Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/catalysis

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Oxidative dehydrogenation of ethane to ethylene over phase-pure M1 MoVNbTeO_x catalystin a micro-channel reactor

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Received (in XXX, XXX) XthXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Phase-pure M1 MoVTeNbO_x catalyst plateshave beenpreparedon a metal-ceramic complex substrate by a dip-coating method. At a temperature of 420°C and atmospheric pressure, the performance of the M1-PVA catalyst plate in a micro-channel reactor approached an ethane conversion of ~ 60% and ethylene selectivity of ~ 85% with a high catalyst productivity of 0.64 $kg_{C2H4}/kg_{cat}/h$. Due to the excellent heat transfer ability, it is demonstrated that a micro-channel reactorcan achieve the same reactor productivity as a traditional fixed-bed reactor within only 20% of the volume. XRD, SEMand ICP characterization indicated that the M1-PVA catalyst plate has a high stability in the micro-channel system.

1. Introduction

Ethylene, is an important bulk chemical being one of the largest consumed worldwide organic products and also one of the indicators used to measure the petrochemical development level of countries[1].It is well-known that ethylene is mostly produced by steam cracking of naphtha and to a smaller extent by the direct catalytic dehydrogenation of ethane[2]. However, obvious drawbacks exist in the steam cracking process, i.e. low selectivity and high energy consumption,as well asin the direct catalytic dehydrogenation, i.e. thermodynamicconstraints and catalyst coking, whichresult in increased operating costs[3].

In contrast to the conventional ethylene production processes, oxidative dehydrogenation of ethane (ODHE) has attracted more and more interest due to several conceptual advantages:

(i) excess heat supply by external means can be avoided by changing the endothermic process (i.e. steam cracking or direct catalytic dehydrogenation) to an exothermic process (i.e. ODHE process);

(ii) a high energyefficiency can be realized by lowering the reaction temperature to 400 - 600°C

(iii) a high ethane conversion and ethylene selectivity can be obtained by using a new chemical equilibrium;

(iv) catalyst coking can be eliminated by introducing oxygen to the reactive system;

Moreover, ethane, as the feed for the ODHE process, is abundant in shale and associated gas, which has becomean increasingly important energy source around the world from the start of the 21st century.

Since the 1970's, some of the catalysts used in the methane coupling reaction have been directly applied in the ODHE process,while more entirely new catalytic systems have been developed during the last 40 years[4, 5]. Among them, the MoVNbTeO_x catalyst shows the highest activity and selectivity at a relatively low temperature of about 400°C[6-18]. MoVNbTeOx catalysts consist 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. The catalyst activity increases with the purity of the M1 phase,where a phase-pure M1 catalyst can be obtained by suitable synthesis methods with a post-treatment procedure[15-17]. In addition to the catalyst preparation,efficient heat removal from the ODHEprocess is a major concernfor reactor design. For instance, temperature gradients can hardly be eliminated in a traditional fixed-bed reactor unless the catalyst bedis diluted withinert particles in a large ratio[19]. This will greatly increase the fixed cost and become a big challenge to realize an economically industrial-scale production of ethylene based on the ODHE process. As a comparison, a micro-channel reactor is inherently suitable for the highly exothermic reaction systems due to the excellent heat transfer and removal capabilities[20, 21]. Meanwhile, gas flow in micro-channel reactorsare close to plug-flow, which could provide a better control of the ethylene selectivity of the oxidative dehydrogenation. The mass production of chemicals in industry can be easily implemented by using the numbering up methodology[22-24].

Recently, *Nguyenet al.* proposed a ceramic catalytic micro-scale reactorcomposed of inverted beaded monoliths (i.e. SiC foam) as catalyst supportfor the MoVTeNbO_x catalyst, and tested this reactor for the oxidative dehydrogenation of ethane[25]. Unfortunately, the reactor performance was still far from that in a fixed-bed reactor under the same conditions, which could be attributed to a low content of the M1 phase and the existence of other phases like $TeMo_5O_{16}$ or MoO_3 in the catalyst.

Our earlier work has demonstrated that using a metal-ceramic complex substrate can successfully maintain the physical stability and chemical activity of a catalyst layer for endothermic and exothermic processes (i.e. methane steam reforming and syngas methanation)[26, 27]. In this work, we will utilize this experience to prepare a phase-pure M1 catalyst layer on the substrate and investigate the ODHE reaction in a micro-channel reactor. Catalyst evaluation will also be carried out in a small-size fixed-bed reactor at the same conditions as a comparison in order to demonstrate the advantages of the micro-channel reactor for improved heat management.

2. Experimental

2.1 Catalyst plate preparation

Firstly, phase-pure M1 MoVNbTeO_x catalysts were prepared by hydrothermal synthesis with a hydrogen peroxide post-treatment procedure[15-17]. Secondly, metal-ceramic complex substrates were used as the supports to load the catalyst which was made by a thermal spray method. Finally, the catalyst powder mixed with an appropriate binder was coated on the substrate by a dip-coating methodto prepare the catalyst layers asdetailedbelow.

(i) Preparation of the phase-pure M1 $MoVNbTeO_x$ catalyst

Phase-pure M1 $MoVNbTeO_x$ catalysts, named as M1, were prepared by hydrothermal synthesis in a 100ml Teflon autoclave. Ammonium heptamolybdate (Sigma-Aldrich, 99.0%), vanadyl sulfate (Sigma-Aldrich, 97%), telluric acid (Sigma-Aldrich, 98%) andammonium niobium oxalate (Sigma-Aldrich, 99.99%) were used as starting materials to prepare the initial slurry precursor containing the metals in a molar ratio of 1Mo:0.25V:0.12Nb:0.23Te. After replacing residual air by nitrogen, hydrothermal synthesis was carried out at a temperature of 175°C for 48 h. The obtained suspensions were filtrated, washed, dried at 80°C for 16 h in air and calcined at 600°C for 2h. Phase-pure M1 catalyst was obtained after a purification process of stirring in the 7.5% H_2O_2 solution at 60°C for 3h.

(ii) Manufacture of the metal-ceramic complex substrate

A layer of α-$Al_2O_3$was thermally sprayed onto a FeCrAlloy plate to manufacture the metal-ceramic complex substrate. Some ceramic particles permeatedin the metal phase during the high temperature process and the binding force between the ceramic layer and metallic layerwas greatly enhanced[28].

(iii) Preparation of the binder solution

Two different binders (i.e. AlOOH sol and polyvinyl alcohol(PVA) solution) were used. The AlOOH sol was prepared in the following procedure: commercialaluminum hydroxide powder (Sinopharm Chemical Reagent Co., Ltd.) was dispersed inwater with a mass fraction of 20% under continuous agitation. A 5 mol/L HNO_3aqueous solution was used to adjust the pHvalue from 7 to 2. The solutionwas stirredfor5hat85 °Canda stablesolwasobtained. The PVA solution was prepared by adding 6.25 wt% PVA powder (Sinopharm Chemical Reagent Co., Ltd.) to water under continuous stirring for 2 h at 60 °Cafter which a stable solution was obtained after cooling down and stirring overnight.

(iv) Coating of catalyst layer

The M1 powder and binder solution was mixed for 24 h at room temperature with a mass ratio of 1:3 and 1:1, respectively, for the PVA solution and AlOOH sol to obtain a stable slurry for dip-coating[29]. The metal-ceramic complex substrate was immersed into this slurry for 3 min, and then withdrawn at a constant speed of 3 cm/min to ensure a uniform coating, dried at room temperature for 2-4 h. The humidity was kept between 60% - 70% to decrease the evaporation rate of water, preventing the formation of cracks. Finally, the catalyst plate wascalcined at 400°C for 6 h in air. The coating procedure was repeated until the catalyst loading reached the required amount of 0.02 g/cm^2.

The M1 catalyst plates were named as M1-Al_2O_3 and M1-PVA, respectively, according to the different binder.

2.2Catalyst plate preparation

X-ray diffraction (XRD) patterns of the catalyst were recorded on a Bruker D8 Advance equipment with a nickel-filtered Cu-Kα radiation (λ = 0.1542 nm) in the 2θ range of 0 - 90°, operating at 40 kV and 45 mA. XRD patterns were analyzed usingMDI Jade 6.5 software forphase identification by comparing the collected pattern with the standard in the PDF2004 database.

The morphology of the bulk catalyst was characterized using a scanning electron microscope (SEM, JEOL, JSM-7401F) and inductively coupled plasma-optical emission spectrometer(ICP-OES, Varian Vista RL spectrometer) to analyze the metal content of the $MoVNbTeO_x$ catalyst. The XRD patterns of catalyst plate were obtained directly from the plate whilst the SEM and ICP analyses were carried out on the powders scrapped off the catalyst plate.

2.2 Catalysttesting

The dimensions and assembly of the reactors used in the ODHE process are illustrated in Fig. 1. In the small-sized fixed-bed reactor, 0.50 g M1 catalyst wasdiluted with SiC powder (Sigma-Aldrich, 99.0%, 0.1-0.2 mm) in a certain mass ratio (e.g. 0.25-10.0) to minimize heat effects during the reaction and, thereafter, loaded in a quartz tube (8 mm i.d. and 750mm length). A removable thermal couple of 1.0 mm diameter was inserted from the reactor outlet to the fixed-bed in order to measure the temperature profile. To facilitate the reaction in the micro-channel reactor, the catalyst plate was first cut into the size of 2 cm ×4 cm. Then four sheets of the catalyst plates, keeping the same catalyst loading as in the fixed-bed reactor,were inserted into the slits of micro-channel reactor separately.As a result the space between the plates formed a channel, with the size of 1.6 cm ×8.0 cm × 0.04 cm, as similarly shown in our previous work [21, 22]. A thermal couple of 1.0 mm diameter was inserted into the reactor to obtain the outlet temperature of the channel.

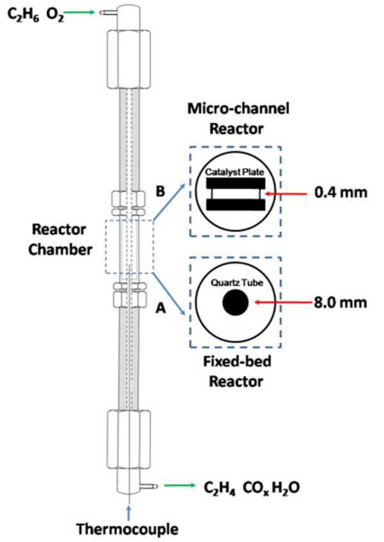


Figure 1 Schematic diagram of (A) fixed-bed reactor and (B) micro-channel reactor

The gas feed consisted of ethane, oxygen and helium with a total flow rate of 30 Nml/min and a $C_2H_6/O_2/He$ molar ratio of 30/20/50. The contact time W/F_{C2H6}(W is the catalyst mass and F_{C2H6} is the ethane molar flow rate) was maintained at20.74 g_{cat}·h/mol$_{C2H6}$.The reaction temperature was varied between340 °C and440 °C. During the reactor heating, helium was the only gas fed through the reactor tube. Once the reaction temperature was reached, the gas feed with the appropriate reaction composition was introduced into the system. The steady-state data of the catalyst performance was obtained 6 h after the beginning of the reaction.

The reactor effluent gases were analyzed by online gas chromatography (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 fixed-bed reactor with only SiC and using the same operating conditions. No ethane conversion was observed, indicating that the effect of the homogeneous gas phase reaction could be neglected.

The conversion and selectivity for ODHE process are defined as follows:

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

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

$$S_{CO_2}=\left(\frac{f_{CO_2}}{2f_{C_2H_4}+f_{CO}+f_{CO_2}}\right)\times 100\% \quad (3)$$

$$S_{CO}=\left(\frac{f_{CO}}{2f_{C_2H_4}+f_{CO}+f_{CO_2}}\right)\times 100\% \quad (4)$$

Where, X is the conversion, S is the selectivity to a certain product, and f is the molar fraction in the effluent gas.

The catalyst productivity and reactor productivity for ODHE process are calculated as follows:

$$Catalyst \quad Productivity=\frac{F_{C_2H_6}\cdot X_{C_2H_6}\cdot S_{C_2H_4}\cdot M_{C_2H_4}}{m_{cat}} \quad (5)$$

$$Reactor \quad Productivity=\frac{F_{C_2H_6}\cdot X_{C_2H_6}\cdot S_{C_2H_4}\cdot M_{C_2H_4}}{V_{reactor}} \quad (6)$$

Where, F is the molar flow, M is the molar mass, $m_{cat}$is the mass of M1 catalyst excluding the mass of diluter or binder and $V_{reactor}$ is the volume of the reactor. In the fixed-bed reactor, $V_{reactor}$ is the volume of catalyst bed including M1 catalyst and SiC diluter. In the micro-channel reactor, $V_{reactor}$ is the constant channel space between the two catalyst plates.

3. Results and discussion

3.1 Catalyst characterization

3.1.1 Crystalline phase identification by XRD

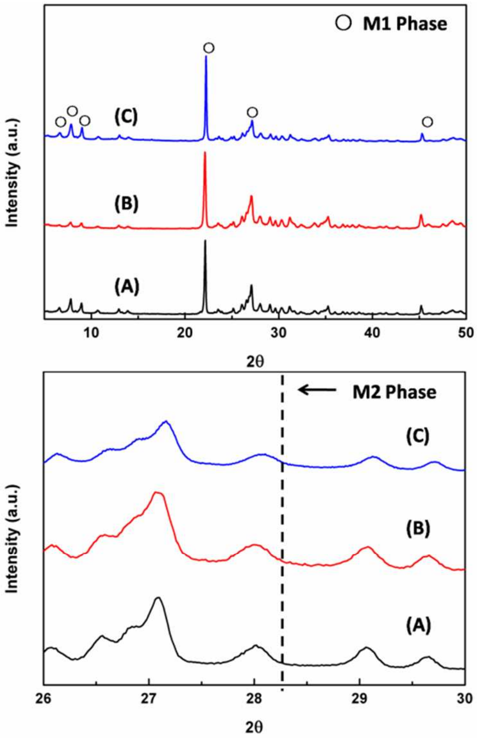
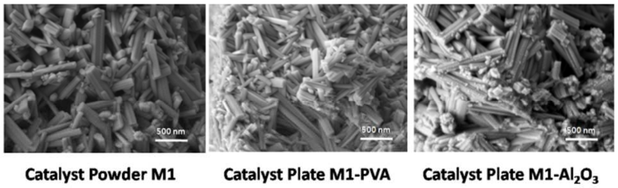


Figure 2 XRD patterns (above) and enlargement of region from 2θ = 26 – 30° (below) of (A) Catalyst plate M1-PVA; (B) Catalyst plate M1-Al_2O_3; (C) Catalyst powder M1

The XRD patterns of the catalyst powder and catalyst plates are shown in Fig. 2. Only the M1 phase (ICSD-55097) exists in both the catalyst powder and catalyst layers and no characteristic peak of the M2 phase (ICSD-55098) can be observed in the enlargement of the region from 2θ = 26-30°. Moreover, no alumina peaks were detected by XRD for the catalyst plate prepared with the AlOOH sol as the binder. It is probably because the signal of the γ-Al_2O_3, which is the main product after calcination of the AlOOH sol, is too weak in comparison to the $MoVNbTeO_x$ crystals.

3.1.2 Crystal morphology detection by SEM

As shown in Fig. 3, the size of $MoVNbTeO_x$ particles on the M1-PVA plates is similar to the original catalyst powder (i.e. ~ 500 nm length and ~ 100 nm widths). The PVA was mostly eliminated after calcination in air for the M1-PVA catalyst plate. However, there was some alumina particles located between the rod-like crystals of the M1 phase.They formed an alumina film with a thickness of approximately 10 nm on the surface of the M1 crystals coatedon the catalyst plate.



Catalyst Powder M1 **Catalyst Plate M1-PVA** **Catalyst Plate M1-Al_2O_3**

Figure 3 SEM images of the fresh $MoVNbTeO_x$ catalyst powder and plates

The chemical and morphology properties of the catalysts are summarized in Table 1. It indicates that phase-pure M1 catalyst plates can be successfully prepared on the metal-ceramic complex substrate based on a dip-coating method. Both the PVA solution and the AlOOH sol have no obvious effect on the M1 phase purity and the M1 particle size during the coating procedure.

Table 1General properties of the $MoVNbTeO_x$ catalyst powder and plates

	Catalyst M1	Catalyst Plate M1-PVA	Catalyst Plate M1-Al_2O_3
Fresh Catalyst Composition	$MoV_{0.19}Te_{0.08}$ $Nb_{0.23}$	$MoV_{0.20}Te_{0.08}$ $Nb_{0.25}$	$MoV_{0.19}Te_{0.08}$ $Nb_{0.22}$ $Al_{0.31}$
Used Catalyst[a]Composition	$MoV_{0.19}Te_{0.08}$ $Nb_{0.24}$	$MoV_{0.20}Te_{0.08}$ $Nb_{0.24}$	$MoV_{0.19}Te_{0.08}$ $Nb_{0.22}$ $Al_{0.31}$
Particle diameter[b](nm)	106±10.4	102±9.8	122±11.5
Particle length[b](nm)	210±31.2	212±32.4	234±35.1

a. ODHE reaction was performed at 420 °C with a contact time of $20.74 g_{cat}\cdot h/mol_{C2H6}$ and a $C_2H_6/O_2/He$ molar ratio at the reactor inlet of 30/20/50 for 36 h.

b. Determined based on the average diameter and length of at least 100 particles from the SEM images.

3.2 Catalyst performance for oxidative dehydrogenation of ethane

The powder catalyst waspacked into a quartz tube and the coated plates were inserted into the slits (Fig. 1). The fixed-bed reactor and the micro-channel reactor were both tested in the ODHE process. Influences of the operation parameters such as (oven) temperature, contact time, diluent amount in the fixed-bed reactorand the influence of binder were investigated.

3.2.1 Influence of diluent in fixed bed reactor

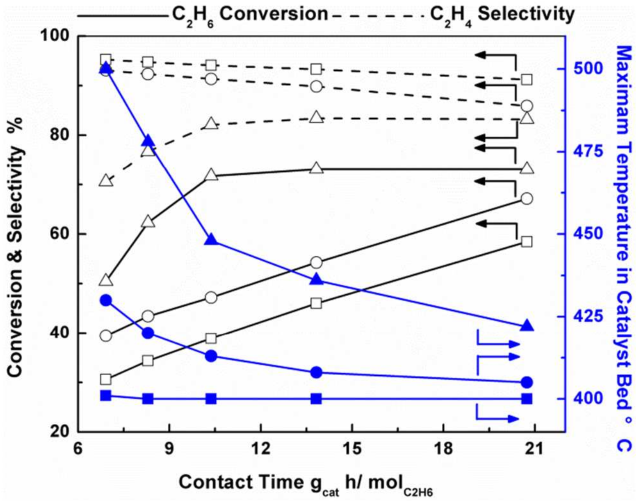


Figure 4 Ethane conversion, ethylene selectivity and hot spot temperature in the catalyst bed as a function of contact time for M1 catalyst powder in the fixed-bed reactor. Experiments were performed at 400 °C and 1.0 atm with a reactor inlet $C_2H_6/O_2/He$ molar ratio of 30/20/50and a diluter to M1 catalyst mass ratio of (▲△) 1:4, (●○) 5:1 and (■□) 10:1.

Fig. 4 shows the influence of the diluent on the reaction performance in the fixed-bed reactor. The hot spot was very apparent in the fixed-bed reactor when the oven temperature was maintained at 400 °C unless the mass of SiC was 10 timesthe M1 catalyst.A similar conclusion was proposed by *Steinfeldt et al.* that the VO_x/Al_2O_3catalyst should be diluted with quartz in a mass ratio of 1:9 to minimize the temperature gradient in the oxidative dehydrogenation of propane[19]. Nearly a 100 °Ctemperature difference between the hot spot and oven temperature was observed at the situation with the least SiC amount (1:4) in use. An obvious deactivation caused by the destruction of the M1 phase crystal structure at high temperature led to a simultaneous decrease of ethane conversion and ethylene selectivity at short contact times[14]. This indicated that the heat effect (i.e. 126.4 kJ/mol C_2H_6) caused by this exothermic process was still very strong although the feed gas was diluted by helium. The following experiments in the fixed-bed reactor were all carried out with the diluter to M1 catalyst mass ratio of 10:1.

3.2.2 Influence of binderin micro-channel reactor

Fig. 5 shows the influence of temperature on the catalytic performance of the M1-PVA and M1-Al_2O_3catalyst platesfor the ODHE reaction. It can be seen that with an increase of temperature, both the ethane conversion and oxygen conversion increase but the ethylene selectivity decreases.The ODHE reaction is not thermodynamically limited but instead controlled by the kinetics. The little difference of catalyst performance in the fixed-bed reactor with the diluter to M1 catalyst mass ratio of 10:1 (Fig. 4) and the micro-channel reactor at 400 °C (Fig. 5) implies a constant temperature profile in the micro-channel reactor. This indicates that the micro-channel reactor is very promising and suitable for kinetics measurement and mechanismdeduction for the ODHE reaction.

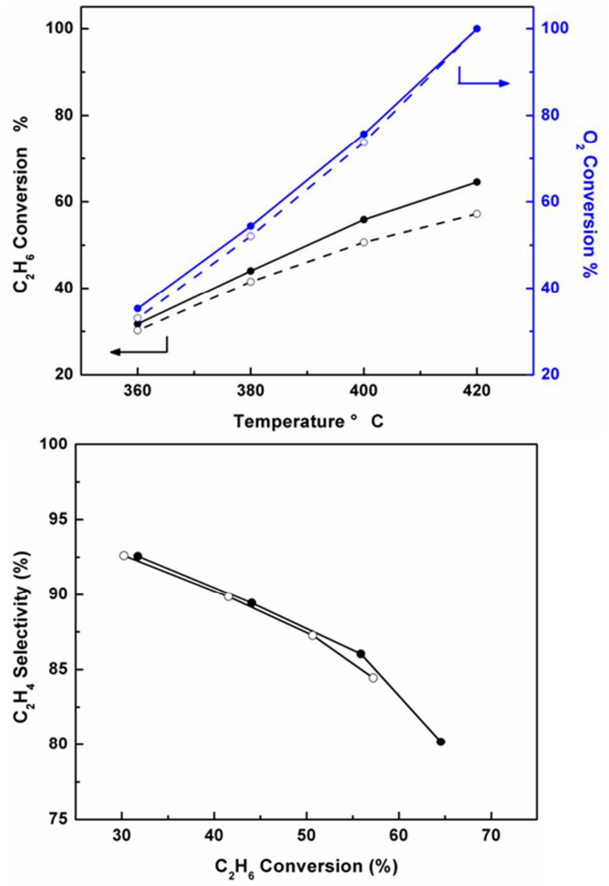


Figure 5 Ethane conversion and oxygen conversion as a function of reaction temperature(above)and ethylene selectivity as a function of ethane conversion (below) for the M1-PVA catalyst plate (●) and M1-Al_2O_3 catalyst plate (○) in a micro-channel reactor. Experiments were performed at 1.0 atmwith a $C_2H_6/O_2/He$ molar ratio of 30/20/50 at reactor inlet and a contact time of 20.74g_{cat}·h/mol_{C2H6}.

At the same time, both the conversions at the same conditions and ethylene selectivity at the same level of conversions on catalyst plate M1-PVA are higher than that of the M1-Al_2O_3catalyst plate. It was speculated that probably the alumina layer (~ 10 nm) formed on the surface of the M1-Al_2O_3 catalyst plate during the calcination would increase the mass transfer resistance and limit the conversions of ethane and oxygen. However, the apparent activation energy of ODHE (> 40 kJ/mol) for M1-Al_2O_3 catalyst plate can rule out the absence of external mass transfer limitations. The main reason for the differences of catalytic performance between these two catalyst plates was caused by the formation of impure phases in Al_2O_3 catalyst plate, which will be further discussed in section 3.3

Moreover, the temperature detected by the thermocouple at the outlet of the channel was always maintained at the same value as the oven temperature during the experiments, which demonstrates the excellent heat transfer capacity of the micro-channel reactor.

3.2.3 Comparison of micro-channel reactor and fixed-bed reactor

According to the above analysis, the micro-channel reactor with the M1-PVA catalyst plate is chosen for comparison with the fixed-bed reactor. Fig. 6 shows the influence of the reactor types on the catalytic performance of the phase-pure M1 catalyst for the ODHE reaction at 400°C with different contact times. The ethane conversion in the micro-channel reactor is very close to that of the fixed-bed reactor. It is sufficient to illustrate that the micro-channel reactor has at least the same temperature control ability as the fixed-bed reactor with a large amount of diluent. The consumption of oxygen is larger in the micro-channel reactor which results in a lower ethylene selectivity and higher carbon oxide's selectivity than the fixed-bed reactor. Usually, the complete decomposition of the PVA is carried out at more than 500 °C in air[30]. However, the calcination of the catalyst plate was carried out at 400 °C to inhibit the phase transformation of the M1 catalyst at high temperature. The high oxygen consumption in the micro-channel reactor is probably due to the slight amount of carbon residue produced by incomplete decomposition of PVA.

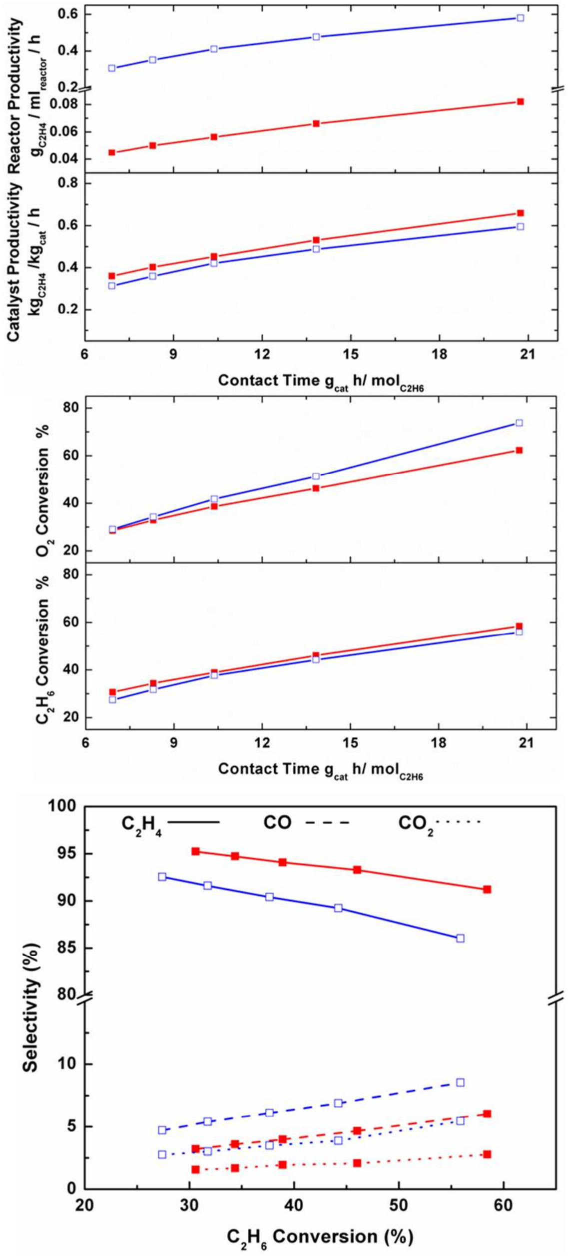


Figure 6 Ethane and oxygen conversion, catalyst productivity and reactor productivity as functions of contact time and product selectivity as functions of ethane conversion for M1 catalyst in fixed-bed reactor (■) and in micro-channel reactor (□). Experiments were performed at 400 °C and 1.0 atm with a C_2H_6/O_2/He molar ratio of 30/20/50 at reactor inlet.

The space-time yields, catalyst productivity and reactor productivity, are defined to compare the productivity of the micro-channel reactor and the fixed-bed reactor. Catalyst productivity refers to the quantity of product produced per unit mass of catalyst per unit time, and reactor productivity refers to the quantity of product produced per volume of reactor per unit time.Different from the catalyst productivity, reactor productivity also considers the temperature-controlled capacity of reactor except for the catalyst performance to evaluate the process productivity. Although the micro-channel reactor did not exceed the fixed-bed reactor in terms of catalyst productivity, it has shown obvious advantages in terms of reactor productivity due to its excellent heat transfer ability. It can be concluded that the M1-PVA catalyst plates prepared in this work show adequate activity and high productivity to catalyze the ODHE reaction in the micro-channel reactors.

3.3 Catalyst stability

Time-on-stream experiments were performed in the above-mentionedreactors in order to investigate the stability of the phase-pure M1 catalyst. As shown in Fig. 7,over a 36 h time-on-stream period, the M1-Al_2O_3 catalyst plate is seen to deactivate from 50 % to 42 % in terms of ethane conversion whilst the M1catalyst powder and M1-PVA catalyst plate remain relativelystable. Generally speaking, the main reasons for catalyst deactivation in the ODHE reaction are leaching of an active component and the formation of impure phases (i.e. MoO_2 and (V, Nb)-substituted θ-Mo_5O_{14})[7, 14].These two possible reasons are analyzed below for a better understanding of the process.

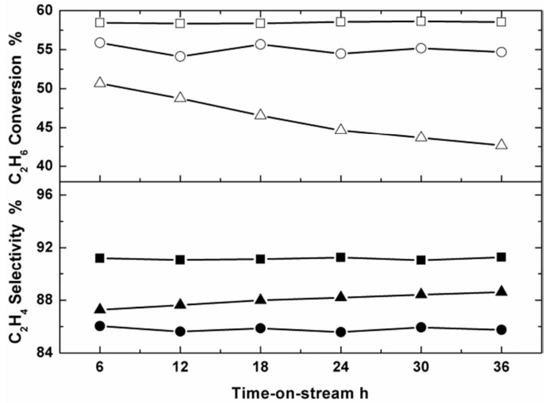


Figure 7 Ethane conversion and ethylene selectivity as functions of time-on-stream for catalyst powder M1 in fixed-bed reactor (■□) and catalyst plate M1-PVA (●○) and M1-Al_2O_3 (▲△) in micro-channel reactor.

3.3.1 Leaching of active component

Among the four active elements, Te is the most unstable and vulnerable one which usually migrates and accumulates during the reaction[14]. However, according to the ICP results of these catalysts before and after the reaction, there was no obvious change in the element content during the experiment. It indicates that the leaching of the active componentis not the main reason for the deactivation of the M1-Al_2O_3catalyst plate.

3.3.2 Formation of impure phases

The XRD patterns of the used catalysts (Fig. 8) showed the formation of a (V, Nb)-substituted θ-Mo_5O_{14} (JCPDS 31-1437) phase inthe M1-Al_2O_3 catalyst plate whilst no visible peaks of other impure phaseswere detected in the M1catalyst powder and M1-PVA catalyst plate.As reported, the (V, Nb)-substituted θ-Mo_5O_{14}phase has less activity and ethylene selectivity in the ODHE process[7]. It was inferredthat the addition of alumina might lead to the formation of impure phases which was also reported by *Solsona et al.*[10] in the study of the ODHE process in a fixed-bed reactor where the deactivation had no difference with the type of reactor. Usually, impure phases should favor the excess oxidation of ethane to carbon oxides during the reaction, which also explained the differences of ethane conversion andethylene selectivity between the two catalyst plates in the micro-channel reactor displayed in section3.2.2.

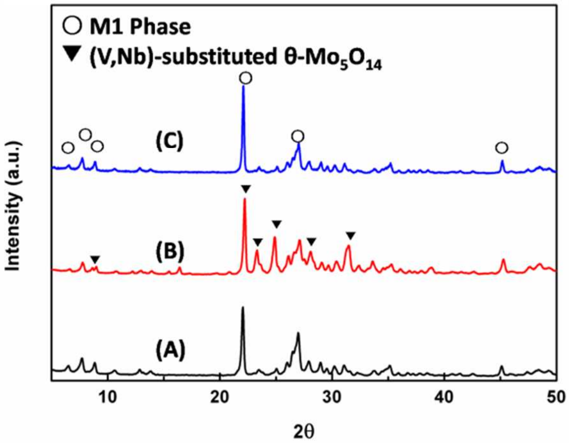


Figure 8 XRD patterns for (A) catalyst powder M1, (B) catalyst plate M1- $Al_2O_3$and (C) catalyst plate M1-PVA after 36 h ODHE reaction. Experiments were performed at 400 °C and 1.0 atm with a space time of20.74g_{cat}·h/mol_{C2H6} and a $C_2H_6/O_2/He$ molar ratio of 30/20/50 at reactor inlet.

Conclusions

This work presents a comprehensive study on the catalytic performance of a phase-pure M1 $MoVTeNbO_x$ catalyst for theODHE reaction in a micro-channel reactor. Astable and active phase-pure M1 catalyst layer was prepared on the metal-ceramic complex substrate by a dip-coating method. The results showed that a PVA solution was a more suitable binder in the coating procedure than the AlOOH sol, which would result in the formation of other impure phases during the reaction. At 420°C and 1.0atm, the performance of the M1-PVA catalyst plate in the micro-channel reactor approached an ethane conversion of ~60% andan ethylene selectivity of ~85% with a high catalyst productivity of 0.64 kg_{C2H4}/kg_{cat}/h. It was demonstrated that a traditional fixed-bed reactor would need about 5 times the amount of volume to achieve the same reactor productivity as a micro-channel reactor. XRD, SEMand ICP characterization indicated that catalyst plate M1-PVA did not show any significant deactivation after being used in the micro-channel system.

It can be concluded that it is feasible to use a phase-pure M1 $MoVNbTeO_x$ catalyst in micro-channel reactors for the ODHE reaction at industrial scale. In addition, the micro-channel reactorwith metal-ceramic complex substrate prepared by the catalyst coating technique opens more opportunities for the study of kinetics and mechanism of the ODHE reaction.

The authors would like to acknowledge the financial support by KNAW (the Netherlands) and Ministry of Education (China).

Notes and references

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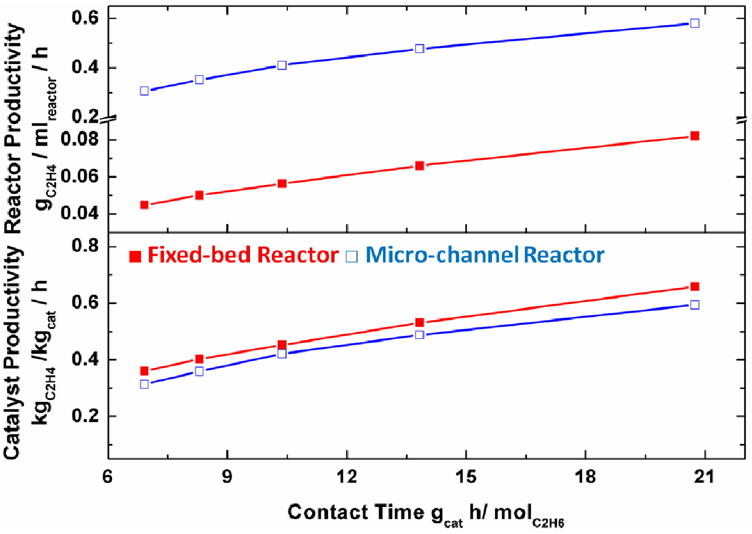

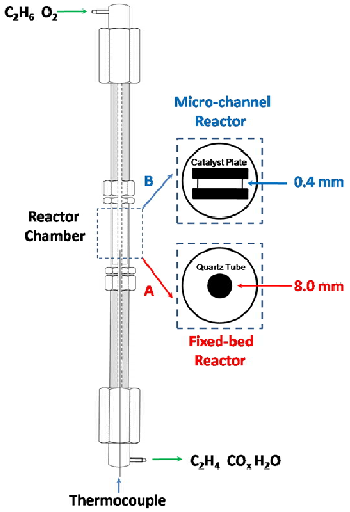

For the excellent heat transfer ability, the micro-channel reactor with coated phase-pure M1 catalyst can achieve nearly 5 times reactor productivity of traditional fixed-bed reactor at the same reaction conditions in the oxidative dehydrogenation of ethane (ODHE) process.