Available online at www.sciencedirect.com
SCIENCE DIRECT®
Catalysis Today 91–92 (2004) 285–288
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Catalyst investigation for applications of oxidative dehydrogenation of ethane in short contact time reactors

Francesco Donsì*, Raffaele Pirone, Gennaro Russo

Istituto di Ricerche sulla Combustione, CNR, P.le Tecchio 80, 80125 Napoli, Italy

Abstract

$LaMnO_3$-based catalysts were tested in a head-to-head comparison with Pt in the oxidative dehydrogenation of ethane at short contact times under the same reactor configuration (400 cpsi honeycomb monolith). The comparison, carried out at varying C_2H_6/O_2 feed ratio and flow rate, showed that on $LaMnO_3$-based catalyst ethylene formation is greatly enhanced in comparison with Pt under a wide range of experimental conditions. Accordingly, product distribution unveils a deeper oxidation of ethane on $LaMnO_3$, resulting in a more efficient heat production and the formation of lower amounts of CO_x.

Keywords: Oxidative dehydrogenation; Short contact time reactors; Non-noble-metal catalyst

1. Introduction

The oxidative dehydrogenation (ODH) of ethane in short contact time reactors (SCTR) was first proposed by Huff and Schmidt [1] in 1993 and, since then, the process was mainly carried out over Pt-based ceramic foam monoliths [1–5].

An initial investigation in the field of partial oxidation of light hydrocarbons on noble metals indeed revealed that Pt-based catalysts amongst the noble metals enhance most ethylene formation [6]. Nevertheless, the presence of Pt influences product distribution to a limited extent in this process, as it was provided clear evidence both by theoretical [5] and experimental works [7] that the catalyst mainly oxidizes the fuel to CO_x and H_2O, while ethylene is primarily formed in the gas phase. Changing the catalyst composition was thus considered a possible means for obtaining performance enhancement. As a matter of fact, the addition of Sn to the Pt-based catalyst raised ethylene yield of about 5% [8]. Flick and Huff [2] instead showed that conversion and selectivities comparable with Pt could be obtained with non-noble-metal catalysts such as Cr_2O_3-based foams, and similarly Beretta and Forzatti [9] claimed good experimental results on hexa-aluminates. Nevertheless, the catalyst lifetime was a serious issue for all of these novel active phases, since Sn is highly volatile, Cr_2O_3 is not stable at high temperature and the hexa-aluminate catalyst quickly cokes. In conclusion, until recently Pt appeared to be the only reliable active phase for the process.

In very recent times we hence proposed the use of non-noble-metal catalysts, which in addition to a fair oxidation activity, show also excellent thermal stability. $LaMnO_3$-based honeycomb monoliths, active and stable in hydrocarbons deep oxidation processes [10], exhibited excellent catalytic properties for ODH of ethane at short contact times [11], with satisfying ethylene yields and resulted stable under many hours of reaction.

In this work the $LaMnO_3$ structured catalytic system is studied in comparison with Pt, with the same support morphology (400 cpsi honeycomb monoliths) and under the same experimental conditions, in order to verify the reliability and profitability of a previously proposed catalyst [11] with respect to the state-of-the-art catalyst.

2. Experimental

Four hundred cpsi cordierite disks, 10 mm long and with a diameter of 18 mm, were used as ceramic supports. Incipient-wetness impregnation was used to deposit Pt onto a α-Al_2O_3 washcoat layer and $LaMnO_3$ onto a La_2O_3-stabilized γ-Al_2O_3 washcoat layer coating the support. The

---

* Corresponding author. Fax: +39-081-5936936.
E-mail address: fradonsi@unina.it (F. Donsì).

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.03.045

catalytic monolith, stacked between two inert monoliths as radiation shields, was placed in a quartz tube inserted in an electric furnace used only for igniting the reacting mixture. Thermocouples were placed in the middle channel of each monolith (radiation shields and catalytic monolith) and downstream of the catalyst.

The head-to-head comparison between Pt and $LaMnO_3$ was carried out at varying, for a constant N_2 dilution (30 vol.%), C_2H_6/O_2 ratio, between 1.5 and 2.5, and the flow rate, between 25 and 125 slph (standard liters per hour), corresponding to a gas hourly space velocity (GHSV) between 1.2×10^4 and $6 \times 10^4\,h^{-1}$ (i.e. the contact time between 294 and 59 ms $cm^3/N\,cm^3$) and to a residence time at the average temperature of 900 °C between 70 and 14 ms.

3. Results and discussion

The catalytic system was ignited heating the reactor at ~200 °C for Pt and ~400 °C for $LaMnO_3$. After ignition the heat source was removed and the reactor worked under auto-thermal conditions, with complete oxygen conversion under all conditions investigated.

In Figs. 1 and 2 and Table 1 the comparison between Pt (black symbols and solid lines) and $LaMnO_3$ perovskite (white symbols and dashed lines) is exploited at varying C_2H_6/O_2 feed ratio in terms of ethane conversion and ethylene selectivity (Fig. 1), selectivity of the main products (Table 1) and temperature profiles (Fig. 2).

Ethane conversion decreases monotonically for increasing C_2H_6/O_2 ratios, and is always higher of about 10% on perovskite than on Pt in the entire range investigated. On $LaMnO_3$ it varies from 90% (at $C_2H_6/O_2 = 1.5$) to 47% (at $C_2H_6/O_2 = 2.5$), while for Pt from 80 to 40%. Conversely, ethylene selectivity is observed to grow at increasing C_2H_6/O_2 ratio. On $LaMnO_3$ it ranges from 60% at $C_2H_6/O_2 = 1.5$, up to about 70% for $C_2H_6/O_2 > 2$. The increase in ethylene selectivity on Pt is less substantial, and starting from about 60% stops below 64%.

The differences observed between the two catalysts in ethylene selectivity are consistent with a different distribution of the main by-products. As shown in Table 1, on Pt larger amounts of CO are formed than on perovskite. Indeed, at increasing C_2H_6/O_2 ratio CO selectivity stays around 25% on Pt, while on $LaMnO_3$ decreases from 17 to 11%. On the contrary, CO_2 selectivity, which shows an increasing trend when C_2H_6/O_2 ratio is increased, is lower on Pt, on which it is observed to range from 6 to 10%, while on the mixed oxide catalyst it varies between 11 and 15% (Table 1). In conclusion, the amount of C_2H_6 converted to CO_x is always lower on perovskite than on Pt, as on $LaMnO_3$ the limiting reactant, oxygen, is preferentially oxidized to CO_2.

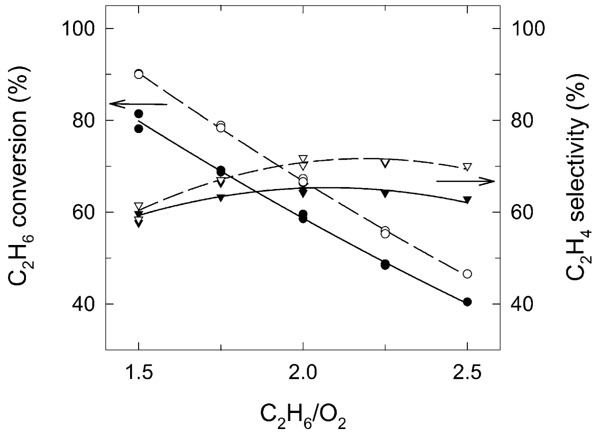

Fig. 1. C_2H_6 conversion and C_2H_4 selectivity at varying C_2H_6/O_2 ratio on Pt-based (black symbols and solid lines) and $LaMnO_3$-based catalysts (white symbols and dashed lines). Experimental conditions: GHSV = $2.4 \times 10^4\,h^{-1}$, N_2 = 30 vol.%.

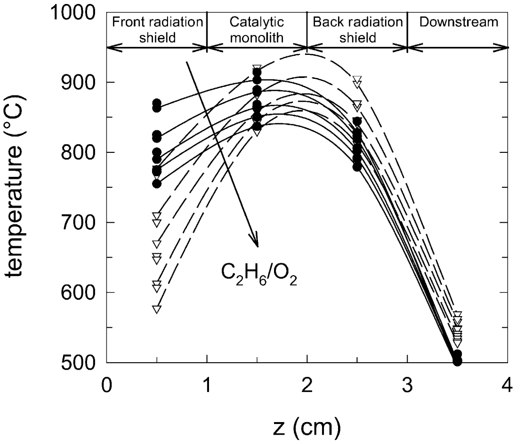

Fig. 2. Temperature profiles of Pt-based (black symbols and solid lines) and $LaMnO_3$-based reactors (white symbols and dashed lines) at different C_2H_6/O_2 ratios under the conditions in Fig. 1.

Table 1
Selectivity (%) of the main products on Pt-based and $LaMnO_3$-based catalysts under the conditions in Fig. 1

C_2H_6/O_2	Pt						$LaMnO_3$					
	CO_2	CO	H_2O	H_2	CH_4	C_2H_2	CO_2	CO	H_2O	H_2	CH_4	C_2H_2
1.5	6	27	29	23	7	2	11	17	21	26	9	3
1.75	6	24	31	20	5	1	11	13	24	22	6	2
2	7	24	31	18	4	1	12	11	25	21	5	1
2.25	9	23	34	16	3	1	14	11	27	19	4	1
2.5	10	24	37	15	3	0	15	11	30	16	3	1

As regards H-atom selectivity, H_2O selectivity grows when C_2H_6/O_2 is increased. On Pt it is comprised between 29 and 37%, while on $LaMnO_3$ the limiting values are respectively 21 and 30%. H_2 selectivity instead at increasing C_2H_6/O_2 ratio decreases, from 26 to 16% on $LaMnO_3$, while it is slightly lower (∼2–3%) on Pt, which varies between 23 and 15%. We can thus observe that on Pt hydrogen oxidation is probably more enhanced than on perovskites.

It is worth to highlight that product distribution upon the variation of the C_2H_6/O_2 ratio does not depend uniquely on the reduced oxygen content of the feed mixture, but also strongly on temperature. Indeed, as previously argued [11], the autothermal nature of the system leads the temperature to play an important role in the process. The larger oxygen content, corresponding to a lower C_2H_6/O_2 ratio, determines the attainment of higher temperatures in the reactor. In Fig. 2 the temperature profiles in the Pt- and $LaMnO_3$-based reactor are reported. The temperature in the catalytic monolith (between $z = 1$ and 2 mm) ranges from ∼820 to ∼910 °C, in dependence on the operating conditions. The back heat shield retains most of the heat of the exothermic catalytic reaction, as shown by its temperature, which is comparable to that of the catalytic monolith in the case of $LaMnO_3$, and slightly cooler for Pt (between 760 and 850 °C). The temperature registered downstream of the monoliths instead shows that at that point the system has considerably cooled down, both because of heat losses from the reactor setup and because of the occurrence of gas-phase endothermic reactions, once oxygen is completely consumed.

Significant differences between the two active phases can be observed in the temperature of the front shield, due to the different temperatures of the front face of the catalytic monolith. The threshold temperature of the ODH reaction on Pt is considerably lower than on $LaMnO_3$ perovskite (200 °C versus 400 °C), due to the higher activity of the noble metal. This implies that the front face of the Pt-based monolith is hotter, and heat is more efficiently transferred by conduction and radiation to the front shield than in the case of the perovskite monolith.

At increasing the C_2H_6/O_2 ratio, the temperature of both catalytic reactors is lowered of ∼100 °C, thus favoring the formation of CO_2 and H_2O, whose selectivities increase notwithstanding the reduction in oxygen content. CO and H_2 are instead more favorably produced at high temperature, as we can observe in Table 1. In addition, other by-products such as CH_4 and C_2H_2, which are formed in gas-phase reactions, are clearly dependent on temperature, and are almost absent at the higher C_2H_6/O_2 ratios.

In Fig. 3 the comparison of two catalysts is exploited at varying space velocity. We did not investigate space velocities as high as 300 slph, usually investigated in most experimental works [1–4], because $LaMnO_3$ catalyst, due to its lower activity, blows out at high flow rates. Differently, Pt-based reactors can be operated at flow rates as high as 900 slph [4].

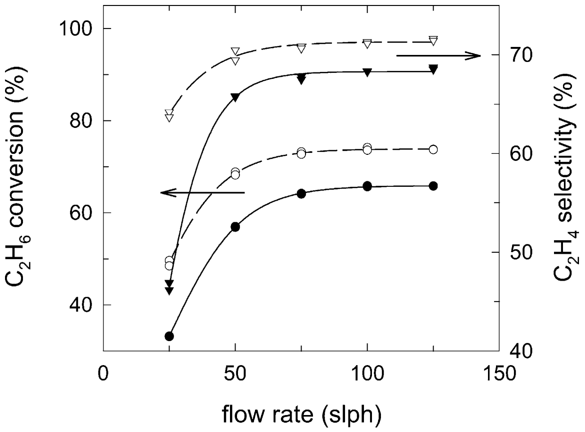

Fig. 3. C_2H_6 conversion and C_2H_4 selectivity at varying the total flow rate on Pt-based (black symbols and solid lines) and $LaMnO_3$-based catalysts (white symbols and dashed lines). Experimental conditions: $C_2H_6/O_2/N_2 = 46.7/23.3/30$.

Experimental results show that on both catalysts ethane conversion and ethylene selectivity are independent on space velocity for flow rates above 50 slph, as are observed to increase between 25 and 50 slph to a steady value maintained up to 125 slph. Similarly, also the other species attain a steady value above 50 slph.

The singular trend observed can be explained taking into account that: (a) contact time is always high enough to attain complete oxygen conversion (limiting reactant); (b) higher flow rates lead to higher temperature, because the system becomes more adiabatic, as already argued in previous investigations [11,12]; (c) mechanisms of heat dispersion become more efficient at increasing temperature (radiation). Consequently, ethane conversion and ethylene selectivity are enhanced by higher flow rates only until the temperature is significantly affected by flow rate, below 75 slph in our case, and after that they do not change further.

On $LaMnO_3$ catalyst, at increasing flow rate, ethane conversion increases from 49 to 74%, while ethylene selectivity from 64 to 72%. On Pt instead, ethane conversion grows from 33 to 66% and ethylene selectivity from 47 to 69%.

Also for a variation in the total flow rate, as shown for C_2H_6/O_2, the use of $LaMnO_3$-based catalyst results in better performance, both in terms of ethane conversion and of ethylene selectivity, even though the range of possible flow rates is limited with respect to Pt by its lower activity.

4. Discussion and conclusions

$LaMnO_3$-based catalysts were tested in a head-to-head comparison with Pt under the same reactor configuration, at varying both the C_2H_6/O_2 ratio and the total flow rate. The mild activity of $LaMnO_3$ turned out to be better than the strong activity of Pt in the ODH process.

The difference in temperature profiles between the two catalysts does not suffice to explain the observed difference in performance, as the $LaMnO_3$-based catalyst always performed better than Pt under a large variety of conditions, which affected diversely the surface temperature of the catalysts. The observed results can be rather explained if we consider some experimental results obtained on Pt and $LaMnO_3$, under conditions such that the homogeneous reactions could be ruled out. In particular, we refer to experimental tests conducted below 600 °C by Beretta et al. [5] on Pt, and to isothermal tests at temperatures up to 550 °C that we carried out on $LaMnO_3$ [11]. Under fuel-rich conditions, on both catalysts in the low temperature range (∼400 °C) CO_2 is the main product. Nevertheless, at increasing temperature, between 400 and 600 °C, on Pt increasing amounts of CO are formed, attaining a selectivity of ∼70% at 600 °C. Instead, on $LaMnO_3$, notwithstanding the presence of a lower amount of O_2 ($C_2H_6/O_2 = 1.7$ in our experimental tests versus $C_2H_6/O_2 = 1$ on Pt) less CO is produced (note that in the case of isothermal reactor, that is not autothermal, the above-discussed temperature effect on product distribution is absent). The selectivity to CO_2 is ∼65% before the ignition of homogeneous reactions, while CO selectivity is ∼15%. On $LaMnO_3$ also small amounts of ethylene (selectivity =∼ 20%) are formed.

Hence, we can conclude that Pt is very active towards hydrocarbon oxidation (its threshold temperature is ∼200 °C), but less selective towards CO_2 formation. The higher activity leads the Pt catalyst to be aggressive towards ethane, oxidizing larger amounts of fuel to CO. Perovskites are instead less active (the threshold temperature is ∼400 °C) but more selective towards CO_2. On $LaMnO_3$ catalyst, the fuel is thus rather oxidized to CO_2, and to consume the same amount of O_2 less C_2H_6 is sacrificed and more heat is produced than on Pt.

In conclusion, we have shown that reliable and competitive catalysts for ethane ODH in SCTR are not necessary noble-metal-based, but that $LaMnO_3$ appears suitable to replace Pt in the ODH reaction of ethane in short contact time reactors. $LaMnO_3$ is indeed a non-noble-metal catalyst, with the advantages stemming from its low cost. Moreover, such perovskite-based catalyst shows a high thermal stability, without any sign of deactivation under many hours (about 100 h) of operation. In addition, what is most important, $LaMnO_3$ performs better than Pt: the higher ethylene selectivity is sustained by the deeper oxidation of the fuel, which results in the production of more CO_2 and less CO than on Pt, sacrificing less ethane.

Nevertheless, the fact that on Pt larger amounts of H_2O are formed (Table 1) suggests that the performance obtained on $LaMnO_3$ is likely to be further improved by a catalyst with similar activity in carbon oxidation but better in hydrogen oxidation.

References

[1] M. Huff, L.D. Schmidt, J. Phys. Chem. 97 (1993) 11815.
[2] D.W. Flick, M.C. Huff, Appl. Catal. A 187 (1999) 13.
[3] A.S. Bodke, S.S. Bharadwaj, L.D. Schmidt, J. Catal. 179 (1998) 138.
[4] A.D. Henning, L.D. Schmidt, Chem. Eng. Sci. 57 (2002) 2615.
[5] A. Beretta, E. Ranzi, P. Forzatti, Chem. Eng. Sci. 56 (2001) 779.
[6] P.M. Torniainen, X. Chu, L.D. Schmidt, J. Catal. 146 (1994) 1.
[7] S.A.R. Mulla, O.V. Buyevskaya, M. Baerns, J. Catal. 197 (2001) 43.
[8] C. Yokoyama, S.S. Bharadwaj, L.D. Schmidt, Catal. Lett. 38 (1996) 181.
[9] A. Beretta, P. Forzatti, J. Catal. 200 (2001) 45.
[10] S. Cimino, L. Lisi, R. Pirone, G. Russo, M. Turco, Catal. Today 59 (1) (2000) 19.
[11] F. Donsì, R. Pirone, G. Russo, J. Catal. 209 (2002) 51.
[12] S. Cimino, A. Di Benedetto, R. Pirone, G. Russo, Catal. Today 69 (2001) 95.