

# Oxidative conversion of ethane to ethylene over supported SrO-promoted Er<sub>2</sub>O<sub>3</sub> catalyst

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## Abstract

Oxidative conversion of ethane to ethylene over a SrO-promoted Er<sub>2</sub>O<sub>3</sub> supported on low-surface area macroporous silica–alumina commercial catalyst carrier (SA5205, obtained from Norton Co., USA) in presence of steam (steam/C<sub>2</sub>H<sub>6</sub> mole ratio = 1.0) and limited O<sub>2</sub> (C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub> mole ratio ≥ 4.0) has been thoroughly investigated. Influence of different process parameters such as temperature (700–850 °C), C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub> feed ratio (4.0–8.0) and space velocity (50, 000–200, 000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>) on the conversion of ethane and product selectivity in the process has been studied. High selectivity (≥80%) of C<sub>2+</sub> olefins at 50–70% conversion of ethane could be obtained at very low contact time without coke deposition on the catalyst at 800–850 °C.

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## 1. Introduction

Oxidative conversion of ethane to ethylene in presence of catalyst is futuristic process of great practical importance. Ethylene is a keystone to petrochemical industry, and is produced commercially from ethane, ethane–propane mixture or naphtha by their thermal cracking in the presence of steam [1]. However, this conventional process is highly endothermic, energy intensive and also involves extensive coke formation. The large amount of coke deposits on the inner walls of tubular cracking reactor because of which the heat transfer from the reactor walls is reduced, requiring higher wall temperature (upto 1100 °C). This consequently requires more energy, reduces the life of reactor tubes and also needs the process shutdown for physical removal of the coke. In order to overcome these problems associated with conventional process, worldwide efforts have been made by many for oxidative conversion of ethane to ethylene, using alkali metal-containing

catalysts [2–8] and alkaline earth metal-promoted La<sub>2</sub>O<sub>3</sub> [9–12] or other rare earth oxide [13] catalysts. The alkali metal-containing catalysts have poor thermal/hydrothermal stability because of the presence of low melting or volatile active components. However, alkaline earth-metal promoted catalysts have no such problem. Since oxidative conversion of ethane is exothermic and also involves formation of water, there is a need to develop a catalyst, which not only is active and selective but also has high thermal and hydrothermal stability. High mechanical strength is a basic requirement of any commercial catalyst. This could be achieved by supporting the catalyst on a porous catalyst carrier having high mechanical strength and high thermal/hydrothermal stability. In this investigation a supported SrO-promoted Er<sub>2</sub>O<sub>3</sub> catalyst satisfying the above requirements and also operating at very low contact time in the process has been reported.

## 2. Experimental

The supported catalyst [SrO (11.6 wt.)/Er<sub>2</sub>O<sub>3</sub> (15.6 wt.)/SA-5205] was prepared by impregnating a commer-

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cial catalyst support SA-5205 (obtained from Norton Co., USA), crushed to 22–30 mesh size particles, first by erbium nitrate (GR LOBA) and then with strontium nitrate (extra pure, LOBA) by using the incipient wetness technique [14]. After each impregnation, the resulting particles were dried at 90 °C for 16 h and then calcined in static air at 900 °C for 4 h. SA-5205 is an inert macro-porous (porosity: 50%) catalyst carrier, having a low-surface area ( $<0.01 \text{ m}^2 \text{ g}^{-1}$ ) and it consists mainly of  $\text{Al}_2\text{O}_3$  (86.1 wt.%) and  $\text{SiO}_2$  (11.8 wt.%).

The oxidative conversion of ethane to ethylene reaction was carried out over the catalyst at atmospheric pressure in a continuous-flow quartz tubular reactor having low dead volume, described elsewhere [15], at different temperatures (700–850 °C),  $\text{C}_2\text{H}_6/\text{O}_2$  feed ratios (4.0–8.0) and gas hourly space velocities (50,000–200,000  $\text{cm}^3 \text{ g}^{-1} \text{ h}^{-1}$ ) in the presence of steam (steam/ $\text{C}_2\text{H}_6$  mole ratio = 1.0). The feed consisted of mixture of pure ethane, oxygen and steam; no feed diluent was used. The space velocity was calculated at 0 °C and one atmosphere pressure. The reaction temperature was measured by a Chromel–Alumel thermocouple located in the catalyst bed. The reactor effluent gases, after the removal of water by condensation at 0 °C were analyzed by an on-line gas chromatograph with TCD detectors using Poropak-Q and Sphercarb columns. The selectivity for  $\text{C}_2\text{H}_4$  and  $\text{C}_2+$  olefins is defined as:

Selectivity for  $\text{C}_2\text{H}_4$  and  $\text{C}_2+$  olefins (%) = (mole of ethane converted to ethylene and other olefins / moles of ethane converted to all the products)  $\times$  100.

### 3. Results and discussion

Results showing the effect of various process parameters such as temperature (700–850 °C),  $\text{C}_2\text{H}_6/\text{O}_2$  feed ratio (4.0–8.0) and space velocity (GHSV = 50,000–200,000  $\text{cm}^3 \text{ g}^{-1} \text{ h}^{-1}$ ) on the conversion of ethane and oxygen, product selectivity (for  $\text{C}_2\text{H}_4$ ,  $\text{C}_2+$  olefins,  $\text{C}_3+$  paraffins,  $\text{CH}_4$  and  $\text{CO}_x$ ) and  $\text{CO}/\text{CO}_2$  product ratio in the process are presented in Figs. 1–3. No coke deposition was observed on the catalyst for all the process conditions.

#### 3.1. Influence of temperature

The results in Fig. 1 show a strong influence of temperature on the conversion of  $\text{C}_2\text{H}_6$  and  $\text{O}_2$ , selectivity for  $\text{C}_2\text{H}_4$ ,  $\text{C}_2+$  olefins,  $\text{CH}_4$ ,  $\text{C}_3+$  paraffins,  $\text{CO}_x$  and the  $\text{CO}/\text{CO}_2$  product ratio, as follows. With the increase in the reaction temperature:

- the conversion of  $\text{C}_2\text{H}_6$  and  $\text{O}_2$  is increased as expected.
- the selectivity for  $\text{C}_2\text{H}_4$ ,  $\text{C}_2+$  olefins and  $\text{CH}_4$  is increased, however, the selectivity for  $\text{C}_3+$  paraffins and  $\text{CO}_x$  is decreased.
- the  $\text{CO}/\text{CO}_2$  ratio is increased, which shows the occurrence of homogeneous reactions in which the formation of CO is favored over  $\text{CO}_2$  more predominantly.

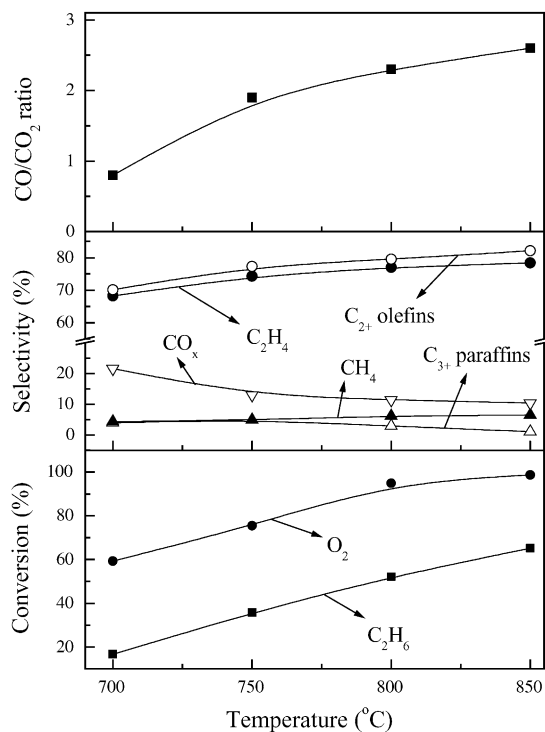


Fig. 1. Influence of temperature on the conversion of ethane and  $\text{O}_2$ , product selectivity and  $\text{CO}/\text{CO}_2$  ratio in the oxidative conversion of ethane to ethylene over supported Sr-promoted  $\text{Er}_2\text{O}_3$  catalyst [reaction condition:  $\text{C}_2\text{H}_6/\text{O}_2 = 6.0$ , steam/ $\text{C}_2\text{H}_6 = 1.0$ , space velocity =  $100,000 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$ ].

#### 3.2. Influence of $\text{C}_2\text{H}_6/\text{O}_2$ ratio

Fig. 2 shows a strong influence of  $\text{C}_2\text{H}_6/\text{O}_2$  feed ratio on the process performance. With increase in the  $\text{C}_2\text{H}_6/\text{O}_2$  feed ratio, the process performance was influenced as follows.

- The conversion of  $\text{C}_2\text{H}_6$  and  $\text{O}_2$  is decreased, however, the decrease in  $\text{O}_2$  conversion is very small.
- The selectivity for  $\text{C}_2\text{H}_4$  and  $\text{C}_2+$  olefins is increased but the selectivity for  $\text{CO}_x$  and selectivity for  $\text{CH}_4$  is decreased. However, the change in the selectivity for  $\text{C}_3+$  paraffins is very small.
- The  $\text{CO}/\text{CO}_2$  ratio is increased, since  $\text{O}_2$  is available at lower and lower concentrations.

#### 3.3. Influence of space velocity

The influence of space velocity on the process performance (at 850 °C) is shown in Fig. 3. The increase in the space velocity (from 50,000 to  $200,000 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$ ) results in:

- a decrease in the conversion of reactants  $\text{C}_2\text{H}_6$  and  $\text{O}_2$  as expected. However, the decrease in the  $\text{O}_2$  conversion is very small.
- a increase in the selectivity for  $\text{C}_2\text{H}_4$ ,  $\text{C}_2+$  olefins and  $\text{C}_3+$  paraffins but a decrease in the selectivity for  $\text{CH}_4$  and  $\text{CO}_x$ , and
- a large increase in the  $\text{CO}/\text{CO}_2$  ratio.

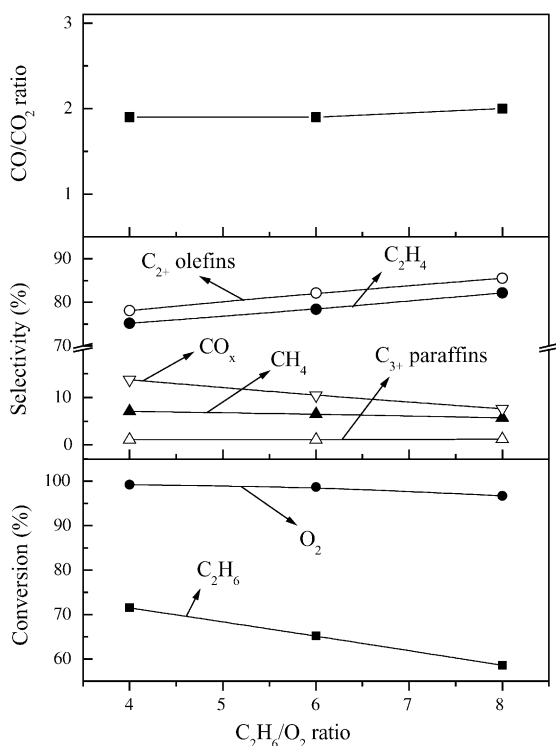


Fig. 2. Influence of  $C_2H_6/O_2$  feed ratio on the conversion of ethane and  $O_2$ , product selectivity and  $CO/CO_2$  ratio in the oxidative conversion of ethane to ethylene over supported Sr-promoted  $Er_2O_3$  catalyst [reaction condition: temperature =  $850^\circ C$ , steam/ $C_2H_6$  = 1.0, space velocity =  $100,000\text{ cm}^3\text{ g}^{-1}\text{ h}^{-1}$ ].

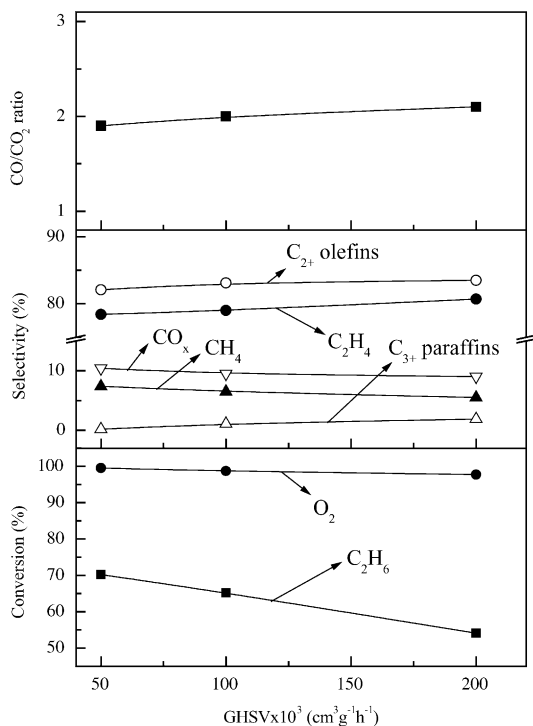
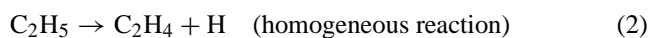
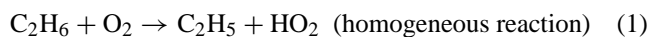


Fig. 3. Influence of space velocity on the conversion of ethane and  $O_2$ , product selectivity and  $CO/CO_2$  ratio in the oxidative conversion of ethane to ethylene over supported Sr-promoted  $Er_2O_3$  catalyst [reaction condition: temperature =  $850^\circ C$ ,  $C_2H_6/O_2$  = 6.0, steam/ $C_2H_6$  = 1.0].

The process is expected to involve a complex network of both heterogeneous and homogeneous reactions such as catalytic and non-catalytic oxidative conversion of ethane reactions (exothermic) and thermal cracking of ethane (endothermic) reactions in the presence of limited  $O_2$  at the high temperature ( $\geq 700^\circ C$ ), as discussed earlier [9]. The catalytic reactions are more predominant at the lower temperatures (below  $750^\circ C$ ). At the higher temperatures (above  $750^\circ C$ ), the homogeneous (non-catalytic) and surface-originated homogeneous reactions also become increasingly important. The homogeneous reactions are simultaneously occurring with heterogeneous reactions. In order to reduce the contribution due to the homogenous reaction, low dead volume reactor packed with inert support was used.

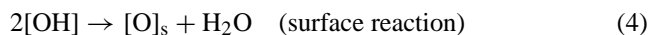
Our earlier studies on non-catalytic oxidative conversion of ethane to ethylene in the presence of limited  $O_2$  [16] showed that because of the activation of ethane by molecular oxygen cracking ethyl radicals and their subsequent decomposition to ethylene [reactions 1 and 2 given below], the conversion of ethane purely by its thermal cracking is drastically increased.



Ethane is expected to be activated on the catalyst surface by the surface oxygen as follows.



and the  $[O]$ , sites are regenerated by the dehydration reaction,



### 3.4. Influence of catalyst support

The support provides not only better dispersion but also a high mechanically strength and thermally/hydro thermally stable porous matrix for the catalyst for practical use in the high temperature process. The particles or pellets of the catalyst without the support undergo disintegration into smaller pieces or powder causing an unacceptable larger pressure drop across the catalyst bed in the reactor, when exposed to humid atmospheres. The supported SrO-promoted  $Er_2O_3$  showed better performance (higher ethane conversion, activity and selectivity for the  $C_{2+}$  olefins) than the unsupported catalyst in the process [13].

## 4. Conclusions

The high ethane conversion (50–70%) and high ethylene selectivity ( $\geq 80\%$ ) in the process can be obtained at very high space velocity (as high as  $200,000\text{ cm}^3\text{ g}^{-1}\text{ h}^{-1}$ ) without formation of coke using the supported SrO-promoted  $Er_2O_3$  catalyst.

The mechanical strength as well as the surface area and the C<sub>2+</sub> olefin selectivity [in the high temperature (>700 °C) oxidative conversion of ethane to ethylene in presence of limited O<sub>2</sub>] of SrO-promoted Er<sub>2</sub>O<sub>3</sub> catalyst are increased significantly because of supporting the catalyst on the low-surface area macro-porous silica–alumina catalyst carrier.

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