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ZnO/MgO Containing ZnO Nanoparticles as a Highly Effective Heterogeneous Base Catalyst for the Synthesis of 4*H*-Pyrans and Coumarins in [bmim]BF_4

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4*H*-Pyrans and coumarins were synthesized through one-pot reactions using ZnO/MgO solid sample containing ZnO nanoparticles as an efficient reusable catalyst in ionic liquid, [bmim]BF_4. The catalyst is inexpensive and readily available, stable and storable, easily recycled and reused for several cycles with consistent activity. The procedure offers advantages in terms of high yields, short reaction times, and mild solvent-free reaction conditions.

Keywords: Coumarin, Heterogeneous catalyst, Pyran, ZnO/MgO, Ionic liquid

INTRODUCTION

Polyfunctionalized 4*H*-pyrans are interesting compounds as they possess biological and pharmacological activities [1]. These compounds are used as anti-coagulants, anticancer agents, spasmolytics, anti-anaphylactics, *etc.* [2-3]. 4*H*-Pyrans containing heterocyclic rings are increasingly used for their pharmacological activities [4]. These compounds can be used for the treatment of neuro-degenerative diseases, including Alzheimer's disease, as well as for the treatment of schizophrenia and myoclonus. Furthermore, a number of 2-amino-4*H*-pyran derivatives are useful as photoactive materials [5]. Thus, in view of their wide utility, researchers have synthesized the 4*H*-pyran unit using different methods including radioactive and non-radioactive techniques such as microwave and ultrasonic irradiation [6]. In addition, the one-pot synthesis of 4*H*-pyrans has been reported using tetrabutylammonium bromide [7], (S)-proline, rare earth perfluorooctanoates, and hexadecyltrimethylammonium bromide [8]. All these catalysts show limitations such as harsh reaction conditions, low yields, tedious work-ups, and poor recyclability.

Coumarins are an important class of natural products with interesting biological and therapeutic properties [9]. Many products, which contain the subunit of coumarin, exhibit useful and diverse biological activity such as molluscacides, anthelmintic, hypnotic, and so on, or serve as anticoagulant agents and fluorescent brighteners [10-11]. Coumarins have been synthesized using several synthetic routes such as Pechmann, Perkin, Knoevenagel, Reformatsky and Wittig reactions. However, due to simple and relatively inexpensive starting materials, the Knoevenagel reaction has been widely used for the synthesis of coumarins. We have already reported the synthesis of coumarin derivatives *via* Knoevenagel reaction of 2-hydroxybenzaldehyde derivatives with some active methylene compounds in aqueous media and also in ionic liquids [12-13].

Recently, mineral oxides have proved to be useful to chemists in the laboratory and industry due to the good activation of adsorbed compounds and reaction rate

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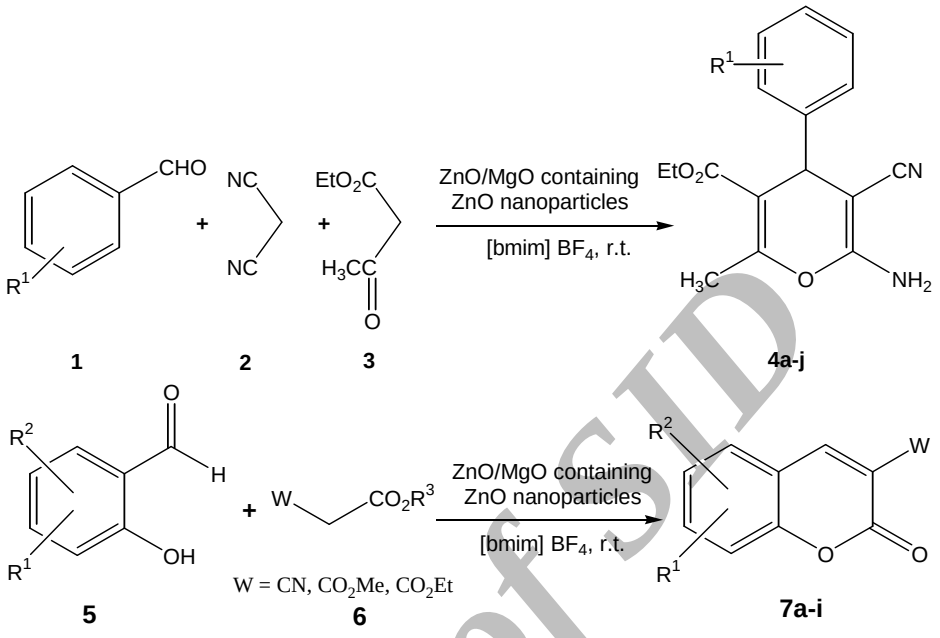

Scheme 1. Synthesis of 2-amino-4*H*-pyrans and coumarins in the presence of ZnO/MgO containing ZnO nanoparticls in [bmim]BF_4

enhancement, selectivity, easier work-up and recyclability of the supports and the eco-friendly, green, reaction conditions [14-19]. Thus, the heterogeneous solid base catalysts have been recognized as potential alternatives to homogeneous organic basic catalysts. In continuation of our interest in using ILs, water or solventless systems as green reaction media [20-26], herein we wish to report the synthesis of 4*H*-pyrane and coumarins from one pot high surface area ZnO/MgO catalyzed reactions in [bmim]BF_4 (Scheme 1).

EXPERIMENTAL

Chemicals and Apparatus

All reagents were purchased from Merck Company and used without further purification. Infrared spectra were recorded in KBr and were determined on a Perkin Elmer FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance AC-400 MHz using $CDCl_3$ or DMSO-d_6 as the deuterated solvents and TMS as internal standard. All melting points are uncorrected and measured in open glass-capillaries using Stuart melting point apparatus.

General Procedure for 4*H*-Pyrans (4a-j)

Benzaldehyde derivative (20 mmol), malononitril (20 mmol), ethylacetoacetate (20 mmol), and ZnO/MgO containing ZnO nanoparticles (10 mol%) were added to [bmim]BF_4 (3 ml) and mixed thoroughly and stirred for 28-40 min at room temperature. After completion of the reaction, as indicated by TLC (ethyl acetate/*n*-hexane, 5/1), the mixture was extracted with ethylacetate. The extracts were concentrated on a rotary evaporator and the crude mixture was purified by silica gel (Merck 230-240 mesh) column chromatography using (ethylacetate/n-hexane:1/5) mixtures as eluent to give pure pyrans (**4a-j**).

General Procedure for Coumarins (7a-i)

Salicylaldehyde (20 mmol), active methylene compound (20 mmol) and ZnO/MgO containing ZnO nanoparticles (10 mol%) were added to [bmim]BF_4 (3 ml) and mixed thoroughly and stirred for 25-40 min at room temperature. After completion of the reaction, as indicated by TLC (ethyl acetate/*n*-hexane, 5/1), the mixture was extracted with ethylacetate. The extracts were concentrated on a rotary

evaporator and the crude mixture was purified by silica gel (Merck 230-240 mesh) column chromatography using (ethylacetate/n-hexane:1/5) mixtures as eluent to give pure coumarins (**7a-**i).

Selected Spectroscopic Data

5-Ethoxycarbonyl-2-amino-4-phenyl-3-cyano-6-methyl-4*H*-pyrans (4a). IR (KBr) (ν_{max}/cm^{-1}): 3428, 3331, 2220, 1712, 1645; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.11 (t, *J* = 7.21 Hz, 3H), 2.44 (s, 3H), 4.09 (q, *J* = 7.21 Hz, 2H), 5.09 (s, 1H), 6.77 (br s, 2H, NH_2), 7.21 (m, 3H), 7.37 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 18.02, 38.00, 58.17, 62.70, 109.02, 123.06, 125.21, 126.32, 127.02, 129.41, 142.01, 148.40, 158.11, 161.63.

5-Ethoxycarbonyl-2-amino-4-(4-nitrophenyl)-3-cyano-6-methyl-4*H*-pyrans (4b). IR (KBr) (ν_{max}/cm^{-1}): 3449, 3291, 2211, 1721, 1680, 1534, 1351; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.15 (t, *J* = 7.23 Hz, 3H), 2.39 (s, 3H), 4.05 (q, *J* = 7.23 Hz, 2H), 5.10 (s, 1H), 6.74 (br s, 2H, NH_2), 7.25 (d, *J* = 7.98 Hz, 2H), 7.41 (d, *J* = 7.98 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 19.12, 39.11, 58.12, 63.52, 110.32, 124.24, 126.01, 126.21, 127.42, 130.08, 142.86, 148.96, 159.00, 162.31.

5-Ethoxycarbonyl-2-amino-4-(3-nitrophenyl)-3-cyano-6-methyl-4*H*-pyrans (4c). IR (KBr) (ν_{max}/cm^{-1}): 3456, 3287, 2215, 1718, 1677, 1531, 1349; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.18 (t, *J* = 7.20 Hz, 3H), 2.35 (s, 3H), 4.11 (q, *J* = 7.20 Hz, 2H), 5.14 (s, 1H), 6.80 (br s, 2H, NH_2), 7.17 (d, *J* = 2.61 Hz, 1H), 7.38 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.6, 40.17, 59.89, 63.50, 111.30, 124.45, 127.42, 127.021, 128.78, 129.02, 130.65, 132.12, 142.16, 148.96, 159.74, 164.30.

5-Ethoxycarbonyl-2-amino-4-(4-chlorophenyl)-3-cyano-6-methyl-4*H*-pyrans (4d). IR (KBr) (ν_{max}/cm^{-1}): 3457, 3288, 2213, 1724, 1685; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.19 (t, *J* = 7.25 Hz, 3H), 2.40 (s, 3H), 4.12 (q, *J* = 7.25 Hz, 2H), 5.09 (s, 1H), 6.71 (br s, 2H, NH_2), 7.19 (d, *J* = 7.85 Hz, 2H), 7.38 (d, *J* = 7.85 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.10, 41.52, 59.72, 63.51, 111.02, 126.24, 127.98, 128.21, 127.42, 131.78, 144.06, 148.16, 161.21, 162.32.

5-Ethoxycarbonyl-2-amino-4-(3-bromophenyl)-3-cyano-6-methyl-4*H*-pyrans (4e). IR (KBr) (ν_{max}/cm^{-1}): 3451, 3282, 2212, 1726, 1686; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.24 (t, *J* = 7.22 Hz, 3H), 2.29 (s, 3H), 4.21 (q, *J* = 7.22 Hz, 2H), 5.24 (s, 1H), 6.82 (br s, 2H, NH_2), 7.23 (d, *J* = 2.31 Hz, 1H), 7.42 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.16, 42.47, 60.63, 64.54, 115.08, 125.45, 127.12, 127.02, 128.08, 130.25, 131.15, 143.17, 148.90, 165.34, 169.85.

5-Ethoxycarbonyl-2-amino-4-(4-hydroxyphenyl)-3-cyano-6-methyl-4*H*-pyrans (4f). IR (KBr) (ν_{max}/cm^{-1}): 3490-3150 (broad), 3448, 3275, 2216, 1718, 1679; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.16 (t, *J* = 7.23 Hz, 3H), 2.39 (s, 3H), 4.16 (q, *J* = 7.23 Hz, 2H), 5.12 (s, 1H), 6.69 (br s, 2H, NH_2), 7.21 (d, *J* = 8.01 Hz, 2H), 7.43 (d, *J* = 8.01 Hz, 2H), 8.32 (br s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 18.10, 42.23, 61.12, 63.11, 113.32, 127.32, 128.08, 128.28, 129.49, 133.18, 144.65, 148.54, 163.21, 164.22.

5-Ethoxycarbonyl-2-amino-4-(4-methylphenyl)-3-cyano-6-methyl-4*H*-pyrans (4g). IR (KBr) (ν_{max}/cm^{-1}): 3451, 3281, 2222, 1726, 1683; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.19 (t, *J* = 7.26 Hz, 3H), 2.35 (s, 3H), 2.91 (s, 3H), 4.26 (q, *J* = 7.26 Hz, 2H), 5.23 (s, 1H), 6.75 (br s, 2H, NH_2), 7.18 (d, *J* = 7.65 Hz, 2H), 7.39 (d, *J* = 7.65 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 19.87, 43.20, 45.36, 62.18, 64.54, 115.30, 127.42, 128.18, 128.76, 130.91, 134.23, 144.54, 148.55, 164.01, 164.87.

5-Ethoxycarbonyl-2-amino-4-(2-methoxyphenyl)-3-cyano-6-methyl-4*H*-pyrans (4h). IR (KBr) (ν_{max}/cm^{-1}): 3403, 3327, 2187, 1691, 1633; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.23 (t, *J* = 7.24 Hz, 3H), 2.32 (s, 3H), 3.78 (s, 3H), 4.24 (q, *J* = 7.21 Hz, 2H), 4.98 (s, 1H), 6.64 (br s, 2H, NH_2), 6.90-7.06 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 18.02, 22.25, 36.24, 58.18, 60.21, 62.41, 109.40, 123.89, 124.21, 126.13, 126.06, 130.01, 141.71, 147.15, 159.55, 161.63, 167.23.

5-Ethoxycarbonyl-2-amino-4-(2-chlorophenyl)-3-cyano-6-methyl-4*H*-pyrans (4i). IR (KBr) (ν_{max}/cm^{-1}): 3428, 3332, 2195, 1686, 1643; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.09 (t, *J* = 7.21 Hz, 3H), 2.43 (s, 3H), 4.06 (q, *J* = 7.21 Hz, 2H), 5.08 (s, 1H), 6.70 (br s, 2H, NH_2), 7.19 (m, 3H), 7.38 (dd, *J* = 7.60 and 2.35 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 16.32, 37.08, 58.18, 61.71, 108.42, 122.27, 123.01, 125.63, 126.56, 128.95, 129.21, 140.01, 148.45, 158.25, 160.16, 168.74.

5-Ethoxycarbonyl-2-amino-4-(2-nitrophenyl)-3-cyano-6-methyl-4*H*-pyrans (4j). IR (KBr) (ν_{max}/cm^{-1}): 3453, 3295, 2209, 1719, 1684, 1530, 1353; ^{1}H NMR (400 MHz, DMSO-

d_6) δ 1.01 (t, *J* = 7.28 Hz, 3H), 2.44 (s, 3H), 3.99 (q, *J* = 7.28 Hz, 2H), 5.24 (s, 1H), 6.75 (br s, 2H, NH_2), 7.36 (m, 1H), 7.61 (dd, *J* = 7.81 and 2.66 Hz, 1H), 7.84 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 15.25, 38.78, 57.58, 60.78, 106.67, 121.27, 123.32, 124.52, 126.23, 127.56, 128.21, 143.91, 149.45, 157.37, 159.06, 169.12.

RESULTS AND DISCUSSIONS

The reaction between benzaldehyde, malononitril and ethyl cyanoacetate was chosen as the test reaction for the synthesis of 4*H*-pyran **4a**, and the reaction between salicylaldehyde and diethylmalonate was chosen as the test reaction for the synthesis of coumarin **7b** because of the large body of literature data available for these reaction systems. The reaction conditions were very mild and carried out in [bmim]BF_4 and the progress of the reaction was monitored by TLC. In the first set of experiments, the catalytic potential of some metal oxides was investigated for this procedure in [bmim]BF_4 at room temperature (Table 1). According to the results obtained, of the metal oxides tested, Al_2O_3, Ag_2O, CaO and SiO_2 were unable to promote the reaction. ZnO nanoparticles were prepared and loaded on MgO to prepare high surface area ZnO/MgO containing ZnO nanoparticles solid sample according to the literature [27]. Using this high surface area solid sample as the catalyst gave large amounts of 5-ethoxycarbonyl-2-amino-3-cyano-6-methyl-4-phenyl-4*H*-pyran **4a** and 3-ethoxycarbonyl coumarin **7b**. When a mixture of benzaldehyde (20 mmol), malononitril (20 mmol), ethyl cyanoacetate (20 mmol) and ZnO/MgO containing ZnO nanoparticles (10 mol %) was stirred at room temperature, the product **4a** was produced in 91% yield.

The scope of this methodology was further extended by the reaction of various benzaldehydes in this procedure. In short reaction times at room temperature, different 4*H*-pyrans were prepared in good yields in [bmim]BF_4 in the presence of ZnO/MgO containing ZnO nanoparticles (10 mol%) (Table 2).

With the optimal catalytic system in hand, we investigated the Knoevenagel reaction of various salicylaldehydes **5** with active methylene compounds **6** (Scheme 1). A variety of structurally diverse salicyaldehydes reacted favorably with active nucleophilic reagents to give the desired coumarins in good to excellent yields. Results are presented in Table 3. It can be easily seen that the condensation of a series of salicyaldehydes and active methylene compounds were conveniently catalyzed by this catalyst in [bmim]BF_4 at room temperature and the reaction completed in short time.

Additionally, the catalytic activity of the reused catalyst, which was readily recovered by extraction of the reaction mixture with ethyl acetate (15 ml × 3), was investigated. 4*H*-Pyran and coumarin derivatives, with catalyst recycled for four times, were synthesized in comparable yields to the fresh catalyst (Table 4).

The SEM images of the catalyst were obtained before the

Table 1. Synthesis of 4*H*-Pyran **4a** and Coumarin **7b** in the Presence of Various Metal Oxides[a]

Entry	Metal oxide (10 mol%)	Product **4a**		Product **7b**	
		Time (min)	Yield (%)[c]	Time (min)	Yield (%)[c]
1	-	50	40	60	42
2	ZnO	35	84	40	80
3	MgO	35	81	40	78
4	SiO_2	40	45	45	38
5	Al_2O_3	45	42	45	35
6	CaO	45	40	50	35
7	Ag_2O	45	42	50	32
8	ZnO/MgO[b]	30	91	35	90

[a]The reactions were made at room temperature in [bmim]BF_4. [b]ZnO/MgO solid sample containing ZnO nanoparticles was prepared according to the procedure reported in the literature [27] at room Temperature in the PH 6. [c]Isolated yield.

Table 2. ZnO/MgO Containing ZnO Nanoparticles Catalyzed Synthesis of 4*H*-Pyrans in [bmim]BF_4[a]

Entry	R^1	Product	Time (min)	Yield (%)[b]
1	Ph	**4a**	30	81
2	4-NO_2	**4b**	32	79
3	3-NO_2	**4c**	30	82
4	4-Cl	**4d**	28	80
5	3-Br	**4e**	40	89
6	4-OH	**4f**	30	90
7	4-Me	**4g**	30	91
8	2-OMe	**4h**	32	83
9	2-Cl	**4i**	33	85
10	2-NO_2	**4j**	30	88

[a]The reaction was made at room temperature. [b]Isolated yield.

Table 3. ZnO/MgO Containing ZnO Nanoparticles Catalyzed Synthesis of Coumarins in [bmim]BF_4[a]

Entry	R^1	R^2	R^3	W	Product	Time (min)	Yield (%)[b]	M.p. (°C)	
								Found	Reported [Ref.]
1	7-OH	H	Me	CO_2Me	**7a**	25	85	264-267	265-267 [28]
2	H	H	Et	CO_2Et	**7b**	28	91	93-96	94-97 [28]
3	7-OH	8-OH	Et	CO_2Et	**7c**	40	82	232-234	233-234 [28]
4	7-OMe	H	Et	CO_2Et	**7d**	38	83	131-134	132-133 [29]
5	7-Et_2N	H	Et	CO_2Et	**7e**	32	80	77-78	77-78 [30]
6	7-OH	8-Br	Et	CO_2Et	**7f**	30	83	270-273	270-271 [29]
7	7-OMe	8-Br	Et	CO_2Et	**7g**	30	84	188-191	189-190 [29]
8	H	8-OMe	Et	CO_2Et	**7h**	35	89	87-90	88-90 [31]
9	H	8-OMe	Me	CN	**7i**	25	78	224-226	224-225 [32]

[a]The reaction was made at room temperature. [b]Yield of isolated product.

Table 4. Reusing of the High Surface Area Basic ZnO/MgO Containing ZnO Nanoparticles Catalyst for the Synthesis of **4a**, **4b**, **7a** and **7b**

Run	Yield (%)[a] Product **4a**	Yield (%)[a] Product **4b**	Yield (%)[a] Product **7a**	Yield (%)[a] Product **7b**
1	81	79	85	91
2	80	79	83	89
3	79	78	84	89
4	78	77	83	88
5	79	78	82	89

[a]Isolated yield.

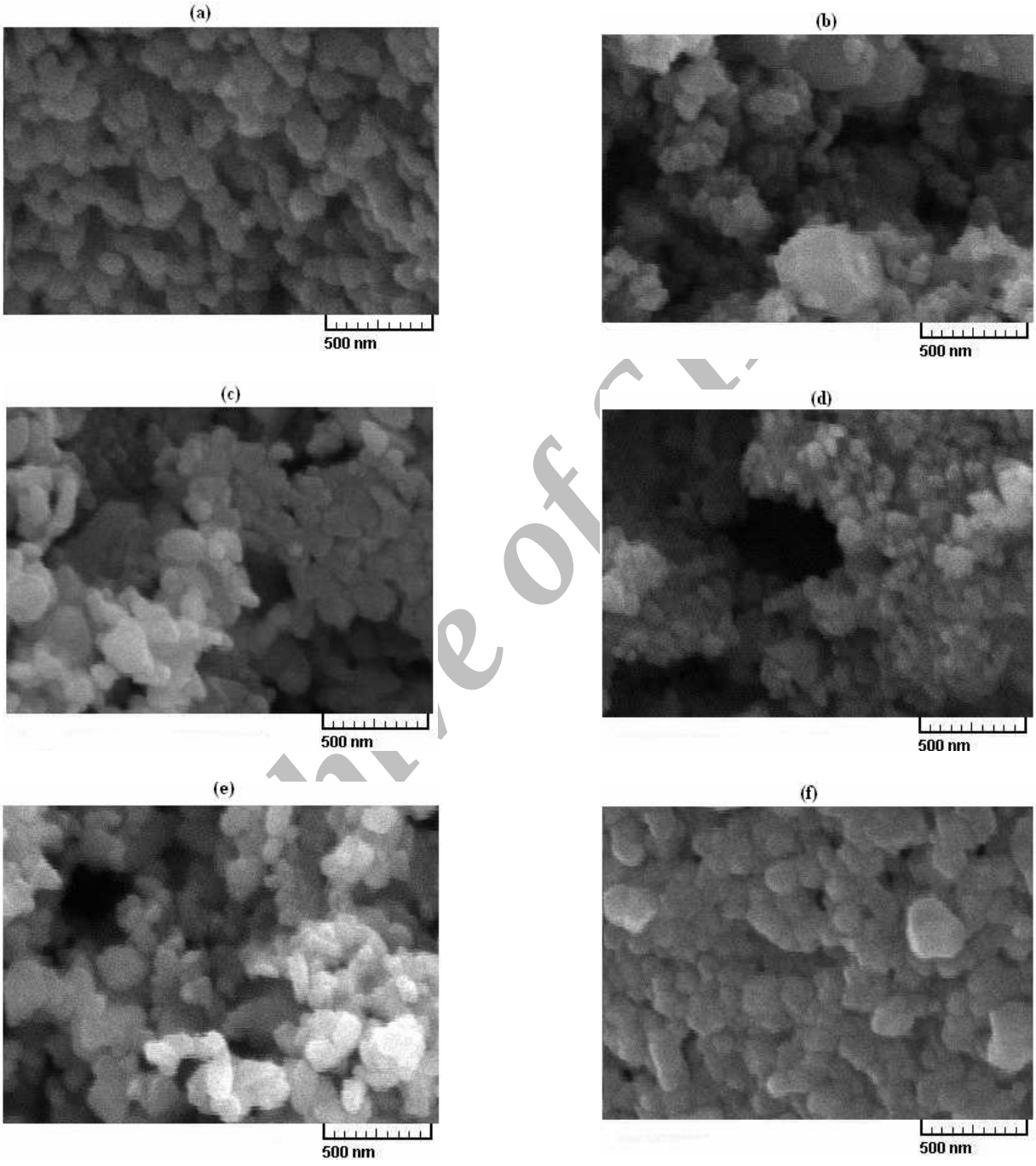

Fig. 1. SEM image of (a) ZnO nanoparticles (b) ZnO nanoparticles in the ZnO/MgO solid before reaction (c) ZnO nanoparticles in the ZnO/MgO solid after reaction to synthesis of **4a** (d) ZnO nanoparticles in the ZnO/MgO solid after the three times recycled to the synthesis of **4a** (e) ZnO nanoparticles in the ZnO/MgO solid after reaction to the synthesis of **74a** (f) ZnO nanoparticles in the ZnO/MgO solid after the three times recycled to the synthesis of **7a**.

reaction and compared with the SEM images of the catalyst recycled for one and three times for the synthesis of **4a** and **7b** (Fig. 1). To the best of our knowledge, this is the first heterogeneous high surface area basic ZnO/MgO containing ZnO nanoparticles catalyst for the synthesis of 4*H*-pyrans and coumarins in [bmim]BF_4.

In conclusion, we have developed a facile and effective procedure for the synthesis of highly substituted 4*H*-pyrans and coumarins in the presence of the high surface area basic ZnO/MgO solid sample containing ZnO nanoparticles as recyclable catalyst in [bmim]BF_4. Compared with other methods in existence, it has the advantages of better yields, inexpensive operation, and environmental friendliness.

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