]
1	5a	NH	H	1.5	88	300-302 (302–304) [31]
2	5b		CH_3	2	85	269-270 (270-271) [43]
3	5c		OCH_3	2	84	234-235 (235–237) [31]
4	5d		NO_2	1.5	91	325-326 (324–326) [31]
5	5e		Cl	2	90	290-292 (289–291) [42]
6	5f		F	2	90	251-253 (249–251) [31]
7	6a	O	H	2	91	100-102 (102–104) [31]
8	6b		CH_3	3	84	113-115 (113–114) [31]
9	6c		OCH_3	3	86	102-103 (102–104) [31]
10	6d		NO_2	2.5	95	273-275 (274–277) [31]
11	6e		Cl	2.5	91	149-150 (147–149) [31]
12	6f		F	3	91	98-101 (98-99) [44]
13	7a	S	H	2	91	112-114 (112-114) [45]
14	7b		CH_3	3	83	85-87 (85) [46]
15	7c		OCH_3	2.5	87	122-124 (123-124) [45]
16	7d		NO_2	2.5	94	225-227 (226-227) [47]
17	7e		Cl	3	92	116–118 (114-115) [48]
18	7f		F	-	-	-

[a] Yields in pure isolated products

Recyclability of the catalyst is an important factor in industrial applications. The reusability of Cu-bentonite was therefore studied. The catalyst was separated by filtration, washed with methanol and calcined at 300°C for 1h. The reusability of the Cu-bentonite was studied in the model reaction (Table 3, Entry 10) between *4*-nitrobenzaldehyde **4d** and *o*-aminphenol **2** in DMF for 2.5h. The results illustrated in (Table 4) showed that the catalyst can be used four times with a slight reduction in its activity. This is because of the saturation of the catalyst active sites during reuse.

Table 4: Studies on the reuse of Cu-bentonite

Entry	Run	Yield [a] (%) 6d
1	Fresh	95
2	Recycle 1	91
3	Recycle 2	88
4	Recycle 3	80
5	Recycle 4	75

[a]Yields in pure isolated products.

Conclusion

The present method is an efficient and selective procedure for the synthesis of benzimidazoles, benzoxazoles, and benzothiazoles comprising the reaction of various aromatic aldehydes with *o*-phenylenediamine, *o*-aminophenol, or *o*-aminothiophenol, in refluxing DMF using Cu-bentonite as catalyst. The salient features of the present method are the mild conditions required, the short reaction times, high yields, and reusability of the catalyst. The method has the advantage of being very stable, non-corrosive, with a low toxicity and high selectivity.

Acknowledgments

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