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Olefins production by catalytic partial oxidation of ethane and propane over $Pt/LaMnO_3$ catalyst

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ABSTRACT

Ethylene + acetylene yields exceeding 68% with selectivities above 80% are obtained over novel doped $Pt/LaMnO_3$ catalysts under self-sustained ethane CPO at short contact time. Insights are presented on the impact of catalyst dopants and type of sacrificial fuel (CH_4, CO, H_2). The study on the novel catalysts is extended to ethylene and propylene production via CPO of propane. Results of an economic analysis for ethylene production from ethane in a 1MtA plant are presented, comparing the traditional steam cracking with CPO technology based on the best achieved experimental data with the $Pt/LaMnO_3$ catalyst.

1. Introduction

Olefins have become the building blocks for the production of polymers and consequently for the manufacture of an impressive number of commodities and specialties for daily use [1,2]. Hence, in the near future the demand for olefins, especially ethylene and propylene, is expected to increase significantly [2]. The selective oxidative dehydrogenation (ODH) of ethane to ethylene over structured catalysts operated at short contact time has attracted some interest as a possible alternative route to steam cracking [1–5]. The typical per-pass ethylene molar yield of an ethane steam cracker unit is 48%, with a selectivity close to 80% (78% molar yield upon recycling of the unconverted ethane) [2,4,5]. Yields reported for ethane ODH through its catalytic partial oxidation (CPO) in short-bed reactors mainly on Pt based catalysts and H_2 addition as sacrificial fuel [2–7 and references therein], are comparable to those of commercial cracking units, and better than yields to olefins (ethylene + propylene) obtained in commercial naphtha steam-cracker units. Due to a simpler reactor system (no need for large external furnaces) and fewer fractionation columns, estimated investment cost for the ethane CPO process is about 20–25% lower than for the corresponding ethane steam cracker. On the other hand, estimated production costs are somewhat higher (10–15%), mainly due to the additional cost of making or purchasing oxygen [4,5]. It was concluded by Shell that economic attractiveness of ethane CPO process is highly sensitive to small yield variations [5].

Requirements for higher performance led our group to the development of a novel catalyst formulation [8], consisting of Pt dispersed onto a layer of $LaMnO_3$ perovskite supported over monolithic structures. Under optimized operating conditions the $Pt/LaMnO_3$ catalyst achieves a total molar yield to ethylene and acetylene in excess of 66% per pass, in correspondence to a C-atom selectivity to ethylene and ethane conversion both above 80%, i.e. significantly better than the best results reported in literature [2,9].

In accordance to recent experimental and numerical investigations [2,5,8–16], the formation of ethylene requires two main steps: a catalytic exothermal oxidation of a fraction of the feed to $CO–H_2$ and/or preferably to $CO_2–H_2O$, followed by an endothermic thermal (uncatalyzed, gas phase) cracking of the remaining ethane to ethylene (oxycracking) [5,11]; the same occurs in the case of propane, in which propylene and ethylene form via gas-phase oxidative pyrolysis [6,11,14,17]. The final olefin yield and selectivity are strongly affected by the way heterogeneous and homogeneous reaction paths are coupled together in the short contact time catalytic reactor, which, in turn, is highly dependent on catalyst formulation and morphology, reactor configuration and operating conditions [7–17].

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In this work we report on further achievements in olefin production via CPO, obtained by doping the Pt/$LaMnO_3$ catalyst with Sn or Ga, in view of their dehydrogenation properties in conjunction with Pt [1]. The study was extended to the impact of the type of sacrificial fuel, in particular comparing the performance of CH_4 and CO as alternatives or partial substitutes to H_2. The novel catalysts were also tested for ethylene and propylene production via CPO of propane with particular emphasis on total olefin yield and ethylene to propylene ratio. The improvement in olefin yields positively affected the economics of the catalytic process in comparison with conventional steam cracking.

2. Experimental

The multilayered catalyst structure consisted of a La_2O_3-stabilized γ-Al_2O_3 washcoat layer of constant average thickness, anchored on a cordierite honeycomb (NGK, 600 cpsi $D \times L = 17\,mm \times 6\,mm$). A $LaMnO_3$ layer was deposited by repeated cycles of co-impregnation with a equimolar solution of the precursor salts and calcination in air at 800 °C. Finally, Pt (2%, w/w of active layer, monolith substrate excluded) and eventual dopants (Sn or Ga, dopant/Pt atomic ratio = 6) were added to the structure by impregnation of the coated monolith with a H_2PtCl_6 (and $SnCl_2$ or $Ga(NO_3)_3{\bullet}xH_2O$) solution. More details on catalyst preparation and characterization were already reported [8,9].

High-purity gases calibrated via mass-flow controllers were pre-mixed at 1.2 atm and fed at a GHSV between 6.0 and $19 \times 10^4\,h^{-1}$ corresponding to residence times as low as 6 ms at an average temp. of 900 °C [9]. Reaction tests with C_2H_6 (or C_3H_8) and O_2 mixtures were undertaken at varying C/O ratio in the range 1.75–2.5 (2–3.25 for C_3H_8); CH_4, CO or H_2 were studied as sacrificial fuels and their quantity was controlled with respect to O_2 feed.

The catalytic honeycomb, in the shape of disk of ~18 mm diameter and 12 mm long, was sandwiched between two inert mullite foam monoliths (45 ppi, same dimensions) as radiation shields: the stack of monoliths was placed in a quartz reactor (id 20 mm) externally heated by an electric furnace to ensure desired pre-heating (up to 400 °C). K-type thermocouples ($d = 0.5$ mm) were used to measure the temperature in the middle of the central channel of the catalyst (Tcat) and in the exit gas downstream of the back heat shield. Further details on the experimental set-up can be found in [8,9].

Product gases passed through a condenser and a $CaCl_2$ trap to selectively remove water, prior to splitting to a ABB continuous analyzer, employed to measure concentrations of H_2 (Caldos17), CO, CO_2 and CH_4 (Uras14), and to an on line gas chromatograph equipped with a RTX Allumina Plot 0.53 mm 30 m column (Restek) and TCD + FID detectors, optimized to measure C_3H_8, C_3H_6, C_2H_6, C_2H_4, C_2H_2, CH_4, CO, CO_2 and other eventual hydrocarbons up to C_4. Using N_2 (5–10 vol.%) as internal standard, the carbon balance was always closed within 2% for ethane feed and 5% for propane, mainly due to the larger number of unmeasured products. Results are generally reported in terms of C-atom selectivity calculated as the ratio of the moles of a specific product to the total moles of converted ethane/propane, with all species scaled by their number of C atoms.

3. Results

3.1. Ethane CPO

Paraffin to olefin conversion over structured catalysts operated at short contact time relies on the combination of three different reaction paths of the paraffinic hydrocarbons: the catalytic partial oxidation (CPO) with oxygen, which is a self-sustaining process, the oxidative dehydrogenation (ODH), in competition with CPO, and the thermal cracking at high temperature, which is driven by the in situ combustion of part of the feed [5–16].

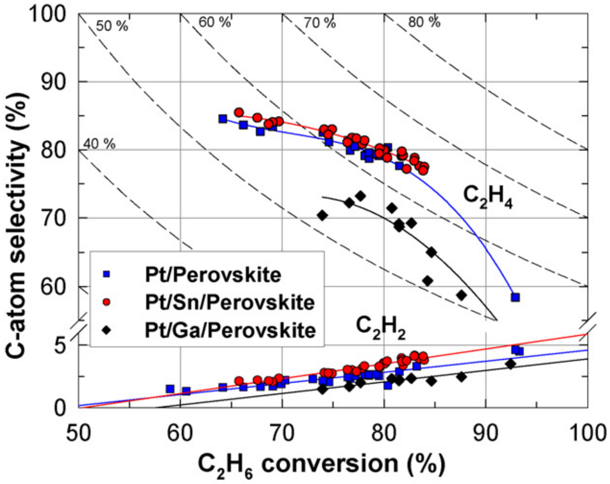

Fig. 1. Effect of dopants on C_2H_4 and C_2H_2 selectivities over Pt/$LaMnO_3$ catalysts during ethane CPO. Dashed lines represent iso-yield curves.

In the conversion-selectivity diagram of Fig. 1 the data obtained on the Pt/$LaMnO_3$ catalyst under optimized process conditions follow a single line and are highly reproducible [9]: C_2H_4 yields above 60% and selectivity above 80%, can be obtained with several combinations of C_2/O_2, H_2/O_2, GHSV and preheat. In fact, it was found that any of the parameters exhibited an opposite effect on conversion and selectivity: when increased, C_2H_6/O_2 ratio, H_2/O_2 ratio and space velocity reduce conversion and enhance selectivity while pre-heating temperature reduces selectivity and enhances conversion [9].

As shown in Fig. 1, doping the catalyst with Ga has a strong negative effect on ethylene selectivity and yield that never exceeds 58% on a molar basis; also C_2H_2 selectivity is reduced with respect to the undoped catalyst. On the other hand, Sn-doping entails a small positive effect since selectivity to C_2H_4 and C_2H_2 are both slightly enhanced probably due to a stronger dehydrogenation activity of the catalyst. Under optimized process conditions the Pt/Sn/$LaMnO_3$ catalyst guarantees a total yield per pass to ethylene and acetylene in excess of 68% molar (above 60% on a mass basis), in correspondence to a C-atom selectivity to ethylene and ethane conversion both above 80%.

A direct comparison of the products distribution obtained over the three catalytic systems (Fig. 2) shows all the major species follow the same qualitative trend as a function of ethane conversion (process severity), whose increment is always accompanied by a corresponding increase of C-atom selectivity to CO, CH_4, C_2H_2 and CO_2 and, consequently, a reduction in C_2H_4 selectivity and O-atom selectivity to H_2O.

At fixed ethane conversion the Sn-doped catalyst shows a strongly reduced formation of CO, which is partly compensated by a larger formation of methane, apart from the already mentioned C_2H_4 and C_2H_6.

CO_2 selectivity is not sensibly affected by catalyst formulation, especially in the presence of H_2 as sacrificial fuel: this is most probably due to the occurrence of the equilibrium RWGS reaction (1), which is shifted towards CO and water due to the high temperatures and large partial pressure of H_2 in the product stream.

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H_r^{25\,^\circ C} = +41\,kJ/mol \tag{1}$$

The plot of O-atom selectivity to H_2O over undoped Pt/$LaMnO_3$ reveals that roughly 80–90% of the oxygen fed to the reactor is

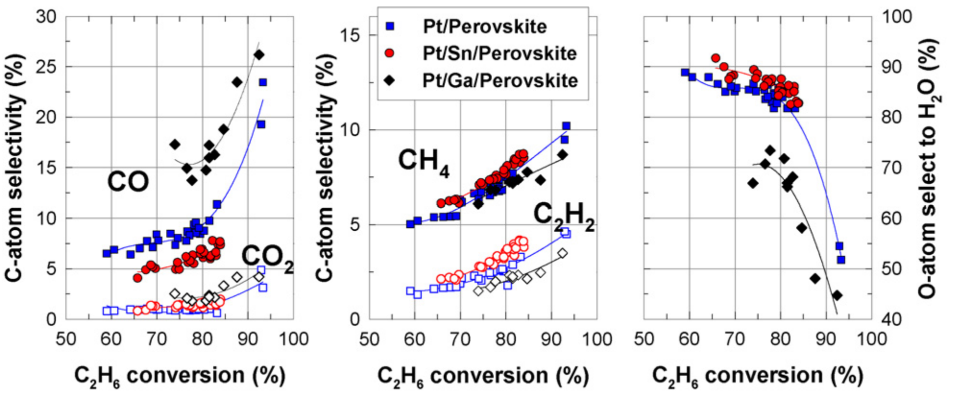

Fig. 2. Effect of dopants on C-atom selectivities to the main by-products and O-atom selectivity to water over Pt/LaMnO$_3$ catalysts during ethane CPO.

used to form water rather than CO_x for conversions <85% and H_2 co-feeding. Sn ensures small but measurable increase of H_2O selectivity in the whole range of conditions, which further confirms a better utilization of the sacrificial H_2. On the other hand, Ga doping shows a marked negative impact.

Overall, the suppressed partial oxidation activity of Pt clusters strongly interacting with the perovskite sublayer or with tin might well be due to the inhibition of secondary unwanted steam reforming reaction consuming both ethane/ethylene and water to form CO and H_2. In fact it was demonstrated by detailed species profiles along Pt catalysts during methane and ethane CPO that steam reforming of residual fuel escaping from the first catalytic oxidation zone contributes to a large extent of the overall syn-gas formation even when the reactor is operated at extremely short contact times [18–19]. Therefore, inhibition of steam reforming is a key issue to keep a high ethylene selectivity in the CPO of ethane: indeed, the poor ethylene yield over Ga doped catalyst mirrors the low O selectivity to water and high syn-gas formation.

The enhancement of olefin yield and selectivity is related to a more favourable product distribution in the first oxidation zone of the reactor, where the sacrificial fuel has to be oxidized selectively with respect to ethane while oxygen has to be consumed to form total rather than partial oxidation products in order to minimize its consumption, required to sustain the optimal surface temperature level slightly below 1000 °C [9,11]; moreover in the second part of the reactor, catalytic steam reforming has to be inhibited by proper catalyst formulation. In the same way CH_4, which is suggested to be formed only at high temperatures at similar rates both in the gas phase and on the Pt surface [20], might be reduced by reducing the extent of hot spot formation on the catalyst [5] (for instance reducing pore size or enhancing thermal conductivity).

Regarding the impact of the type of sacrificial fuel added, CH_4, CO and H_2 are all able to improve process selectivity to C_2H_4 by reducing the amount of C_2H_6 consumed through oxidation reactions to CO_x. Fig. 3a shows that progressively better results are obtained at fixed C_2H_6/O_2 feed ratio over Pt/Sn/LaMnO$_3$ catalyst when adding the sacrificial fuel in the order $CH_4 < CO < H_2$. In particular the increase in selectivity to C_2H_4 with the addition of CO and H_2 more than compensates the simultaneous decrease in ethane conversion so that there is a net increase in olefin yield. The addition of H_2 or CO causes an increase in the temperature measured on the catalysts (not shown), which is consistent with the higher net heat of combustion of the sacrificial fuels per mole of oxygen with respect to ethane (Table 1). From the point of view of minimizing O_2 consumption (cost) to generate in situ the heat necessary to drive the endothermic dehydrogenation reaction, CO and H_2 represent, in this order, the most favourable options. Moreover they do not present any selectivity issue with regards to the products of partial vs. total oxidation.

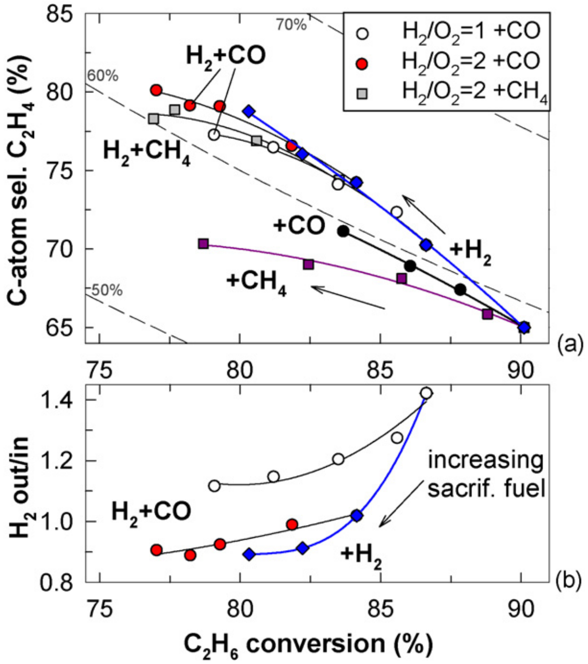

Fig. 3. Effect of sacrificial fuel (CH_4, CO, H_2) addition on ethane CPO performance over Pt/Sn/LaMnO$_3$ catalyst at fixed $C_2H_6/O_2 = 1.9$: (a) C_2H_6 conversion and selectivity to C_2H_4 (dashed lines represent iso-yield curves); (b) H_2 net consumption/production per pass. $CH_4/O_2 = 0–1$; $CO/O_2 = 0–3$; $H_2/O_2 = 0–3$. For mixed fuels: $(CO + H_2)/O_2 = 0–3.5$; $CH_4/O_2 = 0–0.75 + H_2/O_2 = 2$.

Optimal H_2 (or CO) to O_2 feed ratio is found to be well above the stoichiometric value for sacrificial fuel combustion, in particular it is ≥3: the excess of H_2 (or CO) is useful to further increase the oxygen selectivity to form water or CO_2, since at the high catalyst operating temperature, under fuel rich conditions, the oxidation of ethane is fast enough to compete with that of H_2 and CO.

Table 1
Net heat of combustion of selected fuels per mole of O_2 consumed.

	Stoic. O_2 moles for combustion	Net combustion heat per mole O_2 (kJ/mol)
CH_4	2	403.1
C_2H_6	3.5	408.2
C_3H_8	5	408.6
C_2H_4	3	440.0
C_3H_6	4.5	428.0
C_2H_2	2.5	502.0
H_2	0.5	484.0
CO	0.5	566.0

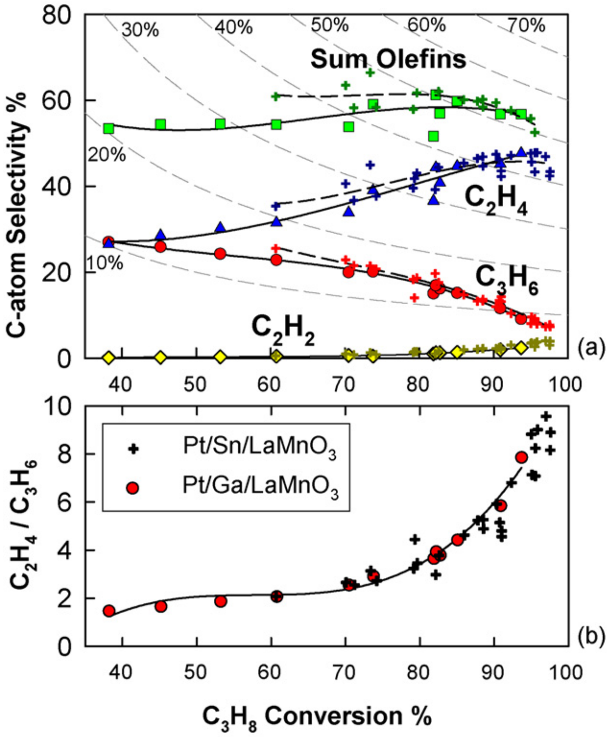

Fig. 4. Results of propane CPO over doped Sn or Ga doped Pt/LaMnO$_3$ catalysts. (a) C-atom selectivities to C_3H_6, C_2H_4 and C_2H_2 (dashed lines represent iso-yield curves); (b) molar C_2H_4/C_3H_6 product ratio as a function of C_3H_8 conversion.

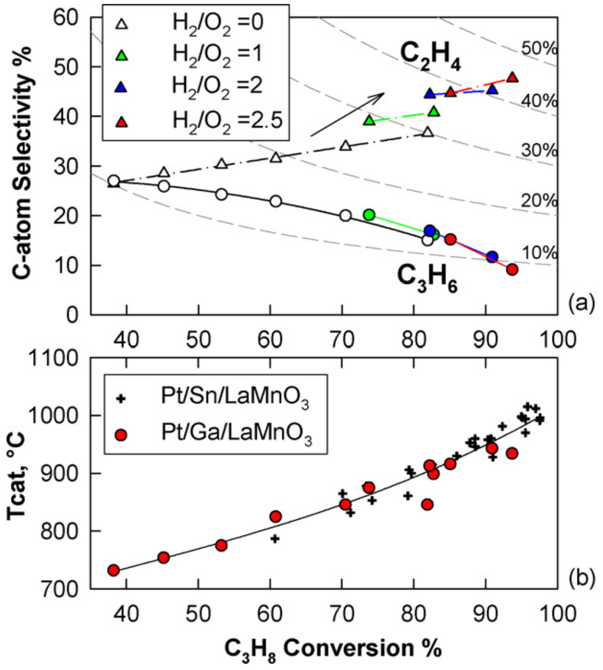

Fig. 5. (a) Effect of H_2 addition on C_2H_4 and C_3H_6 selectivities over Pt/Ga/LaMnO$_3$ catalyst during propane CPO (dashed lines represent iso-yield curves). (b) Correlation between C_3H_8 conversion and catalyst temperature measured over both Sn and Ga doped Pt/LaMnO$_3$ systems.

As shown in Fig. 3b, a net consumption of H_2 is observed at the conditions under which the selectivities of ethylene are maximized: this was already reported over Pt/Sn and Pt/LaMnO$_3$ catalysts [6–9] and represents an economical drawback due to the high cost of H_2 make-up.

However, in the actual catalyst formulation, Pt sites show a marked activity towards H_2 oxidation while LaMnO$_3$ phase is characterized by a high oxidation activity for CO [21]. Thanks to the simultaneous presence of both types of active sites, optimal performance can be achieved with a mix of sacrificial fuels containing both H_2 and CO, in correspondence of a feed $(H_2+CO)/O_2$ ratio around 3 (Fig. 3a). Such strategy helps reducing or completely avoiding the net H_2 consumption per pass (Fig. 3b). In the presence of CO, less H_2 is consumed, since both fuels compete for oxygen at comparable rates; moreover the higher partial pressure of CO limits H_2 conversion to water through the RWGS equilibrium reaction. However a WGS unit downstream of the ODH reactor could be used in order to close the H_2 balance by recycling it after recover from the product stream still rich of water and CO.

3.2. Propane CPO

Results of CPO of propane over doped Pt/LaMnO$_3$ catalysts with or without the addition of H_2 as sacrificial fuel are conveniently summarized in Fig. 4 in the C–S plane: selectivities to each olefin are strongly correlated to propane conversion and tend to follow single lines. Moreover, the Sn-doped catalyst performs only slightly better than the Ga doped one, mainly with regards to C_2H_4 yield, in spite of the large difference which was observed during the CPO of ethane. At increasing process severity (i.e. propane conversion) ethylene, methane and acetylene formation are progressively enhanced whilst the selectivity to propylene is adversely affected. As a consequence the C_2/C_3 olefins molar yield ratio is comprised between 1.5 and 2 up to 70% propane conversion and increases quickly at higher process severity due to a rapid decrease in propylene selectivity in favour to ethylene (Fig. 4b).

The sum of C-atom selectivities to olefins is almost constant at roughly 60% for C_3H_8 conversions up to 90%, before dropping due to lower propylene formation. Propylene (C-atom) yield over Pt/Sn/LaMnO$_3$ catalyst attains a small maximum of roughly 16% in correspondence of a C-selectivity of 23% at 70% conversion, which is slightly better than C_3H_6 13% yield obtained on Pt monoliths at similar conversions [6,11]. Regarding ethylene, the maximum yield of 46% atomic (corresponding to 69% on a molecular basis) is observed at very high propane conversion (~96%).

An important difference with the case of ethane CPO is related to the effect of the sacrificial fuel: Fig. 5a shows clearly that H_2 addition has no direct impact on propylene formation curve, being ineffective to avoid C_3H_8 consumption to form undesired CO_x products. On the other hand, ethylene selectivity and yield are enhanced by the presence of the sacrificial fuel up to a H_2/O_2 feed ratio = 2. In fact, H_2 addition does increase the operating temperature on the catalyst since it is preferentially oxidized instead of the hydrocarbon feed and it has a higher net heat of combustion per mole of O_2. As shown in Fig. 5b, which presents all the data collected under a wide range of experimental conditions (pre-heating, C/O and H/O feed ratios), propane conversion is strictly correlated to the temperature level in the catalytic reactor, and is not influenced by catalyst formulation (doping with Ga or Sn).

The results suggest a less pronounced role of the catalyst in the CPO of propane since propylene formation is only occurring in the gas phase and, above all, is not limited by the selectivity of the catalytic oxidation reactions but only by the low selectivity of the homogeneous dehydrogenation reaction.

3.3. Economics of ethane CPO

An economic analysis of ethane CPO technology was run by Snamprogetti on the basis of its specific engineering knowhow in order to update the previous available evaluations [4,5] by

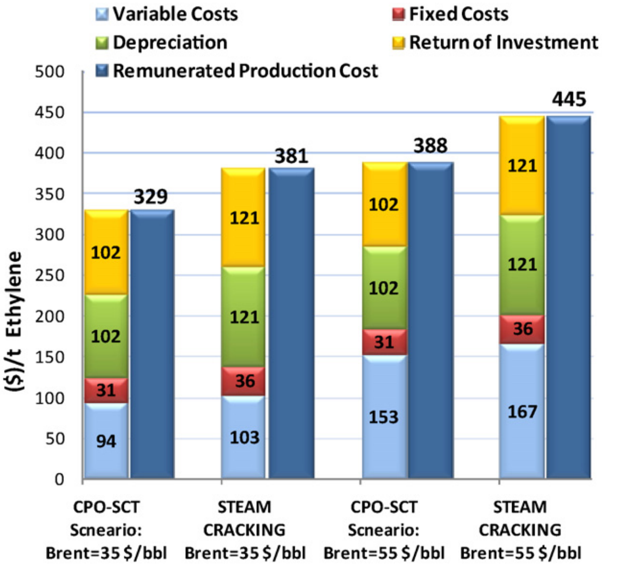

Fig. 6. Economic analysis comparing specific ethylene production costs from ethane by CPO with novel Pt/$LaMnO_3$ catalyst or by steam cracking. Two oil price scenarios were considered: 35 and 55 $/bbl, corresponding to ethane at 1.5 and 2.5 $/MBtu respectively.

including the new experimental results obtained on our best catalyst formulation (with sacrificial H_2 addition). Detailed process schemes for a 1MtA ethylene plant from ethane were developed for both the CPO technology and the last generation of steam cracking, assuming identical site state (brown root) located in the middle east and considering two scenarios for the oil price (low and medium, respectively at 35 and 55 $/bbl, corresponding to ethane price at 1.5 or 2.5 $/MBtu). Investment costs for CPO were estimated taking into proper account the main criticalities of the novel technology and in particular: the manufacturing of a dedicated O_2 plant (ASU), whose cost accounts for roughly 11% of the total of bulk materials; the presence of an acid gas removal unit, not required in the steam cracking scheme; the need for high temperature corrosion resistant heat exchangers and larger compression and refrigeration sections.

Under optimized process conditions, ethane CPO resulted more attractive than steam cracking by roughly 13% of the remunerated production cost, almost independently from the raw material price scenario (Fig. 6). Considering the margin of accuracy of this kind of analysis [4,5], such savings are probably not yet enough for a new technology breakthrough. Nevertheless the economic attractiveness of catalytic partial oxidation process is confirmed to be highly sensitive even to small selectivity (yield) variations [4,5], and there is room for further improvements connected to both catalyst formulation and reactor engineering [22].

Moreover, the scenario can be changed by either a better integration/valorization of the large O_2 plant required or by eventual environmental prizes for CO_2 reduction. In contrast to steam cracking, which is among the biggest user of energy in the chemical industry worldwide [4], the CPO technology is environmentally friendly since heat is generated in situ without NO_x formation through the oxy-combustion of hydrogen extracted from the hydrocarbon feed. As already shown, CO_2 formation per pass is extremely low and the process scheme includes CO_2 capture and removal.

4. Conclusions

Doping Pt/$LaMnO_3$ catalyst with Sn was found to further improve olefin production in ethane CPO with yields to ethylene and acetylene in excess of 68% molar per pass, in correspondence to a C-atom selectivity to ethylene and ethane conversion both above 80%. The beneficial effect is related to a further reduction in syngas formation and improvement of sacrificial H_2 oxidation to form water. On the other hand, Ga doping did not result in the same performance.

Due to the dual site nature of the catalyst formulation, it is possible to profitably use CO in combination with H_2 as sacrificial fuel, boosting ethylene selectivity (and yield), while simultaneously avoiding the previously reported drawback of net hydrogen consumption in the CPO reactor.

The novel catalysts were also tested for ethylene and propylene production via CPO of propane with particular emphasis on total olefin yield and ethylene to propylene ratio. The role of the catalyst formulation was found to be marginal since propylene formation only occurs in the gas phase and is not limited by the selectivity of the catalytic oxidation reactions but exclusively by the low selectivity of the homogeneous dehydrogenation reaction.

The economical viability of ethane CPO process as a compact alternative to steam cracking with lower environmental impact was reconsidered in view of the novel results attained. Under optimized process conditions, ethane CPO resulted to be more attractive than steam cracking by 13% of the remunerated production cost, almost independently from raw material price scenario. The novel technology might results even more attractive by better valorization of the integrated O_2 plant and/or in presence of an environmental prize for the large CO_2 reduction attained with respect to steam cracking.

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