

## Fe doped barium aluminate nano-powder: A versatile catalyst for the epoxidation of $\alpha$ , $\beta$ -unsaturated ketone derivatives

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Received 17 October 2014; accepted 15 September 2015

Fe doped  $\text{BaAl}_2\text{O}_4$  nano powder has been prepared *via* homogeneous precipitation method and was characterized by XRD, FE-SEM and EDAX analysis. The XRD patterns show hexagonal phase of  $\text{BaAl}_2\text{O}_4$ . The particles have an irregular shape with an average size of 32 nm as determined by FE-SEM. The as-prepared nano-powder was used as an efficient catalyst for the epoxidation of  $\alpha$ ,  $\beta$ -unsaturated ketones in aqueous ethanol (70%). The effects of solvent and catalyst concentration on the epoxidation reaction were investigated.

**Keywords:**  $\text{BaAl}_2\text{O}_4$  Fe doped barium aluminate, Chalcone, Epoxidation,  $\alpha$ ,  $\beta$ -unsaturated ketones

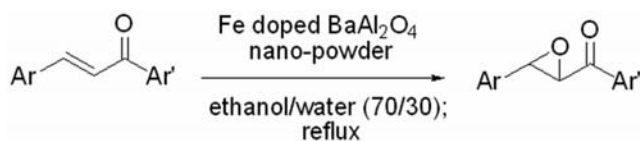
The use of conventional basic or acidic catalysts is started to be removed from the catalytic processes, because of dependable requests for improvement of the environmental aspects of the chemical synthesis by minimizing the waste production and chemical usage. The presence of heterogeneous catalysts to be catalyzed the organic chemistry reactions have been proved important access to environmentally friendly synthesis which has been extensively explored for using of heterogenous metal oxides in synthetic organic chemistry. In contrast, heterogeneous basic catalysts are much more demanded and challenged<sup>1</sup>.

Metal aluminates such as barium aluminate have widespread chemical industrial applications in the fields of catalysts, ceramics, cements, pigments and glazes. Barium aluminate ( $\text{BaAl}_2\text{O}_4$ ) can improve the efficiency of safety and energy-saving and widely utilized as a component of ceramic devices.  $\text{BaAl}_2\text{O}_4$  can also be used as catalyst in the treatment of air pollutions, as well as a component in refractory cements, humidity sensors and phosphor materials<sup>2-8</sup>. However, recent studies showed that the properties of barium aluminate can be reclaimed with the using of expletory elements. To achieve this aim various elements have been doped into the parent structure of barium aluminate. Barium hexaaluminate is a suitable catalyst or catalyst supports because of their high

thermal stability. Rare earth doped aluminates have better phosphorescence and luminescence properties than pure aluminate<sup>2-8</sup>.

On the other hand, many of the natural products or biologically active compounds could be synthesized from the optically active epoxy ketones as versatile building blocks<sup>9,10</sup>. Thus the development of efficient methods for the synthesis of  $\alpha$ -epoxyketones is of great interest. The epoxidation of  $\alpha$ ,  $\beta$ -unsaturated ketones is the most important method for the synthesis of  $\alpha$ -epoxyketones. This method needs an oxidant and a catalyst to be proceeded well<sup>10</sup>. Among various oxidants, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is the most beloved oxidant because it is environmentally benign and has the advantages of cheapness, easy to handle and has a high percentage of available oxygen. Also, it produced water as the only byproduct<sup>11</sup>. Despite of its advantages,  $\text{H}_2\text{O}_2$  has a high activation barrier for its reaction with organic substrates and need to activate.  $\alpha$ ,  $\beta$ -Unsaturated ketone could be easily epoxidized with  $\text{H}_2\text{O}_2$  under alkaline conditions<sup>12-20</sup>.

In continuation of our work on the preparation and application of heterogeneous catalysis<sup>21-24</sup>, the present study involving the investigation of the phase formation of Fe doped barium aluminates nano

Scheme 1—preparation of  $\alpha$ -epoxy ketones

powders and evaluation of their catalytic activity in the epoxidation of chalcones has been taken up (Scheme 1).

### Experimental Section

All reagents were purchased from Merck and Aldrich and used without further purification. All products were characterized by a comparison of their spectra ( $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR) data. The powder X-Ray diffraction patterns were measured with D<sub>8</sub>, Advance, Bruker, axs, diffractometer using Cu-K $\alpha$  irradiation. FE-SEM was taken by a Hitachi S-4160 photograph to examine the shape and morphology of the samples. The NMR spectra were recorded on a Bruker Avance DPX 400 MHz instrument. The spectra were measured in DMSO- $d_6$  relative to TMS (0.00 ppm). TLC was performed on silica gel Polygram SIL G/UV 254 plates.

#### Preparation of Fe doped BaAl<sub>2</sub>O<sub>4</sub> nano-powder

The two different solutions were prepared as follows: Solution A: A solution of Ba(II), Fe(III) and Al(III) was prepared by dissolving of barium chloride (20 mmol), ferric (III) chloride (0.3 mmol) and aluminum chloride (20 mmol) in 50 mL of water. Solution B: A solution of 2-amino ethanol (90 mmol) in 50 mL of ethanol / water (50/50). Solution B was poured into solution A slowly under vigorous magnetic stirring. Next the resulted mixture was aged for 5 h until a gel was formed. Finally, the gel was filtered washed with water for three times, dried and calcinated at 700°C for 2 h.

#### Epoxidation of chalcone: typical procedure

A mixture of chalcone (1 mmol), 30% aqueous hydrogen peroxide (0.5 mL) and Fe doped BaAl<sub>2</sub>O<sub>4</sub> nano-powder (ranged from 0.05 – 0.5 mmol) was refluxed for the appropriate time (Table 1). The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by simple filtration. The filtrate was quenched into ice, followed by extraction with CHCl<sub>3</sub>. Removal of the solvent under reduced pressure afforded the pure product as a white solid.

**Phenyl(3-phenyloxiran-2-yl)methanone (Table 2, Entry 1):**  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  3.94 (d,  $J$  = 7.7 Hz, 1H), 4.20 (d,  $J$  = 7.7 Hz, 1H), 7.36-7.39 (m, 3H),

Table 1 — Catalyst and solvent screening

Entry	Condition	Yield (%) <sup>a</sup>
1	ZnO nanopowder (0.25 mmol), Ethanol (10 ml), reflux	32
2	Al <sub>2</sub> O <sub>3</sub> nanopowder (0.25 mmol), Ethanol (10 ml), reflux	15
3	BaO (0.25 mmol), Ethanol (10 ml), reflux	27
4	BaAl <sub>2</sub> O <sub>4</sub> nanopowder (0.25 mmol), Ethanol (10 ml), reflux	59
5	Fe doped BaAl <sub>2</sub> O <sub>4</sub> nano-powder (0.25 mmol), Ethanol (10 ml), reflux	70
6	Fe doped BaAl <sub>2</sub> O <sub>4</sub> nano-powder (0.25 mmol), Acetonitrile (10 ml), reflux	48
7	Fe doped BaAl <sub>2</sub> O <sub>4</sub> nano-powder (0.25 mmol), Ethyl acetate (10 ml), reflux	40
8	Fe doped BaAl <sub>2</sub> O <sub>4</sub> nano-powder (0.25 mmol), Dichloromethane (10 ml), reflux	-
9	Fe doped BaAl <sub>2</sub> O <sub>4</sub> nano-powder (0.25 mmol), <i>n</i> -hexane (10 ml), reflux	-
10	Fe doped BaAl <sub>2</sub> O <sub>4</sub> nano-powder (0.25 mmol), H <sub>2</sub> O (10 ml), reflux	50
11	Fe doped BaAl <sub>2</sub> O <sub>4</sub> nano-powder (0.25 mmol), Ethanol/water (70/30) (10 ml), reflux	80
12	Fe doped BaAl <sub>2</sub> O <sub>4</sub> nano-powder (0.25 mmol), Solvent-free, (80 °C)	28

<sup>a</sup>Isolated yield, reaction time: 17 h

7.47 (d,  $J$  = 7.9 Hz, 2H), 7.59 (t,  $J$  = 8.1 Hz, 2H), 7.69 (t,  $J$  = 8.1 Hz, 1H), 8.02 (d,  $J$  = 8.0 Hz, 2H).

**4-Chlorophenyl(3-phenyloxiran-2-yl)methanone (Table 2, Entry 2):**  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  3.88 (d,  $J$  = 7.8 Hz, 1H), 4.15 (d,  $J$  = 7.8 Hz, 1H), 7.36-7.39 (m, 3H), 7.48 (d,  $J$  = 7.9 Hz, 2H), 7.56 (d,  $J$  = 8.0 Hz, 2H), 7.97 (d,  $J$  = 8.0 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  59.8, 60.0, 126.0, 128.7, 128.9, 129.0, 130.5, 135.0, 135.1, 135.7, 195.4 ppm. Found: C, 69.77; H, 4.45% C<sub>15</sub>H<sub>11</sub>ClO<sub>2</sub>; requires: C, 69.64; H, 4.29%.

**4-Methoxyphenyl(3-phenyloxiran-2-yl)methanone (Table 2, Entry 3):**  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  3.81 (s, 3H, OCH<sub>3</sub>), 3.88 (d,  $J$  = 7.7 Hz, 1H), 4.14 (d,  $J$  = 7.7 Hz, 1H), 7.09 (d,  $J$  = 7.9 Hz, 2H), 7.36-7.39 (m, 3H), 7.47 (d,  $J$  = 8.0 Hz, 2H), 8.03 (d,  $J$  = 7.9 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  55.5, 59.8, 60.0, 114.0, 125.9, 128.7, 128.9, 130.0, 135.0, 135.1, 160.4, 195.5. Found: C, 75.74; H, 5.77% C<sub>16</sub>H<sub>14</sub>O<sub>3</sub>; requires: C, 75.57; H, 5.55%.

**3-(4-Chlorophenyl)oxiran-2-yl(4-methoxyphenyl) methanone (Table 2, Entry 4):**  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  3.80 (s, 3H, OCH<sub>3</sub>), 3.90 (d,  $J$  = 7.8 Hz, 1H), 4.17 (d,  $J$  = 7.8 Hz, 1H), 7.10 (d,  $J$  = 7.9 Hz, 2H), 7.48-7.52 (m, 4H), 8.03 (d,  $J$  = 7.9 Hz, 2H), ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  55.5, 59.8, 60.0, 114.0,

127.9, 128.6, 130.0, 135.0, 135.3, 135.7, 160.4, 195.5.  
Found: C, 66.73; H, 4.76%  $C_{16}H_{13}ClO_3$ ; requires: C, 66.56; H, 4.54%.

**7-Oxa-bicyclo[4.1.0]heptan-2-one** (Table 8, Entry 3):  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ):  $\delta$  1.80-2.08 (m, 4H), 2.39 (m, 1H), 2.50 (m, 1H), 3.21 (m, 1H), 3.51 (d,  $J = 8.0$  Hz, 1H).

## Results and Discussion

### Catalyst characterization

The crystalline phases of three different catalysts formed at  $700^\circ C$  were identified by XRD. Figure 1 shows the XRD patterns of the  $Al_2O_3$ ,  $BaAl_2O_4$  and Fe doped  $BaAl_2O_4$  nano-powders. Pure alumina showed no crystalline phases while  $BaAl_2O_4$  and Fe doped  $BaAl_2O_4$  nano-powders shown hexagonal phase of  $BaAl_2O_4$  present with peaks at 28.2, 31.1, 34.3 and  $45.0$  [ $2\theta$ ].

The morphology of nano-particles was investigated using the FE-SEM analysis (Fig. 2). As revealed in Fig. 2, it can be seen that Fe doped  $BaAl_2O_4$  nano-powder has an average size of about 32 nm for 20 particles. The FE-SEM image of the Fe doped  $BaAl_2O_4$  nano-powder indicates that the particles have an irregular shape and are relatively agglomerated.

The catalyst compositions were analyzed by Energy dispersive X-ray (EDAX) analysis, providing the average Ba, Al and Fe contents (Fig. 3). The atomic ratio of Ba: Fe: Al is 52, 0.39, 23 based on EDAX analysis, which is consistent with the nominal molar ratio used in the preparation of the catalyst. The chemical formula of Fe doped  $BaAl_2O_4$  nano-powder is  $BaFe_{0.02}Al_{1.98}O_4$  which was calculated from the elemental analysis determined by EDAX analysis.

The dynamic light scattering (DLS) analysis was used to determine the particle size distribution of Fe doped  $BaAl_2O_4$  nano-powder. Before analysis the sample was diluted in ethanol ( $0.5\text{ gL}^{-1}$ ) and sonicated for 2 h. Figure 4 shows the size distribution of nanopowder. Focusing on the results, the intensity-average diameter determined by DLS is about 37 nm.

### Epoxydation of chalcone

Initially, the effect of various catalysts on the epoxydation of chalcone with  $H_2O_2$  was investigated. Various nano-powders including  $ZnO$ ,  $Al_2O_3$ ,  $BaO$ ,  $BaAl_2O_4$  and Fe doped  $BaAl_2O_4$  nano-powder have

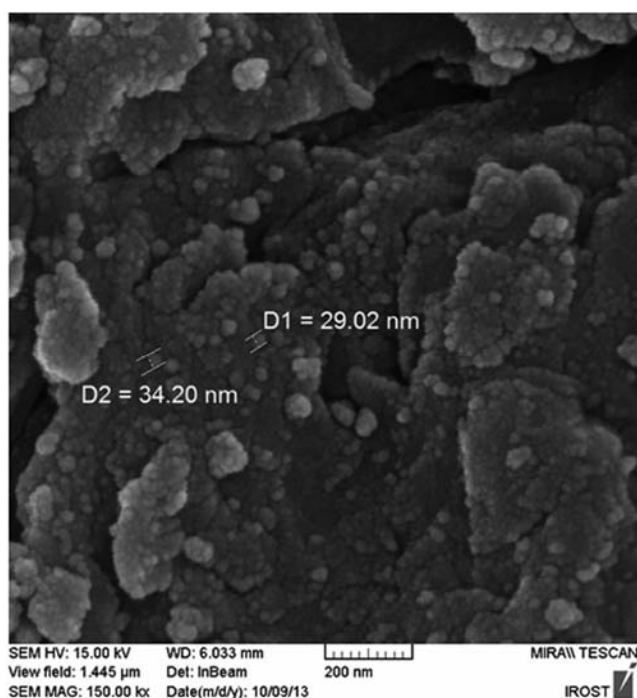


Fig. 2 — FE-SEM photographs of Fe doped  $BaAl_2O_4$  nano-powder

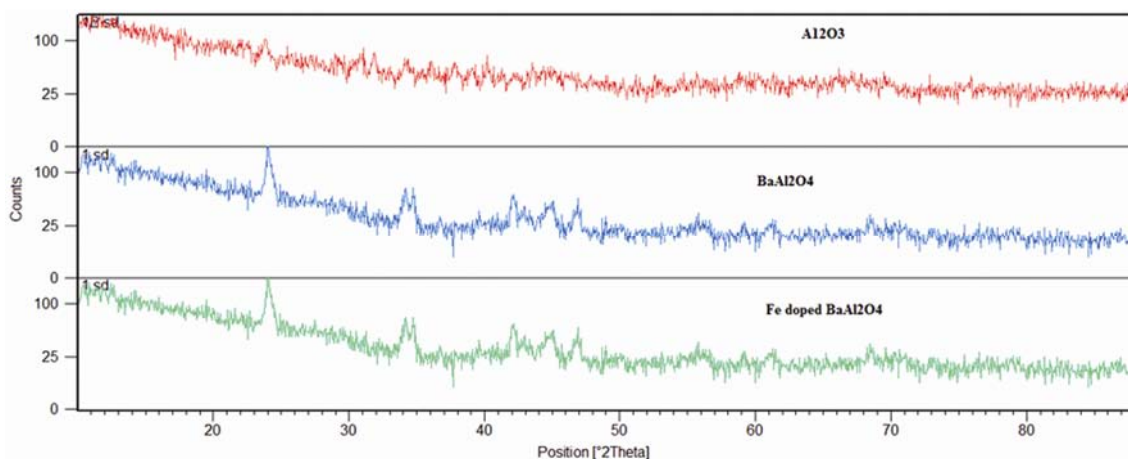


Fig. 1 — XRD pattern of Fe doped  $BaAl_2O_4$  nano-powder

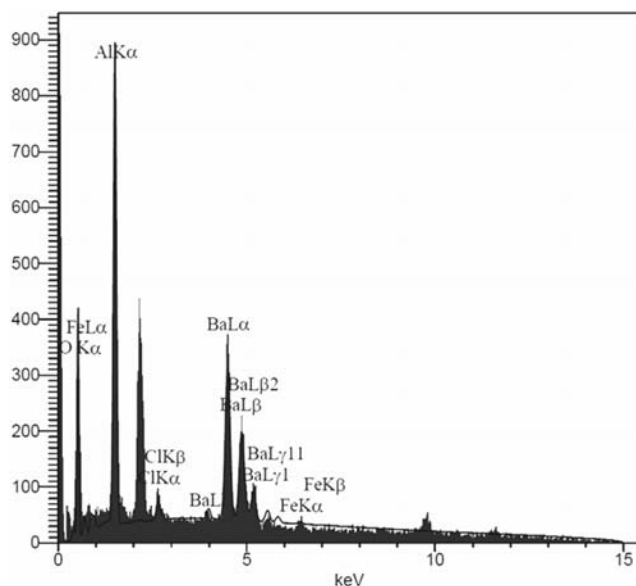


Fig. 3 — EDAX analysis of Fe doped  $\text{BaAl}_2\text{O}_4$  nano-powder

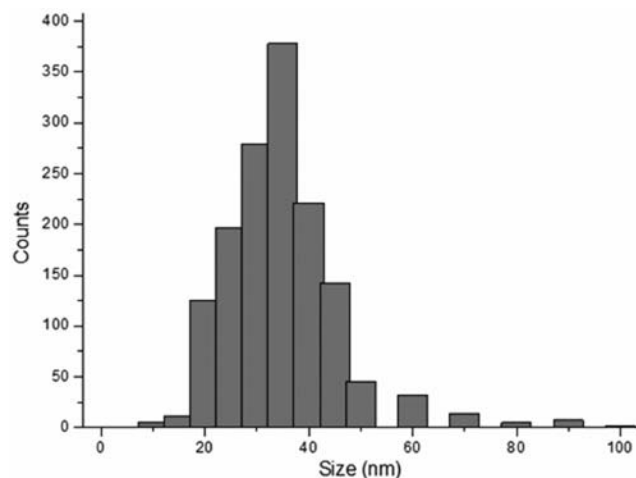


Fig. 4 — particle size distribution of Fe doped  $\text{BaAl}_2\text{O}_4$  nano-powder

the yield (Table 1) while no product was detected in the absence of a catalyst. This shows that the catalyst is essential for the product formation. In all the tested catalysts, Fe doped  $\text{BaAl}_2\text{O}_4$  nano-powder gave the best results and 70% of the desired product (Table 1, Entry 5).

Next, the influence of the solvent on this transformation was checked. Different media including acetonitrile, ethanol, ethyl acetate, dichloromethane, *n*-hexane,  $\text{H}_2\text{O}$ , ethanol/water (70/30) and solvent-free condition were investigated. No product was formed in non-polar solvents (Table 1, Entries 8, 9). Compared with solvent-free condition, polar solvents showed increased yields

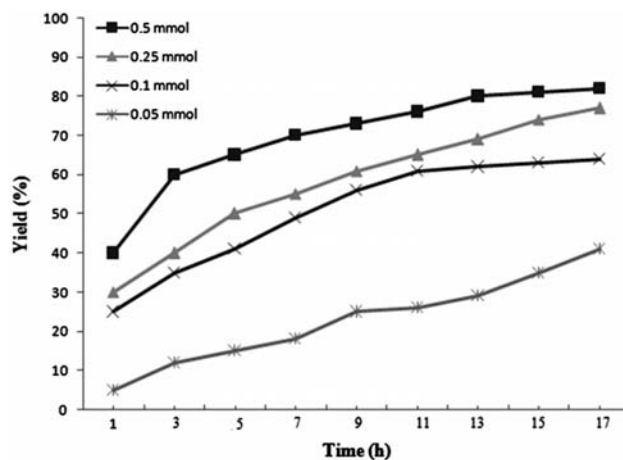


Fig. 5 — effect of the amount of Fe doped  $\text{BaAl}_2\text{O}_4$  nano-powder as catalyst

(Table 1). Finally, ethanol/water (70/30) was chosen as the approved reaction media due to its higher yield of product.

To clarify the effect of catalyst concentration, the reaction was carried out in a range of 0.05-0.5 mmol of the catalyst amount (Fig. 5). The complete conversion of the starting material was achieved using different concentrations of the catalyst. However, increasing the catalyst concentration to 0.5 mmol led to a significant improvement in the product yield after 17 h. Higher yield was obtained using 0.5 mmol of catalyst and increasing the amount of catalyst did not improve the yield significantly. Finally, we achieved an optimized condition using 0.5 mmol of Fe doped  $\text{BaAl}_2\text{O}_4$  nano-powder as the catalyst and ethanol/water (70/30) as solvent under reflux condition.

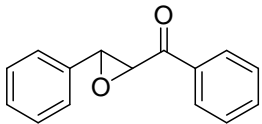
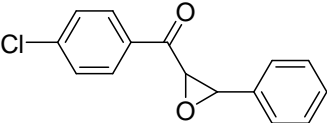
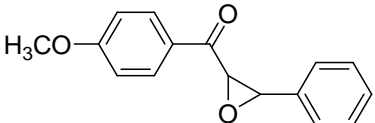
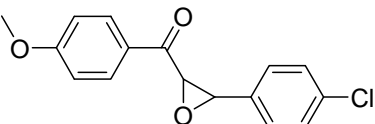
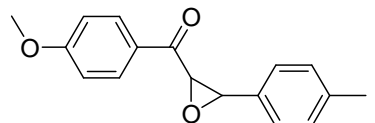
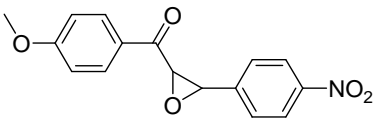
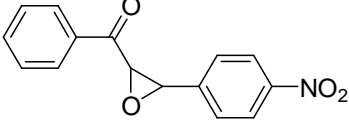
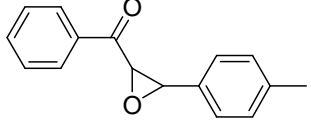
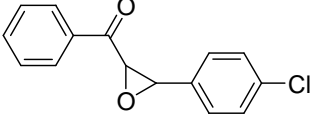
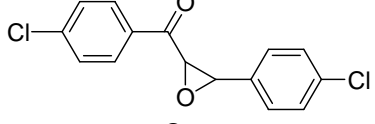
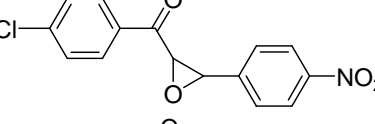
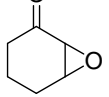
#### Catalyst reusability

Our attention was then turned to the possibility of recycling the catalyst from the reaction media since the recovery and reuse of the catalyst are highly preferable for a greener process. At the completion of the reaction, the reaction mixture was poured into  $\text{CHCl}_3$  and stirred for 5 min. The solid catalyst separated was filtered via simple filtration, dried and reused for subsequent reactions. The reusability of the catalyst was investigated by using chalcone as model substrates. After 8 recycles, the catalyst still had a high activity and gave the corresponding product in good yield.

#### Scope and limitations

Using ethanol/water (70/30) as optimum media and 0.5 mmol of catalyst at reflux condition a variety of  $\alpha,\beta$ -unsaturated ketones were investigated in the

Table 2 — Preparation of  $\alpha$ -epoxy ketones

Entry	Product structure	Time (h)	Yield (%)
1		17	84
2		18	87
3		15	86
4		16	91
5		15	89
6		20	80
7		20	85
8		17	88
9		18	87
10		20	89
11		21	79
12		15	89

epoxidation reaction. The results are summarized in Table 2. The electron repelling and electron donating groups attached to aromatic rings were successfully epoxidized, and the product was obtained in an excellent yield (Table 2).

### Conclusion

The *in-situ* preparation of the Fe doped  $BaAl_2O_4$  nano-powder *via* homogeneous precipitation method was reported. The prepared sample has been characterized using XRD, FE-SEM and EDAX analysis. The XRD pattern shows only hexagonal phases of  $BaAl_2O_4$ . The average particle size determined by FE-SEM is about 32 nm. The Fe doped  $BaAl_2O_4$  nano-powder shows to be a highly efficient catalyst for the efficient epoxidation of chalcone under reflux conditions in ethanol/water (70/30) as solvent.

### Acknowledgement

The authors are thankful to the Najafabad Branch, Islamic Azad University research council for partial support of this research

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