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A novel Schiff base of Mn(III) complex supported on magnetic cobalt nanoparticles as a highly efficient retrievable heterogeneous catalyst in oxidation of alcohols and sulfides compounds

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Graphical abstract



Highlights

- A novel magnetic hybrid catalyst was synthesized.
- Oxidation reactions were run with an environmentally friendly oxidant.
- The catalyst was capable of running different oxidation reactions.
- The heterogeneous catalyst could be easily recoverable from the system.
- The heterogeneous catalyst was capable of running oxidation reaction several times without significant loss in its activity.

Abstract

A novel Schiff base Mn(III) complex was successfully synthesized and covalently immobilized on silica-coated magnetic cobalt nanoparticles as a support. The prepared heterogeneous catalyst showed a high catalytic activity in the oxidation of alcohols with high yield and in a milder conditions. The synthesized hybrid nanomaterials were fully characterized by FT-IR spectra, XRD and EDAX analysis. Morphology of the nanomaterials was determined by SEM and TEM. Also, the metallic magnetic cobalt and silica in the core-shell structure were determined by XPS analyses. The synthesized catalyst shows a high catalytic activity in the oxidation of alcohols and sulfides to the corresponding aldehydes and sulfoxides. Also the magnetic properties of the magnetic support and hybrid nanomaterials were measured by AGFM analysis. Keywords: Schiff base, manganese, magnetic cobalt, nanoparticles, sulfide oxidation, alcohol oxidation.

1. Introduction

Generally, hybrid organic-inorganic materials are a linkage between two classes of chemistry. In hybrid materials, each part has considerably significant contributions to the field of materials science, and each has specific properties that all together manifest distinct advantages [1]. The separation of the catalyst-product mixture is a huge problem in catalytic system. Thus, to overcome this problem heterogenization of homogeneous catalyst has been recommended. To date, several methods have been proposed for this issue which involves anchoring the metal complexes on inorganic and organic supports through the formation of a covalent bond between a linkage and the complex [2,3] or immobilizing metal complexes into or onto inorganic supports [4-6].

More recently, salen and salophen ligands have attracted considerable attention due to their widespread applications in the fields of catalysis and synthesis [7]. Besides, metal complexes of salen and salophen ligands have been used as catalysts in organic reactions such as nucleic acid modification, electrochemical reduction, olefin epoxidation, Diels-Alder transformations, hydroxylation of alkane, carboxylic acid decarboxylation and amine oxidation [8-10]. However, these reactions generally proceed in homogeneous systems and the major disadvantages of homogeneous catalysis systems is the problem of separation and recovery of the catalysts from the reaction mixture at the end of the process [11-17]. From the environmental and economic point of view, the development of suitable processes running by a heterogeneous catalyst is of great interest.

It has been proved that the immobilization of homogeneous metal complexes onto/in solid supports is one of the most efficient methods for preparation of heterogeneous metal

complexes. Various solid supports include organosilica materials [18,19], carbon materials [20,21], silica materials [22-24], zeolites [25] and layered compounds [26,27]. The immobilization occurs through covalent, dative, electrostatic, encapsulation or adsorption binding onto/in the solid supports [28-33].

In recent years, immobilization of Mn(III) complexes on solid supports has attracted considerable attention due to the some of the advantages such as easy separation from the reaction mixture and simple recycling of heterogeneous catalysts in the reaction system [34-37].

The best point about Mn(III) complexes is that these complexes are easily synthesized, need milder reaction condition and shorter reaction time [38].

Until now various supports have been synthesized and reported for the immobilization of Mn(III) complexes. These supports include activated carbon [39,40], polymers [41,42] and mesoporous silica [43-47]. Generally, organosiliconic materials are necessary for the fabrication of heterogeneous Mn(III) catalysts immobilized on inorganic materials as support. The efficient alcohol oxidations with O₂ using the magnetically-recoverable heterogeneous catalyst have been already investigated by researchers [48,49].

Very recently some publication have been reported for sulfides oxidation using phthalazinebased diiron complexes [50], β-brominated meso-tetraphenylporphyrinatomanganese(III) acetate [51], Copper-Schiff base complex [52], immobilized metalloporphyrins [53], TsOH by phenyliodine diacetate as an oxidant [54], dendritic bis(acylamino)pyridines [55], PyHBr₃/TBN/H₂O [56], MWW-type titanosilicate zeolite [57] and ruthenium porphyrins with iodobenzene diacetate [58].

Herein, we report the synthesis of novel magnetic hybrid organic-inorganic nanomaterials as an efficient catalyst for alcohols and sulfides oxidation. To the best of our knowledge this is the first report of the synthesis of Mn(III) Schiff base complex immobilized on Co@SiO₂ as a magnetic support.

2. Experimental

2.1. Synthesis of magnetic cobalt nanoparticles

Cobalt nanoparticles were synthesized by a modified method [59]. In a typical procedure, 1 g CoCl₂ 6H₂O was dissolved in 60 ml doubly distilled water. Then 0.07 g citric acid was added to the solution followed by argon bubbling into the solution for 2 minutes. In a beaker, 3 g NaBH₄ was dissolved in 100 ml water and drop wise added to the stock solution under argon atmosphere. With the first drop of NaBH₄, the color of the solution was rapidly changed to black indicating the formation of cobalt nanoparticles.

2.2. Synthesis of magnetic Co@SiO₂ core-shell nanoparticles,

The solution containing magnetic Co nanoparticles was left to be stirred for 30 minutes. Then 200 ml ethanolic solution of 200 μ l 3APTES and 800 μ l TEOS was added to the stock solution under argon atmosphere. The argon atmosphere was cut off and the solution was left to be strongly stirred for 24 h. After this period, a puffy black precipitate with strong magnetic property was obtained, separated by magnet, washed with ethanol and water several times. Then the precipitate was left to be dried at 50 °C in the oven.

2.3. Synthesis of Schiff base ligand

Typically, an equimolar amount of 3-aminopropyl triethoxysilane (3APTES) and 2-hydroxy benzaldehyde was mixed as follows: 1 mmol of 3-aminopropyl triethoxysilane along with 1

mmol of 2-hydroxy benzaldehyde was added to 10 mmol methanol. The obtained mixture stirred for 30 minutes. A yellow solution was obtained which is indicative of the formation of an immine bond in Schiff base ligand.

2.4. Synthesis of Schiff base Mn(III) complex

A methanolic solution (10 ml) of Mn (acac)₃ (1mmol) was added to 5 ml methanolic solution of Schiff base ligand and the total volume was reached to 40 mL by adding the same solvent. The mixture was refluxed for an hour to complete the reaction. A darkish green precipitate was obtained and washed with water and ethanol and filtered by Whatman paper and dried at 60 °C.

2.5. Synthesis of magnetic hybrid nanomaterial

The magnetic hybrid nanomaterials were synthesized as following procedures: 0.3g of magnetic $Co@SiO_2$ nanoparticles were ultrasonically dispersed in 10ml ethanol. Then 0.4g of the Schiff base complex of Mn (III) was added to the solution and total volume was reached to 30 ml of solvent. The mixture was refluxed for 10 hours. The obtained light green magnetic precipitate was collected by a magnet and washed with water and dried in an oven at 60 °C for 12h.

2.6. Typical procedure for oxidation of alcohols

All the reactions were carefully carried out at 40 °C in a 25 ml flask. In a typical procedure an amount of catalyst along with H_2O_2 was used for the oxidation process under mild conditions. The oxidation process was monitored by thin layer chromatography technique.

3. Results and discussion

Fig. 1 Shows the XRD pattern of magnetic $Co@SiO_2$ support and immobilized Schiff base on the support. the diffraction peaks at 2Θ = 44.2, 51.5 and 75.9 are attributed to the (111), (200) and (220) reflections of fcc metallic cobalt (15-0806). As it is observed, XRD pattern of the immobilized Schiff base on the support also shows three peaks related to metallic cobalt. This shows that the magnetic support does not change during immobilization of the Schiff base complex.

Further confirmation was carried out by EDAX analysis. As shown, characteristic peaks containing Si, O and Co are indicative of the formation of silica coated magnetic support. Also, the EDAX analysis of magnetic catalyst shows the elements Si, O, Co, Mn, C and nitrogen, which confirm the fabrication of Co@SiO₂@Mn (III) Schiff base catalyst (Fig. 2). Also, another point taken from the EDAX analyses is that there are no any extra peaks related to any impurity such as Co_3O_4 , CoO or Co_3B_2 were observed.

To further confirm the formation of the catalyst and surface modification of the support, FT-IR spectra were provided (Fig. 3). The synthesized Co@SiO₂ possesses the main peak at 1090 cm⁻¹ which indicates the formation of silica layer on magnetic cobalt NPs. The peak at 3471 cm⁻¹ is assigned to the OH groups on the surface of cobalt nanoparticles. Obvious different bands can be seen among the FT-IR spectra of the free Schiff base ligand and Schiff base complexes of metal ion. The free Schiff base ligand shows u(C-N) stretch at 1630-1635 cm⁻¹ while this band shifts to lower frequency in the complex and manifests at 1623 cm⁻¹ which is due to the coordination of the nitrogen with the metal. Vibrations in the range of 1475-1608 cm⁻¹ are

attributed to aromatic rings. Also the bands in the range of 2770-2900 cm⁻¹ are related to the C-H stretching vibration of methylene groups.

3.1. Morphological study

To investigate the morphology of the hybrid nanomaterials SEM and TEM images were provided (Fig. 4). TEM images confirm the formation of cobalt nanoparticles coated with silica layer. It is seen that the thickness of the silica layer is about 12 nm. As it is clear the nanoparticles are spherical and the size of the nanoparticles is in the range of 25-50 nm. The magnetic properties of the synthesized hybrid nanomaterials were also investigated by alternative gradient force magnetometer (AGFM) at room temperature. Fig. 5 shows the magnetization curves of prepared materials. The magnetization curve of magnetic Co@SiO₂ nanoparticles shows no remanence which indicates their superparamagnetic properties. Also, magnetization curve of the hybrid nanomaterials shows superparamagnetic behavior. The decreased saturation magnetization further confirms the immobilization of the Schiff base complex of Mn(III) ion on the silica-coated cobalt nanoparticles. Thus, the synthesized catalyst can still be separated from the product by applying an external magnetic field.

3.2 X-ray photoelectron spectroscopy (XPS)

XPS analysis is a technique that is sensitive to the surface of the materials. In order to investigate the chemical states of the elements XPS analyses were performed. To investigate the stability of the magnetic support it was placed in an oven and heated an hour at 100 °C. Fig 6a depicts the Si 2p XPS spectra of the magnetic Co@SiO₂ nanoparticles at two temperatures (50 and 100 °C). As seen, in the XPS spectra of the Si 2p there is no change by rising temperature. In the XPS spectra of the Co 2p (Fig 6b) at 50 °C the peak at 778.2 eV can be assign to the metallic

cobalt. By rising the temperature to 100 °C a sholder is appeared which is attributed to cobalt oxide (779.0 eV). Thus, the XPS measurments show that the magnetic support has been made of metallic cobalt and there is no any trace of cobalt oxide.

3.2. Effect of reflux time on loading of metal content over magnetic support To synthesize the hybrid material, the Schiff base complex of Mn(III) ion and silica-coated magnetic support were refluxed in ethanolic solution. To find the effect of reflux time on the metal content immobilized on magnetic support the mixture was refluxed for different period of time. The results have been summed up in table 1. As it is shown by increasing the reflux time the amount of loaded metal on the support has been increased. The maximum metal content is 7.19 wt% after 360 minutes of reflux. Thus, this amount was chosen as a catalyst for the oxidation reactions.

4. Catalytic activities of the synthesized catalyst

4.1. Oxidation of alcohols

The catalytic activity of the Co@SiO₂@[Mn(III)SB] was investigated in the reaction of alcohol oxidation. Benzyl alcohol was used as a sample. The reaction was run in different solvents and in solvent free conditions. As an initial test, different amounts of the catalyst and ethyl acetate as a solvent was mixed in a glass tube and stirred with a magnet. Then, hydrogen peroxide (30%) was added to the solution. The reaction progress was monitored by thin layer chromatography in a regular alternative time. The results have been summed up in table 2. The obtained results show that the magnetic catalyst is considerably selective and transforms alcohols to the corresponding aldehydes. To improve the yield of the reaction and find the optimized conditions, several reactions were carried out in the same conditions with changing

parameters (table 2, entry 2-9). Also, the oxidation reaction was run in the absence of the catalyst and it was found that the reaction proceeds only 4%, which confirms the importance of the catalyst for the reaction completion (table 2, entry 10).

The yield of the reactions was determined by extraction method as follows: The heterogeneous catalyst was separated from the reaction mixture. Then the organic phase was separated by water/ethyl acetate extraction method and the solvent was dried. Next, in order to isolate the aldehyde from the remaining alcohol the mixture was stirred in warm n-hexane several times. Thus, the aldehyde was dissolved in warm n-hexane and isolated from remaining alcohol. The aldehyde was weighted and the yield of the reaction was calculated.

According to the metal content turn over number (TON) and turn over frequency (TOF) of the catalyst were calculated (table 2, entry 11). The amount of metals loaded on magnetic support determined by flame atomic absorption spectrophotometer (FAAS).

To investigate the performance capability of the magnetic catalyst in solution the oxidation reaction was carried out in various solvents. The results show that the catalyst is highly active in different solvents and convert alcohols to the corresponding aldehyde with high yield (Table 3). Also the highest yield was obtained in acetonitrile and ethyl acetate. An important point is that the catalyst acts selectively in various solvent which is of great importance.

4.2. Effect of temperature on the reaction of alcohol oxidation

To investigate the effect of temperature on the oxidation process the reaction was run at different temperature in the range of 20 to 60 °C (Fig. 7a). By raising the temperature from 20 to 60 °C the yield of the reaction is increased from 35 to 92%. Upper than 45 °C no considerable

change in the yield of the reaction occurs. So, the optimized temperature was chosen 45 °C for further reactions.

Table 4 shows the results of the oxidation of the variety of aromatic and aliphatic alcohols in the presence of the catalyst $Co@SiO_2@[Mn(III)SBC]$. As it is seen the selectivity is 100% in any case of alcohol. A slight difference in the time of the reactions is probably due to the presence of electron-donating and electron-withdrawing groups on the benzene ring which cause the alcohols to be slightly active or inactive.

4.3. Separation and recyclability

The supported catalyst was applied in the oxidation reaction. Totally, to evaluate the performance of the catalyst, after recycling the reaction was carried out for several times. After each run the magnetic catalyst was separated by external magnetic field and applied in another run. As it is seen (Fig. 7b) the synthesized catalyst is capable to run the oxidation reaction after 8 runs without any considerable loss in its catalytic activity.

5. Oxidation of sulfides

To further evaluate the performance of the synthesized catalyst, oxidation of sulfides was also investigated. Methyl (phenyl) sulfide was used as a sample and hydrogen peroxide was used as an oxidant. The reaction was carried out in different solvents and in solvent free conditions. Firstly, different amounts of the magnetic Schiff base complex along with methyl phenyl sulfide were stirred in a glass tube. Then ethyl acetate as a solvent was added and the mixture was

stirred with a magnet. After some minutes hydrogen peroxide (30%) was added to the solution. Thin layer chromatography was used for monitoring the reaction progress in a regular alternative time. The results summed up in table 5. As the results show the magnetic catalyst is considerably selective and transforms methyl phenyl sulfide to the corresponding sulfoxide and there is not any trace of second order oxidation product like sulfone which is a great advantage of this catalyst.

To confirm the necessity of the catalyst presence for completion of the reaction (table 5, entry 8) the oxidation reaction was carried out in the absence of the catalyst. The result showed that reaction is not completed and only 7% of the reaction proceeds which shows the importance of the catalyst in oxidation reaction.

In continue, the effect of solvents on the oxidation reaction was investigated. To do this, oxidation of methyl phenyl sulfide was carried out in different solvent. It was found that the synthesized catalyst is capable to act selectively in different solvents and produce the desired product with high yield. As observed, the maximum conversion with 100% selectivity is obtained in acetonitrile and dimethylformamide solvent.

To evaluate the performance capability of the magnetic Mn(III) Schiff base complex, different sulfides compounds were subjected to the catalyst. The results show that the catalyst is capable of oxidizing all sulfide compounds and convert them to the corresponding sulfoxides with high yield and 100 % selectivity (Table 7).

5.1. Sheldon's test for heterogeneous catalyst

To determine whether the reaction is truly carried out in a heterogeneous way or not, hot filtration test was investigated [60]. The result is as follows. In the half way of the reaction process the reaction media were filtered in hot condition. The magnetic catalyst remained on the filter paper and the filtrate came through. In the next step the reaction was continued. It was found that the conversion remained the same of the filtrate. This showed that there was no leaching of the immobilized Schiff base complex. Thus, this confirms that the synthesized catalyst acts heterogeneously.

5.2 Utilization efficiency of hydrogen peroxide

Table 8 shows the results of the hydrogen peroxide utilization efficiency in oxidation reactions of alcohol and sulfide. As indicated above, in the oxidation of alcohols and sulfides the amount of substrates were 0.5 mmol and 1 mmol respectively, and the amount of consumed hydrogen peroxide was 90 μ l and 130 μ l for alcohols and sulfides.

Table 8.

The utilization efficiency of the hydrogen peroxide in alcohol oxidation is 69% and in sulfide oxidation is 78%.

Conclusion

Synthetic processes for magnetic nanomaterials are currently undergoing quick improvement and open tremendous possibilities for the fabrication of magnetically-recoverable catalysts. Separation and recovery of catalysts by external magnetic field is an environmentally friendly alternative because not only it minimizes the use of auxiliary materials, but also prevents mass loss and reduces the operation time. We have synthesized a highly active catalyst based on

Schiff base complexes of Mn(III) ion supported on magnetic cobalt nanoparticles for the first time. This synthesized catalyst was capable to run the oxidation reactions of alcohols and sulfides with high yield. Also investigation of other catalytic reactions with this synthesized nanocatalyst is in progress.

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References

- [1] P. Gomez-Romero, Adv. Mater. (2001) 163-174.
- [2] A.R. Silva, J.L. Figueiredo, C. Fieire, B.D. Castro, Micropor. Mesopor. Mater. 68 (2004) 83-89.
- [3] C. Venkatesan, A.P. Singh, , J. Catal. 227 (2004) 148-163.
- [4] A[^]. Zsigmond, K. Boga[^] r, F. Notheisz, J. Catal. 213 (2003) 103-108.
- [5] D. Gournis, M. Louloudi, M.A. Karakassides, C. Kolokytha, K. Mitopoulou, N. Hadjiliadis, ,
- Mater. Sci. Eng. C 22 (2002) 113-116.
- [6] T. Joseph, S.B. Halligudi, C. Satyanarayan, D.P. Sawant, S. Gopinathan, J. Mol. Catal. A: Chem.168 (2001) 87-97.
- [7] L. Canalai, D.C. Sherrington, Chem. Soc. Rev. 72 (1999) 603.
- [8] W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen, J. Am. Chem. Soc. 112 (1990) 2801-2803.
- [9] S.B. Routier, J.L. Bernier, M.P. Catteau, C. Bailly, Bioorg. Med. Chem. Lett. 7 (1997) 63-66.
- [10] (a) V. Mirkhani, S. Tangestaninejad, M. Moghadam, M. Moghbel Bioorg. Med. Chem. 12(2004) 903-906.

⁽b) V. Mirkhani, S. Tangestaninejad, M. Moghadam, M. Moghbel, Bioorg. Med. Chem. 12 (2004) 4673-4677.

- [11] M. Moghadama, S. Tangestani nejada, V. Mirkhani, I. Mohammadpoor-Baltork, A. Mirjafari,N.S. Mirbagheri, J. Mol. Catal. A: Chem. 329 (2010) 44-49.
- [12] S.L. Weia, Y.H. Tang, X.Q. Xu, G.J. Xu, Y. Yu, Y. Sun, Y.S. Zheng, Appl. Organometal. Chem.25 (2011) 146-153.
- [13] M.E. Amato, F.P. Ballistreri, A. Pappalardo, G.A. Tomaselli, R.M. Toscano, D.J. Williams, Eur.J. Org. Chem. (2005) 3562-3570.
- [14] J.Y. Yang, S.Y. Liu, I.V. Korendovych, E.V. Rybak-Akimova, D.G. Nocera, Chem Sus Chem. 1 (2008) 941-949.
- [15] K. Yu, L.L. Lou, F. Ding, S.J. Wang, Z.L. Wang, S.X. Liu, Catal. Commun. 7 (2006) 170-172.
- [16] P.A. Ulmann, A.B. Braunschweig, O. Lee, M.J. Wiester, G.C. Schatz, C.A. Mirkin, Chem.Commun. (2009) 5121-5123.
- [17] J. Huang, X.K. Fu, G. Wang, Y.Q. Ge, Q. Miao, Sci. Technol. 2 (2012) 1040-1050.
- [18] J.L. Hu, Q.Y. Wu, K.X. Li, W. Li, F.Y. Ma, S.Q. Zhang, F. Su, Y.H. Guo, Y.H. Wang, Catal.
- Commun. 12 (2010) 238-242.
- [19] J.L. Hu, Q.Y. Wu, W. Li, L. Ma, F. Su, Y.H. Guo, Y.Q. Qiu, Chem Sus Chem. 4 (2011) 1813-1822.
- [20] A.R. Silva, V. Budarin, J.H. Clark, C. Freire, Carbon 45 (2007) 1951-1964.
- [21] A.R. Silva, V. Budarin, J.H. Clark, Carbon 43 (2005) 2096-2105.
- [22] H. Zhang, Y. Zhang, C. Li, J. Catal. 238 (2006) 369-381.
- [23] R.I. Kureshy, I. Ahmad, N.H. Khan, S.H.R. Abdi, K. Pathak, R.V. Jasra, J. Catal. 238 (2006) 134-141.
- [24] H. Zhang, S. Xiang, C. Li, Chem. Commun. (2005) 1209-1211.

[25] M. Salavati-Niasari, M.R. Ganjali, P. Norouzi, J. Porous Mater. 14 (2007) 423-432.

[26] B.M. Choudary, T. Ramani, H. Maheswaran, L. Prashant, K.V.S. Ranganath, K.V. Kumar, Adv.

Synth. Catal. 348 (2006) 493-498.

[27] S. Bhattacharjee, T.J. Dines, J.A. Anderson, J. Phys. Chem. C 112 (2008) 14124-14130.

[28] M. Beigi, R. Haag, A. Liesec, Adv. Synth. Catal. 350 (2008) 919-925.

[29] A. Zulauf, M. Mellah, X. Hong, E. Schulz, Dalton Trans. 39 (2010) 6911-6935.

[30] L. Saikia, D. Srinivas, P. Ratnasamy, Micropor. Mesopor. Mater. 104 (2007) 225-235.

[31] I. Kuz niarska-Biernacka, O. Rodrigues, M.A. Carvalho, I.C. Neves, A.M. Fonseca, Appl.

Organometal. Chem. 26 (2012) 44-49.

[32] A.R. Silva, J.L. Figueiredo, C. Freire, B.D. Castro, Micropor. Mesopor. Mater. 68 (2004) 83-89.

[33] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, I. Ahmad, S. Singh, R.V. Jasra, J. Catal. 221 (2004) 234-240.

[34] A.F. Trindade, P.M.P. Gois, C.A.M. Afonso, Chem. Rev. 109 (2009) 418-514.

[35] J.M. Fraile, J.I. García, C.I. Herrerías, J.A. Mayoral, E. Pires, Chem. Soc. Rev. 38 (2009) 695-706.

[36] N.C. Maity, S.H.R. Abdi, R.I. Kureshy, N.H. Khan, E. Suresh, G.P. Dangi, H.C. Bajaj, J. Catal. 277 (2011) 123-127.

[37] R. Tan, D. Yin, N. Yu, Y. Jin, H. Zhao, D. Yin, J. Catal. 255 (2008) 287-295.

[38] W. Sun, H. Wang, C. Xia, J. Li, P. Zhao, Angew. Chem. Int. Ed. 115 (2003) 1072-1074;

[39] A.R. Silva, C. Freire, B. De Castro, Carbon 42 (2004) 3027-3030.

[40] A.R. Silva, V. Budarin, J.H. Clark, C. Freire, B. de Castro, Carbon 45 (2007) 1951-1964.

- [41] B. Gong, X. Fu, J. Chen, Y. Li, X. Zou, X. Tu, P. Ding, L. Ma, J. Catal. 262 (2009) 9-17.
- [42] X. Tu, X. Fu, X. Hu, Y. Li, Inorg. Chem. Commun. 13 (2010) 404-407.
- [43] H. Zhang, Y.M. Wang, L. Zhang, G. Gerrtsen, H.C.L. Abbenhuis, R.A. van Santen, C. Li, J.Catal. 256 (2008) 226-236.
- [44] H. Zhang, Y. Zhang, C. Li, J. Catal. 238 (2006) 369-381.
- [45] R.I. Kureshy, I. Ahmad, N.H. Khan, S.H.R. Abdi, K. Pathak, R.V. Jasra, J. Catal. 238 (2006) 134-141.
- [46] R.I. Kureshy, I. Ahmad, N.H. Khan, S.H.R. Abdi, K. Pathak, R.V. Jasra, Tetrahedron:
- Asymmetry. 16 (2005) 3562-3569.
- [47] X. Tang, Y. Tang, G. Xu, S. Wei, Y. Sun, Catal. Comm. 10 (2008) 317-320.
- [48] K. Mori, S. Kanai, T. Hara, T. Mizugaki, K. Ebitani, K. Jitsukawa, K. Kaneda, Chem. Mater. 19 (2007) 1249-1256.
- [49] V. Polshettiwar, R.S. Varma, Org. Biomol. Chem. 7 (2009) 37-40.
- [50] M. Szávuly, S.D. Szilvási, R. Csonka, D. Klesitz, G. Speier, M. Giorgi, J. Kaizer, Journal of Molecular Catalysis A: Chemical 393 (2014) 317-324
- [51] S. Rayati, F. Nejabat, S. Zakavi, Inorganic Chemistry Communications 40 (2014) 82-86.
- [52] P. Gogoi, M. Kalita, T. Bhattacharjee, P. Barman, Tetrahedron Letters 55 (2014) 1028-1030
- [53] X.T. Zhou, H.B. Ji, Catalysis Communications 53 (2014) 29-32.
- [54] B. Yu, C.X. Guo, C.L. Zhong, Z.F. Diao, L.N. He, Tetrahedron Letters 55 (2014) 1818-1821.
- [55] Y. Imada, T. Kitagawa, S. Iwata, N. Komiya, Takeshi Naota, Tetrahedron 70 (2014) 495-501.
- [56] H. Zhang, G. Wang, Tetrahedron Letters 55 (2014) 56-58.

[57] Y. Kon, T. Yokoi, M. Yoshioka, S.Tanaka, Y. Uesaka, T. Mochizuki, K. Sato, T. Tatsumi,

- Tetrahedron 70 (2014) 7584-7592
- [58] T.H. Chen, Z. Yuan, A.Carver, R. Zhang, Applied Catalysis A: General 478 (2014) 275-282.
- [59] M. Aslam, S. Li, and V. P. Dravid, J. Am. Ceram. Soc. 90 [3] (2007) 950-956.
- [60] H.E.B. Lempers, R.A. Sheldon, J. Catal. 175 (1998) 62-69.

Figures caption

Scheme 1. Synthesis of magnetic metallic cobalt nanoparticles in water

Fig. 1. XRD patterns of Co nanoparticles coated with silica layer (a) and catalyst (b).

Fig. 2. EDAX analyses of Co@SiO₂ nanoparticles and catalyst Co@SiO2@[Mn(III)SB].

Fig. 3. FT-IR spectra of magnetic metallic Co NPs, Schiff base ligand and synthesized magnetic.

Fig. 4. TEM image of Co NPs , silica-coated cobalt nanoparticles and the magnetic catalyst $Co@SiO_2@[Mn(II)SB]$.

Fig. 5. AGFM analysis of Co@SiO₂ and catalyst Co@SiO₂@[Mn(III)SB].

Fig 6. XPS analyses of the Co@SiO₂ and high resolution TEM image of Co@SiO₂.

Fig. 7. The effect of temperature on the oxidation of benzyl alcohol by $Co@SiO_2@Mn(III)SBC$ (a) and number of recycling of the catalyst (b).



Scheme 1

Fig. 1.



Fig. 2.



Fig. 3.



Fig. 4.





Fig. 5.



Fig. 6.



Fig. 7.



Entry	Reflux time (min)	Support (Co@SiO ₂)	Anchoring group (Mn(II)SBC)	Catalyst	Metal loaded (wt%)
1	120	0.3 g	0.4 g	Co@SiO ₂ @[Mn(II)SBC]	4.34
2	180	0.3 g	0.4 g	Co@SiO ₂ @[Mn(II)SBC]	5.87
3	240	0.3 g	0.4 g	Co@SiO ₂ @[Mn(II)SBC]	6.17
4	300	0.3 g	0.4 g	Co@SiO ₂ @[Mn(II)SBC]	7.18
5	360	0.3 g	0.4 g	Co@SiO ₂ @[Mn(II)SBC]	7.19

Table 1. Effect of reflux time on loading of metal content on magnetic support.

Table 2. The optimized amounts of the catalyst and oxidant in oxidation reaction.

	Initial test						
Entry	Co@SiO ₂ @[Mn(III)SB]	H ₂ O ₂ (30%)	Product	Selectivity	/ Isolated		
		µI, (mmol)			Yield %		
1	0.02 g	30, (0.293 mmol)	benzaldehyde	100	32		
	Experir	nents to obtain optin	nized conditions				
2	0.02 g	40, (0.391 mmol)	benzaldehyde	100	44		
3	0.02 g	50, (0.489 mmol)	benzaldehyde	100	51		
4	0.02 g	60, (0.587 mmol)	benzaldehyde	100	63		
5	0.03 g	60, (0.587 mmol)	benzaldehyde	100	72		
6	0.03 g	70, (0.685 mmol)	benzaldehyde	100	81		
7	0.03 g	80, (0.783 mmol)	benzaldehyde	100	89		
8	0.03 g	90, (0.881 mmol)	benzaldehyde	100	92		
9	0.03 g	100, (0.979 mmol)	benzaldehyde	100	94		
10	Not used	90, (0.881 mmol)	benzaldehyde	100	4		
The amount of metal loaded on magnetic support and calculation of TON and TOF numbers							
Entry	Catalyst	The amount of Meta	TON ^a	TOF (h ⁻¹) ^b			
11	Co@SiO ₂ @Mn(III)SBC	7.19		95	87		

Reaction conditions: benzyl alcohol (0.6 mmol), temperature 45 °C, solvent: ethyl acetate 3ml. ^a Moles of substrate converted per moles of metal in the catalyst ([substrate]/[metal]×100).

Entry	catalyst	solvent	product	Time (min)	Selectivity (%)	lsolated Yield
2	Co@SiO ₂ @Mn(III)SBC	Acetone	benzaldehyde	40-45	100	81
3	Co@SiO ₂ @Mn(III)SBC	Acetonitrile	benzaldehyde	40-45	100	91
4	Co@SiO ₂ @Mn(III)SBC	DMF	benzaldehyde	40-45	100	88
5	Co@SiO2@Mn(III)SBC	Ethyl acetate	benzaldehyde	40-45	100	94

Table 3. The effect of various solvents on the oxidation of benzyl alcohol to benzaldehyde.

Reaction conditions: benzyl alcohol (0.6 mmol), temperature 45 °C, 90 μ l H_2O_2 (30%) (0.881 mmol).

Table. 4. Oxidation of the variety of aromatic and aliphatic alcohols in the presence of the catalyst $Co@SiO_2@[Mn(III)SBC]$.



Entry	Sulfides	Catalyst	product	Time (min)	Selectivit y %	lsolated yield %
1	HO	CSMn(III)S B	0	40-45	100	92
2	HO	CSMn(III)S B		40-45	100	90
3	HO	CSMn(III)S B	o a	40-45	100	87
4		CSMn(III)S B		40-45	100	86
5	ON*-OH	CSMn(III)S B		40-45	100	90
6	HO	CSMn(III)S B	O F	40-45	100	98

7	HO	CSMn(III)S B		40-45	100	94
8	ОН	CSMn(III)S B	→	40-45	100	87
9	ОН	CSMn(III)S B	O H	40-45	100	89

Amount of catalyst CSMn(III)SB 0.03 g, Substrate: Benzyl alcohol (0.6 mmol), 90 µl H₂O₂ 30% (0.881 mmol), temperature 45 °C, solvent: Ethyl acetate.

Table 5. Oxidation of methyl phenyl sulfide using an aqueous solution of hydrogen peroxide 30%.

Entry	Catalyst	H_2O_2	Time	Sulfoxide ^a	Sulfone
	amount (mg)	µI, (mmol)	(min)	%	%
1	30	60, (0.587 mmol)	40-45	42	N.P ^b
2	40	70, (0.685 mmol)	40-45	51	N.P
3	40	90, (0.881 mmol)	40-45	60	N.P
4	40	100, (0.979 mmol)	40-45	76	N.P
5	40	110, (1.07 mmol)	40-45	87	N.P
6	40	120, (1.17 mmol)	40-45	92	N.P
7	40	130, (1.27 mmol)	40-45	93	N.P
8	No	100, (0.979 mmol)	40-45	7	N.P

Substrate (1 mmol), catalyst: Co@SiO₂@[Mn(III)SBC], Ethyl acetate (3ml), temperature 45 °C. a Isolated yield. b No Product.

Entry	catalyst	solvent	product	Time (min)	Selectivity (%)	lsolated Yield
2	Co@SiO ₂ @Mn(III)SBC	Acetone	methyl phenyl sulfoxide	40-45	100	83
3	Co@SiO ₂ @Mn(III)SBC	acetonitrile	methyl phenyl sulfoxide	40-45	100	93
4	Co@SiO ₂ @Mn(III)SBC	DMF	methyl phenyl sulfoxide	40-45	100	86
5	Co@SiO ₂ @Mn(III)SBC	ethyl acetate	methyl phenyl sulfoxide	40-45	100	92

Table 6. The effect of various solvents on the oxidation of methyl phenyl sulfide.

Table 7. Oxidation of the variety of aromatic and aliphatic sulfides in the presence of the catalyst $Co@SiO_2@[Mn(III)SBC]$.

$\mathbf{R} \xrightarrow{\mathbf{S}} \mathbf{R} \xrightarrow{\mathbf{Catalyst} (0.040 \text{ g})} \underbrace{\mathbf{H}_2 O_2 (30\%)}_{\mathbf{H}_2 O_2 (30\%)} \mathbf{R} \xrightarrow{\mathbf{O}} \mathbf{R}$						
	K	temprature 45	C, 40 min	R		
Entry	Sulfides	Catalyst	Product	Selectivity %	lsolated yield %	
1	S S	Co@SiO₂@Mn(III)S BC	O=S	100	92	
2	∫) ^S ∕∕	Co@SiO₂@Mn(III)S BC	O=S S	100	90	
3	S Ph	Co@SiO₂@Mn(III)S BC	O S Ph	100	89	
4	∫ S ∕	Co@SiO₂@Mn(III)S BC		100	93	
5	S S	Co@SiO₂@Mn(III)S BC	O=S S	100	91	
6	S C U O O O O Me	Co@SiO₂@Mn(III)S BC	O S C O Me	100	87	

7	H₃C ^{−S} −CH₃	Co@SiO2@Mn(III)S BC	0 Ш Н ₃ С ^{-S} -СН ₃	100	89
8	H ₃ C S CH ₃ H ₂ H ₂	Co@SiO₂@Mn(III)S BC	$\begin{array}{c} O \\ = \\ H_3C \\ C \\ H_2 \\ H_2 \\ H_2 \end{array} \begin{array}{c} CH_3 \\ H_2 \\ CH_3 \\ CH_$	100	88

Reaction conditions: methyl phenyl sulfide (1 mmol), H₂O₂ 120 µl (1.17 mmol), solvent: ethyl acetate 3ml.

Table 8. Utilization efficiency of hydrogen peroxide in the oxidation of alcohol and sulfide in the presence of catalyst $Co@SiO_2@Mn(III)SBC$.

Oxidation reaction of alcohol							
Substrate	Hydrogen peroxide	Yield %	Selectivity	Efficiency % ^a			
Benzyl	90 µl (0.881 mmol)	94	100	69			
alcohol							
	Oxidation reaction of sulfide						
Substrate	Hydrogen peroxide	Yield %	Selectivity	Efficiency % ^b			
Methyl	130 µl (1.17 mmol)	92	100	78			
phenyl sulfide							

([Aldehyde)/[H_2O_2]_c × 100 (%), where [H_2O_2]_c is the concentration of H_2O_2 used. ([Sulfoxide)/[H_2O_2]_c × 100 (%), where [H_2O_2]_c is the concentration of H_2O_2 used.