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Crossing the breakthrough line of ethylene production by short contact time catalytic partial oxidation

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Abstract

A novel catalyst (Pt-$LaMnO_3$) for the oxidative dehydrogenation of ethane to ethylene in short contact time reactors was developed by Istituto di Ricerche sulla Combustione (CNR) in cooperation with Snamprogetti, with a multi-layered structure consisting of a thin layer of Pt deposited onto a layer of $LaMnO_3$ perovskite supported over monolithic carriers. Such structured catalyst was tested in a head-to-head comparison with state-of-the-art Pt and Pt-Sn systems, under autothermal process conditions, showing enhanced performances both in terms of high temperature stability and yields to ethylene. The development of a durable, high-performance catalyst undertaken in this work may be beneficial to making catalytic ethane ODH more economically viable and represents a further step towards its pre-commercial implementation.

Keywords: Olefin production; Catalytic partial oxidation; Ethane ODH; Pt-perovskite; Structured catalysts; Short contact time reactors

1. Introduction

The oxidative dehydrogenation of ethane (ODH) is an emerging technology, which has been thoroughly investigated in recent years and evaluated as alternative to the steam-cracking route to produce ethylene [1]. High olefins yields can be attained by the partial catalytic oxidation of hydrocarbons in structured autothermal reactors operated at high space velocity using Pt based catalysts [2,3,4,5]. In particular, doping Pt with tin or copper resulted in improved performance for ethane ODH, with a significant increase in ethylene yield up to 55% on a carbon atom basis [6], which was even greater (around 60%) when H_2 was added as a sacrificial fuel [7]. Nevertheless, the use of such state-of-the-art bi-metallic catalysts is penalized by the elevated cost of Pt and by the volatility of the active phase at the high operating temperatures, which reduces the thermal stability and the durability of the catalytic system [4,7].

From the standpoint of industrial application, the simpler autothermal reactor and fewer fractionation columns of the ethane catalytic partial oxidation process result in about 20–25% lower estimated investment cost with respect to a corresponding ethane cracker. On the other hand, estimated production costs are somewhat higher (10–15%) at present levels of performance of the catalytic route, mainly due to the additional cost of oxygen [8].

Hence, the condition for the short contact time catalytic ODH of ethane to cross the breakthrough line is represented by the development of a durable and cheap catalytic system, exhibiting enhanced thermal and mechanical stability at the high process temperature and capable of attaining ethylene selectivity and yield significantly higher than the steam cracking (85% selectivity at 60% conversion [8]).

$LaMnO_3$ perovskite-like catalyst, recently developed at the Istituto di Ricerche sulla Combustione (IRC), CNR, Italy, is more economical than Pt-based and represents a good alternative for its higher thermal stability and interesting process performance, leading to ethylene yields larger than those obtainable on Pt [9,10], even though not yet

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beyond the breakthrough line for industrial application, not even by adding CO or H_2 as secondary fuels [11].

Requirements for higher performance has led to the development of a novel catalyst (Pt-$LaMnO_3$), patented in cooperation with Snamprogetti [12], with a multi-layered structure consisting of a thin layer of Pt deposited onto a layer of $LaMnO_3$ perovskite supported over monolithic structures. The deposition of Pt onto $LaMnO_3$ results in a fine dispersion of the noble metal, which is hence required in smaller amounts, and can be effectively stabilized at the operation temperature. In this work, we present a head-to-head comparison between state-of-the-art catalysts (Pt and Pt-Sn) and the novel bi-functional system Pt-$LaMnO_3$, tested in the short contact time autothermal ODH of ethane with or without addition of H_2 as sacrificial fuel.

2. Experimental

The multi-layered catalyst structure consists of a La_2O_3-stabilized γ-Al_2O_3 washcoat layer of constant average thickness, anchored on a monolithic α-Al_2O_3 ceramic substrate with foam morphology and pore density of 45 ppi (pores per inch), provided by Vesuvius Hi-Tech Ceramics. $LaMnO_3$ perovskite is deposited onto the washcoat layer by repeated cycles of co-impregnation with a solution of the precursor salts, as previously described [11]. Finally, Pt is added to the structure by impregnation of the coated monolith with a H_2PtCl_6 solution. The catalysts were calcined in air at 800 °C after the deposition of each layer and at 1000 °C for 3 h before testing. The catalytic monoliths, in the shape of disks of 17 mm diameter and 10 mm long, were stacked between two inert monoliths as radiation shields and placed in a quartz tube, thermally insulated with ceramic wool.

Reaction tests were undertaken at varying C_2H_6/O_2 and H_2/O_2 ratios, constant pressure (1.3 atm) and a total flow rate of 5 slpm (standard liters per minute), corresponding to a gas hourly space velocity (GHSV) of $2 \times 10^5\ h^{-1}$ and to a residence time of about 5 ms at the average reactor temperature of 900 °C. All results were checked twice for repeatability. The carbon balance was always closed within 2% using N_2 (fixed at 30 vol.%) as internal standard.

The reactor operated autothermally without pre-heating under steady state conditions and heat was supplied only for the purpose of obtaining ignition. In addition to the products indicated in the figures, methane, acetylene, propane, propene, butane and butene were measured in the gaseous stream at the outlet. All the results were repeatable over numerous hours of operation.

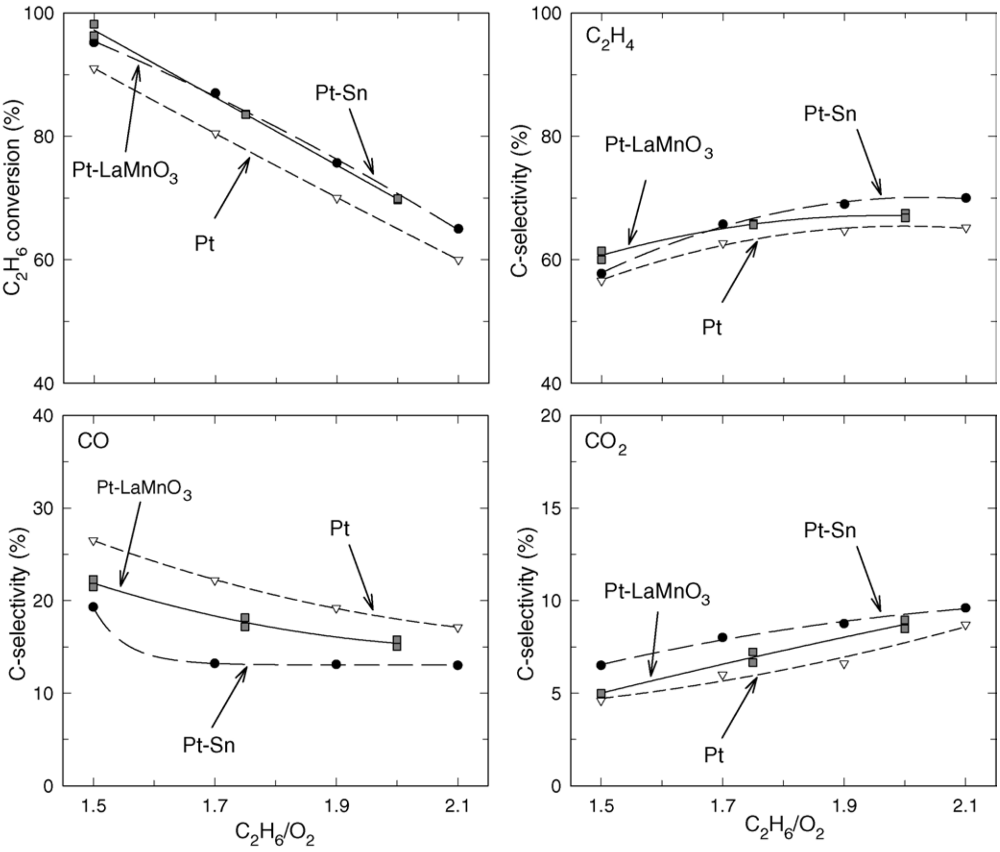

Fig. 1. C_2H_6 conversion and carbon atom selectivity to C_2H_4, CO and CO_2 for Pt-$LaMnO_3$ catalyst as a function of C_2H_6/O_2 ratio in the feed, in comparison with literature data for Pt and Pt-Sn catalysts [6].

3. Results and discussion

The performance of the Pt-$LaMnO_3$ catalyst is compared with data provided in the literature for Pt and Pt-Sn [6,7] on the same ceramic substrates (45 ppi α-Al_2O_3 foam monoliths, from Vesuvius Hi-Tech Ceramics) and under the same experimental conditions (flow rate of 5 slpm). Fig. 1 shows the ethane conversion and the C-atom selectivity to the main products at varying the C_2H_6/O_2 ratio in the feed. In the range examined, the ethane conversion attained on the Pt-$LaMnO_3$ catalyst is comparable to that observed on Pt-Sn, decreasing linearly with C_2H_6/O_2 from above 95% at $C_2H_6/O_2 = 1.5$ to 70% at $C_2H_6/O_2 = 2$. Conversely, the highest values of ethylene selectivity are attained at $C_2H_6/O_2 = 2$ (68%) and are only slightly lower than those observed on Pt-Sn (around 70%). At $C_2H_6/O_2 = 1.5$ a higher selectivity is exhibited by Pt-$LaMnO_3$ (60% versus 58% on Pt-Sn).

On Pt, the ethane conversion is always 6–7 points percent lower than on the other catalysts, while the ethylene selectivity is around 5% lower (Fig. 1). It was demonstrated that the oxidation of a fraction of ethane takes place on the catalytic surface [4,5,9] and is needed to generate the heat to drive the endothermic dehydrogenation of the remaining ethane in the gas phase.

Clearly, the higher the fraction of oxygen that is converted to total oxidation products (CO_2 and H_2O) the lower the amount of ethane sacrificed to produce heat, and the higher the ethylene selectivity.

The difference in performance among the catalysts can be hence explained by their different intrinsic activity and selectivity towards deep oxidation products, which in turn affect gas phase dehydrogenation of the remaining fraction of ethane.

Coherently, larger quantities of CO and smaller quantities of CO_2 are produced on the worst performing Pt catalyst. On the other hand, both the addition of Sn or the dispersion of Pt on the perovskite sub-layer reduce the formation of CO in favour of CO_2 (Fig. 1), with a corresponding increase in the formation of H_2O.

The experimental data relating to mixtures containing hydrogen as sacrificial fuel on supported Pt-$LaMnO_3$ are compared in Fig. 2 with the experimental data of Bodke et al. [7], for Pt and Pt-Sn. The progressive addition of hydrogen at fixed $C_2H_6/O_2 = 2$ causes a decrease in the ethane conversion, extremely significant on Pt, and less dramatic on Pt-$LaMnO_3$ and on Pt-Sn. Correspondingly, the selectivity to ethylene increases with an increase in the quantity of hydrogen present in the feed, but such an increase is less pronounced in the case of the Pt catalyst.

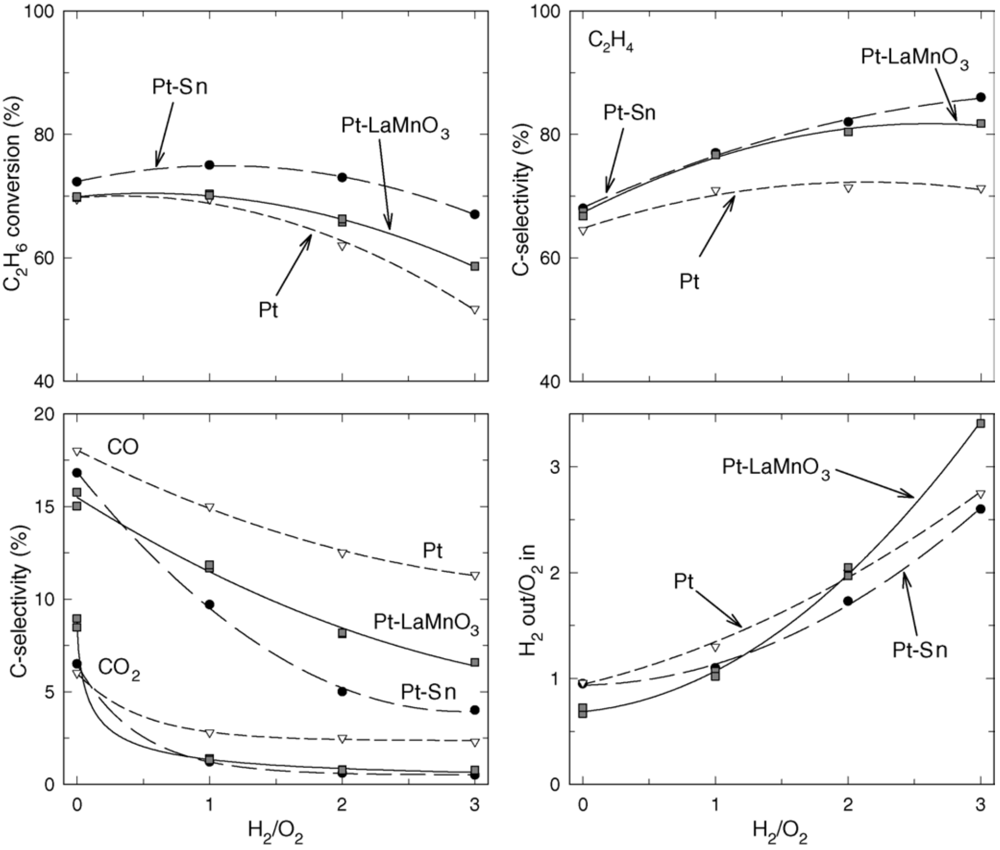

Fig. 2. C_2H_6 conversion, carbon atom selectivity to C_2H_4, CO and CO_2 and moles of H_2 produced per mole of H_2 fed for Pt-$LaMnO_3$ catalyst as a function of H_2 added in the feed (H_2/O_2), in comparison with literature data for Pt and Pt-Sn catalysts [7].

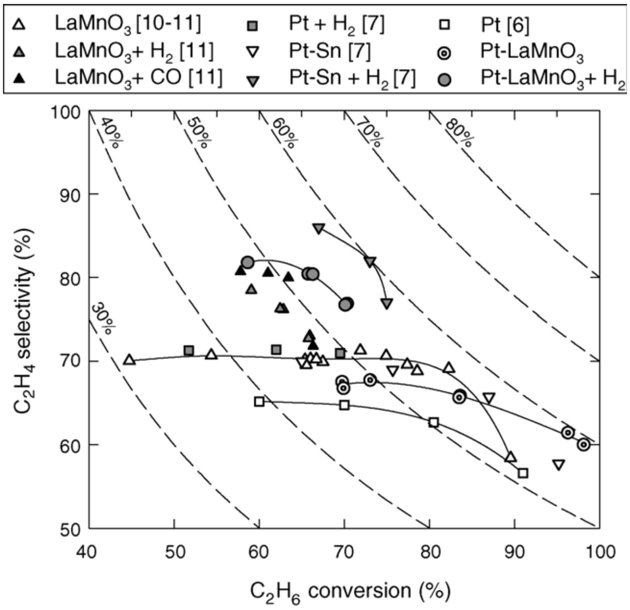

Fig. 3. Ethylene selectivity vs. ethane conversion for Pt-$LaMnO_3$ based catalyst in comparison with literature data.

Hence, the yields to ethylene show an optimum for H_2/O_2 ratios ranging from 1 to 2.

It can also be seen that higher quantities of CO and CO_2 are formed on Pt, whereas on Pt-Sn and on Pt-$LaMnO_3$ the selectivities to these species are substantially analogous.

It should be noticed that only in the case of Pt-$LaMnO_3$ the moles of H_2 consumed are balanced by the moles of H_2 produced in the reaction (Fig. 2), and consequently the possibility of recycling H_2 to the reactor becomes feasible.

Due to a lower activity for oxidizing hydrogen, the moles of H_2O produced on Pt are less than those produced on Pt-Sn and on Pt-$LaMnO_3$, and are substantially constant for H_2/O_2 feed ratios between 1 and 3.

Interestingly, Pt-$LaMnO_3$ catalyst does not show intermediate performance between Pt and $LaMnO_3$, but exhibits an improvement, primarily in terms of ethane conversion and secondarily in ethylene selectivity. This is clearly shown in Fig. 3, where the comparison of Pt-$LaMnO_3$ with other catalysts is focused on the dependence of the ethylene selectivity with respect to the ethane conversion. This form of comparison is preferred due to the heterogeneity of conditions of experimental testing and different ceramic supports reported in the literature. In particular, results on $LaMnO_3$ perovskite catalyst were obtained on 400 cpsi honeycomb monoliths operated at six times lower space velocity ($3.3 \times 10^4\ h^{-1}$), since the lower activity of $LaMnO_3$-based reactor requires longer residence times if no preheating is applied.

Without sacrificial fuel addition, the performance of Pt-$LaMnO_3$ (5 slpm) is comparable to $LaMnO_3$ and Pt-Sn and

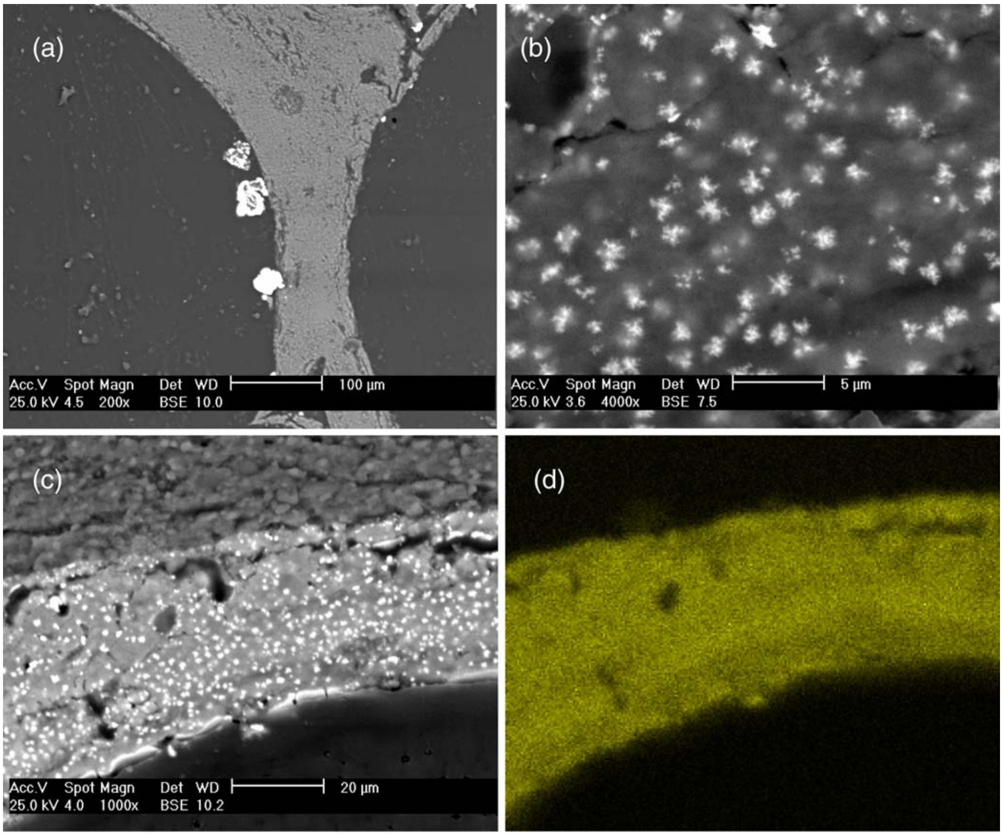

Fig. 4. SEM images of ceramic foam catalysts: (a) Pt particles on bare α-Al_2O_3; (b) details of Pt-$LaMnO_3$ on γ-Al_2O_3 washcoat; (c) Pt-$LaMnO_3$ on γ-Al_2O_3 washcoat layer; (d) EDS map of Mn distribution in the Pt-$LaMnO_3$/γ-Al_2O_3 active layer.

remarkably better than Pt. Upon hydrogen addition, Pt-$LaMnO_3$ (5 slpm) performs better than $LaMnO_3$, much better than Pt and slightly worse than Pt-Sn.

Noticeably, the synergy between the Pt particles and the $LaMnO_3$ active phase becomes even more evident at lower space velocity, where perovskite active sites might play a more important role. Indeed preliminary data, obtained optimizing the operating conditions by means of the reduction of the space velocity, the modification of the C_2H_6/O_2 and H_2/O_2 ratios and preheating of the feed, show that yields exceeding 65%, while preserving selectivities above 80%, are easily achievable. Such results, which are significantly better than industrial steam cracking performance, exceed the best results ever reported on Pt/Sn [7], but with a superior high temperature durability, suggesting that the breakthrough line for industrial application may be crossed in terms of both catalyst performance and stability.

The increased performance of the Pt-$LaMnO_3$ catalyst results from the strong interaction between the Pt particles and the perovskite active phase. The scanning electron microscopy (SEM) analysis summarized in Fig. 4, gives clear evidence of different distribution of Pt, when it is dispersed on the bare macroporous alumina support (Pt catalyst, Fig. 4a), and when it is dispersed onto the intermediate perovskite layer (Pt-$LaMnO_3$ catalyst, Fig. 4b and c).

On the bare alumina support (BET surface area $<1\ m^2/g$), Pt forms large cluster particles, whose dimensions range between 10 and 30 μm, and which tend to grow even further at longer times under reaction conditions at high temperature.

The active catalyst layer in Pt-$LaMnO_3$ system (BET surface area $\sim 50\ m^2/g$), whose average thickness is $\sim 20\ \mu$m, is shown in Fig. 4c, where the ceramic foam support is depicted in darker colours and the washcoat layer (Pt-$LaMnO_3$ on porous γ-Al_2O_3) appears brighter. $LaMnO_3$ is uniformly distributed on the porous γ-Al_2O_3 layer, as demonstrated by EDS maps collected on the cross-section of the active layer: for example, the Mn distribution inside the washcoat layer is depicted in Fig. 4d.

Pt is uniformly distributed in the whole depth of the washcoat in the form of fine particles with fringed edges (white aggregates in Fig. 4b and c), whose characteristic dimension are $\leq 1\ \mu$m, even after exposure to high temperature.

The deposition of Pt onto the perovskite layer not only results in the fine dispersion of the noble metal, but in a strong interaction, which positively affects the catalyst activity and that is not observed when Pt is deposited onto a porous γ-Al_2O_3 layer. The fine dispersion of Pt onto a γ-Al_2O_3 layer does result in an increase of activity of surface reaction, but it is accompanied by a shift of the main products from ethylene to syn-gas [13].

On the contrary, the interaction of Pt with the perovskite layer produces a synergetic effect, resulting from coupling the high activity of Pt towards ethane activation with the marked activity of $LaMnO_3$ towards CO oxidation, which in turn results in higher ethylene selectivity and higher conversion with respect to either Pt or $LaMnO_3$ alone.

Furthermore, Pt is stabilized within the perovskite structure. Pt-$LaMnO_3$ catalyst did not show signs of deactivation after 100 h under reaction. The dispersion of Pt in very small particles and the strong interaction with the perovskite appears effective in preventing sintering phenomena between the particles themselves. The catalyst based on Pt-Sn, on the other hand, begins to show after a few operating hours signs of deactivation mainly due to the high volatility of tin [4,7].

4. Conclusion

A novel catalyst was developed with a multi-layered structure consisting of a thin layer of Pt deposited onto a layer of $LaMnO_3$ perovskite supported over monolithic carriers. The deposition of Pt onto $LaMnO_3$ results in a fine dispersion of the noble metal, which is required in small amounts, and its stabilization at the operation temperature. Moreover, due to the strong interaction of the two active phases, Pt and $LaMnO_3$, the catalyst performance is greatly enhanced, resulting in higher ethylene selectivity and higher conversion with respect to either Pt or $LaMnO_3$ alone.

Preliminary data obtained during the search for optimum operating conditions and adding H_2 as a sacrificial fuel show that the ethylene yields exceeding 65% preserving selectivities above 80% are easily achievable. Such results approach and even exceed the best results ever reported on Pt-Sn catalysts [7], but with a superior high temperature stability.

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