

Barium Hexaferrite ($\text{BaFe}_{12}\text{O}_{19}$) Nanoparticles as Highly Active and Magnetically Recoverable Catalyst for Selective Epoxidation of Styrene to Styrene Oxide

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Herein, we are reporting the use of pure single phase barium hexaferrite ($\text{BaFe}_{12}\text{O}_{19}$) nanoparticles as an efficient catalyst for epoxidation of styrene. $\text{BaFe}_{12}\text{O}_{19}$ nanocatalysts exhibit high conversion of styrene with excellent selectivity of styrene oxide formation. Easy method of preparation, capability of catalyzing the epoxide reaction of styrene to styrene oxide with excellent styrene conversion (~91%) and high styrene oxide selectivity (~86.5%), easy magnetic separation and very good reusability make the synthesized $\text{BaFe}_{12}\text{O}_{19}$ nanocatalyst an excellent catalyst for this reaction. To the best of our knowledge, this is the first time the use of $\text{BaFe}_{12}\text{O}_{19}$ as catalyst for this reaction has been reported.

Keywords: Barium Hexaferrite Nanoparticles, Styrene Epoxidation, Magnetic Separation.

1. INTRODUCTION

Selective oxidation of olefin (particularly styrene) is an industrially important reaction because of the products of this reaction (e.g., epoxides) have myriad applications such as in the manufacturing of pharmaceuticals, plasticizer, perfumes, fine chemicals, commodity products etc.^{1–3} The conventional processes for synthesis of epoxides (e.g., chlorohydrins, peracid routes) are associated with several limitations, such as generation of large quantity of hazardous waste, unsafety, environment unfriendliness etc.^{4,5} Therefore, selective oxidation of olefinic $\text{C}=\text{C}$ by using an oxidant (e.g., H_2O_2 , tert-butyl hydroperoxide) has been exploited as greener approach for this reaction.^{3–5} Owing to the large surface area, nanoparticles exhibited excellent catalytic activities for variety of organic reactions.^{6,7} Various types of heterogeneous catalysts (such as Au supported BaTiO_3 nanotube,³ TS-1,⁸ Au/ TiO_2 ,⁹ Ag–Cu/ Cu_2O on carbon fiber,¹⁰ Au/CNTs,¹¹ Titania-supported Au nanoparticles¹² etc.) have been developed by several researchers. However, poor stability of the catalyst, leaching of catalytically active species from support, same times low styrene conversion and styrene oxide formation selectivity, difficulty in recovery and recycling

of the catalyst are some of the limitations which are associated with these heterogeneous catalysts. To overcome these limitations, particularly recovery and recycling of the catalyst, development of magnetically separable catalyst is an attractive solution.^{13–15} Some ferrite based catalysts, such as $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ supported Co(II) or Cu(II) acetylacetonate,¹⁶ Ag– $\text{M}_{1-x}\text{Fe}_{2-x}\text{O}_4$ (M = Co, Ni, Mn, Zn),² Au on $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{hollow mSiO}_2$,¹⁷ Au/L– Fe_3O_4 ¹⁸ etc. have been reported for epoxidation of styrene. In these catalysts Fe_3O_4 has been used to provide necessary magnetic character in the catalysts so that they can be recovered magnetically. However, complicated method of preparation and use of Au or Ag make these catalysts costly and limit their large scale application.

Though some of the pure ferrite nanoparticles (e.g., $\text{Mg}_x\text{Fe}_{3-x}\text{O}_4$,¹⁹ $\text{Mg}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$,²⁰ Gd substituted NiFe_2O_4 ,²¹ $\text{Sr}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4$,²² CaFe_2O_4 ,²³ SrFe_2O_4 ,²⁴ NiFe_2O_4 and ZnFe_2O_4 ²⁵) have been employed as catalyst for styrene oxidation but very poor styrene conversion and very less yield for styrene oxide formation (in most of the cases styrene oxide does not form and benzaldehyde forms as major product) are major issues with these catalysts. To the best of our knowledge, till date the use of a single phase pure ferrite, which is capable of catalyzing selective epoxidation of styrene with high conversion of styrene

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and good selectivity of styrene oxide formation along with excellent magnetic property, has not yet reported.

Herein, we report the use of pure barium hexaferrite (BaFe₁₂O₁₉) nanoparticles as catalyst for the epoxidation of styrene. Synthesized BaFe₁₂O₁₉ exhibited excellent catalytic property with high styrene conversion as well as styrene oxide formation selectivity. Moreover, unique magnetic property of BaFe₁₂O₁₉ nanoparticles was exploited for their easy magnetic separation. Recovered BaFe₁₂O₁₉ nanoparticles also exhibited very good catalytic property.

2. EXPERIMENTAL DETAILS

2.1. Materials Used

Barium carbonate (BaCO₃), iron nitrate (Fe(NO₃)₃ · 9H₂O), ethylenediaminetetraacetate (EDTA) and acetonitrile were purchased from Merck, India. Styrene and tert-butyl hydroperoxide (TBHP) were purchased from Sigma-Aldrich. All the chemicals were used without further purification. Deionized water was used throughout the experiment.

2.2. Synthesis and Characterization of BaFe₁₂O₁₉

BaFe₁₂O₁₉ nanoparticles were synthesized by employing an EDTA precursor based method in aqueous medium, which is developed by us.²⁶ In a typical synthetic protocol, in an aqueous slurry of barium carbonate aqueous solution of HNO₃ was added drop wise to make an aqueous solution of barium nitrate. Then stoichiometric amount of iron nitrate was added into it. After that, an aqueous solution of EDTA was mixed with this metal nitrate solution keeping total metal ion: EDTA molar ratio 1:4. The pH of this mixture was maintained at ~6. When this solution was evaporated to dryness on a hot plate at 110 °C a black color precursor was formed. This precursor was calcined in air at 850 °C for 4 h to obtain BaFe₁₂O₁₉ nanoparticles.

2.3. Materials Characterization

Synthesized BaFe₁₂O₁₉ nanoparticles were characterized by using X-ray diffraction (XRD, Mini Flex II, Rigaku), particle size analyzer (Delsa Nano S, Beckman Coulter), transmission electron microscope (TEM, Jeol JEM 1400) and field emission scanning electron microscope (FESEM, Quanta 250 FEG, FEI). Magnetic property of synthesized BaFe₁₂O₁₉ nanoparticles was determined by employing a vibrating sample magnetometer (VSM, EV5, ADE Technology).

2.4. Catalytic Activity Test

The catalytic activity of synthesized BaFe₁₂O₁₉ nanoparticle was tested towards epoxidation reaction of styrene. In a typical catalysis reaction, 0.575 ml (5 mmol) styrene, 25 mg of BaFe₁₂O₁₉ and 2.5 ml (12.5 mmol) TBHP were mixed with 4 ml acetonitrile in a round bottom flask with constant stirring. Reaction was performed in N₂ atmosphere. The reaction mixture was placed in an oil bath and

temperature was maintained at 100 °C. To determine the optimum reaction condition, catalysis reactions were performed by varying the reaction parameters (such as reaction time, temperature, catalyst dose and styrene: TBHP molar ratio). Progress of the reaction was monitored by drawing 0.1 ml reaction aliquot from the reaction mixture in every 1 h interval. The aliquot was analyzed using a gas chromatography (GC-2014 Shimadzu Gas Chromatograph), which was equipped with a capillary column (30 m × 0.25 mm × 0.25 mm) and a flame ionization detector (FID) detector.

The conversion of styrene and styrene oxide selectivity were calculated by using Eqs. (1) and (2):

$$\text{Conversion (\%)} = \frac{\text{Mole of reactant converted}}{\text{Mole of reactant in feed}} \times 100 \quad (1)$$

$$\begin{aligned} \text{Product Selectivity (\%)} \\ = \frac{\text{Mole of the product formed}}{\text{Mole of the reactant converted}} \times 100 \quad (2) \end{aligned}$$

3. RESULTS AND DISCUSSION

3.1. Structural Characterization of Barium Hexaferrite (BaFe₁₂O₁₉)

XRD pattern of synthesized BaFe₁₂O₁₉ is shown in Figure 1. Here, diffraction peaks at $2\theta = 17.79, 18.91, 23.09, 30.39, 32.24, 34.22, 35.57, 37.17, 40.51, 42.73, 50.38, 54.09, 55.19, 56.68$ and 63.34° which are corresponding to (101), (102), (006), (110), (107), (114), (200), (203), (205), (206), (209), (300), (217), (2011) and (220) planes of BaFe₁₂O₁₉ [JCPDS card no. 84-0757] are observed. This observation clearly indicates the formation of single phase BaFe₁₂O₁₉. The crystallite size of BaFe₁₂O₁₉ nanoparticle was calculated using Scherrer's equation and was found to be ~48 nm.

The morphology of synthesized BaFe₁₂O₁₉ nanoparticles was examined by TEM micrograph (Fig. 2(a)) and

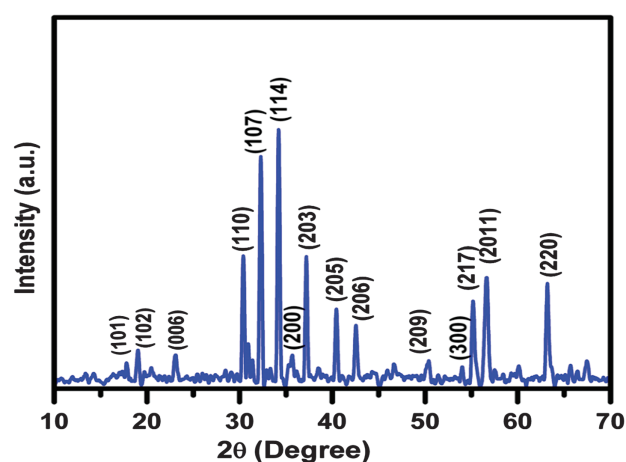


Figure 1. Powder XRD patterns of synthesized BaFe₁₂O₁₉ nanoparticles.

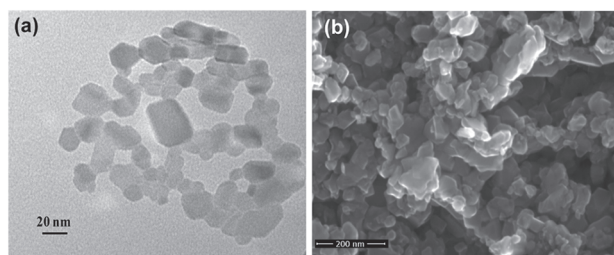


Figure 2. (a) TEM micrographs and (b) FESEM micrograph of synthesized $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles.

FESEM image (Fig. 2(b)). These micrographs show the hexagonal structure of the synthesized $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles and particle size of $\text{BaFe}_{12}\text{O}_{19}$ is $\sim 15\text{--}25$ nm. Dynamic light scattering (DLS) study also indicates the cumulant mean diameter of $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles is 13.3 nm with polydispersity index of 0.439 (Fig. 3).

Magnetic property measurement of the sample reveals that, the synthesized $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles possess saturation magnetization (M_s) of 56.50 emu g^{-1} and coercivity (H_c) of 4914 Oe (Fig. 4).^{26,27}

3.2. Catalytic Activity Study

To determine the optimum reaction condition of $\text{BaFe}_{12}\text{O}_{19}$ catalyzed epoxidation reaction of styrene, catalysis reactions were performed with various reaction conditions. Reactions were conducted at various reaction temperatures ($80\text{--}120$ °C), reaction times (4–12 h), catalyst dose (10–50 mg) and styrene: TBHP ratio (1:1.5–1:3). The effects of various reaction parameters on the % of styrene conversion and selectivity of styrene oxide formation have been listed in Table I. The important observations are as follows:

(i) When reaction temperature was increased from 80 °C to 100 °C, the styrene conversion was increased from 63.2% to 91% but selectivity of styrene oxide formation remain almost same ($\sim 86\%$). However, further increase in

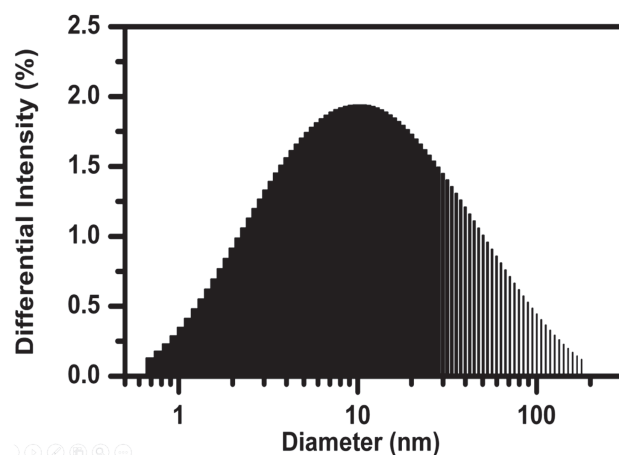


Figure 3. Particle size distribution of synthesized $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles.

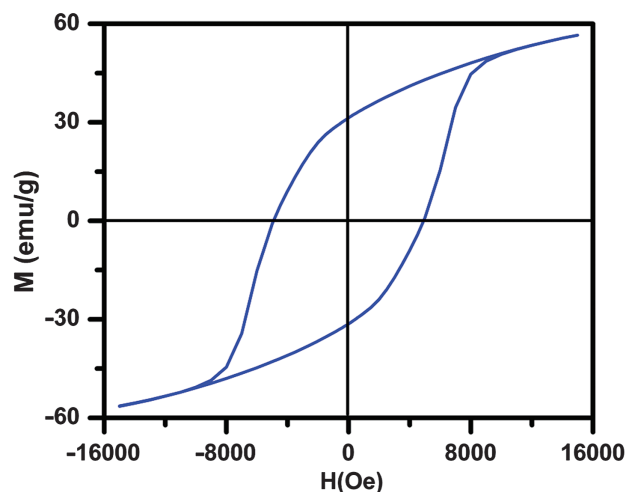


Figure 4. Room temperature hysteresis loop for $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles.

temperature resulted in decrease of both conversion and selectivity.

(ii) With increasing reaction time styrene oxide conversion was increased. After 4 h of reaction, though styrene oxide selectivity was $\sim 91\%$ but styrene conversion was very low ($\sim 22\%$). Styrene conversion was reached up to $\sim 91\%$ with 86.5% styrene oxide selectivity, when the reaction was allowed to carry for 10 h. No significant enhancement in conversion and selectivity was observed when the reaction was conducted for 12 h (Fig. 5).

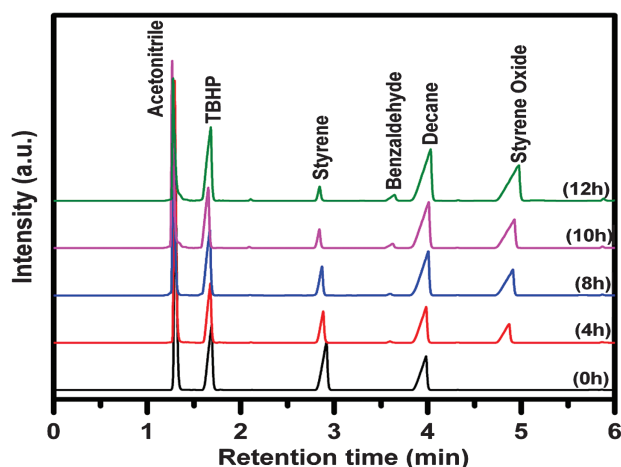
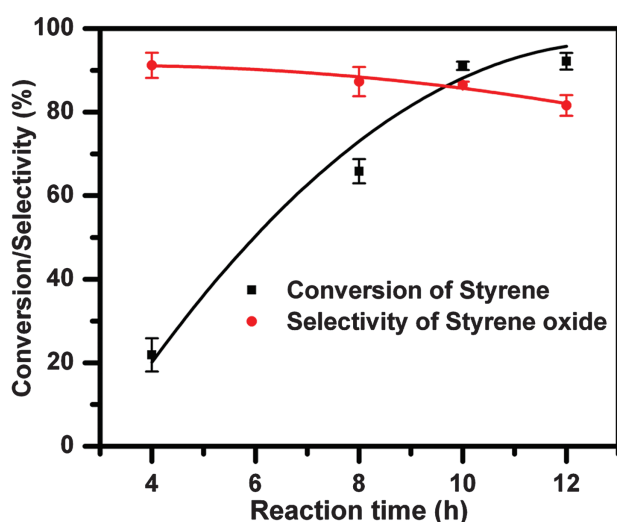
(iii) When reactions were performed with different catalyst amount (10–50 mg), maximum amount styrene conversion and styrene oxide selectivity were achieved (i.e., 91% and 86.5% respectively) when 25 mg of $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles were used as catalyst. Further increase of catalyst dose decreased the styrene conversion. This might be because of formation of agglomeration when catalyst amount was in excess and agglomeration caused to reduce the access of catalytically active site to the reactant molecules.

(iv) With increasing amount of TBHP in reaction mixture (Styrene: TBHP ratio varies from 1: 1.5 to 1: 3) styrene conversion was increased from 52.4% to 92%. However, highest % of styrene oxide selectivity was achieved when styrene: TBHP ratio was 1: 2.5. Further increase of TBHP amount resulted in reduction of styrene oxide formation selectivity and enhanced the formation of other oxidation products. Therefore, the optimum reaction conditions for $\text{BaFe}_{12}\text{O}_{19}$ catalyzed styrene epoxidation were achieved when reaction was performed at 100 °C for 10 h with 25 mg catalyst dose and styrene: TBHP ratio 1: 2.5. In this condition $\sim 91\%$ styrene conversion was obtained with 86.5% styrene oxide formation selectivity (Fig. 6).

Comparison of catalytic activity of synthesized $\text{BaFe}_{12}\text{O}_{19}$ with various reported catalyst is shown in Table II. The catalytic activity of $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles

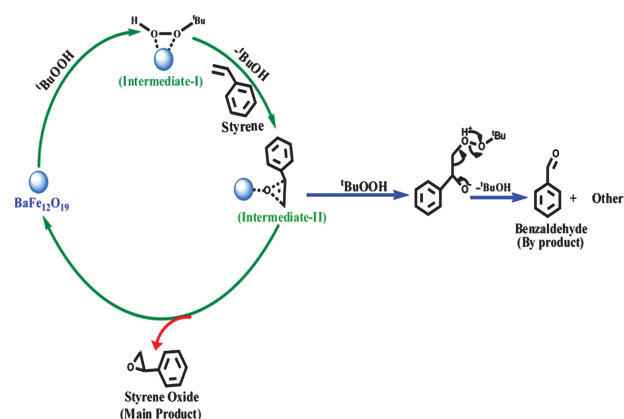
Table I. Changes in styrene conversion and selectivity of styrene oxide formation in BaFe₁₂O₁₉ catalyzed epoxidation of styrene with changing reaction parameters.

Entry	Reaction temperature (°C)	Reaction time (hours)	Catalyst amount (mg)	Styrene: TBHP molar ratio	Conversion (%)	Selectivity styrene oxide (%)	Selectivity PhCHO (%)	Selectivity other (%)
1	80	10	25	1:2.5	63.2	85.7	4.6	9.7
2	100	10	25	1:2.5	91.0	86.5	6.1	7.4
3	120	10	25	1:2.5	89.6	70.3	14.7	15.0
4	100	10	10	1:2.5	65.9	84.4	6.4	9.2
5	100	10	50	1:2.5	81.3	85.2	7.6	7.2
6	100	10	25	1:1.5	52.4	83.7	7.4	8.9
7	100	10	25	1:2.0	63.6	87.2	6.3	6.5
8	100	10	25	1:3.0	89.1	69.7	13.2	17.1
9	100	4	25	1:2.5	21.9	91.2	4.3	4.5
10	100	8	25	1:2.5	65.8	87.3	5.8	6.9
11	100	12	25	1:2.5	92.2	81.6	7.9	10.5

**Figure 5.** Gas chromatography analysis of progress of BaFe₁₂O₁₉ catalyzed styrene epoxidation reaction with time.**Figure 6.** Change of styrene conversion and styrene oxide formation selectivity with time in BaFe₁₂O₁₉ catalyzed epoxidation of styrene.**Table II.** Catalytic activity of different reported catalysts towards epoxidation of styrene.

Sr. No.	Catalyst	Styrene conversion/ yield (%)	Selectivity of styrene oxide formation (%)	Ref.
1	CaFe ₂ O ₄	38 ± 2	0*	[23]
2	SrFe ₂ O ₄	51.0	0*	[24]
3	NiFe ₂ O ₄	31.4	0*	[25]
4	ZnFe ₂ O ₄	26.1	0*	[25]
5	Fe ₃ O ₄	36.5	0*	[25]
6	Ni _{0.5} Zn _{0.5} Fe ₂ O ₄	30.7	0*	[25]
7	Ce _{0.3} Co _{0.7} Fe ₂ O ₄	90.3	0*	[29]
8	Mg _{0.5} Cu _{0.5} Fe ₂ O ₄	21.8	0*	[20]
9	NGF 1	46.3	0*	[21]
10	Mg _{0.4} Fe _{2.6} O ₄	32.0	3.82	[19]
11	Sr _{0.2} Ca _{0.8} Fe ₂ O ₄	49.6	95.8	[22]
12	Ag-Fe ₃ O ₄	100	84.0	[1]
13	Ag-Co _{0.79} Fe _{2.51} O ₄	56.2	68.9	[2]
14	Ag-Ni _{0.81} Fe _{2.19} O ₄	69.8	84.8	[2]
15	Ag-Mn _{0.42} Fe _{2.58} O ₄	49.2	90.5	[2]
16	Ag-Zn _{0.60} Fe _{2.40} O ₄	18.7	67.5	[2]
17	Fe ₃ O ₄	43.1	74.1	[18]
18	Au/L-Fe ₃ O ₄	76.1	70.1	[18]
19	Fe ₃ O ₄ @SiO ₂ -NH ₂ -Cu	85.9	51.4	[16]
20	Fe ₃ O ₄ @SiO ₂ -NH ₂ -Co	90.8	63.7	[16]
21	YS-320-Au	91.4	83.1	[17]
22	Barium Oxide	40.7	78.7	[30]
23	Au/CaO(HDP)	67.6	78.3	[31]
24	Ag-γ-ZrP	44.7	92.9	[32]
25	AgNps/CNFs(1/10)	43.4	38.9	[33]
26	Ag CNFs	61.4	81.5	[10]
27	Cu/Cu ₂ O	99	9	[10]
28	Ag-Cu/Cu ₂ O CNFs	99	41.9	[10]
29	MgO-AgNPs-CNFs (1/10/100)	43	33.10	[34]
30	Al ₂ O ₃ -AgNPs-CNFs(1/10/100)	46.45	34.45	[34]
31	Fe ₂ O ₃	17.9	60.6	[35]
32	Ag/SBA-15	77.7	73.7	[36]
33	Ag/LDH	80.8	91.1	[37]
34	CuO-1	100	44	[38]
35	Cu-S-SBA-15	84.5	15.3	[39]
36	Au-Silica	98.5	82.8	[40]
37	Au(6.6 wt%)/Yb ₂ O ₃ (HDP)	63.5	54.8	[4]
38	TiO ₂ -Ag	83.9	66.8	[41]
39	Cu-10-600	77.7	76.9	[28]
40	CuO/nanotubes-450	94.5	46.9	[42]
41	Au(1wt. %)/BaTNT	60.5	80.1	[3]
42	Ag/4A Zeolite	80.8	89.2	[43]
43	BaFe ₁₂ O ₁₉	91.0	86.5	This work

Note: *Benzaldehyde as major product.



Scheme 1. Plausible mechanism of $\text{BaFe}_{12}\text{O}_{19}$ catalyzed epoxidation reaction of styrene.

is comparable and in some cases even better than the previously reported catalysts.

As no reaction took place in absence of catalyst ($\text{BaFe}_{12}\text{O}_{19}$) the possibility of the reaction due to thermal decomposition of TBHP was ruled out. To explain the epoxidation of styrene a proposed mechanism is shown in Scheme 1. Initially, TBHP was activated in presence of $\text{BaFe}_{12}\text{O}_{19}$ and generated metal-oxy complex (Intermediate-I) on the surface of the catalyst. The reaction proceeded via formation of an Intermediate-II, when styrene reacted with Intermediate-I. Ultimately styrene oxide was formed from Intermediate-II. The formation of benzaldehyde can be explained by the reaction of another molecule of TBHP with intermediate-II. Similar mechanism was proposed by Wang et al. for epoxidation of styrene where different metal-ion doped TiO_2 was used as catalyst.²⁸

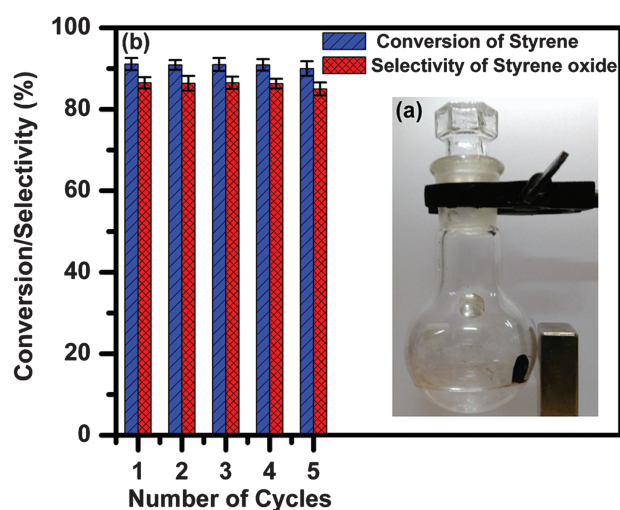


Figure 7. (a) Magnetic separation of $\text{BaFe}_{12}\text{O}_{19}$ nanocatalyst by applying a magnet externally after completion of reaction and (b) Recycling results of styrene epoxidation reaction catalyzed by recovered $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles.

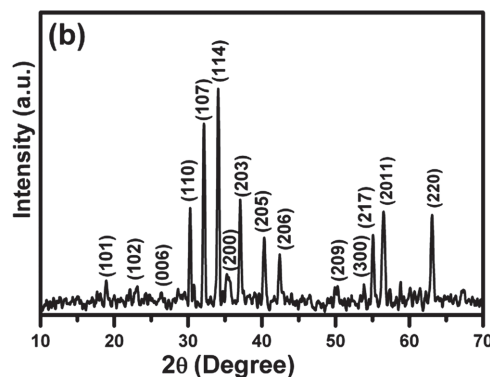
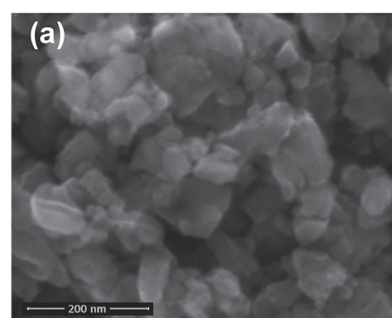


Figure 8. (a) FESEM micrograph and (b) powder XRD patterns of recovered $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles after catalysis reaction.

3.3. Magnetic Recovery of the Catalyst and Reusability

As $\text{BaFe}_{12}\text{O}_{19}$ nanocatalyst exhibited good magnetic property (in terms of M_s and H_c) $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles were recovered from the reaction mixture after completion of catalysis reaction by using a simple magnet externally (Fig. 7(a)). After recovery, $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles was washed thoroughly with distilled water and acetone, dried and then reused for next cycle. No significant change in catalytic activity (in terms of styrene conversion and styrene oxide selectivity) was observed till 5th catalytic cycle (Fig. 7(b)). After that, slight reduction ($\sim 2\text{--}5\%$) in catalytic activity was observed. FESEM micrograph and XRD pattern of the recycled $\text{BaFe}_{12}\text{O}_{19}$ nanocatalyst are shown Figure 8 and no significant change in crystal structure or morphology in the recycled $\text{BaFe}_{12}\text{O}_{19}$ was observed. Therefore, it has been concluded that, $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles are fairly stable in the reaction conditions.

4. CONCLUSION

In summary, here we have reported the excellent catalytic activity of $\text{BaFe}_{12}\text{O}_{19}$ nanocatalyst towards epoxidation of styrene to styrene oxide. To the best of our knowledge, this is first time the use of $\text{BaFe}_{12}\text{O}_{19}$ as catalyst for this reaction has been reported. The catalytic activity of $\text{BaFe}_{12}\text{O}_{19}$ is comparable and in some cases even better than the previously reported ferrite based catalysts for this reaction (Table II). The advantages $\text{BaFe}_{12}\text{O}_{19}$ offer as catalyst are: (i) it does not require any surface modification or attachment of catalytically active center (e.g., Au, Ag).

Therefore, no complicated catalyst preparation methodology is required.

(ii) As BaFe₁₂O₁₉ is a very stable single phase material, the chance of leaching out of catalytically active sites is almost negligible.

(iii) Along with excellent catalytic property BaFe₁₂O₁₉ also exhibits good magnetic property. The capability of catalyzing the epoxide reaction of styrene to styrene oxide with high styrene conversion (~91%) and very good styrene oxide selectivity (~86.5%), along with easy magnetic separation and very good reusability make the synthesized BaFe₁₂O₁₉ nanocatalyst an excellent catalyst for this reaction.

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References and Notes

1. D.-H. Zhang, G.-D. Li, J.-X. Li, and J.-S. Chen, *Chem. Commun.* 29, 3414 (2008).
2. D.-H. Zhang, H.-B. Li, G.-D. Li, and J.-S. Chen, *Dalton Trans.* 47, 10527 (2009).
3. D. Nepak and D. Srinivas, *Appl. Catal. A* 523, 61 (2016).
4. V. Choudhary, D. Dumbre, N. Patil, B. Uphade, and S. Bhargava, *J. Catal.* 300, 217 (2013).
5. V. R. Choudhary and D. K. Dumbre, *Top. Catal.* 52, 1677 (2009).
6. H. S. Nalwa, (ed.), *Handbook of Nanostructured Materials and Nanotechnology*, Academic Press, San Diego, CA (2000), Vols. 1–5.
7. H. S. Nalwa, (ed.), *Encyclopedia of Nanoscience and Nanotechnology*, American Scientific Publishers, Los Angeles, CA (2004), Vols. 1–10.
8. S. B. Kumar, S. Mirajkar, G. C. Pais, P. Kumar, and R. Kumar, *J. Catal.* 156, 163 (1995).
9. N. S. Patil, B. S. Uphade, P. Jana, R. S. Sonawane, S. K. Bhargava, and V. R. Choudhary, *Catal. Lett.* 94, 89 (2004).
10. Q. Wang, C. Li, J. Bai, W. Sun, and J. Wang, *J. Inorg. Organomet. Polym Mater.* 26, 488 (2016).
11. J. Liu, F. Wang, T. Xu, and Z. Gu, *Catal. Lett.* 134, 51 (2010).
12. M. Nemanashi and R. Meijboom, *Catal. Lett.* 143, 324 (2013).
13. F. Shirini and M. Abedini, *J. Nanosci. Nanotechnol.* 13, 4838 (2013).
14. F. Shirini, M. Abedini, and M. Seddighi, *J. Nanosci. Nanotechnol.* 16, 8208 (2016).
15. S. Hazra and N. Ghosh, *J. Nanosci. Nanotechnol.* 14, 1983 (2014).
16. J. Sun, G. Yu, L. Liu, Z. Li, Q. Kan, Q. Huo, and J. Guan, *Catal. Sci. Technol.* 4, 1246 (2014).
17. Q. Yue, Y. Zhang, C. Wang, X. Wang, Z. Sun, X.-F. Hou, D. Zhao, and Y. Deng, *J. Mater. Chem.* 3, 4586 (2015).
18. C. Huang, H. Zhang, Z. Sun, Y. Zhao, S. Chen, R. Tao, and Z. Liu, *J. Colloid Interface Sci.* 364, 298 (2011).
19. N. Ma, Y. Yue, W. Hua, and Z. Gao, *Appl. Catal. A* 251, 39 (2003).
20. X. Cai, H. Wang, Q. Zhang, and J. Tong, *J. Sol-Gel Sci. Technol.* 69, 33 (2014).
21. R. Ramanathan and S. Sugunan, *Catal. Commun.* 8, 1521 (2007).
22. R. Y. Pawar, P. V. Adhyapak, and S. K. Pardeshi, *Appl. Catal. A* 1 478, 129 (2014).
23. S. K. Pardeshi and R. Y. Pawar, *Mater. Res. Bull.* 45, 609 (2010).
24. S. K. Pardeshi and R. Y. Pawar, *J. Mol. Catal. A: Chem.* 334, 35 (2011).
25. D. Guin, B. Baruwati, and S. V. Manorama, *J. Mol. Catal. A: Chem.* 242, 26 (2005).
26. A. B. Rajput, S. Hazra, G. F. Fernando, and N. N. Ghosh, *Synth. React Inorg. M.* 41, 1114 (2011).
27. S. Hazra, M. K. Patra, S. R. Vadera, and N. N. Ghosh, *J. Am. Ceram. Soc.* 95, 60 (2012).
28. A. Wang and H. Jing, *Dalton Trans.* 43, 1011 (2014).
29. J. Tong, W. Li, L. Bo, H. Wang, Y. Hu, Z. Zhang, and A. Mahboob, *J. Catal.* 344, 474 (2016).
30. V. R. Choudhary, R. Jha, and P. Jana, *Green Chem.* 8, 689 (2006).
31. D. K. Dumbre, V. R. Choudhary, N. S. Patil, B. S. Uphade, and S. K. Bhargava, *J. Colloid Interface Sci.* 415, 111 (2014).
32. J. Liu, F. Wang, Z. Gu, and X. Xu, *Catal. Commun.* 10, 868 (2009).
33. H. Liu, J. Bai, S. Wang, C. Li, L. Guo, H. Liang, T. Xu, W. Sun, and H. Li, *Colloids Surf. A* 448, 154 (2014).
34. H. Liu, J. Bai, C. Li, W. Xu, W. Sun, T. Xu, Y. Huang, and H. Li, *RSC Adv.* 4, 3195 (2014).
35. V. R. Choudhary, R. Jha, and P. Jana, *Catal. Commun.* 10, 205 (2008).
36. Y. Tang, M. Yang, W. Dong, L. Tan, X. Zhang, P. Zhao, C. Peng, and G. Wang, *Microporous Mesoporous Mater.* 215, 199 (2015).
37. X. Wang, Z. Liang, F. Zhang, L. Yang, and S. Xu, *J. Mater. Sci.* 48, 5899 (2013).
38. G. Qiu, S. Dharmarathna, Y. Zhang, N. Opembe, H. Huang, and S. L. Suib, *J. Phys. Chem. C* 116, 468 (2011).
39. Y. Yang, S. Hao, P. Qiu, F. Shang, W. Ding, and Q. Kan, *Reac. Kinet. Mech. Cat.* 100, 363 (2010).
40. J. Liu, F. Wang, S. Qi, Z. Gu, and G. Wu, *New J. Chem.* 37, 769 (2013).
41. D. Yang, N. Yang, and J. Ge, *Cryst. Eng. Comm.* 15, 7230 (2013).
42. C. Hu, L. Zhang, J. Zhang, L. Cheng, Z. Zhai, J. Chen, and W. Hou, *Appl. Surf. Sci.* 298, 116 (2014).
43. X. Hu, J. Bai, C. Li, H. Liang, and W. Sun, *J. Inorg. Chem.* 22, 3758 (2015).

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