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A self-redox pure-phase M1 $MoVNbTeO_x/CeO_2$ nanocomposite as a highly active catalyst for oxidative dehydrogenation of ethane

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ABSTRACT

The M1 phase of $MoVNbTeO_x$ mixed metal oxide is one of the most attractive catalysts for the oxidative dehydrogenation of ethane (ODHE). This work presents the performance of pure-phase $M1/CeO_2$ nanocomposite catalysts in the ODHE process. Nanosized CeO_2 is successfully added to pure-phase M1 catalysts by physical mixing and by a sol–gel method, so that $M1/CeO_2$ nanocomposites with different CeO_2 particle sizes are formed. The experimental results show that the introduction of CeO_2 can increase the abundance of V^{5+} on the catalyst surface by a self-redox solid-state reaction during activation at 400 °C in air. Improvement of catalyst performance can be observed with the decrease of CeO_2 dimensions. The nanocomposite catalyst consisting of M1 particles and 4.4 nm CeO_2 exhibits the best catalyst productivity of 0.66 $kg_{C_2H_4}/kg_{cat}$ h with 20% lower cost than for pure-phase M1 catalysts at 400 °C. It is anticipated that a high-throughput and low-cost ODHE process could be realized on $M1/CeO_2$ nanocomposites.

1. Introduction

Ethylene, as one of the indicators that measure the petrochemical development level of countries all over the world, is the principal chemical commodity in the world and an important raw material for polymers [1]. The oxidative dehydrogenation of ethane (ODHE) has been extensively considered as an attractive and interesting process for ethylene production over the past few decades due to its great benefits of high theoretical ethane conversion, low energy consumption, and low risk of catalyst deactivation caused by carbon deposition [2–7]. The ODHE reaction network consists of selective oxidation of ethane to ethylene,

$$C_2H_6 + 0.5O_2 = C_2H_4 + H_2O \quad \Delta_rH^\theta = -105.5\ \text{kJ/mol}, \tag{1}$$

as the main reaction and the overoxidation of ethane and ethylene,

$$C_2H_6 + 3.5O_2 = 2CO_2 + 3H_2O \quad \Delta_rH^\theta = -1429\ \text{kJ/mol} \tag{2}$$

$$C_2H_6 + 2.5O_2 = 2CO + 3H_2O \quad \Delta_rH^\theta = -137.0\ \text{kJ/mol} \tag{3}$$

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O \quad \Delta_rH^\theta = -1323\ \text{kJ/mol} \tag{4}$$

$$C_2H_4 + 2O_2 = 2CO + 2H_2O \quad \Delta_rH^\theta = -31.5\ \text{kJ/mol}, \tag{5}$$

as side reactions. Supported catalysts (NiO-based [8,9] and VO_x-based [10–12] metal oxide catalysts) and unsupported catalysts ($NiWO_x$-based [13], $NiNbO_x$-based [14–17], $NiSnO_x$-based [18], and $MoVO_x$-based metal mixed oxide catalysts [19,20]) both show high activity in the ODHE reaction at a relatively low temperature (<500 °C). Among all the catalytic systems above, a mixed metal oxide catalyst, $MoVNbTeO_x$, is one of the most outstanding catalysts for ODHE [21–32].

The $MoVNbTeO_x$ catalyst usually consists of M1 and M2 crystalline phases and minor amounts of other phases such as Mo_5O_{14}-type structures or binary MoV and MoTe oxides [21–24]. M1 is an orthorhombic phase with space group Pba2, while M2 is a pseudo-hexagonal phase with space group P6mm [33–36]. Previous studies have indicated that the M1 phase possesses the only V^{5+} ions as ethane activation sites [24,37,38], and the performance of $MoVNbTeO_x$ catalysts increases with the purity of the M1 phase [25]. It is acknowledged that the ODHE process with pure-phase M1 $MoVNbTeO_x$ catalyst seems to be the most competitive choice nowadays in comparison with the traditional industrial processes (steam cracking and catalytic dehydrogenation) in ethylene production. The high activity (ethane conversion >80%) and selectivity (ethylene selectivity >90%) of the $MoVNbTeO_x$ catalyst can easily reach the economic feasibility of a 65–70% ethylene yield [39–42]. However, the ethylene productivity achieved with the reported catalyst is still much lower than the industrial

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requirements for commercialization (1.00 $kg_{C_2H_4}/kg_{cat}$ h catalyst productivity) [41].

Pure-phase M1 catalyst can be prepared by hydrothermal synthesis or a slurry method with a suitable purification process [43–46,28]. Due to the expensive chemical source for catalyst preparation and mass leaching caused by the post-treatment, the high price of this catalyst will also be one of the vital reasons for the industrial implementation of the ODHE process. Therefore, addition of low price promoters/active components naturally becomes an easy and effective method for catalyst improvement and cost reduction. Several different metal oxides (SiO_2, γ-Al_2O_3, α-Al_2O_3, Nb_2O_5, or ZrO_2) have been introduced into the $MoVNbTeO_x$ catalysts. However, the improvement is limited because they can only function as diluters with little influence on the surface chemistry of the catalyst [26,28].

In the present work, pure-phase M1 $MoVNbTeO_x/CeO_2$ (M1/CeO_2) nanocomposites for the ODHE reaction were prepared by physical mixing and a sol–gel method. CeO_2 itself is an excellent oxygen storage material due to its unique redox properties [47]. Moreover, CeO_2 is a catalyst with low activity and selectivity in the ODHE reaction at a temperature lower than 500 °C [48,49]. We utilized CeO_2 as an oxidant in the pure-phase M1 catalyst on the nanoscale to increase the oxidative state of active sites (i.e., V^{5+} abundance) on the catalyst surface with the aim of catalytic performance improvement. The introduced CeO_2 was expected to replace the M1 catalyst of the same mass to realize higher catalyst productivity in the ODHE reaction at lower catalyst cost. All the catalyst evaluations were carried out in a laboratory-scale fixed-bed reactor and the properties of the catalyst were characterized by XRD, BET, ICP, XPS, H_2 TPR, and TEM.

2. Experimental methods

2.1. Catalyst preparation

$MoVNbTeO_x$ catalysts were prepared by hydrothermal synthesis in a 100-ml Teflon autoclave [45,46]. Ammonium heptamolybdate (Sigma–Aldrich, 99.0%), vanadyl sulfate (Sigma–Aldrich, 97%), telluric acid (Sigma–Aldrich, 98%), and ammonium niobate oxalate hydrate (Sigma–Aldrich, 99.99%) were used as starting materials to prepare the initial slurry precursor containing the metals in a molar ratio of Mo/V/Te/Nb = 1/0.25/0.23/0.12. Portions of 4.46 g ammonium heptamolybdate, 1.63 g vanadyl sulfate, and 1.35 g telluric acid were dissolved in 50 mL of deionized water as solution 1, and 1.18 g ammonium niobium oxalate was dissolved in 25 mL of deionized water as solution 2 at 80 °C. Solution 1 was stirred at 80 °C for 30 min till it turned into a yellow slurry. Solution 2 was added to solution 1 after it was cooled down to 40 °C and stirred for 10 min. After residual air in the slurry precursor was replaced by nitrogen, hydrothermal synthesis was carried out at a temperature of 175 °C for 48 h. The obtained suspensions were filtrated and the precipitate was washed with 200 mL deionized water. The solid precursor material was then filtered, dried at 80 °C overnight in air, and calcined at 600 °C for 2 h in nitrogen. A 7.5% H_2O_2 solution was used to purify the $MoVNbTeO_x$ mixture of the M1 and M2 phases. As a result, the M2 phase was totally dissolved during the stirring at 60 °C for 2 h. About 1.5 g of pure-phase M1 catalyst was finally obtained after filtration, washing, and drying at 110 °C overnight.

Two methods were employed to prepare M1/CeO_2 catalysts.

- The physical mixing method: M1 catalyst was mixed and ground with CeO_2 (Sigma–Aldrich, 99.95%) at mechanically for 15 min in a mass ratio of 4:1. Then the mixture was calcined at 400 °C in air for 2 h to enhance the dispersion of CeO_2. A nanocomposite catalyst with 20 wt.% CeO_2, namely M1-Ce-PM, was obtained.
- The sol–gel method: Cerium nitrate (Sigma–Aldrich, 99%) and citric acid (Sigma–Aldrich, 99.5%) were dispersed in water at a molar ratio of 1:3 with continuous agitation for 24 h at 65 °C. A stable transparent sol with 10 wt.% CeO_2 was obtained. Catalyst M1 was added to the sol at a mass ratio of 2:5, stirred for 2 h, and dried overnight at 110 °C. Finally, a nanocomposite catalyst with 20 wt.% CeO_2 was obtained after the activation by calcination in air for 2 h at 400 °C. The prepared nanocomposite catalyst was named M1-Ce-SM.

CeO_2 powder was also prepared by drying of CeO-$_2$ sol and calcination in air for 2 h at 400 °C. Its catalytic performance was also tested in the ODHE reaction in comparison with other catalysts.

2.2. Catalyst testing

Portions of catalysts of 0.5 g (M1, M1-Ce-PM, M1-Ce-SM, and CeO_2) were loaded into a small fixed-bed reactor (a quartz tube with 8 mm i.d. 750 mm in length) for catalyst testing of the ODHE process. The catalysts were diluted with 5.0 g SiC particles (Sigma–Aldrich, 99.0%, diameter 0.1–0.2 mm) to minimize heat effects during the reaction. A movable thermocouple of diameter 1.0 mm was inserted into the reactor outlet of the packed catalyst bed in order to measure the temperature profile. The gas feed consisted of ethane, oxygen, and helium at a total flow rate of 30 ml/min and a C_2H_6/O_2/He molar ratio of 30/20/50. The reaction temperature was maintained at 400 °C. The contact time, defined as $W/F_{C_2H_6}$ (W is the mass of the M1 phase in catalyst and $F_{C_2H_6}$ is the ethane molar flow rate) was varied between 6.91 and 20.74 g_{cat} $h/mol_{C_2H_6}$. During the heating of the fixed-bed reactor, helium was the only gas fed through the reactor tube. Once the reaction temperature was reached, a gas feed with the appropriate composition was introduced into the system. The steady-state data on catalyst performance were recorded 6 h after the beginning of the reaction, because there is usually an induction period for the catalysts in oxidative dehydrogenation of alkanes. The catalytic activity of catalysts M1, M1-Ce-PM, and M1-Ce-SM at 350 °C was also measured to estimate their observed activation energy.

The reactor effluent was analyzed by an online gas chromatograph (GC) equipped with two columns. A PorapakQ column was used to separate the CO_2, C_2H_4, and C_2H_6 and a 5A molecular sieve column was used to separate the O_2, N_2, CH_4, and CO. A blank run was conducted by loading the reactor with only SiC under the same operating conditions. No ethane conversion was observed, indicating that the effect of the homogeneous gas phase reaction can be neglected.

The conversion and selectivity for the ODHE process are defined as

$$X_{C_2H_6} = \left(1 - \frac{2f_{C_2H_6}}{2f_{C_2H_6} + 2f_{C_2H_4} + f_{CO} + f_{CO_2}}\right) \times 100\% \tag{6}$$

$$S_{C_2H_4} = \left(\frac{2f_{C_2H_4}}{2f_{C_2H_4} + f_{CO} + f_{CO_2}}\right) \times 100\% \tag{7}$$

$$S_{CO_2} = \left(\frac{f_{CO_2}}{2f_{C_2H_4} + f_{CO} + f_{CO_2}}\right) \times 100\% \tag{8}$$

$$S_{CO} = \left(\frac{f_{CO}}{2f_{C_2H_4} + f_{CO} + f_{CO_2}}\right) \times 100\%, \tag{9}$$