Applied Catalysis B: Environmental 237 (2018) 554–562

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Promoting effect of cerium on MoVTeNb mixed oxide catalyst for oxidative dehydrogenation of ethane to ethylene

Yang Sik Yun[a,1], Minzae Lee[a,1], Jongbaek Sung[a], Danim Yun[a], Tae Yong Kim[a], Hongseok Park[a], Kyung Rok Lee[a], Chyan Kyung Song[a], Younhwa Kim[a], Joongwon Lee[b], Young-Jong Seo[b], In Kyu Song[c], Jongheop Yi[a,*]

[a] World Class University Program of Chemical Convergence for Energy & Environment, Institute of Chemical Processes, School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Republic of Korea
[b] Lotte Chemical Corporation, Gajeongbuk-ro, Yuseong-gu, Daejeon 305-726, Republic of Korea
[c] School of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University, Shinlim-dong, Kwanak-gu, Seoul 151-744, Republic of Korea

ARTICLE INFO

Keywords:
Oxidative dehydrogenation
Ethane
Ethylene
Ce
MoVTeNbO

ABSTRACT

Ce-incorporated MoVTeNbO catalysts were developed to enhance ethylene productivity of oxidative dehydrogenation of ethane (ODHE) to ethylene. Structural characterizations (XRD, TEM, STEM, Raman, and UV–vis DRS) and DFT calculations revealed that Ce atoms were incorporated into MoVTeNbO framework with maintaining its unique structure (*M1* phase), which is active phase for ODHE. The reducibility of the catalysts was enhanced and both V^{5+} and the lattice oxygen species available to ODHE reaction were enriched by incorporation of Ce, confirmed by TPR, XPS, and pulse injection method, respectively. These improved properties enhanced the conversion of ethane while maintaining their excellent selectivity to ethylene for MoVTeNbCeO catalysts. It is noteworthy that 56.2% of ethane conversion and 95.4% of ethylene selectivity were retained for 200 h over MoVTeNbCeO-0.1 catalyst. Ethylene productivity was calculated to be 1.11 kgC_2H_4/kg_{cat} h. The developed catalyst exhibits substantial level of ethylene productivity and stability having the possibility with low production of CO_x to make a step forward for industrialization of oxidative dehydrogenation of ethane.

1. Introduction

Ethylene is a primary building block for the production of value-added chemicals such as polyethylene, ethylene oxide, and, styrene [1–3]. Most of ethylene has been produced by steam cracking of ethane and thermal cracking of petrochemicals (e.g. naphtha) in commercial process. However, the processes are operated at high temperature (> 800 °C), resulting in high energy consumption and undesired side reactions [1]. In addition, the processes suffer from coke depositions and environmentally harmful gases (CO_2 and NO_x) emissions [2]. Especially, large production of greenhouse gas (CO_2, 1.5–3 times per ethylene production) is considered as one of major drawbacks in conventional processes [3]. The increasing demand for minimizing the negative environmental impact and the necessity of efficient process promote a development of alternative reaction process for the production of ethylene.

The oxidative dehydrogenation of ethane (ODHE) has attracted considerable attention as an efficient process due to its low energy costs, low deactivation, availability of the reactant from shale gas instead of petrochemical feedstock, and low greenhouse-gas emission [4–6]. A variety of metal oxide catalysts have been studied for the ODHE reaction, as exemplified by Ni-based [1,7–11], Mo-V-based [12–15], and L a–b ased mixed oxides [16], supported alkali chlorides [17–19], and supported noble metals [20,21], etc. Among them, MoVTeNbO catalyst is one of the most promising catalysts for ODHE as well as propane selective oxidation [22,23]. In previous researches, it shows high ethane conversion and ethylene selectivity at relatively low reaction temperature (< 500 °C), resulting in high ethylene yield (> 60%) [5,24]. Despite the advantages of the ODHE process and the high ethylene yield of MoVTeNb mixed oxide catalyst, the process has not been commercialized yet. For commercial implementation, several key requirements should be simultaneously satisfied: ethylene selectivity (> 90%), long-term stability, and ethylene productivity (> 1.0 kgC_2H_4/kg_{cat} h) [4,25]. However, the requirements are restrictedly and/or partially satisfied by most conventional catalysts. Especially, such high criteria of ethylene productivity have been considered as major obstacle for commercialization of the process.

* Corresponding author.
E-mail address: jyi@snu.ac.kr (J. Yi).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.apcatb.2018.06.025
Received 8 March 2018; Received in revised form 5 June 2018; Accepted 8 June 2018
Available online 15 June 2018