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

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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.

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There have been various attempts to improve the ethylene productivity using MoVTeNb-based mixed oxide catalysts. For example, supports such as Al_2O_3, SiO_2, and CeO_2 [13,26,27], post treatments [25], size control [6], and the introduction of additives [28,29] are used. Unfortunately, the ethylene productivity of them is still lower than the industrial criteria for the commercialization.

In this study, we developed Ce-incorporated MoVTeNbO catalysts for the production of ethylene via the ODHE reaction. Ce can be a proper hetero-atom as a dopant due to its high oxygen storage capacity and unique redox properties [30]. The active structure (*M1* phase) was maintained after Ce was incorporated into the MoVTeNbO framework, which was confirmed by XRD, TEM, STEM, Raman, and UV–vis DRS. DFT calculation results also provided an evidence for the incorporation of Ce into the framework. XPS and TPR analyses revealed that the incorporated Ce induced an abundance of V^{5+} species within the catalysts and an enhancement in reducibility of catalysts, which promotes conversion of ethane. In addition, it was confirmed that the amounts of available lattice oxygen to participate in the ODHE reaction became abundant in MoVTeNbCeO catalysts. The results of reaction tests proved that the catalytic activity was remarkably increased by the incorporation of Ce without losing its high ethylene selectivity. The catalytic performance was retained for 200 h with exhibiting commercially feasible ethylene productivity (1.11 kgC_2H_4/kg_{cat} h). As far as we can ascertain, this is the first report developing a catalyst with the excellent ethylene productivity (> 1.00 kgC_2H_4/kg_{cat} h), ethylene selectivity (> 94%), and long-term stability (> 200 h).

2. Methods

2.1. Catalyst preparation

MoVTeNbCeO catalysts were prepared by a hydrothermal method. A aqueous solution containing ammonium molybdate hydrate (10.07 g, 81.0–83.0% MoO_3 basis, Sigma-Aldrich), 2.18 g of telluric acid (2.18 g, 99.0%, Sigma-Aldrich), cerium nitrate hexahydrate (0.50–3.00 g, 99%, Sigma-Aldrich), vanadium oxide sulfate hydrate (5.11 g, 97.0%, Sigma-Aldrich) with deionized water (58 mL) was prepared with vigorous stirring at 80 °C for 1 h (Solution 1). The color of mixture turned into green. Solution 2 was prepared with niobium oxide hydrate (1.22 g, CBMM), oxalic acid dehydrate (3.03 g, 99.0%, Sigma-Aldrich), deionized water (14 mL) at 80 °C for 30 min. The solutions were cooled down to room temperature. Then, solution 2 was added to solution 1, and the mixture was stirred for 30 min. The aqueous solution containing Mo, V, Te, Nb, and Ce precursors was heated at 175 °C for 48 h. The obtained precipitate was washed 3 times with deionized water by centrifugation (12,000 rpm), and dried overnight at 80 °C. The prepared samples were activated under inert atmosphere (N_2, 50 mL/min) at 600 °C for 2 h. The catalysts are denoted as MoVTeNbCeO-X where X indicates molar ratio of Ce to V in aqueous solution in preparation step. A reference sample (MoVTeNbO) was also prepared following previous procedure [31].

2.2. Characterization

XRD analysis was performed by a powder X-ray diffractometer (Rigaku d-MAX2500-PC, CuK_α radiation, 50 kV, 100 mA). The morphology and lattice were characterized using a high-resolution transmission electron micrograph (HR-TEM) (JEOL JEM-3010, 300 kV). EDS chemical mapping images of the catalyst were obtained using Bright field scanning transmission microscopy (BF-STEM) (JEOL JEM-2100F). Ultraviolet-visible diffuse reflectance spectroscopy (UV–vis DRS) (Jasco V670 spectrometer) was conducted to obtain the spectra at room temperature. Raman shifts were collected using a HORIBA LabRAM HV Evolution (CCD detector, 532 nm of laser). The surface areas were measured on by a Micromeritics ASAP-2010 with N_2 adsorption at −196 °C. Field emission electron probe microanalysis (EPMA) was performed to investigate the elemental compositions (Mo, V, Te, Nb, Ce, and O) of the catalysts using JEOL JXA-8530F. X-ray photoelectron spectroscopy (XPS) spectra were recorded using AXIS SUPRA (Kratos). C 1s peak (284.5 eV) was used as a standard. Peak deconvolution for vanadium oxidation state (V^{4+} and V^{5+}) was conducted based on previous researches [6]. H_2 temperature-programed reduction (H_2-TPR) was carried out by Micromeritics Autochem II chemisorption analyzer. The catalyst (0.1 g) was used in the analysis, and heated at 150 °C for 1 h under Ar flow. After that, it cooled to 50 °C. The gas flow was switched to 10% H_2/Ar flow (30 mL/min), and the temperature was then ramped from 50 °C to 800 °C at 10 °C/min. TCD detector was used to measure H_2 consumption during ramping step.

Lattice oxygen capacity measurement was applied to investigate the lattice oxygen species of catalysts available for the reaction. The measurement was conducted in a flow reactor system with 6 port valves for the rapid introduction of an ethane pulse. 0.2 g of powders was placed on a quartz bed reactor (8 mm i.d.). He (26.6 mL/min) was used as a carrier gas. The signals of the outlet gas were detected by an on-line mass spectrometer (QGA, Hiden Analytical). Prior to the measurements, the samples were heated at 400 °C in O_2 (2.4 mL/min) and He (26.6 mL/min) for 1 h. Then, the sample was purged in He for 30 min to remove residual oxygen from the system. 250 μL of ethane was injected along with carrier gas (He) to the samples 12 times. Instantaneous ethane consumption was monitored as a function of time. Lattice oxygen capacity was calculated as micromoles of ethylene produced per gram of the sample.

2.3. Reaction test

A 0.2 g of catalyst was used for oxidative dehydrogenation of ethane using a quartz reactor (8 mm i.d.). Before the reaction, pre-heating step was carried out at 250 °C under an inert flow (He: 39.2 mL/min and N_2: 16.3 mL/min) for 1 h. Then, O_2 and ethane was introduced. The molar composition of feed mixture was [Ethane/O_2/N_2/He] = [5.0/2.5/27.2/65.3]. N_2 was used as internal standard for analyzing the gas-phase products. Due to the induction time for ODHE reaction, reaction data were collected at 6 h. The products were analyzed by an online GC (Younglin ACME 6100 model) equipped with both a flame ionization detector (FID) and a thermal conductivity detector (TCD). Two columns were used in the analysis (Porapak Q for CO_2, C_2H_4, C_2H_6 and Molsieve 13X for N_2, O_2, CO. Ethane conversion, ethylene yield, selectivity, and productivity, and CO_x selectivity were calculated as follows:

$$\text{Ethane conversion (\%)} = \frac{\text{mole of ethane reacted}}{\text{mole of ethane fed}} \times 100$$

$$\text{Ethylene yield (\%)} = \frac{\text{mole of ethylene produced}}{\text{mole of ethane fed}} \times 100$$

$$\text{Ethylene Selectivitiy (\%)} = \frac{\text{mole of ethylene produced}}{\text{mole of ethane reacted}} \times 100$$

$$\text{CO}_x \text{ Selectivitiy (\%)} = \frac{\text{mole of CO}_x \text{ produced}}{\text{mole of ethane reacted}} \times \frac{1}{2} \times 100$$

$$\text{Ethylene productivity } (kg_{C_2H_4}/kg_{cat}\cdot h) = \frac{F_{C_2H_6}\cdot X_{C_2H_6}\cdot S_{C_2H_4}\cdot MW_{C_2H_4}}{m_{cat}}$$

where F_{C2H6} is the molar flow of ethane, X_{C2H6} is conversion of ethane, S_{C2H4} is selectivity to ethylene, MW_{C2H4} is molecular weight of ethylene (28.05 g/mol), and m_{cat} is the mass of the catalyst. The carbon balance was closed to 100% for each run.

2.4. DFT calculations

Density functional theory (DFT) calculations were performed by The Vienna Ab-initio Simulation Package (VASP) [32]. For exchange-correlation functional, the Perdew–Burke–Ernzerhof (PBE) of the