

## Epoxidation of styrene over MgO-rice derived carbon composite catalyst prepared by *in situ* transformation technique

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With a view to develop eco-friendly and metal-free catalysts, herein we report MgO-rice derived carbon composite for epoxidation of styrene to styrene epoxide. MgO-C catalysts prepared via *in situ* transformation technique are characterized by powder XRD, BET-surface area, Raman spectroscopy, CO<sub>2</sub>-TPD, CHNS analysis and TGA techniques. Under optimized reaction conditions, MgO-C0.5 catalyst efficiently catalyzed the reaction with 84% conversion of styrene yielding 82% selectivity to styrene epoxide. The characterization results suggest that the catalytic activity is attributed to the presence of well dispersed accessible basic sites obtained through *in situ* dispersion of MgO over rice derived carbon. MgO-C0.5 catalyst is recyclable up to four cycles without significant loss in the activity and selectivity.

**Keywords:** Catalysts, Composites, Carbon composites, Epoxidation, Styrene, Styrene epoxide

Epoxidation of alkenes is a promising route to convert hydrocarbons into functionalized molecules which are used as chemical intermediates. Among the epoxidation reactions, selective conversion of styrene into styrene epoxide is an interesting reaction due to ample industrial applications of the product, viz., styrene epoxide, which is used in manufacturing of pharmaceuticals, polyethers, surfactants and agro chemicals<sup>1-3</sup>. Owing to its versatile significance, production of styrene epoxide has been challenging for both academia and industrial research. In general, styrene epoxide has been produced by dehydrochlorination of chlorohydrins or oxidation of alkenes with formic acid or peracids. The complications associated with these processes such as high cost operations, unwanted reactions and corrosive nature of peracids limit their practical application<sup>4, 5</sup>. In the search for sustainable catalytic systems for the epoxidation of styrene, many researchers have been involved with the oxidant (such as H<sub>2</sub>O<sub>2</sub>, *tert*-butyl hydroperoxide (TBHP), O<sub>2</sub>) assisted epoxidation of styrene.

Various catalytic systems such as Co-SBA-15<sup>5</sup>, Co/ZIF-67<sup>6</sup>, Mn<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub><sup>7</sup>, Cr(III) complexes<sup>8</sup>, heteropolyacid/SBA-15<sup>9</sup>, Au/SiO<sub>2</sub><sup>10</sup>, Au/TS-1<sup>11</sup>, Cu-NH<sub>2</sub>-MCM-41<sup>12</sup> have been studied with encouraging results. Apart from these, Yang *et al.*<sup>13</sup> examined the Si/Ti/SiO<sub>2</sub> catalyst performance for the titled reaction

with *tert*-butyl hydroperoxide (TBHP) and H<sub>2</sub>O<sub>2</sub> as oxidants. Choudhary *et al.*<sup>14</sup> investigated the epoxidation of styrene with anhydrous H<sub>2</sub>O<sub>2</sub> over TS-1 and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. Kumar *et al.*<sup>15</sup> had also reported the epoxidation of styrene with TS-1 with dilute H<sub>2</sub>O<sub>2</sub> as oxidizing agent. The selective formation of acid sensitive styrene epoxide is quite problematic with the acidic supports. The catalytic epoxidation of styrene has been achieved over metals with basic supports such as Au/CaO<sup>16</sup>, Au<sub>25</sub> clusters supported on hydroxyapatite<sup>17</sup>, Au/LDH<sup>18</sup>, and Au/MgO<sup>19</sup>. The same reaction was also tested with the conventional basic oxides and satisfactory results were obtained. Beena *et al.*<sup>20</sup> reported the use of Mg-Al and Co-Al LDH as efficient solid base catalysts for epoxidation of styrene with molecular O<sub>2</sub>. Pavel *et al.*<sup>21</sup> investigated Y<sup>3+</sup> modified Mg, Al hydrotalcites and their memory effect on the epoxidation reaction with H<sub>2</sub>O<sub>2</sub> as oxidant and reported that the catalytic activity is correlated to their basicity<sup>21</sup>. Vasant *et al.*<sup>22</sup> examined the catalytic activity of alkaline and rare earth metal oxides in presence of TBHP and found that unsupported or Ga<sub>2</sub>O<sub>3</sub> supported BaO is highly active and selective for this epoxidation reaction.

The literature reports discussed above show that basic oxide supports and/or modified basic oxides are effective in catalyzing oxidant assisted

epoxidation of styrene. One of the major disadvantages of conventional basic oxides is their lower surface area. MgO is one of those basic oxides with potential catalytic applications, functioning as catalyst and catalyst support<sup>23-26</sup>. Some of the researchers have explored the synthesis of high surface area MgO by sol-gel technique<sup>27, 28</sup>, chemical vapour deposition<sup>29, 30</sup> and exo-templating methods<sup>31, 32</sup>. Although these methods offer high surface area, the catalyst preparation procedures are expensive and complicated to execute.

Recently, the use of rice grains as template and carbon source for the synthesis of high surface area and dispersed MgO catalysts has been increasing due to its simple and inexpensive preparation method<sup>33-35</sup>.

In this, rice grains are cooked in boiling water and MgO precursor is dispersed along with the absorption of water. This *in situ* transformation technique offers high surface area and enhanced accessibility to active basic sites. In order to develop metal free-epoxidation of styrene, a series of rice-derived MgO-C catalysts were prepared and subjected to the titled reaction (Scheme 1). Various reaction parameters were optimized to achieve the best results. Further, the catalytic activity is correlated with the characterization results.

## Experimental

### Catalyst preparation

Rice derived MgO-Cx catalysts were prepared according to a reported method by using magnesium acetate tetrahydrate ( $\text{Mg}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ ; 98%, Sigma Aldrich) as MgO precursor and rice grains as carbon precursor (procured from a rice store in Hyderabad, India)<sup>33-35</sup>. In a typical synthesis, the requisite amount of prewashed rice grains was added to an aqueous solution containing the requisite amount of magnesium acetate tetrahydrate, and covered with a suitable watch glass and dried on a hot plate at 60 °C. It was then allowed to dry at ambient temperature for 12 h and then calcined at 500 °C for 3 h followed by 700 °C for 1 h under  $\text{N}_2$  flow (80 mL  $\text{min}^{-1}$ ). The resultant solid was labelled

as MgO-Cx, where x denotes the mass ratio of  $\text{Mg}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$  and rice grains.

### Catalyst characterization

TGA measurements were carried out on a TGA/SDTA 851e thermal system (Mettler Toledo, Switzerland). The samples were heated in air with a heating rate of 10 °C  $\text{min}^{-1}$ . Powder X-ray diffraction (XRD) patterns were collected on a Ultima IV diffractometer (Rigaku Corporation, Japan) using Ni filtered Cu-K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) and a scintillation counter detector with a scan speed of 4°  $\text{min}^{-1}$  and a scan range of 10°–80° at 40 kV and 20 mA. BET surface area was calculated using a Quadrasorb-SI V 5.06 adsorption unit (Quanta Chrome Instruments Corporation, USA) under  $\text{N}_2$  adsorption. The samples were out-gassed at 300 °C for 4 h prior to the measurement. The basicity of the catalysts was measured by TPD of  $\text{CO}_2$ . In a typical experiment, 0.1 g of catalyst was loaded on the vertical fixed bed reactor and pre-treated in a helium gas flow (99.9%, 50 mL  $\text{min}^{-1}$ ) at 300 °C for 1 h. After pre-treatment, the physisorbed  $\text{CO}_2$  was flushed out. TPD- $\text{CO}_2$  of the catalysts was carried out at 100–700 °C under helium gas flow (99.9 %, 30 mL  $\text{min}^{-1}$ ) with a temperature ramping rate of 10 °C  $\text{min}^{-1}$ . The desorbed  $\text{CO}_2$  was monitored using GC equipped with a thermal conductivity detector (TCD). Raman spectra were recorded on Horiba Jobin-Yvon Lab Ram HR spectrometer with a 17 mW internal He-Ne (Helium-Neon) laser source of excitation wavelength of 632.8 nm at room temperature in the range of 200–1200  $\text{cm}^{-1}$ .

### Catalyst activity

Catalytic activity of the rice derived MgO-Cx catalysts in epoxidation of styrene was investigated in a 25 mL round bottom flask with a reflux condenser. In a typical experiment, 100 mg of the catalyst, 10 mmol of styrene and 20 mmol aqueous TBHP were added into the flask. The reaction mixture was heated at 100 °C for 18 h under constant stirring. Unless otherwise specified, the applied reaction conditions were the same as mentioned above. The products were identified on a FID equipped GC-17A (Shimadzu Instruments, Japan) with a EB-5 capillary column (30 m×0.53 mm×5.0 mm) and confirmed by GC-MS (M/s. QP-2010, Shimadzu Instruments, Japan) with EB-5 MS capillary column (30 m×0.25 mm×0.25 mm).



## Results and Discussion

### Characterization of the catalyst

The powder XRD patterns of MgO-C0.125, MgO-C0.25, MgO-C0.5, and MgO-C1 catalysts are presented in Fig. 1. A broad diffraction peak at about  $2\theta = 22\text{--}25^\circ$  in all the samples shows the presence of (002) plane of graphite lattice, which is formed from the rice grains<sup>33, 36</sup>. The diffraction peaks at  $2\theta$  values around  $43^\circ$  and  $62^\circ$  correspond to the pure phase of periclase MgO (PCPDF#: 711176). The intensity of these MgO peaks increases with the increase in mass ratio while the carbon peak intensity decreases. The crystallite size of MgO was calculated by Scherer's equation and the results show a linear correlation between the crystallite size and MgO content (Table 1). BET-surface area values of the MgO-Cx catalysts are also reported in Table 1. The surface area decreases with the increase in the mass ratio. BET surface areas of the MgO-Cx catalysts are proportional to the amount of MgO precursor.

Raman spectra of all the the MgO-Cx catalysts show two absorption bands at around  $1360$  and  $1585\text{ cm}^{-1}$  (Supplementary Data, Fig. S1). The absorption band at  $\sim 1360\text{ cm}^{-1}$  represents the D band which corresponds to the two-dimensional hexagonal lattice of all  $sp^2$  carbon atoms vibrations. The other

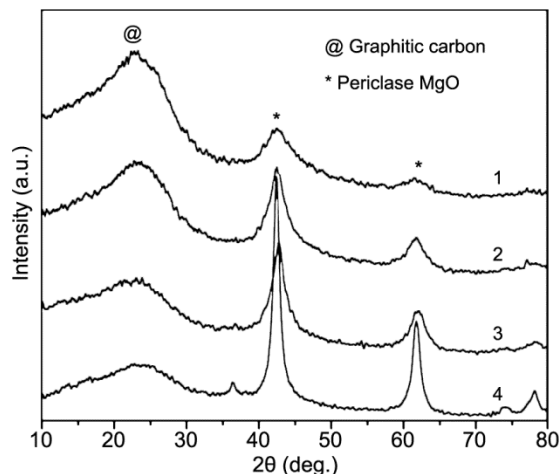


Fig. 1 – Powder XRD patterns of (1) MgO-C0.125, (2) MgO-C0.25, (3) MgO-C0.5, and, (4) MgO-C1 samples.

band at  $\sim 1585\text{ cm}^{-1}$  represents the G band related to the  $sp^3$  hybridized carbons<sup>33, 37</sup>.

Figure 2 shows the thermogravimetric analysis (TGA) of calcined MgO-Cx catalysts. All the samples show a similar trend in weight loss with increase in temperature. The minor weight loss in the region of  $\sim 50\text{--}200^\circ\text{C}$  is attributed to loss of physisorbed water. All the samples show a major weight loss in the  $\sim 300\text{--}580^\circ\text{C}$  region, which is assigned to the loss of carbon present in the samples.

The strength and number of basic sites present in MgO-Cx catalysts was evaluated by temperature programmed desorption of  $\text{CO}_2$  ( $\text{CO}_2$ -TPD) and results are presented in Fig. 3. Based on the desorption temperature, the basic sites are classified into three categories such as weak ( $<250^\circ\text{C}$ ) moderate ( $250\text{--}400^\circ\text{C}$ ) and strong basic sites ( $>400^\circ\text{C}$ ). MgO-Cx catalysts contain these three types of basic sites with the majority being the medium strength basic sites. The total basicity values are presented in Table 1. The number of basic sites increases with the increase in amount of MgO content and found to be optimum for MgO-C0.5 samples. On further increase in the MgO content (i.e., MgO-C1), no significant increase was observed in the  $\text{CO}_2$  uptake. In addition, it is also interesting to note that there is development

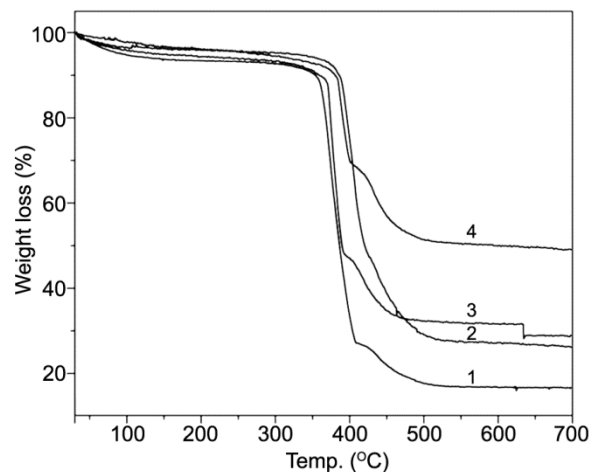


Fig. 2 – TGA profiles of (1) MgO-C0.125, (2) MgO-C0.25, (3) MgO-C0.5, and, (4) MgO-C1 samples.

Table 1 – Physicochemical properties of MgO-Cx catalysts

Catalyst	Carbon (wt%) <sup>a</sup>	BET-surface area (m <sup>2</sup> /g)	MgO crystallite size (nm) <sup>b</sup>	CO <sub>2</sub> uptake (mmol g <sup>-1</sup> ) <sup>c</sup>
MgO-C0.125	71	2	-	0.48
MgO-C0.25	64	44	3.3	0.62
MgO-C0.5	56	186	4.0	0.89
MgO-C1	45	235	6.7	0.93

<sup>a</sup>From CHNS elemental analysis; <sup>b</sup>From XRD; <sup>c</sup>From  $\text{CO}_2$ -TPD analysis.

of strong basic sites with increase in MgO amount (Fig. 3).

#### Catalytic activity of MgO-C<sub>x</sub> catalysts

The catalytic activity of MgO-C<sub>x</sub> catalysts on epoxidation of styrene was studied and results are presented in Fig. 4. Both the pure MgO and carbon exhibited low activity with 31% and 53% conversion of styrene with 64% and 0% selectivity to styrene epoxide respectively. The dispersion of MgO over rice derived carbon via *in situ* transformation results in enhanced catalytic activity in the epoxidation of styrene. The results showed an increase in conversion of styrene from 28% to 89% with the increase in mass ratio from MgO-C<sub>0.125</sub> to MgO-C<sub>1</sub>. The selectivity

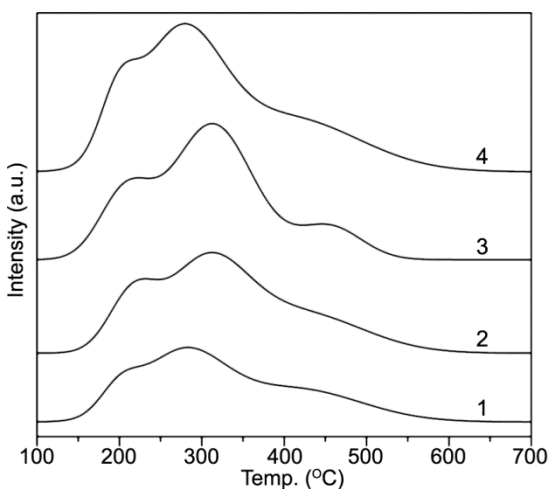


Fig. 3 – CO<sub>2</sub>-TPD profiles of (1) MgO-C<sub>0.125</sub>, (2) MgO-C<sub>0.25</sub>, (3) MgO-C<sub>0.5</sub>, and, (4) MgO-C<sub>1</sub> samples.

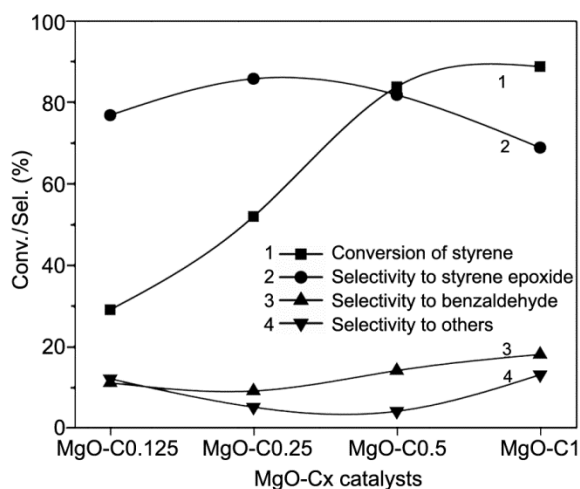


Fig. 4 – Catalytic activities of MgO-C<sub>x</sub> catalysts on epoxidation of styrene. [React. cond.: styrene: 10 mmol; TBHP: 20 mmol; catalyst: 100 mg; temp.: 100 °C; time: 18 h].

to styrene epoxide increased from 77% to 82% up to MgO-C<sub>0.5</sub>, and thereafter a decrease in selectivity to styrene epoxide was noticed. The decrease in selectivity of styrene epoxide with MgO-C<sub>1</sub> is due to increase in amount and distribution of basic sites which may promote the formation of other products, viz., benzaldehyde, benzoic acid, and condensation products. These results suggest that the increase in both activity and selectivity to styrene epoxide is associated with increase in amount of MgO in MgO-C<sub>x</sub> catalysts. The *in situ* dispersion of MgO over rice derived carbon results in increase in the number of accessible basic sites which are responsible for the epoxidation of styrene.

The reaction temperature plays a decisive role on the catalytic epoxidation of styrene. Figure 5 shows the effect of temperature on epoxidation of styrene over MgO-C<sub>0.5</sub> catalyst. The conversion of styrene increased linearly with the increase in temperature up to 100 °C. At 60 °C the styrene conversion was 60% and reached a maximum of 84% at 100 °C. The same trend is followed in the case of selectivity to styrene epoxide also. Initially, the selectivity to styrene epoxide was 59% and reached at a maximum of 82% selectivity to styrene epoxide at 100 °C. The remaining 18% comprised benzaldehyde (14%), phenyl acetaldehyde (2%), condensation product of benzaldehyde (0.8%), benzoic acid (0.4%) and unidentified products (0.8%). On further increase in the reaction temperature to 120 °C, the conversion of styrene increased, while the selectivity to styrene epoxide decreased. The increase in temperature

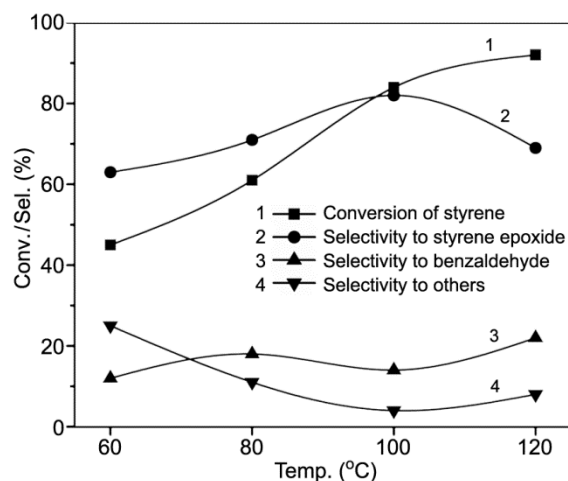


Fig. 5 – Effect of reaction temperature on epoxidation of styrene over MgO-C<sub>0.5</sub> catalyst. [React. cond.: styrene: 10 mmol; TBHP: 20 mmol; catalyst: 100 mg; time: 18 h].

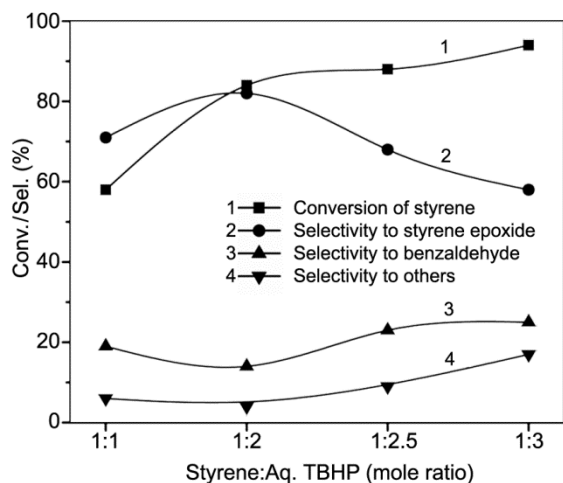


Fig. 6 – Effect of styrene:aqueous TBHP mole ratio on epoxidation of styrene over MgO-C0.5 catalyst. [React. cond.: catalyst: 100 mg; styrene: 10 mmol; temp.: 100 °C; time: 18 h].

enhances the rate of nucleophilic attractions which promotes the ring opening of styrene epoxide and subsequent formation of other products. Hence, the optimum reaction temperature for this reaction over MgO-C0.5 is 100 °C.

The effect of mole ratio of styrene to aqueous TBHP on the epoxidation of styrene was studied over MgO-C0.5 catalyst (Fig. 6). The results show that the conversion of styrene is influenced by the amount of the oxidant, TBHP. When the mole ratio of styrene to aqueous TBHP was 1:1 the conversion of styrene was 57% with 71% selectivity to styrene epoxide. With the increase in mole ratio from 1:1 to 1:2, the conversion of styrene increased from 57% to 84% with increase in selectivity to styrene epoxide reaching a maximum of 82%. With further increase in mole ratio of styrene to aqueous TBHP, the conversion of styrene increased at the expense of selectivity to styrene epoxide. The low selectivity to styrene epoxide at 1:1 mole ratio (styrene:aqueous TBHP) is due to lack of sufficient amount of oxidant molecules to convert the styrene into styrene epoxide. At molar ratios higher than 1:2, the decline in selectivity to styrene epoxide is related to over-oxidation of the formed styrene epoxide by more number of oxidant molecules.

The effect of catalyst amount on the epoxidation of styrene was studied over MgO-C0.5 catalyst (Supplementary Data, Fig. S2). It can be observed that the conversion of styrene increased with the increase in the catalyst amount. As the catalyst amount was increased from 50 mg to 200 mg, the conversion of

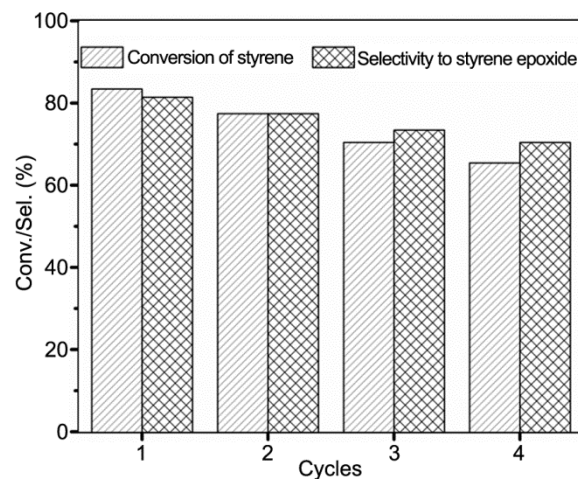


Fig. 7 – Reusability of MgO-C0.5 catalyst for epoxidation of styrene. [React. Cond.: styrene: 10 mmol; TBHP: 20 mmol; catalyst: 100 mg; temp.: 100 °C; time: 18 h].

styrene increased from 57% to 98% and the selectivity to styrene epoxide decreased from 83% to 57%. The increase in the amount of catalyst offers more active sites for the reactant as well as the product molecules. The higher number of accessible active sites allows increased contact between the reacting molecules. With increase in catalyst amount, styrene and styrene epoxide are promoted to participate in further reactions which results in increase in conversion of styrene and decrease in selectivity to styrene epoxide.

### Recyclability

The catalyst recyclability is one of the important parameters from the industrial point of view. Recycling experiments were performed with the MgO-C0.5 catalyst (Fig. 7). After completion of each cycle, the catalyst was collected by means of centrifugation and washed thoroughly with methanol and dried at 100 °C for 3 h and then used for the next run. It is evident from the results that the catalyst is active up to four cycles with only a slight decrease in the conversion. The selectivity to styrene epoxide is consistent during four cycles which shows the efficiency of MgO-C0.5 catalyst in the epoxidation of styrene.

### Conclusions

In conclusion, a low-cost and eco-friendly MgO-C0.5 catalyst has been synthesized and applied for the first time for the epoxidation of styrene with aqueous TBHP under solvent-free conditions. MgO-C0.5 catalyst is active and selective for the

epoxidation of styrene with 84% conversion and 82% selectivity to styrene epoxide. The high activity of this catalyst is due to presence of a large number of basic sites which have resulted due to the dispersion of MgO over rice derived carbon via *in situ* transformation technique. MgO-C0.5 catalyst is recyclable up to four cycles without much loss in activity and selectivity.

### Supplementary data

Supplementary data associated with this article are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA\\_57A\(8-9\)1106-1111\\_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_57A(8-9)1106-1111_SupplData.pdf).

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