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Catalytic performance of phase-pure M1 $MoVNbTeO_x/CeO_2$ composite for oxidative dehydrogenation of ethane

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The introduction of cerium oxide to phase-pure M1 $MoVNbTeO_x$ with CeO_2 loading from 0 up to 90 wt.% results in highly active catalysts for oxidative dehydrogenation of ethane (ODHE). These catalysts are characterized with BET, ICP, XRD, TEM, SEM and XPS techniques and tested for ODHE process. The results show that the increase of active site, V^{5+}, is one of the dominant factors to improve the ethane conversion. In addition, the easier re-oxidation of V^{4+} to V^{5+} due to the presence of Ce^{4+} makes an extra contribution to the increase of turn-over frequency. Among all the catalysts, M1 catalyst with 30 wt.% CeO_2 loading obtains the best productivity of 0.69 $kg_{C2H4}/kg_{cat}{\cdot}h$ while the corresponding performance of phase-pure M1 catalyst is 0.34 $kg_{C2H4}/kg_{cat}{\cdot}h$ at 400 °C with the contact time of 18.52 $g_{cat}{\cdot}h/mol_{C2H6}$. It is further demonstrated that $M1/CeO_2$ catalyst (e.g., with 50 wt.% CeO_2 as a representative) loading remains highly active after 3 cycles of refreshment in situ, and its crystal structure and surface morphology keep stable compared to the fresh catalyst.

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1. Introduction

Ethylene is one of the most important building blocks in the chemical industry [1]. The oxidative dehydrogenation of ethane (ODHE) to ethylene has received considerable attention because of its distinct advantages (e.g., thermodynamically favored, lower reaction temperature, no coke formation, etc.) over steam cracking process [2–4]. In recent years, mixed metal oxides seem to be the most promising catalytic system for ODHE reaction [4–14]. Among them, $MoVNbTeO_x$ catalyst exhibits attractive performances (i.e., activity, selectivity and productivity) at the reaction temperature of about 400 °C.

Usually, $MoVNbTeO_x$ catalyst is prepared by slurry method [14–18] or hydrothermal method [4,19,20]. This multicomponent metal oxide is nanocrystalline solid mainly composed of phase-M1 and phase-M2 [21]. The M1 phase has a needle-like crystal morphology in which the (0 0 1) planes are arranged perpendicular to the long axis of the needles [22]. While the M2 phase has characteristic hexagonal rings hosting the Te-O units without any pentagonal or heptagonal rings in the (0 0 1) planes [20,23]. Previous studies have indicated that the M1 phase is the most efficient phase in ethane oxidation, assuming V^{5+} ions as ethane activation sites [4,24,25]. The performance of $MoVNbTeO_x$ catalysts increases with the purity of M1 phase [26]. It is reported that the $MoVNbTeO_x$ catalyst has a considerable potential for industrial application when the catalytic activity obtains ethane conversion >80% and ethylene selectivity >90% [27–30]. However, according to the reported catalysts, the industrial requirements for commercialization (e.g, 1.00 $kg_{C2H4}/kg_{cat}{\cdot}h$ catalyst productivity) is far from achieved [29]. Since the catalytic activity of phase-pure M1 is related with the amount of V^{5+} ions, increasing their amount could be an important working direction. Meanwhile, because of the expensive raw material for catalyst preparation and mass loss caused by post-treatment, the high cost of $MoVNbTeO_x$ catalysts is one of the crucial reasons hindering the industrial implementation in the ODHE process [11]. As a result, introduction of cheap promoters naturally becomes a simple and effective method for catalyst improvement and cost reduction. At present, α-Al_2O_3, SiO_2, and ZrO_2 have been added into the $MoVNbTeO_x$ catalysts [11,31] as diluters with little influence on the surface chemistry of the composite catalyst [14,31]. In our previous work, the introduction of CeO_2 significantly improved the catalytic efficiency and reduced the cost of catalyst in ODHE process, which provides a promising idea and preliminary verification on improvement of $MoVNbTeO_x$ catalysts. However, further detailed and thorough research on the addition of CeO_2 to $MoVNbTeO_x$ catalysts is still needed.

In this work, M1 $MoVNbTeO_x/CeO_2$ ($M1/CeO_2$) catalysts are synthesized for the ODHE reaction. As a matter of fact, pure CeO_2

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shows low activity of ethane conversion and low selectivity to ethylene in the ODHE process at a temperature lower than 500 °C [11,34,35]. However, CeO_2 itself has high oxygen-storage capacity (OSC) and easy oxidation/reduction of the Ce^{4+}/Ce^{3+} redox couple [32,33]. Therefore, the essential idea of this paper is to use CeO_2 as an oxidant, added to the phase-pure M1 catalyst, to increase the number of vanadium active sites so as to improve the catalytic performance [23]. The catalytic performance is evaluated for the ODHE in a laboratory-scale fixed-bed reactor and the characterization of the catalysts are achieved by using XRD, BET, ICP, XPS, SEM and TEM techniques.

2. Experimental section

2.1. Catalyst preparation

$MoVNbTeO_x$ catalysts are prepared by hydrothermal synthesis [11,20,36,37]. Ammonium heptamolybdate (Sigma-Aldrich, 99.0%), vanadyl sulfate (Sigma-Aldrich, 97%) telluric acid (Sigma-Aldrich, 98%) and ammonium niobium oxalate (Sigma-Aldrich, 99.99%) are used to prepare an aqueous slurry comprising Mo, V, Te and Nb at the molar ratio of Mo:V:Te:Nb = 1:0.25:0.23:0.18. The slurry is put into a 100 ml Teflon autoclave, where the air inside the autoclave is replaced by nitrogen for 15 min. Then the autoclave is placed in an oven at 175 °C for 48 h. The obtained suspension is filtered and washed by 500 ml deionized water, dried overnight at 80 °C and calcinated in nitrogen at 600 °C for 2 h with the heating rate of 5 °C/min. The formed lump solid is grinded to powder form, which is the mixture of phases M1 and M2. After removal of phase M2 by using 30% HNO_3, the phase-pure M1 is obtained accordingly.

The $M1/CeO_2$ catalysts are synthesized by a sol–gel method [11]. Cerium nitrate (Sigma-Aldrich, 99%) and citric acid (Sigma-Aldrich, 99.5%) are dissolved in deionized water at a molar ratio of 1:3 with continuous agitation for 24 h at 65 °C and obtained a stable transparent sol with 10 wt.% CeO_2. Powder phase-pure M1 is introduced to the CeO_2 sol at different mass ratios, stirred in 60 °C water bath for 2 h, and dried overnight at 80 °C. Finally, a series of catalysts with 10 wt.%, 20 wt.%, 30 wt.%, 40 wt.%, 50 wt.%, 70 wt.%, 90 wt.% CeO_2 are obtained after the activation by calcination in air for 6 h at 400 °C with the heating rate of 5 °C/min in muffle furnace. The prepared catalysts are named $M1/10CeO_2$, $M1/20CeO_2$, $M1/30CeO_2$, $M1/40CeO_2$, $M1/50CeO_2$, $M1/70CeO_2$, $M1/90CeO_2$, respectively. The pure CeO_2 is also prepared by drying of CeO_2 sol and calcination in air at 400 °C for 6 h. Its catalytic activity is also tested in the ODHE reaction in comparison with other catalysts.

2.2. Catalyst characterization

Metal contents are measured by inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian Vista RL spectrometer).

Specific surface areas of the samples are determined by nitrogen adsorption carried out at 77 K on a Quantachrome Autosorb-6B analyzer. The data are calculated by multipoint BET analysis method in the pressure range of $P/P_0 = 0.05–0.30$. Prior to the measurement, the samples are degassed in vacuum at 300 °C for 2 h.

X-ray diffraction (XRD) patterns of samples are obtained using a Bruker D8 Advance equipment with Cu Kα radiation. 2θ scans are run from 5 to 70° at a rate of 0.5 degree per minute. The spectra are identified with JCPDS database (Joint Committee of Powder Diffraction Standards) and the ICSD database (Inorganic Crystal Structure Database). M1 phase (ICSD 55097) has characteristic diffraction lines located at 2θ = 6.6°, 7.7°, 8.9°, 22.1°.

The morphology of the synthesized catalysts are studied by scanning electron microscopy (SEM, Zeiss, GeminiSEM 500) and JEOL JEM2010 high-resolution transmission electron microscopy (HR-TEM).

X-ray photoelectron spectra (XPS) measurements with a PHI Quantera SXM system equipped with Al Kα X-ray source are made to analyze the ion concentration on catalyst surface. Survey scans (0–1200 eV) and high-resolution Mo (3d), V (2p), Te (3d), Nb (3d), Ce (3d) and C (1s) spectra are obtained. During the scanning for vanadium and cerium, the dwell time is increased from 300 ms to 500 ms and the number of scan times is increased from 6 to 10. The binding energy scale is corrected by setting the C (1s) signal at 284.8 eV. The XPS data analysis for vanadium is performed with XPSPEAK 4.1 software and that for cerium is performed with Thermal Advantage 4.88 software. The binding energy data of reference materials are obtained from NIST X-ray Photoelectron Spectroscopy Database.

2.3. Catalyst test

All of the catalysts for ODHE reaction are evaluated in a fixed-bed quartz tubular reactor (8 mm i.d., 750 mm in length) heated by a furnace, in which the temperature in the middle of the catalyst bed is measured with a thermocouple. The catalyst particles with 0.3 g in mass are diluted with 3.0 g quartz particles with the size of about 200 μm to achieve the isothermal operation. The feed composition is $30C_2H_6/20O_2/50He$. The contact time is defined as W/F_{C2H6} (W is the catalyst mass and F_{C2H6} is the ethane molar flow rate), and the total flow rate is varied from 22 ml/min to 66 ml/min.

The reactants and products are analyzed with an online Shimadzu GC 2014 gas chromatograph equipped with A PorapakQ column for identifying CO_2, C_2H_4 and C_2H_6 and a 5A molecular sieve column for O_2, N_2, CH_4 and CO. A blank run is conducted by loading the reactor with only quartz sands at the same reaction conditions. No ethane conversion is detected, indicating that the homogeneous gas phase reaction can be neglected.

The conversion of ethane and the selectivity to products are calculated as follows:

$$X_{C_2H_6} = \left(1 - \frac{2f_{C_2H_6}}{2f_{C_2H_6} + 2f_{C_2H_4} + f_{CO} + f_{CO_2}}\right) \times 100\% \tag{1}$$

$$S_{C_2H_4} = \frac{2f_{C_2H_4}}{2f_{C_2H_4} + f_{CO} + f_{CO_2}} \times 100\% \tag{2}$$

$$S_{CO} = \frac{f_{CO}}{2f_{C_2H_4} + f_{CO} + f_{CO_2}} \times 100\% \tag{3}$$

$$S_{CO_2} = \frac{f_{CO_2}}{2f_{C_2H_4} + f_{CO} + f_{CO_2}} \times 100\% \tag{4}$$

where X_{C2H6} is the ethane conversion, S is the selectivity to a certain product, and f is the molar fraction in the effluent gas.

3. Results and discussion

3.1. Catalyst performance for ODHE

3.1.1. Effect of contact time

The performances of catalysts M1 with and without addition of CeO_2 in ODHE process at 400 °C with different contact times are presented in Figs. 1–3. The detailed experiment data tested at 400 °C and 18.52 $g_{cat}·h/mol_{C2H6}$ are listed in Table 1. Each data is collected after 2 h since the change of flow rate. Ethylene, carbon

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