Dehydrogenation of ethylbenzene over $La_{0.8}Ba_{0.2}Fe_{0.4}Mn_{0.6}O_{3-\delta}$ perovskite oxide catalyst working by redox mechanism using steam and lattice oxygen

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ABSTRACT

Details of the reaction mechanism of ethylbenzene (EBDH) dehydrogenation were investigated using kinetic analyses of highly active and stable $La_{0.8}Ba_{0.2}Fe_{0.4}Mn_{0.6}O_{3-\delta}$ (LBFMO) perovskite oxide catalyst with a quadrupole mass spectrometer by measuring the instantaneous behavior. Under EBDH with a steam condition, the stoichiometric factor of oxygen in LBFMO catalyst in the steady-state reaction was found to be 2.927, which is lower than 3. The catalyst worked in the reduced state in which a few layers of lattice oxygen were consumed, supported by X-ray photoelectron spectroscopic analyses. Additionally, the reactive lattice oxygen and vacancy were involved with the reduction–oxidation (redox) mechanism of EBDH with steam. The respective amounts were 17.0 mmol mol-cat^{-1} for available lattice oxygen and 68.5 mmol mol-cat^{-1} for vacancy over LBFMO under the steady state condition. LBFMO catalyst showed high and stable EBDH activity by virtue of the redox mechanism using this lattice oxygen and vacancy.

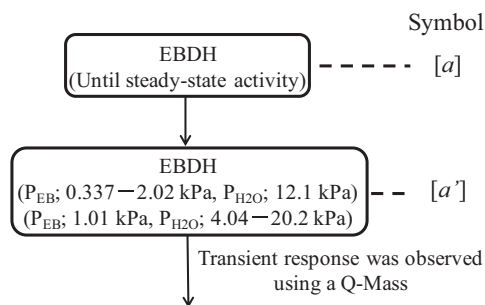© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Styrene, used for polymeric materials such as polystyrene resin, acrylonitrile–butadiene–styrene resin, and styrene–butadiene rubber, is an important monomer associated with petrochemistry. Styrene production volume is about 30 million tons annually, more than 90% of which is produced by dehydrogenation of ethylbenzene (EBDH), as expressed in the following chemical equation (1) [1,2].

$$C_8H_{10} \rightarrow C_8H_8 + H_2 \quad \Delta H_{298} = 124\,kJ\,mol^{-1} \quad (1)$$
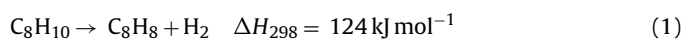
EBDH is an endothermic reaction. Therefore, high temperatures are necessary for high ethylbenzene conversion because of its thermodynamic limitation. The catalyst of Fe–K, an often-used industrial catalyst [3], contains promoters such as Cr_2O_3 [3–5], CeO_2, MoO_3 [6,7], and Pd [8]. Addition of Mn to Fe–K catalyst enhances its catalytic activity [9–11]. Generally, radial-type adiabatic reactors have been applied in commercial processes for EBDH [12]. Superheated steam is supplied to the catalyst bed with ethylbenzene as a heating source to control the reaction temperature. Steam also acts as a diluent for shifting the equilibrium conversion higher, and suppresses overreduction of the Fe–K catalyst in the reductive atmosphere. Additionally, steam suppresses carbon

deposition on the surface of the Fe–K catalyst [13,14]. In a preliminary study, we investigated the reaction mechanism of EBDH on the Fe–K catalyst with periodic pulse experiments using a quadrupole mass spectrometer (Q-Mass) [15]. Results showed that the industrial Fe–K catalyst for styrene production works with a redox mechanism using the lattice oxygen in the catalyst. Perovskite-type oxides (ABO_3), which also have high redox ability [16–20], are applicable for EBDH thanks to their redox ability [21–23]. Few reports have investigated perovskite oxide as a dehydrogenation catalyst. Moreover, the roles of the A-site and B-site in perovskite-type oxide have not been elucidated clearly. In general, A-site and B-site elements in ABO_3 are determined by ionic radii of these elements. The catalytic activity for the reaction is determined mainly by the transition metals. The selection of A-site elements such as lanthanide metal affects the catalytic properties; B-site elements determine the catalytic activity and stability. Fe-based and Mn-based materials have superior redox properties, which imply their higher activity and better stability. In an earlier study, we developed a novel catalyst for EBDH based on $LaMnO_3$ perovskite-type oxide [22]. By the substitution of A-site with the low-valence metal ion of Ba and of B-site with Fe, the LBFMO catalyst was found to show higher activity and better stability for EBDH than the industrial Fe–K catalyst. Generally, incorporation of the alkaline earth metal of Ba^{2+} in perovskite structure engenders the generation of electron holes and oxygen vacancies as the charge compensation, which can induce high oxygen mobility derived from the mixed

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Symbol

EBDH
(Until steady-state activity) ----- [a]

↓

EBDH
(P_{EB}; 0.337 – 2.02 kPa, P_{H_2O}; 12.1 kPa) -- [a']
(P_{EB}; 1.01 kPa, P_{H_2O}; 4.04 – 20.2 kPa)

Transient response was observed
using a Q-Mass

↓

Scheme 1. Flow chart of a transient response test for dependence of the styrene/hydrogen formation rate on partial pressure of ethylbenzene/H_2O.

conduction by electrons and oxygen ions. Additionally, the incorporation of Ba in perovskite structure engenders the large free volume in the lattice, which decreases the activation energy of oxygen ion migration. These effects promote the release rate of lattice oxygen as the following equation (2).

$$C_8H_{10} + O^{2-}_{lat} \rightarrow C_8H_8 + H_2O + V_{ox} + 2e^- \qquad (2)$$

In this equation, O_{lat} denotes the lattice oxygen in/on the perovskite oxide, and V_{ox} denotes the lattice vacancy. Stability was improved by the incorporation of Fe in $La_{0.8}Ba_{0.2}MnO_{3-\delta}$ structure. We investigated the reaction mechanism of EBDH over LBFMO perovskite-type oxide catalyst [23], which revealed that the redox mechanism proceeded on the catalyst. The oxidative dehydrogenation of ethylbenzene uses lattice oxygen (2) and regeneration consumes lattice oxygen (i.e. vacancy) by H_2O (3).

$$H_2O + V_{ox} + 2e^- \rightarrow H_2 + O^{2-}_{lat} \qquad (3)$$
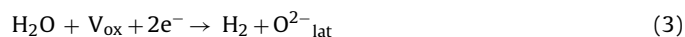
The rate-determining step of EBDH with steam was found to be lattice vacancy regeneration. The role of Fe was found to be enhancement of the regeneration rate derived from high redox nature of Fe. The optimal substitution ratio of 0.4 in B-site produced the well-balanced relation between the rate of releasing lattice oxygen and the rate of regenerating lattice vacancy. Therefore, in this study, we conducted detailed kinetic studies of the release/regeneration of lattice oxygen to elucidate the characteristics of high activity/stability of LBFMO catalyst.
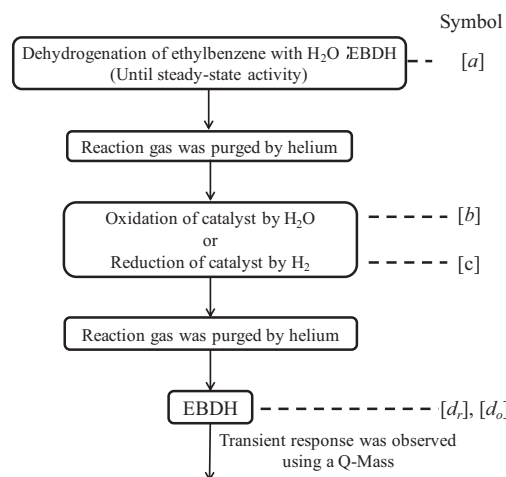
2. Experimental

2.1. Catalyst preparation and characterization

$La_{0.8}Ba_{0.2}Fe_yMn_{1-y}O_{3-\delta}$ ($y = 0$, 0.4) was prepared using a polymerized complex method. $La(NO_3)_3 \cdot 6H_2O$, $Ba(NO_3)_2$, $Fe(NO_3)_3 \cdot 9H_2O$, and $Mn(NO_3)_2 \cdot 6H_2O$ (Kanto Chemical Co. Inc.) were dissolved in distilled water. Citric acid and ethylene glycol were added to the solution to produce a molar ratio of metal ions/citric acid/ethylene glycol of 1/3/3. The obtained solution was dried and pre-calcined at 673 K for 2 h, then calcined at 1123 K for 10 h. The crystalline structure of the calcined product was ascertained using X-ray powder diffraction with Cu$K\alpha$ radiation ($\lambda = 1.54$ Å, Rint-2000; Rigaku Corp.). The specific surface area of perovskite oxide was measured using N_2 adsorption at 77 K. Then the sample was outgassed at 573 K for 2 h before N_2 adsorption.

2.2. Transient response experiments

2.2.1. Effect of partial pressure of ethylbenzene or H_2O on release/regeneration of lattice oxygen

Other transient response experiments were conducted to ascertain the reaction order of ethylbenzene and H_2O for the release/regeneration rate of lattice oxygen. Scheme 1 presents a

Symbol

Dehydrogenation of ethylbenzene with H_2O ÆBDH
(Until steady-state activity) -- [a]

↓

Reaction gas was purged by helium

↓

Oxidation of catalyst by H_2O ----- [b]
or
Reduction of catalyst by H_2 ----- [c]

↓

Reaction gas was purged by helium

↓

EBDH --------- [d_r], [d_o]

Transient response was observed
using a Q-Mass

↓

Scheme 2. Flow chart of a transient response test for dependence of the styrene/hydrogen formation rate on the amount of lattice oxygen/lattice vacancy.

flow chart for transient response tests. First, ethylbenzene and H_2O were introduced to the catalyst bed (operation [a] in Scheme 2). Then a steady-state activity on EBDH was obtained. Reaction conditions of [a] were the following: 813 K reaction temperature, 0.2 g catalyst weight, 3 ml min^{-1} ethylbenzene flow, 36 ml min^{-1} H_2O flow, and 3 ml min^{-1} internal standard gas (Ar) flow. The total flow rate was 300 ml min^{-1}, as balanced with helium flow (partial pressure of ethylbenzene, $P_{EB} = 1.01$ kPa; partial pressure of H_2O, $P_{H_2O} = 12.1$ kPa). Next, another EBDH was conducted without purging (operation [a']) under different conditions to operation [a]. Reaction [a'] was the following: (1) ethylbenzene at various partial pressures ($P_{EB} = 0.34$–2.02 kPa) and H_2O at a constant partial pressure ($P_{H_2O} = 12.1$ kPa) were introduced to the catalyst bed to investigate the ethylbenzene reaction order; or (2) ethylbenzene at a constant partial pressure ($P_{EB} = 1.01$ kPa) and H_2O at various partial pressures ($P_{H_2O} = 4.04$–20.2 kPa) were introduced to the catalyst bed to elucidate the reaction order of H_2O. Here, the initial styrene/H_2 flow rate was obtained at the time [a'] started. We defined the initial styrene/H_2 flow rate as the lattice oxygen release/regeneration rate referring Eqs. (2) and (3).

2.2.2. Evaluation of the lattice oxygen release/regeneration rate

We conducted some transient response experiments to evaluate the lattice oxygen release/regeneration rate on the catalyst. Scheme 2 presents a flow chart for transient response tests. First, steady-state EBDH was conducted in the presence of H_2O (operation [a] in Scheme 1). Reaction conditions of [a] were the same as those described in Section 2.2.1. We have already confirmed that these conditions were suitable for the determination of kinetic parameters considering diffusion and kinetics. After a stable catalytic activity on EBDH was obtained, adsorption species on the catalyst surface were purged and desorbed using helium flow. Next, H_2O or H_2 alone was supplied to the catalyst bed to control the amount of lattice oxygen in the catalyst (operation [b] or [c]). Then the gas was purged using helium to remove the adsorbed H_2O or H_2 on the catalyst surface. Finally, EBDH was conducted under the same condition as those of the operation [a] in the presence of H_2O (operation [d_r] or [d_o]). We measured the reaction order of lattice oxygen for its release rate during the steady-state reaction of EBDH. We defined the styrene formation rate at the time when [d_r] or [d_o] started as the lattice oxygen release rate. To determine the reaction order with respect to amounts of available lattice oxygen on/in the catalyst N_o, kinetic data were fitted to rate law expression (4).

Release rate of lattice oxygen = k_r[ethylbenzene]$^\alpha$[H_2O]$^\beta$$N_o^\gamma$ (4)