Lanthanoid-free perovskite oxide catalyst for dehydrogenation of ethylbenzene working with redox mechanism

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INTRODUCTION

Styrene, an important monomer in petrochemistry, is used for polymeric materials such as polystyrene resin, acrylonitrile–butadiene–styrene resin and styrene–butadiene rubber. The production volume of styrene is 30 million tons per year worldwide (Meima and Menon, 2001; Su et al., 2005; Won and Jang, 2011). Styrene is produced via catalytic dehydrogenation of ethylbenzene (EBDH) according to the following chemical equation (Equation 1) (Cavani and Trifirò, 1995).

\[ C_8H_{10} \rightarrow C_8H_8 + H_2 \]  

(1)

As an endothermic reaction, EBDH requires high temperatures for high conversion of ethylbenzene because of thermodynamic limitations. An iron-based catalyst promoted by potassium and many kinds: Cr2O3, MoO3, CeO2, and Pd is used as an industrial catalyst (Kearby, 1945; Eggertsen and Voge, 1947; Pitzer, 1958; Lee, 1974; O’Hara, 1975; Riesser, 1979; Hirano, 1986; Rokicki et al., 2004). In the industrial process, steam is supplied with EB for increasing the equilibrium conversion by decreasing the partial pressure of EB. Additionally, steam has roles of heating up the reactant fluid, supplying heat for the endothermic reaction, and inhibiting coke deposition on the catalyst. A disadvantage of EBDH with steam is a large amount of energy loss because of the supply of superheated steam. Therefore, development of a catalyst that can work under low steam conditions and at low temperatures has been pursued.

For energy resource conservation, oxidative dehydrogenation of ethylbenzene (ODH) has recently been emphasized and investigated widely. Because ODH is an exothermic reaction, high conversion can be achieved at lower temperatures than from non-oxidative dehydrogenation. Meso-structured CeO2 (Xu et al., 2009), V2O5/CeO2/Al2O3 (Reddy et al., 2007), and Mg(VO4)2-MgO (Chang et al., 1995) catalysts were reported as highly active catalysts working at low temperatures of around 723 K for ODH. Onion-like carbon (Su et al., 2005, 2007, 2010) and carbon fibers (Zhao et al., 2007) have also been reported as catalysts showing high activity for ODH. However, because of the combustion of EB and styrene, ODH processes presented some problems such as the decrease of selectivity to styrene. Therefore, the selectivity
to styrene was low in the ODH process: about 68% at the EB conversion rate of 91% (Keller et al., 2002). An application of \( \text{N}_2\text{O} \) and \( \text{CO}_2 \) to ethylbenzene dehydrogenation has been conducted to attain high selectivity to styrene, \( \text{N}_2\text{O} \), and \( \text{CO}_2 \) were used instead of \( \text{O}_2 \) to avoid the combustion of styrene and EB, to \( \text{CO} \) and \( \text{CO}_2 \) (Sugino et al., 1995; Sakurai et al., 2000a, 2002; Shiju et al., 2005). As for using \( \text{N}_2\text{O} \) as the oxidant for ODH of ethylbenzene, high styrene yield was obtained at low temperature, however the selectivity to styrene was low due to the production of styrene oxide as well as benzene and toluene (Shiju et al., 2005). Vislovskiy et al. (2002) and Park et al. (2003) investigated EBDH in the presence of \( \text{CO}_2 \) over V–Sb/Al-oxide catalyst. They stated that a redox-type mechanism proceeded on V–Sb/Al-oxide catalyst, which achieved high activity and selectivity to styrene. \( \text{CO}_2 \) was considered to be a desirable oxidant for EBDH. Although high activity and stability was acquired over activated carbon-supported vanadium catalyst which was promising dehydrogenation catalyst, deactivation proceeded on the catalyst due to coke deposition. Sakurai et al. investigated the catalytic properties of V/AC catalyst for EBDH with \( \text{CO}_2 \) (Sakurai et al., 2000b). The catalyst revealed high activity and selectivity to styrene, but deactivation was not prevented. From these backgrounds, development of a novel dehydrogenation catalyst which has high stability as well as high activity is considered to be required.

We previously investigated the reaction mechanism of EBDH with steam over the industrial potassium promoted the iron catalyst (Fe–K) catalyst, and found for the first time that oxidative dehydrogenation of EBDH (Equation 2) proceeded on the Fe–K catalyst and \( \text{H}_2\text{O} \) can regenerate the consumed lattice oxygen in the catalyst (Equation 3) (Sekine et al., 2008).

\[
\begin{align*}
\text{C}_8\text{H}_{10} + \text{O}_2^{\text{lat}} & \rightarrow \text{C}_8\text{H}_8 + \text{H}_2\text{O} + \text{V}_{\text{ox}} + 2e^- \quad (2) \\
\text{H}_2\text{O} + \text{V}_{\text{ox}} + 2e^- & \rightarrow \text{H}_2 + \text{O}_2^{\text{lat}} \quad (3)
\end{align*}
\]

Here, \( \text{O}_2^{\text{lat}} \) denotes the lattice oxygen and \( \text{V}_{\text{ox}} \) shows the lattice vacancy in the catalyst. In other words, the catalytic activity and stability depended on redox characteristics of the lattice oxygen in the catalyst. Therefore, investigations of catalytic activity for EBDH with steam over some perovskite-type oxides whose mobility of lattice oxygen in perovskite-type oxide could be controlled, were conducted. As a result of investigations, \( \text{La}_{0.8}\text{Ba}_{0.2}\text{Fe}_{0.4}\text{Mn}_{0.6}\text{O}_3 – \delta \) (LBKMO) catalyst had high activity and stability and revealed superior performance to the Fe–K catalyst at 813 K (Watanabe et al., 2009). In addition, we found that oxidative dehydrogenation using lattice oxygen (Equation 2) proceeded and \( \text{H}_2\text{O} \) could regenerate the consumed lattice oxygen in the catalyst (Equation 3). The high regeneration rate of lattice oxygen enhanced the activity and stability of EBDH (Watanabe et al., 2011).

However, elemental La contained in LBKMO catalyst is an expensive rare-earth metal that is distributed unevenly throughout the world. Therefore, lanthanoid elements such as La are best not included in the catalyst for industrial applications. Additionally, the catalyst must work under low reaction temperatures and low steam conditions from the viewpoint of energy saving. These severe operations might be possible thanks to high redox property of perovskite-type oxides, which could achieve a low-cost dehydrogenation process.

In this work, to develop a novel La-free perovskite-type oxide catalyst, \( \text{BaMnO}_3 – \delta \)-based catalysts that are well known for high redox properties, were applied to EBDH with steam. For acquiring high-activity catalysts, the low-valence metal ion such as \( \text{Ba}^{2+} \), \( \text{Sr}^{2+} \), or \( \text{Ca}^{2+} \) was incorporated in A-site in the structure. The valence of B-site cation was fixed at higher-valence state for keeping the charge neutralization conditions by introduction of the low-valence metal ion in A-site, which affected enhancement of the catalytic property of the catalyst. In addition, introducing the low-valence metal ion into the A-site in perovskite was expected to produce oxygen vacancies in the structure, and it would bring high oxygen ionic conductivity. We optimized the structure of the \( \text{BaMnO}_3 – \delta \)-based catalyst by the substitution of A-site with \( \text{Sr} \) and B-site with \( \text{Fe} \). Additionally, the activity and robustness of the optimized catalyst at low reaction temperature and low steam/EB condition were examined for exploring the possibility as the industrial catalyst.

**EXPERIMENTAL**

**CATALYST PREPARATION**

Screening tests revealed that Ba–Ca–Fe–Mn–Ox and Ba–Sr–Fe–Mn–Ox perovskite were active and selective catalysts for EBDH as shown in Table 1. Therefore, we used some perovskite oxides in this study: \( \text{Ba}_{0.2}\text{Ca}_{0.8}\text{Fe}_{0.4}\text{Mn}_{0.6}\text{O}_3 – \delta \), and \( \text{Ba}_{1-x}\text{Sr}_x\text{Fe}_y\text{Mn}_{1-y}\text{O}_3 – \delta \) \((x = 0, 0.2, 0.4, 0.6, 0.8, \text{and } 1, \ y = 0, 0.2, 0.4, 0.6, \text{and } 0.8) \). They were prepared using a complex polymerization method as follows: \( \text{Ba(NO}_3)_2 \), \( \text{Sr(NO}_3)_2 \), \( \text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O} \), \( \text{Fe(NO}_3)_2 \cdot \text{H}_2\text{O} \), and \( \text{Mn(NO}_3)_2 \cdot \text{H}_2\text{O} \) (Kanto Kagaku) were dissolved in distilled water. Then, citric acid and ethylene glycol were added to the solution to produce a molar ratio of total metal ions: citric acid: ethylene glycol = 1:3:3. The obtained solution was dried up to produce a gel at 353 K. Then the gel was pre-calcined at 673 K for 2 h, and then calcined at 1123 K for 10 h.

**CHARACTERIZATION OF THE CATALYST**

The crystalline structure of the prepared catalyst was ascertained using X-ray powder diffraction with CuKα radiation (\( \lambda = 1.54 \text{ Å}, \text{Rint-2000; Rigaku Corp.)} \). The specific surface area of perovskite oxide was measured using \( \text{N}_2 \) adsorption at 77 K using Autosorb-1 (Quantachrome Corp.). The sample was outgassed at 2.5 K for 10 h. The sample was outgassed at

\[
\begin{align*}
\text{EB conversion} & = \frac{\text{EB reacted}}{\text{EB total}} \times 100 \\
\text{Selectivity} & = \frac{\text{Selectivity product}}{\text{EB reacted}} \times 100
\end{align*}
\]

Table 1 | EB conversion and selectivity to products for EBDH over perovskite catalysts.

| Catalyst | EB Conv./% (0.5 h) | Selectivity (0.5 h)/% |
|----------|-------------------|----------------------|
| BaFe\textsubscript{0.4}Mn\textsubscript{0.6}O\textsubscript{3} – \delta | 4.9 | 77.9 | 17.3 | 4.8 |
| SrFe\textsubscript{0.4}Mn\textsubscript{0.6}O\textsubscript{3} – \delta | 17.1 | 91.9 | 6.5 | 1.7 |
| BaFe\textsubscript{0.4}Mn\textsubscript{0.6}O\textsubscript{3} – \delta | 33.2 | 94.4 | 2.4 | 3.2 |
| Ba\textsubscript{0.2}Ca\textsubscript{0.8}Fe\textsubscript{0.4}Mn\textsubscript{0.6}O\textsubscript{3} – \delta | 28.2 | 96.6 | 2.0 | 1.4 |
| Ba\textsubscript{0.2}Sr\textsubscript{0.8}Fe\textsubscript{0.4}Mn\textsubscript{0.6}O\textsubscript{3} – \delta | 28.8 | 95.4 | 2.9 | 1.7 |
573 K for 2 h before N₂ adsorption. Redox property of the catalyst was measured using thermogravimetric analysis with TGA-50 (Shimadzu Corp.). The catalyst sample was set on the center of the muffle. Then the temperature of the catalyst was raised with a 10 K min⁻¹ heating rate from room temperature to 783 K in N₂ atmosphere. Thermogravimetric measurements were conducted under 10 vol% H₂ in N₂ atmosphere and also conducted under 10 vol% H₂ + 1 vol% H₂O or 2.5 vol% H₂O in N₂ atmosphere at 783 K to elucidate the effect of steam on the reduction profile of the catalyst. Weight loss “0” was the starting weight of the catalyst.

ACTIVITY TEST

Catalytic activity, selectivities to products and stability were examined in a conventional fixed bed reactor. The reactor used for this study comprised a quartz tube (10-mm o.d.) containing a catalyst bed, which was fixed by quartz wool. A type-K thermocouple enclosed in a quartz thermowell (3-mm o.d.) was positioned inside the catalyst bed for the measurement of the catalyst temperature. Reactions were conducted at 783 or 813 K at atmospheric pressure in the presence of steam; the molar ratio of steam to ethylbenzene was 2 or 12. The weight hourly space velocity (WHSV) was 1.2 h⁻¹; the catalytic weight was 1 g. Liquid products such as ethylbenzene, benzene, toluene, and styrene were analyzed using off-line flame ionization detection (FID) gas chromatograph (GC-2014; Shimadzu Corp.). Gaseous products such as H₂, CO, and CH₄ were analyzed using off-line thermal conductivity detection (TCD) gas chromatograph (GC-8A; Shimadzu Corp.). The conversion (Equation 4) and styrene yield (Equation 5) were evaluated using following equations.

\[
\text{EB conversion/\%} = \frac{([\text{Sty}] + [\text{Bz}] + [\text{Tol}]) / ([\text{EB}] + [\text{Sty}] + [\text{Bz}] + [\text{Tol}] ) \times 100}{(4)}
\]

\[
\text{Styrene yield/\%} = \frac{[\text{Sty}] / ([\text{Sty}] + [\text{Bz}] + [\text{Tol}]) \times 100}{(5)}
\]

\[
\text{Styrene selectivity/\%} = \frac{[\text{Sty}] / ([\text{Sty}] + [\text{Bz}] + [\text{Tol}]) \times 100}{(6)}
\]

Here, [EB], [Sty], [Bz], and [Tol] were, respectively, the concentration of EB, styrene, benzene and toluene in the effluent gas. Carbon balances in this work were over 95% through all the experimentally obtained results.

XPS MEASUREMENT FOR CHARACTERIZATION OF CATALYST SURFACE

X-ray photoelectron spectroscopy (XPS, ESCA1800; Ulvac-Phi Inc.) measurement was performed using a non-monochromatic Al-Kα radiation. The pass energy of the analyzer was set at 23.5 eV. Binding energies obtained for an identical sample were reproducible within ±0.1 eV in general. Binding energy of C1s was corrected to 284.7 eV.

SURFACE EXCHANGE REACTION

For clarifying redox properties of perovskite catalyst, surface exchange reaction using isotope was performed as the following method. First, 100% of H₂¹⁶O was supplied to the catalyst for 30 min in order to fill O²⁻ in the perovskite. After adequately feeding H₂¹⁸O in the catalyst, the mixed gas of H₂¹⁸O (30%) and H₂¹⁶O (70%) was fed to the catalyst as a step at 783 K for substitution of lattice oxygen from O²⁻ to O¹⁸⁻. Temporal changes of concentrations of H₂¹⁸O and H₂¹⁶O were monitored using a quadruple mass spectrometer (Q-Mass).

RESULTS AND DISCUSSION

DEHYDROGENATION ACTIVITY AND SELECTIVITY TO PRODUCTS OVER BaMnO₃₋₈-BASED CATALYSTS

Previous studies revealed that Mn-based and Fe/Mn-oxide catalysts showed high activity for EBDH thanks to the well-balanced rates of release and regeneration of lattice oxygen (Watanabe et al., 2009, 2011). In addition, Ba-based perovskite was well known to give better performance for oxygen-ion diffusivity (Wang et al., 2005; Vente et al., 2006; Zeng et al., 2007; Cheng et al., 2008). As mentioned in the introduction, high oxygen ionic conductivity was obtained by incorporating low-valence metal ions, such as Ba²⁺, Sr²⁺, and Ca²⁺ into the A-site in perovskite-type oxides. As shown in Table 1, BaMnO₃₋₈-based catalysts showed high activity, compared with CaMnO₃₋₈-based and SrMnO₃₋₈-based catalyst. Incorporation of the alkaline earth metal of Ba in perovskite structure would lead to the generation of electron holes and oxygen vacancies as the charge compensation, which could induce the high oxygen mobility derived from the mixed conduction by electrons and oxygen ions. Also, the incorporation of Ba in perovskite structure would engender the large free volume in the lattice, which could decrease the activation energy of oxygen ion migration. Therefore, to develop novel La-free perovskite catalysts for EBDH, BaMnO₃₋₈-based perovskite oxides were applied as catalysts.

Table 2 presents results for catalytic activities over BaMnO₃₋₈, Ba₀.2Sr₀.8MnO₃₋₈, and Ba₀.2A₀.8Fe₀.4Mn₀.6O₃₋₈(A = Ca²⁺, Sr²⁺) at 813 K with the steam/EB molar ratio of 12. Styrene yield over BaMnO₃₋₈, Ba₀.2Sr₀.8MnO₃₋₈, Ba₀.2Ca₀.8Fe₀.4Mn₀.6O₃₋₈, and Ba₀.2Sr₀.8Fe₀.4Mn₀.6O₃₋₈ catalysts at 0.5 h were, respectively 22.0, 27.1, 26.9, and 27.5%. BaMnO₃₋₈-based catalysts showed high activity for EBDH. The substitution of Sr²⁺ for Ba²⁺ enhanced dehydrogenation activity; however, the stability was not improved by the substitution. The reason for improving high catalytic activity by

| Table 2 | Durability and the amount of deposited carbon on Ba₁₋ₓSrxFe₀.₄Mn₀.₆O₃₋₈ (0 ≤ x ≤ 1) catalyst. |
| --- | --- | --- |
| Catalyst | Durability* | Amount of carbon deposition/mg g⁻¹cat⁻¹ |
| BaFe₀.₄Mn₀.₆O₃₋₈ | 0.48 | 6.4 |
| Ba₀.₈Sr₀.₂Fe₀.₄Mn₀.₆O₃₋₈ | 0.37 | 4.6 |
| Ba₀.₆Sr₀.₄Fe₀.₄Mn₀.₆O₃₋₈ | 0.46 | 4.6 |
| Ba₀.₄Sr₀.₆Fe₀.₄Mn₀.₆O₃₋₈ | 0.59 | 4.8 |
| Ba₀.₂Sr₀.₈Fe₀.₄Mn₀.₆O₃₋₈ | 0.65 | 5.8 |
| SrFe₀.₄Mn₀.₆O₃₋₈ | 0.60 | 7.6 |

*Durability = Styrene yield at 2 h/Styrene yield at 0.5 h.
the substitution of Sr$^{2+}$ for Ba$^{2+}$ might be enhancement of high releasing rate of lattice oxygen (Equation 2). In other words, ionic conductivity might increase by the substitution of Sr$^{2+}$. Shao et al. investigated the O$_2$ permeability property of Ba$_{0.2}$Sr$_{0.8}$Fe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$ catalyst. Comparison of the catalytic performance between Ba$_{0.2}$Sr$_{0.8}$Fe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$ and Ba$_{0.2}$Sr$_{0.8}$Fe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$ catalysts. The slightly substitution of Sr$^{2+}$ for Ba$^{2+}$ might decrease an activation energy for releasing rate of lattice oxygen. Therefore, initial dehydrogenation activity of the Ba$_{0.2}$Sr$_{0.8}$Mn$_{0.6}$O$_{3−δ}$ catalyst was higher than that of the BaMnO$_3$ catalyst. However, the rate for regenerating lattice oxygen (Equation 3) might not be improved, so stability was not improved.

While, the substitution of Fe for Mn improved the stability, and the initial activity showed similar values on Ba$_{0.2}$Sr$_{0.8}$Mn$_{0.6}$O$_{3−δ}$, and Ba$_{0.2}$Sr$_{0.8}$Fe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$ catalysts. Comparison of the catalytic performance between Ba$_{0.2}$Ca$_{0.8}$Fe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$ and Ba$_{0.2}$Sr$_{0.8}$Fe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$, a catalyst substituted with Sr (Ba$_{0.2}$Sr$_{0.8}$Fe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$) showed better activity and stability. Ba$_{0.2}$Sr$_{0.8}$Fe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$ catalyst showed comparable initial activity with Fe–K catalyst. The incorporation of Fe in perovskite-type oxide was found to suppress the lattice oxygen release (Equation 2) and promote the lattice oxygen regeneration (Equation 3) in the previous investigation (Watanabe et al., 2011). Therefore, the Fe/Mn-oxide catalyst showed higher stability for EBDH than Mn-based oxide thanks to the well-balanced rates of release and regeneration of lattice oxygen.

Styrene selectivity over Ba$_{0.2}$Sr$_{0.8}$Mn$_{0.6}$O$_{3−δ}$ catalyst was 94.1% and that over Ba$_{0.2}$Sr$_{0.8}$Fe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$ was 95.4%. Introducing Fe in the B-site of Ba$_{0.2}$Sr$_{0.8}$Mn$_{0.6}$O$_{3−δ}$ perovskite catalyst enhanced the activity, stability, and selectivity to styrene. After 2 h of reaction, styrene selectivity was improved a little. The reason for improvement of the styrene selectivity of all catalysts in Table 3 after 2 h of reaction was that the formation rate of benzene and toluene degraded faster than that of styrene formation rate. Further investigations by optimizing the structure of Ba-Sr-Fe-Mn-perovskite catalyst were conducted to improve the activity/selectivity to styrene.

### Table 3 | Catalytic performances for EBDH over perovskite catalysts: reaction times.

| Catalyst      | BET specific surface area/m² g⁻¹ | Styrene yield/% at 0.5 h | Styrene yield/% at 2.0 h | Styrene selectivity/% at 0.5 h | Styrene selectivity/% at 2.0 h |
|---------------|----------------------------------|--------------------------|--------------------------|--------------------------------|---------------------------------|
| BaMnO$_3$−δ   | 2.8                              | 22.0                     | 5.1                      | 94.5                           | 96.0                            |
| Ba$_{0.2}$Sr$_{0.8}$O$_{3−δ}$ | 8.4                              | 271                      | 3.6                      | 94.1                           | 94.0                            |
| Ba$_{0.2}$Ca$_{0.8}$O$_{3−δ}$ | 9.7                              | 26.9                     | 13.2                     | 96.6                           | 97.8                            |
| Ba$_{0.2}$Sr$_{0.8}$Fe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$ | 13.1                             | 275                      | 17.9                     | 95.4                           | 97.8                            |
| Fe–K          | 2.0                              | 271                      | 29.4                     | 978                            | 98.3                            |

### Table 4 | Selectivity to styrene, benzene and toluene for EBDH over Ba$_{1−x}$Sr$_{x}$Fe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$ (0 ≤ x ≤ 1) catalysts and Fe–K catalyst.

| Catalyst                  | BET specific surface area/m² g⁻¹ | Selectivity (0.5 h)% | Selectivity (2 h)% |
|---------------------------|----------------------------------|----------------------|--------------------|
| BaFe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$ | 7.1                              | 94.3                 | 2.0                |
| Ba$_{0.8}$Sr$_{0.2}$Fe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$ | 6.5                              | 95.2                 | 2.6                |
| Ba$_{0.6}$Sr$_{0.4}$Fe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$ | 7.9                              | 96.3                 | 2.1                |
| Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$ | 9.0                              | 96.1                 | 2.4                |
| Ba$_{0.2}$Sr$_{0.8}$Fe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$ | 13.1                             | 95.4                 | 2.9                |
| SrFe$_{0.4}$Mn$_{0.6}$O$_{3−δ}$ | 11.6                             | 91.9                 | 6.5                |
| Fe–K                      | 2.0                              | 97.8                 | 1.1                |
oxidation was conducted to measure the amount of carbon deposition over Ba$_{1-x}$Sr$_x$Fe$_{0.4}$Mn$_{0.6}$O$_{3-δ}$ (0 ≤ x ≤ 1) catalysts after 2 h reaction. Results showed that the amount of deposited carbon was very little for each catalyst about 5 mg g-cat$^{-1}$, and no relation was found between stability and the amount of carbon deposition as shown in Table 2. Therefore, carbon deposition does not seem to be the reason for deactivation of the catalyst. Next, the structure of as-made and used catalysts was evaluated using XRD. Figures 2A,B respectively depict XRD patterns of Ba$_{1-x}$Sr$_x$Fe$_{0.4}$Mn$_{0.6}$O$_{3-δ}$ (0 ≤ x ≤ 0.4) catalysts and of Ba$_{1-x}$Sr$_x$Fe$_{0.4}$Mn$_{0.6}$O$_{3-δ}$ (0.6 ≤ x ≤ 1) catalysts. From Figures 2A,B, the peak position was shifted between the fresh catalyst and used one. The shift in peak position seemed to be caused by producing oxygen vacancies. The peak at about 2θ = 24°, small peak was observed after reaction, although the peak was not observed over the as-made catalyst. The appeared peak was attributable to the BaMnO$_3$ structure from SrMnO$_3$ structure from Ba$_{1-x}$Sr$_x$Fe$_{0.4}$Mn$_{0.6}$O$_{3-δ}$ (0 ≤ x ≤ 0.4) catalysts include BaMnO$_3$ and BaMnO$_3$–δ after 2 h reaction. BaMnO$_3$–δ perovskite structure had lattice vacancy in the structure. However, the structure of used Ba$_{1-x}$Sr$_x$Fe$_{0.4}$Mn$_{0.6}$O$_{3-δ}$ (0.6 ≤ x ≤ 1) catalysts were almost identical structures to those of as-made catalyst derived from SrMnO$_3$ structure from Figure 2B. For Figure 2A at about 2θ = 24°, small peak was observed after reaction, although the peak was not observed over the as-made catalyst. The appeared peak was attributable to the BaMnO$_3$–δ structure. The reason for the appearance of small peak was the difference of sharing state of perovskite unit cell. The as-made catalyst has a cubic type structure with corner-sharing MnO$_6$ octahedral. In contrast to the stoichiometric BaMnO$_3$, oxygen-deficient BaMnO$_3$–δ has different hexagonal/rhombohedral structures with variable ratios of corner-sharing (cubic) and face-sharing (hexagonal) layers (Adkin and Hayward, 2006, 2007). These differences produced the new peak after dehydrogenation reaction. Such created lattice vacancy under dehydrogenation atmosphere might be due to the fact that the release rate of lattice oxygen (Equation 2) was higher than the regeneration rate of lattice oxygen. Therefore, lattice oxygen in BaMnO$_3$ was consumed and the BaMnO$_3$–δ structure appeared. However, lattice vacancy was not created by low content of Ba$_{2+}$ in the perovskite, as shown in Figure 2B. This fact might be explained by the well-balanced rates of release and regeneration of lattice oxygen. Therefore, the imbalance of release rate and regeneration rate of lattice oxygen is attributable to the deactivation of the catalyst and change of structure attributable to the reduction by EB on Ba$_{1-x}$Sr$_x$Fe$_{0.4}$Mn$_{0.6}$O$_{3-δ}$ (0 ≤ x ≤ 0.4).

From these results and consideration, the Sr$_{2+}$ substitution ratio of 0.6 was better in terms of high initial activity and stability for EBDH. However, Fe–K industrial catalyst still shows higher stability, as described above. Therefore, we controlled the stability by changing the substitution amount of Fe in Ba$_{0.4}$Sr$_{0.6}$Fe$_y$Mn$_{1−y}$O$_{3−δ}$ (0.2 ≤ y ≤ 0.8) catalysts in the next section.

**OPTIMIZATION OF B-SITE SUBSTITUTION RATIO IN Ba$_{0.4}$Sr$_{0.6}$Fe$_y$Mn$_{1−y}$O$_{3−δ}$ CATALYST FOR EBDH**

For further enhancement of stability, the Fe substitution ratio (y) in Ba$_{0.4}$Sr$_{0.6}$Fe$_y$Mn$_{1−y}$O$_{3−δ}$ was optimized. Activity tests were performed over Ba$_{0.4}$Sr$_{0.6}$Fe$_y$Mn$_{1−y}$O$_{3−δ}$ (y = 0.2, 0.4, 0.6, and 0.8) catalysts at 813 K. Figure 3 shows the styrene yield as a function of reaction time. Results showed that
the stability was enhanced with increasing Fe cation substitution ratio, as we expected. Figures 4A, B show XRD patterns for these catalysts. As-made Ba$_{0.4}$Sr$_{0.6}$Fe$_2$O$_{3}$ catalyst contained perovskite-type oxide and undesired BaFe$_2$O$_4$ phase. After 2h reaction, Ba$_{0.4}$Sr$_{0.6}$Fe$_2$O$_{3}$ catalyst contained many impurity phases because Eb reduced the catalyst during the reaction by imbalance of release rate and the regeneration rate of lattice oxygen. However, as-made catalyst during the reaction by imbalance of release rate contained many impurity phases because EB reduced the regenerating rate of lattice oxygen by Fe substitution. Enhancement of stability was regarded as improving the catalytic performance of partially Mn-substituted Fe–K catalysts (Miyakoshi et al., 2001). They reported that styrene selectivity was almost invariable in whole range of Mn-substitution. In this work, styrene selectivity over Ba$_0$ catalyst did not change from 0.4 to 0.6, and 0.8 catalysts showed almost identical structure to that of the as-made catalyst. After 2h reaction, Ba$_0$ catalyst showed characteristic peaks for perovskite-type oxide. As-made Ba$_0$ catalyst revealed higher initial activity and almost identical selectivity, as shown in Figure 3 and Table 5.

Table 5 presents the effect of the Fe substitution with Mn on the selectivity to products. Fe substitution increased selectivity to benzene and decreased selectivity to toluene slightly, although styrene selectivity did not change from $y = 0.2$ to $y = 0.6$ on Ba$_{0.4}$Sr$_{0.6}$Fe$_2$O$_{3}$ catalysts. Miyakoshi et al. investigated the catalytic performance of partially Mn-substituted Fe–K catalysts (Miyakoshi et al., 2001). They reported that styrene selectivity was almost invariable in whole range of Mn-substitution. In this work, styrene selectivity over Ba$_{0.4}$Sr$_{0.6}$Fe$_2$O$_{3}$ catalyst was also invariable within the range: $0.2 \leq y \leq 0.8$ as shown in Table 5. The trend was almost the same. The reason for low styrene selectivity over the Ba$_{0.4}$Sr$_{0.6}$Fe$_2$O$_{3}$ catalyst was significantly low styrene yield, compared with Ba$_{0.4}$Sr$_{0.6}$Fe$_2$O$_{3}$ catalyst (0.2 $\leq y \leq 0.6$) catalysts. Low activity might be derived from low mixed conductivity of the catalyst.

Among these catalysts, Ba$_{0.4}$Sr$_{0.6}$Fe$_2$O$_{3}$ catalyst showed superior catalytic performance. Comparing the activity and selectivity to styrene on Ba$_{0.4}$Sr$_{0.6}$Fe$_2$O$_{3}$ catalyst with that on Fe–K industrial catalyst, Ba$_{0.4}$Sr$_{0.6}$Fe$_2$O$_{3}$ catalyst revealed higher initial activity and almost identical selectivity, as shown in Figure 3 and Table 5.

**CHARACTERIZATION OF SURFACE ANALYSES OF Ba$_{0.4}$Sr$_{0.6}$Fe$_2$O$_{3}$ CATALYST BY X-RAY PHOTOELECTRON SPECTROSCOPY MEASUREMENT FOR CHARACTERIZATION OF CATALYST SURFACE**

XPS measurement was carried out to evaluate the concentration of lattice vacancy in the Ba$_{0.4}$Sr$_{0.6}$Fe$_2$O$_{3}$ catalyst as-made catalyst and during EBDH reaction, and to investigate the oxidation state of B-site cation in the catalyst. XPS spectra of Mn2p and Fe2p are shown in Figure 5. Table 6 shows binding energies of Mn2p$_{3/2}$ (Mn2p) and Fe2p$_{3/2}$ (Fe2p) core-levels of as-made catalyst, the catalyst after 10 min reaction and the catalyst after 2h reaction. The concentration of oxygen vacancy at the surface calculated from the surface atomic ratio is shown in Table 6. Here, the peak percentage of components is in parenthesis. As for as-made catalyst, the peak of Mn2p included two components at 641.94 and 640.98 eV. Former and latter peaks were attributed to Mn4+ and Mn3+, respectively (Carver et al., 1972; Oku and Hirokawa, 1976; Ponce et al., 2000). The peak of Fe2p included components at 711.71 and 709.56 eV which were attributed to Fe3+ and Fe2+, respectively (Ghaffari et al., 2012). The peak percentage of components was as follows; Mn4+: 51.5%, Mn3+: 48.5%, Fe3+: 30.3%, and Fe2+: 69.7%. The concentration of oxygen vacancy; $\delta$ was 2.88. The composition of perovskite which has no lattice vacancy, is AB0$_3$, in other words d = 0. In this work, the low valence cation; Ba was doped in A-site of Ba$_{0.4}$Sr$_{0.6}$Fe$_2$O$_{3}$ catalyst.

**Table 5 | Selectivity to styrene, benzene, and toluene on EBDH over Ba$_{0.4}$Sr$_{0.6}$Fe$_2$O$_{3}$ catalyst (0.2 $\leq x \leq 0.8$) and Fe–K catalyst.**

| Catalyst | BET specific surface area/m$^2$ g$^{-1}$ | Selectivity (0.5 h)/% | Selectivity (2 h)/% |
|----------|-------------------------------------|---------------------|--------------------|
|          |                                      | Sty     | Bz       | Tol     | Sty     | Bz       | Tol     |
| Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.2}$O$_{3}$ | 8.9    | 95.9  | 2.1     | 2.0     | 98.2  | 0.3     | 1.5     |
| Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.4}$O$_{3}$ | 9.0    | 96.1  | 2.4     | 1.5     | 98.0  | 0.4     | 1.6     |
| Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$O$_{3}$ | 10.1   | 96.6  | 1.7     | 1.7     | 97.8  | 0.6     | 1.6     |
| Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.8}$O$_{3}$ | 5.7    | 89.7  | 8.2     | 2.2     | 92.4  | 4.7     | 2.9     |
| Mn$_2$O$_{3}$ | 2.0    | 978   | 1.1     | 1.1     | 98.3  | 0.9     | 0.8     |

**Table 6 | Surface analyses of Ba$_{0.4}$Sr$_{0.6}$Fe$_{2}$O$_{3}$ catalyst.**

| Catalyst | Mn2p$_{3/2}$ (eV) | Fe2p$_{3/2}$ (eV) |
|----------|-------------------|-------------------|
| Ba$_{0.4}$Sr$_{0.6}$Fe$_{2}$O$_{3}$ | 641.94 | 711.71 |
| Ba$_{0.4}$Sr$_{0.6}$Fe$_{2}$O$_{3}$ | 640.98 | 709.56 |
perovskite-type oxides, in order to maintain the electrical neutrality, the electrical charge unbalance could be compensated via following ways: (a) the increase of valence state of B-site metal cation and (b) the production of lattice vacancy in the structure. Therefore, the result indicated the presence of lattice vacancy.

As for the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3−δ}$ catalyst after 10 min reaction, the peak of Mn$_{2p}$ was 642.25 and 640.86 eV. These values were attributed to the Mn$^{4+}$, Mn$^{3+}$, respectively in Figure 5B. The Fe$^{2p}$ peak can be divided into two peaks, namely Fe$^{4+}$ at 711.59 eV and Fe$^{3+}$ at 709.49 eV. The peak percentage of components was as follows; Mn$^{4+}$: 36.4%, Mn$^{3+}$: 63.6%, Fe$^{4+}$: 29.5%, and Fe$^{3+}$: 70.5%. The Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3−δ}$ catalyst was reduced by EB and high valence cation of Mn$^{4+}$ was reduced to lower valence cation of Mn$^{3+}$. While, the oxidation state of Fe did not almost change after the reaction. In fact, the Fe cation in the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3−δ}$ catalyst was not reduced by EB. The concentration of oxygen vacancy, $δ$ was 2.83. The catalyst also had lattice vacancy in the perovskite structure. The peak of Mn$^{2+}$ and Fe$^{2+}$ in the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3−δ}$ catalyst after 2 h reaction contained Mn$^{4+}$, Mn$^{3+}$, Fe$^{4+}$, and Fe$^{3+}$. The mixed valence of Mn and Fe was not almost changed, compared with the catalyst after 10 min reaction. The peak percentage of components was as follows; Mn$^{4+}$: 35.9%, Mn$^{3+}$: 64.1%, Fe$^{4+}$: 30.3%, and Fe$^{3+}$: 69.7%.

We considered the role of Fe from the results of XPS results. Preliminary studies showed that redox-type mechanism proceeded on the catalyst; (Equation 2) oxidative dehydrogenation of ethylbenzene using lattice oxygen and (Equation 3) regenerating lattice vacancy by H$_2$O (Watanabe et al., 2011, 2013). In this work, Mn-based catalyst showed high initial activity, but low stability. While, stability of the catalyst was improved by Fe substitution of Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{1−γ}$O$_{3−δ}$ catalyst. Therefore, we proposed that the role of Mn and Fe might be the site for releasing lattice oxygen and the site for regenerating lattice vacancy, respectively. The oxidation state of Fe and Mn on Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3−δ}$ catalyst was Mn$^{4+}$/Mn$^{3+}$ and Fe$^{4+}$/Fe$^{3+}$, respectively. So, the aromatic ring of EB was adsorbed onto Mn$^{4+}$. Then, styrene and H$_2$O were produced via oxidative dehydrogenation of ethylbenzene, following that Mn$^{4+}$ and Fe$^{4+}$ were reduced to Mn$^{3+}$ and Fe$^{3+}$. Co-feeding steam was adsorbed on reduced Fe$^{3+}$ site. Lattice oxygen was regenerated by oxidation of Fe$^{3+}$ to Fe$^{4+}$ and of Mn$^{3+}$ to Mn$^{4+}$. Summarily, the role of Fe was considered to be the promotion of regenerating lattice oxygen derived from high redox property of Fe$^{4+}$/Fe$^{3+}$.

**DEHYDROGENATION ACTIVITY AND ROBUSTNESS OF Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3−δ}$ CATALYST UNDER LOW-TEMPERATURE OR LOW STEAM/EB CONDITION**

To examine the dehydrogenation activity and robustness of the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3−δ}$ catalyst under low temperature or low steam/EB condition, catalytic activity tests were conducted. The Fe–K oxide catalyst was used as the control. Figure 6A presents results for activity tests at 783 K (i.e., lower temperature) under steam/EB of 12. The styrene yield of the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3−δ}$ catalyst was 16.3% and that of the Fe–K catalyst was 10.4% at 30 min. The initial activity of the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3−δ}$ catalyst was 1.57 times higher than that of the Fe–K oxide catalyst at such a low temperature.

Next, the robustness of the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3−δ}$ catalyst for low steam/EB operation was examined, and catalytic activity tests were performed at 813 K with steam/EB molar ratio of 2. Figure 6B presents results for the activity test over the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3−δ}$ and the Fe–K catalysts under the condition of steam/EB molar ratio of 2. From Figure 6B, the

![Image](59x255 to 163x316)

![Image](59x339 to 163x400)

![Image](59x422 to 164x483)

**FIGURE 5 |** XPS spectra of Mn$_{2p}$ (left) and Fe$_{2p3/2}$ (right) for Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3−δ}$: (A) as-made, (B) after 10 min of reaction, (C) after 2 h of reaction.

| Condition                      | Mn$_{2p}$/eV | Fe$_{2p}$/eV | Surface composition                  |
|--------------------------------|-------------|-------------|--------------------------------------|
|                                | Mn$^{4+}$   | Mn$^{3+}$   | Fe$^{4+}$   | Fe$^{3+}$   |                        |
| As-made                        | 641.94 (51.5)| 640.98 (48.5)| 711.71 (30.3)| 709.56 (69.7)| Ba$_{0.53}$Sr$_{0.48}$Fe$_{0.61}$Mn$_{0.50}$O$_{2.88}$ |
| After 10 min reaction          | 642.25 (36.4)| 640.86 (63.6)| 711.59 (29.5)| 709.49 (70.5)| Ba$_{0.62}$Sr$_{0.47}$Fe$_{0.54}$Mn$_{0.47}$O$_{2.83}$ |
| After 2 h reaction             | 642.19 (35.9)| 641.17 (64.1)| 711.71 (30.3)| 709.68 (69.7)| Ba$_{0.81}$Sr$_{0.20}$Fe$_{0.63}$Mn$_{0.51}$O$_{2.87}$ |

*Peak percentage of components is in parenthesis.*
Ba_{0.4}Sr_{0.6}Fe_{0.8}MnO_{3−8} catalyst showed high robustness under low steam conditions. However, the activity of Fe–K oxide catalyst gradually decreased with time on stream. These results might be derived from the superior ability for steam activation over the Ba_{0.4}Sr_{0.6}Fe_{0.8}MnO_{3−8} catalyst compared to that of the Fe–K catalyst. For the Fe–K catalyst, low steam/EB conditions caused a low regeneration rate of lattice oxygen, and deactivation was observed.

The reason for the higher activity of the Ba_{0.4}Sr_{0.6}Fe_{0.8}MnO_{3−8} catalyst was investigated in terms of the redox property of the catalyst. An isotope exchange reaction from O_{16} to O_{18} in the catalyst by switching H_{16}O to H_{18}O at 783 K was conducted over the Ba_{0.4}Sr_{0.6}Fe_{0.8}MnO_{3−8} catalyst. We have already found that the Fe–K catalyst works on a redox mechanism during EBDH (Sekine et al., 2008). Figure 7 presents the time profile of H_{18}O by the time that the stable flow rate of H_{18}O was confirmed. Here, time “0” was the starting time at which H_{18}O (30%) and H_{16}O (70%) were supplied to the catalyst. H_{18}O was monitored sooner after the feeding of H_{18}O on a blank test and over α-Al_{2}O_{3} as a non-redox control, respectively. The isotope exchange reaction did not proceed over α-Al_{2}O_{3} in accordance with the profile of the blank test.

Figure 7 presents the normalized temporary profile of H_{18}O flow rate over α-Al_{2}O_{3} or Ba_{0.4}Sr_{0.6}Fe_{0.8}MnO_{3−8} catalyst. Here, “surf” and “bulk” respectively signify the surface and bulk of the catalyst. The surface exchange reaction proceeded on the catalyst, and then the surface lattice oxygen diffused to bulk with redox of the catalyst. Figure 8 shows the result of H_{2}-temperature programmed reduction (TPR) measurement of Ba_{0.4}Sr_{0.6}Fe_{0.8}Mn_{1−y}O_{3−8} (y = 0.2, 0.6, 0.8) catalysts. The weight loss of the catalyst was measured by heating to 1173 K (10 K min−1) under 10 vol% H_{2} atmosphere. The start of the reduction was considered to reflect the consumption of lattice oxygen on the vicinity of the surface. From this Figure, Ba_{0.4}Sr_{0.6}Fe_{0.8}MnO_{3−8} catalyst was less likely to be reduced. Namely, reducibility of the catalyst was low, comparing with other catalysts. Low releasing ability of lattice oxygen might cause low activity for dehydrogenation of ethylbenzene. Based
on these results, the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3-\delta}$ catalyst enabled redox at low temperature of 783 K. Consequently, high activity is apparently derived from high redox property of the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3-\delta}$ catalyst.

For elucidating the greater robustness of the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3-\delta}$ catalyst than that of the Fe–K catalyst, redox properties of the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3-\delta}$ and the Fe–K catalysts were examined using thermogravimetric measurement under H$_2$ atmosphere and H$_2$/H$_2$O atmosphere. Figure 9A portrays the thermogravimetric profile of the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3-\delta}$ catalyst under various partial pressures at 783 K and Figure 9B shows that of the Fe–K catalyst under the same condition. From Figure 9A, 3.1 wt% of the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3-\delta}$ catalyst was reduced under 10 vol% H$_2$/N$_2$ atmosphere. The reduced amount was equivalent to 405 mmol mol-cat$^{-1}$, which was 13.5% of lattice oxygen in perovskite-type oxide. However, 2.5 wt% of the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3-\delta}$ was reduced under 10 vol% H$_2$ and 1 vol% H$_2$O. The value corresponded to 330 mmol mol-cat$^{-1}$ of lattice oxygen, which was 11% of lattice oxygen in perovskite-type oxide. Further increase of the partial pressure of steam decreased the value to 308 mmol mol-cat$^{-1}$ under 10 vol% H$_2$ and 2.5 vol% H$_2$O. The lattice oxygen of 10.3% was released under this condition. Figure 9B showed that the Fe–K was reduced to Fe metal under 10 vol% H$_2$/N$_2$ atmosphere. Also, the Fe–K was reduced to Fe metal under 10 vol% H$_2$ and 1.0 vol% H$_2$O. Compared with the case in the absence of H$_2$O (10 vol%H$_2$/N$_2$), the reduction rate was suppressed by H$_2$O. Even if the partial pressure of steam further increased, the Fe–K was reduced to Fe$_3$O$_4$ and additional reduction gradually proceeded from Fe$_3$O$_4$ to Fe metal with reaction time under 10 vol% H$_2$ and 2.5 vol% H$_2$O condition. The nature of the structural stability of the Fe–K catalyst was low in reducing atmosphere. From these results, coexisting H$_2$O in the atmosphere affected the reduction behavior of the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3-\delta}$: i.e., reduction was suppressed by H$_2$O compared to the case in the absence of H$_2$O. We confirmed that the regeneration of consumed lattice oxygen by H$_2$O proceeded on the catalyst in our previous study (Watanabe et al., 2011). Therefore, the suppression of the reduction was derived from the increased regeneration rate of the consumed lattice oxygen by H$_2$O. These results showed that the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3-\delta}$ catalyst revealed high robustness under a reductive atmosphere and activated H$_2$O more easily than the Fe–K catalyst.

For low reaction temperature and low steam/EB reaction conditions, the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3-\delta}$ catalyst had high activity and robustness. Results show that the Ba$_{0.4}$Sr$_{0.6}$Fe$_{0.6}$Mn$_{0.4}$O$_{3-\delta}$ is a promising catalyst for industrial dehydrogenation processes.

**CONCLUSION**

For EBDH, the substitution of Ba$^{2+}$ for Sr$^{2+}$ over Ba$_{1-x}$Sr$_x$Fe$_y$Mn$_{1-y}$O$_{3-\delta}$ (x = 0, 0.2, 0.4, 0.6, 0.8, and 1, y = 0, 0.2, 0.4, 0.6, and 0.8) catalysts enhanced the initial activity for EBDH, but activity decreased with time on stream. Optimization of B-site substitution ratio of Fe in Ba$_{0.4}$Sr$_{0.6}$Fe$_y$Mn$_{1-y}$O$_{3-\delta}$ catalyst was conducted, and results showed that the stability
for EBDH was improved by an increase of Fe substitution ratio. Optimized Ba$_{0.4}$Sr$_{0.5}$Fe$_{0.5}$Mn$_{0.2}$O$_{3-\delta}$ catalyst showed high styrene yield of 29.2% and selectivity to styrene of 96.6% at 813 K. The dehydrogenation activity and robustness of Ba$_{0.4}$Sr$_{0.5}$Fe$_{0.6}$Mn$_{0.4}$O$_{3-\delta}$ catalyst were investigated under low-temperature and low steam/EB reaction conditions. Consequently, the catalyst of Ba$_{0.4}$Sr$_{0.5}$Fe$_{0.6}$Mn$_{0.4}$O$_{3-\delta}$ revealed high activity and superior robustness under these severe conditions derived from high redox property of the catalyst. From the evaluation of redox property of the Ba$_{0.4}$Sr$_{0.5}$Fe$_{0.6}$Mn$_{0.4}$O$_{3-\delta}$ catalyst, thermogravimetric profile was measured under H$_2$/H$_2$O atmosphere at 783 K. The result showed that reduction was suppressed by the presence of H$_2$O, implied that the lattice oxygen in perovskite-structure was consumed by H$_2$, subsequently the consumed lattice oxygen was regenerated by H$_2$O. Additional support for this result was confirmed by H$_2$O surface exchange reaction. The lattice oxygen was exchanged with steam by redox of the catalyst at low temperature of 783 K.

Therefore, Ba$_{0.4}$Sr$_{0.5}$Fe$_{0.6}$Mn$_{0.4}$O$_{3-\delta}$ was identified as a promising catalyst for EBDH with steam under severe conditions.

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