VO$_x$-Nb/La-γAl$_2$O$_3$ catalysts for oxidative dehydrogenation of ethane to ethylene

AbdAlwadood H. Elbadawi, Mogahid S. Osman, Shaikh A. Razzak, Mohammad M. Hossain*

Department of Chemical Engineering, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia

ARTICLE INFO

ABSTRACT

The present study deals with oxidative dehydrogenation (ODH) of ethane to ethylene in absence of gas phase oxygen using VO$_x$-Nb/La-γAl$_2$O$_3$ catalysts. In catalyst formulation, La is used to modify γ-Al$_2$O$_3$, stabilizing its bulk phase transformation. Nb is introduced as a promoter of VO$_x$ species. The prepared catalysts are characterized using various physicochemical techniques in order to demonstrate reducibility, oxygen carrying capacity, stability, metal–support interaction and acidity of the catalysts. TPR shows that VO$_x$-Nb/La-γAl$_2$O$_3$ is highly active and stable over repeated reduction and oxidation cycles. XRD analysis indicates that VO$_x$ appears both as amorphous and crystalline phases. The presence of Nb minimizes the formation of crystalline V$_2$O$_5$ phases, which is undesirable for ODH reaction. The NH$_3$-TPD analysis reveals an intermediate acidity of the VO$_x$-Nb/La-γAl$_2$O$_3$ catalysts. NH$_3$-TPD kinetics analysis shows that the addition of Nb increases the activation energy of ammonia desorption, suggesting increased V–support interaction and minimized V–V interaction. The ODH of ethane activity and stability is evaluated in a CREC fluidized riser simulator. The addition of Nb increased ethylene selectivity (85.7%) at 20.1% conversion comparatively at low reaction temperature (550 °C) and short contact time. Thus, Nb enhances VO$_x$ isolation and forms a secondary oxide, resulting a superior catalyst activity.

1. Introduction

Ethylene is a starting material for several industrial syntheses. The majority of worldwide ethylene production has been consumed as a monomer to produce polyethylene [1]. Conventionally, ethylene is produced by steam cracking of petroleum hydrocarbons. Ethylene is also obtained as by product of the catalytic cracking of heavy oil. Both the steam cracking and catalytic cracking processes require high-energy consumption, which contribute to high production cost of ethylene. On the other hand, catalytic oxidative dehydrogenation (ODH) is an emerging technology that can overcome the drawbacks associated with conventional processes. A metal based ODH catalyst can play an important role achieving high ethylene selectivity by minimizing the undesired CO$_x$ formation. Due to this reason, there are many research groups including the present research group have devoted efforts to develop highly active, ethylene selective and stable catalysts for ODH reactions.

In selective oxidation, both the supported and unsupported metals catalysts have been studied. For example, iron phosphates FePO$_4$, Fe$_2$P$_2$O$_7$, α-Fe$_3$(P$_2$O$_7$) and β- Fe$_3$(P$_2$O$_7$) and FePO$_4$/Al$_2$O$_3$ were found to be active as ODH catalysts [2]. The supported catalysts show several advantages over the unsupported catalysts, including better control of metal loading and metal dispersion. The supported catalysts are also flexible for adjusting their physicochemical properties. In supported catalysts, the support has an important role to determine the ultimate catalyst characteristics. For example, TiO$_2$ supported VOPO$_4$ catalysts gives higher ethylene selectivity than the unsupported VO$_x$ and (VO)$_2$P$_2$O$_7$ catalysts [3,4]. Ni–Co/Al$_2$O$_3$ powder catalysts are active and selective for ODH reaction with lower conversion and selectivity (less than 30%) [5]. V, Co, Mg and Mn supported on ALPO-5 structure, showed good activity at low temperature although their ethylene selectivity was within the 60–65% range [6]. On the other hand, vanadium on Ti, Sn or Zr pyrophosphates support exhibited good ethylene selectivity (approximately 90 %) at low ethane conversion level [7]. Therefore, the selection of support is an important aspect of formulating a suitable ODH catalyst.

Another way to improve catalyst performance is the addition of promoters. Generally, the promoters isolate the active species and form secondary metal oxides on support surface [8,9]. For instance, phosphorous promoted V based catalysts show better performance than the un-promoted V based catalysts [8]. Cr containing pillared zirconium phosphate, synthesized by fluoro-complex, displayed good activity due to the presence of Cr oxide [9].

* Corresponding author. Tel.: +966 13 860 1478; fax: +966 13 860 4234.
  E-mail address: mhossain@kfupm.edu.sa, mhossai4@alumni.uwo.ca
  (M.M. Hossain).

Notation

f	fraction of reduced vanadium
E_{des}	energy of desorption, kJ/mol
k_{d0}	pre-exponential factor
k_d	adsorption constant
S	selectivity
T_m	centering temperature, K
T	temperature, K
r_{des}	rate of desorption
V_m	volume of ammonia desorbed, ml/g
n	order of the desorption rate
R	the universal gas constant
VO_x	vanadium oxide surface species
x	ethane conversion

*Greek letters*

α	catalyst activity function
β	rate of temperature increase, °C/min
θ_{des}	surface coverage of adsorbed species

Abbreviations

ODH	oxidative dehydrogenation
XRD	X-ray diffraction
XRF	X-ray Fluorescence
TPR	temperature-programmed reduction
TPO	temperature-programmed oxidation
TPD	temperature-programmed desorption

Fig. 1. Schematic diagram of fluidized-bed oxidative dehydrogenation under gas phase oxygen free conditions.

A multicomponent $BaCl_2$–TiO_2–SnO_2 catalyst shows very high ethylene selectivity even at higher ethane conversion [10]. The presence of Cl^- ions in the catalyst helped to minimize the CO_x selectivity (7%) and enhancing ethylene selectivity. The major shortcoming of the $BaCl_2$–TiO_2–SnO_2 catalyst is its fast deactivation. La, Nd, Sm and Gd based catalysts, synthesized by modified sol–gel method, provides approximately 50% ethylene selectivity relatively at higher ethane conversion (56%) [11]. Cobalt-titania based catalysts, investigated with and without presence of phosphorous, although these catalysts were found to be not very promising with respect to ethylene selectivity [12].

Ni, Cu, and Fe treated Y-zeolites are also studied as ODH catalyst [13]. Among the three catalysts, Ni modified Y-zeolites showed superior activity and ethylene selectivity. On the contrary, the ethylene selectivity drastically dropped by 50% when only the oxides of these metals (unsupported) were used as catalysts [14]. Li, Mg, Al, Ga, Ti, Nb and Ta were used to enhance the properties of Ni-based mixed metal oxides [15]. NiO and Nb–NiO nano composites were prepared based on the slow oxidation of a nickel-rich Nb–Ni gel obtained in citric acid [16, 17]. The resulting materials have higher surface areas than those obtained by the classical evaporation method from nickel nitrate and ammonium niobium oxalate. Nano-sized Ni–Zr–O catalysts prepared by sol–gel method, showed good ethylene selectivity [15]. V_2O_5/Nb_2O_5 catalyst with various V_2O_5 contents was studied [18]. At high ethane conversion, the ethylene selectivity remains within 40% level. Excessive use of Nb_2O_5 might have contributed to the low yield with these catalysts. MoO_3–V_2O_5/Al_2O_3 is an effective catalyst in ethane dehydrogenation [19]. The catalyst synthesis method also has great effects on the catalyst structure and performance. It has been reported that $MoVNbTeO_x$ catalyst gave a good results after it was post treated with oxalic acid, improving catalyst surface area, and hence product selectivity and feed conversion up to 85% and 73%, respectively [20,21].
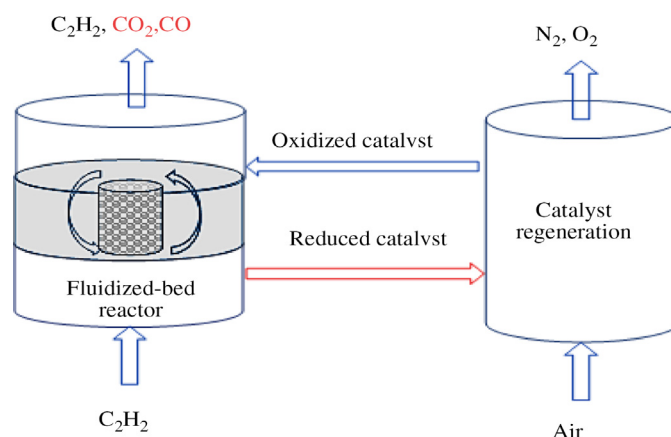
In addition to the catalysts type, the reactor can also play an important role enhancing both ethane conversion and ethylene selectivity [12,22,23]. Most of the literature studies considered fixed bed type reactor for ODH reactions, mainly for its simplicity. In addition, the previous studies considered gas phase oxygen (from air) as oxidative agent for ODH reaction, which also favors the combustion of both the feed ethane and product ethylene. Consequently, selectivity of ethylene significantly decreased. On the other hand, membrane and fluidized bed reactor can be more interesting to improve both the ethane conversion and ethylene selectivity.

The present research group has been investigating a novel gas phase oxygen free ODH using a circulating fluidized beds system [24,25]. In this approach, the ODH reactor system consist of two fluidized bed reactors called as: (i) the gas phase oxygen free dehydrogenation reactor and (ii) the catalyst oxidizer (as shown in Fig. 1). In this arrangement, ethane can be dehydrogenated in presence of the fluidizable solid oxide catalysts, which also acts as the source of lattice oxygen. The oxygen depleted catalyst can be circulated to the oxidizer to re-oxidize them by flowing air and the recycle back to the dehydrogenation reactor to maintain continuous operation. In this fashion the gas phase oxygen will never be allowed to enter into the dehydrogenation reactor, thus diminishes the possibility of complete combustion of both the feed and product. The remaining outstanding challenge for this process is to obtain a catalyst which is fluidizable, selective for ethylene formation and capable of supplying enough oxygen for dehydrogenation but limits the complete oxidation.

Taking into considerations of the advantages of the above gas phase oxygen free ODH process, the present study is aimed at developing a fluidizable VO_x-Nb/La-γAl_2O_3 catalyst suitable for ODH of ethane to produce ethylene. Generally, in vanadium based catalysts, the crystalline V_2O_5 forms at higher vanadium loading, which is less selective to ethylene and more selective to CO_x. The isolated VO_x species are desirable to achieve high ethylene selectivity. On the other hand, the gas phase oxygen free ODH requires appreciable oxygen carrying capacity to attain substantial ethane conversion rate. Therefore, the challenge is to develop a catalyst with highest possible amount of isolated VO_x and minimum crystalline V_2O_5. In this regard, Nb is introduced as a promoter to isolate the VO_x species and prevent their crystal formation. Nb also improves ethylene selectivity by enhancing the V=O and V–O–Al forms of lattice oxygen in the catalyst [26,27]. In catalyst formulation a small amount of (1 wt. %) La is employed to provide thermal stability of γAl_2O_3.