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Synthesis and characterization of Nanoparticles Poly Ethylene Imine-Functionalized MCM-41by Covalent Anchoring as a Solid Catalyst for Multi-Component Reactions

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Abstract- A novel magnetically immobilized polyethyleneimine (PEI) fabricated by covalently anchoring on MCM-41 (MCM-41@PEI) was prepared. The synthesized catalyst was characterized by Fourier transform infrared (FT-IR), thermogravimetric analysis (TGA), X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The immobilized PEI was shown to be an efficient heterogeneous catalyst for the synthesis of spiro-oxindole and benzopyranes derivatives *via* multi-component reaction (MCR), in ethylene glycol as a green solvent. No leaching problem was observed after several runs, while the catalyst can be recovered and reused without loss of reactivity under the described reaction conditions.

Keywords: Polyethylenimine, Catalyst, Microwave, MCM-41 supported catalyst, spiro-oxindole, benzopyranes.

Introduction

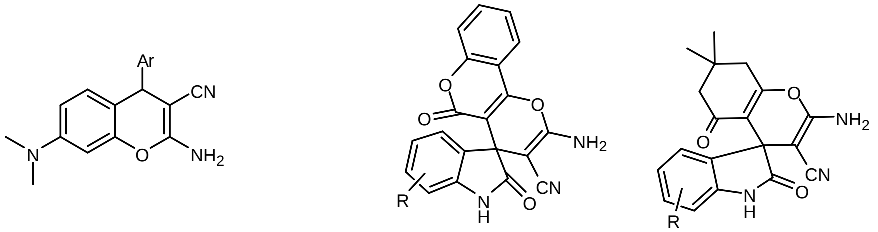
Solid-supported catalysts are an important and growing arena in heterogeneous catalysis which has attracted increased attention in organic transformation due to their easy separation from the reaction mixture and possible reuse and has become strategically vital for the efficient and ecofriendly organic transformations over the past few decades [1-5].Surface fictionalization allows a number of groups to introduce onto the surfaces through co-condensation or post-synthesis. The advancement of heterogenized catalysis by Solid-supported catalysts, such as various organic/inorganic polymer-supported catalysts, zeolites, mixed metal oxides, hydrotalcites, mesoporous siliceous molecular sieve, resins, etc combine the advantages of both homogeneous and heterogeneous catalytic systems.

In the last few decades, mesoporous materials have received much attention in the field of catalysis, especially for their use as solid supports. One of the well-ordered mesoporous solid structures is MCM-41 that has some interesting properties such as high surface area, uniform pore size (20–100A˚) and relatively hydrophobic nature [6]. The MCM-41 in pure silica form exhibits only weak hydrogen bonding [7, 8] and hasenormous specific surface area.It can be easily modified with organic groups and metal complexes to form discreteand uniform active sites for substrates [9, 10].

In recent years, functionalization of MCM-41 by using the reaction with the surface silanol groups, to form MCM-supported catalysts, have been successfully deployed in organic synthesis for a variety of important reactions such as heteropolyacids (HPW) [11–13] and other mineral acids (H_3PO_4, H_2SO_4) supported on MCM-41 [14–16], pyridine-functionalized MCM-41 [17], SO_3H-MCM-41 [18, 24].

Polyethyleneimine (PEI) or polyaziridine is a branched polymer and an available synthetic polycation with a high-density amine group. Linear PEIs contain all secondary amines, in contrast to branched PEIs which contain primary, secondary and tertiary amino groups by ratio 1:2:1. The branched PEIs have a strong protonation capacity and they are liquids at all molecular weights. It has been widely used in drug/gene delivery [26-28], CO_2 adsorption [29], nucleic acid precipitation, protein coagulation/flocculation [30], nucleotide, cell and enzyme immobilization as well as modified surface agent of nanoparticles [31-34].

In this work, we used PEI as water soluble and cationic polymer consisting of large number of terminal amino groups in combination with MCM-41(MCM-41@PEI), with the maximum catalytic activity in the multi-component reaction (MCR) by optimizing reaction conditions.This catalyst is tested for the preparation of biologically interesting chromene, benzopyranes and spiro-oxindole derivatives via multi-component reaction (MCR), invarious conditions (Scheme 1).



Scheme 1.

Experimental

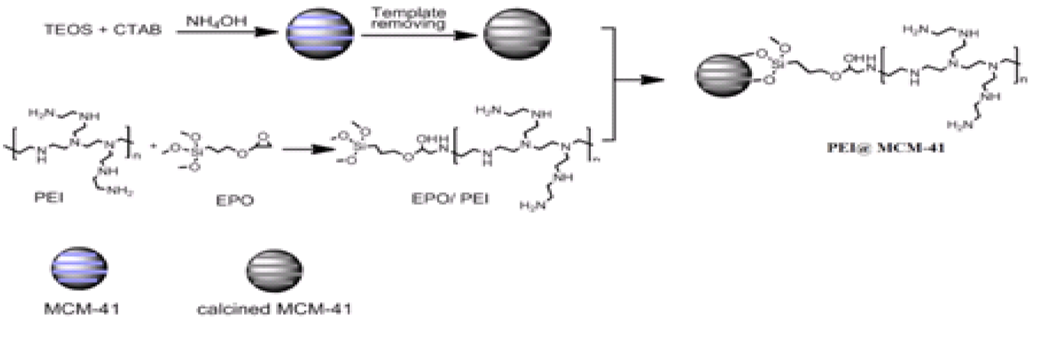
Preparation of MCM-41 and MCM-41@PEI

MCM-41 was prepared according the previous work [41]. Briefly, Cetyltrimethylammonium bromide (CTAB) (13.0 g) was dissolved in deionized water (167.0 mL). Then, aqueous ammonia (163.7 mL) and absolute ethanol (131.5 mL) were added to the surfactant solution, and stirred for 15 min. Subsequently, tetraethyl orthosilicate (TEOS) (24.8 mL) was added to the mixture. After 2 h of vigorous stirring at 1500 rpm and subsequent filtration, the white precipitate was washed with deionized water and dried at 60 °C for 24 h. The prepared MCM-41 was successfully calcinated under oxygen atmosphere by heat treatment at a rate of 1 °C.min^{-1} up to 600 °C. This temperature was maintained for 6 h.

PEI was grafted onto the prepared MCM-41 as follows. [3-(2,3-epoxypropoxy) propyl] trimethoxysilane (EPO) (1.0 mmol) was added to PEI solution (3.0 mmol) in dry toluene (150 mL). The resultant mixture was allowed to react at 80 °C for 24 h. The calcined MCM-41 (2.5 g) and ethanol (25 mL) were added to the mixture and then stirred at 80 °C for 24 h. The produced PEI@MCM-41 was filtered and washed several times with deionized water and ethanol. It was subsequently Soxhleted with ethanol for 24 h to remove physically bonded compounds, filtered, and dried at 50 °C for several days [42] (Scheme 2).

Catalytic experiments

Multi-component reactions of an active carbonyl compound (isatin or aldehyde, 1 mmol), malononitrile (1.2 mmol) and an enolizable compounds (dimedone, or 3-(dimethylamino) phenol) were performed with microwave irradiation assistance for the preparation of spiro-oxindole, benzopyranes and chromene derivatives (Scheme 1).



Scheme 2. Schematic representation of the formation of MCM-41@PEI

Prior to reaction, Benzaldehyde (Merck, 1.0 mmol), Malononitrile (MN, Merck, 1.2 mmol), 3-(dimethylamino) phenol (Merck, 1.0 mmol) and freshly activated MCM-41@PEI catalyst (0.1 g, 100 ◦C, 20 min) in PEG were loaded into a reactor. The reaction was realized in the microwave oven (ETHOS 1600, Milestone) with a power of 300 W.After completion of the reaction, the reaction mixture was allowed to cool at room temperature and diluted with ethyl acetate and the catalyst was easily separated bycentrifuge and washed twice with ethyl acetate. The combined organic layers were concentrated and the residue was purified by recrystallization from ethanol.

Characterization of PEI@MCM-41

The as-synthesized PEI@MCM-41catalyst was characterized by various techniques. The FT-IR spectra of MCM and PEI@MCM-41 are shown in Figs. 1a and 1b. The FT-IR spectrum of the PEI@MCM-41, shows weak peaks at 1079, 796, and 467 cm^{-1} assigned to the dissymmetry, symmetry, and bending vibration of the Si-O-Si group, respectively [48] and The strong peaks at 3410 cm^{-1} attributed to the stretching and bending vibration of OH, indicate the presence of a large number of hydroxyl groups and H_2O molecules on the surface of the particles (Fig. 1a). In addition, the characteristic peaks of the stretching vibrations of C-H and C-N bonds at 2940 and 1466 cm^{-1} were also observed in the FT-IR spectrum of the PEI grafted onto MCM-41(Fig. 1b).

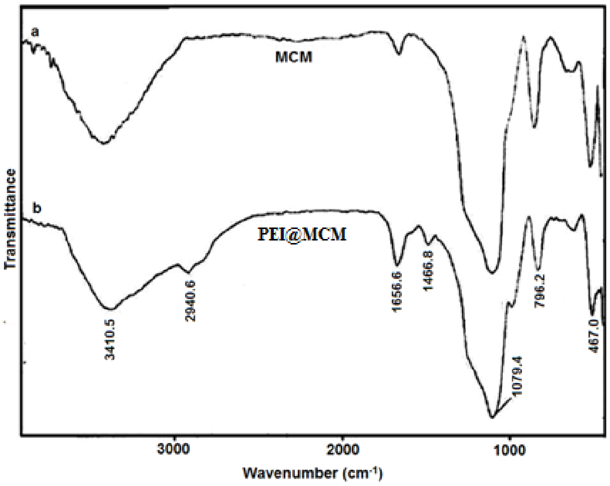


Figure 1. FT-IR spectra of the prepared (a) MCM-41 and (b) PEI@MCM-41

The ordered mesoporosity of MCM-41 solids was determined by XRD analysis. The XRD pattern of calcined MCM-41 exhibits an intense signal at 2θ= 2.2◦ corresponding to (1 0 0) plane and three small signals between 3.5◦ and 6.5◦ due to (1 1 0), (2 0 0) and (2 1 0) planes which confirms the presence of well-defined hexagonal MCM-41 (Fig. 2a) [49].

The Fig. 2b presents the thermal properties of PEI@MCM-41 (TGA) which shows 38% weight loss up to 800 ºC. The weight loss of FCNT can be described to decomposition of PEI groups, EPO and intrinsic structure of MCM. The most part of this weight loss belongs to thermal degradation of PEI grafted onto MCM and less part of it belongs to thermal degradation of the other materials. The mass loss of 5.2 % (below 100 ◦C) may be due to removal of surface adsorbed water of the catalyst.

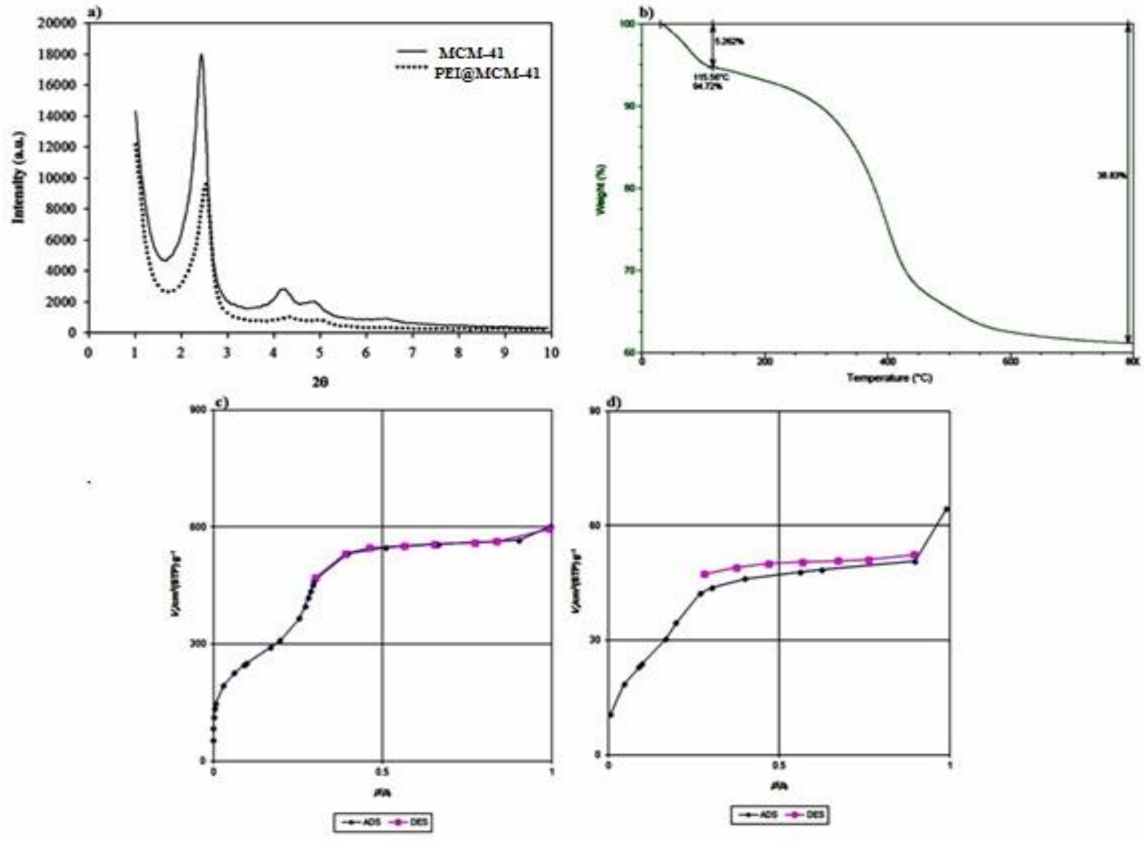


Figure 2. (a) XRD spectra of MCM and PEI@MCM-41, (b) TGA for PEI@MCM-41, and Nitrogen sorption isotherm obtained at 77 K for (c) MCM and (d) PEI@MCM-41.

The SEM image of MCM-41 and PEI grafting MCM-41 presented in Fig. 3a and Fig. 3b, showing a nearly smooth spherical MCM surface. The high-resolution TEM images exhibit identical MCM coating by PEI and the formation of a core-shell structure (Figs. 3c and 3d). The TEM microphotographs show the core-shell structure of mesoporous silica in the polymer matrix and nanosized mesoporous MCM particles with diameters of 200-400 nm.

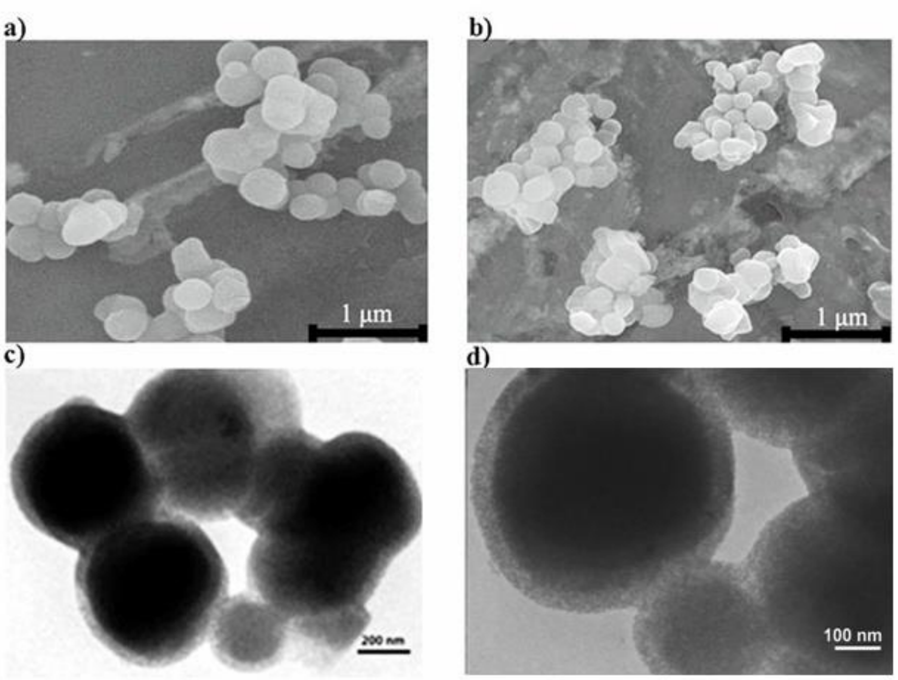


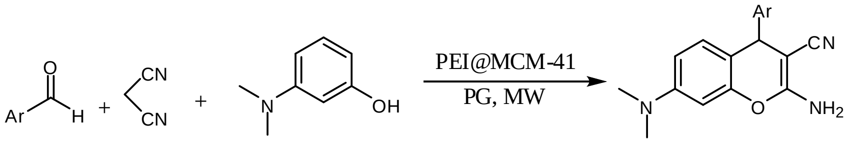
Figure 3. SEM images of the (a) MCM, (b) PEI@MCM-41; TEM image of the core-shell structure of PEI@MCM-41 (c) low magnification and (d) high magnification

Catalytic study

The reaction was caused by the 3-(dimethylamino) phenol which resulted in the formation of 4H-benzo[b]pyran derivatives in excellent yields. Thus the PEI@MCM-41 as a catalyst by microwave irradiation shows excellent procedure for preparation of 4H-benzo[b]pyran derivatives (Table 1).

A reusability test for PEI@MCM-41 was performed and it was found that the reactivity of the recovered PEI@MCM-41 was preserved after the second, third and fourth runs. This strongly suggests that little to no leaching took place as the PEI are covalently bonded to the mesoporous support. This is consistent with the results obtained from both thermogravimetry and IR spectroscopy analyses.

Table 1. Synthesis of Chromene derivatives usingPEI@MCM-41



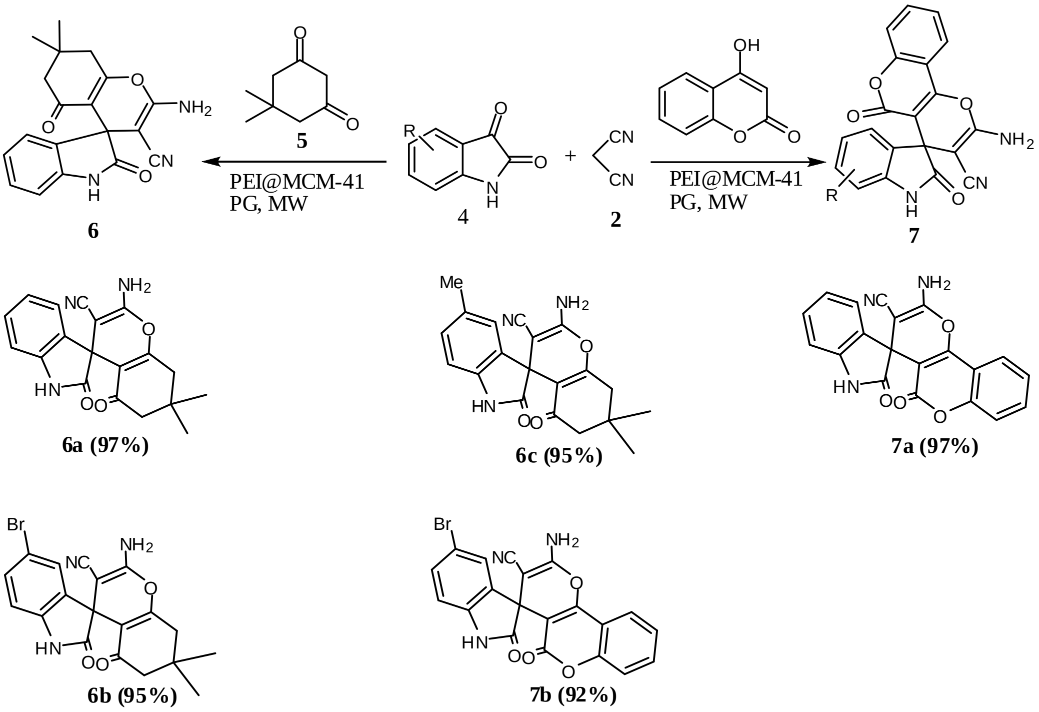
Entry	Ar	Yield[a]	m.p[b]	Entry	Product	Yield [a]	m.p.[b](°C)
1	4-NO_2-C_6H_4	94	224-226	7	2,4-di-Me-C_6H_3	89	155-157
2	3-Br-C_6H_4	91	194-196	8	2,3-di-Cl-C_6H_3	85	220-222
3	3-F-C_6H_4	88	163-166	9	4-F-C_6H_4	87	174-178

4	3-CF_3-C_6H_4	92	214-218	10	4-Br-C_6H_4	89	212-214
5	2,3-di-OMe-C_6H_3	86	158-160	11	2,6-di-Cl-C_6H_3	83	>250
6	3-NO_2-C_6H_4	93	207-209	12	2-OMe-C_6H_3	82	182-184

[a] Isolated yield

[b] literature m.p. [43-47]

In continuation to this research, a simple and an efficient one pot synthetic approach was used for the preparation of biologically interesting spirooxindole derivatives by means of three-component reactions of isatin, malononitrile, and dimedone or 4-hydroxycoumarin catalyzed by mentioned catalytic system in PG (Scheme 5).



Scheme 5. PEI@MCM-41 catalyzed three-component synthesis of spirooxindole derivatives

Conclusions

In summary, we showed that PEI grafted on silica coated MCM-41fabricated by covalently anchoring, was a novel and effective heterogeneous catalyst for the one-pot synthesis of benzopyranes and spiro-oxindoles derivatives from commercially available starting materials. The present method requires remarkably small amounts of non-toxic and environmentally friendly PEI@MCM-41 as catalyst. This procedure offers several worthy advantages including generality, simplicity, easy work up, clean reactions and improved yields. Based on these observations, it could be concluded that this green and cost-effective catalyst, with simple experimental and work-up procedure, which avoids the use of large volumes of hazardous organic solvents, makes it a useful alternative for the scale-up of these three component reactions.

REFERENCES

[1] N. T. S. Phan, C. S. Gill, J. V. Nguyen, Z. J. Zhang and C. W. Jones, Angew. *Chem., Int. Ed.*, 2006, **45**, 2209–2212.

[2] S. Shylesh, V. Schunemann, W.R. Thiel, Angew. *Chem. Int. Ed*. 2010, **49**, 3428.

[3] A. Kong, P. Wang, H. Zhang, F. Yang, S.P. Huang, Y. Shan, *Appl. Catal*. 2012, **A 417**, 183.

[4] A. Baiker, *Chem. Rev*., 1998, **99**, 453–474.

[5] H. Hamadi, M. kooti,

[6] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature. 1992,**359**, 710–712.

[7] W. Zhang, T.R. Pauly, T.J. Pinnavaia, *Chem. Mater*. 1997, **9**,2491–2498.

[8]E.P. Ng, S. Mintova, Micropor. Mesopor. Mater. 2008, **114**,1–26.

[9] Beck J. S., Vartuli J. C., Roth W. J., Leonowicz M. E., Kresge C. T., Schmitt K. D., Chu C. T. W., Olson D. H., Sheppard E. W., McCullen S. B., Higgins J. B., Schlenker J. L., *J. Am. Chem. Soc.*, 1992, **114**, 10834—10843.

[10] Song C. E., Lee S. G., *Chem. Rev*., 2002, **102**, 3495-3524.

[11] P. Selvam, S.E. Dapurkar, *Catal. Today*,2004, **96**, 135–141.

[12] J.C. Juan, J. Zhang, M.A. Yarmo, *J. Mol. Catal. A: Chem*. 2007, **267**,265–271.

[13] G. Karthikeyan, A. Pandurangan, J. Mol. *Catal. A: Chem*. 2009, **311**,36–45.

[14] E.-P. Ng, H. Nur, K.-L. Wong, M.N.M. Muhid, H. Hamdan, *Appl. Catal. A*: Gen. 2007,**323,** 58–65.

[15] D.P. Sawant, A. Vinu, F. Lefebvre, S.B. Halligudi, J. Mol. *Catal. A: Chem*. 2007, **262**, 98–108.

[16] N.E. Poh, H. Nur, M.N.M. Muhid, H. Hamdan, *Catal. Today*. 2006, **114**,257–262.

[17] A. Shaabani, M. Mohammadpour, S. Ghasemi, R. Ghadari, A. H. Rezayan, Y. Fazaeli, S. Feizi, *Chem. Pharm. Bull*. 2010, **58**, 270—272.

[18] J.-P. Dacquin, H.E. Cross, D.R. Brown, T. Duren, J.J. Williams, A.F. Lee, K. Wilson, *Green Chem*. 2010, **12**, 1383–1391.

[19] X. Sheng, J. Gao, L. Han, Y. Xia, W. Sheng, Micropor. Mesopor. Mater. 2011, **143**, 73–77.

[20] S. Shylesh, P.P. Samuel, C. Srilakshmi, R. Parischa, A.P. Singh, J. Mol. *Catal. A: Chem.* 2007, **274**, 153–158.

[21] F. Adam, K.M. Hello, T.H. Ali, Appl. *Catal. A: Gen.*2011, **399**, 42–49.

[22] B. Rac, P. Hegyes, P. Forgo, A. Molnar, Appl. Catal. A: Gen. 2006, **299**,193–201.

[23] E-P. Ng, S. N. M. Subari, O. Marie, R. R. Mukti, J-C. Juan Appl. *Catal. A: Gen*. 2013, **450**, 34– 41

[24] R.V. Hangarge, S.A. Siddiqui, S.R. Shengule, M.S. Shingare, *Mendeleev Commun*. 2002, **12**, 209–210.

[25] K-Z. Hossain, C. M. Monreal, A. Sayari,*Colloids and Surfaces B: Biointerfaces*, 2008, **62**, 42–50

[26] C. Rudolph, J. Lausier, S. Naundorf; RH. Müller, J. Rosenecker, *J. Gene. Med.*,2000, **4**, 269.

[27] B. Chertok, A. E. David, V. C. Yang, Biomat. 2010, **31**, 6317.

[28] A. Barnard, P. Posocco, S. Pricl, M. Calderon, R. Haag, M. E. Hwang, V. W. T. Shum, D. W. Pack, D. K. Smith, J. Amr. *Chem. Soc*, 2011, **133**, 20288.

[29] S. Satyapal, T. Filburn, J. Trela, J. Strange, Energy & Fuels, 2001, **15**, 250.

[30] J.J. Karimpil, J.S. Melo, S.F. D’Souza, *Int. J. Biol. Macromol*. 2012, **50**, 300.

[31] C. T. Chen, L. Y. Wang, Y. P. Ho, Anal Bioanal Chem. 2011, **399**, 2795.

[32] W-J. Song, J-Z. Du, T-M. Sun, P.-Z. Zhang, J. Wang, Small. 2010, **6**, 239.

[33] H. J. Lee, S. G. Lee, E. J. Oh, H. Y. Chung, S. I. Han, E. J. Kim, S. Y. Seo, H. D. Ghim, J. H. Yeum, J. H. Choi, Coll. *Surf B Biointerfaces*. 2011, **88**, 505.

[34] X. Wang, L. Zhou, Y. Ma, X. Li, H. Gu, *Nano Res*. 2009,**2**, 365.

[35] X. Wang, L. Zhou, Y. Ma, X. Li; H. Gu, *Nano Res*.2009,**2**, 365.

[36]A. J. Amali, R. K. Rana, *Green Chem*. 2009, **11**,1781.

[37] S. M. Ribeiro, A. C. Serra, A.M. d’A. Rocha Gonsalves, *App. Catal*. 2011, **A 399**, 126.

[38] Z. Shen, Y. Chen, H. Frey, S-E. Stiriba, *Macromol*. 2006, **39**, 2092.

[39] Y. Chi, S. T. Scroggins, E. Boz, J. M. J. Fre´chet, *J. Ame. Chem. Soc*, 2008,**130**, 17287.

[40]M-L. Wang, T-T. Jiang, Y. Lu, H-J. Liu, Y. Chen, *J. Mater. Chem*. A, 2013,**1**, 5923-5933.

[41] L. Martins, W. Hölderich, P. Hammer, D. Cardoso,*J Catal*.2010,**271**,220-227.

[42] D. Zois, C. Vartzouma, Y. Deligiannakis, N. Hadjiliadis, L. Casella, E. Monzani, *J Mol Catal A: Chem.***261** (2007) 306-317.

[43] M. Khoobi, L. Ma'mani, F. Rezazadeh, Z. Zareie, A. Foroumadi, A. Ramazani, A. Shafiee, J. Mol. *Catal A: Chem*. 2012,**359**, 74– 80.

[44] D. Zois, C. Vartzouma, Y. Deligiannakis, N. Hadjiliadis, L. Casella, E. Monzani, M. Louloudi, *J. Mol. Catal. A: Chem*. 2007,**261**, 306.

[46] D. Fang, H.B. Zhang, Z.L. Liu, *J. Heterocycl. Chem*. 2010,**47**, 63.

[47] D. Kumar, V.B. Reddy, B.G. Mishra, R.K. Rana, M.N. Nadagouda, R.S. Varma, *Tetrahedron*, 2007,**63**, 3093.

[48] J.M. Khurana, B. Nand, P. Saluja, *Tetrahedron*, 2010, **66**, 5637.

[49] Z. Deng, J. Wei, X. Xue, J. Wang, L. Chen, *J Porous Mater*. 2001,**8,** 37-42.

[50] P. Tartaj, *Chem Commun*. 2011,**47,** 256-258.

[51] HL .Pang, J. Liu, D. Hu, XH. Zhang, JH.Chen, *Electrochim Acta*. 2010,**55**, 6611-6616.