An experimental study of the partial oxidation of ethane to ethylene in a shallow fluidized bed reactor

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Abstract: The partial catalytic oxidation of ethane to ethylene was investigated experimentally in a shallow fluidized bed. The performaces of two catalyst types, pure γ-Al_2O_3 and V_2O_5/ γ-Al_2O_3 particles 1.8 mm in diameter, were analyzed. A pilot fluidized bed reactor with rectangular cross-section of 100 mm × 100 mm was used. The experiments were carried out under atmospheric pressure in a dilute system under oxygen excess conditions. V_2O_5/γ-Al_2O_3 showed good catalytic performances regarding ethylene selectivity. The influence of the temperature (in the range of 400–600 °C) and the contact time (in the range of $35 - 85$ kg s m^{-3}) on the conversion of ethane and the selectivity to ethylene was analyzed. The highest yield of ethylene was 18 %.

Keywords: catalytic oxidation of ethane, ethylene, shallow fluidized bed.

INTRODUCTION

Ethylene is the main feedstock in industrial organic chemistry. It is the basic raw material for the production of polyethylene, acetaldehyde, vinyl acetate and ethanol. Ethylene is conventionally obtained by thermal cracking of oil, which is a highly endothermic process with a large energy consumption. This energetic drawback of thermal cracking, together with the oil supply crisis, implies growing industrial interest the development of alternative processes for ethylene production.

Therefore, in the last decade, of lot of research was carried out in the field of catalytic oxidation of ethane to ethylene.[1–5] Natural gas could be a potential source of ethane. The poor reactivity of ethane is the first problem to overcome, with regards to its catalytic oxidation. The ethane molecule is stable with a dissociation enthalpy of the C – H bond of 420 kJ/mol and a moderately positive charge of the H atoms.[6] Therefore, it can be expected that a catalyst with Broensted basic properties would promote the polarization and breakage of the C–H bond, thus activiting the ethane molecules.

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Another important point is that the mechanism of the catalytic oxidation of ethane is complex going through several steps. The obtained products and their distribution depend on the operating conditions and the type of catalyst. A classification of catalytic materials for the oxidation of ethane (and other light alkanes) has been given by Cavani and Trifiro.[7] Detailed information on the structure and performances of supported metal oxide catalysts was given by Banares.[6] Several reacton nets for the catalytic oxidation of ethane have been proposed in the literature.[8–12] The reaction net proposed by Klose *et al.*[12] followed by the appropriate activation energy of every step is shown in Fig. 1. This reaction net is based on an experimental investigation of the partial oxidation of ethane over a V_2O_5/Al_2O_3 catalyst in a laboratory packed bed reactor.
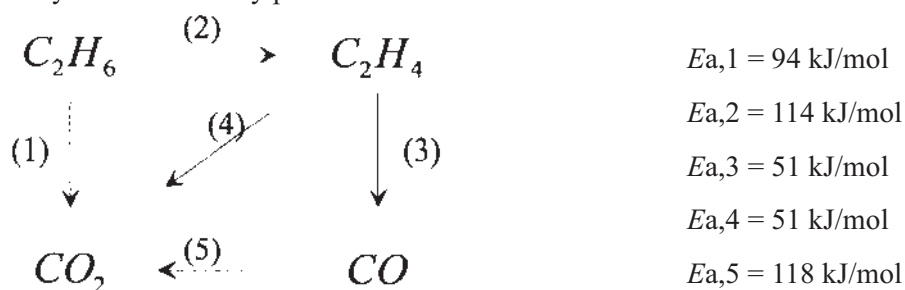
$C_2H_6 \xrightarrow{(2)} C_2H_4$

$(1) \quad (4) \quad (3)$

$CO_2 \xleftarrow{(5)} CO$

$E_{a,1} = 94$ kJ/mol

$E_{a,2} = 114$ kJ/mol

$E_{a,3} = 51$ kJ/mol

$E_{a,4} = 51$ kJ/mol

$E_{a,5} = 118$ kJ/mol

Fig. 1. Reaction net of the partial oxidation of ethane according to Klose *et al.*[12]

From the reaction net shown in Fig. 1, it can be seen that the formation of ethylene as an intermediate product is limited by consecutive and parallel deep oxidations. Therefore, optimization of the operating conditions is very important. Furthermore, Klose suggested that step (2), which provides the desired ethylene, goes through a redox-reaction between ethane and the lattice oxygen from the surface of the catalyst, which is reduced. This means that the ability of the catalyst to be reduced would make it selective for ethylene.

In order to enhance the ethylene yield, different types of catalysts, as well as different reactor designs, have been investigated. Their overview is presented in Table I.

TABLE I. Experimental investigation of the partial oxidation of ethane to ethylene

Author	Reactor configuration	Catalyst
Lopez Nieto *et al.*[4]	Fixed-bed reactor	Mo–V–Te–Nb mixed oxide
Donsi *et al.*[5]	Monolith reactor	$LaMnO_3$
Klose *et al.*[1]	Packed bed reactor, Packed bed membrane reactor	$VO_x/\gamma–A\lambda_2O_3$
Zhang *et al.*[2]	Fixed-bed flow quartz glass micro reactor	NiO/Al_2O_3
Panizza *et al.*[3]	Fixed-bed flow tubular quartz reactor	$V_2O_5–K_2O/Al_2O_3$

In this work, the applicability of a fluidized bed reactor for this reaction was explored. In principle fluidized bed reactors have the advantage of temperature uniformity due to mixing of the particles, even for highly exothermal reactions. On

the other hand, complex hydrodynamics and back-mixing effects might be their disadvantages.

In this work, an investigation of the catalytic partial oxidation of ethane was performed in a shallow fluidized bed reactor (the height of the bed was less than the bed diameter), in order to provide short contact times. Coarse particles of pure γ-Al$_2$O$_3$ and V$_2$O$_5$/γ-Al$_2$O$_3$ were employed and their catalytic performance were investigated and compared. The hydrodynamic behavior of the shallow fluidized bed of coarse particles was previously investigated.[13] The temperature and contact time effects on the conversion and product distribution were also investigated and analyzed.

The aim of this work was to contribute to the development of catalytic partial oxidation of ethane as an alternative method to thermal cracking for the industrial production of ethylene. The advantages of the catalytic oxidation process, such as utilization of natural gas instead of oil as well as large savings of energy due to its highly exothermal nature, make it worth investigating.

EXPERIMENTAL

Experimental set-up

The experimental set-up is schematically show in Fig. 2. The experiments were performed in a pilot fluidized bed reactor made of stainles steel, with a square cross-section area of 100 nm $\times$ 100 mm and the total column height of 1.5 m (Fig. 2). A perforated plate with 4.2 % open area was used as the gas distributor.
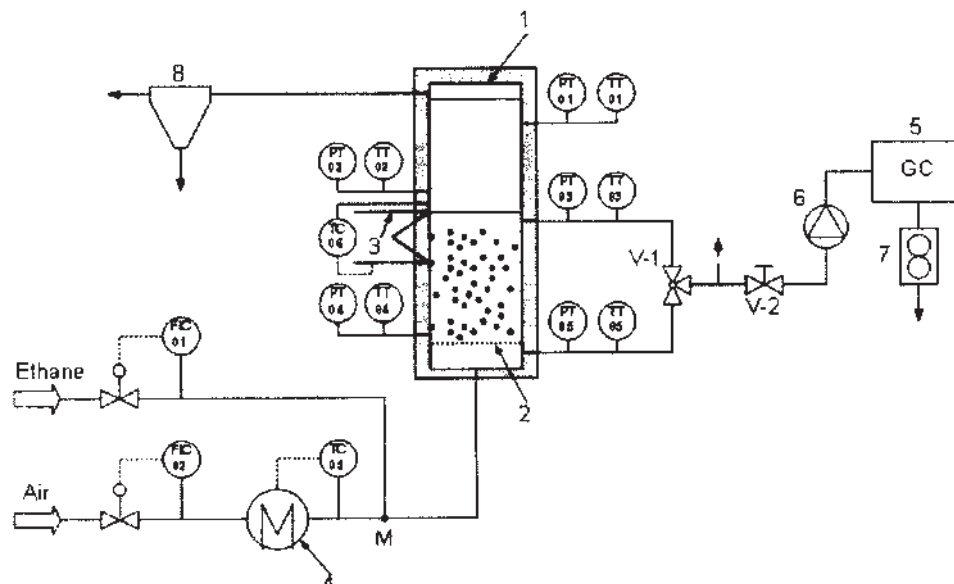

Fig. 2. Experimental apparatus: 1 – fluidized bed reactor, 2 – gas distributor, 3 – spiral heater, 4 – electrical pre-heater, 5 – gas chromatograph, 6 – pump, 7 – flowmeter, 8 – cyclone.

Porous γ-Al$_2$O$_3$ particles (Condea Chemie, Germany) were used as the fluidized particles as well as the catalyst support. Some important features of the catalyst particles are given in Table II. Detailed descriptinos of the preparation of the catalyst and the characterization procedures can be found elsewhere.[1]

TABLE II. Properties of the catalyst particles

γ-Al$_2$O$_3$	Diameter	1.8	mm
V$_2$O$_5$/γ-Al$_2$O$_3$	Density	1040	kg m^{-3}
	Minimum fluidization velocity*	0.5	m s^{-1}
	Terminal velocity*	9.0	m s^{-1}
	Mean pore diameter[12]	10.9	nm
	Specific area (BET)[12]	168	m^2 g^{-1}
V$_2$O$_5$/γ-Al$_2$O$_3$	Vanadium content[12]	1.4	%

*at 500 °C

A spiral heater wound around the outside wall of the column was used for heating the bed, which was thermally insulated in order to prevent heat losses. Ambient air (the source of oxygen) was preheated in an electrical pre-heater before mixing with ethane (point M, Fig. 2) and entering the column. Electronic mass flow controllers (HITEC, Bonkhorst, Netherlands) were used for adjusting the air and ethane, flows thus providing the desired concentration of ethane.

NiCr–Ni thermocouples (Therma, Germany) and pressure sensors (Huba Control, Germany) were isntalled at five positions along the reactor, which provided continuous temperature and pressure measurements. DIAdem 8.1 (National Instruments) software was used for data acquisition.

Gas samples were taken before the bed (reactants) and after the bed (products). A gas chromatograph HP 6890 (Agilent, Germany), equipped with Plot Molsieve and Paraplot Q columns followed by an FID detector, was used for the analysis of the gas composition, supported by ChemStation software.

Operating conditions and data processing

Three serries of experiments were carried out, in which th catalyst type, bed temperature and the contact time, were varied. An overview is shown in Table III.

TABLE III. Experimental operating variables

Series	Catalyst	Mass of the catalyst/kg	Bed temperature/°C	Gas velocity/m s^{-1}	Contact time kg s m^{-3}
1	γ-Al$_2$O$_3$	0.3	400 – 500	0.6 – 2	46 – 15
2	V$_2$O$_5$/γ-Al$_2$O$_3$	0.3	400 – 550	0.6 – 2	46 – 15
3	V$_2$O$_5$/γ-Al$_2$O$_3$	0.6	500 – 590	0.6 – 1.7	85 – 36

The contact time was calculated on the basis of the mass of the catalyst as follows:

$$\tau_{\mathrm{m}} = \frac{m_{\mathrm{cat}}}{V(T)} = \frac{m_{\mathrm{cat}}}{UA_{\mathrm{c}}} = \frac{1}{WHSV} \tag{1}$$

Variation of the contact time was achieved by changing the volumetric flow-rate of the gas at a constant mass of the catalyst. The volumetric flow-rate at the bed temperature was used in Eq. (1).

All experiments were performed under oxygen excess conditions (ambient air) and with an inlet ethane concentration of 1 mol %. Higher concentrations were not used due to flammability limits.[14] Experimental runs in an empty column (at the highest tested temperature of 590 °C) showed that reaction on the walls of the column, as well as in the gas phase could be neglected under the employed operating conditions.

Gas samples were taken in steady state, 15 min after commencing the ethane flow, when the temperature in the bed had ceased to change. Two runs were performed for every set of experimental conditions and the mean values of the two measured concentrations were taken for further calculations. Measurements giving a carbon balance of less then 0.95 were excluded. The pressure drop over the bed (without the pressure drop over the distributor plate) was about 300 Pa.

On the basis of the measured concentrations of reactants and products, the conversion of ethane (X), selectivity (S_i) and yield (Y_i) to certain products were calculated using the following equations:

$$X = \frac{c_{C_2H_6}^{in} - c_{C_2H_6}^{out}}{c_{C_2H_6}^{in}} \, 100 \tag{2}$$

$$S_i = \frac{c_i^{out} - c_i^{in}}{c_{C_2H_6}^{in} - c_{C_2H_6}^{out}} \, 100, \quad i = C_2H_4, CO_2, CO \tag{3}$$

$$Y_i = X \, S_i \tag{4}$$

RESULTS AND DISCUSSION

Influence of the catalyst

Ethylene, carbon monoxide and carbon dioxide were detected as the products of catalytic oxidation of ethane for both the tested catalyst particles, which is in agreement with the results reported by Klose[12] under similar operating conditions.

The temperature dependence of the conversion of ethane for pure γ-Al_2O_3 and V_2O_5/γ-Al_2O_3 particles for two contact times is presented in Fig. 3. Higher conversions (on average two times higher) were achieved with pure γ-Al_2O_3 particles. The increase of conversion with increasing temperature and contact time is also
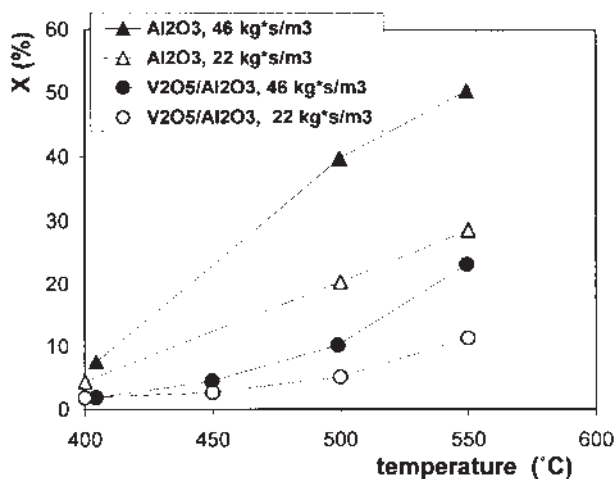

Fig. 3. Conversion of ethane *vs.* temperature over γ-Al_2O_3 and V_2O_5/γ-Al_2O_3 for two contact times: 46 kg s m^{-3} and 22 kg s m^{-3} (Series 1 and 2).
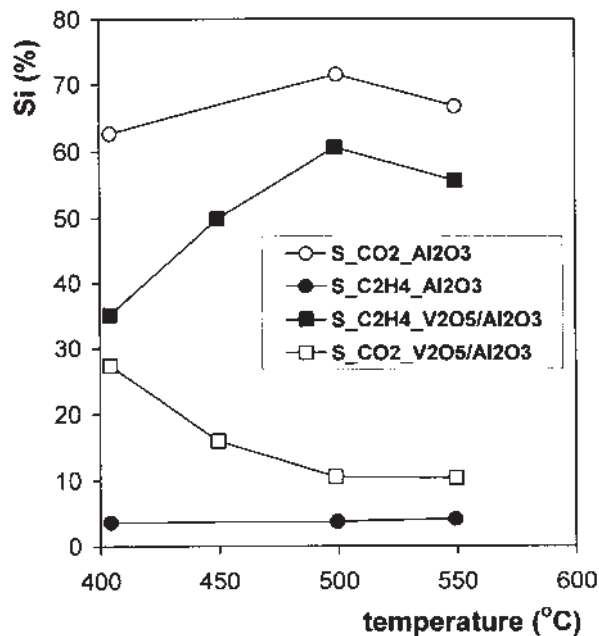
Fig. 4. Selectivity to C_2H_4 and CO_2 over γ-Al_2O_3 and V_2O_5/γ-Al_2O_3 for a contact time of 46 kg s m^{-3}

more pronounced with γ-Al_2O_3. Obviously, γ-Al_2O_3 shows higher activity as a catalyst than V_2O_5/γ-Al_2O_3. This can be attributed to its more basic properties.

However, regarding the selectivity to ethylene, γ-Al_2O_3 is practically useless. Figure 4 shows that with γ-Al_2O_3 the selectivity to ethylene is extremely low, re-
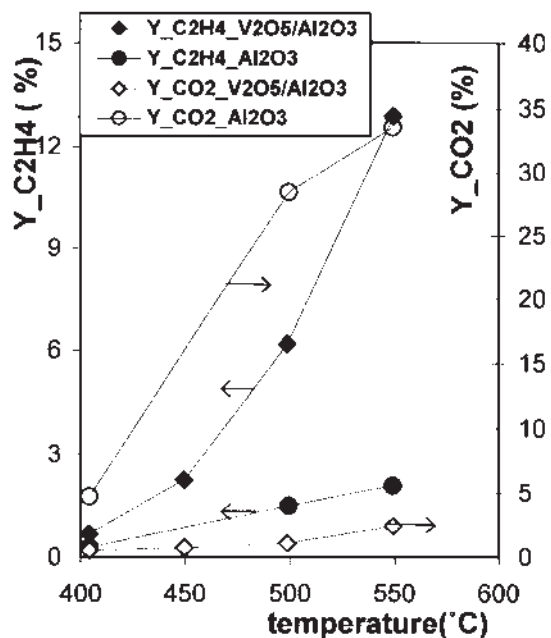
Fig. 5. Yield of C_2H_4 and CO_2 over γ-Al_2O_3 and V_2O_5/γ-Al_2O_3 for a contact time of 46 kg s m^{-3}
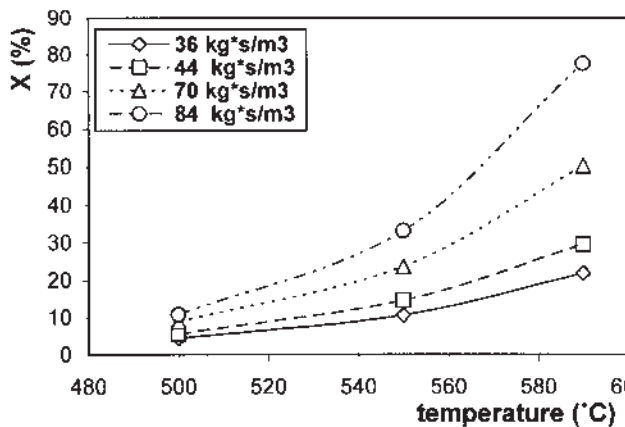
Fig. 6. Conversion of ethane *vs.* temperature over V_2O_5/γ-Al_2O_3 for different contact times.
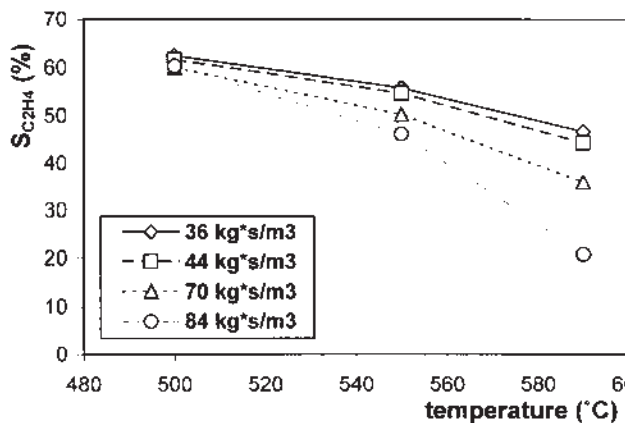

Fig. 7. Selectivity to ethylene *vs.* temperature over V_2O_5/γ-Al_2O_3 for different contact times.
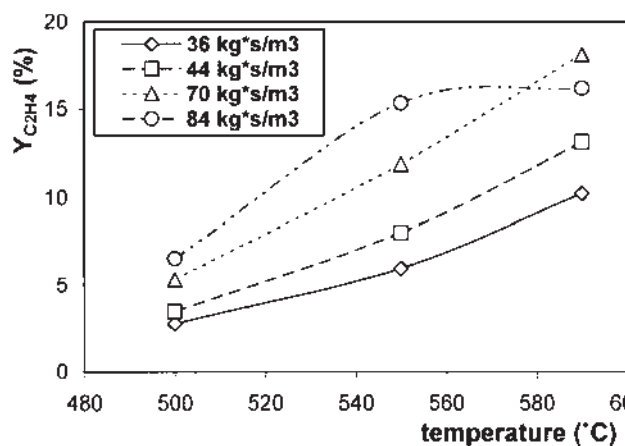

Fig. 8. Yield of ethylene *vs.* temperature over V_2O_5/γ-Al_2O_3 for different contact times.

gardless of the temperature. The corresponding yields of ethylene are less then 3 % (Fig. 5). The main product is CO_2 with a selectivity of up to 70 % (Fig. 4) and yield

up to 35 % (Fig. 5), which leads to the conclusion that deep oxidation occurs (reaction 1 in Fig. 1) with γ-Al_2O_3 which is thus non-selective towards ethylene.

On the other hand, although V_2O_5/ γ-Al_2O_3 provides low conversions (up to 20 %, Fig. 3), it shows greatly enhanced performances regarding ethylene selectivity. Under oxygen excess conditions, a selectivity to ethylene of up to 60 % is achieved (Fig. 4), and ethylene is the main product with a maximum yield of 14 % in the tested temperature range (Fig. 5). V_2O_5 belongs to the reducable transition metal oxides. This ability to be reduced in reaction with ethane makes it a suitable catalytic agent in terms of ethylene selectivity, unlike γ-Al_2O_3 which can not be reduced.

Influence of the temperature and the contact time

Since V_2O_5/γ-Al_2O_3 showed better performances regarding ethylene selectivity, additional measurements were performed with this catalyst for contact times in the range 36 – 85 kg s m^{-3} and temperatures in the range 500 – 590 °C (Series 3). The results are presented as conversion of ethane (Fig. 6), selectivity to ethylene (Fig. 7) and yield of ethylene (Fig. 8) *vs*. temperature, for different contact times.

As expected, the conversion of ethane increased with both increasing temperature and contact time (Fig. 6). The maximum achieved conversion was 80 %, corresponding to the highest temperature (590 °C) and the highest contact time (84 kg s m^{-3}).

However, the selectivity to ethylene shows the opposite trend (Fig. 7). With increasing temperature, the selectivity to ethylene decreased. It is a known fact[15] that, in the case of parallel reactions, higher temperatures favor reactions with higher activation energies. In the present case, deep oxidation of ethane (Step (1) in Fig. 1) has a a higher activation energy (114 kJ/mol) than the desired Step (2) (94 kJ/mol), and, therefore, the formation of ethylene is suppressed at higher temperatures.

Increasing the contact time leads to a decrease in the ethylene selectivity. Longer contact times enable further reaction of the formed ethylene through consecutive reactions (Reactions 3 and 4, Fig. 1), thus causing its loss and decreasing its fraction in the reaction products.

In Fig. 8, it can be seen that the yield of ethylene increase more slowly with increasing temperature than the conversion of ethane. For the highest contact time of 84 kg s m^{-3}, the yield levels off a 560 °C reaching a value of 18 % (corresponding to a selectivity of 40 % in Fig. 7), which is the maximum achieved yield under the conditions investigated in this work. Maximums on the yield-temperature curves, typical for intermediates, were not achieved in the tested range of temperature. The reasons for the low ethylene yields could be:

– the shallow fluidized bed of coarse particles operating at gas velocities of up to 4U_{mf} (employed in this work) is mainly in the rapidly growing bubble regime,[13] with poor gas-particles contact, resulting in low conversion

– the employed oxygen excess conditions support ethylene loss through consecutive steps, thus decreasing the selectivity towards ethylene.

A fluidized bed with smaller particles, which exhibits smoother bubbling, would probably enhance the ethane conversion. Also, reactor designs which would enable a closed oxygen supply could contribute to an increase in the ethylene selectivity.

CONCLUSIONS

Although numerous studies have been reported regarding catalytic oxidation of ethane, there is still no satisfactory efficient model system which would enable commercialization of the process. This work presents a contribution in this field showing directions for further investigations. The results of this study show that γ-Al_2O_3 exhibits high activity as a catalyst due to its Brönsted base properties but it is non-selective to ethylene. On the contrary, V_2O_5/γ-Al_2O_3 provides lower conversions but higher selectivity to ethylene due to its reducibility.

The experiments over V_2O_5/γ-Al_2O_3 show that increasing both the temperature and contact time increases the conversion but simultaneously decreases the selectivity to ethylene. Therefore, optimization regarding the operating conditions would be required. The temperature at which the ethylene yield has a maximum would be the optimal temperature for a certain contact time.

In a shallow fluidized bed of coarse particle under oxygen excess conditions, yields of ethylene of up to 18 % are achieved. If smaller catalyst particles were employed and the quantity of added oxygen was adjusted according to stoichiometry, higher yields might be achieved.

NOMENCLATURE

τ_m – Contact time, kg s m^{-3}
m_{cat} – Mass of the catalyst, kg
$V(T)$ – Volumetric flow of the gas at the bed temperature, m^3 s^{-1}
U – Superficial gas velocity, m s^{-1}
U_{mf} – Minimum fluidization velocity, m s^{-1}
A_c – Cross-sectional area of the column, m^2
$WHSV$ – Weight hourly space velocity, m^3 kg^{-1} s^{-1}
X – Conversion, %
S_i – Selectivity to component i, %
Y_i – Yield of component i, %
c_i^{in} – Inlet concentration of component i, mol m^{-3}
c_i^{out} – Outlet concentration of component i, mol m^{-3}

И З В О Д

ЕКСПЕРИМЕНТАЛНО ИСПИТИВАЊЕ ПАРЦИЈАЛНЕ ОКСИДАЦИЈЕ ЕТАНА ДО ЕТИЛЕНА У РЕАКТОРУ СА ПЛИТКИМ ФЛУДИЗОВАНИМ СЛОЈЕМ

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У овом раду експериментално је испитивана парцијална каталитичка окидација етана до етилена у реактору са плитким флуидизованим слојем (висина слоја мања од пречника реактора). Као честице катализатора коришћене су честице чистог γ-Al_2O_3 као и V_2O_5/γ-Al_2O_3 пречника 1.8 mm и упоређена су њихова својства у погледу активности и селективности ка етилену. Реакција је испитивана у реактору квадратног попречног пресека 100 mm × 100 mm под атмосферским притиском, у разблаженом систему у условима вишка кисеоника. V_2O_5/ γ-Al_2O_3 је показао добра каталитичка својства у смислу високе селективности ка етилену. Анализирани су утицаји температуре (у опсегу 400–600 °C) и времена контакта (у опсегу 35 – 85 kg s m^{-3}) на конверзију етана и селективност ка етилену. Максимални остварени принос етилена је 18 %.

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